Effect of addition ferrous chloride ($FeCl_2$) on some A.C and D.C electrical properties of polystyrene

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Abstract

In this work, effect of addition ferrous chloride($FeCl_2$) on some A.C and D.C properties of polystyrene have been investigated .For this purpose ,the PS films with ($FeCl_2$) additive prepared with different percentages and different thicknesses. The experimental results showed that the dielectric constant, dielectric loss, A.C electrical conductivity are changed with change the concentration of additional salts and frequency of applied electrical field ,also, the results showed that the D.C electrical conductivity and activation energy are effected with change the concentration of additional salt and temperature .

الخلاصة

تم في هذا البحث دراسة تأثير إضافة كلوريد الحديدوز $FeCl_2$ على بعض الخصائص الكهربائية المستمرة والمتناوبة للبولي ستايرين .ولهذا الغرض تم تحضير أغشيه بتراكيز واسماك مختلفة من المضاف . النتائج العملية أظهرت أن ثابت العزل وفقدان العزل والتوصيلية الكهربائية المتناوبة تتغير بتغيير تركيز الملح المضاف والتردد للمجال الكهربائي المسلط .أظهرت النتائج أيضا إن التوصيلية الكهربائية المستمرة وطاقة التنشيط تتأثر بتغيير تركيز الملح المضاف ودرجة الحرارة

Introduction

Electrical properties of polymers are the responses when an electric field applied and the subject of electrical properties of polymers covers a diverse range of molecular phenomena.

In contrast to metals, when the electrical response is one of electronic conduction polymers display a much less striking response. These absences of any over riding conduction dose allow, however, a whole set of more suitable electrical effects to be observed more easily, for example, polarization phenomena resulting from distortion and alignment of molecules under the influence of the applied field becomes apparent. Examination of such polarization not any gives valuable insight into the nature of the electrical response itself, but it also provides an effective way to probe molecular dynamics. For this, reassign electrical studies form a desirable supplement to studies of purely mechanical properties aimed at reaching an understanding of the behavior of polymers on a molecular level. The study of electrical properties will also facilitate the fundamental understanding of the thermal and optical properties of polymer [A.R.Blyth 1979].

As consequence of the characteristically insulating nature of solid polymers, any electrostatic charges that they acquire are retained for along time. Since charges may be deposited by mere contact with different material, the charge conditions are frequently encountered with articles made from polymers.

It is worth pointing out here that, although contact charges represent only slight imbalance of charge compared with the total amounts of positive and negative charge present in matter, they can never be less to give arise to electric fields which are high enough to cause sparking in air [R.G. Arridge 1967].

In recent years, there has been a resurgence of interest in electrostatic and new experimental techniques have vastly improved the scope for scientific study. The stimulus has come partly from recognition of the possible benefits to be gained commercially from control and exploitation of static charges on polymeric materials [W.Bolton 1998].

Polymers is not completely free of conduction processes, small quantity of charge carriers it may posses low-level conduction, is essentially insulating polymers can take variety of forms.

Conduction may very often be contributed by impurities that provide small concentration of charge carriers in the form of electrons or ions. At high fields, the electrodes may inject new carriers (holes and electrons) into the polymers, causing the current to increase more rapidly with voltage than in accord with Ohm's law. At very high fields, these and other processes will lead to complete breaking down of polymers as insulating materials [A.R.Blyth 1979and D.A.Seanor 1982].

The most important property of PS polymers as dielectric polymers is their ability to be polarized under the action of an external electric field [B.Tarev 1979].

Dielectrics are materials in which polarization effects are strong [R.A.Leve 1970]. The difference between the dielectric constant of polymer and that of free space is due to the restricted movements of charges within the polymer matrix or molecules.

Under the influence of the applied field, positive charges move with the electric field and an equal number of negative charges move against it, resulting in no net positive charge at the surface where the positive direction of the field emerges and negative charge at the surface where the field enters. Thus, the fields within the polymers produced by larger field outside it and the normal components have the ratio given by the dielectric constant. This general process is called polarization [D.A.Seanor 1982].

There are several types of polarization, each of which can be explained by its intrinsic physical mechanism. Thus, the total polarization of dielectric solid is due to four different sources[Z.D.Jastrzebski 1977]: -

a. Electronic polarization (P_e).
b. Atomic polarization (P_a).
c. Orientation polarization (P_o).
d. Interfacial polarization (P_I).

Experimental Part

The materials used in this paper are polystyrene as matrix and ($FeCl_2$) as a filler.

