Influence of B ion irradiation on the dielectric properties of conductive PPy on PVC/PMMA composites

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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. In the present study the Influence of B ion irradiation on the dielectric properties is examined with varying parameters, the filler content and the frequency in the case of ac field. The effect of irradiation on the dielectric constant of pure PVC/PMMA and PVC/PMMA loaded with conductive PPy filler blends was studied. Ɛ' obviously increase after ion implantation. The behavior of ε' – frequency curves does not change appreciably with irradiation fluence but its values are highly affected especially for samples loaded with 2 and 3 wt. % of PPy filler. It can be readily noted that irradiation at 1.62 x 1014 ions cm-2 increases ε' of sample PVC/PMMA loaded with 2 and 3 wt. % PPy by approximately seven times its initial value. Irradiation at 5.97 x 1014 ions cm-2 increases ε' of sample PVC/PMMA loaded with 3 wt. % PPy by 3 orders of magnitude.

Keywords: Dielectric constant, ion implantation, conductive PPy, electrical Properties, PVC/PMMA composites

INTRODUCTION

The process of ion implantation appeared on the metallurgical scene in the 1970s as a result of the pioneering work at Harwell in the UK [1] and the Naval Research Laboratory in the USA [2]. This work was driven by the desire for improved wear resistance in industrial tools and the initial focus was on the implantation of the nitrogen into steels using accelerating voltages of around 100 kV and at temperatures of 100C or lower, resulting in penetration of the ions to depths of the order of 0.1 μm[3].

The interest in ion bombardment of polymers arises from the possibility to alter their near-surface properties in a controlled way. For example, implantation of B, C, N or Fe ions with energies of several hundreds of keV, considerably improves the hardness and wear resistance of Kapton and other polymers [4]. These property changes are the consequence of irreversible modifications of the polymer structure. The major processes which alter the chemical composition and the molecular weight during irradiation are (1) radical formation, (2) formation of carbon-carbon multiple bonds, (3) loss of volatile molecules, (4) main chain scission, and (5) intermolecular crosslinking. In particular, main-chain scission produces effectively molecules of smaller molecular weight, an effect which is detrimental for mechanical strength. Vice versa, intermolecular crosslinking leads to an increase in the molecular weight via the formation of a chemically bonded network. Therefore, crosslinking enhances the mechanical strength, resistance to solvents and thermal stability [5-7].

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 dielectric constantof composite systems is examined with varying parameters 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 employed and

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applied on ac data. The observeddielectric response of the composites will be examinedusing models for Effective Dielectric Constant.

2. EXPERIMENTAL
2.1 Materials and Preparation of sample[(8)]

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 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 the dielectric constant ε' (real part of the dielectric constant) of the samples was calculated by using the relation (2.1)at different frequencies.

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

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 voltage 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.

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 1.62×10^{14} to 5.95×10^{14} ion/cm^2.

3. RESULTS AND DISCUSSION
3.1 frequency dependence

Dielectric relaxations are present in these composites and can be investigated via dielectric spectroscopy. However, because of the presence of conductive particles, dielectric relaxations may be obscured, as for example in the case of interfacial polarization observed in heterogeneous systems [9].

The dielectric constant ε′ versus frequency of the composites with 0,1, 2, 3, 4, 5, and 15 wt. % conductive polypyrrole particles at different fluenciesare shown in Figures (1 a-f) at room temperature(30 °C). In the low frequency region, ε′

reaches value which drop to the normal one for these composites, as the frequency increases, indicating the existence of the dielectric relaxation. This could be explained on the bases that when conductive particles are dispersed in a non-conductive matrix, the dielectric constant of the resulting composites increases with the weight fraction of the filler, as theory predicts [10, 11], and has been experimentally found [12-14].

