Influence of B ion irradiation on the ac conductivity of conductive PPy on PVC/PMMA composites

F.S. Shokr[1]

Abstract. In this study, thin films from poly(vinyl chloride) (PVC) – poly (Methyl methacrylate) (PMMA)composites with different amounts of Polypyrrole (PPy) / carbon nano-particles were prepared. Influence of B ion irradiation on the ac conductivity σis examined with varying parameters, the filler content and the frequency in the case of ac field. The effect of irradiation on the ac conductivity σof pure PVC/PMMA and PVC/PMMA loaded with conductive PPy filler blends was studied. A.c conductivity σobviously increase after ion implantation. The higher σ_{ac} of PVC/PMMA after implantation will be got by implantation for samples loaded with 3 wt. % PPy conductive filler. The irradiation with B ions at 4.87 x 10^{14} ions cm^{-2} increases σ_{ac} of sample PVC/PMMA loaded with 3 wt. % PPy by 3 orders of magnitude. B ion fluences change the type of conduction mechanism for samples pure PVC/PMMA at different fluences, 1, and 2 wt. % loading at 5.95x10^{14} ions cm^{-2}.

Keywords:ac conductivity, ion implantation, conductive PPy, electrical Properties, PVC/PMMA composites

INTRODUCTION

The effects of high-energy irradiation on polymers can lead to changes in their properties, and their interaction with high-energy electrons is a complex and random process [1]. The changes resulting from irradiation are mainly a consequence of electron absorption followed by bond cleavage to give radicals, radical recombination leading to the formation of crosslinks and end-links or disproportionation to give chain scission and gas evolution, mainly by radical recombination [2,3]. The final result depends on the nature of the material, on the dosage, dosage rate and the radiation energy. Thus, there are many ways to exploit these processes technologically, such as cross-linking [4-7] and surface modification [8-10].

Ion beam surface modification has shown great potential for improving the tribological behaviour as well as surface and electrical properties of polymeric materials. As a result, the past few years have seen many advances in the field of ion beam surface modification of polymeric materials in terms of applying conventional ion beam techniques to various types of polymers, and introducing innovative plasma-enhanced ion implantation techniques.

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). Theemphasis 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 such as the filler content and frequency in the case of the ac field under the effect of ion beam implantation. In order to investigate further, the physical origin of the occurring charge transport in granular composite systems, different models have been applied on ac data.

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ISSN 2229-5518

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 10^2-10^6 Hz. The samples were in the form of disks of 0.2-0.3 cm thick and 1.0 cm in diameterthen sandwiched between two brass electrodes and the a.c conductivity $\sigma_{ac}$of the samples was calculated by using the relations [11] at different frequencies.

$$\varepsilon' = \frac{d}{\varepsilon_o A} C \quad (2.1)$$

$$\sigma ac = \omega \varepsilon o \varepsilon'' \quad (2.2)$$

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

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, ε_o: The permittivity of free space which is equal to 8.85×10^{-12}F/m,

2.3 Exposure to Plasma Irradiation

The polymer samples of circular shape with common size (1 cm diameter) were fixed inside the vacuum ended tube with diameter 21mm. The full length between the accelerated voltages along the evacuated tube was 57 cm. This tube was evacuated several times after refreshing it with oxygen gas to minimize air contamination.

The ignition of microwave (at frequency 2.45 GHz) lunched to boron oxide powder to generate boron ion plasma at fixed gas flow rate that was kept at constant pressure about 0.5 torr. After these steps the ions driving high voltage was applied between the two accelerating plates through a charging capacitor C = 0.5 μF and current control resistance of 6 kΩ.

ISSN 2229-5518

The samples was irradiated with different numbers of ions shoots with constant accelerating voltage 12 KV between the two copper electrodes of 20 and 10 mm outer and inner diameter respectively. The fluence of boron gas irradiation is in the range of 1.62 x 10^{14} to 5.95 x10^{14} ion/cm^2.

3. Results and Discussion

3.1 frequency dependence [12]

The frequency dependence of Ac conductivity versus frequency of the composites with 0,1, 2, 3, 4, 5, and 15 wt. % conductive polypyrrole particles at different fluencies can be expressed by equation (3.1), where the n parameter determines the ac conduction.

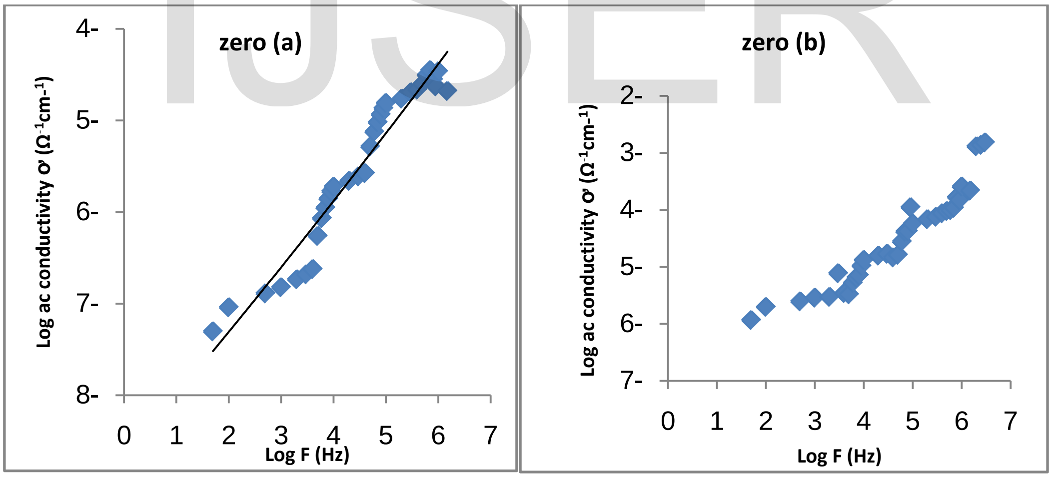
It is evident that all samples have a frequency dependence of the ac conductivity σac given by

σ_{ac} (ω) α ω^n (3.1)

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 logarithmic a.c conductivity are shown in Figures (1 A-F) at room temperature(30 °C) at different B ion fluence for all samples from which it is clear that σ_{ac} (ω) increases linearly with increasing frequency and the conductivity of the implanted layer, in general, increases with fluence beyond a certain value (dependant on the filler loading) and saturates or diminishes after higher fluences of implantation.



