Temperature and Electron beam dependence on A.C. electrical conductivity of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends

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Abstract: Polymer blends of polypyrrole (PPy)-conducting particles dispersed in poly (ethylene -co-vinyl acetate) (EVA) matrix were prepared. The effect of temperature and electron beam on A.C. electrical conductivity of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends were studied. These properties depend on the relative concentration of the conducting (PPy) and dielectric (EVA) blends. All samples show a decreasing behavior of its ε′ with electron-beam dose indicating the dangling bonds formation. Moreover, the aspect ratio and the depolarizing factor increases with electron beam doses.

1. Introduction

Recently the scientific interest in polymer blends has intensified [1–3]. Most plastics are dielectrics or insulators (poor conductors of electricity) and resist the flow of a current. This is one of the most useful properties of plastics and makes much of our modern society possible thought the use of plastics as wire coatings, switches and other electrical and electronic products. Despite this, dielectric breakdown can occur at sufficiently high voltages to give current transmission and possible mechanical damage to plastics.

Elastomers, unlike fibers or plastics, are normally useful only after fillers and other compounding ingredients have been added [4]. Restricted properties and limited use of homopolymers alone, has given rise exploration of composites, copolymers, blend, etc. copolymer such as poly (Ethylene-co-vinyl acetate) (EVA) has wide range of usages in different industries. Among the numerous ethylene copolymers, due to its wide range of properties depending on its vinyl acetate (VA) content, EVA has become one of the most useful copolymers in the transportation industry as an insulator, in the electric industry as a cable insulator and in many other industries as a hot melt adhesive, coating, etc.

EVA acts as host material in the prepared conducting composite polymer containingconductive PPy as was investigated by FS Shokr*et al.*[5]. The concentration of the dopant polymer was varied in order to investigate the influence of the PPy on the dielectric properties of the polymer blends. To our knowledge no researcher had discussed the effect of electron beam on following the recipe of the preparing condition by FS Shokr, this article studied the effect of temperature and electron beam on A.C. electrical conductivity of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends

2. Experimental

2.1 Materials and *Preparation of sample*

EVA, containing 12% VA which used throughout this work was supplied by Aldrich Company in the form of pellets. Polypyrrole / carbon nano-particles used for the study was supplied from Aldrich Company also. EVA was melt-mixed in a Brabender Plasticorder PLE-319 (Brabender co., Germany) at a temperature $80^{o}C$ and 80 rpm rotor speed for 5 minutes which was followed by the addition of polypyrrole / carbon nano-particles and the mixing lasted for another swing. The formulations of the mixes are given in Table (1). The resultant mixtures were sheeted on a two roll mill at ambient temperature. The sheets were then compression moulded between smooth teflon sheets at a temperature of $110^{o}C$ and a pressure of 5 MPa in an electrically heated press (type carver M-154). In order to ensure predetermined sheet size, the hot pressed sheet was cold pressed afterward in another press at the same pressure and cooled with water.

2.2. Electrode coating

The electrode coating on the film of measured thickness was done by using quick drying and highly conducting silver paint supplied by TAAB. A mask of circular aperture of 1.0 cm diameter was used while coating, to ensure uniformity in the size of the coated silver electrode.

Table (1): Shows the composition of the blend

Ingredients	Phr*					
EVA	100	95	90	85	80	70
PPY	0	5	10	15	20	30

* Parts per hundred parts by weight of rubber.

2.3. Structural characterization

For structural characterization the x-ray diffract grams of films were obtained on XPERT – PRO – PAN analytical – Netherland. The x-ray diffract grams of all the samples ensures the amorphous nature.

2.4. Electron-beam Irradiation:

The electron irradiation was performed in air at room temperature using a 1.5 MeV electron beam from the ICT-type electron accelerator (NCRRT, AEA, Cairo, Egypt). The conveyer was attached to a cooling system in order to avoid temperature heating of the samples. The films were subjected to various integral irradiation dose levels, up to 100 kGy. The irradiation dose levels were 10, 25, 50, 75 and 100 KGy respectively. The dose determined by the FWT 60-00 dosimeter that was calibrated using the CERIC/CEROUS dosimeter. The uncertainty in the delivered dose was estimated to be 1.15%.

2.5. Measurements

The dielectric properties were measured using a bridge (LCR-821, Instek LCR meter) in the frequency (f) range 10^2-10^5 Hz. The prepared 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 δ) 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

$$\varepsilon' = \frac{d}{\varepsilon_\circ A} C$$

(1)

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon''$$ (2)

$$\varepsilon'' = \varepsilon' \tan \delta$$ (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,

$\varepsilon_\circ$: The permittivity of free space.

ε″: The dielectric loss.

ω: The angular frequency ($\omega = 2\pi f$)

3. Results and Discussion

Studies of the transport mechanisms in intrinsically conductive polymers and polymer blends have gained importance in recent years owing to the potential applications in various devices technologies [6-8]. Polypyrrole is one of the most widely studied conducting polymers. It exhibits relatively high conductivity and good environmental stability like other polymers. Polypyrrole is electro active and can acts as an anion exchanger. During the synthesis of PPy, do pant anions are incorporated in the structure of PPy to balance the positive charge developed on the oxidized polymer chain [9].

