

## Electrical and Dielectric properties of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin films prepared by casting method.

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### **ABSTRACT**

In this study, 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film was prepared by casting method. The study consists of two parts: the first includes the measurement of electrical conductivity and activation energy range (303-353) °K. The second part deals with the dielectric properties that were measured at temperatures ranging from 303 to 353°K and frequency in the range (120Hz - 2MHz).

Dielectric properties (dielectric permittivity, loss tangent and Ac. conductivity ( $\sigma_{ac}$ ) have also been investigated. It is found that the system obeys the Maxwell-Wagner Sillars relaxation of space charge phenomenon. Permittivity, loss tangent and Ac. conductivity increase with increasing the temperature and the permittivity decreases with the increasing of frequency. The values of ac conductivity and dc conductivity were compared.

**Keyword:** conductivity, activation energy, permittivity, loss tangent.

دراسة الخواص الكهربائية و العازلية لأغشية 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) المحضرة بطريقة الصب

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جامعة البصرة

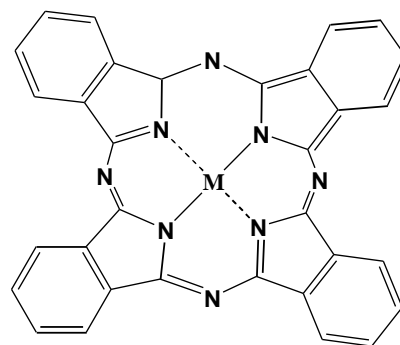
## الخلاصة

تم في هذه الدراسة تحضير البوليمر 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) بطريقة الصب الاعتيادية. وقد شملت هذه الدراسة على جزئين رئيسيين: يتضمن الجزء الأول منها قياس كل من التوصيلية الكهربائية المستمرة وطاقة التنشيط للبوليمر المحضر من خلال رسم مميزة الخصائص الكهربائية (الفولتية- التيار) ضمن مدى درجة الحرارة  $303-353^{\circ} K$ . حسبت قيمة التوصيلية الكهربائية وطاقة التنشيط بواسطة معادلة ارهينوس . حيث لوحظ زيادة في التوصيلية الكهربائية وطاقة التنشيط مع زيادة درجة الحرارة. أما الجزء الثاني من هذه الدراسة فقد تضمن دراسة الخواص العازلية للبوليمر المحضر التي قيست ضمن نفس المدى، وضمن التردد في المدى (120Hz - 2MHz). فحصت خواص العزل الكهربائي مثل ( سماحية العزل الكهربائي وفقد العازل والتوصيلية الكهربائية المتناوبة)، ووجد من خلال النتائج ان النظام الحاصل يخضع إلى استرخاء (ماكسويل - وينر سايرز أو ما يسمى ظاهرة شحنة الفراغ). لوحظ من النتائج العملية إن قيم السماحية الكهربائية وفقد العازل والتوصيلية الكهربائية المتناوبة تزداد بصورة عامة مع زيادة درجة الحرارة، بينما تقل السماحية مع زيادة التردد. كما تم المقارنة بين قيمة التوصيلية المستمرة والمتناوبة.

## 1.Introduction

The phthalocyanines are a class of organic semiconductors which are chemically and thermally stable, and, thus, suitable for the preparation of thin film [1]. Electrically conductive organic and metalloorganic polymers are of great interest and they have applications in electronic, optical, photonic, photoelectric, electrochemical, and dielectric devices. Phthalocyanines and their polymers are well known for their unique photoconducting and semiconducting properties [2-7]. Though the discovery of these materials is accidental, the phthalocyanine ring is a good ligand and every element in the periodic table, including nonmetallic elements such as silicon and phosphorous, form a complex with phthalocyanine ring [1, 5, 8]. Materials based on phthalocyanines have been of particular significance in many fields concerning energy conversion (photovoltaic and solar cells), chemical sensors, rectifying devices, electrochromism, optical data storage, laser dyes, liquid crystals, nonlinear optics electrophotography and photosensitizers for photodynamic therapy [9,10]. The electrical properties of polymeric phthalocyanine are of interest because of their conjugated structure and stability against light, heat, moisture, and air. Hence polymeric phthalocyanines are suitable candidates for use as environmentally stable electrically conductive materials [11-14]. Polymeric

metallophthalocyanines of copper, nickel, iron and cobalt possess large extended conjugated structures and exhibit high conductivity. To understand the electrical and dielectric properties of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) compound, a systematic investigation on these properties and their variation with temperature and frequency is attempted in this paper.