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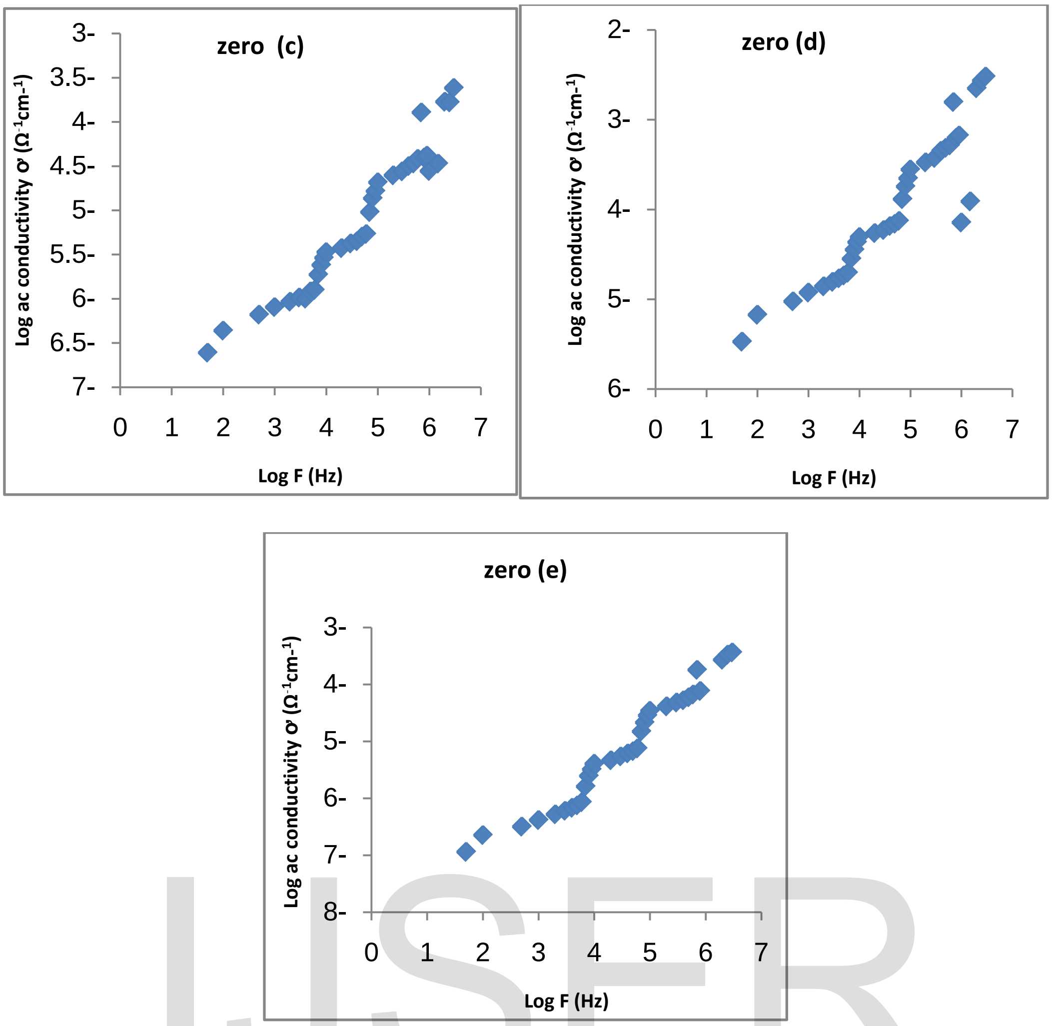
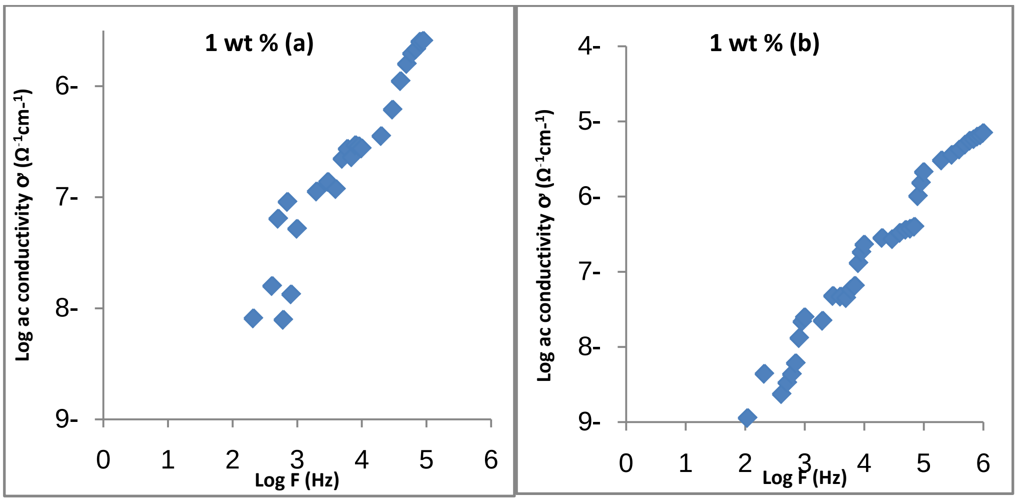
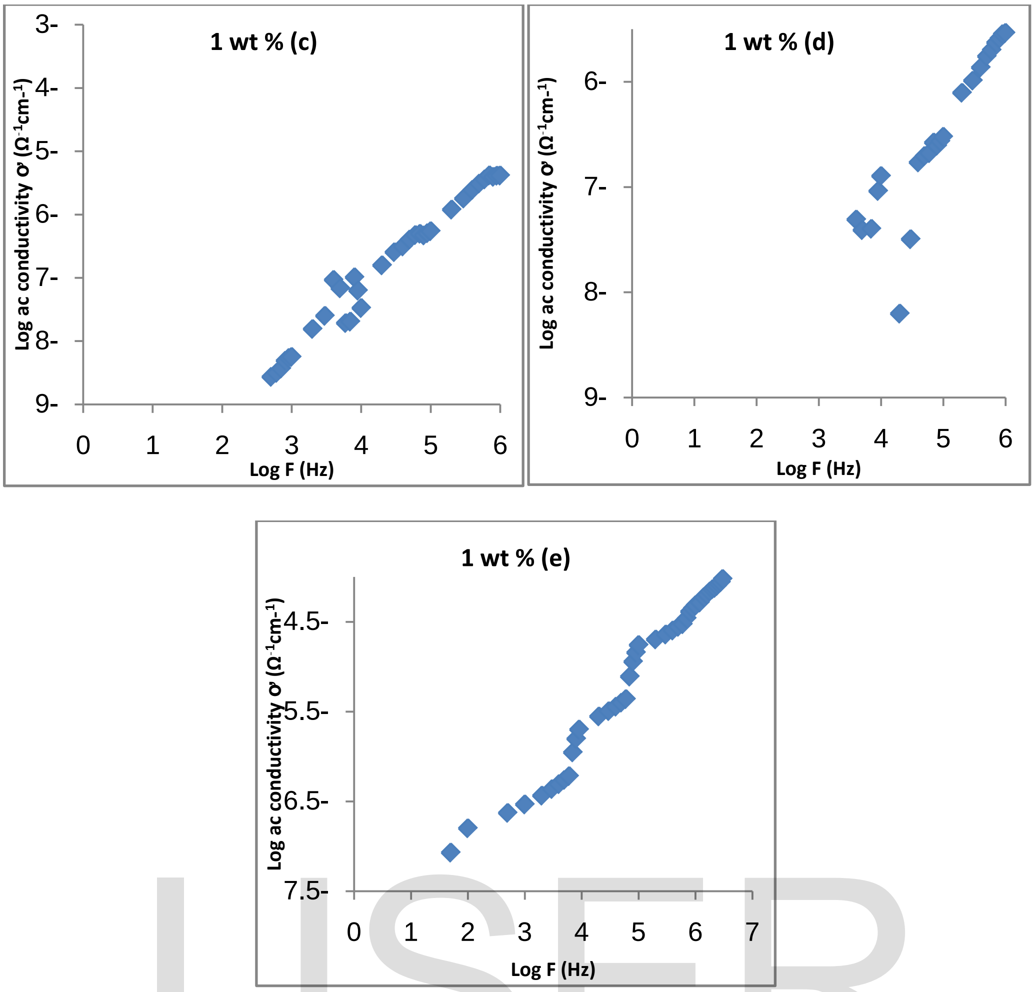
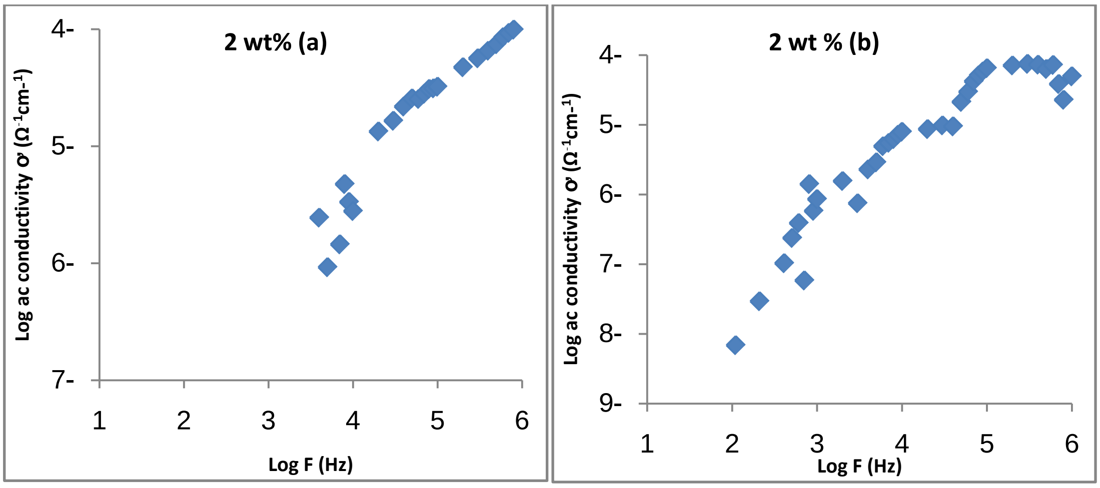