Radiation induced changes in polymeric materials continue to draw attention for practical reasons. For production, utilizing radiation chemistry alters the chemical and physical structures in order to improve some physical properties, For applications, the search mode for polymers that are not destructively affected by radiation, even at low doses, often undergo structural changes accompanied by both molecular cross linking and scission (degradation) reactions [10].

a. Filler dependence:

The dielectric constant and ac conductivity are important parameters in the selection of an insulating material. The variation of dielectric constants and losses of pure EVA and the blends of conductive PPy /EVA as a function of frequency was shown by FS Shokr Generally the dielectric constant of a material arises due to polarization of molecules, and the dielectric constant increases with the increase in polarizability.

The different types of polarizations possible in a material are the polarizations arising from electronic polarization, atomic polarization, and orientation polarization due to the orientation of the dipoles parallel to the applied field [11]. For heterogeneous materials, there is also the possibility for interfacial polarization that arises due to the difference in conductivities of the two phases [12].

The dependence of έ, upon HAF/PPy content and frequency at different electron-beam doses for PPy/EVA samples are shown in Figures [(3.1) & (3.2 a-e)]. The frequency dependence of έ is highly affected by both HAF/PPy contents and the electron-beam irradiation dose. From Figure (3.1) it is clear that έ increases sharply after a critical concentration (around 15 Phr) of HAF/PPy. Also, it is of great interest to notice that the values of έ at the peak decreases with electron-beam doses 25 KGy and 75 KGy.

The deposition of energy in polymers promotes, amongst other processes, bond breakage with

emission of atomic and molecular species [13]. It was verified that H groups are preferentially lost since they constitute side groups or chain termination in polymers [14]. Once it is a weakly bonded species, just its progressive emission enhances the medium strength of the structure. Moreover it induces dangling bonds, which are unstable species and tend to vanished through chain un-saturation and cross linking.

Consumption of radicals through these processes depends on a number of factors, including their concentration, separation and chain mobility. The more radicals are generated, the higher is the probability of recombination and then of cross linking and unsaturation. Structure strength is strongly affected by these processes. As the bombardment proceeds, polymeric chain crosslink, turning the structure rigid. Polymer mobility is essential to the

cross linking processes and then, if further bombardment is performed, new radicals are generated but recombination is hindered by the immobile structure [15]. In this case dangling bonds are generated and are not re-established. Radicals keep active and the solid prone to oxidation as the sample is exposed to the atmosphere.

Figure (3.3) represent the electron-beam dose dependence of the dielectric constant of all pure EVA and EVA loaded conductive PPy. All samples show a decreasing behavior of its ε' with electron-beam dose indicating the dangling bonds formation. Meanwhile, sample loaded with 15 phr conductive PPy shows an anomalous behavior in its ε' & electron-beam dose dependence arise as a maximum at around 25 KGy indicating the completion between the above mechanical mechanisms.
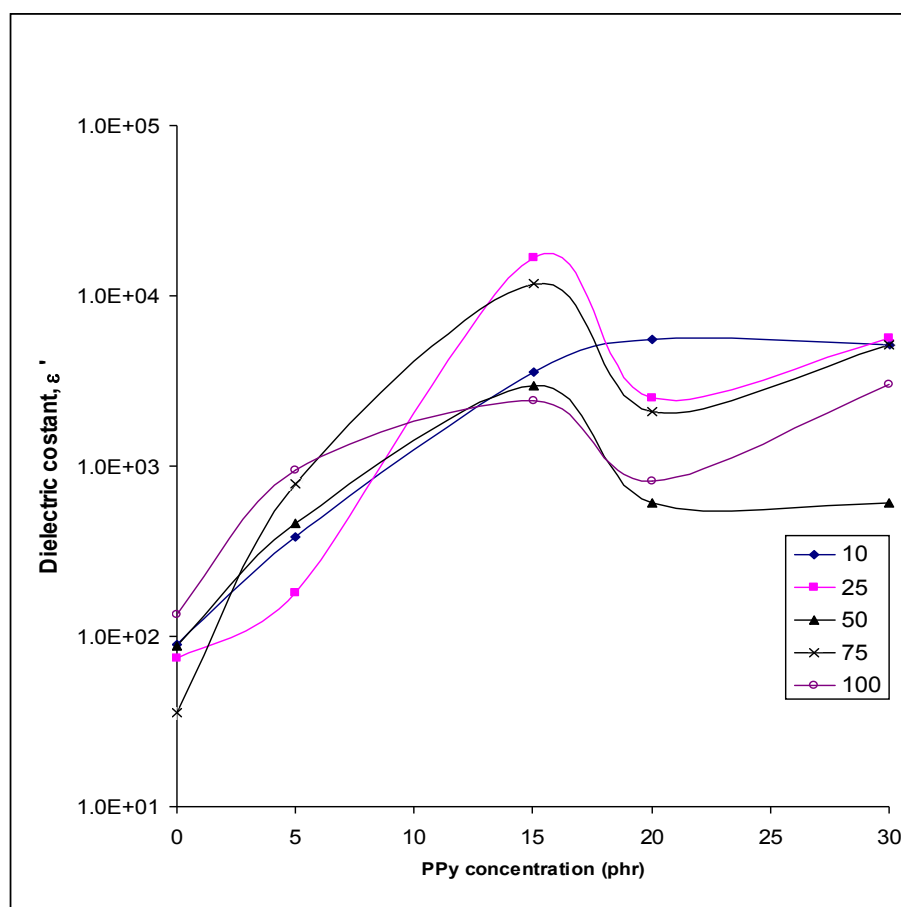