In the region of low frequency, dielectric constant attains high values which decreases as frequency increases as shown in Figure (1 a-f). This behaviour depicts a relaxation process that is attributed to an interfacial polarization, known as Maxwell-Wagner-Sillars (MWS) effect [15, 16], and a phenomenon appearing in heterogeneous media due to the accumulation of charges at the interfaces.
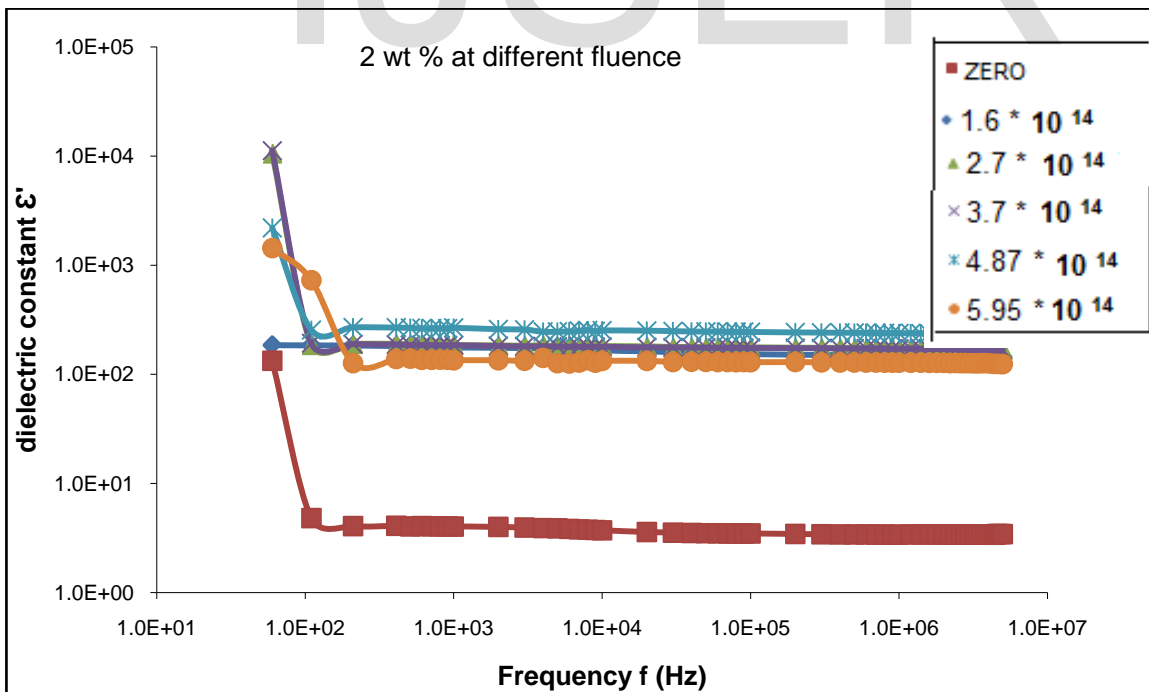All irradiated samples have been subjected to test the dependence of its