Conductivity spectra analysis behaviour of conductive PPy on PVC/PMMA composites

F.S. Shokr[1] and S.A. Al-Gahtani[2]

Abstract. A series of thin films from poly (vinyl chloride) (PVC) – poly (Methyl methacrylate) (PMMA) composites with different amounts of Polypyrrole (PPy) / carbon nano-particles were prepared. Charge transport properties, such as the frequency dependent conductance, of polymer matrix–conductive filler particles composites, are investigated. In the present study Ac conductivity is examined with varying parameters, the filler content and the frequency in the case of ac field. The examined systems, though they are characterized as dielectrics, exhibit considerable conductivity, which alters by several orders of magnitude with frequency. The frequency dependence of conductivity gives evidence for the charge carriers transport mechanism via the occurred agreement of experimental results with the employed QML model. The ac conductivity increases as with the incorporation of conductive PPy and the proposed model by Tsangaris et al fit well the experimental values more closely for low PPy contents.

Keywords: Conductivity, conductive PPy, Electrical Properties, PVC/PMMA composites

INTRODUCTION

Composite systems consisting of an insulating matrix and randomly dispersed fine conductive particles have generated significant research interest, mostly, due to their electrical and electromagnetic performance [1–2]. The essential applications for conductive phase-polymer have composites allude to electromagnetic interference (EMI) shielding, radio frequency interference (RFI) shielding and electrostatic dissipation of charges (ESD). Furthermore, conductive polymer composites are utilized as electrical conductive adhesives and circuit elements in microelectronics [3] and have been reported to possess anticorrosive behaviour as metal parts coatings [4]. Composite materials of an amorphous polymeric matrix and randomly dispersed metal particles are considered as heterogeneous disordered systems. The electrical performance of granular materials, as these frameworks are once in a while alluded to, is directly related to the permittivity and conductivity of the constituent phases, the size, shape and volume fraction of the inclusions and can be experimentally investigated by means of Dielectric Spectroscopy (DS) and dc conductivity measurements [5–12].

Polymers and polymer matrix composites are fundamentally electrical insulators, due to their low concentration of free charge carriers. Thus their electrical response is, mainly, associated with relaxation phenomena occurring under the influence of ac field. The observed relaxation processes are related to dipolar orientation effects or space charge migration [13]. Molecular mobility and interfacial polarization are regarded as the origin of dielectric effects. At adequate high temperature, in the vicinity of the glass transition temperature, large segments of the polymer chain are able to move trying to follow the alternation of the field, while at lower temperatures polar side groups are contributing to the electrical performance of the system. Interfacial polarization is the aftereffect of the heterogeneity of the system, such as mobile charges accumulated at the metal particles–polymer matrix interface, form large dipoles.

On the other hand the, locally restricted or extended through the whole system, migration of charges gives rise to materials conductivity. The concentration of the conductive inclusions has been proved to be a crucial parameter, governing the electrical behaviour of the composites.

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At the point when the filler content is low, the mean separation between metal particles or clusters is sufficient large and conductance is limited by the presence of the dielectric matrix. However, by increasing the conductive phase content, the metal ''islands'' get closer and at a critical concentration of the filler, a physical path is formed, through which the current can flow percolating the whole system. Percolation theory describes the transition from the state of limited and spatially restricted connections of conductive elements to the state of an infinite network of connections.

The present investigation is concerned with detailed studies on the ac electrical properties of PVC/PMMA composites filled with conductive PPy nano filler (loaded with constant concentration (30 phr) of HAF black). The emphasis was addressed to the recorded electrical relaxations, under the influence of ac field. In the present work ac conductivity of composite systems is examined with varying parameters the filler content and frequency in the case of the ac field. In order to investigate further, the physical origin of the occurring charge transport in granular composite systems, different models have been employed and applied on ac data. The observed dielectric response of the composites will be examined using the proposed model of Tsangaris et al. [25]

2. Experimental

2.1 Materials and Preparation of sample

Poly vinyl chloride (PVC) of standard grade provided by Fluka, and poly methyl methacrylate (PMMA) provided by Alfa Aesar, were utilized as a part of the study. The conducting polymer (polypyrrole) likewise provided from Aldrich. For the preparation of polypyrrole doped thin film, the two polymers, PVC (1.5 g) and PMMA (0.5 g), were taken in the ratio 3: 1 by weight, 1.5 g of PVC in 15 ml of tetrahydrofuran (THF) and 0.5 g of PMMA in 5 ml of THF dissolved separately and subsequently mixed together. Polypyrrole was taken in various wt % as mentioned in Table (1), and was dissolved in 5 ml of THF to produce polypyrrole solution. After allowing them to dissolve completely, the three solutions were mixed together. The solution was slightly heated to allow polymers to dissolve completely to yield a clear solution. A glass plate altogether cleaned with heated water and afterward with acetone was utilized as a substrate. The arrangement was poured on the glass plate and permitted to spread consistently every which way on the substrate. The entire get together was set in a tidy free chamber kept up at a room temperature (25°C). In this way, the film was set up by isothermal evaporation technique. Finally, the film was expelled from the glass plate. It was cut into little bits of reasonable size, which were washed with ethyl liquor to expel any surface impurities

Table (1): Shows the composition of the blend

Ingredients	Wt
PVC	1.5 gm
PMMA	0.5 gm
PPY(HAF) 30% (nanoparticles)	0,0.02,0.04,0.06,0.08,0.10,0.30 gm

2.2 Measurements

The dielectric properties were measured using a bridge (HIOKI 3538-50 LCR Hi Tester) in the frequency range 102-106 Hz. The crosslinked samples were in the form of disks of 0.2-0.3 cm thick and 1.0 cm in diameter.

The samples were sandwiched between two brass electrodes and both their capacitance and their dielectric loss tangent ($\tan\delta$) values were measured at different frequencies.

The dielectric constant ε' (real part of the dielectric constant) of the samples and the a.c conductivity σ_{ac} were calculated by using the relations [14]

$$\varepsilon' = \frac{d}{\varepsilon_\circ A} C \qquad (2.1)$$

$$\sigma_{ac} = \omega\, \varepsilon_o\, \varepsilon'' \qquad (2.2)$$

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (2.3)$$

Where C: The capacitance of the sample, d: The thickness of the sample, A: The cross-sectional area of each of the parallel surfaces of the sample, εo: The permittivity of free space which is equal to 8.85×10^{-12} F/m,

ε'': The dielectric loss (imaginary part of the dielectric constant) and ω : The angular frequency (ω = 2πf).