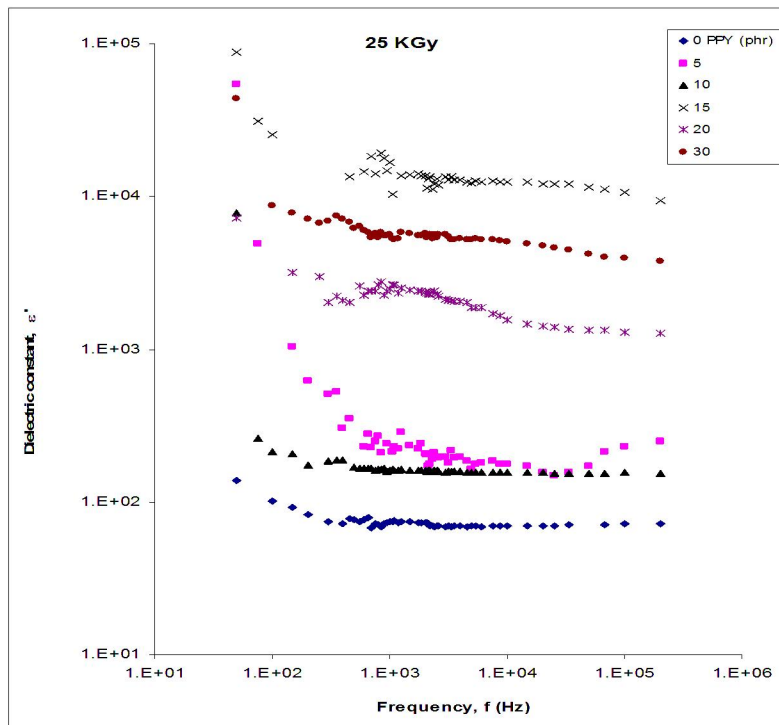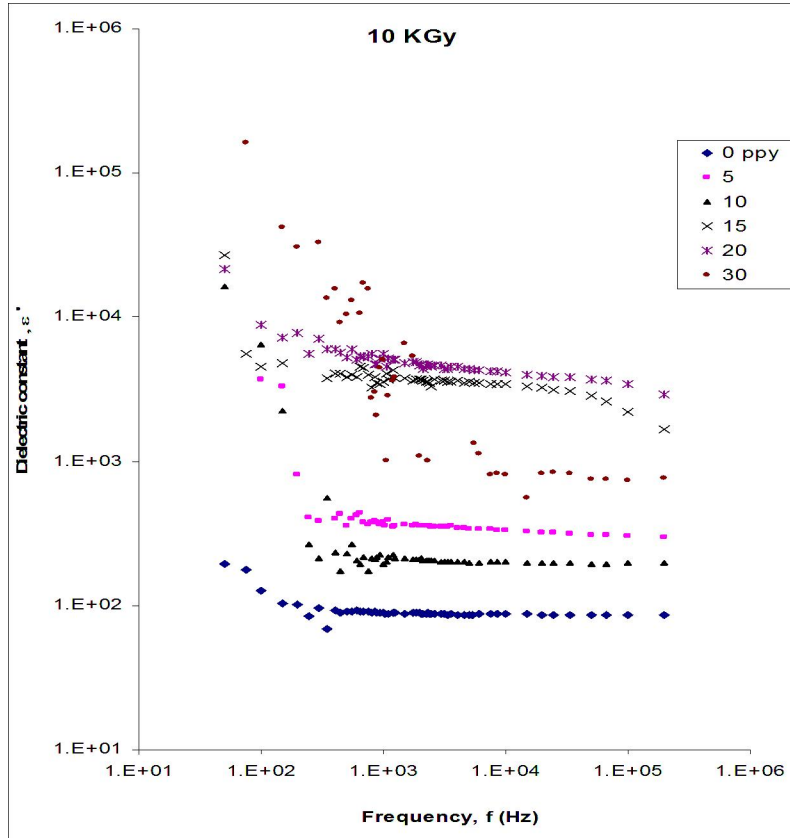Figure (3.1): The dependence of the dielectric constant on the PPy concentration for all irradiated samples at constantfrequency 1 KHz
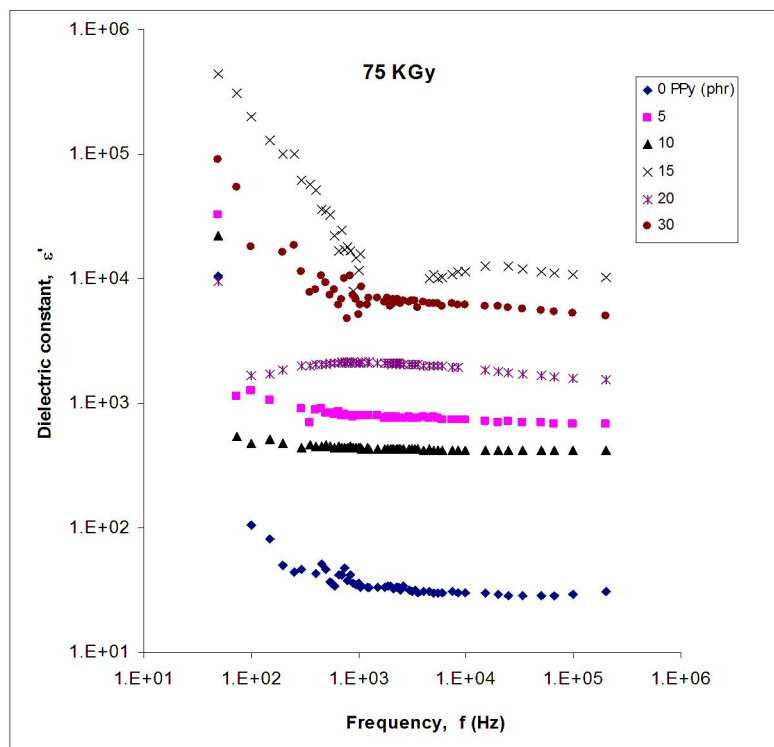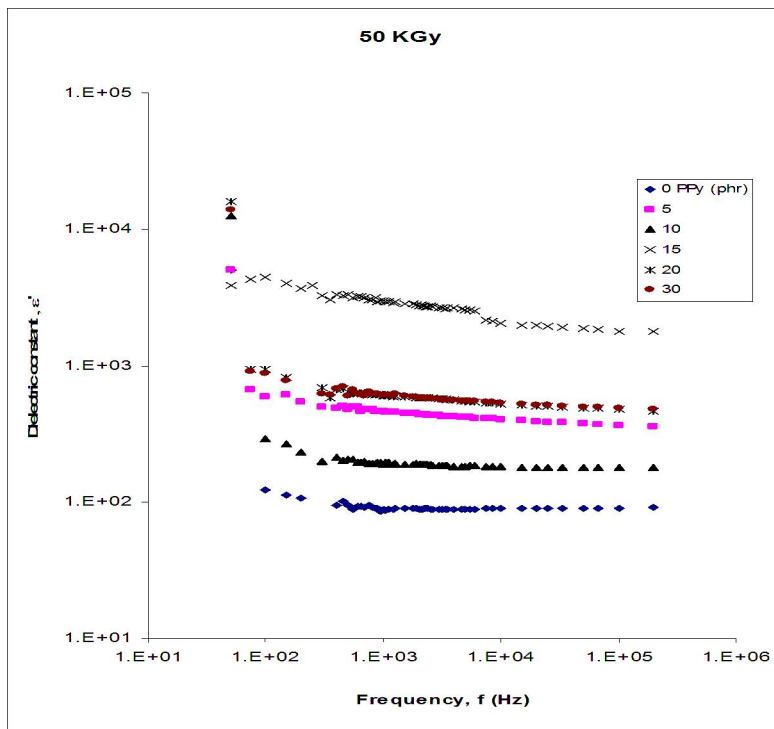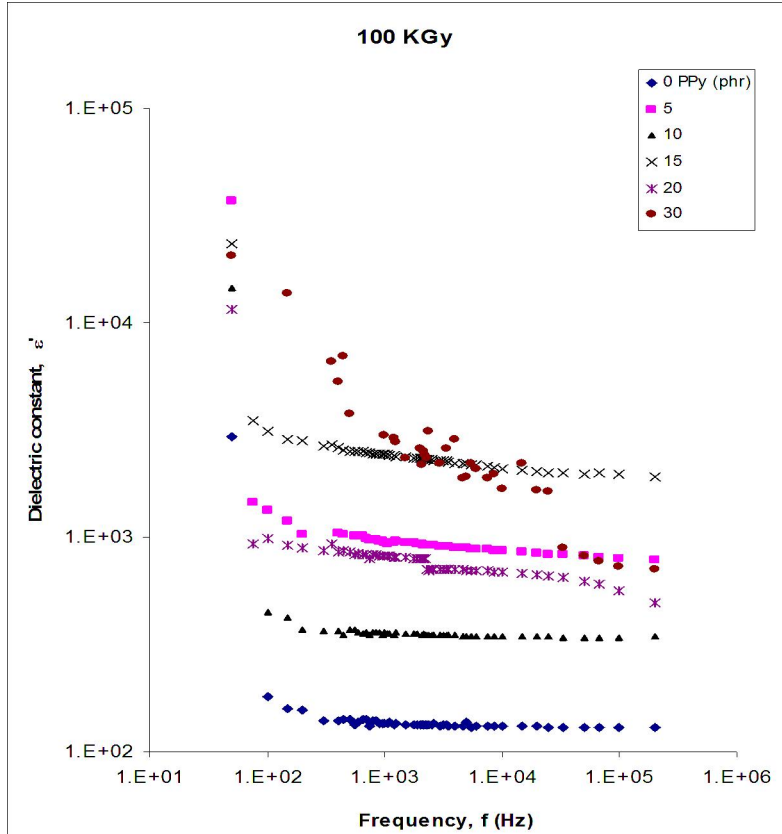
Figure (3.2 b)