dielectric constant on frequency at different fluenceand The behavior of ε' – frequency curves does not change appreciably with irradiation fluence but its values are highly affected especially for samples loaded with 2 and 3 wt. % of PPy filler.
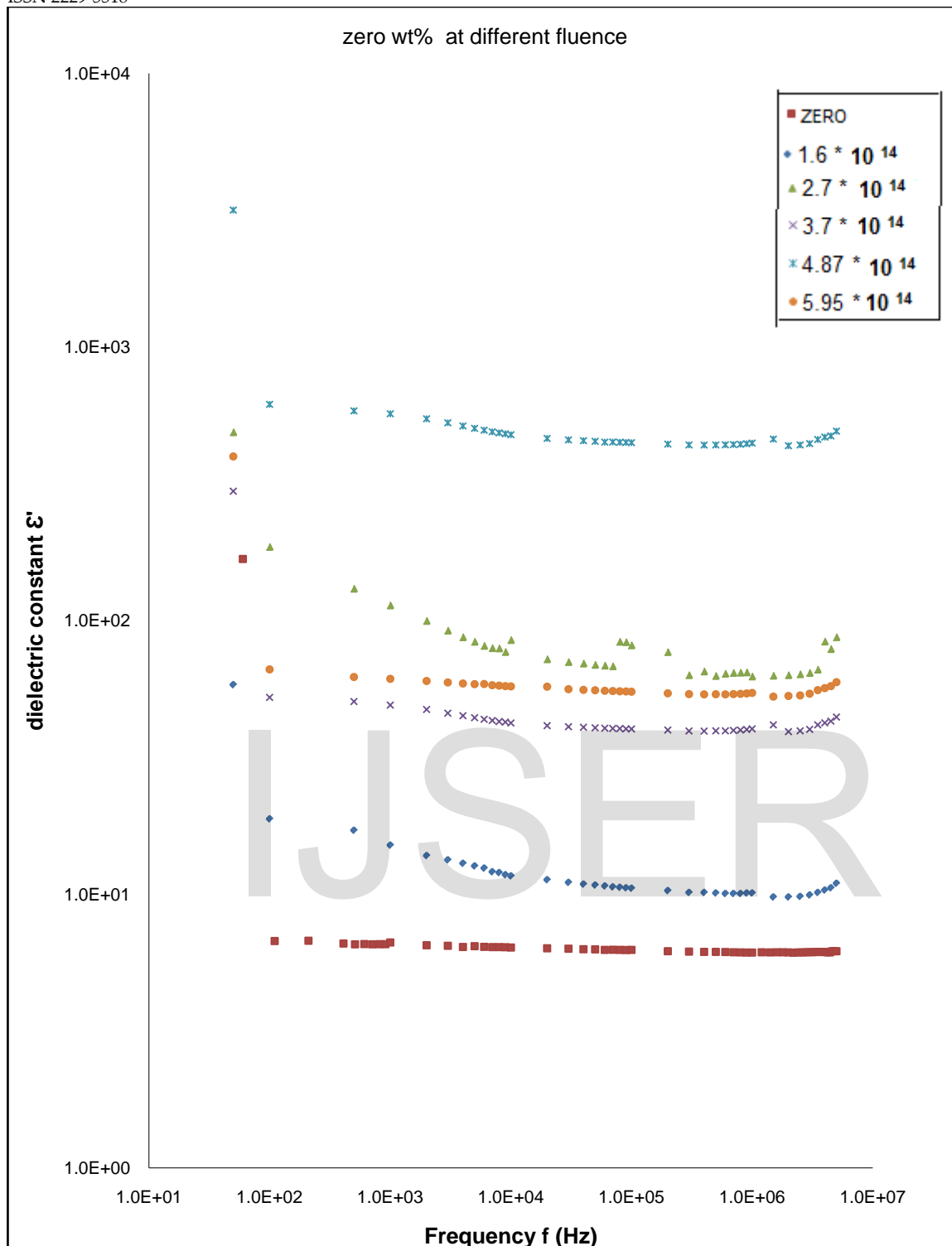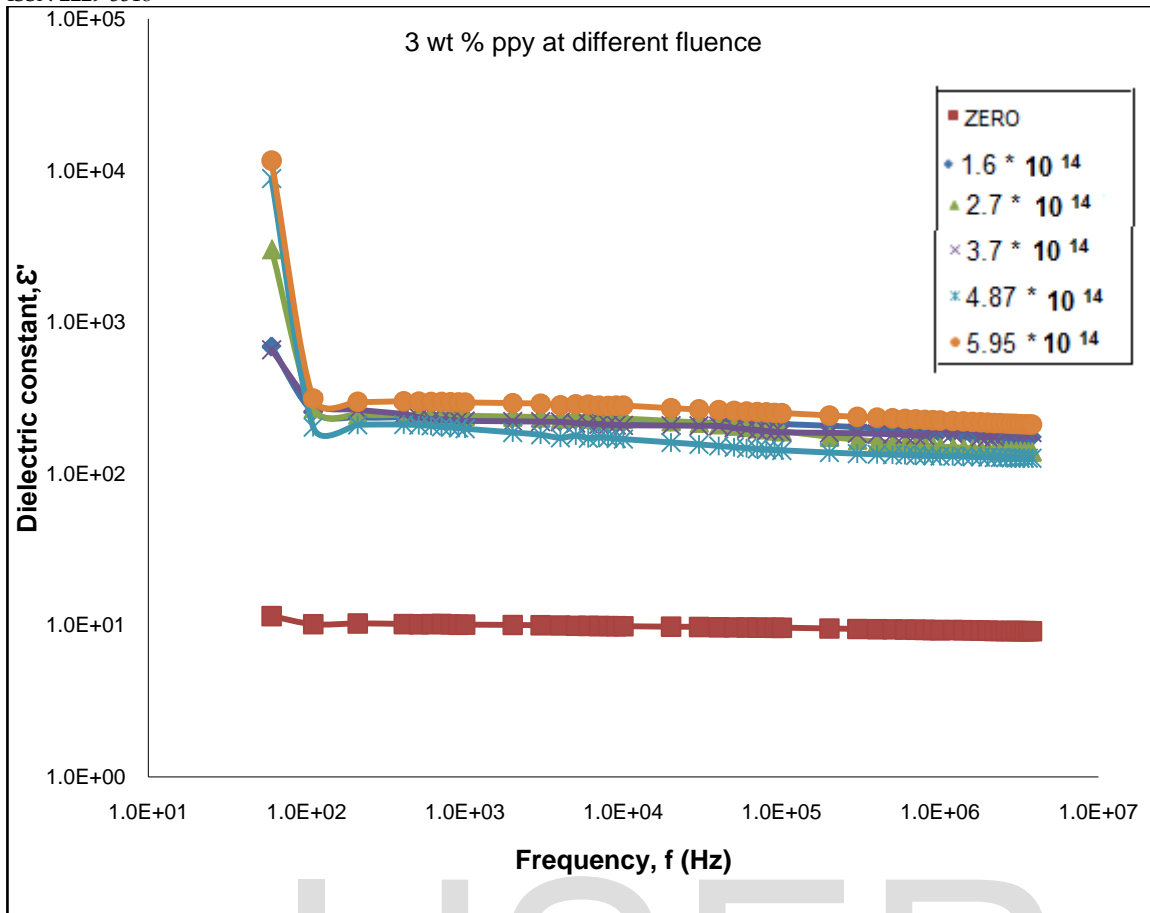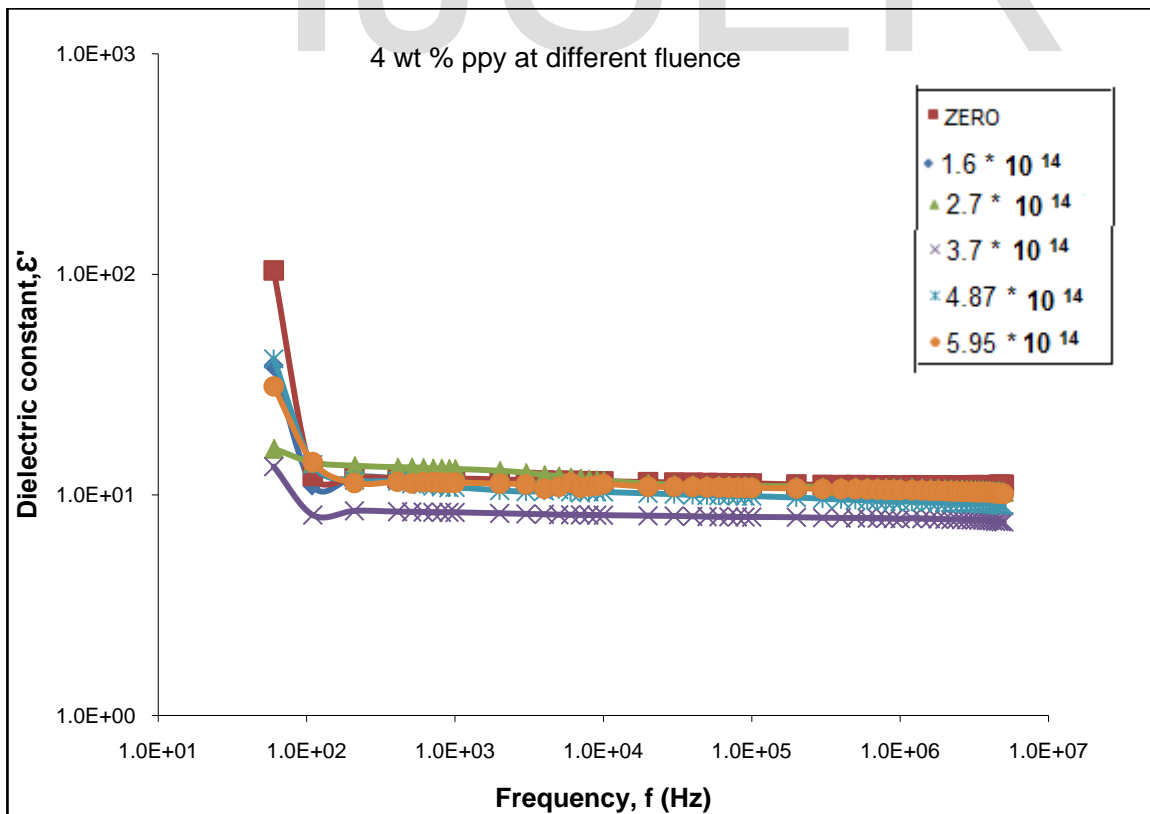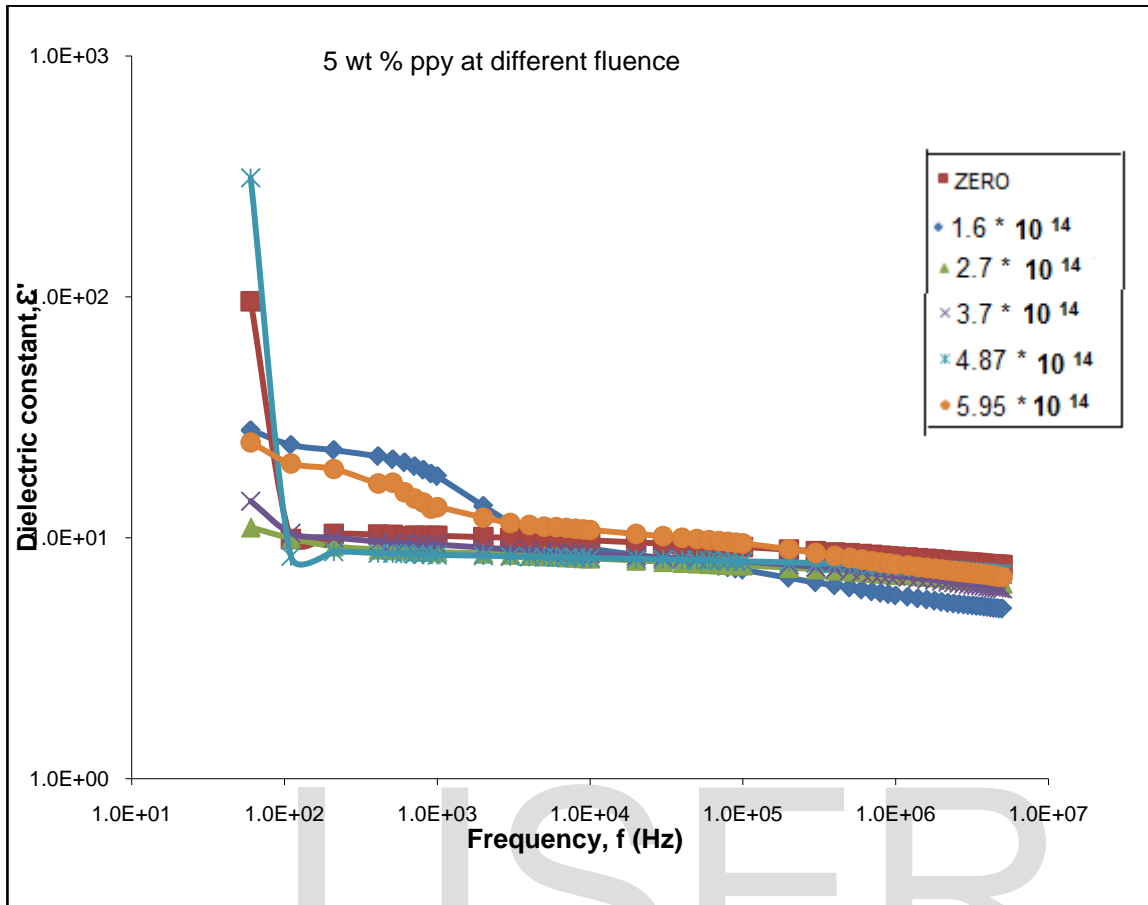
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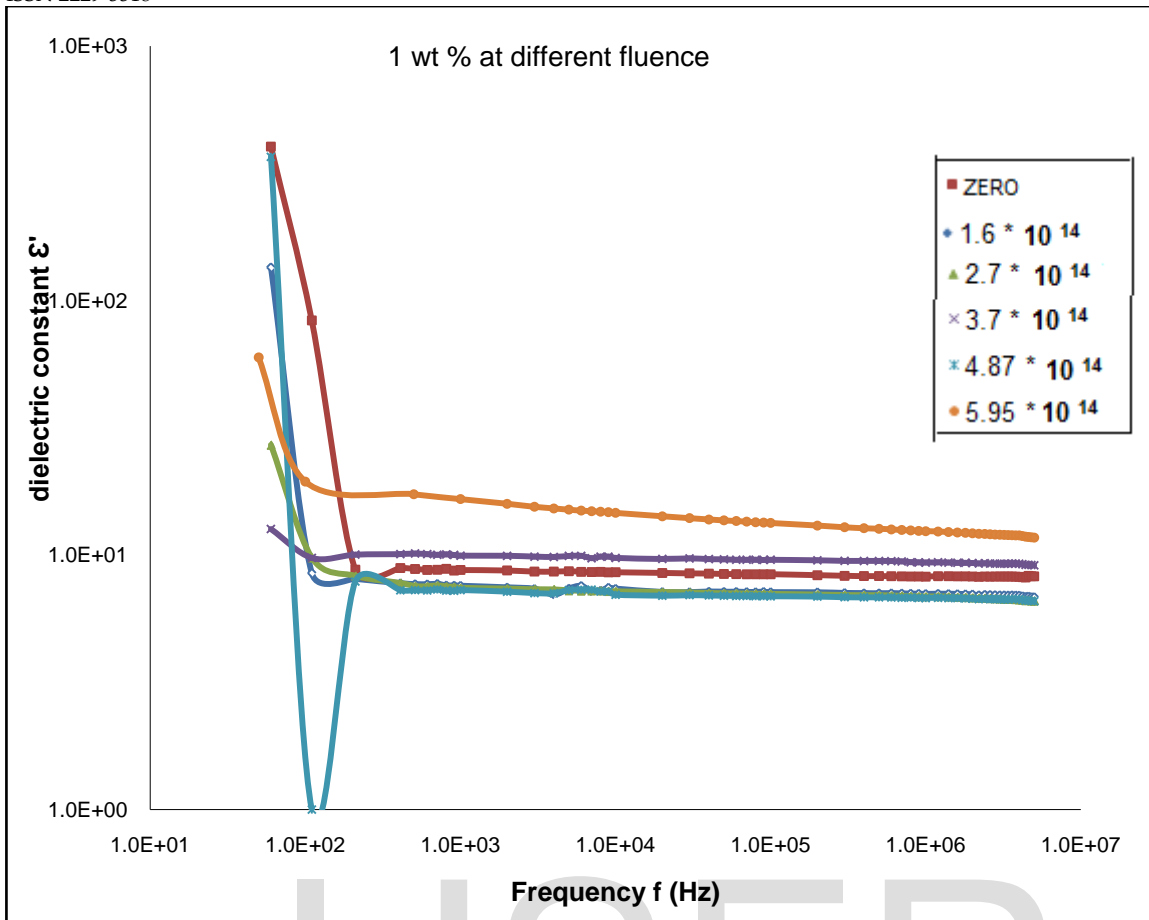
(b)