3. Results and Discussion

3.1 Conductivity spectra analysis [15]

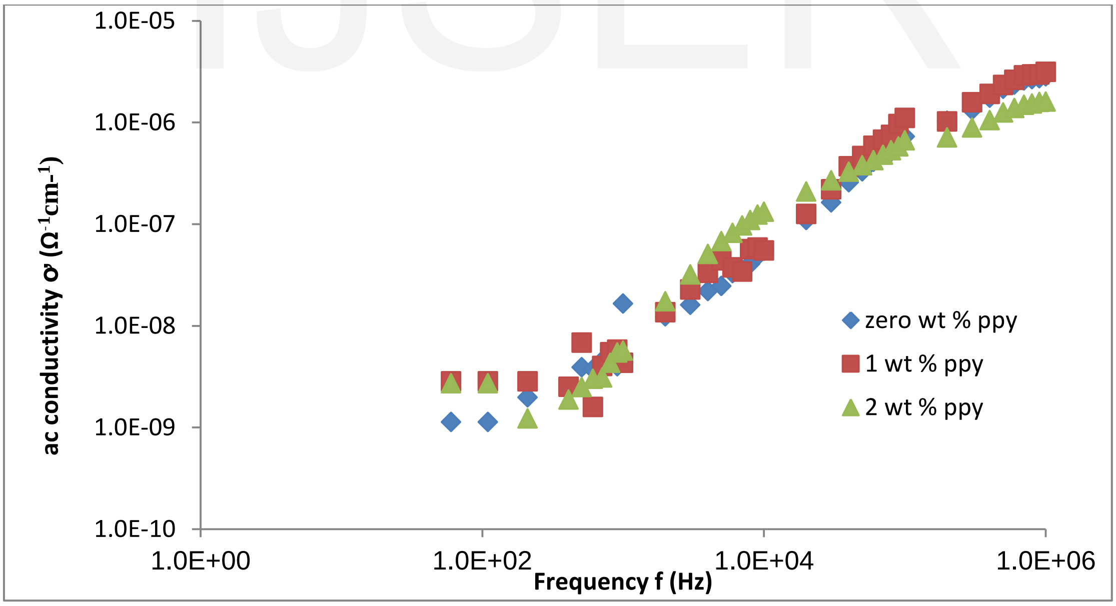
The logarithmic plots of the conductivity as a function of angular frequency for all polymer composites at room temperature as shown in Figure (3.1 a, b) can be divided into a frequency – independent plateau region in the low frequency and a dispersive region at high frequencies. The ac conductivity, σ (ω), obeys the Jonscher's power law [16] and it is found to vary with angular frequency ω 1 according to:

$$\sigma(\omega) = \sigma_{dc} + A\, \omega^{\,n} \qquad (3.1)$$

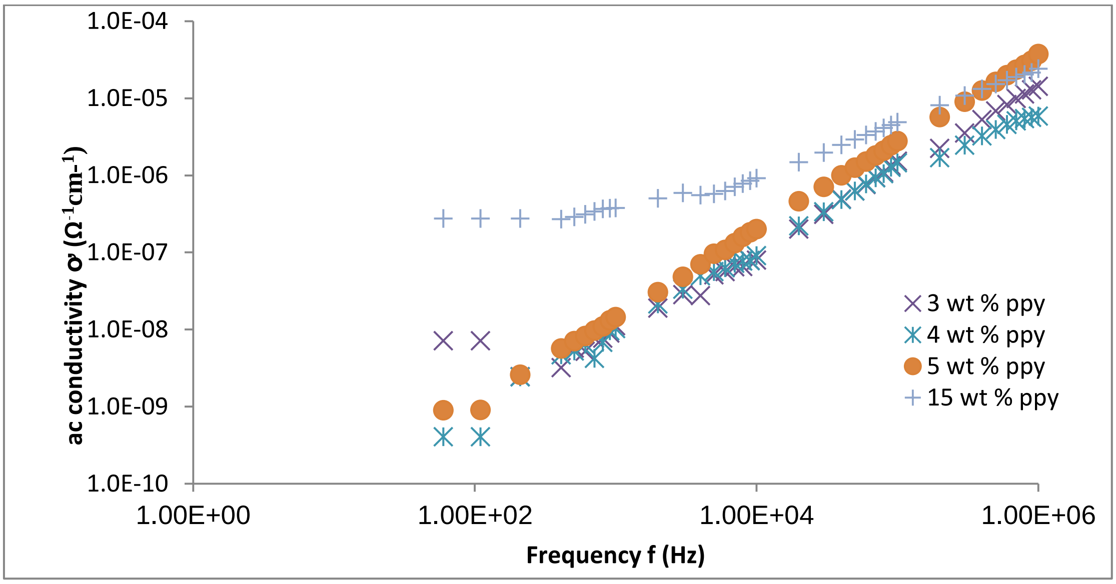
where σ_{dc} is the dc conductivity and A and n are temperature dependent parameters.

The dc conductivity values have been calculated by fitting experimental data with Jonscher's equation and the conductivity values for all the polymer composites lie in the range 2.79 x 10-9 — 3.67 x 10-7 at room temperature as shown in table (3.2).

To analyze the ac conductivity data of these samples, we extracted the σ_{dc} plateau values at different frequencies by subtracting σ_{dc} from σ_{total} data. Curves resulting from this procedure are shown in figure (3.2 a, b) for all samples at room temperature (25 °C).



(a)



(b)

Figures (3.2 a, b): Shows the relation between the logarithmic a.c. conductivity and the frequency for all sample.

TABLE (3.2): THE VALUES OF DC CONDUCTIVITY AND WEIGHT % OF POLYPYRROLE.

Weight % of polypyrrole	Dc conductivity
Zero	2.79 x 10-9
1	6.83 x 10-9
2	4.33 x 10-9
3	3.19 x 10-9
4	4.69 x 10-9
5	5.68 x 10-9
15	3.67 x 10-7

It is evident that all samples has an frequency dependence of the ac conductivity σac given by

$$\sigma_{ac}(\omega) \; \alpha \; \omega^{n} \qquad (3.2)$$

Where the exponent n is seen to be a function of ω. One can determine n from the shape of log σ_{ac} – log ω curve for various samples. The log σ_{ac} – log ω can be fitted by a polynomial equation of the form:

$$\log \sigma_{ac} = a + b \log \omega + c \log (\omega)^2 \qquad (3.3)$$

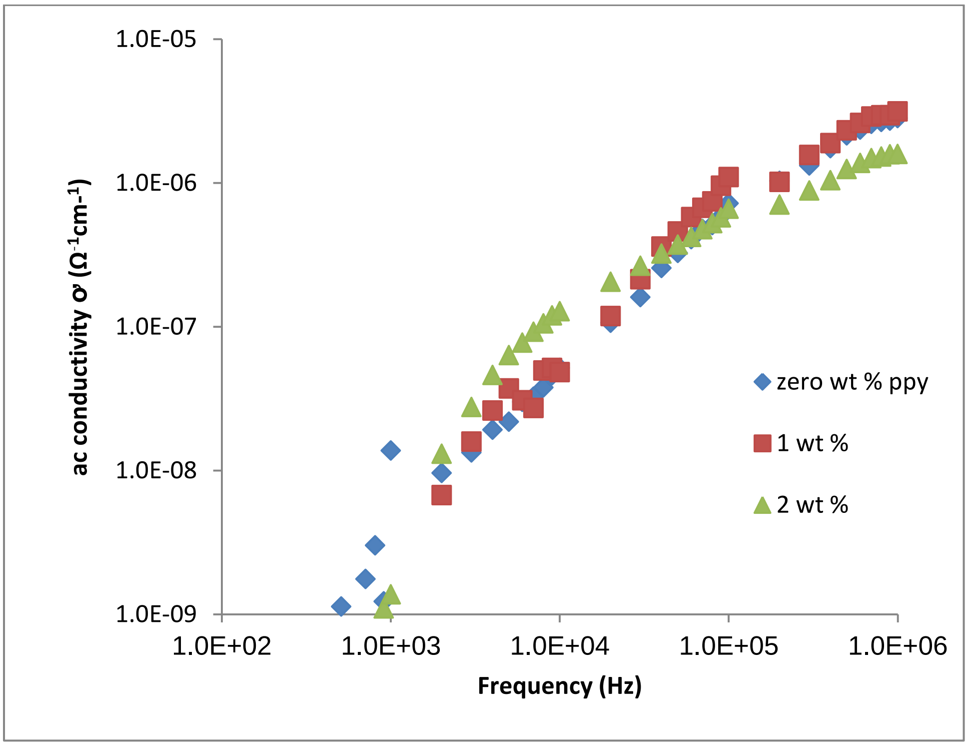
The slope at any ω was obtained from the equation

$$n = \frac{d \log \sigma ac}{d \log \omega} \qquad (3.4)$$

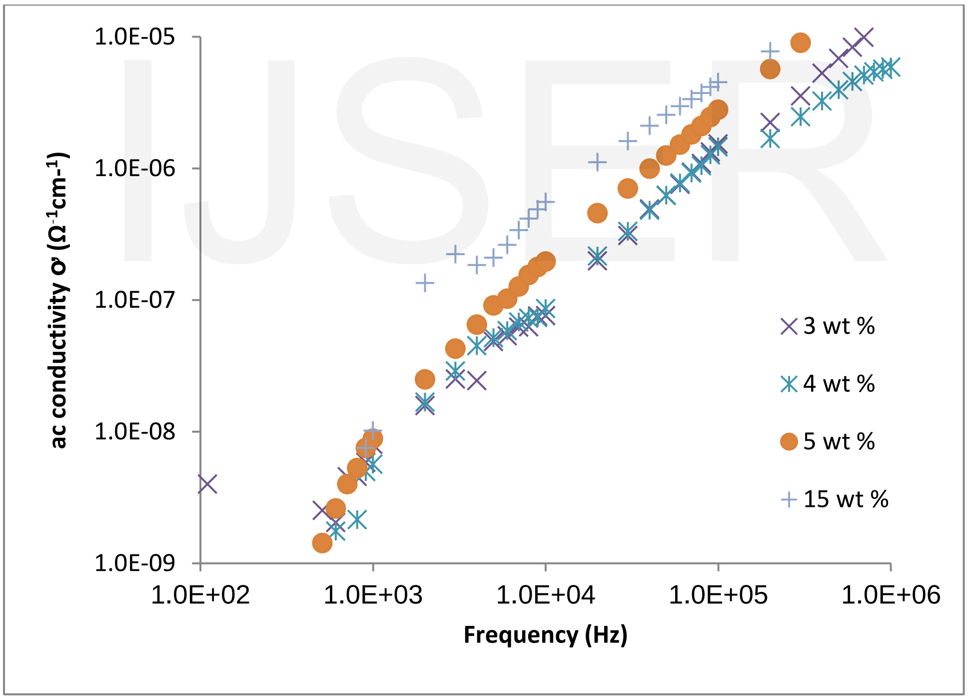
Using equation (3.14) and (3.15), one can obtain

$$n = b + 2\, c \log \omega \qquad (3.5)$$

Figures (3.3 a -f) show the typical fitting data for PVC/PMMA and PVC/PMMA loaded conductive polypyrrole composites.

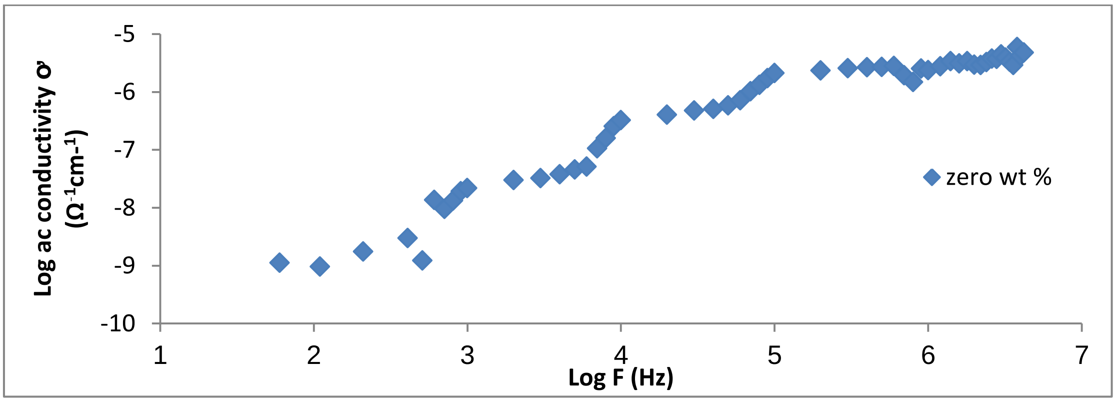


(a)