Figure (3.2 d)

Figure (3.2 e): The frequency dependence on the dielectric constant for all irradiated samples.
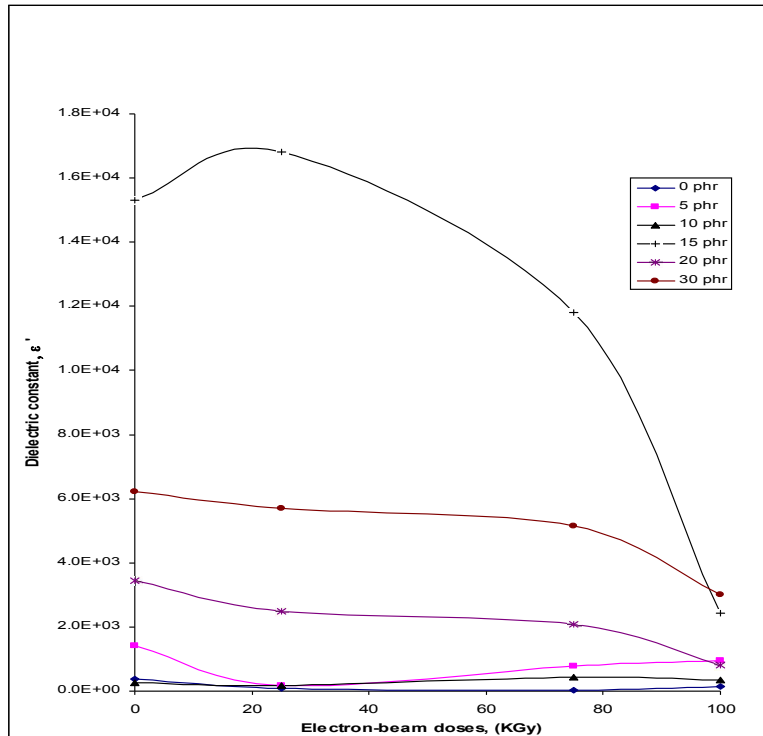

Figure (3.3): The dependence of dielectric constant on electron-beam dose for all irradiated samples at different PPy concentrations.

b. Temperature dependence.

In measuring the temperature dependence of έ, sufficient time was allowed for PPy/EVA samples to reach equilibrium with its temperature-controlled environment. The unloaded EVA sample initially shows an increase in its έ value with increasing electron-beam dose D as a result of crosslinking (D ≤ 50 KGy). But decreases appreciably after an irradiation dose of about 5 Mrad presumably due to degradation. Meanwhile, for loaded EVA samples with (15, 20and 30 Phr) conductive PPy powder,

[Figures 3.4(a-e)] the un-irradiated samples manifested relatively sharp beak of the dielectric constant as a function of temperature, this peak occurred at around 55 ^{0}C before irradiation. By electron beam irradiation dose the dielectric constant appreciably decreases at the peak value.