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(f)

Figures (1 a-f): frequency dependence of the dielectric constant for conductive PVC/PMMA samples irradiated at differentfluencies.
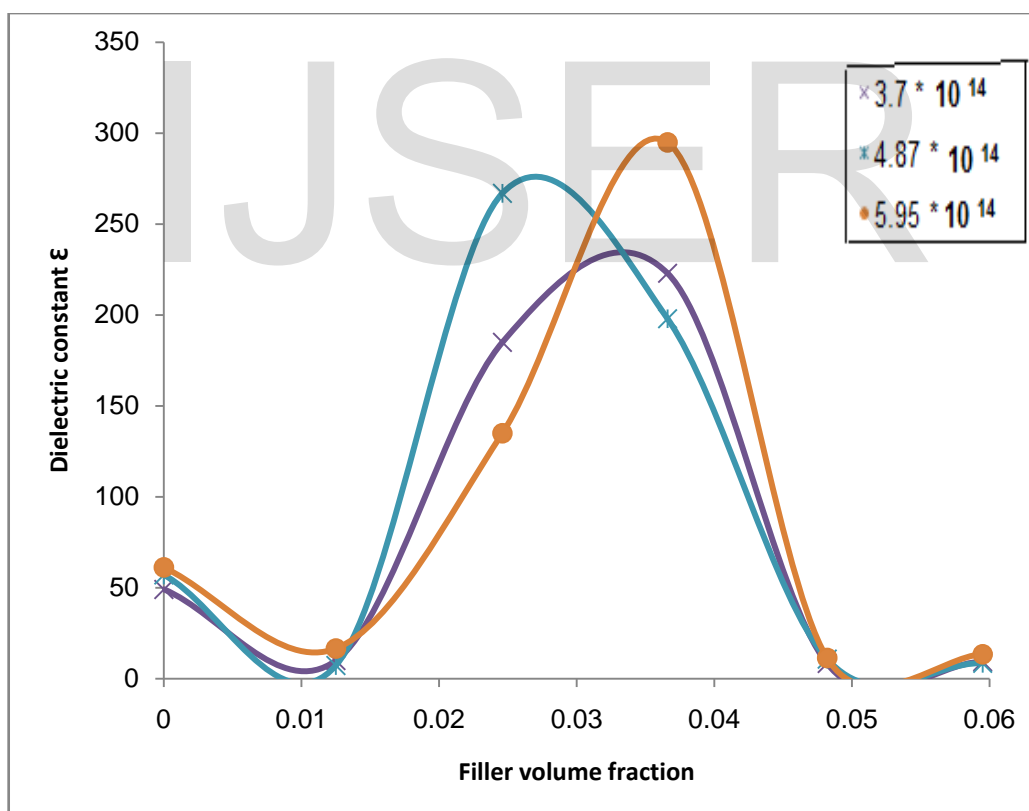
3.2 volume fraction dependence

It is found that the dielectric constant ε' of implanted PVC/PMMA unloaded and loaded samples with conductive polypyrrole are influenced by the ion species and implanting dose. The relations between ε' of implanting PVC/PMMA composites and PPy contents at a dose of 1.62×10^{14} ion cm^{-2} to 5.95×10^{14} ions cm^{-2} are given in Figures (2 a, b).