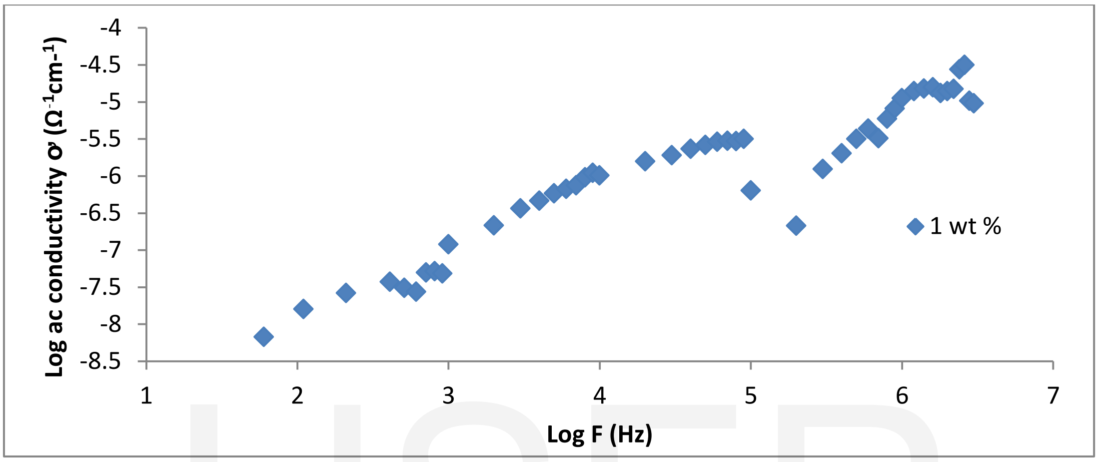


(b)

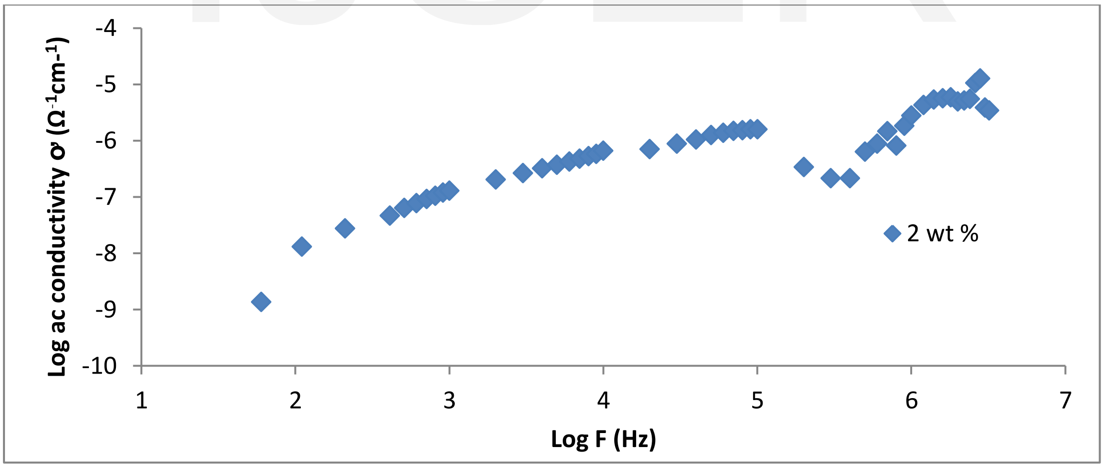
Figures (3.2 a, b): Frequency dependence of σ_{ac} for all samples after subtracting the σ_{dc} values from σ_{total} according to equation (3.1).


Log ac conductivity σ' ($\Omega^{-1}cm^{-1}$)
-5
-6
-7
-8
-9
-10
1
2
3
4
5
6
7
Log F (Hz)
zero wt %

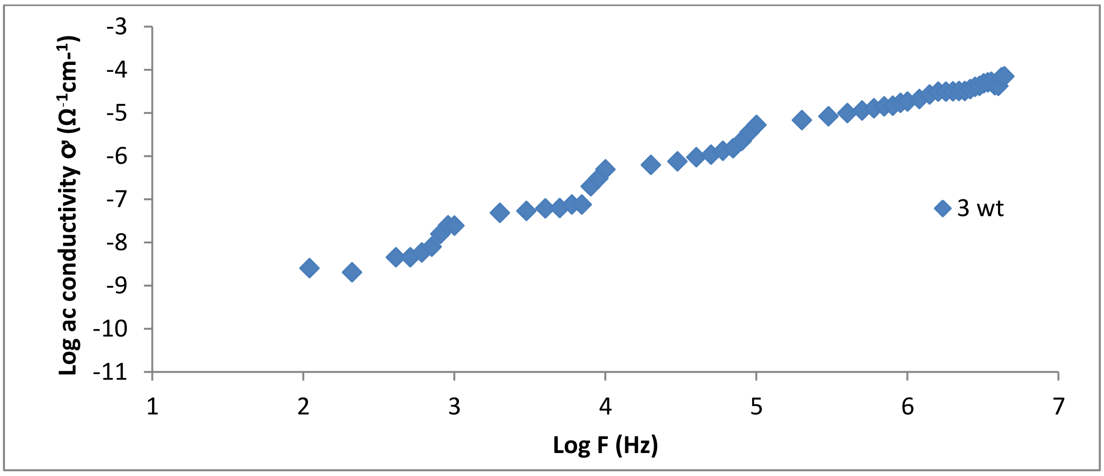
(a)


Log ac conductivity σ' ($\Omega^{-1}cm^{-1}$)
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
1
2
3
4
5
6
7
Log F (Hz)
1 wt %

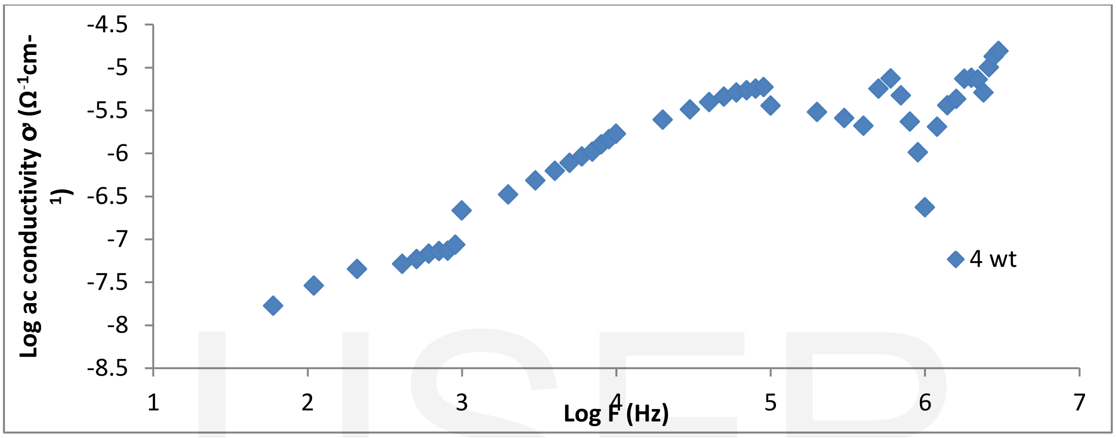
(b)


Log ac conductivity σ' ($\Omega^{-1}cm^{-1}$)
-4
-5
-6
-7
-8
-9
-10
1
2
3
4
5
6
7
Log F (Hz)
2 wt %