The dielectric anomaly seemed to disappear for exposure dose of approximately 50 KGy, (for 15 and 20 Phr of conduction PPy), the έ (t) relation was approximately a straight line with a slight curvature.
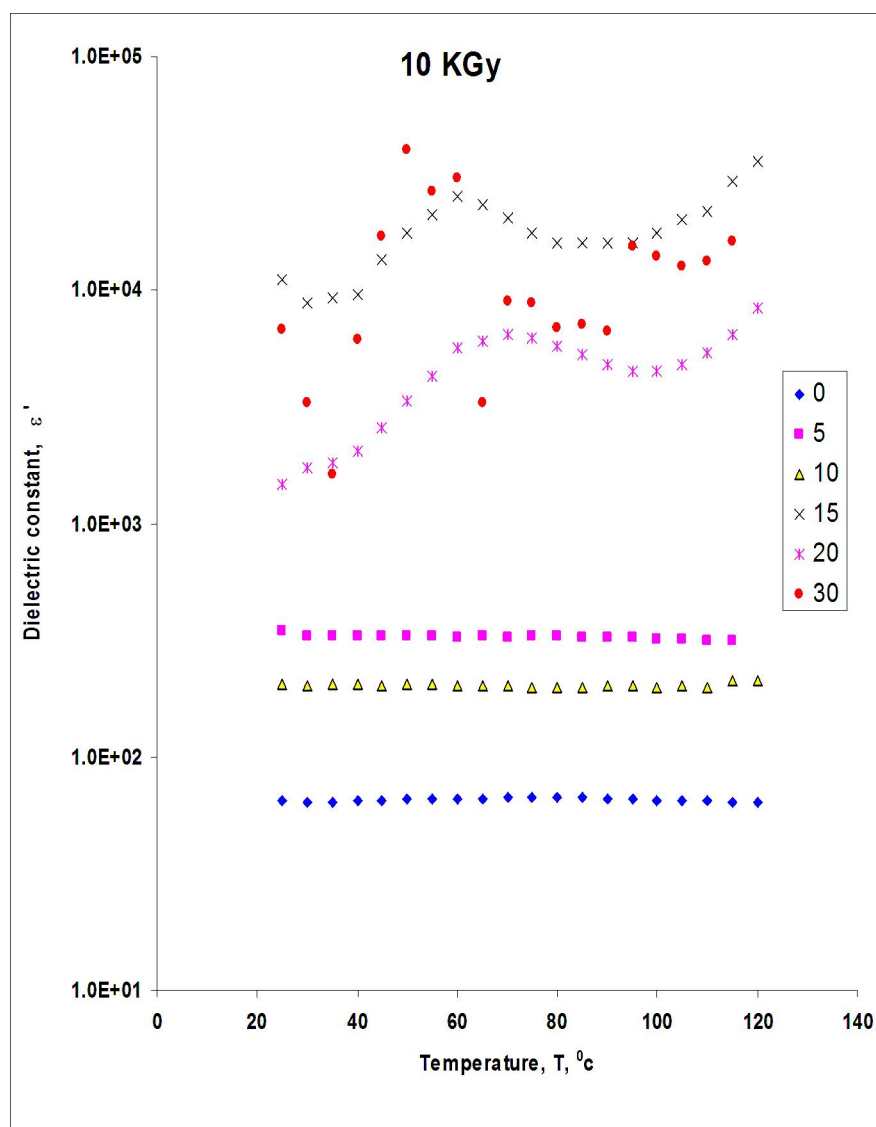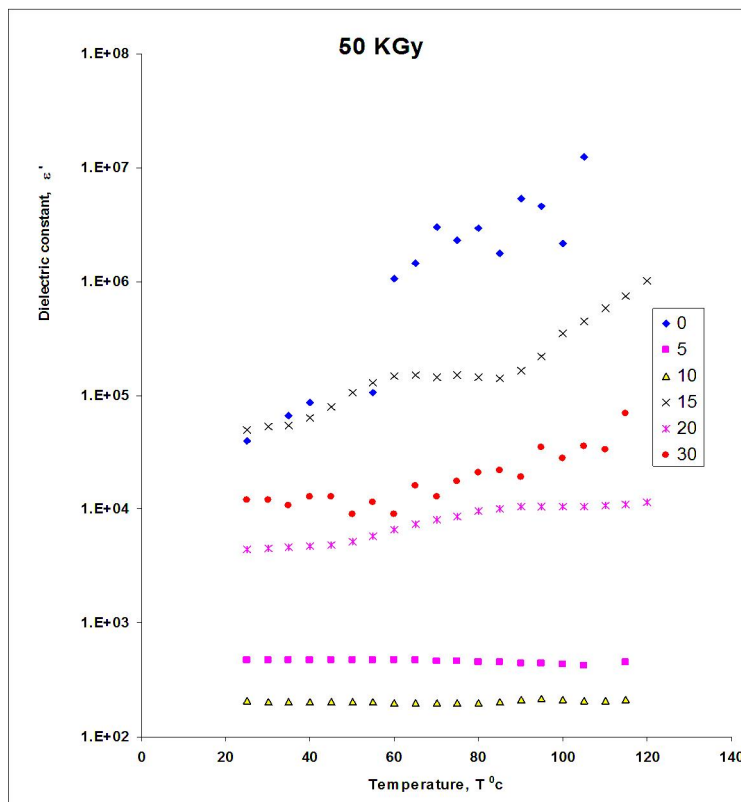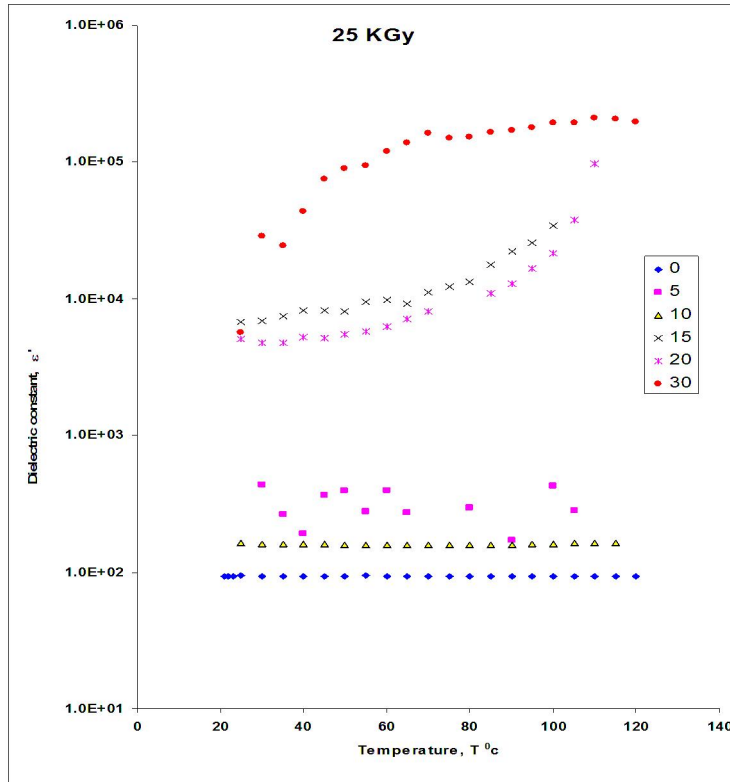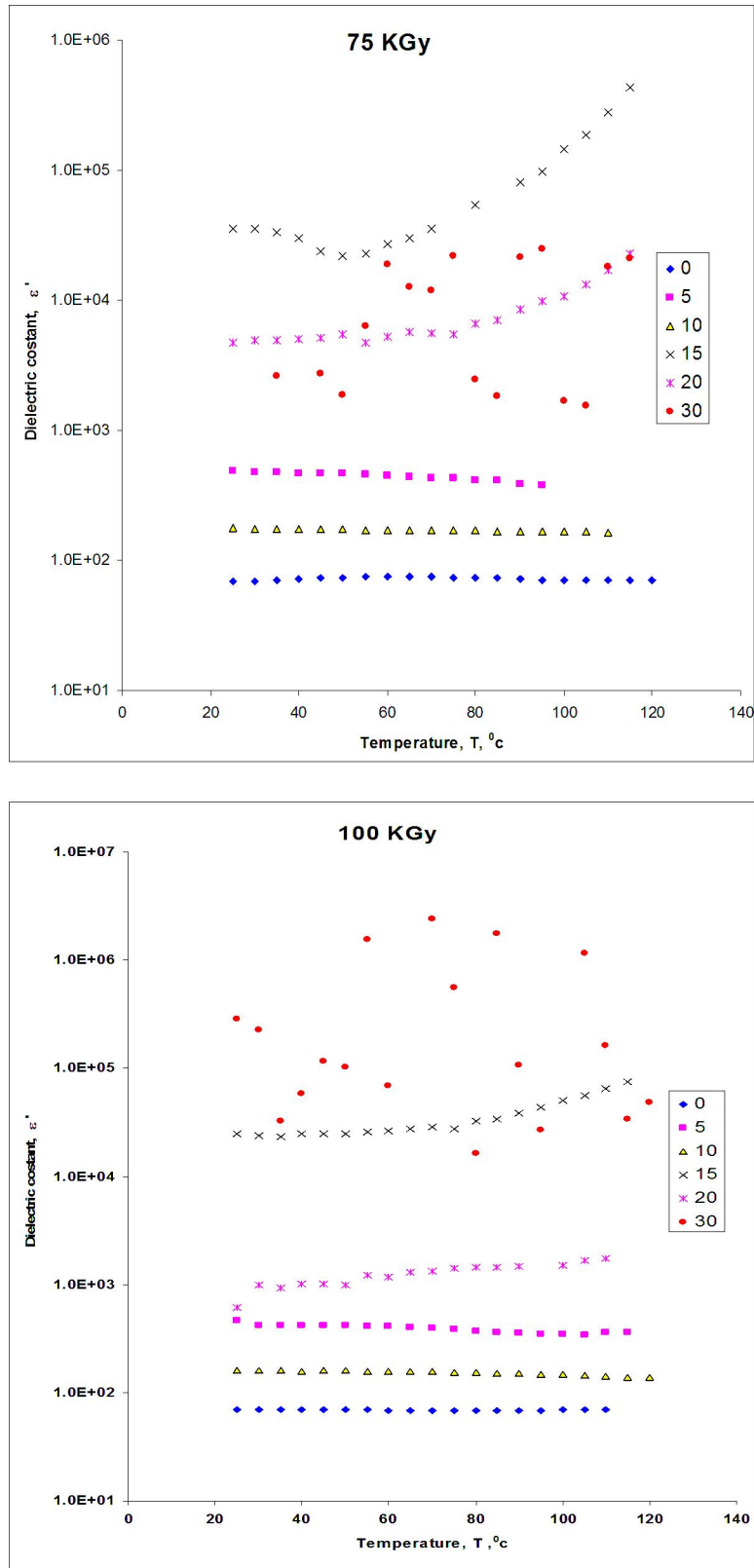