**Metallophthalocyanine**

Fig. (1) Structure of Metallophthalocyanine

**2. Theoretical**

Activation energy of the sample was calculated using the relation [15]

$$\sigma = \sigma_0 e^{-E_a / K_B T} \dots\dots\dots (1)$$

where  $\sigma$  represents the dc conductivity,  $\sigma_0$  is the pre exponential factor,  $k_B$  is the Boltzmann constant,  $E_a$  is the activation energy and  $T$  is temperature.

The dielectric studies of the 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film were calculated using the relation [16, 17]

$$C = \epsilon_0 \epsilon' A / d \dots\dots\dots (2)$$

where  $C$  is the capacitance of the film,  $\epsilon_0$  is the permittivity of the free space,  $d$  is the separation between the capacitor electrodes,  $A$  is the area of the electrodes and  $\epsilon'$  is the dielectric permittivity of the film. The ac conductivity ( $\sigma_{ac}$ ) was calculated according to the relation [18, 19]

$$\sigma_{ac} = \epsilon_0 \omega \epsilon'' \dots\dots\dots (3)$$

**3. Experimental**

**3.1 Materials**

Phtalic anhydride, Acetyl chloride, ammonium molybdate, tetrahydrate Sulphuric acid, nitric acid, acetic anhydride, HCl, NaOH, sodium polysulphide, and Thionylchloride were purchased from Aldrich chemical company.

**3.2 Synthesis**

**Preparation of copper (II) – 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine**

To a suspension of poly (1, 4-diaminobenzen phthalate) 10 mmole) in 25 ml of chloroforme added to (2mmole) of copper (II)– 3,3',3'',3'''-tetraaminophthalocyanine in 25 ml of chloroforme in 25°C . The mixture was stirred at 25°C with vigorous stirring for 5 hrs. Then the solid precipitate was collected by centrifuge and washing with chloroforme. Blue solid of copper (II)-3, 3',3'',3'''-tetra poly(1,4-diaminobenzen phthalate) phthalocyanine was obtained yield 87%.

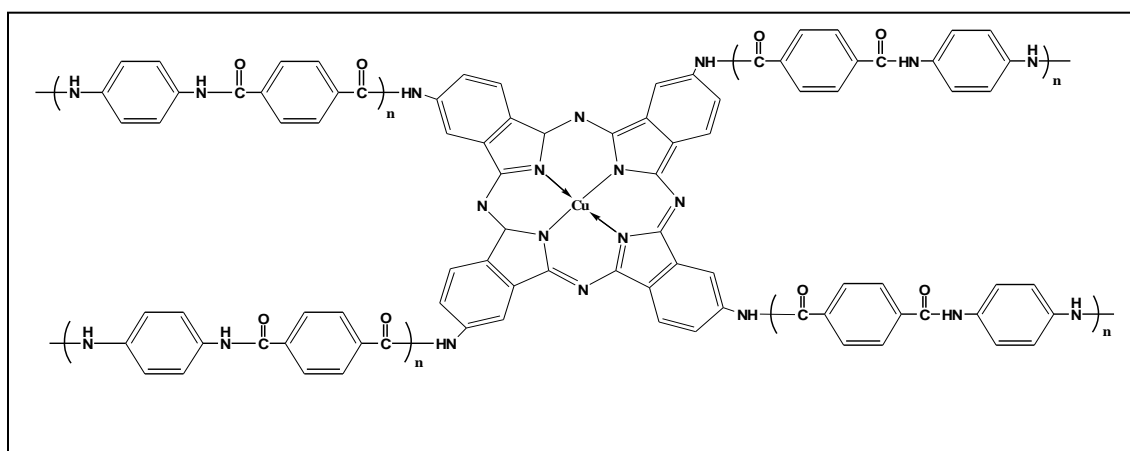


Fig. (2): The suggested structure of prepared complex.

