Tensile stress – strain behaviour of conductive PPy on Mechanical Properties of PVC/PMMA composites

N. I. Aljuraide

Faculty of Medical Applied Sciences and Scientific Departments, Department of Physics, Turabah Branch, Taif University, Al-Haweiah, P.O. Box 888, 21974, Saudi Arabia,
Tel. +966(02)8224377, Fax +966(02)8221115, E-mail : n.aljuraied@gmail.com.

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. Tensile strength and elongation at break were estimated from stress strain curves measured by a tension meter.The mechanical properties of these filled PVC/PMMA samples show that Young's modulus is obviously improved by the addition of conductive PPy till 2 wt. % and begins to decrease with further conductive PPy loading till 5 wt. %. The cycle rank calculated from Gaussian affine model was found to increase by the addition of conductive PPy till 2 wt. % and begins to decrease with further conductive PPy loading till 5 wt. %. Then increase again at 15 wt. % loading.

Keywords. Tensile stress – strain behaviour, conductive PPy, Mechanical Properties, PVC/PMMA composites

Introduction

High molecular weight compounds constitute one of the major fields of modern technology. Thus high polymers either natural or synthetic participate in a wide range of industrial applications (1).

During the recent years there has been an explosive growth of research in the field of conducting polymers owing to their interesting electrical properties and their potential applications in various fields like electrochromic displays, electronic devices, modified electrodes, chemical and bio-sensors etc. Most of the works with conducting polymers have been focussed on three main classes of polymeric materials viz. polyacetylene and its derivatives, polyphenylenes and its derivatives and poly heterocyclics such as polypyrrole, polythiophene etc.

These polymeric materials can be obtained in various forms like powders, thin films etc (2). In order to set a material suitable for applications in various technological fields one has to overcome certain limitations such as poor mechanical properties and processability, instability in ambient conditions. Several approaches have been made by many researchers to improve these properties.

PVC has high hardness and mechanical properties. The mechanical properties enhance with molecular weight increasing, but decrease with temperature increasing. The mechanical properties of rigid PVC (uPVC) is very good, the elastic modulus can reach to 1500-3,000 MPa. The soft PVC (Flexible PVC) elastic modulus is 1.5-15 MPa. However, elongation at break is up to 200 -450%. PVC friction is ordinary, the static friction factor is 0.4-0.5, and the dynamic friction factor is 0.23(3).

Polypyrrole is regarded as one of the most investigated conducting polymers. It is a chemical compound formed from a number of connected pyrrole ring structures. Understanding of mechanical 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 device performance.

PPy and related conducting polymers have two main applications in electronic devices and in chemical sensors (4) . PPy is also used in potential vehicle for drug delivery. The polymer matrix serves as a container for proteins (5) .

Conducting polymers composites, resulting from the association of an insulating polymer matrix with conductive fillers, exhibit several interesting features due to their resistivity variation with thermal, mechanical or chemical solicitations.

This versatility of compounds is used for "intelegent" applications such as self regulated heating or vapour detections.

The main significant factor is the filler distribution within the matrix which can result from processing conditions (temp. shearing, viscosity and orientation).

Electronic transport in conjugated polymers has become an increasingly interesting area of research, partly because of the unique electronic properties of compounds, and partly because these materials posses great potential for device applications such as Schottky junctions batteries, displays, sensors and microelectronics.

These applications are hampered by the poor mechanical properties of these conducting polymers embedded in some insulating polymer matrices with higher mechanical properties.

Poly (methyl methacrylate) PMMA is one of the well-known brittle materials, in order to enhance the physical and mechanical properties of PMMA, numerical studies on the improvement methods have been extensively carried out in the past three decades. The most common method for promoting toughness of PMMA is blending with modifier (PVC).

The present investigation is concerned with detailed studies on the mechanical properties of PVC/PMMA composites filled with conductive PPy nano filler (loaded with constant concentration (40 phr) of HAF black).