Figure (3.4 a)

Figure (3.4 c)

Figure (3.4 e): The temperature dependence on the dielectric constant for all irradiated samples at different electron beam doses.

c. Theory:

The calculation of ε′ of dielectric mixtures and the variety of proposed formulae have been reviewed by Reynolds and Hough [16] Van Beek[17] Bőttcher and Bordwijk [18], Grosse and Graffe [19], and Kraszewski [20]. 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 [21]. Tsangaris et al. [22] 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:

$$\varepsilon'_{eff} = \frac{\varepsilon'_1}{[(\varepsilon'_1 - 1)^Y + 1]}\left\{ [(\frac{\sigma}{\omega\varepsilon_\circ})^{v_2}(\varepsilon'_1 - 1)^{(1-v_2)}\cos\frac{\pi v_2}{2}]^Y + 1\right\} \quad (4)$$

$$\varepsilon''_{eff} = \varepsilon'_1 \{[(\sigma/\acute{\omega}\varepsilon_\circ)^{v2-1}(\varepsilon'_1-1)^{1-v2}\sin(\pi v_2/2)]^y + 1\} \qquad (5)$$

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

$$y = \frac{1}{1-(a/b)^2} - \frac{a/b}{[1-(a/b)^2]^{\frac{3}{2}}}\cos^{-1} a/b \quad (6)$$

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 (4) which gives ε'_{eff} of the composites as a function of frequency for various volume fraction of the conductive PPy is shown in Figure (3.5), 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} with the experimental ones and tabulated for all samples in Table (2). It is clear from this table 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.

Applying Tsangaris et al. model, the application of equation (6) which gives $\acute{\varepsilon}_{eff}$ of the composites as a function of frequency for various volume fraction of conductive PPy is tested also for the case of different electron-beam doses as shown in [Figure3.5].

The proposed model approaches the experimental values more closely for both lower and higher PPy contents at all irradiation doses. The changes of the values of the polarizing factor are tabulated in table (2). The aspect ratio and the depolarizing factor increases with electron beam doses.