It is found that ε' obviously increase after ion implantation. The higher ε' of PVC/PMMA after implantation were affected by implantation of samples loaded with 3 wt % and 4 wt. %PPy conductivefiller.
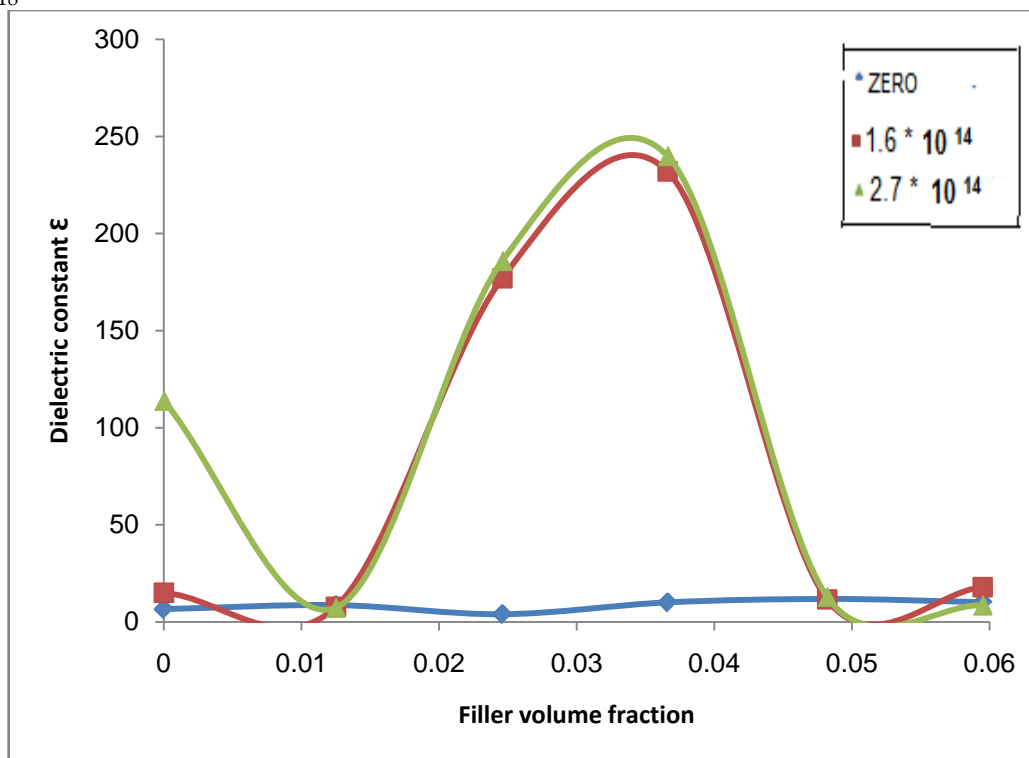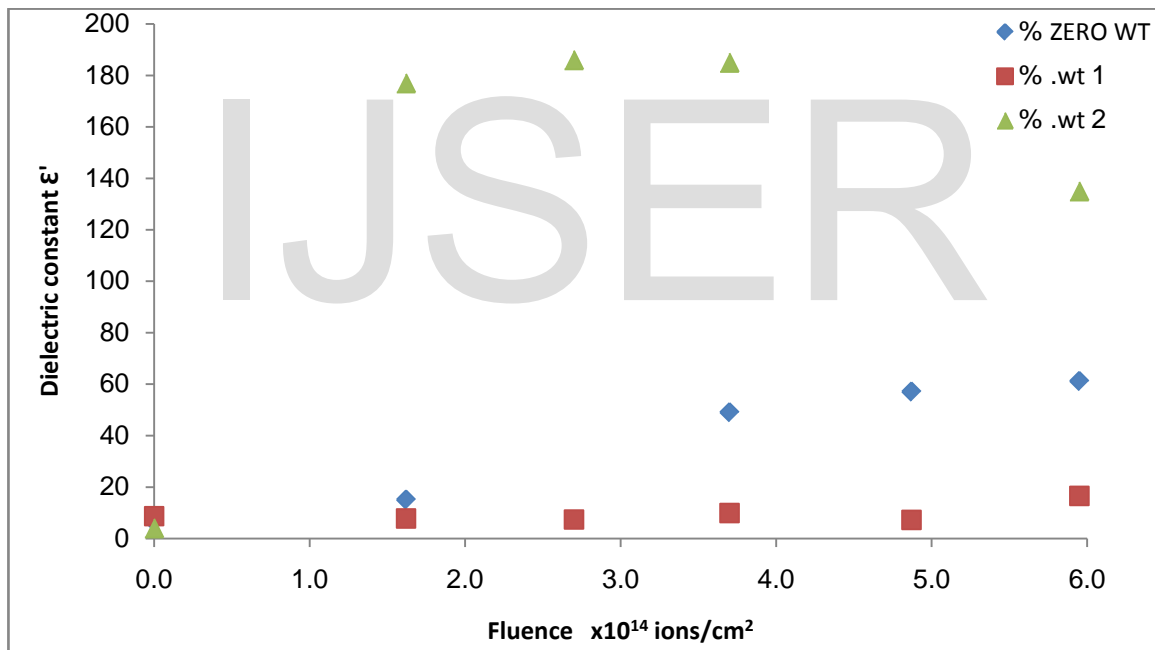
(a)

(b)

Figures (2 a, b): Dependence of dielectric constant on the volume fraction ofconductive PPyfor PVC/PMMA

composites irradiated at different fluences.

Figures (3a, b) show the experimental results of the relation between ε' with implanting dose of B in PVC/PMMA composites with dose range from 1.62 x10^{14} ions cm^{-2} to 5.95 x10^{14} ion cm^{-2}. Samples of PVC/PMMA loaded with 1, 4, and 5 wt. % of PPy show approximately independent behavior of its dielectric constant on the B ion fluence (in the studied range) and still show the characteristics of the pristine samples. Meanwhile, samples loaded with 2 and 3 wt. % show an appreciable change of their dielectric constant with implanting dose.

It can be readily noted from Figures (3 a, b) that irradiation at 1.62 x 10^{14} ions cm^{-2} increases ε' of sample PVC/PMMA loaded with 2 and 3 wt. % PPy by approximately seven times its initial value.

The increase in ε' with B ion irradiation arises from some structural changes that contribute to the increase in ε' likes the formation of crosslinks since the charge carrier mobility is enhanced by the connected paths across the polymer chains.