2. Experimental

2.1 Materials and Preparation of sample

Poly vinyl chloride (PVC) of standard grade supplied by Fluka, and poly methyl methacrylate (PMMA) supplied by Alfa Aesar, were used in the study. The conducting polymer (polypyrrole) also supplied 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 different 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 thoroughly cleaned with hot water and then with acetone was used as a substrate. The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at a room temperature (25°C). In this way, the film was prepared by isothermal evaporation technique. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove 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*

Tensile strength and elongation at break were estimated from stress strain curves measured by a tension meter (carried out with the use of SLFL-100KN Shimadzu Co.); tension speed was 1mm/min. Samples in a rectangular shape (specimens of 50mm long and 2.6mm neck width of different degrees of crosslinking gas calculated from the Mooney Rivlin equation were used for a mechanical test. By using the dimensions of samples the stress and strain were calculated.

3. Results and discussion

3.1 Tensile stress – strain behaviour of PVC/PMMA composites

In practice, the tensile stress- strain measurements are usually done under non- equilibrium conditions. They belong to fundamental and most frequently used tests; the data obtained give basics, important and manifold information which is being exploited for quality control, material specification and developmental work (6).

3.1.1 Theoretical (6):

Low elongation region

a- Gaussian theory

The equilibrium stress – strain dependence of elastomeric networks in the region of low elongation was qualitatively explained on the basis of the classical Gaussian rubber elasticity theory as early as 1936 (7) and developed further in a number of papers (8, 9). The only parameter of the theory is the shear modulus G which due to the incompressibility of the network determines the initial slope of stress – elongation dependents (SED): (dσ/dt) = 3 G; σ is the nominal stress, i.e force per unit undeformed area of cross- section.

The Gaussian result for the stress in simple extension is given by

$$\sigma = G\,D \qquad (3.1)$$

$$D = \lambda - 1/\lambda^2 \qquad (3.2)$$

λ is the extension ratio: $\lambda = L/L_o = Ɛ+1$

where L is the change of length, L_o is the initial length

The shear modulus G of the Gaussian network is predicted to be proportional to the concentrations ʒ (mole/m^3) of independent circuitous paths in the network, called the cycle rank (10).

$$G = ʒ\,RT \qquad \text{phantom theory} \qquad (3.3)$$

$$G = \frac{\Phi}{\Phi-2}\,ʒ\,RT \qquad \text{affine theory} \qquad (3.4)$$

Φ is the junction functionality, R the universal gas constant, and T the absolute temperature. In a perfect network with a concentration of C junctions, the cycle rank $ʒ = \frac{C\,(\Phi-2)}{2}$ and the concentration of network chains, υ = CΦ/2. The modulus of a perfect phantom network devoid of imperfections of any kind (dangling chains, intramolecular loops, entanglements) and containing C (mole/ m^3) tetrafunctional junctions is G = CRT = (υ/2) RT; that of an affine network is equal to

$$G = 2\,CRT = \upsilon RT. \qquad (3.5)$$

For an imperfect network , Flory (11) defined the term " effective chains " to be those that effectively contribute to the elasticity of the network and related their number υ_{eff} to the cycle rank by $\upsilon_{eff} = 2$ ʒ.

Deviations from the Gaussian equations (3.1) and (3.2) at low elongations, a general definition of the so called reduced stress σ_{red} is given by the relation:

$$\sigma_{red} = \frac{\sigma}{D} \qquad (3.6)$$

In the simple Gaussian theory the reduced stress is independent of the extension ratio. This is not supported by the experiment: at low elongation virtually unswollen rubber like networks shows a decrease in the reduced stress with increasing extension ratio.

b) Phenomenological theory

A simple satisfactory description of the low- elongation behaviour of most single phase networks is offered by Phenomenological two – parameters equation of Mooney and Rivilin (12, 13).

