International Journal of Scientific & Engineering Research, Volume 7, Issue 9, September-2016
ISSN 2229-5518

Effect of electron-beam irradiation on the Mechanical properties of Poly (Ethylene-co-Vinyl Acetate) (EVA) - PPy polymer blends

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Abstract.

Films of EVA, containing 12% VA and Polypyrrole / carbon nano-particles 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. Tensile strength and elongation at break were estimated from stress strain curves measured by using a tension meter. The mechanical properties of these filled EVA samples show high initial elastic modulus increases with PPy contents up to 15 phr. Moreover, the elastic moduli and strength increases with electron-beam irradiation dose. The degree of reinforcement achieved through incorporation of conductive PPy is the highest at 15 phr loading and at 100 KGy electron-beam irradiation dose. The crosslinking density calculated from the Mooney-Rivlin equation is found to be maximized at PPy loading of 30 phr at (75 KGy). Finally, a trial to compare the experimental results with theoretical models were tested.

Keywords: Mechanical properties, (EVA), **conductive PPy, polymer blend, electron-beam and radiation.**

1. Introduction

The effect of radiation on polymeric materials is an area of rapidly increasing interest. Several high technology industries require specialty polymers that exhibit a specific response upon exposure to radiation. For instance, the electronics industry requires materials that undergo radiation induced scission or crosslinking for resist applications, while aerospace and medical applications require highly radiation stable materials. The design and development of appropriate chemistry for these applications requires full understanding of the effects of radiation on polymeric materials. It is through fundamental understanding of the radiation chemical processes occurring in polymers that the technological advances required by today's industries can be realized. The study of the effect of radiation on polymer materials is an area of rapidly increasing interest [(1-3)]. The radiation regimes of primary utility are either high

energy, ionizing radiation such as from gamma or neutron sources, or ultraviolet radiation from arc lamps, excimer lasers or synchrotron sources. The major difference between the two types of radiation is the initial or primary event following absorption of the radiation. In the case of ionizing radiation, the initial absorption is typically a spatially random process and leads to free radical or ionic species production, whereas, ultraviolet absorption is molecular site specific and often leads to electronically excited states. Subsequent events in both cases can involve side group or main chain scission or crosslinking. Even small amounts of radiation can induce significant changes in the physical or mechanical properties of a polymer, with the extent of these changes being dependent upon the chemical structure of a particular polymer. In some cases, even a few crosslinks or scission sites per molecule can dramatically affect the strength or solubility of a polymer. These changes, in turn, will determine whether a particular polymer will have application in a particular industry. Applications that are covered include microelectronics, radiation sterilization, modified polymers and surface coatings.

The most important feature that affects the interfacial adhesions believed to be the mechanical stresses, chemical interactions and physico-chemical weak boundary layers. Chemical interactions involve covalent bonding and filler/matrix wetting [(4)].

Conducting polymeric composites (CPCs) are traditionally prepared by the blending of conventional polymers with electrically conductive fillers, and they have important applications in antistatic materials, low temperature heaters, electromagnetic radiation shielding, and electric field grading.

Following the previous work [(5)], The present investigation is concerned with detailed studies on the mechanical properties of EVA composites filled with conductive PPy nano filler (loaded with constant concentration (40phr) of HAF black) under the effect of electron beam irradiation doses [(6)]. Finally the detected different properties of the prepared EVA composites are evaluated in the light of various theoretical models, to examine the applicability of these models to the present systems and its modification owing to the electron beam irradiation doses.

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.

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.

2.2.*Measurements*

Tensile strength and elongation at break were estimated from stress strain curves measured by using a tension meter (carried out with the use of H10KS Hounsfield Co. UK); tension speed was 50mm/min. tensile tests were carried out on dumbbell shaped specimens. Three samples per formulation were tested. By using the dimensions of samples the stress and strain were calculated.

The system used in measuring mechanical properties is illustrated elsewhere [(5)]

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%.

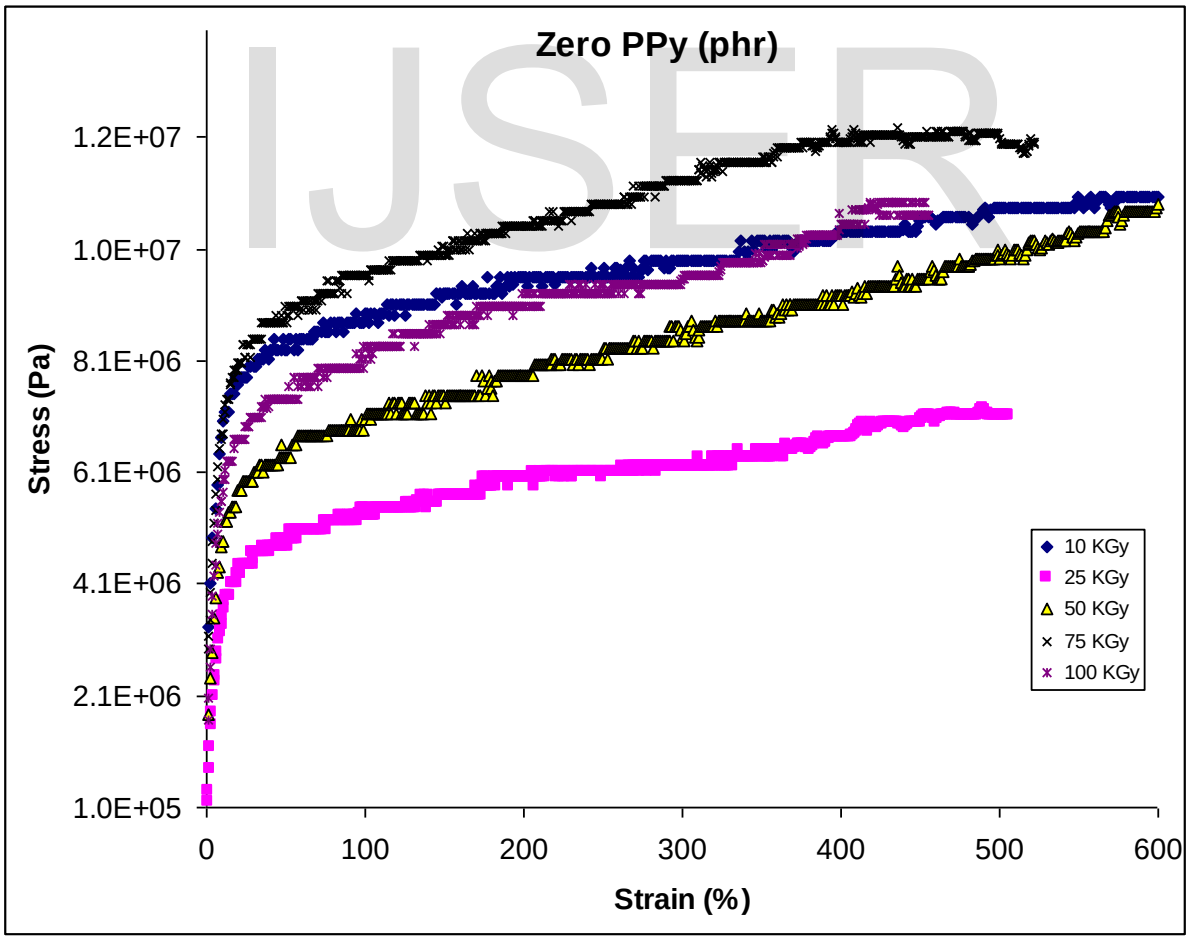
3. Results and discussion

The stress –strain behaviors of the composites of PPy and EVA exposed to different doses are shown in Figures (1 a-f). Both the gum sample and the filled samples show similar trend. One notices that, the overall extensibility of the samples is lower than those of an unirradiated sample as estimated from our previous work [(5)]. The initial moduli and strength are higher for irradiated samples with higher electron-beam dose (100 KGy).