### 3.3 Characterization and measurements

#### 3.3.1 DC conductivity measurements

Electrical conductivity (I-V characteristic) measurement was carried out on the samples of 3, 3', 3'', 3'''-tetra poly (1,4-diaminobenzen phthalate) phthalocyanine copper (II) using a multimeters Fluke 8846A and a conductivity cell in the temperature range (303-358) °K by employing a two-probe technique. The thickness of prepared films was measured (0.7 mm).

#### 3.3.2 Dielectric permittivity measurements

The samples capacitance and the dielectric loss of composites were measured by RCL bridge type (Metrapoint-RLC2 and ME 1634 function generator) continuous frequencies in the range (120Hz -2MHz) and digital RCL bridge type (Megger B131), at the frequencies 120 Hz and 1 kHz.

## 4. Result and Discussion

Fig. (3) shows the plots of current against applied voltage at different temperature (303-353) °K. At the low field rang (1-10V), the current shows Ohmic behaviour which indicates that thermally generated charge carriers are effected by the current limits [20]. The dc conductivity ( $\sigma_{dc}$ ) in the rang 303 to 353°K was calculated and plotted in fig.(4).

The dc conductivity of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film at room temperature was equal to  $2.08 \times 10^{-5}$  S/cm and the activation energy is (0.27eV). In general, in phthalocyanine the electrical conductivity is associated with mobile  $\pi$  electrons of the phthalocyanine ring and the conductivity is due to thermal excitation of  $\pi$  electrons from the highest filled to lowest empty  $\pi$  orbitals [21].

Fig. (5) shows dielectric permittivity with frequency in the rang (120Hz -2MHz) for different temperatures (303-353) °K. It can be seen that the dielectric permittivity increases as the temperature increases but a decrease with frequency.

Normally, metallophthalocyanine are highly conjugated and have a large planar structure. The  $\pi$  electrons are completely delocalized over the entire molecule. If the applied field is increased the probability of tunneling of electrons between molecules is also increased causing high dielectric permittivity and dielectric loss [22]. The decrease of dielectric permittivity with increase in frequency can be explained using Koop's phenomenological theory [23]. According to this theory the dielectric structure is considered as an inhomogeneous medium of two layers of Maxwell-Wagner Sillars type (MWS)/ or interfacial effect [24].

The variation of dielectric loss with frequency for different temperatures is shown in figure (6). It is obvious that, Dielectric loss ( $\epsilon''$ ) shows a loss peak characterized by a relaxation frequency for all temperatures. After the dielectric loss reaches a maximum, it decreases almost linearly at lower temperatures and there is not much variation at higher temperatures. Also from the figure it is observed that, when the temperature increases, the value of maximum dielectric loss shifts toward higher frequency. Here dielectric loss depends on both frequency and temperature. The increase in dielectric loss is related to the increased segmental mobility and ionic conductivity [25].

Fig. (7) shows the variation of ac conductivity with frequency for different temperatures (303-353) °K. It can be seen that the ac conductivity increases with the increase of frequency and temperature. This is because, as the temperature increases, the mobility of charge carriers also increases. When frequency increases, the dielectric permittivity decreases (Fig. 5), dielectric loss is also found to increase with increase of frequency. However, the rate of decrease of dielectric permittivity with frequency is lower than the rate of increase of loss factor with frequency and hence there is a net increase of AC conductivity with increase of both frequency as well as temperature [26].

## 5. Conclusions

The electrical and dielectric properties of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film have been investigated. It was found that the Dc. conductivity  $2.08 \times 10^{-7}$  S/cm and activation energy 0.27eV.

Dielectric permittivity, dielectric loss and Ac. conductivity have also been investigated. It is found that the dielectric Permittivity, dielectric loss and ac. conductivity increases with increasing temperature and permittivity decreases with increasing frequency.