The electronic balanced of accuracy 10^{-4} have been used to obtain a weight amount of ($FeCl_2$) powder and polymer powder . The weight percentages of ($FeCl_2$) are (0 , 3 , 6 ,9 and 12) wt% . The casting method has been used for prepared of film in room temperature.

The dielectric properties of(PS- $FeCl_2$) composites were measured using (Agilent impedance analyzer 4294A),in the frequency(f) range ١٠0-6×10^6 Hz at room temperature. The measured capacitance, (C)was used to calculate the dielectric constant (έ), using the following expression:

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where d is the thickness of the films and A is surface area of the films . whereas for dielectric loss ε":

$$\varepsilon''=\acute{\varepsilon}\times\tan\delta \qquad \text{......................(2)}$$

where tanδ is dissipation factor .

The A.C conductivity (σ_{ac}) can be calculated by the following equation:

$$\sigma_{ac} = \varepsilon_o w \varepsilon'' \qquad \text{..................(3)}$$

where ε_o is the permittivity of free space and (*w*) is the angular frequency (*w*=2πf).

The resistivity was measured over range of temperature from (40 to 80)°C using Keithly electrometer type (616C) . The volume electrical conductivity σ_v defined by :

$$\sigma_v = \frac{1}{\rho_v} = \frac{L}{RA} \qquad \text{........................(4)}$$

where :

A = guard electrode effective area.

R = volume resistance (Ohm) .

L = average thickness of sample (cm) .

In this model the electrodes have circular area A= π D^2/4 where D= 2.5 cm^2. The conductivity increases exponentially in polymers with the increase of temperature according to the relation:

$$\sigma = \sigma_0 EXP\left(-E_{act}/KT\right) \qquad \text{........................(5)}$$

where σ is electrical conductivity at T temperature , σ_o is electrical conductivity at absolute zero of temperature, K_B is Boltzmann constant and E_{act} is Activation Energy.

Results and Discussion

Figure (1) shows the variation of the dielectric constant of (PS-$FeCl_2$) composites with angular frequency. The figure shows that the dielectric constant values decrease with increasing applied frequency . The increase of frequencies results is decreasing of space charge polarization to the total polarization .Space charge polarization becomes more contributing type of polarization at low frequencies, and less contributing with the increase of frequency, this would result in the decrease of dielectric constant values with the increase (2×10^6)Hz .

The other types of polarizations appear at subsequent frequencies. The ionic polarization reacts slightly to the variation in the field frequencies compared with electronic polarization, this is because the mass of ion is greater than that of the electron. The electrons respond to even the high frequencies of the field vibrations. The low mass of electron makes the electronic polarization has only type of polarization at higher frequencies, this makes the dielectric constant approximately constant for all samples at high frequencies [C. Chiteme *et.al* 2005]

Figure (2) shows the effect of adding the Ferrous chloride on the dielectric constant at 100Hz and 298K. The dielectric constant is approximately constant at low concentrations, it increases with the increase of the concentration of Ferrous Chloride to concentrations ranging 6wt.% - 9 wt.%. The reason for this increase in the value of dielectric constant is the formation of a continuous network of $FeCl_2$ ions inside the composite. At low concentrations, the ions of Ferrous Chloride take the form of clusters or separated groups, hence, the dielectric constant becomes approximately constant. At a level equals to 9 wt.% or higher $FeCl_2$ ions forms a continuous network inside the composite, and so the value of dielectric constant increases with the weight rate of the added Ferrous Chloride. This is similar to the results reached by the researchers [S.H.Kwan *et.al.*١٩٤٨, M. Hamzah *et.al* 2008 and S. C. Raghavendra *et.al.*].