(A)




1 wt % (c)
1 wt % (d)
1 wt % (e)
Log ac conductivity σ' (Ω^{-1}cm-^{1})
Log F (Hz)

(B)


2 wt% (a)
2 wt % (b)
Log ac conductivity σ' (Ω^{-1}cm-^{1})
Log F (Hz)

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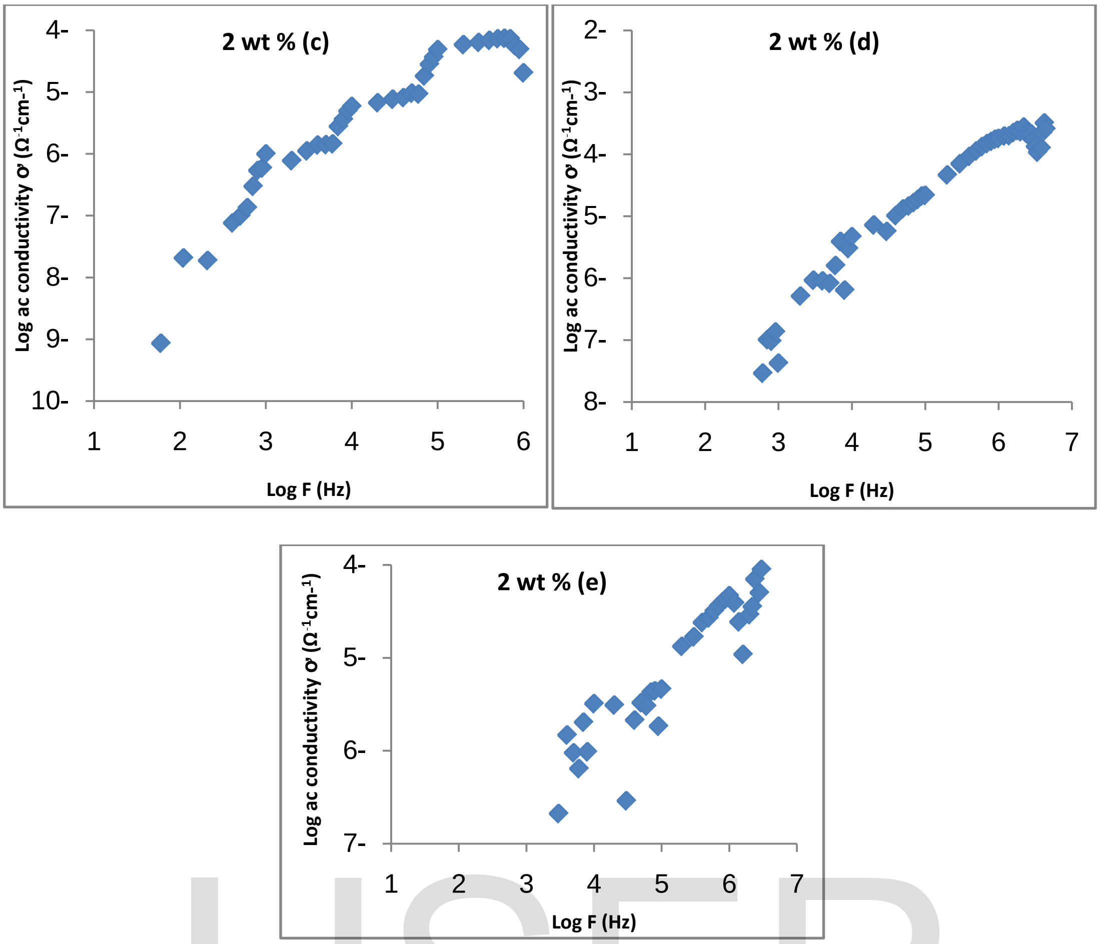
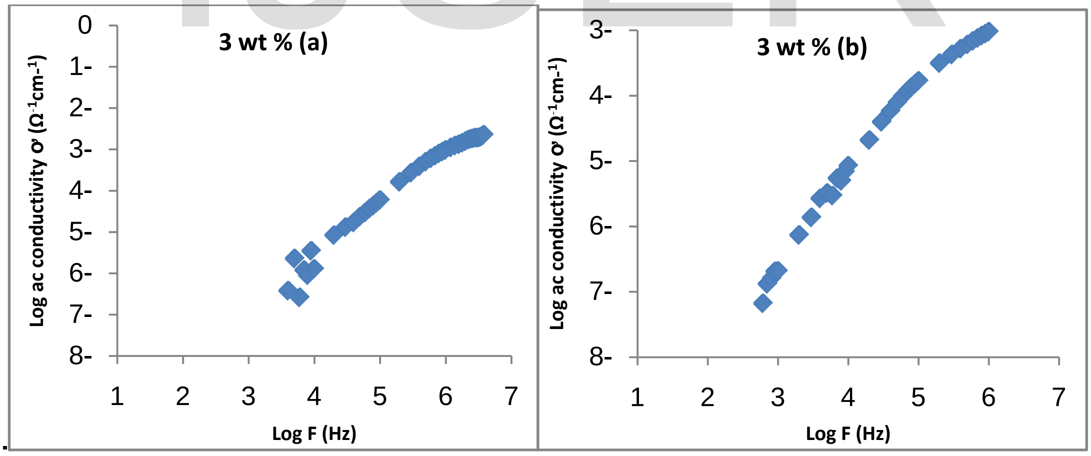
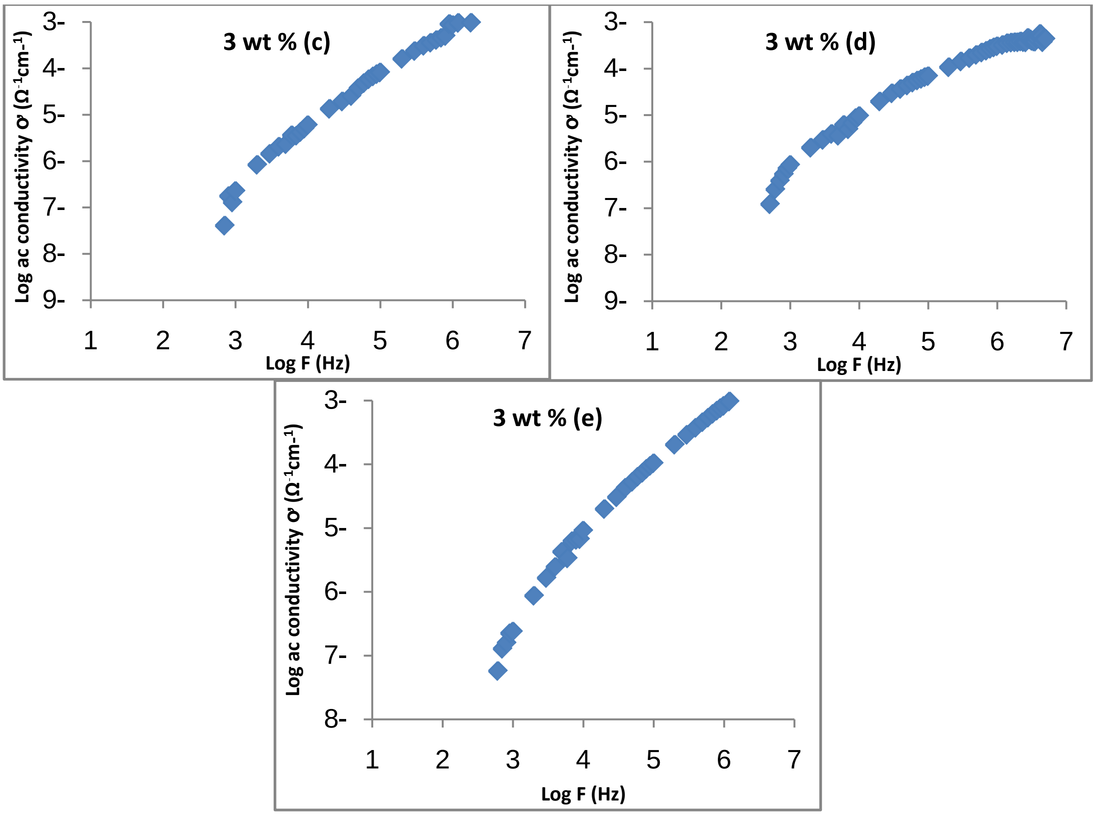
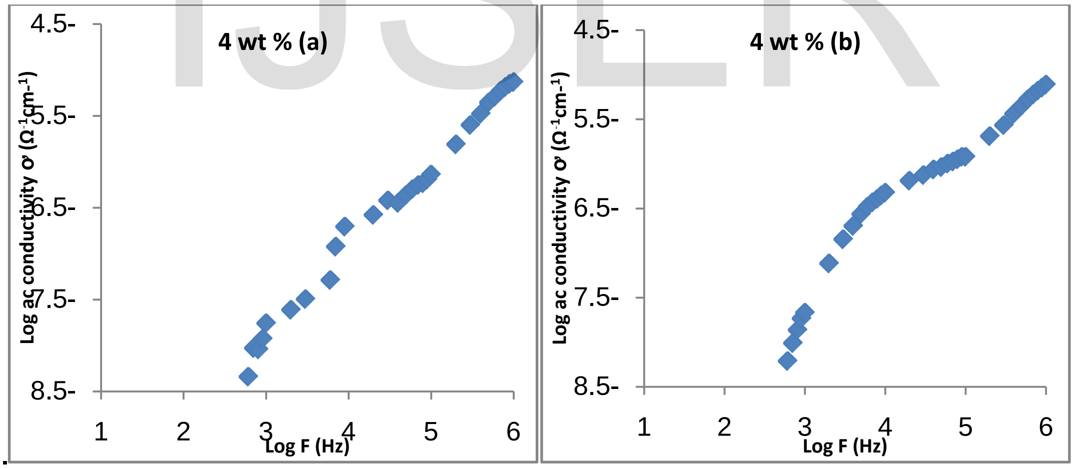