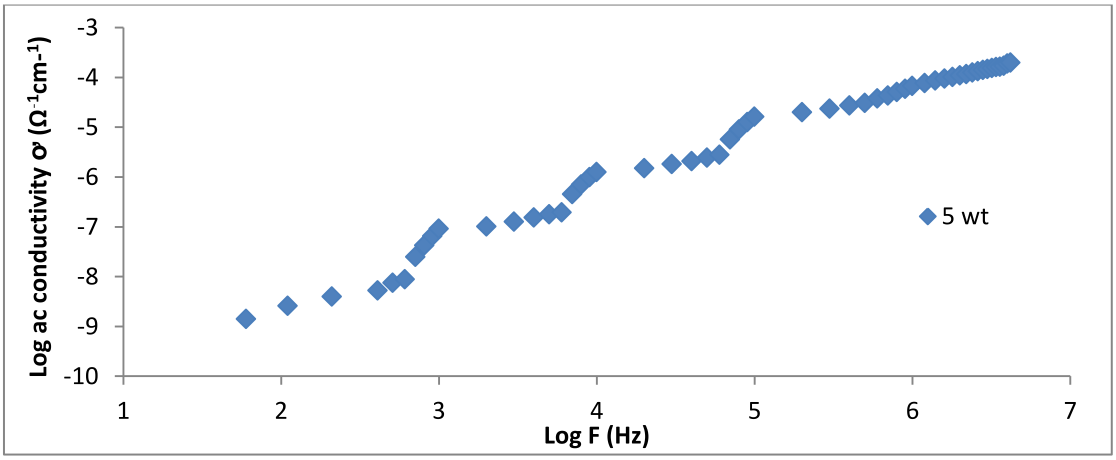
(c)


Log ac conductivity σ' (Ω-1cm-1)
-3
-4
-5
-6
-7
-8
-9
-10
-11
1
2
3
4
5
6
7
Log F (Hz)
3 wt

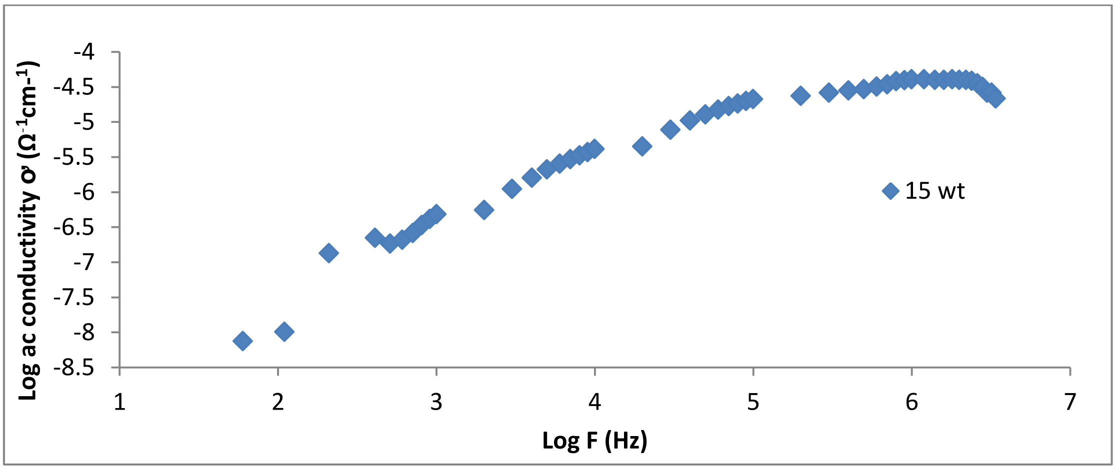
(d)


Log ac conductivity σ' (Ω-1cm-1)
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
1
2
3
4
5
6
7
Log F (Hz)
4 wt

(e)


Log ac conductivity σ' (Ω-1cm-1)
-3
-4
-5
-6
-7
-8
-9
-10
1
2
3
4
5
6
7
Log F (Hz)
5 wt

(f)



(g)

Figures (3.3 a -f): Typical fitting data for PVC/PMMA and PVC/PMMA loaded conductive polypyrrole composites.

Several theoretical models have been proposed for ac conduction in amorphous semiconductor. It is commonly assumed that dielectric loss occurs because of localized motion of charge carriers within a pairs of sites. Two distinct mechanisms have been proposed for the relaxation phenomenon: (1) quantum mechanical tunneling (QMT) of electrons or polarons through the barrier separating localized states and (2) classical hopping over the same barrier.

For (QMT) of electrons, the frequency exponent's n in this model is deduced to be:

$$n = 1 - \frac{4}{\ln(\frac{1}{\omega T})} \quad (3.6)$$

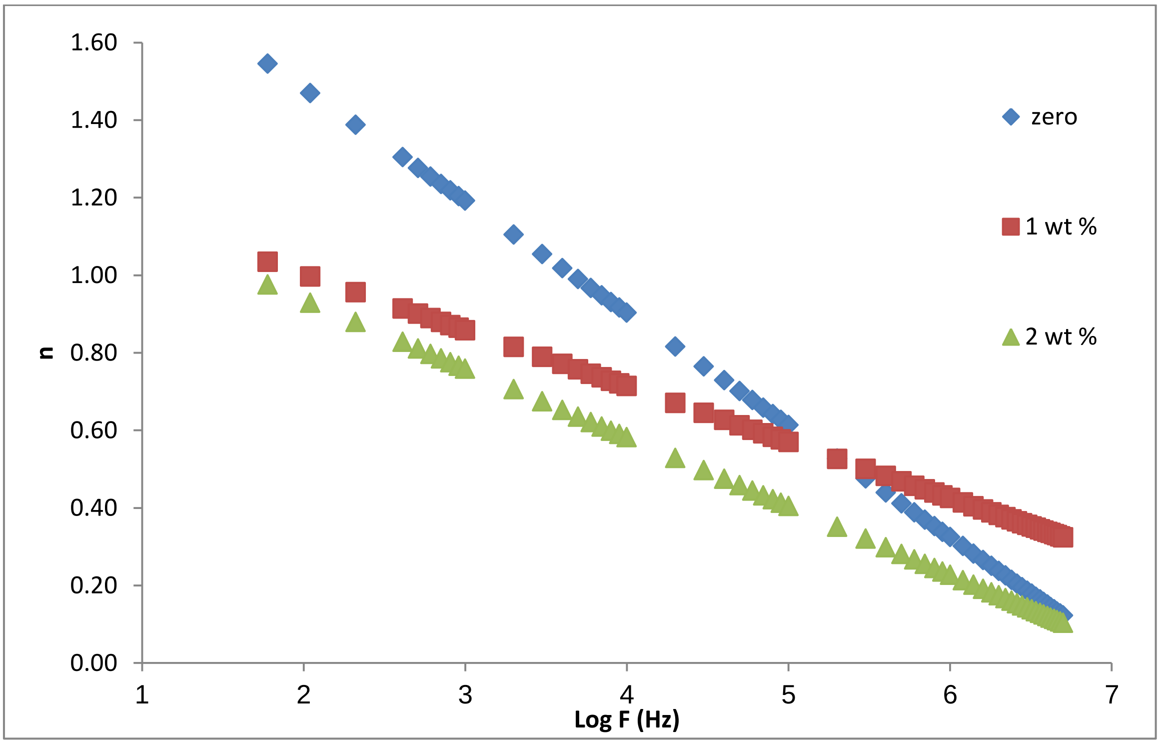
Thus σ (ω) is linearly depended on temperature and n is temperature independent [16].