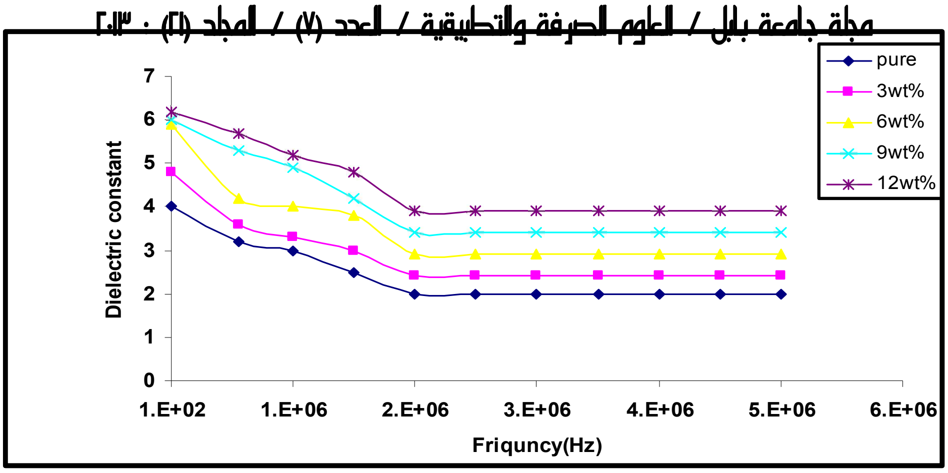

Figure (1) : Variation of the dielectric constant of (PS-$FeCl_2$) composites with angular frequency

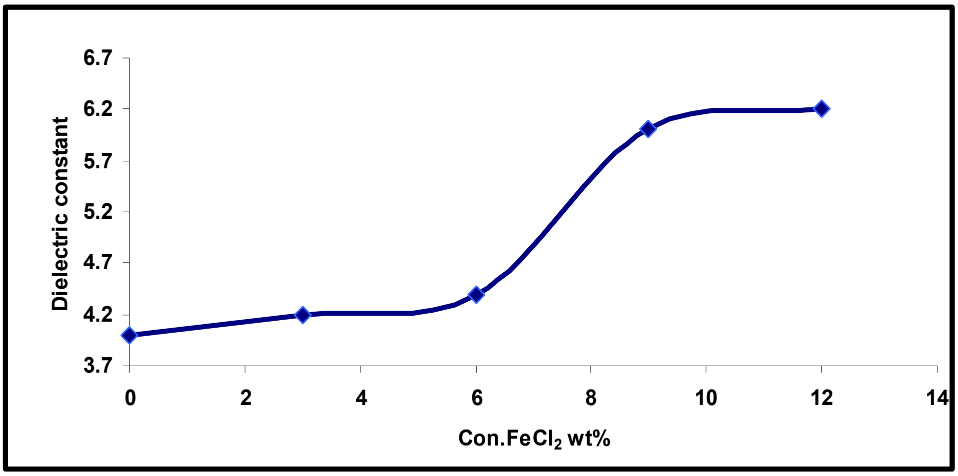

Figure (2) : Effect of adding the Ferrous Chloride on the dielectric constant at 100Hz and 298^{o}k

Figure (3) shows the dielectric loss as a function of the angular frequency of (PS-$FeCl_2$)composites. When the applied field frequency is low, the dielectric loss value is high, and it is decreasing when increasing the frequency . This is attributed to the decrease of the space charge polarization contribution when increasing the frequency. The dielectric loss increases again till it reaches to the highest value at (f=0.5 MHz). This value represents the highest dielectric loss at certain frequency, that is the highest absorption of applied field. This absorption happens due to Maxwell- Wagner phenomenon which is caused by A.C current due to the difference of dielectric constant and conductivity of the phases in the composite. This electric current has the same phase as that of the applied field [B. H *et.al.* AL-Khayat 1985 and M. Revanasiddappa *et.al.* 2007].

When the frequency(f) is increasing to (1 MHz), the dielectric loss is approximately constant. This is attributed to the mechanisms of other types of polarization that occurs at high frequencies. This is similar to the results reached by the researchers[P. K. Pillal *et.al.*1986 and S. Satapathy *et.al.* 2008].