(C)




3 wt % (c)
3 wt % (d)
3 wt % (e)
Log ac conductivity σ (Ω-1cm-1)
Log F (Hz)
3-
4-
5-
6-
7-
8-
9-
1
2
3
4
5
6
7

(D)


4 wt % (a)
4 wt % (b)
Log ac conductivity σ (Ω-1cm-1)
Log F (Hz)
4.5-
5.5-
6.5-
7.5-
8.5-
1
2
3
4
5
6

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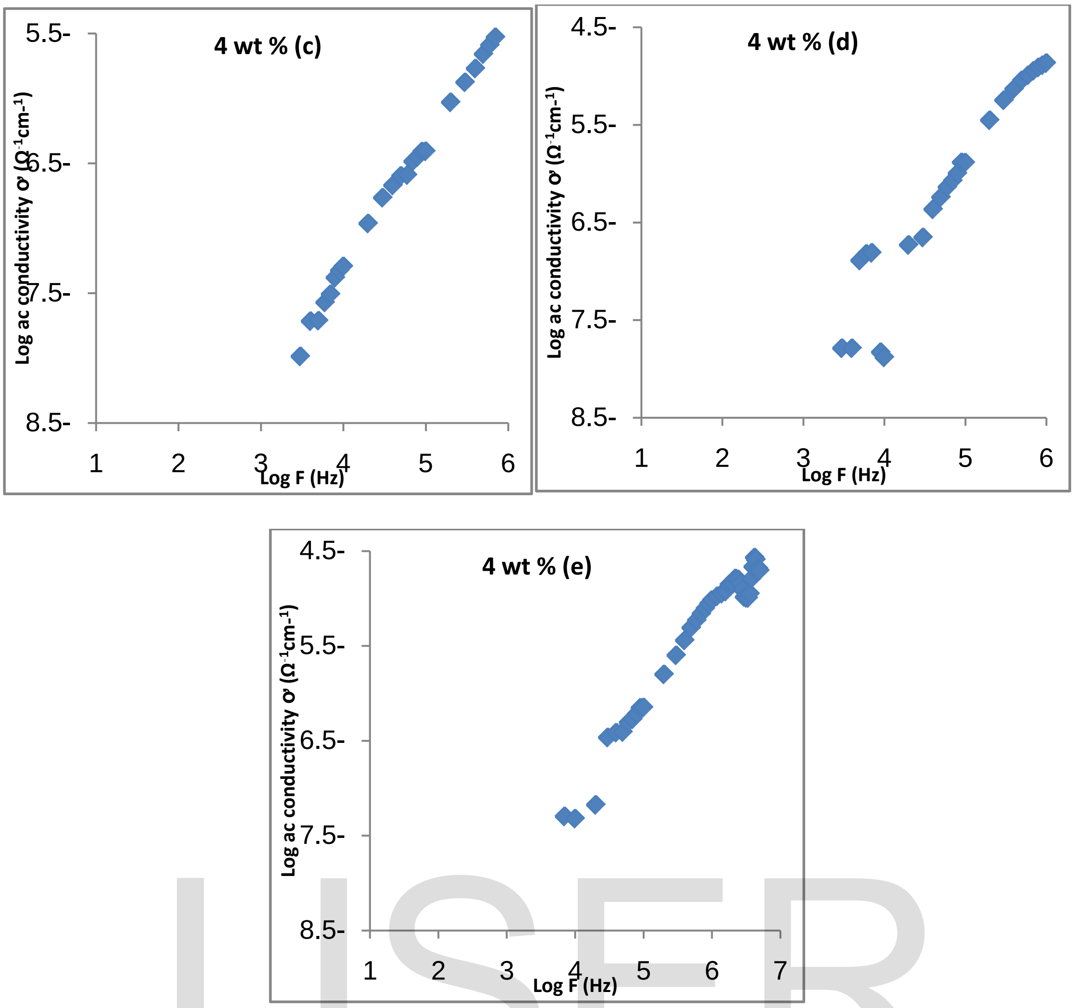