The correlated barrier hopping model (CBH) was proposed by Pika [17] and the frequency exponent n in this model is evaluated to be:

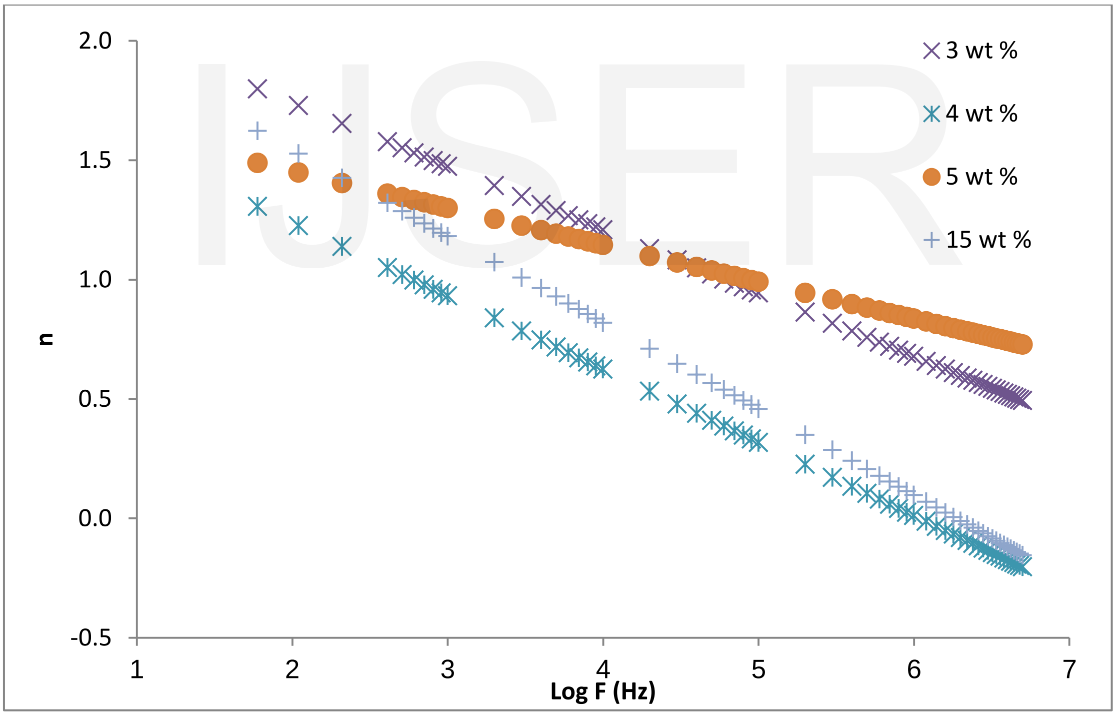
$$n = 1 - \frac{6\,KT}{(Fm - KT\ln(\frac{1}{fT}))} \quad (3.7)$$

Where F_m is the maximum barrier height.

From Figures (3.4 a,b) at 25 °C, it is evident that n decreases as a function of frequency for all samples, this suggests that variation follow equation (3.6), indicating a (QMT) mechanisms is operative in these samples.



(a)



(b)

Figures (3.4a, b): Variation of frequency exponent n with frequency for all samples.

3.2 filler dependence

The ac conductivity increases as the conductive PPy content increases as presented in Figure 5. This increase in ac conductivity with the incorporation of conductive PPy is due to the increase in the free charge, which increase the interfacial as well as the orientation polarization and also due to the fact that the carbon particles in the PPy matrix associated with a conjugated bonding structure present in the crystalline regions and also due to the presence of polar groups in carbon black.

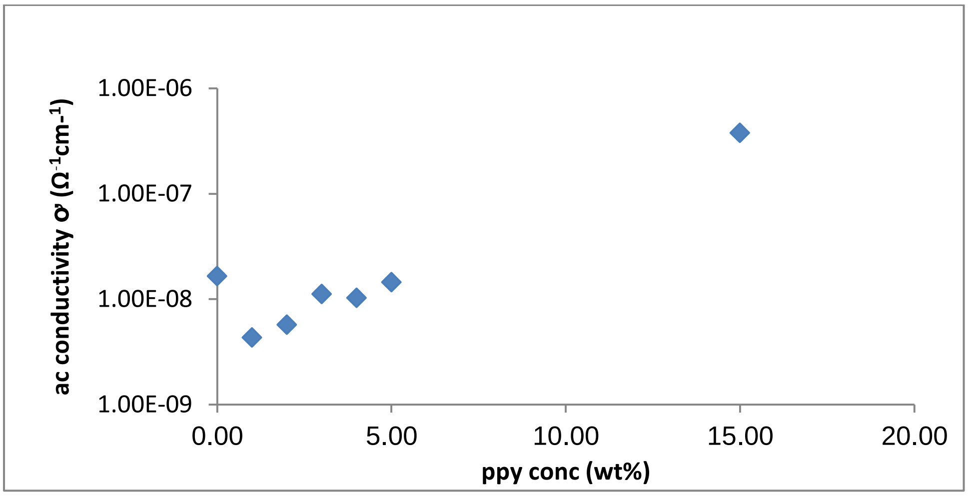


Figure (5): shows the relationship between ac conductivity and conductive PPy at 1 kHz frequency.