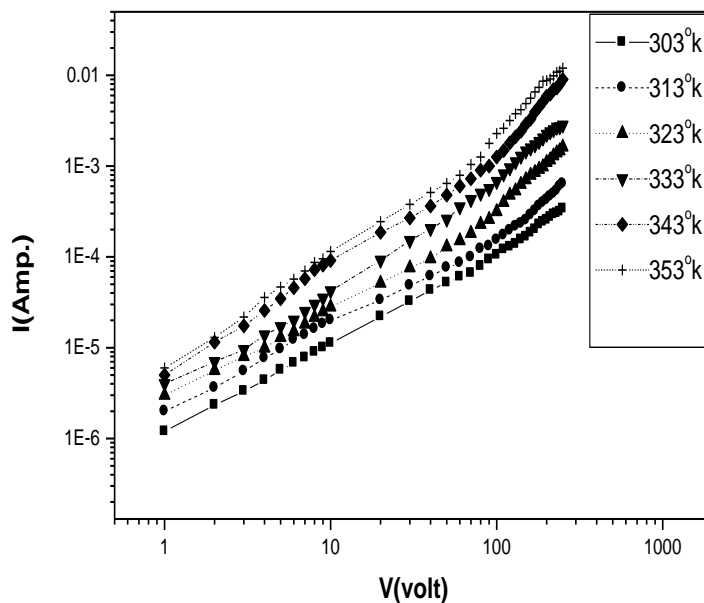


Fig. (3) (I-V) characteristic of 3, 3', 3'', 3'''-tetra poly(1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film.

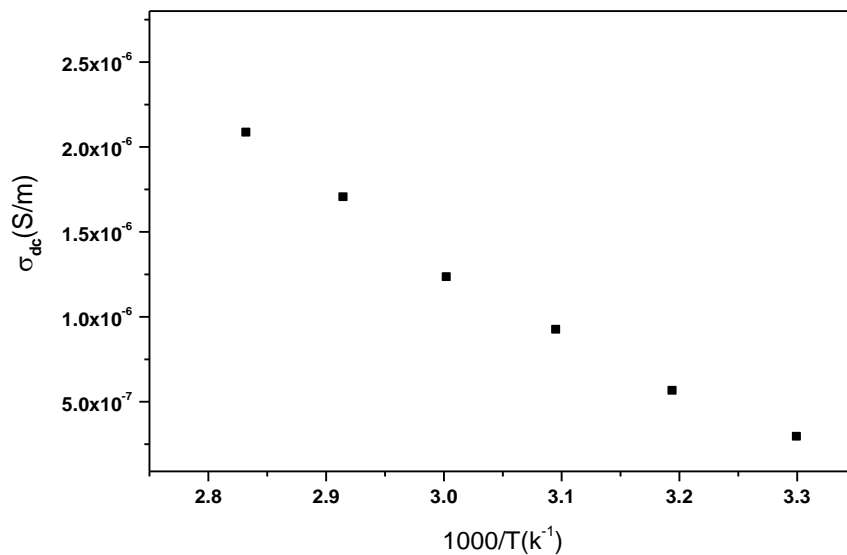


Fig. (4) The  $\sigma_{dc}$  of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film.

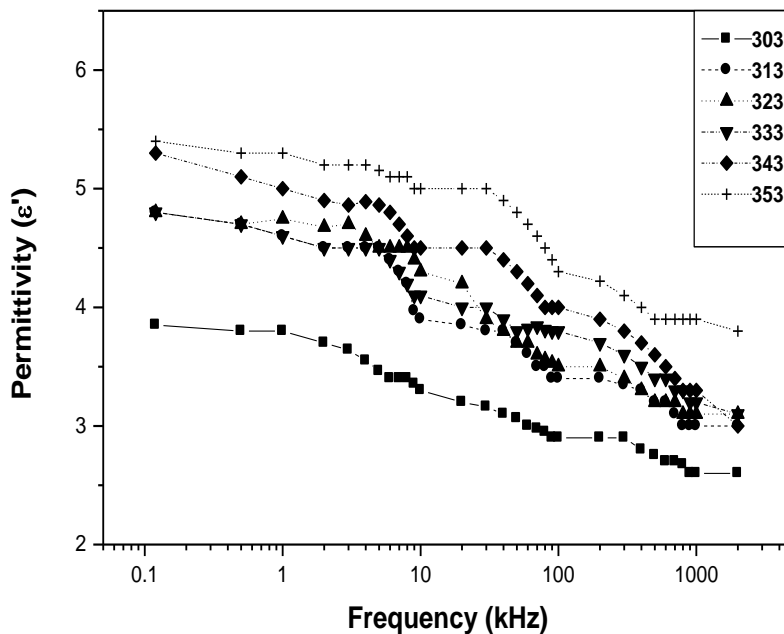


Fig. (5): The permittivity as a function of frequency for different temperatures of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film.