3.1 Young's modulus:

Young's modulus of the composites is the bulk property that attracted more attention in this area of research .Young's modulus is the ratio of stress to strain in the linear region of the stress – strain curve. After electron-beam irradiation, the modulus values showed an increasing trend up to 15 % PPy content followed by a decrease beyond 15 % depends on the dose values. For all the composition except samples irradiated by doses 25, 50 KGy, the modulus values are lower than those un-irradiated samples. The electron-beam dose enhances the reinforcement between EVA matrix and the PPy conductive contents. The increase in modulus with e-beam irradiation dose is attributed to the various parameters of PPy added as filler to the EVA matrix. They include the aspect ratio of the PPy, the orientation of the PPy, interfacial interaction, the nature of the filler and the cross linking density.

Concerning the decreasing behavior of the modulus after certain electron-beam dose for all samples. This may be due to the saturation of the reinforcing action of the PPy and the degradation predomination of the electron-beam irradiation dose.



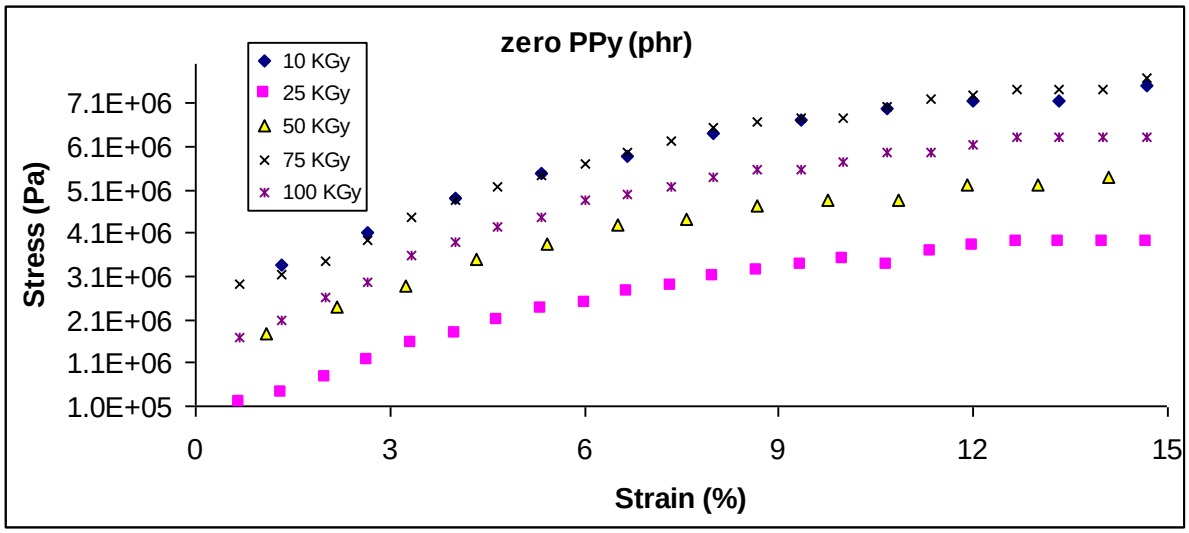
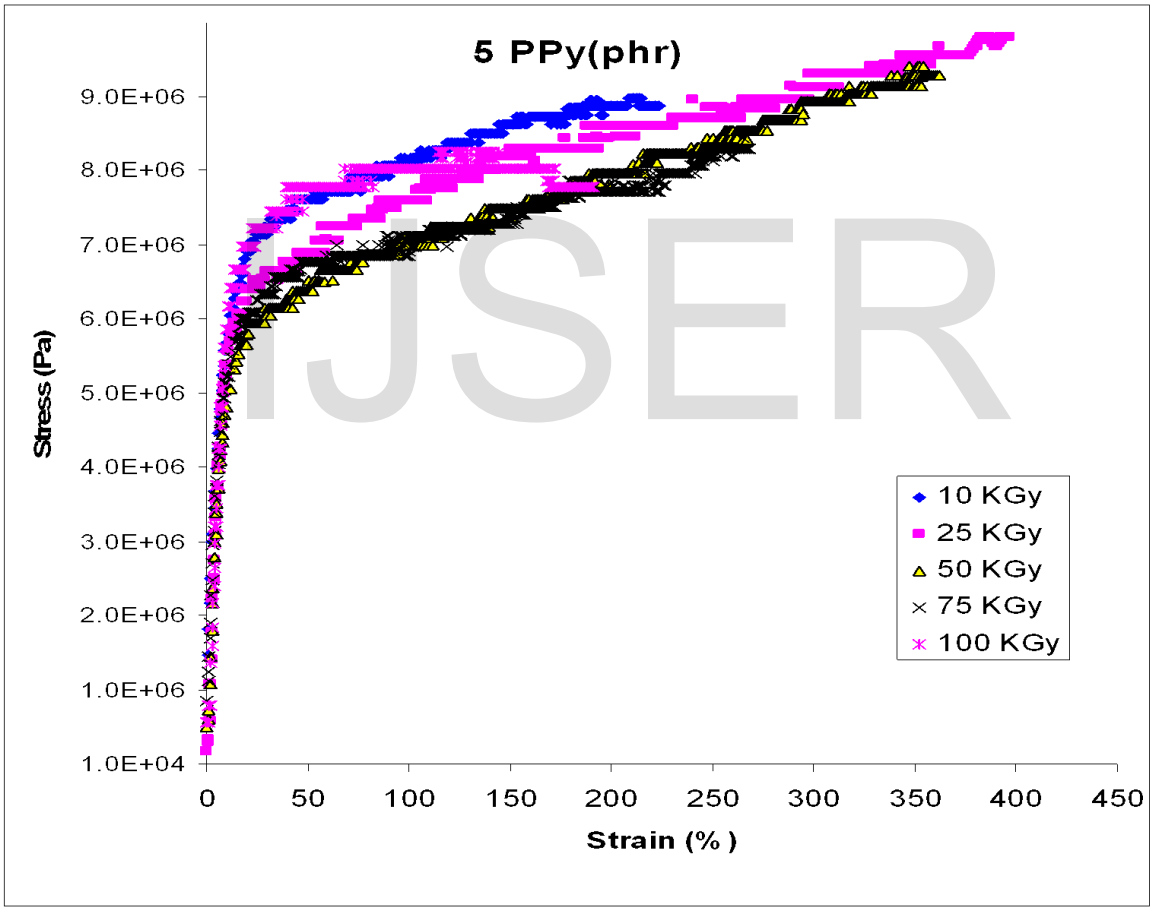
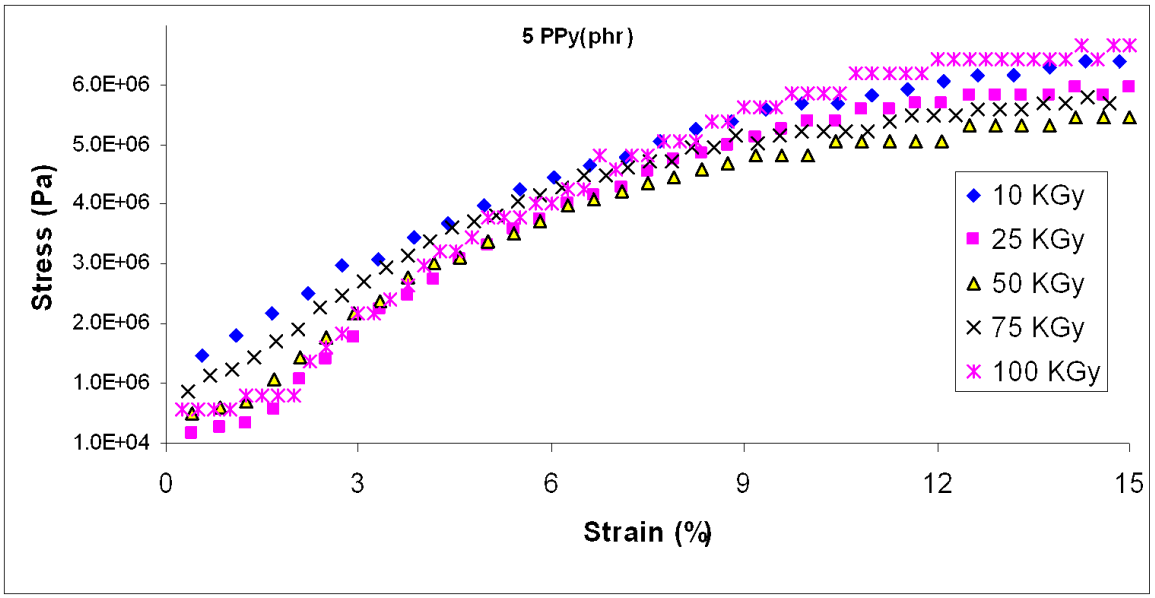


