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

A.M. Abd Elbary[(1)] and N.I. Aljuraide[(2)]

[1]Higher Institute of Engineering and Technology, Department of Physics and Mathematical Engineering science, New Cairo Academy, 5th settlement, New Cairo City, Egypt.
[2]Faculty of Medical Applied Sciences and Scientific Departments, Department of Physics, Turabah Branch, Taif University, Al-Haweiah, P.O. Box 888, 21974, Saudi Arabia,
dr_ah_abdelbary2005@yahoo.com,; n.aljuraied@gmail.com.

Abstract: Films of EVA, containing 12% VA and Polypyrrole / carbon nano-particles used for this study were prepared. The x-ray diffract grams of films were obtained for all the samples and ensures the amorphous nature. 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 30 phr. The degree of reinforcement achieved through incorporation of conductive PPy is the highest at 30phr loading. The cross linking density calculated from the Mooney-Rivlin equation is found to be maximized at PPy loading of 30 phr. 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.
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1. Introduction

An important attribute of polymers is the ability to modify their inherent physical properties by the addition of fillers while retaining their characteristics processing ease. These fillers, present in varying degrees, also affect the basic mechanical properties of the polymer. In many cases, the changes in the mechanical properties of the filled polymer can be predicted from basic principles. In other cases, the property changes must be experimentally measured, because there is not much sufficient knowledge about the polymer filler interactions to calculate the effect of filler concentration on polymer changes [(1)].

The effect of fillers on the properties of the composites depends on their concentration and particle size and shape as well as the interaction with the matrix. The theory of filler reinforcement of the polymers predicts the formation of the boundary layer of a matrix material on the surface of the filler [(2-5)].

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 [(6)].

Elastomers, unlike fibers or plastics, are normally useful only after fillers and other compounding ingredients have been added [(7)]. Restricted properties and limited use of homo polymers 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 [(8)].

Ethylene-co-vinyl acetate has Boor tensile strength**,** Resistant to heat deformation, Flexibility, low temperature performance. EVA copolymer with approximately 12 % VA_c is widely used in the hot-melt coatings and adhesives arena where the additional intermolecular bonding promoted by the polarity of the vinyl-acetate ether and carbonyl linkages enhances melt strength, while still enabling low melt processing temperatures[(8)].

Polypyrrole is an especially promising conductive polymer for commercial applications, a wing to high conductivity, good environmental stability, and ease of synthesis. However, PPy is insoluble and infusible, which restricts its fabrication, and it has poor mechanical properties. Understanding of electrical properties, morphology and crystal structure of PPy composites may be useful in improving the stability characteristics of these materials which are the key factors in governing the device performance.

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 shown in Figure (1).