Its first term (the C_1 term) has the same λ- dependence as the result of the Gaussian theory (equation 3.8), the second term (the C_2 term) introduces the necessary decrease in reduced stress with increasing extension ratio.

$$\sigma_{MR} = 2C_1 D + 2 C_2 (1- \lambda^{-3}) \qquad (3.7)$$

$$\sigma_{MR} / D = 2 C_1 + 2 C_2/\lambda \qquad (3.8)$$

Relations between the experimentally determined Mooney – Rivilin parameters, C_1, C_2, and the structural parameters of the network were studied in a number of papers (14 -17). As a rule, the measured modulus is higher than that calculated from the knowledge of the network structure and using the Gaussian equations (3.1 - 3.4). The latter effect has often been ascribed to the presence of chain entanglements trapped between chemical crosslinks (18).

The stress – strain curves of different loading PPy in PVC/PMMA composites are shown in Figure (1).

Table (2) shows the summarized results of tensile tests. Young's modulus is obviously improved by the addition of conductive PPy till 2 wt. % and begins to decrease with further conductive PPy loading till 5 wt. %.

The total area under the stress – strain (force - displacement) curve, which represents the fracture energy (as tabulated in table (3)), firstly decreases with PPy contents till 2 wt. % and begins to increase with further PPy loading till 5 wt. %.

The modulus of 2 wt. % PVC/PMMA loading samples is approximately 195 % of the neat PVC/PMMA. Meanwhile, upon loading PVC/PMMA with PPy greater than 2 wt. % and less than 15 wt. % the modulus decreases approximately by 84 %. With further PPy loading (15 wt. %) young's modulus increases by 415%.

Table (2): The summarized results of tensile tests.

PPy %	Young's Modulus (MPa)	Fracture energy (Joule) (x10^6)
Zero	1135	0.92
1	1922	0.21
2	3353	0.17
3	171.8	2.63
4	262.44	1.68
5	415.38	2.50
15	5842.5	0.05

c) Comparison of Experimental with Theoretical Equations.

1) Gaussian theory

A measure of agreement of Gaussian equation with our data on loaded PVC/PMMA network in simple extension is presented in Figures (3.2) for all samples where the data are plotted in linear coordinates. The deviation of the data from the fitting curve does not seem to be large especially for samples PVC/PMMA unloaded and loaded with 3 wt. %, 5 wt.% and 15 wt. %.