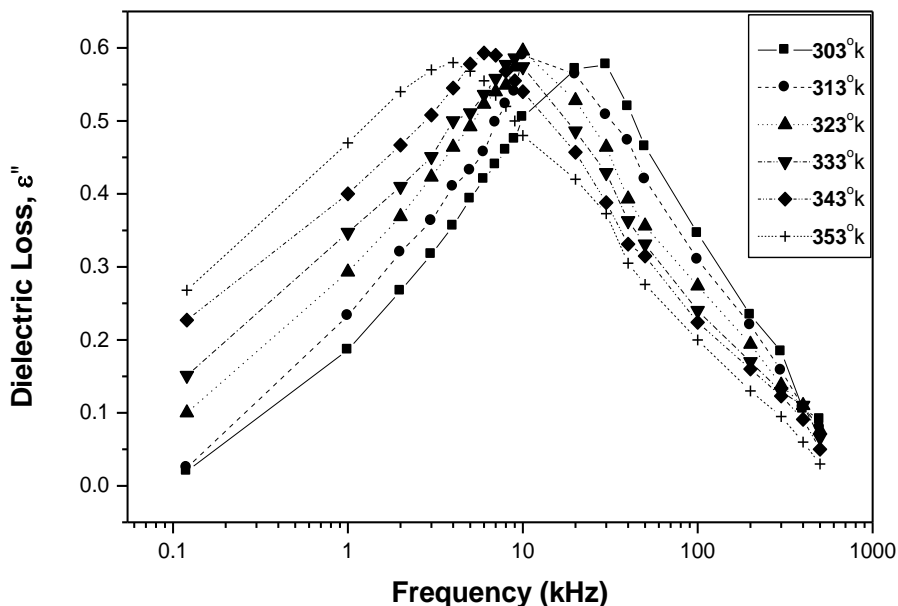


Fig. (6): The dielectric loss as a function of frequency for different temperatures of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film.

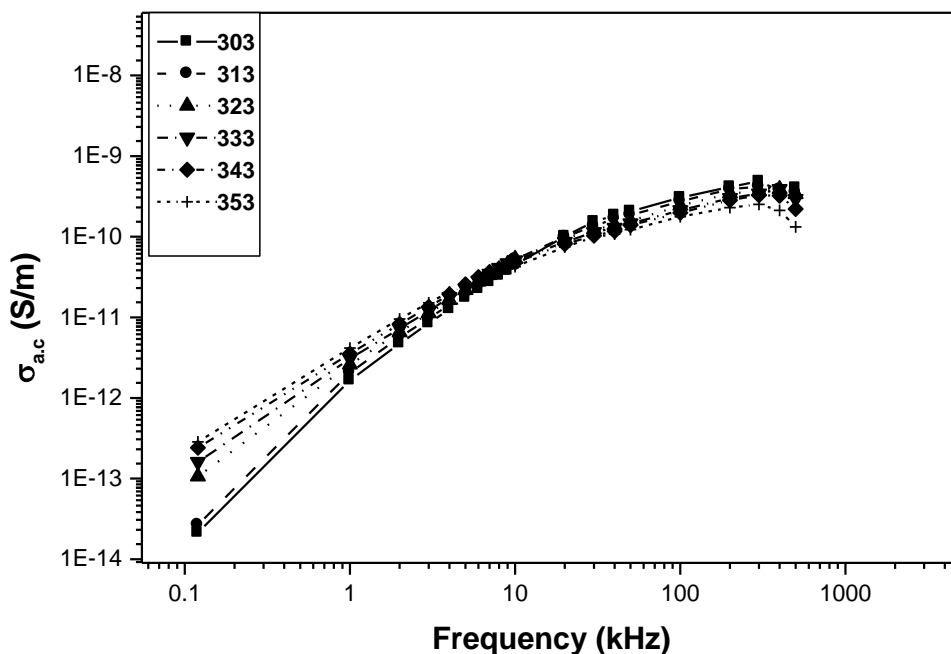


Fig. (7) The  $\sigma_{ac}$  as a function of frequency for different temperatures of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) film.