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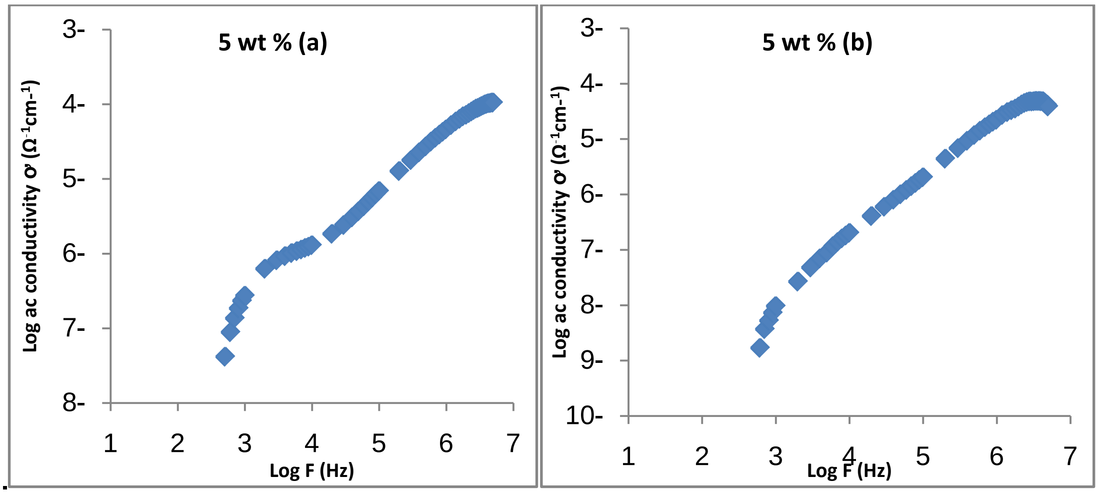

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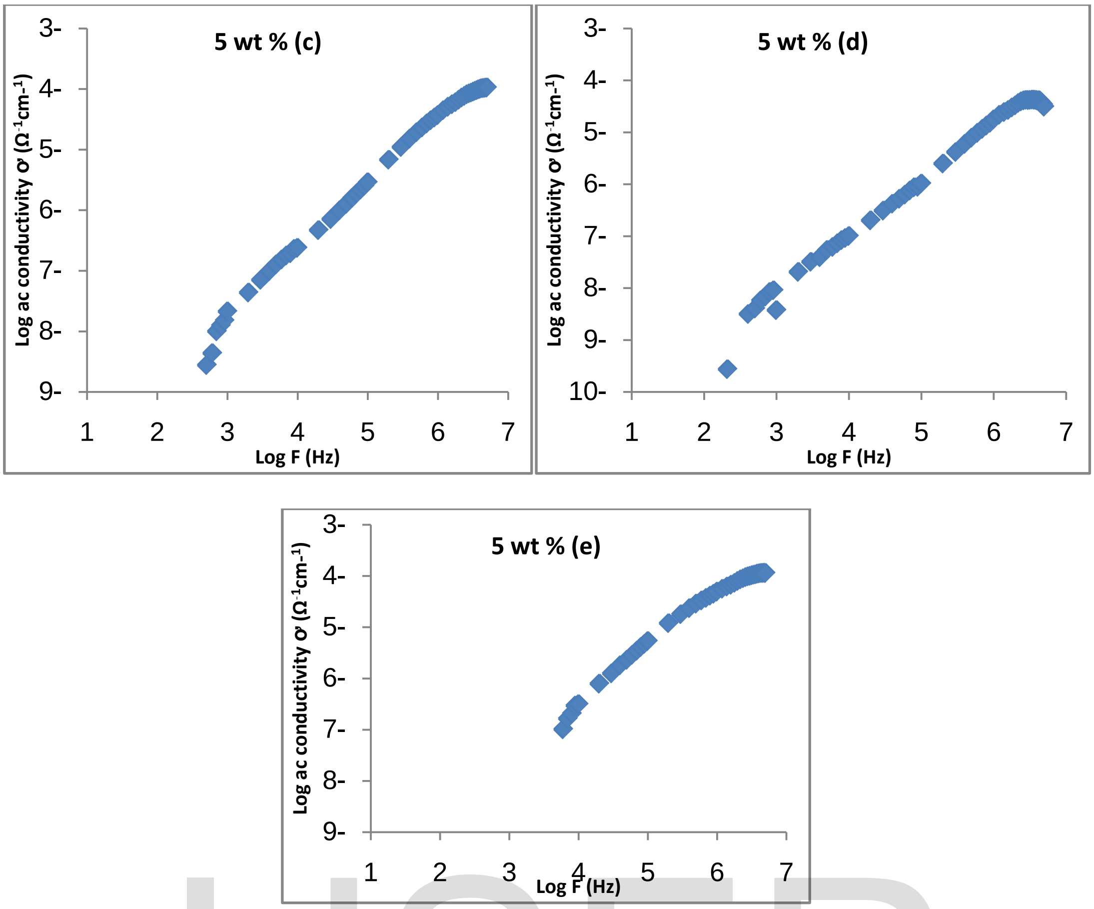


(F)

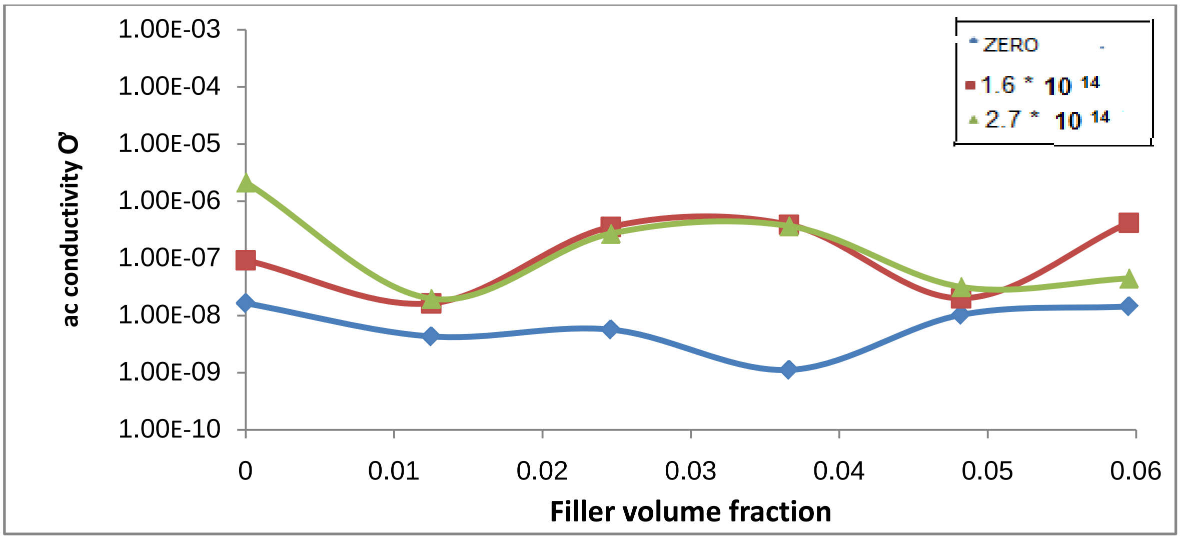
Figures (1 A-F): Dependence of a.c. conductivity on the frequency (on log – log scale) for pure and conductivePVC/PMMA irradiated samples at different fluences (a)1.62x10^{14} ions cm^{-2} (b) 2.7 x10^{14} ions cm^{-2} (c) 3.7 x10^{14} ions cm^{-2} (d) 4.87 x10^{14} ions cm^{-2} (e) 5.95 x10^{14} ions cm^{-2}.