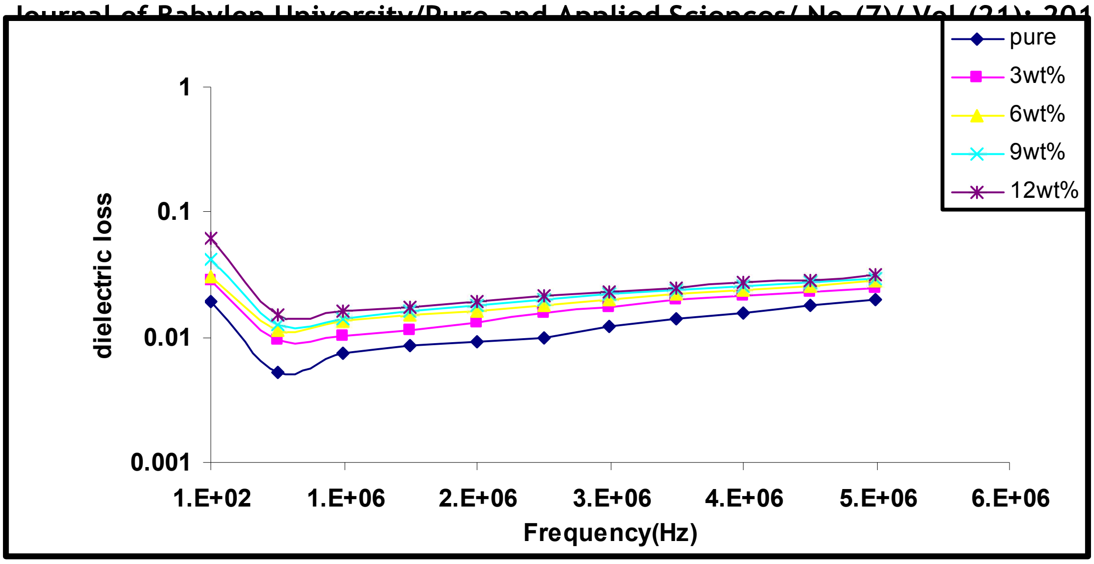

Figure (3) : Dielectric loss as a function of the angular frequency of (PS-FeCl$_2$)composites

Figure (4) shows the variation of the conductivity for (PS- FeCl$_2$) composites with angular frequency. The figure shows that A.C conductivity increases considerably with the increase of frequency from (100Hz) to (0.5 MHz). This is attributed to the space charge polarization that occurs at low frequencies, and also to the motion of charge carriers by hopping process. The increasing of the conductivity is small at high frequencies, this is attributed to the electronic polarization and the charge carriers which travel by hopping process. Consequently, the conductivity is increasing when increasing the frequency for all different rates of the FeCl$_2$. This is similar to the results reached by the researchers [N. Jovic *et.al*. 2007and S. karmakar *et.al*. 2008].

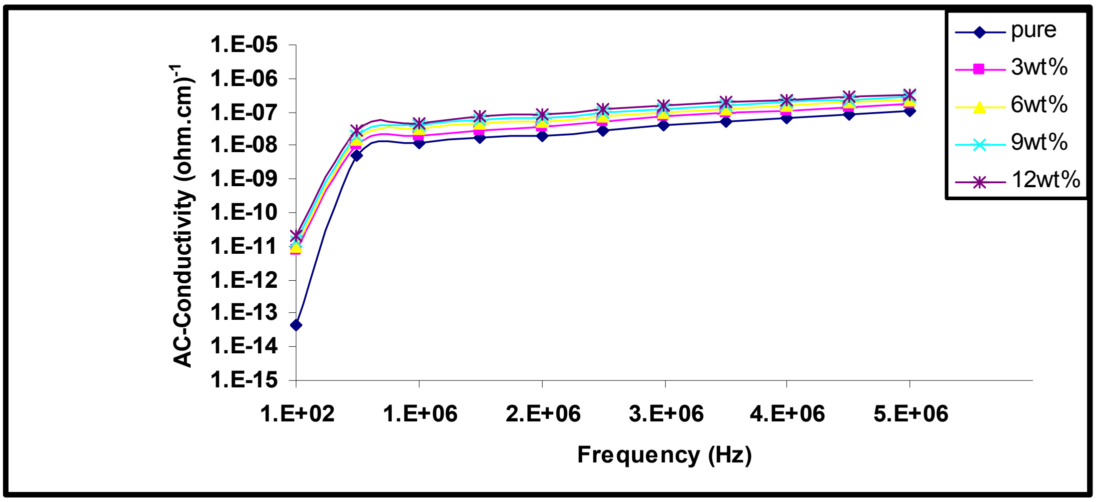

Figure (4) : Variation of AC conductivity for PS- FeCl$_2$ composites with angular frequency

Figure (5) shows the variation of A.C conductivity of (PS-$FeCl_2$) composites, with Ferrous Chloride concentration at 100Hz and 298^{o}k. The A.C conductivity is slightly increasing at low concentrations of the $FeCl_2$. This increase is due to the effect of the space charge. The ions of Ferrous Chloride take the form of clusters or separated groups. The conductivity is increasing with the increase of the concentration of $FeCl_2$ as a result of the increase of the ionic charge carriers and the formation of a continuous network of $FeCl_2$ ions inside the composite. Consequently, the conductivity is increasing with the increase of $FeCl_2$ concentration for (PS- $FeCl_2$) composites[G. Shui *et.al.* 2004 and M. P. Alvarez *et.al.* 2008].