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)
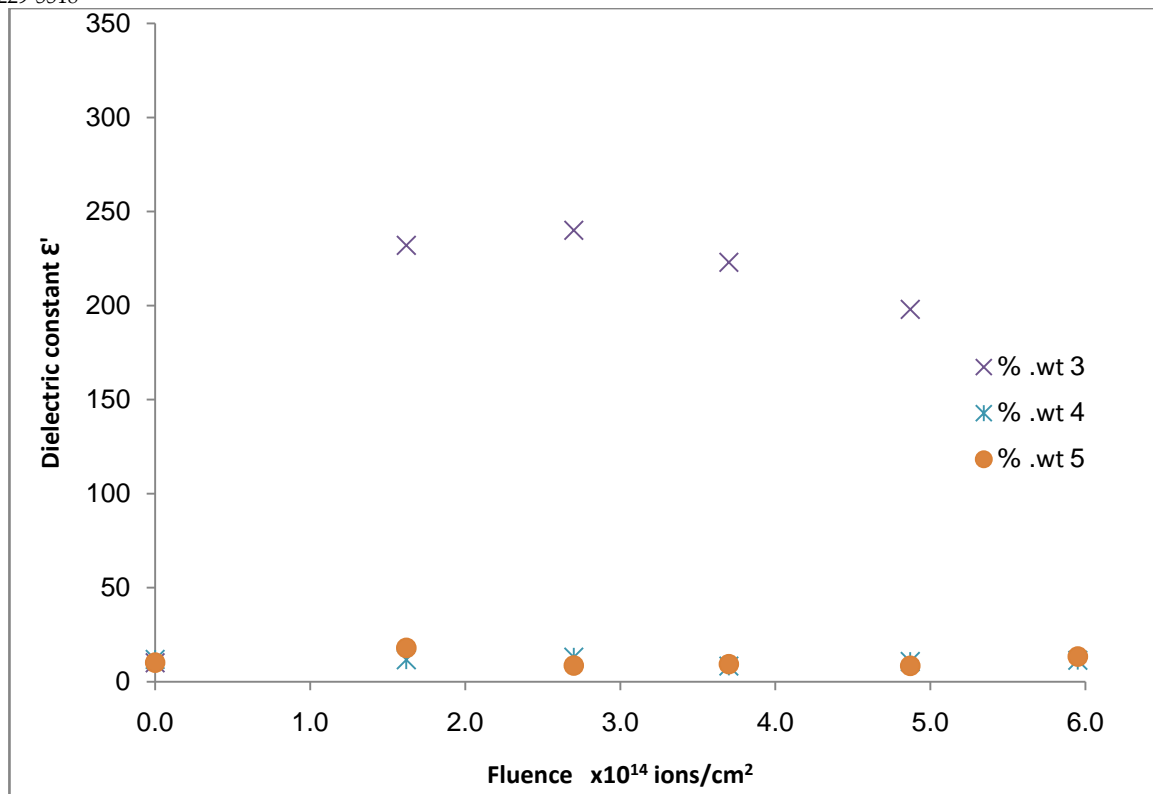
(b)

Figures (3a, b): Dependence of dielectric constant on thefluence for pure and conductive PVC/PMMA

composites irradiated at different fluences.

3.3 Theoretical background

3.3.1. Models for Effective Dielectric Constant [17]

There are different models for computing the effective dielectric constant of nanocomposites. These models are summarized as follows:

a- Maxwell–Garnett (MG) model

In this model, the effective dielectric constant of the composite (ε_c) can be computed using equation. (3.1). This model is based on a mean field approximation of a single spherical inclusion surrounded by a continuous matrix of polymer [18].

$$\varepsilon_c = \varepsilon_2 \frac{\varepsilon_1(1 + 2\varphi_1) - 2\varepsilon_2(\varphi_1 - 1)}{\varepsilon_2(2 + \varphi_1) + \varepsilon_1(1 - \varphi_1)} \quad (3.1)$$

Where ε_1 and ε_2 are the filler and matrix dielectric constants, respectively. Φ_1 is the filler volume fraction. This model did not take into consideration the effect of interaction zone between the filler particles and the base polymer matrix .As well as the effect of particle shape and orientation.

b- BŌttcher Mixture (BM) model

Another mean field theory, known as the BŌttcher model, treats the binary mixture as being composed of repeated unit cells composed of the matrix phase with spherical inclusions in the center. According to this model, the effective dielectric constant of the composite (ε_c) can be calculated using equation. (3.2).

$$\varphi_1 \frac{\varepsilon_1 - \varepsilon_c}{\varepsilon_1 + 2\varepsilon_c} + (1 - \varphi_1) \frac{\varepsilon_2 - \varepsilon_c}{\varepsilon_2 + 2\varepsilon_c} = 0. \quad (3.2)$$

Similar to MG model, BM model did not give accurate results for the same reasons mentioned in MG model.

The Power –Law model was developed to overcome this disagreement.

c- Power-law model

According to Power - Law model [19], the effective dielectric constant of a composite (ε_c) can be calculated using equation. (3.3).

$$\varepsilon_c^\beta = \varphi_1 \varepsilon_1^\beta + (1 - \varphi_1)\varepsilon_2^\beta \tag{3.3}$$

Where ß is a dimensionless parameter depending on the shape and orientation of the filler and can be computed from equation (3.4) [20].

$$\beta = 1 - 2\left[\frac{1}{1 + 1.6(a:b) + 0.4(a:b)^2}\right] \tag{3.4}$$

Where a and b are the axial dimensions of the particle. When a = b this means a spherical particle. At this condition ß = 1/3.

More generally, for a composite comprised m number of mixtures, the PL model can be rewritten as:

$$\varepsilon_c^\beta = \sum_1^m \varphi_i \varepsilon_i^\beta \tag{3.5}$$

Where Φ_i and ε_i are the volume fraction and the dielectric constant of each constituent material, respectively. The accuracy of this model was found to be higher than the two above-mentioned models due to the inclusion of particle shape and orientation. However, this model again did not take into consideration the interaction between filler particles and the base material.

d- Interphase power-law model

According to this model, the effective dielectric constant of a composite (ε_c) can be calculated as [21]:

$$\varepsilon_c^\beta = \varphi_1 \varepsilon_1^\beta + \varphi_2 \varepsilon_3^\beta + (1 - \varphi_1 - \varphi_2)\varepsilon_2^\beta \tag{3.6}$$

Where ε_3 and Φ_2 are the interphase dielectric constant and the interphase volume fraction, respectively. The interphase volume fraction depends on the filler volume fraction and can be computed from equation. (3.7).

$$\varphi_2 = k\varphi_1 \frac{1 - \varphi_1}{1 + k\varphi_1} \tag{3.7}$$

Where k is a factor depending on the interphase thickness. The increase in k means larger thickness and vice versa.