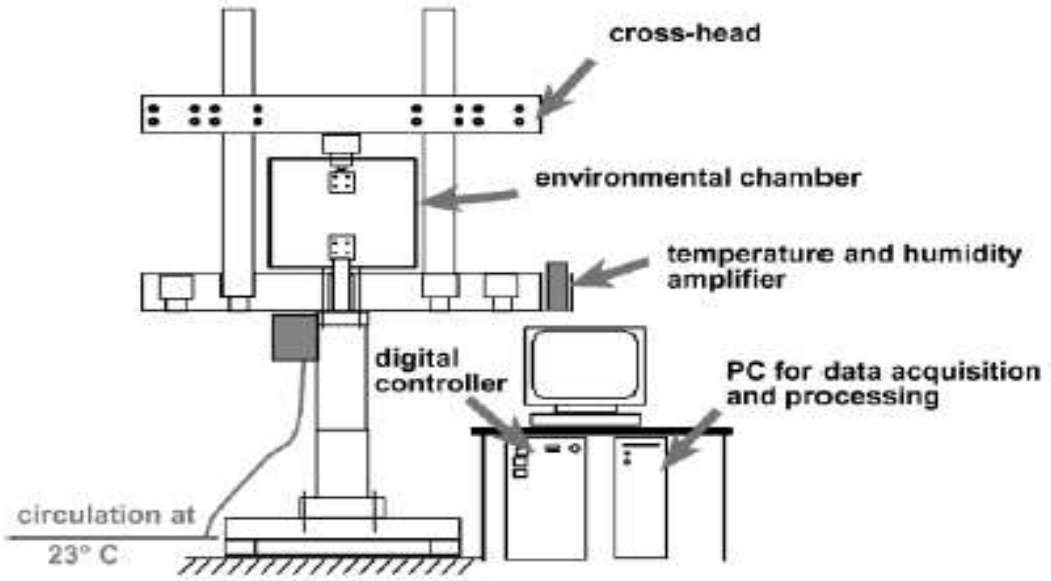

Figure (1): Shows the system used in measuring mechanical properties

3. Results and Discussion

The stress –strain behaviors of the composites of PPy and EVA are shown in Figure (2).

All filled samples show similar trend. In the initial stages of the strain, the stress goes on increasing linearly (Hookean region). In the plastic deformation stage, the strain increases but there is not an appreciable amount of increase in stress value as in the linear region. After this the samples break. All the filled system shows high initial moduli.

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.

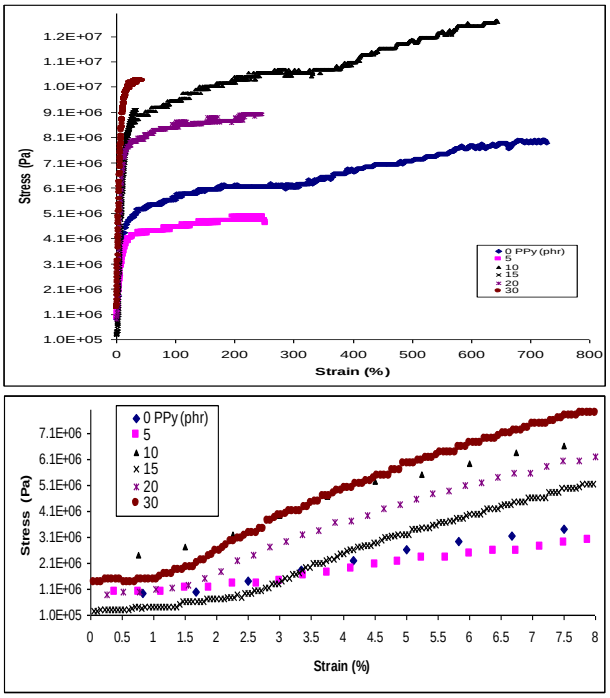

Figure (2): The nominal stress –strain curves for the composite up to 30 phr of PPy.

On increasing the PPy conductive contents, the modulus value increased (Figure 3). For the addition of 30% of PPy, it was noticed that a 259% increases in Young's modulus occurred. The increase in Young's modulus is governed by the fact that the PPy filler gives good reinforcement with the EVA matrix. Further, the particle size of the PPy is very small (40nm) so that the aspect ratio is high.

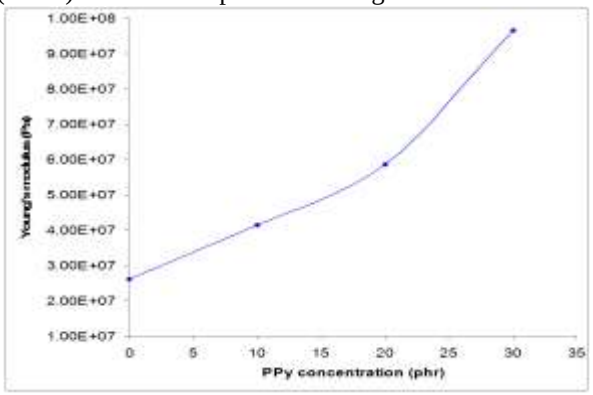

Figure (3): The dependence of Young's modulus on PPy concentration (phr).