3.2 volume fraction dependence

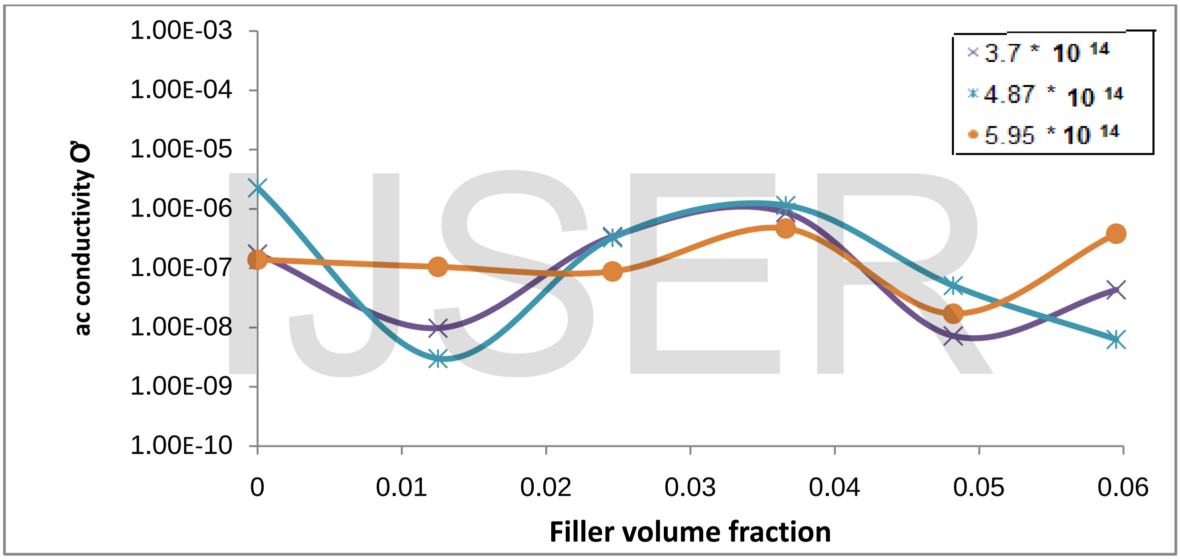
It is found that the ac conductivity σ_{ac} of implanted PVC/PMMA unloaded and loaded samples with conductive polypyrrole are influenced by the ion species and implanting dose. The relations between $\sigma_{ac}$of implanting PVC/PMMA composites and PPy

contents at a dose of 1.62 x 10^{14} ion cm^{-2} to 5.95 x 10^{14} ions cm^{-2} are given in Figures (2 a, b).

It is known that any ion passing through an organic polymer produces both degradation and crosslinking of the carbon chains. Chain degradation is a consequence of nuclear collisions causing atomic displacements and breaking of the C-C bonds. Crosslinking is due to the formation of dangling bonds by electronic excitation and joing of these bonds when they are in neighboring chains.



(a)



(b)

Figures (2 a, b): Dependence of ac conductivity σ_{ac} on the volume fraction ofconductive PPyfor PVC/PMMA composites irradiated at different fluences.

3.3 Theoretical background

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:

$$n = 1 - \frac{4}{\ln\left(\frac{1}{\omega T}\right)} \quad (3.2)$$

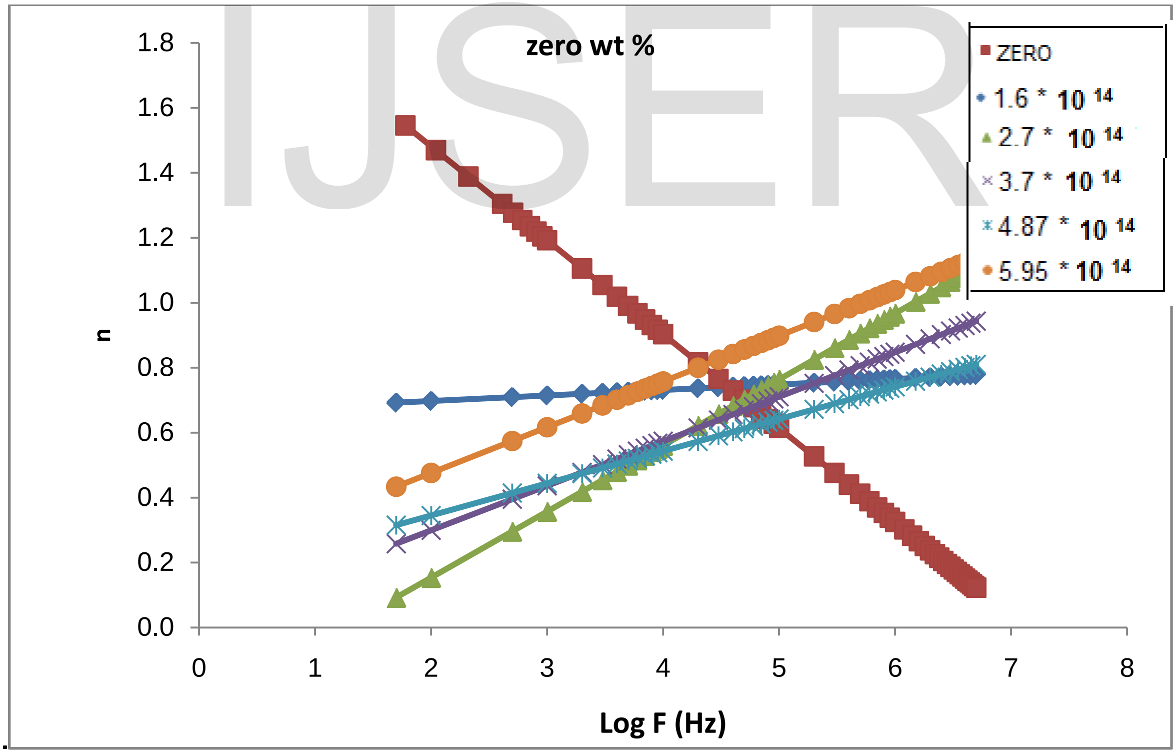
Thus σ (ω) is linearly depended on temperature and n is temperature independent [13].

The correlated barrier hopping model (CBH) was proposed by Pika[14] and the frequency exponent n in this model is evaluated to be:

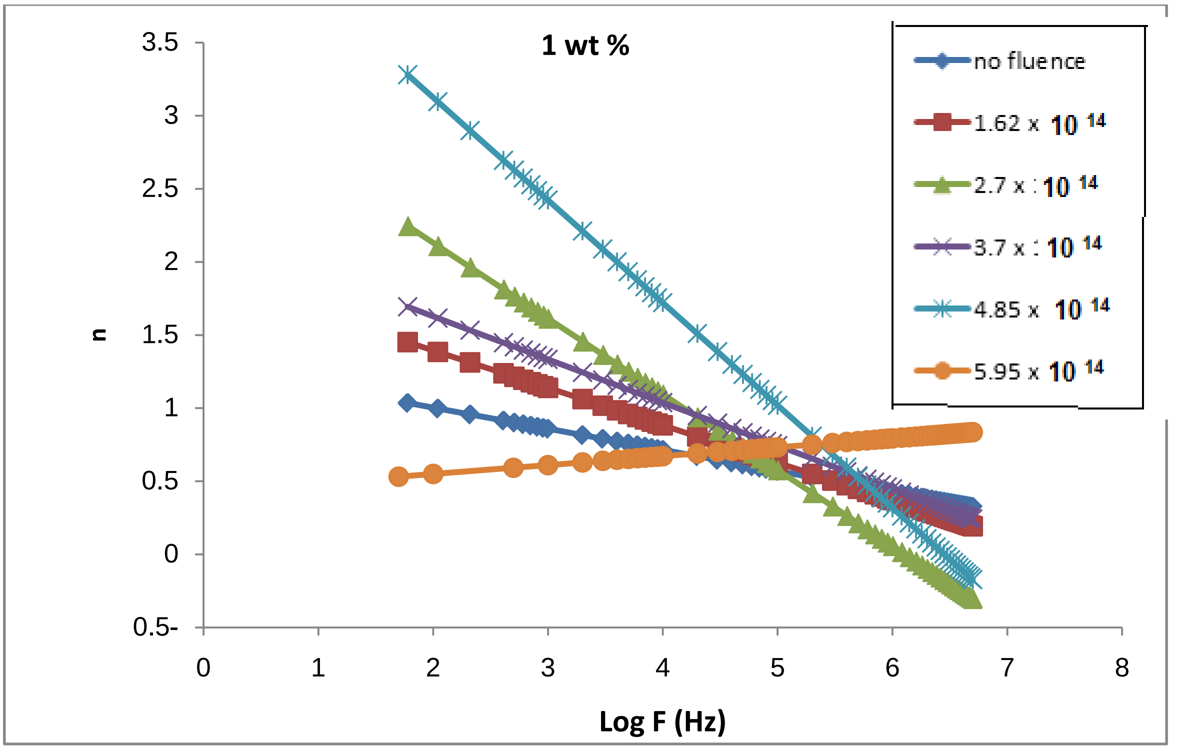
$$n = 1 - \frac{6\,KT}{\left(Fm - KT\ln\left(\frac{1}{fT}\right)\right)} \qquad (3.3)$$