Figure (1- a)





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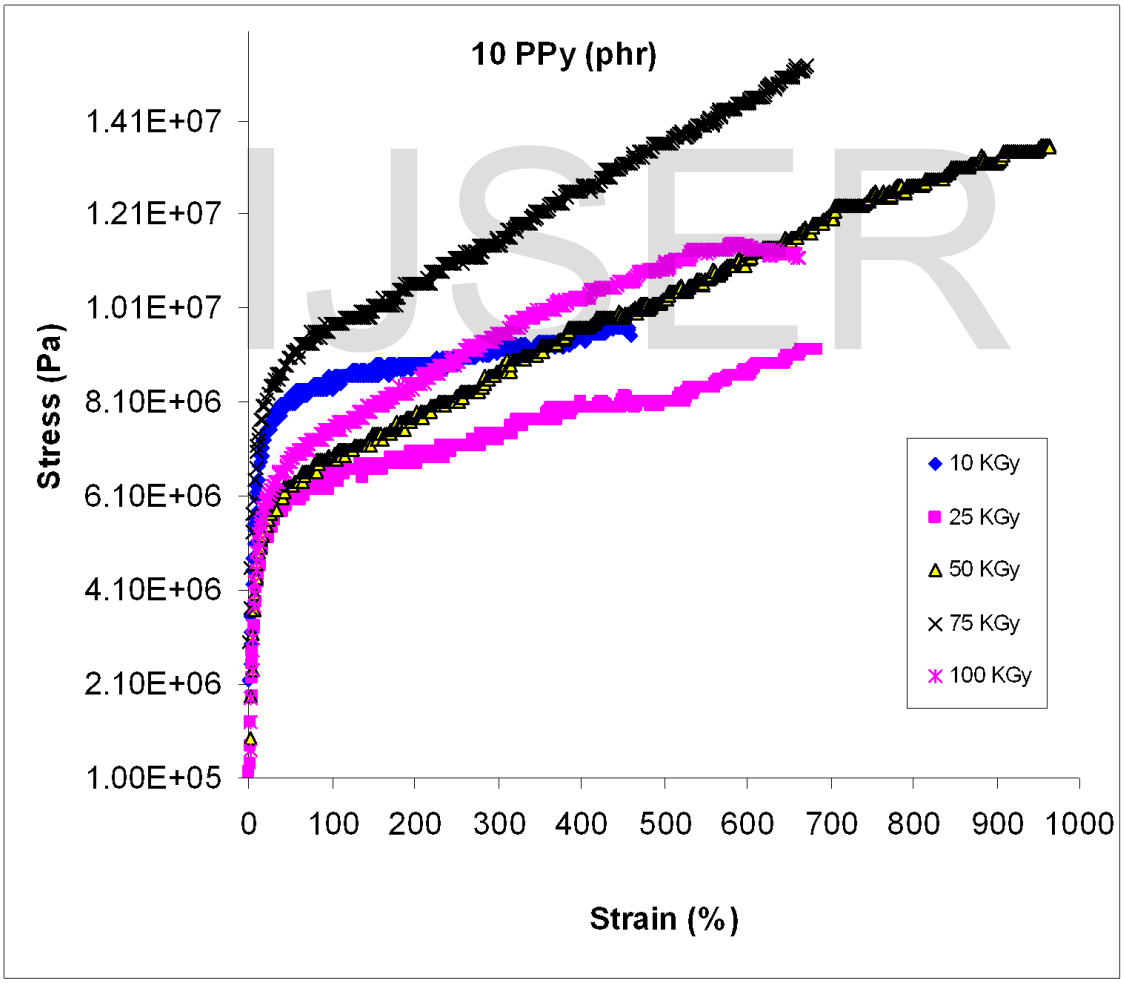