3.3 Theoretical background [18]:

The calculation of ε' of dielectric mixtures and the variety of proposed formulae have been reviewed by Reynolds and Hough [19] Van Beek [20] Bőttcher and Bordwijk [21], Grosse and Graffe [22], and Kraszewski [23]. The size and shape of inclusions have not been considered in the above trials of the calculations of the permittivity of the dielectric mixtures. Equations which take into accounts the inclusions characteristics, giving the dielectric permittivity and conductivity of a conductor loaded dielectrics have been proposed by Neelakanta [24]. Tsangaris et al [25] formulated suitable equations expressing the dielectric permittivity ε', and dielectric loss ε'' of the composite material in terms of the applied field frequency and the components characteristics as follow:

$$\varepsilon'_{eff} = \frac{\varepsilon'_1}{[(\varepsilon'_1 - 1)^Y + 1]} \left\{ [(\frac{\sigma}{\omega\varepsilon_\circ})^{v_2} (\varepsilon'_1 - 1)^{(1-v_2)} \cos\frac{\pi v_2}{2}]^Y + 1 \right\} \quad (3.8)$$

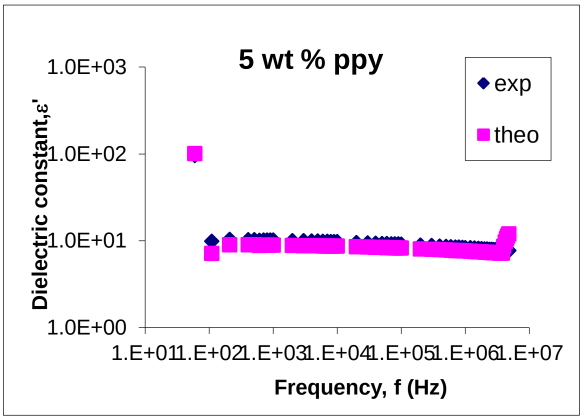
$$\varepsilon''_{eff} = \varepsilon'_1 \{[(\sigma/\dot{\omega}\,\varepsilon_\circ)^{v_2^{-1}} (\varepsilon'_1 - 1)^{1-v_2} \sin(\pi v_2/2)]^y + 1\} \quad (3.9)$$

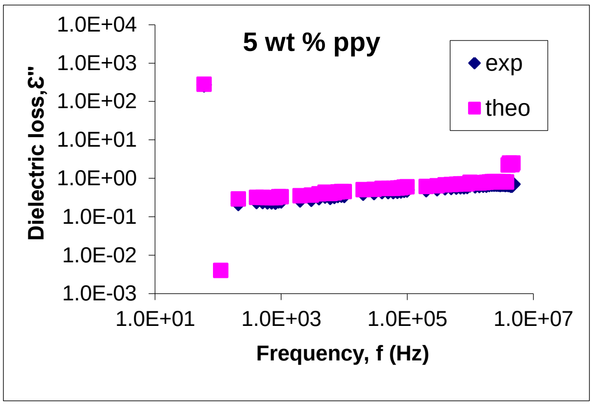
Where y is the depolarizing factor [26], which depends on the aspect ratios and orientation of the inclusions [27]. The depolarizing factor is given by [28]:

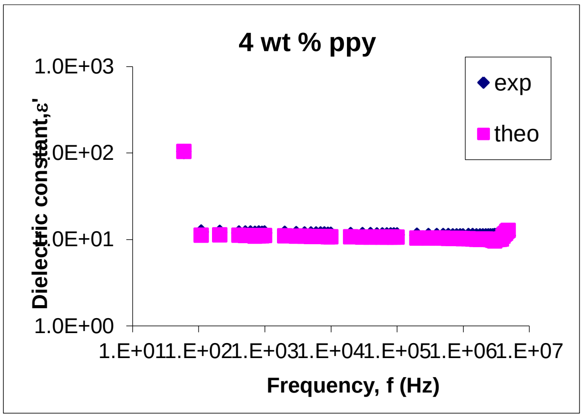
$$y = \frac{1}{1-(a/b)^2} - \frac{a/b}{[1-(a/b)^2]^{\frac{3}{2}}} \cos^{-1} a/b \quad (3.10)$$

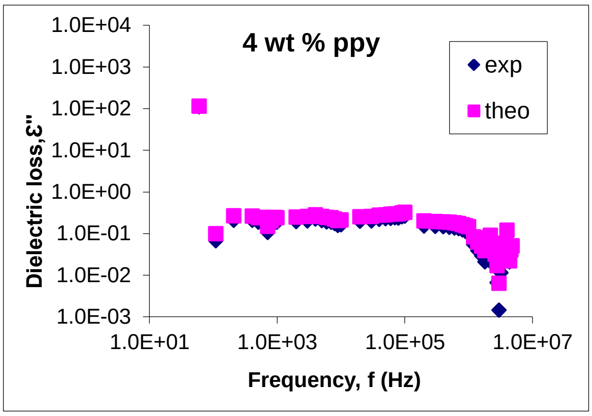
Where a/b is the aspect ratio of the inclusions , ω is the angular frequency, σ is the ac conductivity of the conductive inclusions, $\varepsilon_\circ$ is the permittivity of the free space, ε is the dielectric permittivity of the matrix and v_2 is the volume fraction of the conductive inclusions. The application of equation (3.8) which gives ε'eff and ε''eff of the composites as a function of frequency for various volume fraction of the conductive PPy is shown in Figure (3.6), together with experimental values at room temperature. The proposed model by Tsangaris et al approaches the experimental values more closely for low PPy contents. The shape of filler inclusion particles may be transformed from spherical to ellipsoidal or even to a long rod shape according to the volume fraction. The values of y were chosen to fit the calculated ε'eff and ε''eff with the experimental ones. It is clear from that the aspect ratio and the depolarizing factor increases with PPy particles and takes the shape of oblate ellipsoids with the minor axes (a) parallel to the applied frequency.

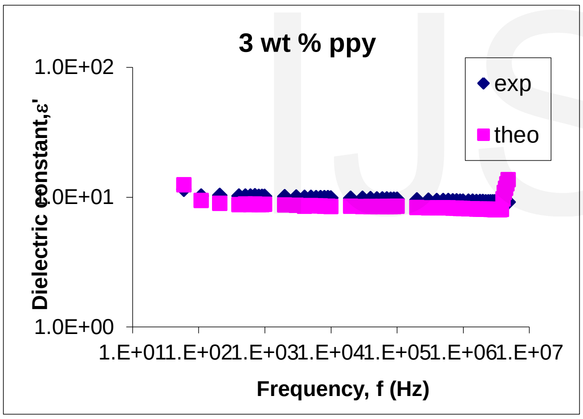
International Journal of Scientific & Engineering Research, Volume 7, Issue 11, November-2016
ISSN 2229-5518