Table (2): The values of depolarizing factor (Y) chosen to fit the calculated ε'_{eff} with the experimental ones for all samples

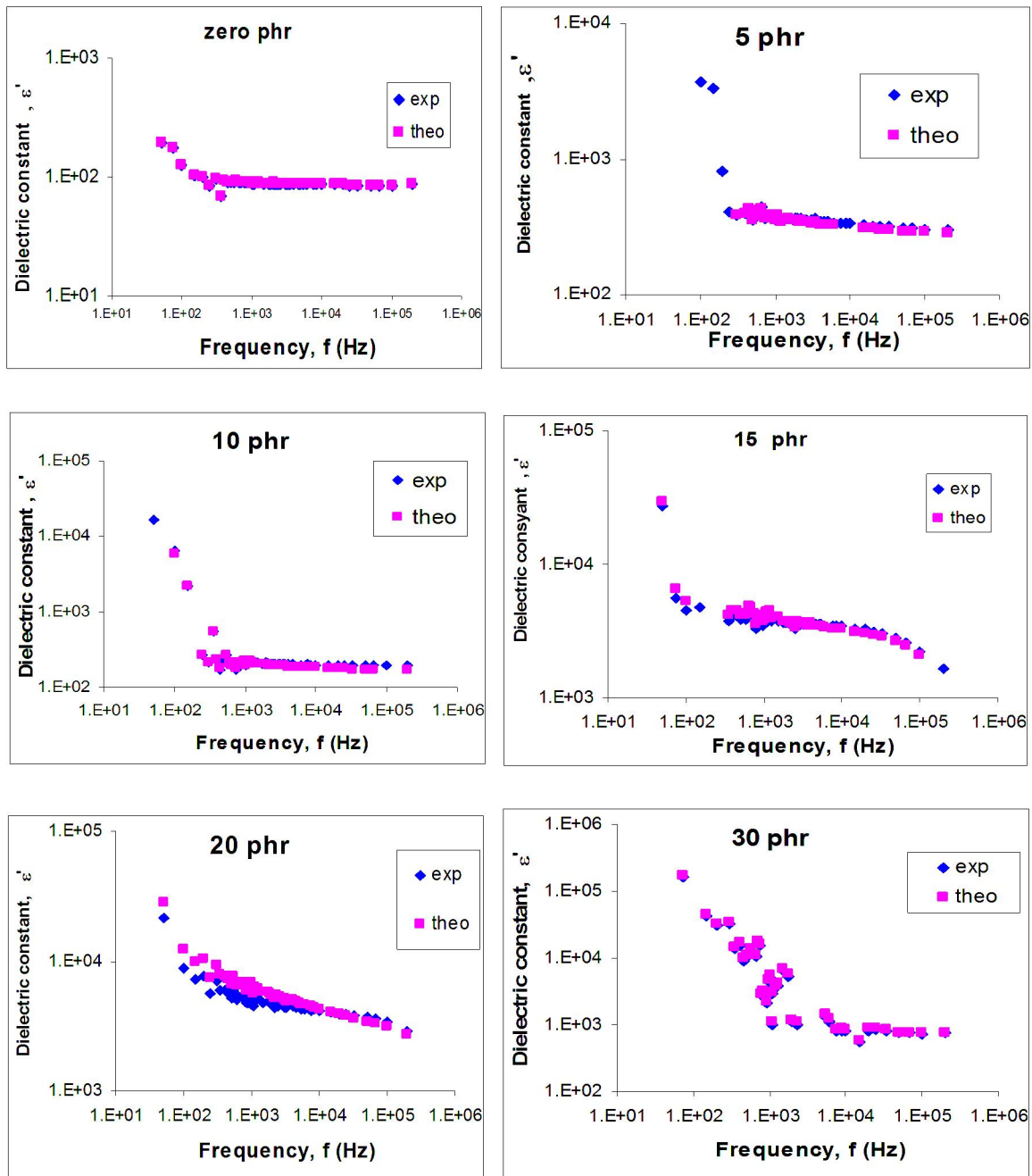| Sample (phr) \ Dose	Depolarizing factor (Y)					
	Un-irradiated samples	10 KGy	25KGy	50KGy	75KGy	100 KGy
Zero	0.25	0.30	0.34	0.40	0.42	0.45
5	0.30	0.33	0.38	0.44	0.46	0.48
10	0.35	0.40	0.43	0.47	0.49	0.51
15	0.40	0.42	0.48	0.50	0.52	0.53
20	0.43	0.47	0.51	0.53	0.55	0.58
30	0.48	0.50	0.52	0.54	0.57	0.61

Figure (3.5): The experimental and theoretical relation between the dielectric constant and the frequency for irradiated samplesat10 KGy.

4. Conclusion

The dielectric constant of the pure EVA and conductive PPy/EVA blends decreases with an increase in frequency. Variation in the dielectric constant is in two stages due to the relaxation in interfacial and orientation polarizations. The experimental dielectric constant values where compared with Tsangaris model, which fit well with that model. The dielectric constant increases on the addition of conductive PPy, and the increase ismore pronounced at 15 phr PPy loaded EVA composites. The effect of irradiation on the dielectric constant of all pure EVA and EVA loaded by conductive PPy were studied. All samples show a decreasing behavior of its ε′ with electron-beam dose indicating the dangling bonds formation. Moreover, the aspect ratio

and the depolarizing factor increases with electron beam doses.

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