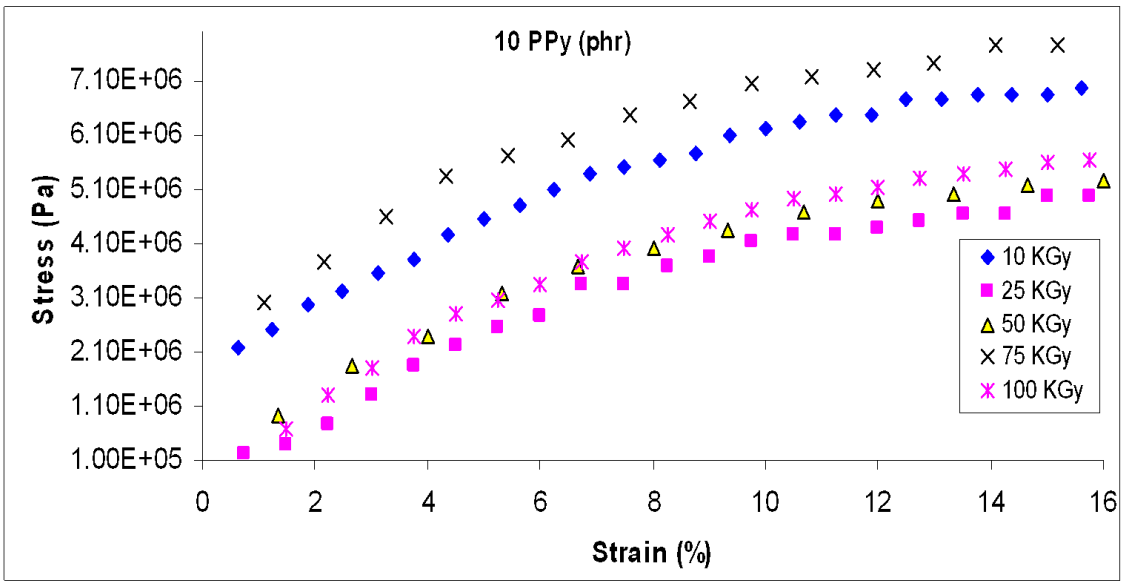

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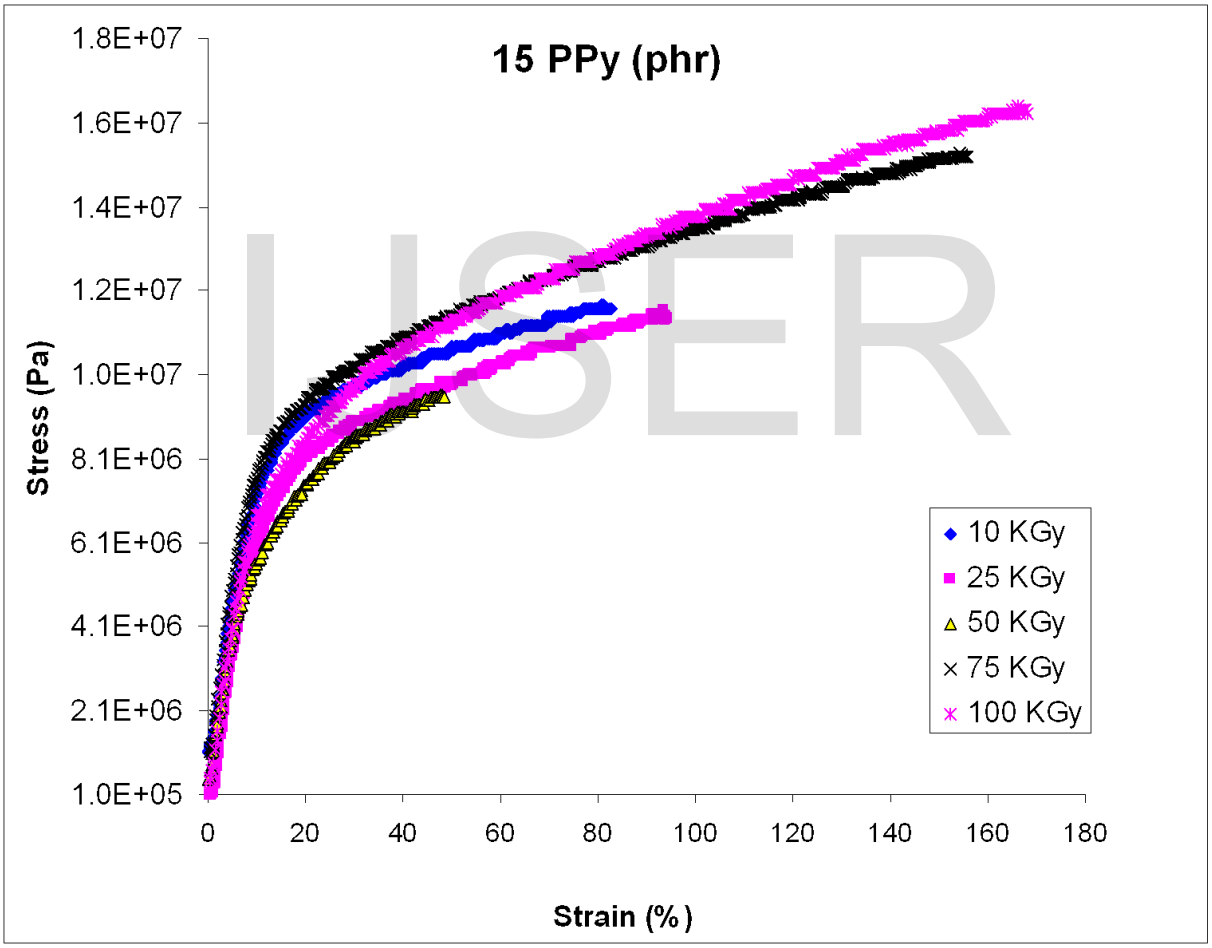

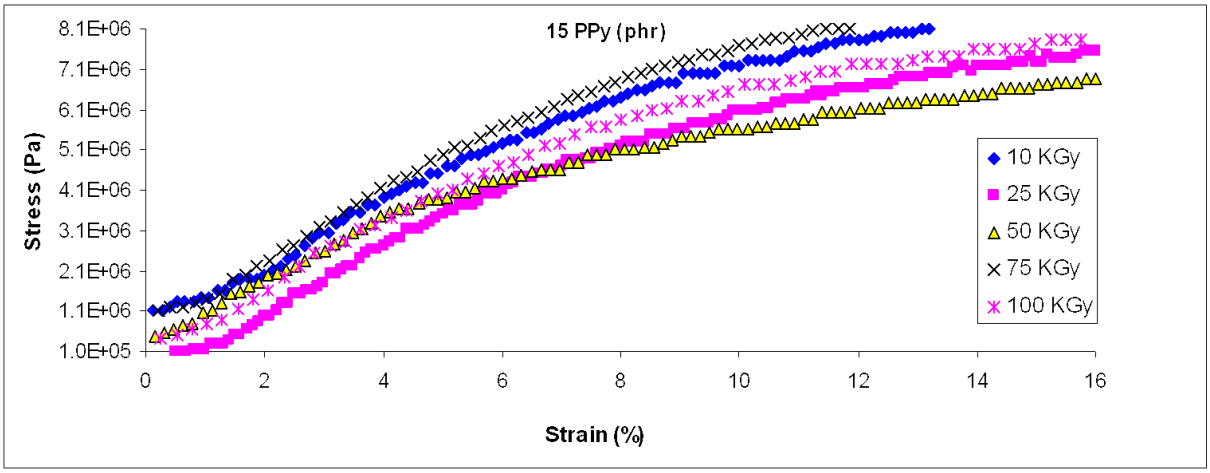

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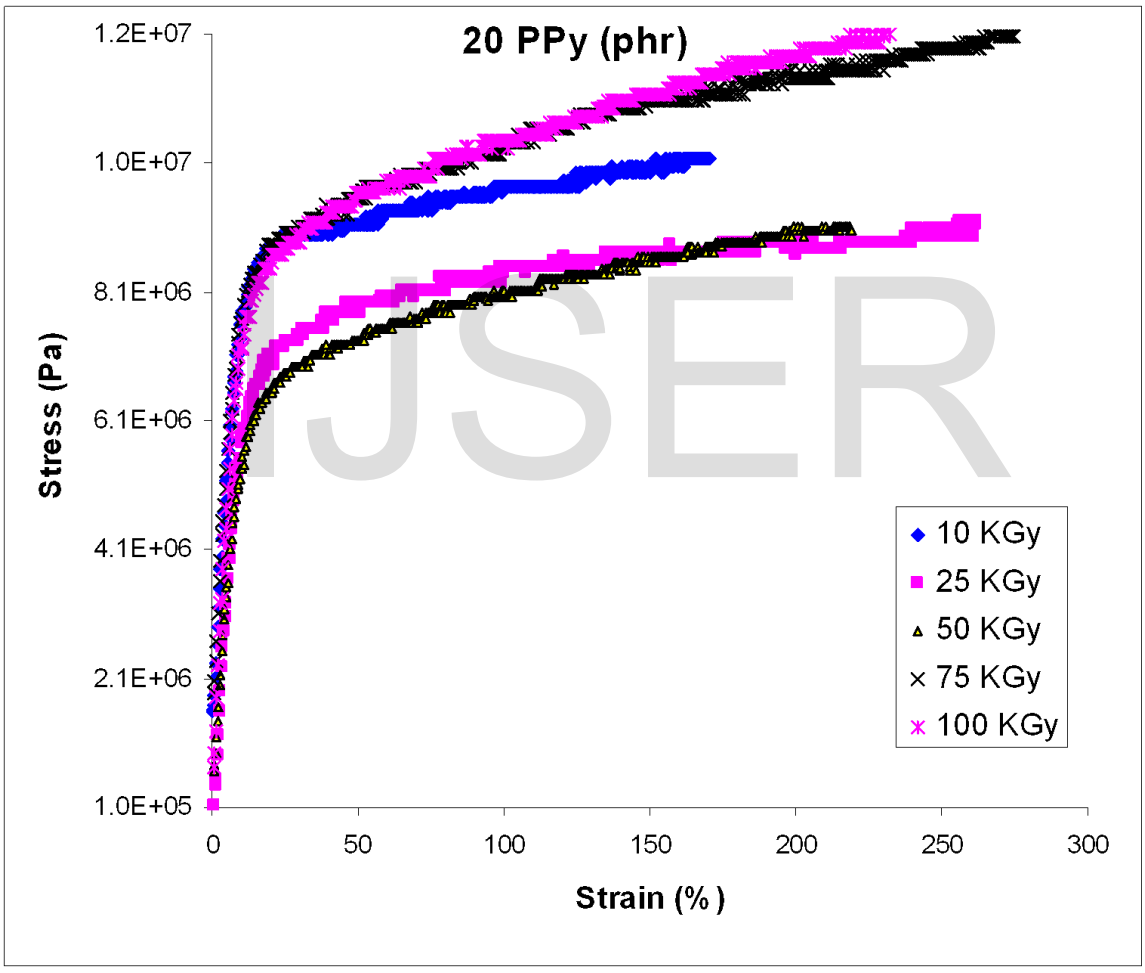