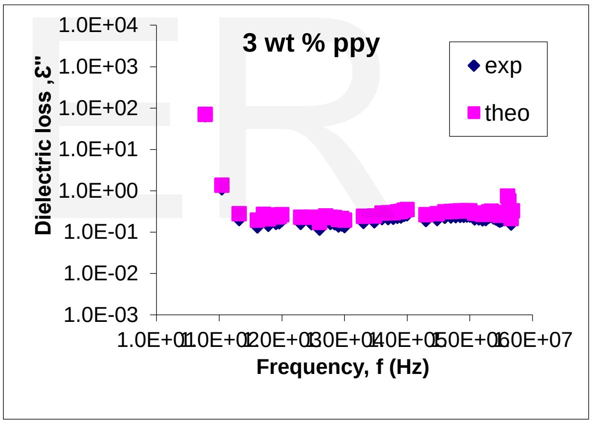


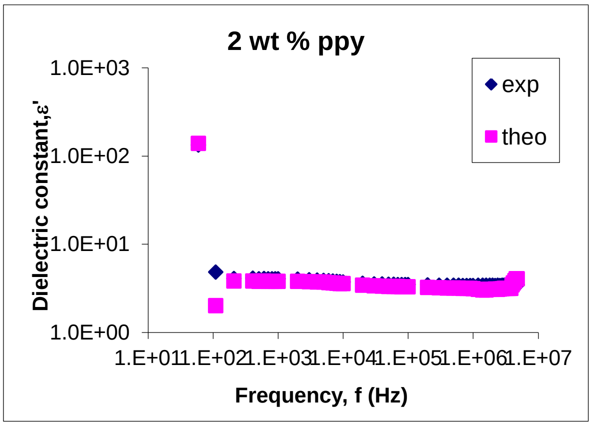


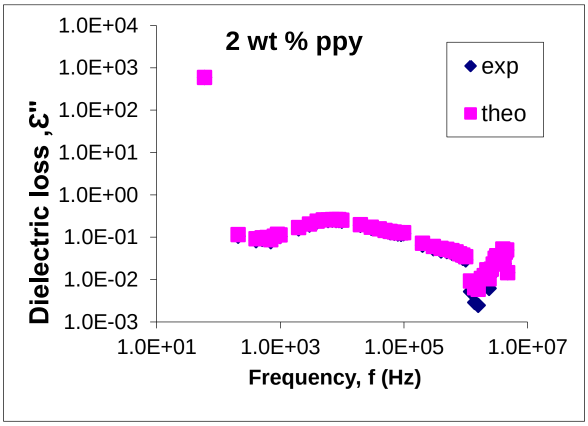












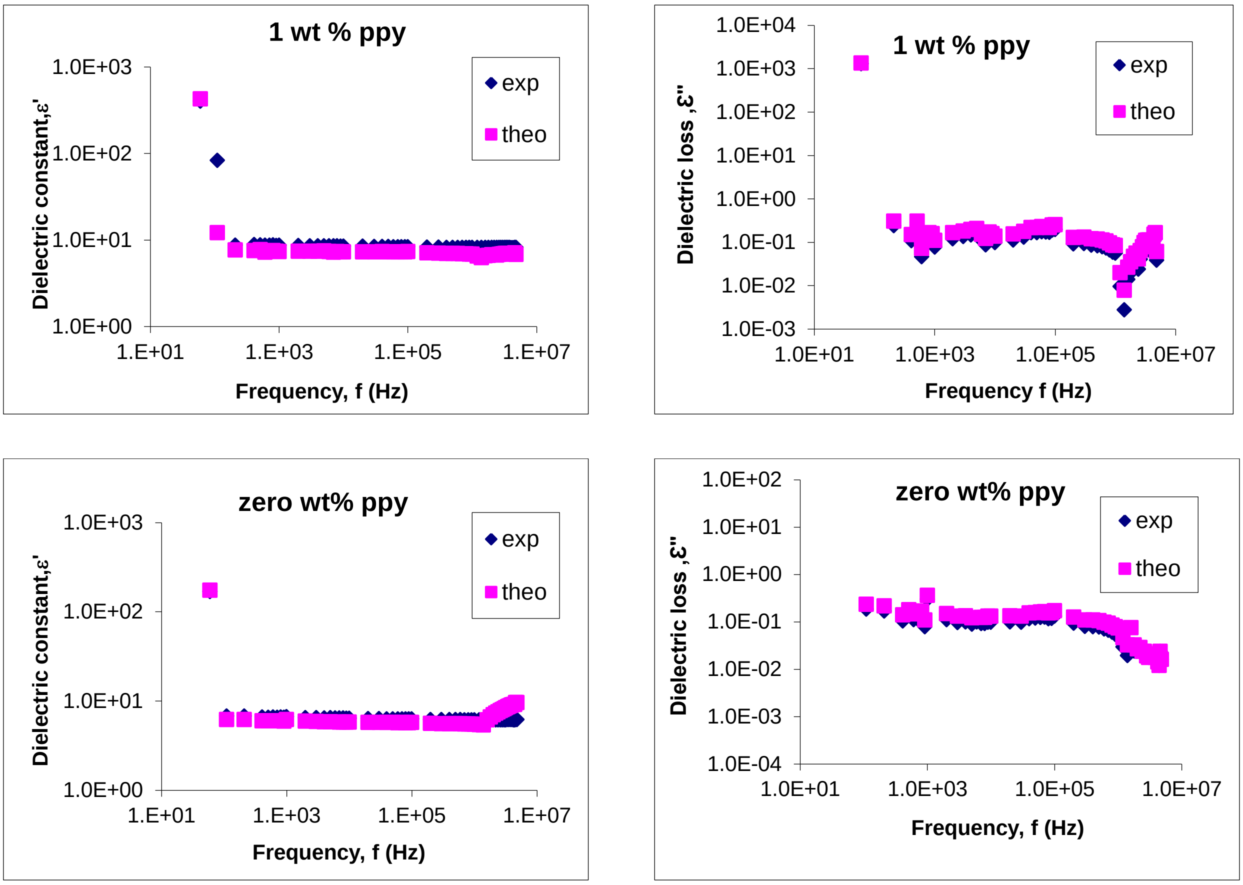


Figure (6): The experimental and theoretical relationship between dielectric constant and the frequency for all samples

4. Conclusions

An experimental method is utilized to draw a reliable picture of the physical properties of PVC/PMMA loaded with different concentrations of conductive PPy nano filler (loaded with constant concentration (30 phr) of HAF carbon black). Electrical behaviors of such materials were investigated. The frequency exponent value, n, was calculated. This decreased with increasing frequency for all samples indicating the existences of QML model. The ac conductivity increases as with the incorporation of conductive PPy due to the increase in the free charge, the proposed model by Tsangaris et al approaches the experimental values more closely for low PPy contents. The shape of filler inclusion particles may be transformed from spherical to ellipsoidal or even to a long rod shape according to the volume fraction.

Acknowledgement

The authors are thankful to and express their sincere gratitude to Prof. G. M. Nasr, Professor of Solid State, Phys. Dept., Faculty of Science, Cairo University, for providing necessary laboratory facilities during the course of this work, supervision, encouragement and fruitful discussion. Also to Dr. Ah. Abd Elbary, Doctor of experimental physics, Higher Institute of Engineering and Technology, New Cairo Academy for his help to finish this work.

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