Where Fm is the maximum barrier height.

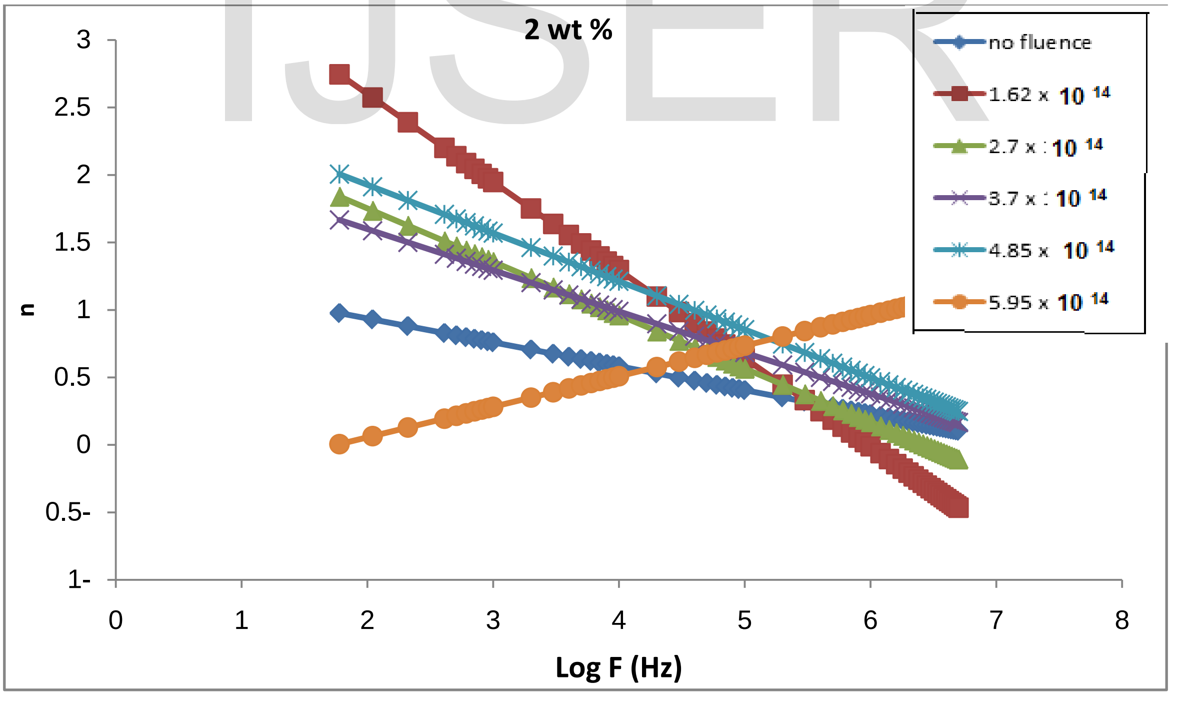
The frequency exponent value, n, was calculated. The change of n with frequency at different B ion fluence for all samples are shown in Figures (3a-f) from which it is apparent that the values of n decrease with increasing frequency for all samples indicating the applicability of the QML model. Meanwhile, it increases with frequency for samples pure PVC/PMMA at different fluences, 1 wt % loaded at fluence of 5.95×10^{14} ions cm^{-2}, and 2 wt % at fluence of 5.95×10^{14} ions cm^{-2}, indicating the predomination of hopping conduction mechanism. B ion fluences change the type of conduction mechanism for samples PVC/PMMA at different fluences, 1, and 2 wt. % at 5.95×10^{14} ions cm^{-2}.



(a)

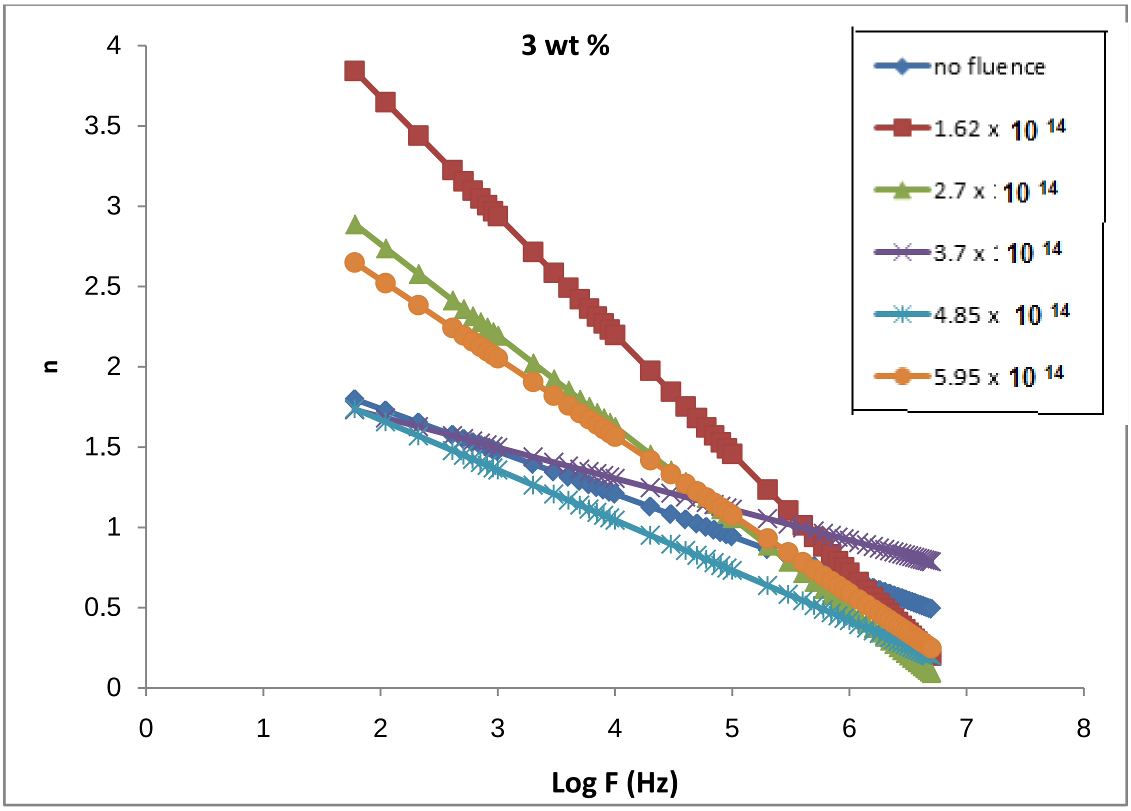

1 wt %
n
Log F (Hz)
no fluence
1.62 x 10 14
2.7 x 10 14
3.7 x 10 14
4.85 x 10 14
5.95 x 10 14