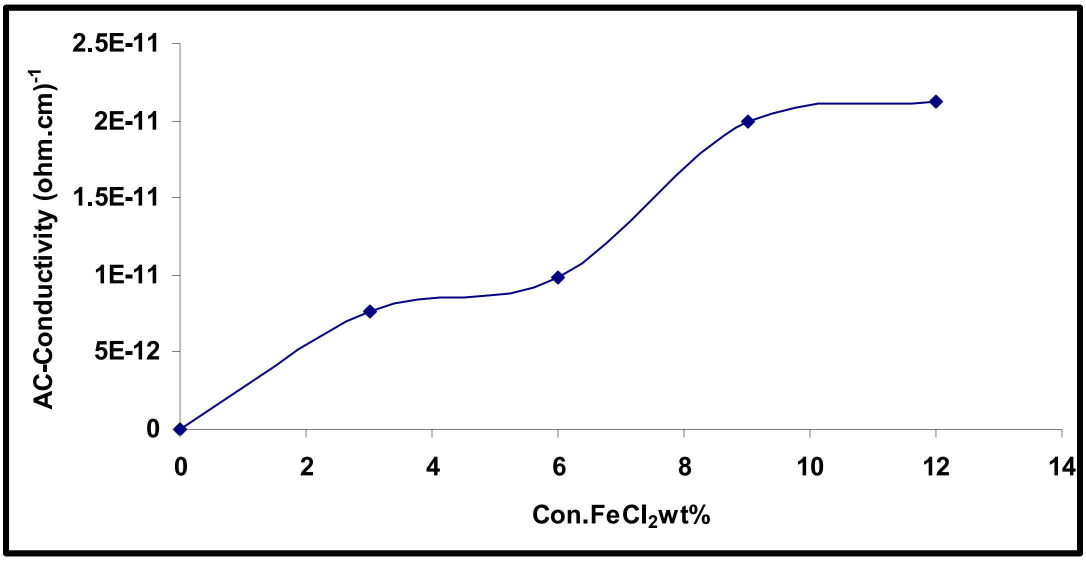

Figure (5) : Variation of A.C conductivity of (PS-$FeCl_2$) composites with Ferrous Chloride concentration at 100Hz and 298K

Figure (6) shows the electrical volume conductivity $\sigma_V(\Omega.cm)^{-1}$ as a function of the concentration of ferrous chloride ($FeCl_2$) at a temperature of (40^{o}C), from the figure we note that the electrical conductivity is slightly increasing with increase the concentration of ($FeCl_2$) . When increasing the concentration more than that, the electrical conductivity to a large increase to the value 1×10^{-14} $(\Omega.\ cm)^{-1}$ at the concentration (9 wt%) of ($FeCl_2$) and an increase in the concentration of ($FeCl_2$) to(12wt%), the conductivity reach to 2.1×10^{-14} $(\Omega\ .cm)^{-1}$.

The increase of conductivity with increasing concentration of ($FeCl_2$)caused by the increase of the charge carriers ions in which they increased with increasing filler content when the ($FeCl_2$) ions at low concentrations and become large when the ferrous chloride ($FeCl_2$) content increases but when the concentration of ($FeCl_2$) reaches to (9wt%), the network will be connected to each other containing the overlapping paths to allow the charge carriers to pass through, where the charge carriers with routes through which the electrical resistance be less [S. Bhattacharya *et.al.* 2008 and N. K Srivastava *et.al.* 2003].