e- Ezzat et al Model (ESI) model

To predict the interphase dielectric constant, a model proposed by Ezzat, Sabiha and Izzularab (ESI) was suggested. They suggested that for polymers, especially those of large molecules, formation of air voids in the interphase region is dominant as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and air bubbles. So, the interphase dielectric constant can be assumed to be function of resin and air dielectric constants only, and the interphase dielectric constant can be computed from:

$$\varepsilon_3^\beta = \varepsilon_2^\beta + \varphi_a\left(1 - \varepsilon_2^\beta\right) + \varphi_f\left(\varepsilon_1^\beta - \varepsilon_2^\beta\right) \tag{3.8}$$

For ceramic and polymers of smaller molecules, the formation of air voids in the interphase region can be neglected as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and filler molecules. So, the interphase dielectric constant can be assumed to be function of resin and filler dielectric constants only, and the interphase dielectric constant will be computed from:

$$\varepsilon_3^\beta = \varepsilon_2^\beta + \varphi_f\left(\varepsilon_1^\beta - \varepsilon_2^\beta\right) \tag{3.9}$$

Also, the effective dielectric constant of a composite can be calculated from Eq. (3.10).

$$\varepsilon_c^\beta = \varphi_1 \varepsilon_1^\beta + (1 - \varphi_1)\varepsilon_2^\beta + \varphi'\left(\varepsilon^\beta - \varepsilon_2^\beta\right) \tag{3.10}$$

Where ε is the dielectric constant of air (1), for polymers of large molecules, ε is the dielectric constant of the filler for ceramics and polymers of smaller molecules. Φ' can be computed from:

$$\varphi' = \varphi_1 \frac{1 - \varphi_1}{1 + \varphi_1} \quad (3.11)$$

If the dielectric constant of the matrix is greater than the dielectric constant of the filler then ε and ε_2 must be reversed in the last term of Eq. (3.10).

Figures(4 a-e) represents the experimental filler dependence of the effective dielectric constant data of PVC/PMMA composites and the corresponding calculated values on the basis of the mentioned four models. By looking at all the pre-mentioned models, MG, PL, IPL and ESI models and comparing the effective dielectric constant as a function of conductive polypyrrole particle contents, one found that the ESI model gives a better accuracy than the other models at low filler loading (≤ 0.06 volume fractions). Meanwhile the interphase model gives better fitting at higher loading ≥ 0.06 volume fraction.
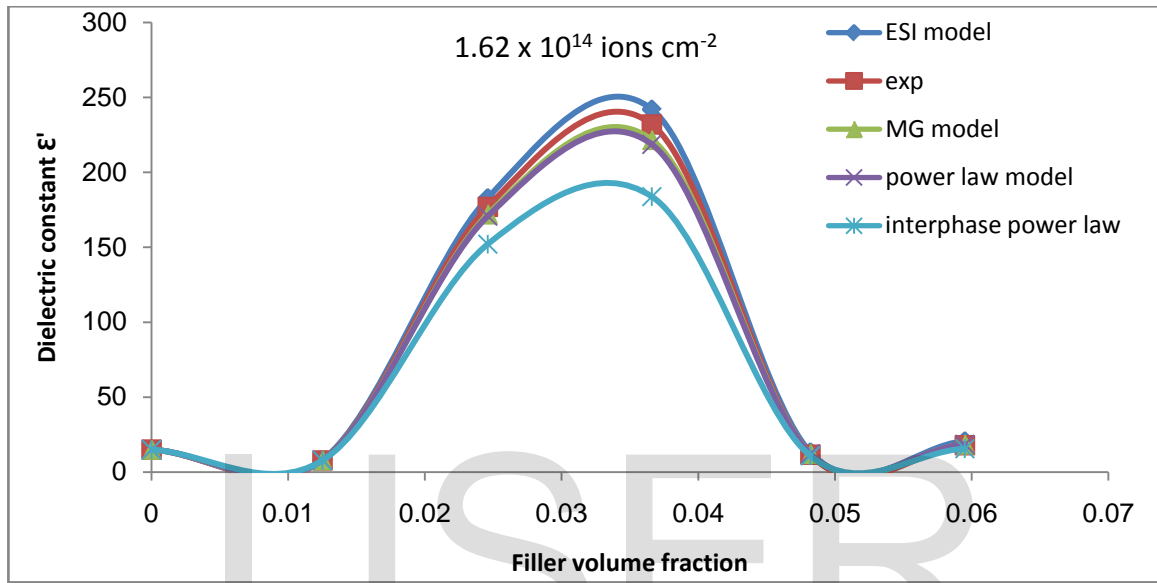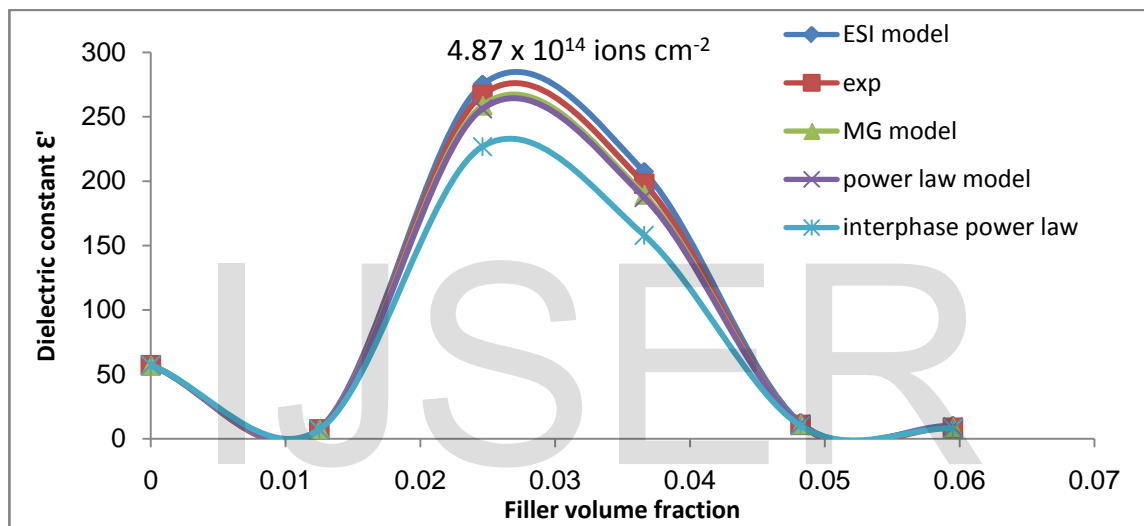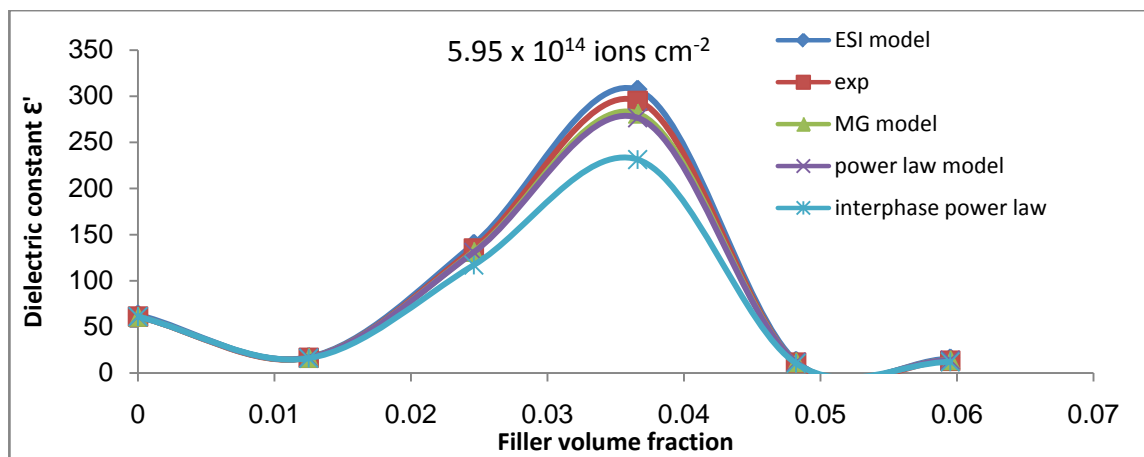