(b)

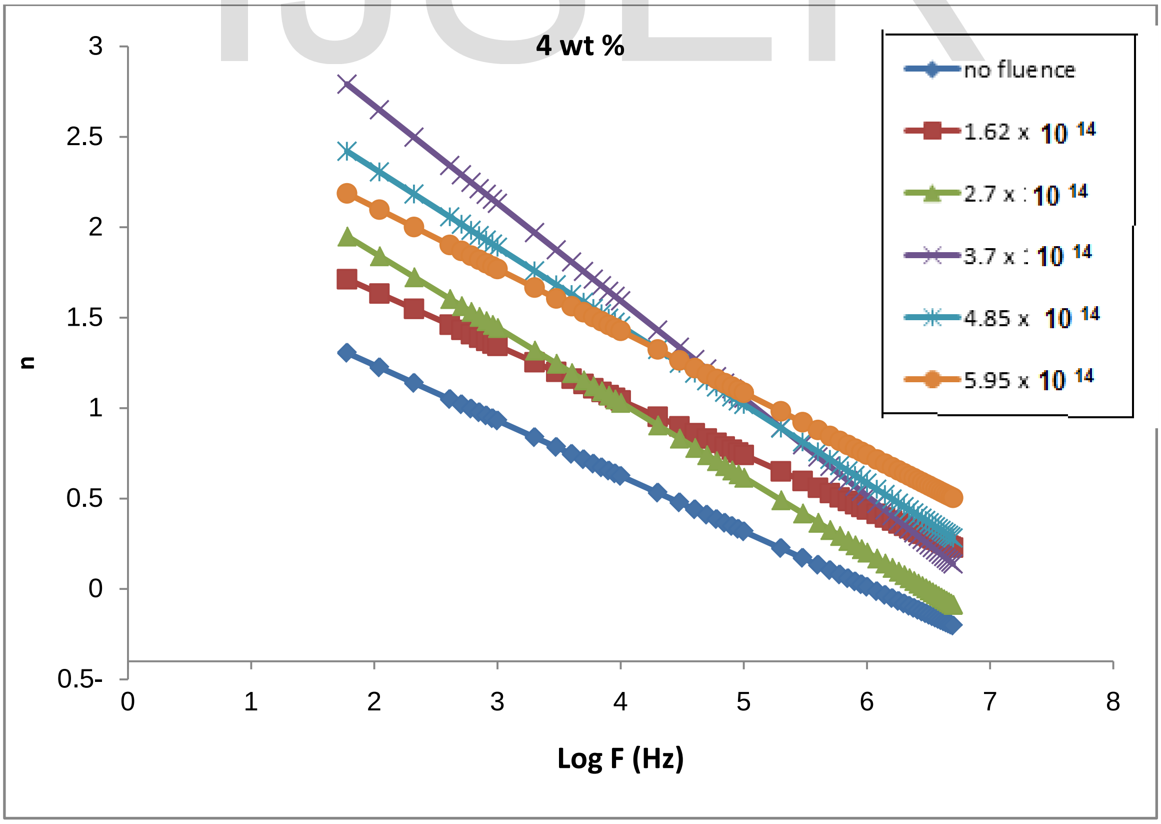

2 wt %
n
Log F (Hz)
no fluence
1.62 x 10 14
2.7 x 10 14
3.7 x 10 14
4.85 x 10 14
5.95 x 10 14

(c)

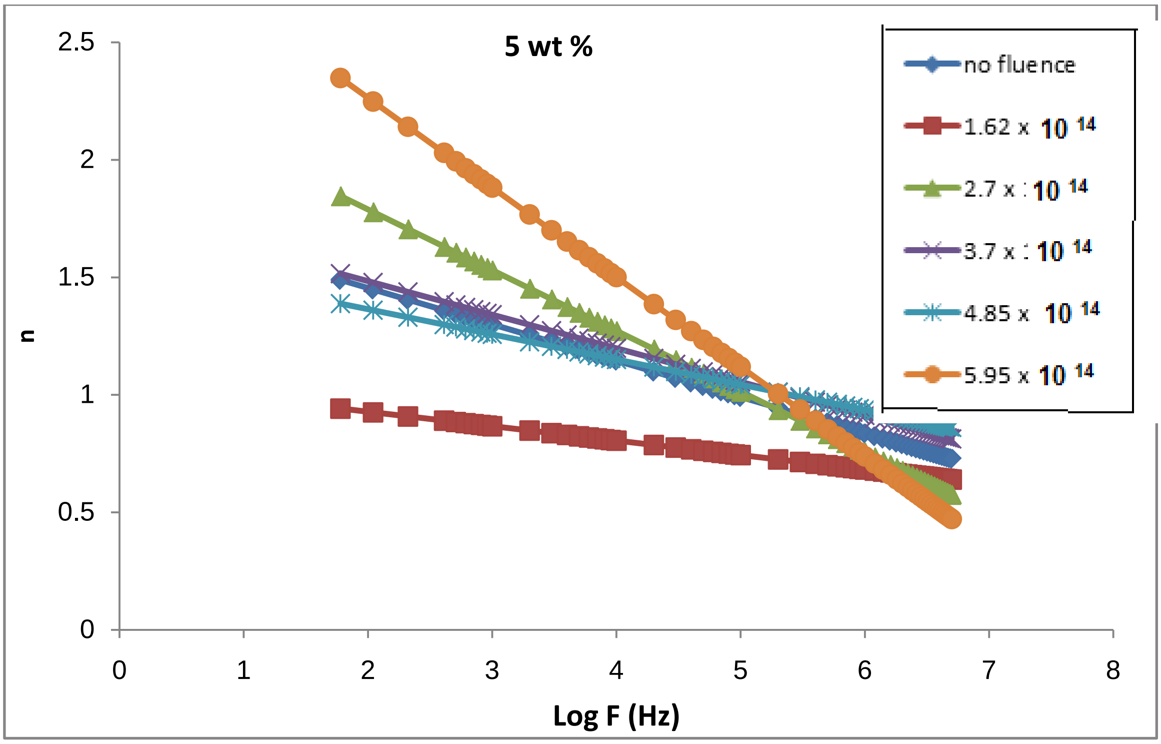
ISSN 2229-5518



(d)



(e)



(f)

Figures (3a-f): The variation of frequency exponent n with frequency for pure and conductive PVC/PMMA samples under different fluences.

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). A. C Electrical behaviors of such materials were investigated.

A.c conductivity σ_{ac} obviously increases after ion implantation. The higherσ_{ac} of PVC/PMMA after implantation will be got by implantation for samples loaded with 3 wt. % PPy conductive filler.The irradiation with B ions at 4.87 x 10^{14} ions cm^{-2} increases σ_{ac} of sample PVC/PMMA loaded with 3 wt. % PPy by 3 orders of magnitude.The frequency exponent value, n, was calculated.

The values of n decreased with increasing frequency for all samples indicating the applicability of QML model. Meanwhile, it increases with frequency for pure PVC/PMMA at different fluences, 1 wt. % at fluence of 5.95x10^{14} ions cm^{-2}, and 2 wt. % at fluence of 5.95x10^{14} ions cm^{-2} indicating the predomination of hopping conduction mechanism. B ion fluences change the type of conduction mechanism for samples pure PVC/PMMA at different fluences, 1, and 2 wt. % loading at 5.95x10^{14} ions cm^{-2}.

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 toDr. Ah.AbdElbary, Doctor of experimental physics, Higher Institute of

Engineering and Technology, New Cairo Academy for his help to finish this work.

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