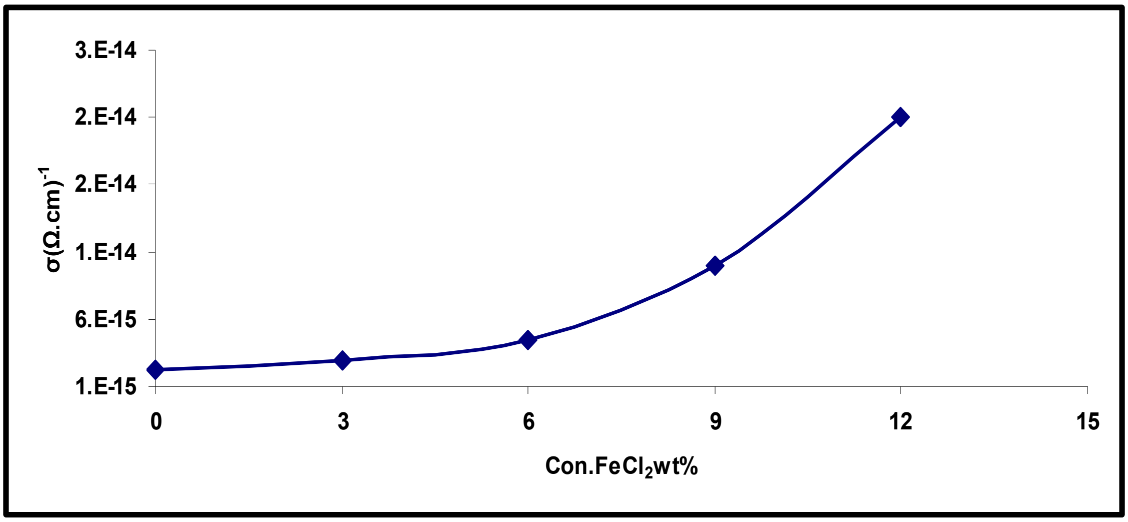

Figure (6) : Electrical volume conductivity $\sigma_v(\Omega.cm)^{-1}$ as a function of the concentration of ferrous chloride ($FeCl_2$) at a temperature of (40^oC)

Figure (7) shows the relationship of electrical volume conductivity of the composite $\sigma_v(\Omega.cm)^{-1}$ with the temperature. We note that the electrical conductivity increases with increasing the temperature that any of this material has a positive thermal coefficient of conductivity ,the interpretation of this is that the polymeric chains and ($FeCl_2$) salts act as traps the charge carriers which transited by hopping process. On increasing the temperature, segments of the polymer being to move , releasing the trapped charges. The released of trapped charges is intimately associated with molecular motion. The increase of conductivity with temperature is attributed to two main parameters , charge carriers and mobility of these charges. The mobility depends on the structure and the temperature [A. H. Muheisin 2009, K. M. Gabur2010 and Z .Al-Ramadhan 2008].

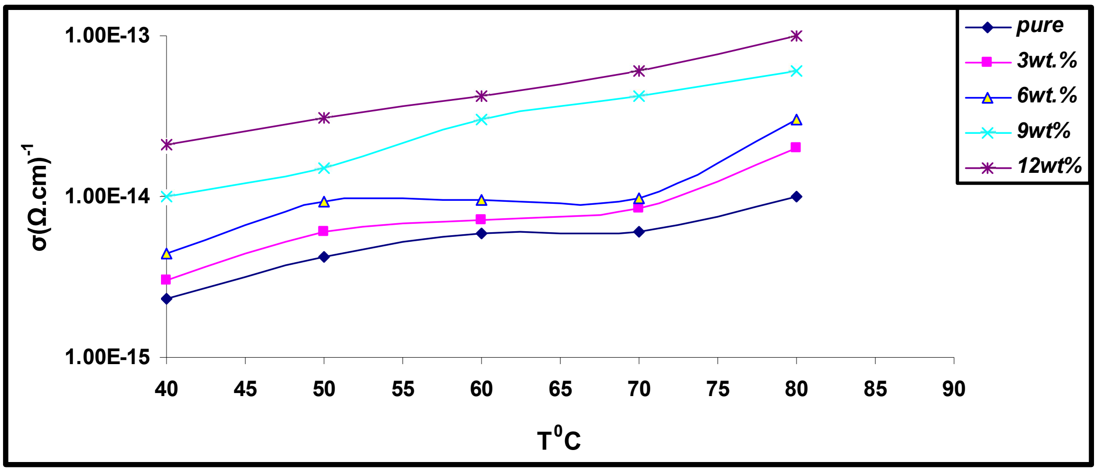

Figure (7) : the relationship between electrical volume conductivity of the composite $\sigma_v(\Omega.cm)^{-1}$and temperature

Figure (8) shows the relation between $\ln\sigma_v$ and the inverse of absolute temperature for (PS-$FeCl_2$) Composites. The activation energy was calculated by using equation (5). From these calculations, it can be seen that high activation energy occure in the range (0.623-0.6) eV .

By adding low concentrations of $FeCl_2$, the values of the activation energy are decreasing as a result of the impact of space charge. The addition of low concentrations creates local energy levels in the forbidden energy gap which act as traps for charge carriers when move thy among these levels.

By increasing the ferrous chloride concentrations, the activation energy decreases as a result of the increase of local centers, as shown in figure (9). Thus, the mechanism of conduction in the samples having low concentrations is the hopping .