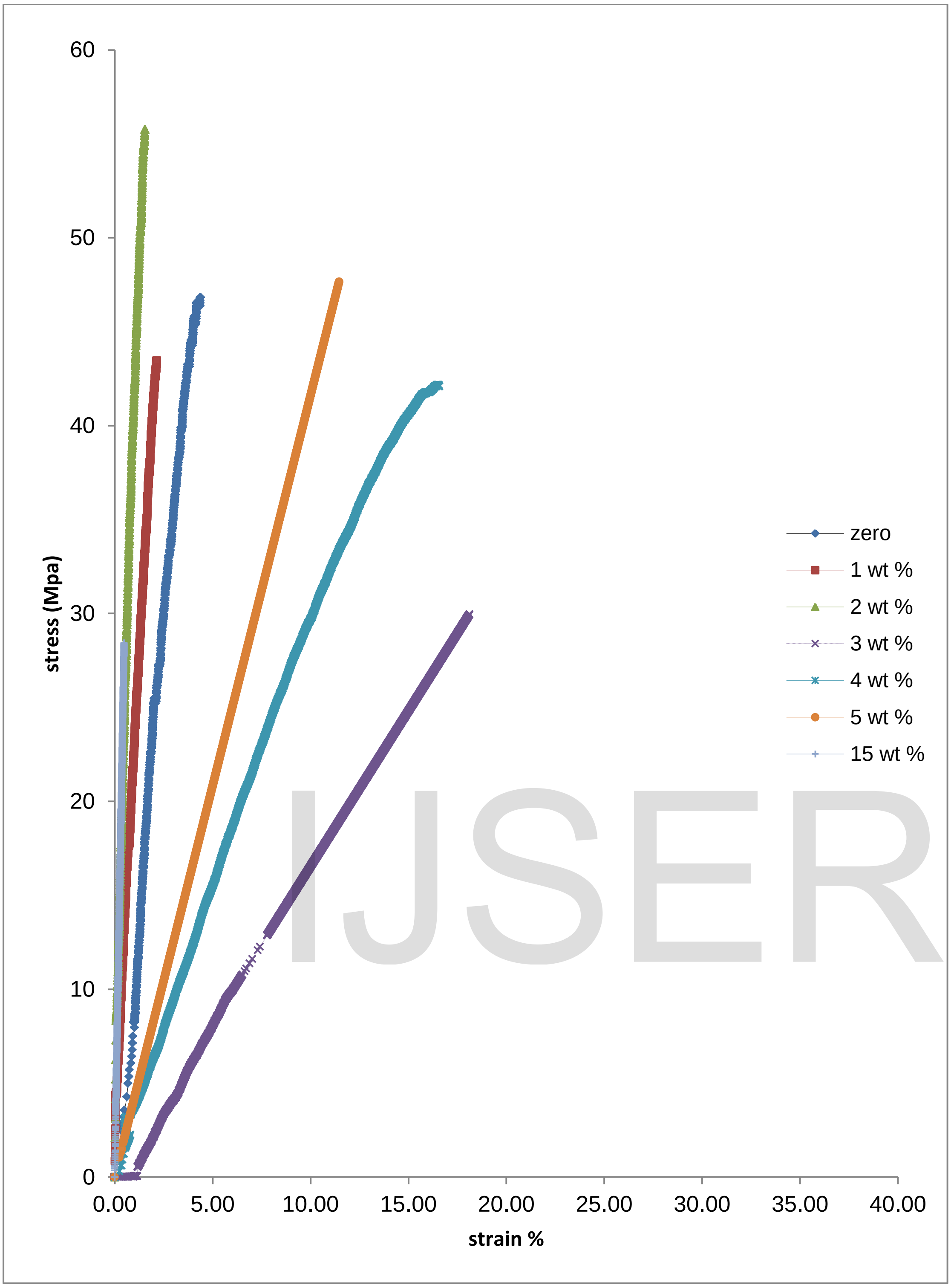


Figure (3.1): The stress – strain curves of different loading PPy in PMMA/PVC composites.