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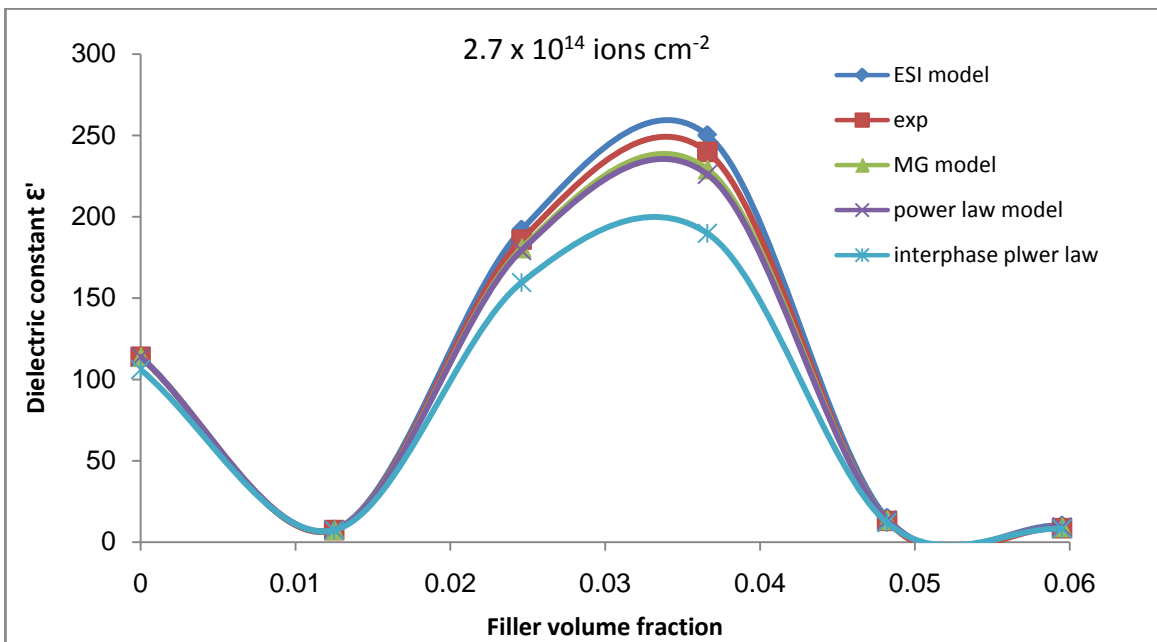
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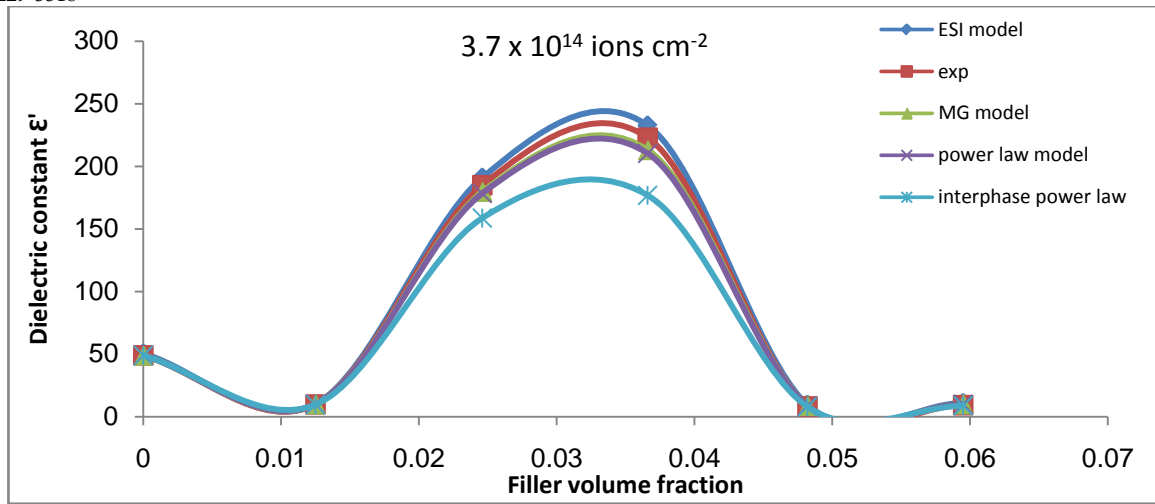
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Figures (4 a-e): Comparison of the experimental data (ε′ with frequency dependence) with all studied theoretical

models for PVC/PMMA composites irradiated at different fluences.

4. Conclusions

Electrical behaviors of PVC/PMMA loaded with different concentrations of conductive PPy nano filler (loaded with constant concentration (30 phr) of HAF carbon black)were investigated.Dielectric constant obviously increases after ion implantation. The higher ε' of PVC/PMMA after implantation will be got by implantation for samples loaded with 3 wt. % PPy conductive filler.

It can be readily noted that irradiation at 1.62×10^{14} ions cm^{-2} increases ε' of sample PVC/PMMA loaded with 2 and 3 wt. % PPy by approximately seven times its initial value.Irradiation at 5.97×10^{14} ions cm^{-2} increases ε' of sample PVC/PMMA loaded with 3 wt. % PPy by 3 orders of magnitude.

ACKNOWLEDGEMENT

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