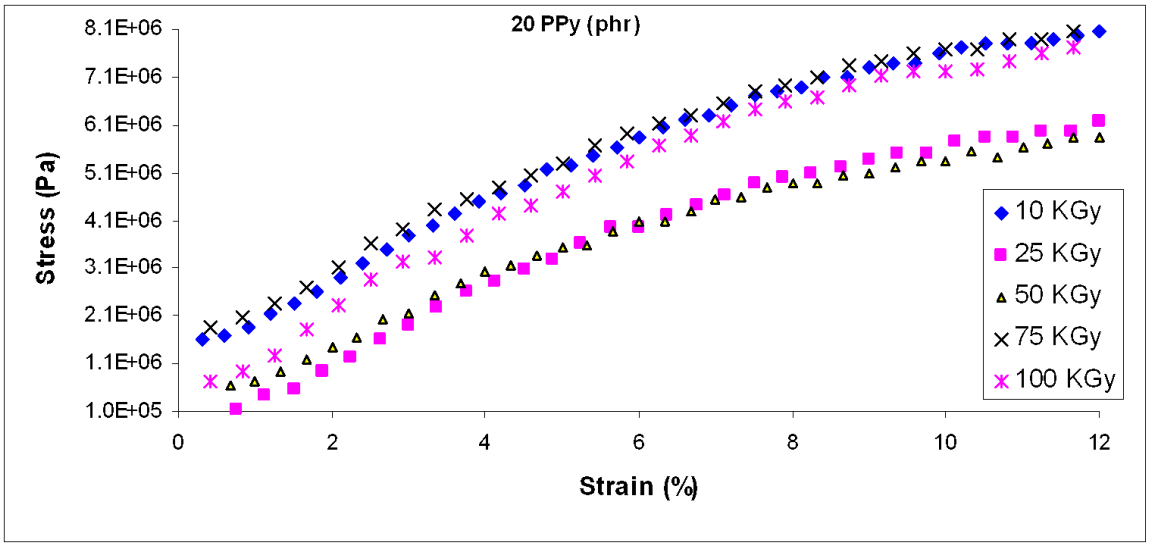

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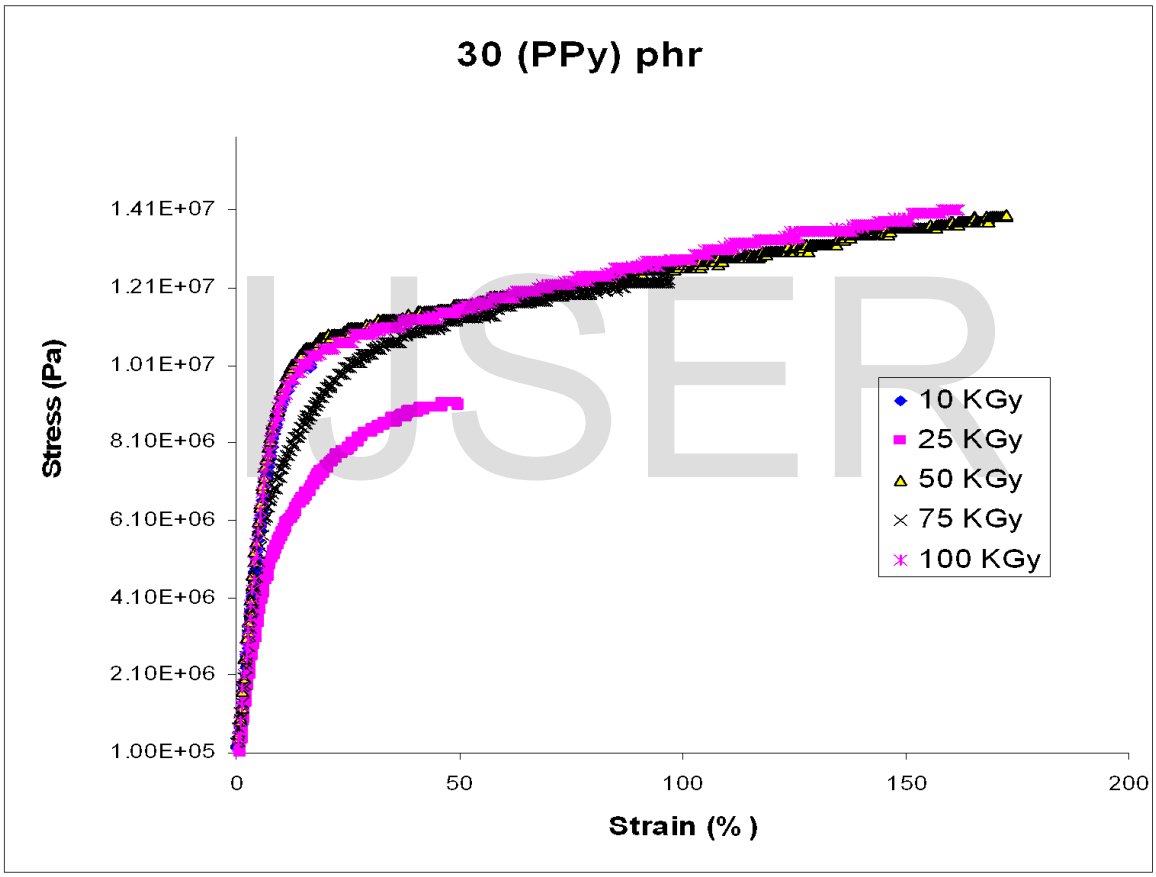


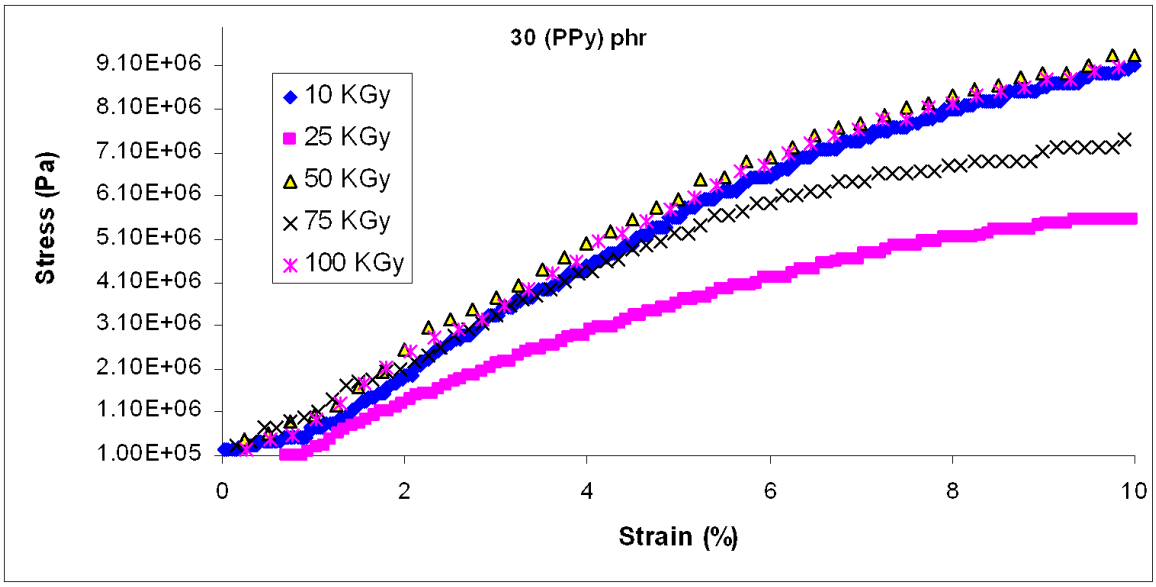


Figure (1- f): The nominal stress –strain graphs for the composite up to 30 phr of PPy with electron - beam irradiation dose (10, 25, 50, 75& 100 KGy).