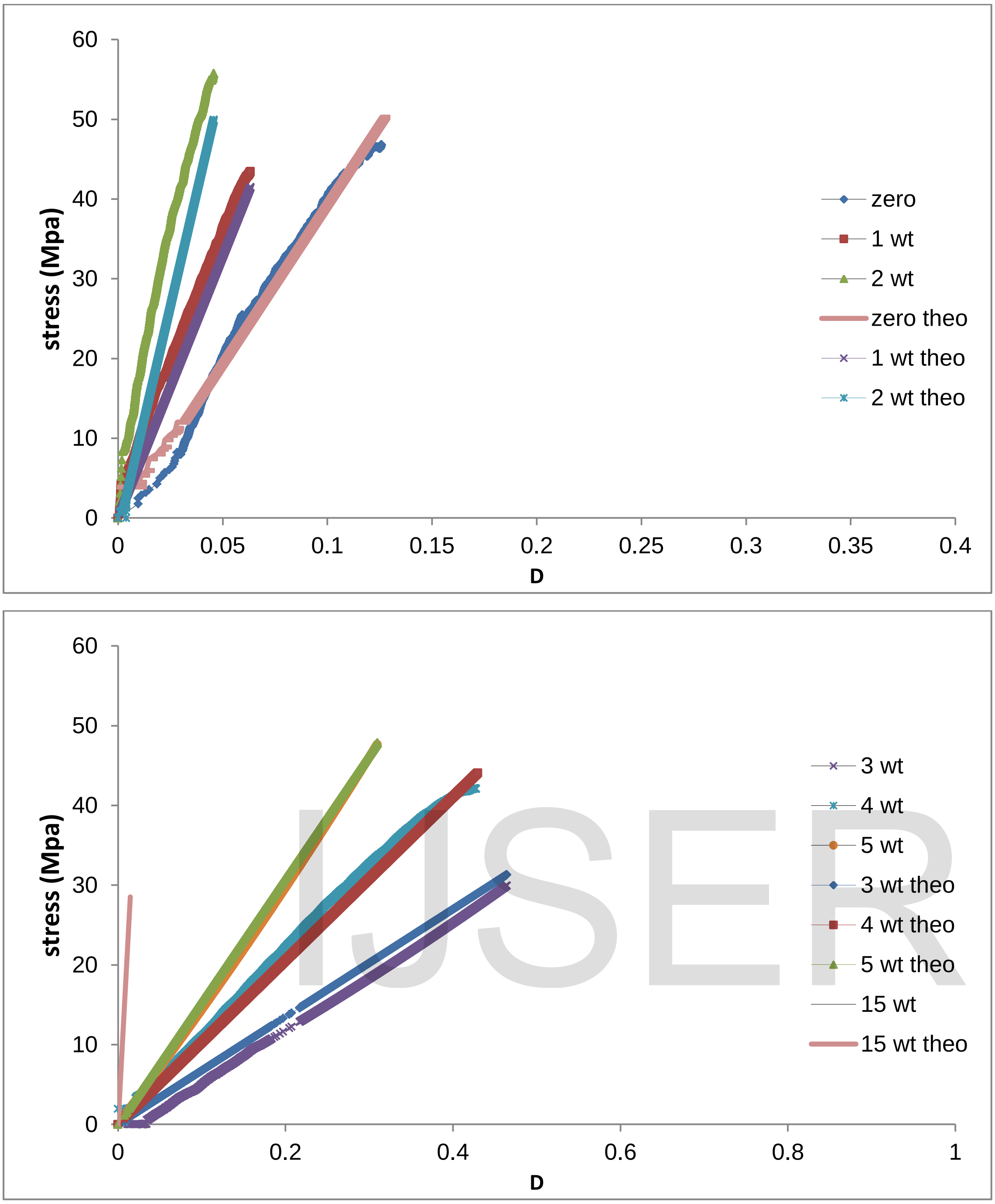


Figure (3.2): The stress – D curves of PMMA/PVC samples loaded with different contents of conductive PPy as a filler.

From Figure (3.2), one can calculate the shear modulus G of all samples which tabulated in Table (3.5). The same detected behaviour of the young's modulus on the PPy conductive loading is also observed for the shear modulus, one can also observe that the shear modulus G is approximately equal to one third of young's modulus for all measured samples. From Table (3), one also observes that the number of effective chains increases with PPy loading up to 15 wt. % except for samples loaded with 3 wt. % and 5 wt. %.

Table (3): The summarized results of shear calculations.

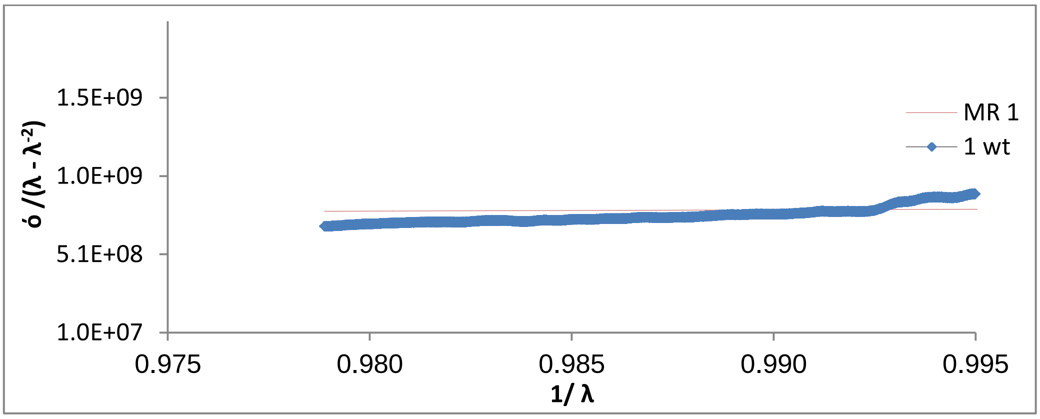
PPy %	**Shear Modulus (MPa)**	**Effective chains $\upsilon_{eff}= 2\xi$((mole/m^3) (x10^4)**	**Cycle rank ξ (mole/m^3) (x10^4)**
Zero	399.2	16.01	8.005
1	655.03	26.26	13.13
2	1130.3	45.32	22.66
3	67.426	2.70	1.35
4	102.54	41.11	20.55
5	154.4	6.19	3.095
15	1957.3	78.47	39.24