The low values of the activation energy for (PS- $FeCl_2$) composites range from (0.4-0.420) eV , this is attributed to the formation of a continuous network of ferrous chloride that contains paths inside the composite and allows the charge carriers to pass through and this leads to decrease the activation energy. Increasing of the concentration of the additive, the activation energy decreases[K. M. Gabur2010 and M. S. Ahmed 1992], as shown in the figure (9).

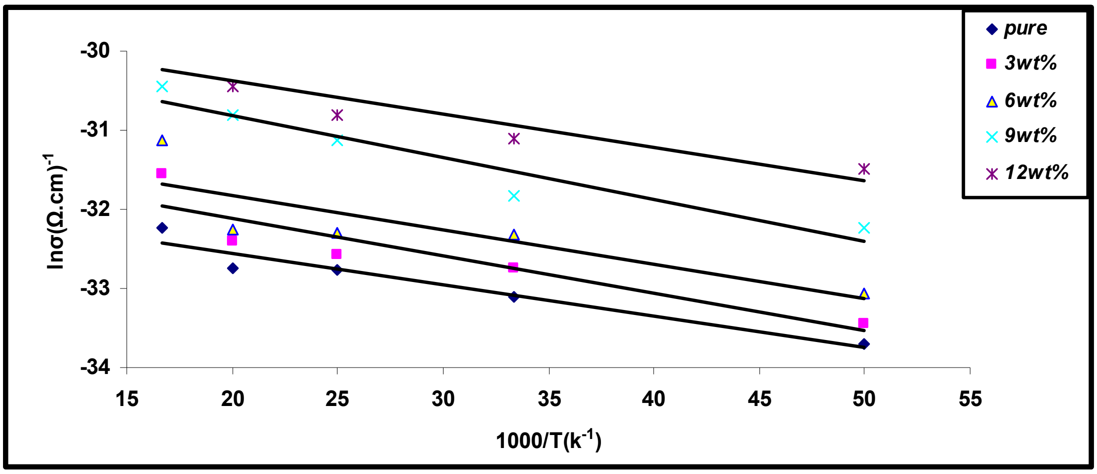

Figure (8) : the relation between $\ln\sigma_v$ and the inverse of absolute temperature for (PS-$FeCl_2$) Composites

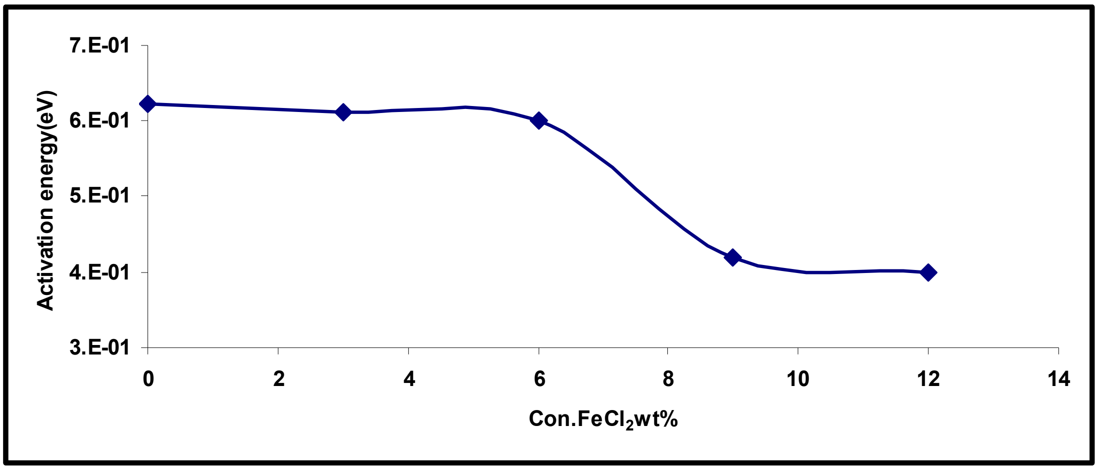

Figure (9) : the relationship between activation energy and concentration of $FeCl_2$ wt%.

Conclusions

1-The dielectric constant, dielectric loss, ,A.C electrical conductivity and the D.C electrical conductivity are increasing with the increasing of the filler.

2-The dielectric constant is decreasing with the increase of frequency of the applied electric field .

3-The dielectric loss of low and high concentrations is oscillatory with the frequency of applied electric field .

4-The A.C electrical conductivity at all concentrations is increasing with the increase of the frequency of the applied electrical field .

5-The D.C electrical conductivity are increasing with the increasing of the filler wt.% content.