3.2 Tensile strength:

Tensile strength for all samples of PPy/EVA composites were reported in Figure (4) from the Figure one can see that the tensile strength values increasing linearly up to 10 % then it falls. However, all the compositions showed a tensile strength higher than the origin EVA polymeric matrix.

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.

3.3 Cross linking density:

On the basis of phenomenological theory of rubber elasticity and derived from the Mooney Rivlin equation [9], 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

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

The cross linking density values calculated by the above equation for all samples are given in Table (2).

It can be seen that the crosslink density is found to be maximum at 30 phr filler contents of PPy/EVA and this in good agreement with the increase in c_1 value. As the concentration of conducting PPy/EVA shows the presence of higher chain entanglement [10], a higher chain entanglement shows better molecular level mixing. The crosslink density increases with the amount of filler thus the observed tensile strength variation can be correlated with the variation of υ from Mooney-Rivlin equation.

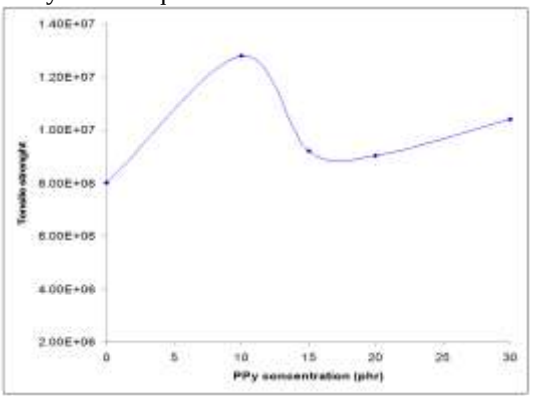

Figure (4): The tensile strength for all samples of PPy/EVA composites with sample concentration.

Table (2).The crosslinking density values for all samples are given

Sample (phr)	C_1 (MPa)	C_2 (MPa)	Crosslinking density$\nu_e x10^3$ (mol/m^3)
0	0.4	4.0	0.748
5	1.1	6.0	2.06
10	1.2	8.0	2.24
15	1.5	50	2.81
20	1.7	6.0	3.18
30	3.0	15.0	5.61

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 [11-15].

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:

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

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 (5). 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 (5)].

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

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

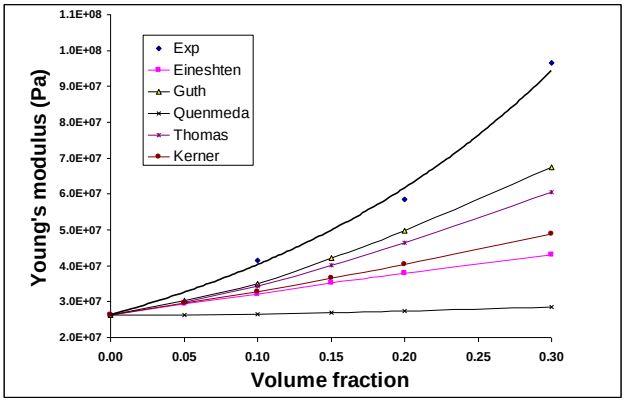

Figure (3.5): The relation between Young's modulus and volume fraction of PPy concentration (phr) with the theoretical models for all samples.

4. Conclusions

From the mechanical properties all the filled systems show high initial moduli. By adding of 30 phr of PPy, it was noticed that a 259% increases in

Young's modulus occurred. the tensile strength values increasing linearly with PPy loading up to 10 phr then it falls. The crosslinking density values (υ) were calculated for all samples by using the Mooney- Rivlin equation. It can be seen that the crosslink density is found to be maximum at 30 phr filler contents of PPy/EVA and this in good agreement with the increase in c_1 value as presented in Mooney- Rivlin equation. The crosslink density increases with the amount of filler. Thus the observed tensile strength variation can be correlated with the variation of υ from Mooney-Rivlin equation.

Finally, some theoretical models where used to describe the dependence of Young's modulus on the volume fraction of PPy concentration filler. None of these models fit well the experimental results. An empirical polynomial equation was proposed to fit the experimental results.

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