2) Mooney Rivilin

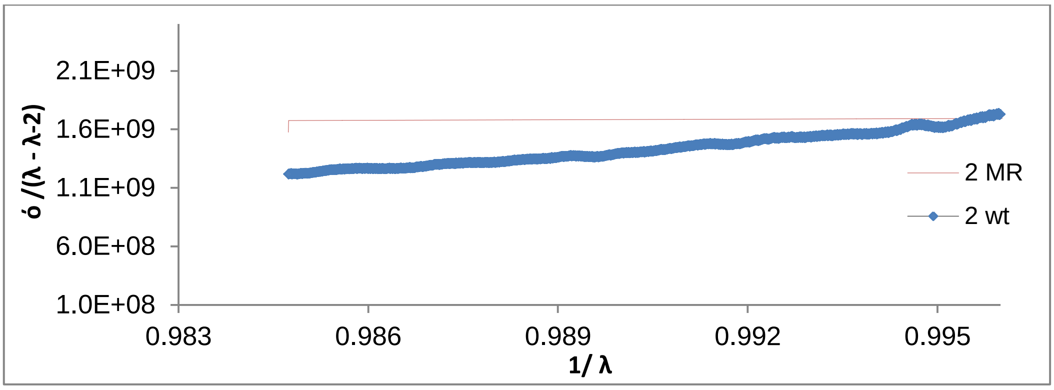
Figures (3 a-c) represent a comparison of an experiment – theory according to the phenomenological theory as in equation (3.8). From these Figures it was possible to calculate both fitting parameters C_1 and C_2 for samples loaded with 1 wt. %, 2 wt. % and 4 wt. %. The fit of equation (3.8) to the SED of these samples is satisfactory.

Table (4): The summarized results of the fitting parameters of equation (3.8) for samples loaded with 1, 2, and 4 wt. %.

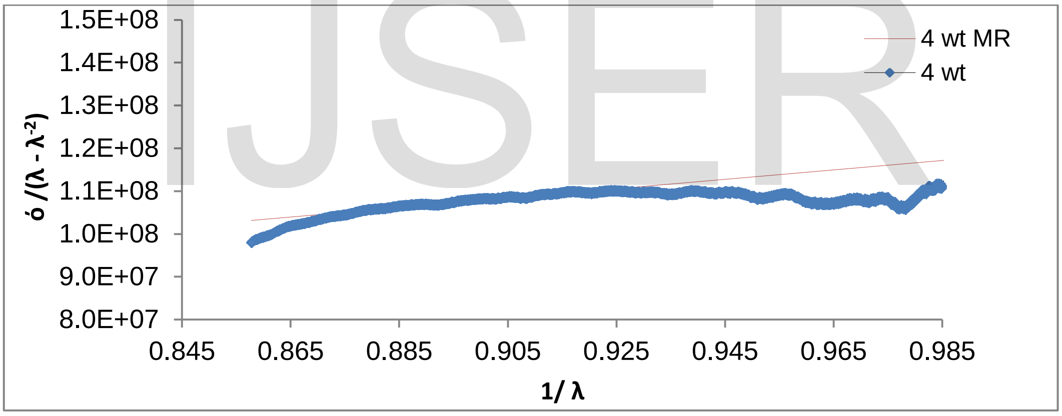
PPy %	**C_1 (10 ^{6})**	**C_2 (10 ^{6})**
1	1	400
2	50	900
4	4.4	55



(a)



(b)



(c)

Figure (3 a-c): A comparison of an experiment data and theory according to the phenomenological theory with different loading PPy in PVC/PMMA composites.