3.2 Tensile strength:

Tensile strength for all samples of PPy/EVA composites were reported in Figure (2) The reinforcement acquired by the EVA matrix by the incorporation of the PPy filler is evident from this behavior. This can be attributed to the interaction of PPy with the EVA matrix. In the case of irradiated samples (Figure 2) all the composition showed an improved strength. Here the maximum value is attained at 15 % of PPy loading according to the e-beam dose 100 KGy respectively. By the use of PPy and electron-beam irradiation dose one can achieve best mechanical properties by the incorporation of small amount of the filler. (For irradiated samples with 100 KGy).

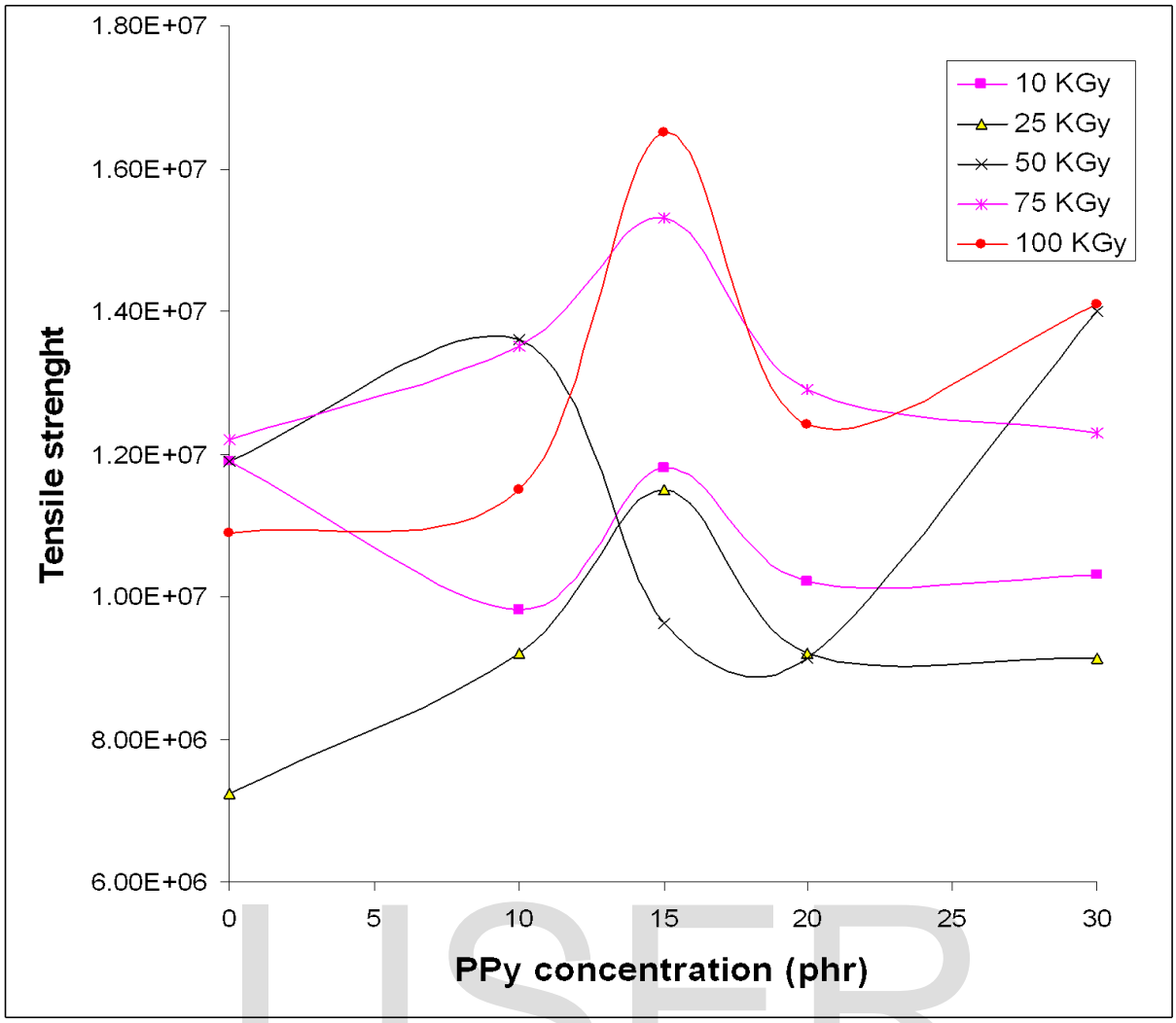


Figure (2): The tensile strength for all irradiated samples of PPy/EVA composites with sample concentration.

3.3 Cross linking density:

On the basis of phenomenological theory of rubber elasticity and derived from the Mooney Rivlin equation [7], stress - strain measurement can be used for measuring the crosslink density of rubber. This can be obtained using equations below. From the plot of $\sigma/ (\lambda - \lambda^{-2})$ and $1/\lambda$, the constants C_1 and C_2 can be determined, the intercept of the curve on the $\sigma/ (\lambda - \lambda^{-2})$ axis corresponds to C_1 value and its slope corresponds to the value of C_2

$$F=2 A_0 (C_1 + C_2 \lambda^{-1}) (\lambda - \lambda^{-2}) \quad (3.1)$$

$$\sigma/ (\lambda - \lambda^{-2}) = 2C_1+2C_2/\lambda \quad (3.2)$$

Where F is the tensile extension force required for stretching a specimen, A_0 is the cross sectional area of the unstretched specimen, λ is the extension ratio (which is $1+\varepsilon$, where ε is the strain) σ_0 is identifiable with F/A_0 and C_1 and C_2 characteristic constants of the vulcanizate.

C_1 is directly related to the physically effective crosslink density υ_ℓ by the equation

$$C_1 = \rho RT \upsilon_\ell \qquad (3.3)$$

The crosslinking density values calculated by the above equation for all samples are given in Tables (2- 4).

Table (2)**: The calculated values of C_1 (MPa)**

Radiation dose / Sample phr	Un-irradiated samples	10 KGy	25 KGy	50 KGy	75 KGy	100 KGy
	C_1 (MPa)					
0	0.4	0.5	0.7	1.7	1.5	1.4
5	1.1	1.5	1.6	1.8	1.7	1.8
10	1.2	1.7	1.8	2.0	1.9	2.0
15	1.5	1.9	2.0	2.8	2.0	2.5
20	1.7	2.1	2.2	3.0	2.2	2.8
30	3.0	3.5	4.0	5.0	7.0	3.0

Table (3): The calculated values of C_2 (MPa)

Radiation dose / Sample phr	Un-irradiated samples	10 KGy	25 KGy	50 KGy	75 KGy	100 KGy
	C_2 (MPa)					
0	4.0	4.0	4.0	1.0	5.0	4.0
5	6.0	7.0	5.0	0.6	4.0	4.0
10	8.0	7.5	7.5	5.0	5.0	4.45
15	50	30.0	20	30.0	8.0	6.0
20	6.0	8.5	8.5	8.5	6.0	6.5
30	15.0	12.5	30.0	10.0	50.0	5.5

Table (4): The calculated values of crosslinking density ע $_\ell$ (mol/m^3).