**References**

- [1] M.M. El-Nahass, F.S. Bahabri, A.A. AL Ghamdi and S.R. Al-Harbi, *Egypt. J. Sol.*, (2002), Vol. 25, No. 2.
- [2] S. Saravanan, C. Joseph Mathai, M. R. Anantharaman, S. Venkatachalam, P. V. Prabhakaran, *J. Applied Polymer Science*, (2004), Vol. 91, P.2529–2535.
- [3] D. Wohrle, *Adv Polym Sci*, (1983), Vol.50, No.75.
- [4] M. Kaneko,; Wohrle, D. *Adv Polym Sci*, (1988), Vol.84, No.141 .
- [5] C.C. Leznoff, Lever, A. B. P., Eds. *Phthalocyanine Properties and Applications*, VCH: New York, (1989).
- [6] J. Simon,; Andre, J. J. *Molecular Semiconductors*, Springer: Berlin, (1985).
- [7] M. Ottmar,; Hohnholz, D.; Wedel, A.; Hanack, M. *Synth Met*, (1999), Vol.105, No.145 .
- [8] W. J. Pietro, *Adv Mater*, (1994), Vol.6, No. 3, P.239 .
- [9] E. Orti,; Bredas, J. L. *J Am Chem Soc*, (1992), Vol.114, No. 22, p.8669 .
- [10] N. D. Mckeown, *Phthalocyanine Materials*, Cambridge University Press: Cambridge, UK, (1998).
- [11] B. N. Achar,; Jayasree, P. K. *Synth Met*, (1999), Vol.104, No.101 .
- [12] S. Venkatachalam,; Rao, K. V. C.; Manoharan, P. T. *J Polym Sci Part B Polym Phys*, (1994), Vol. 32, No. 37 .
- [13] B. Sanjai,; Raghunathan, A.; Natarajan, T. S.; Rangarajan, G.; Venkatachalam, S. *Bull Mater Sci*, (1997), Vol.20, No.2, P. 279 .
- [14] H. Xu,; Bai, Y.; Bharti, V. Cheng, Z. Y. *J Appl Polym Sci*, (2001), Vol.82, No. 70.
- [15] E. Riando, "Electric Properties of Polymer", Marcel Dekker, Inc, (2004).
- [16] H. J. Park, S.M. Hong, S.S. Lee and M. Park, *IEEE Trans. Adv. Pack.*, (2008), Vol. 31.
- [17] S.J. Mahantappa and S. Ducharme, *Current Since*, (2002), Vol.83, No.4, P. 472-476.
- [18] L. Ramajo, M. Catro and M. Reboredo, *J. Appl. Sci. Manuf* (2007), Vol.38, P.1852-1959 .
- [19] S.A. Saq'an, A.S. Ayesh, A.M. Zihlif, E. Martuscelli and G. Ragosta, *Polym. Test.*, (2004) Vol.23, P.739–745.
- [20] I. Jacqueline and Kroschwitz, *Electrical and Electronical Properties Polymers*, John Willey and Sons, Astate of Art Compendium, (1988), p. 140.
- [21] S. Roth, *Hopping Transport in Solids*, Elsevier Science Publishers: Amsterdam, The Netherlands, (1991), p.377.
- [22] P. Kalugasalam, Dr.S. Ganesan. *Chalcogenide Letters*, (2009), Vol. 6, No. 9, p. 469 – 476 .
- [23] C. G. Koops, *Phys Rev*, (1951), Vol. 83, No.1, P.121.
- [24] H. J. Park, S.M. Hong, S.S. Lee and M. Park, *IEEE Trans. Adv. Pack.*, (2008), Vol. 8331.
- [25] S. Sindhu, M.R. Anantharaman, B.P. Thampi, K.A. Malini and P. Kurian, *Bull. mater. Sci.*, (2002), Vol.25, No.599, P.8325.
- [26] G.C. Psarras, E. Manolakaki and G.M. Tsangaris, *Composites part A*, (2002), P. 375.