6-The D.C electrical conductivity is increasing with the increasing of temperature.

7-The activation energy for D.C electrical conductivity is decreasing with the increase of the filler wt.% content

References

Ahmed M. S. and A. M. Zihilif , " The electrical conductivity of polypropylene and Nickel- Coated carbon Fiber composite ",J. Mater. Sc ,University of Jordan , Amman , Jordan Vol. 25 , No. 706, , (1992) .

AL-Khayat B. H and F. A. Awni ,J. Am. Ceram. Soc. Bull. 64(4), p(598-601) , 1985.

Al-Ramadhan. Z.. ,"Effect of Nickel salt on Electrical Properties of PMMA" , J. of college of education , University of Mustansiriah. No.3,(2008).

Alvarez , M. P. V. H. poblete , M. E. pilleux and V. M. Fuenzalida , "Submicron Copper- Low- Density polyethylene conducting composites: Structural , Electrical and percolation Threshold" , Comision Chilena de Energia Nuclear, Chile, 2008.

Arridge, R.G. , "j.Appl.phys.",Vol.(18),P.(1311),(1967).

Bhattacharya, S. V.K.Sachdev & R.P.Tandon, "Electrical properties of Graphite Filled Polymer Composites",2nd National Conference Mathematical Techniques, Dilhi University (2008).

Blyth, A.R."Electrical Properties of Polymers", London-NewYork, (1979).

Bolton, W. "Engineering Material Technology", 3rd Edition , Oxford, (1998).

Chiteme , C. S. Lowther and S. Harrison , J. of Polym. Science, Vol. 43, p (3273-3287), (2005).

Gabur , K. M. " Preparation and Study The Electrical and Optical Properties of (PS-Ni)Composites", M.Sc .Thesis, Babylon University, college of science, (2010).

Hamzah , M. E. Saion , A. Kassim and M. Yousuf , MPJ. Vol. 3, No. 2 , p(24-31) , 2008 .

Jastrzebski, Z.D."The Nature and Properties of Engineering Materials", New York, (1977)

Jovic, N. D.Dudic , A. Montone , M. Vittori and V. Djokovic "Electrical conductivity behaviour of the Epoxy / Graphite nanosheets composites " , XVII Symposium on condensed Matter physics ,Vrsac- Serbia , 2007 .

karmakar , S. H. Nagar , J. P. Jog , S. V. Bhoraskar and K. Das ," A.Cconductivity of polymer composites : an efficient confirmatory tool for qualifying crude multi-walled carbon nanotube-samples"Svb @Physics.Unipune.ernet.in,India, 2008 .

Kwan , S. H. F.G. Shin and W.L . Tsul , J. of materials science , P(4093- 4098), 19,1984.

Leve, R.A."Principles of Solid State Physics",4th edition, Academic Press ,(1970).

Muheisin, A. H. "study of electrical conductivity for amorphous and semi crystalline polymers filled with lithum fluoride additive", M.Sc. Thesis , University of Mustansiriah ,college of science,(2009).

Pillal , P. K. P. Khurana and A. Tripathi , J. of materials Sci. letters, Vol. 5, p(629-632) , 1986 .

Raghavendra , S. C. V. Dmitriev , T. K. Vishnuvardhan , V.R. Kulkarni and C. Basavaraja," conductivity and dielectric properties of polypyrrole/ La_2O_3composites " , Indian Institute of science, Bangalore, India, 2008 .

Revanasiddappa, M. S.C. Raghavendra , S. Khasim and T. KVishnuvardhan , J.Bull. Korean chem.. Soc. Vol. 28 , No.7P(1104-1108), 2007 .

Satapathy , S. P. K. Gupta , K. B. R. Varma , P. Tiwari andV. Ganeshan , "study on dielectric behavior of Lithium Tantalate (LT) nano particl filled poly(vinylidene fluoride) (PVDF) nano composites", Institute of Science, Srinu73@cat.ernet.in, India, 2008.

Seanor, D.A."Electrical Properties of Polymers", New York, (1982).

Shui , G. J. Hu , M. Qiu , M. Wei and D. Xiao , J.Chinese chem.. letters, Vol. 15 , No. 12 , pp 1501-1504 , 2004 .

Srivastava N. K,R. M and Mehra ," Study of Electrical Properties of Polystyrene / Foliated graphite Composite " , Delhi University South Campus , (2003).

Tarev, B. "Physics of Dielectric Materials ", Moscow, (1979).