Radiation dose / Sample phr	Un-irradiated samples	10 KGy	25 KGy	50 KGy	75 KGy	100 KGy
	Crosslinking density ע$_\ell$ x10^3 (mol/m^3)					
0	0.748	0.935	1.31	3.18	2.81	2.62
5	2.06	2.81	2.99	3.55	3.18	3.37
10	2.24	3.18	3.37	3.74	3.55	3.74
15	2.81	3.55	3.74	5.24	3.74	4.68
20	3.18	6.55	4.12	5.69	4.02	5.24
30	5.61	7.10	7.48	9.35	13.1	5.61

It can be seen that the crosslink density is found to be maximum at 30 phr filler contents of PPy/EVA (at 75 KGy electron-beam dose) and this in good agreement with the increase in c_1 value. As the concentration of conducting PPy/EVA (at 75 KGy) shows the presence of higher chain entanglement [8, 9], a higher chain entanglement shows better molecular level mixing. The crosslink density increases with the amount of filler and electron-beam dose ≤ 75 KGy thus the observed tensile strength variation can be correlated with the variation of υ from Mooney-Rivlin equation

3.4 Theoretical models:

Mechanical properties of particulate filled composites are widely studied through a comparison of experimental results and predictions based on various theoretical models. Different theoretical models selected to predict the mechanical behavior of conductive PPy/EVA blends. Include Einstein and Guth equations, Guth equation, Kerner equation, Querneda equation and Thomas equation [10-14].

i) Einstein and Guth equation:

These equations are mainly used for theoretical calculations of the properties of particulate (spherical) reinforced polymer composites. According to the Einstein equation

$$M_c=M_m (1+ 2.5V_p) \quad (3.4)$$

Where M_c and M_m are the Young's modulus of composite and matrix, respectively, and V_p is the particle volume fraction. Einstein's equation is applicable only for material filled with low concentrations of non interactive spheres. Einstein's equation implies that the stiffened or reinforcing actions of filler are independent of the size of the filler particles. This equation shows that the volume occupied by the filler, not its weight, that is the important variable. The equation also assumes that filler is very much more rigid than the matrix.

ii) Guth equations:

$$M_c=M_m (1+ 2.5V_p+14.1V^2_p) \quad (3.5)$$

Guth′s equation is an expansion of Einstein, to account for the interpartical interactions at higher filler concentrations.

iii) Kerner equation:

Young′s modulus of spherically shaped particulate-filler polymer composites is given by Kerner′s equation:

$$M_c=M_m \left[1+\frac{15V_p(1-\sigma_m)}{V_m(8-10\sigma_m)}\right] \quad (3.6)$$

Where V_m is the matrix volume fraction and σ_m is the Poisson's ratio of the matrix.

iv) Querneda equation:

$$Mc = [\frac{M_m}{(1-0.5KV_p^2)}] \quad (3.7)$$

Where K is a constant normally 2.5 this variable coefficient is introduced to account for the interpartical interactions and differences in particle geometry.

V) Thomas equation:

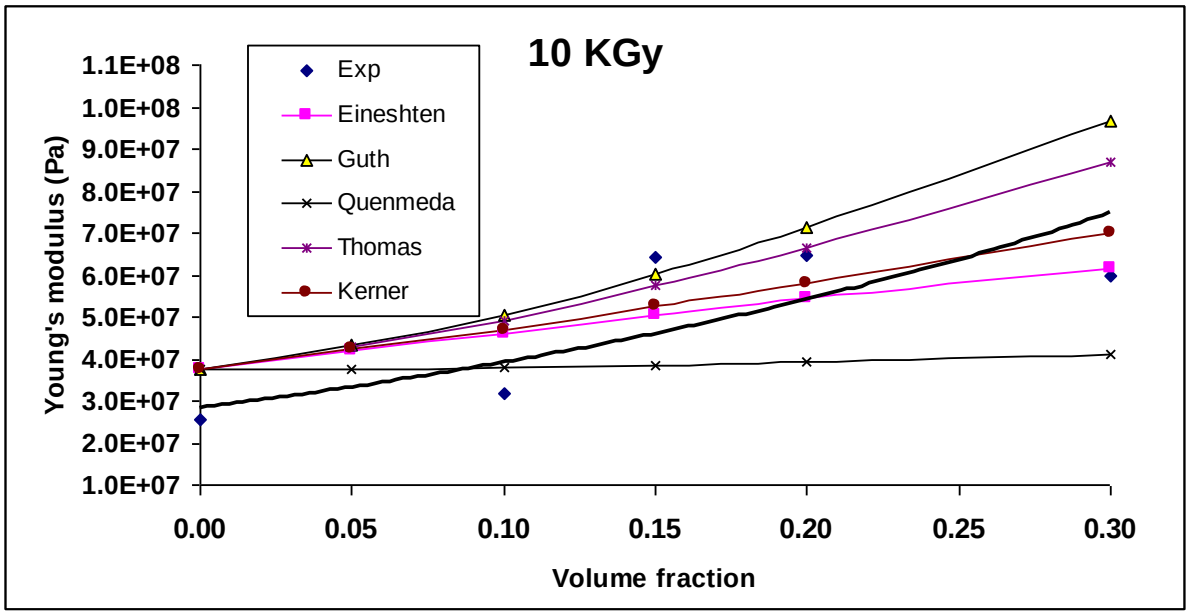
$$M_c=M_m [1+2.5V_p+10.05V^2_p+0.00273 \exp (16.6V_p)] \quad (3.8)$$

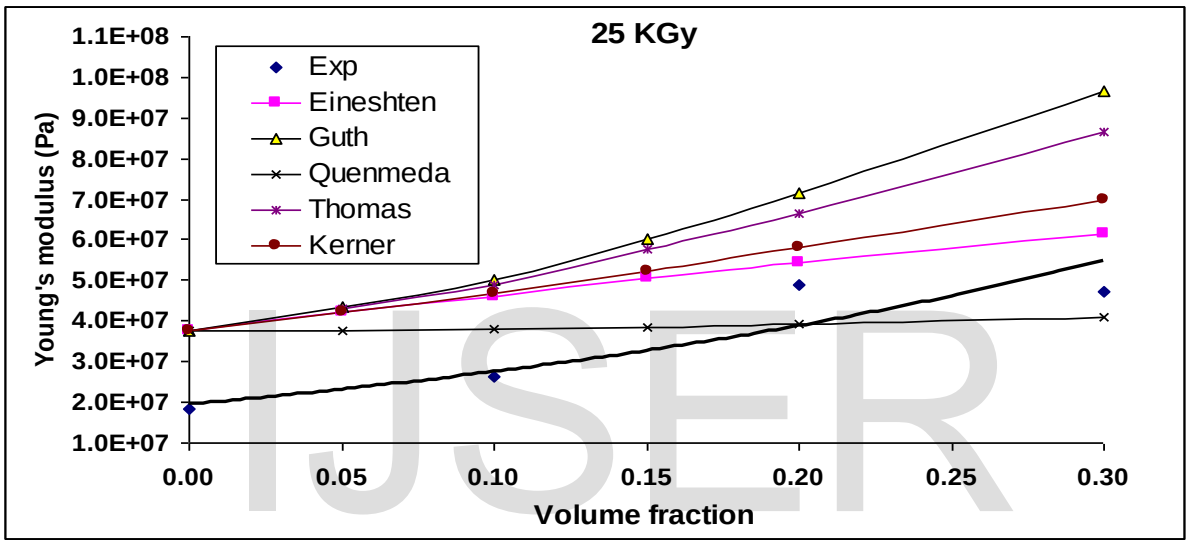
Thomas equation is an empirical relationship based on the data generated with dispersed spherical particles. These theoretical predictions have been plotted with the experimental results in Figure (3). One can see that none of these fit with experimental results. all these predictions assume that the matrix and filler have no appreciable degree of interaction. However, from the mechanical properties, one can see that there is considerable interaction. So, the modulus values differ with the theoretical values. However, in the present system, there is interaction between the matrix and filler. This enables the modulus value to shoe a different behavior at lower and higher loading. The experimental results could be fitted well with polynomial equation [as shown in Figure (3)].