4. Conclusions

An experimental technique is employed to draw a consistent 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). Mechanical, behaviors of such materials were investigated.

The mechanical properties of these filled PVC/PMMA samples show that Young's modulus is obviously improved by the addition of conductive PPy till 2 wt. % and begins to decrease with further conductive PPy loading till 5 wt. %. The modulus of 2 wt. % PVC/PMMA loading samples is approximately 195 % of the neat PVC/PMMA. Meanwhile, upon loading PVC/PMMA with PPy greater than 2 wt. % and less than 15 wt. % the modulus decreases with approximately 84 %. With further PPy loading (15%) young's modulus increases by 415%. The cycle rank calculated from Gaussian affine model was found to increase by the addition of conductive PPy till 2 wt. % and begins to decrease with further conductive PPy loading till 5 wt. % .then increases again at 15 wt. % loading.

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 to Dr. Ah. Abd Elbary, Doctor of experimental physics, Higher Institute of Engineering and Technology, New Cairo Academy for his help.

References

(1) A Elwy, MM Badawy, GM Nasr, "Electrical properties and penetration rate of solvent into irradiated LDPE/SBR conductive blend" Polymer Degradation and stability, 1996

(2) GM Nasr, M Amin, HM Shaker , "mechanical properties of natural rubber nano composites" International Journal of Academic Research, 2014

(3) Properties of PVC (polyvinyl chloride). Jt-extrudermachine.com

(4) Janata, Jiri; Josowicz, Mira "Progress Article: Conducting polymers in electronic chemical sensors" Nature Materials, 2(1), 19-24, (2003).

(5) S. Geetha, Chepuri R.K. Rao, M. Vijayan, D.C. Trivedi, "Biosensing and drug delivery by polypyrrole" "Molecular Electronics and Analytical Chemistry Analytica Chimica Acta, 568, 119–125, (2006).

(6) B. Meissner, "Tensile stress–strain behaviour of rubberlike networks up to break. Theory and experimental comparison ", Polymer, 41, 7827 (2000).

(7) W. Kuhn, Kolloidz, 76, 258 (1936).

(8) L. R. G. Treloar," The physics of rubber elasticity", 3rd ed. Oxford, Clarendon press (1975).

(9) B. Erman, and J. E. Mark, "Structure and properties of rubber like networks", New York, Oxford

University press, 1997.

(10) F.T. Wall, P. J. Flory," Silicon-Containing Polymers: The Science and Technology of Their Synthesis " J. chem. Phys., 19, 1435 (1951).

(11) P. J. Flory, Macromolecules," Elastic activity of imperfect networks " 15, 99 (1982).

(12) M. Mooney, J. Appl. Phys., 11, 582 (1940).

(13) R. S. Rivilin, Philos Trans. R. Soc., A241, 379 (1948).

(14) M Amin, GM Nasr, G Attia, AS Gomaa, "Determination of the crosslink density of conductive ternary rubber vulcanizates by solvent penetration". Materials Letters, 1996

(15) GM Nasr, M Madani ," Mechanical properties of irradiated rubber-blends". Arab Journal Of Nuclear Sciences And Applications, 2005

(16) HH Hassan, GM Nasr, MA El-Waily , "Electrical and mechanical properties of aluminum-loaded NBR composites". Journal of Elastomers and Plastics, 2012

(17) B. Meissner, "Structure and properties of rubber networks ", J. Polym. Sci., c16, 781 (1967).

(18)C. G. Moore, W. F. Waston, J. Appl. Polym. Sci., 19, 237 (1956).