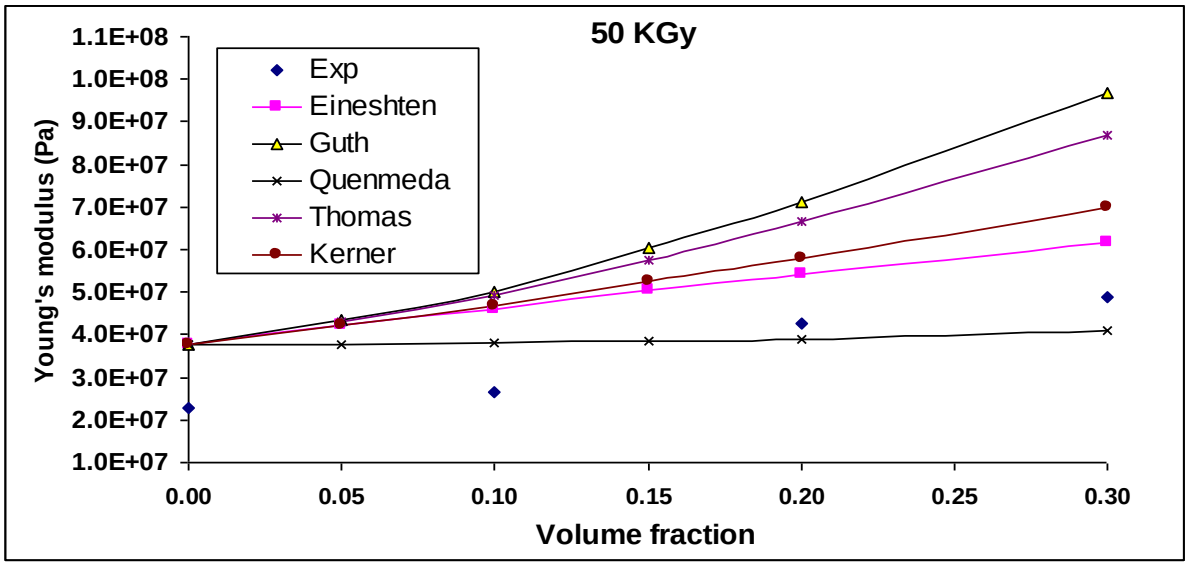
$$Y=Y_o (AX^2+By+ c) \quad (3.9)$$

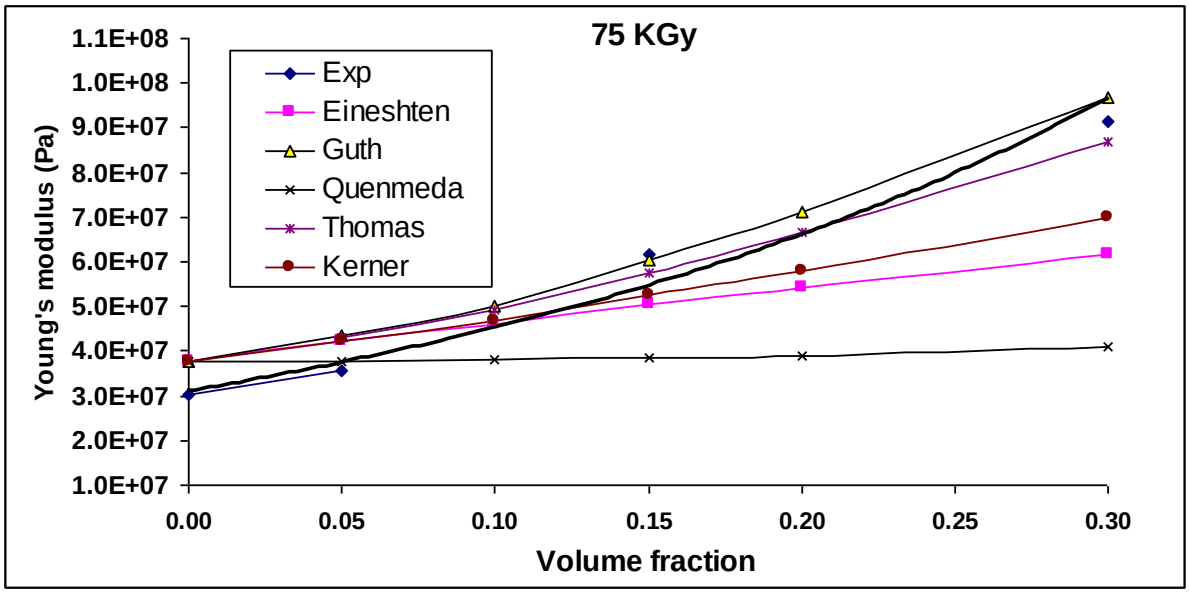
Where Y_o is young's modulus for the unloaded EVA sample, A, B, and C are fitting parameters.

the modification of electron-beam dose to the values of Young's modulus of these samples (at 75 KGy) contribute to the degree of interaction of the filler with the EVA matrix and this could be observed through the fact that none of these theoretical models fit with the experimental results [as shown in figure (3)] .









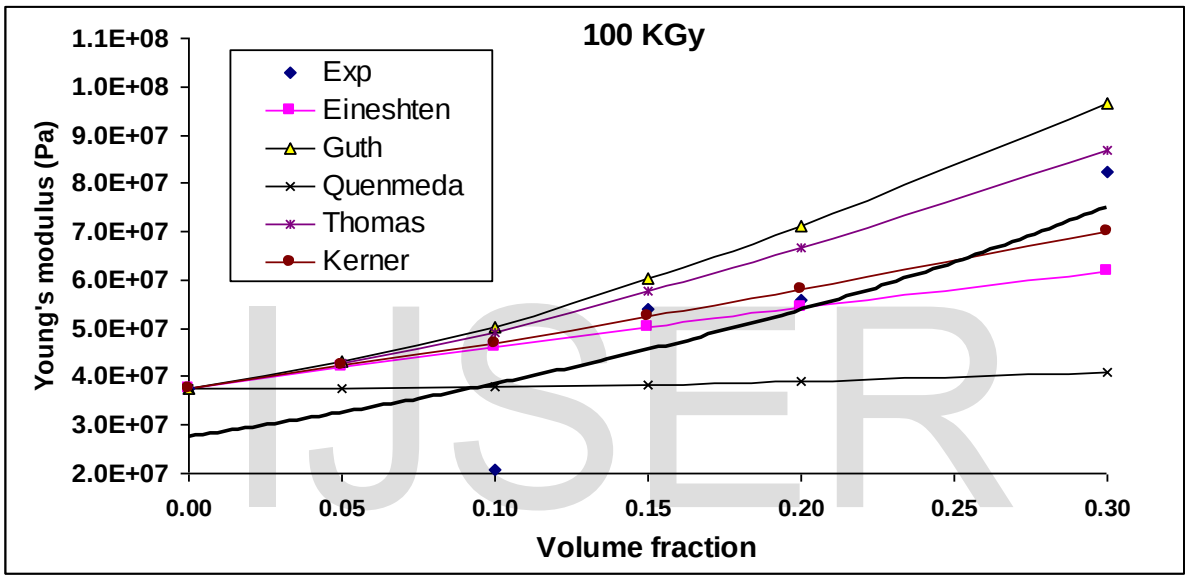


Figure (3): The relation between Young's modulus and volume fraction of PPy concentration (phr) with the theoretical models for all irradiated samples.

4. Conclusions

The mechanical properties of these filled EVA samples show high initial elastic modulus increases with PPy contents up to 15 phr. Moreover, the elastic moduli and strength increases with electron-beam irradiation dose. The degree of reinforcement achieved through incorporation of conductive PPy is the highest at 15 phr loading and at 100 KGy electron-beam irradiation dose. The crosslinking density calculated from the Mooney-Rivlin equation is found to be maximized at PPy loading of 30 phr at (75 KGy). Finally, the experimental results were compared with theoretical a prediction, which indicates the absence of fitting between them. Meanwhile, polynomial empirical formula fit well the experimental results.

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.

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