Effect of Temperature and Frequency on the Dielectric Properties of PVC/$MnCl_2$ Composite

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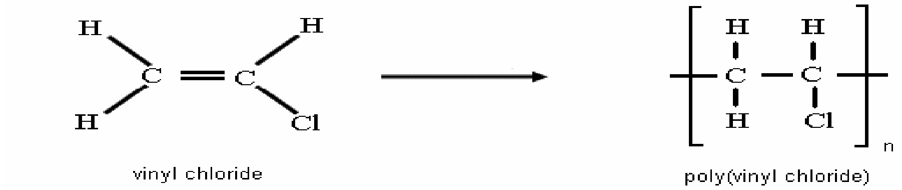
Abstract

The dielectric properties of polyvinyl chloride (PVC)-$MnCl_2$ composite were studied by using the impedance technique. The measurements were carried out as a function of frequency in the range from 10 Hz to 13 MHz and temperature range from 27^oC to 55^oC. Using a composite of 20 wt. % $MnCl_2$ by weight, it was found that the dielectric constants and the dielectric loss of the prepared films increase with the increasing temperature at law frequency and the enhancement of the ionic conduction which is confirmed by the increase the of AC. conductivity and the decrease of the activation energy of the conduction mechanism at high applied frequency. The observed relaxation and polarization effects of composite are mainly attributed to the dielectric behavior of the $MnCl_2$ filler and polarity of the polymer PVC. However, the results were explained on the basis of the interfacial (space charge) polarization dipolar polarization and the decrease of the hindrance of the polymer matrix with the ionic mobility and impurities in the composite.

Keywords: Electrical properties; PVC matrix; $MnCl_2$ filler; Composite; Impedance; Field frequency; Dielectric constant; AC-Conductivity; Polarization; Activation Energy.

Introduction

Polymeric materials were given a great interest in many industrial applications owing to their desirable characteristics and properties which made them favorable compared to other commercial materials .The vast majority of polymers used today as plastics, rubbers, adhesives and paints are synthetic petrochemicals (1). The unbeatable combination of characteristics such as ease of fabrication, low cost, light weight, ease of chemical modification and excellent insulation or good conduction properties have made the polymer one of the most desirable materials for application (2). Many studies showed that physical properties of polymers have clearly depended on many factors concerning their preparation methods and chemical structure (3). Understanding these dependencies and their effect on conducting mechanism will help to a large degree the ability to control the electrical conductivity, which in turn, trials the proper application. Poly(vinyl chloride) or (PVC) is formed from vinyl chloride in a special heat driven plastics manufacturing process that polymerizes toxic short gaseous vinyl chloride monomers $[C_2H_3Cl]$ into non -toxic solid PVC $[(C2H3Cl)_n]$ long polymer chains as shown in picture (1).



Picture (1): Structure of vinyl chloride monomer and polymer of PVC.

PVC is a semicrystalline polymer i.e., it has crystalline and amorphous regions within it. The thermal stabilities of crystalline PVC-$MnCl_2$ system depend on the salt molar ratio, the PVC molecular weight, the choice of solvent and concentration, and the thermal history. The melting temperatures also, depend on the nature of the complexion salts. (4)

The addition of fillers into PVC polymer matrix improves both the mechanical strength of the polymer (5) and their ionic conductivities (6). The additives which are used include SiO_2 (7), TiO_2 (8), SiC (9), Al_2O_3 (10) etc., and in most work on composite polymer electrolytes, the electrolyte is usually based on PEO (8, 11, 12). PVC has been successfully prepared as polymer electrolytes by the blending of two polymers (13, 14), and addition of plasticizers (15).

Previous studies were centered on the enhancement of its ionic conductivity with the aim of developing the material to have a promising electrical application (16, 17). Considerable efforts were focused on the applied research in the field of polymer composites to turn these materials into useful products for electronic industry. This is mainly because they possess interesting properties which can be utilized to develop a lot of related potentials. Recently, many reports have appeared in literature dealing with the effects of frequency of the applied field and temperature on the physical properties of the conductive polymer composite such as impedance, dielectric behavior and electrical conduction (18, 19, 20). Sangawar and Chikhalikar (21) studied the electrical properties of PVC treated by charcoal and others; they found that the increase of temperature enhances the electrical conductivity through the ion conduction process and the activation energies equal about 0.7 eV for sample of higher properties of filler and 0.3 eV for sample with lower properties, i.e. when the filler decreases in the composite, the thermal activation energy decreases. Eid et al (13) studied the effect of temperature, frequency and PEO concentration on the Ion-Selective conduction in PVC/PEO blend as membranes in electrolyte electrodes, and she found that temperature, frequency and PEO content affect the dielectric behavior of the blended membrane.

In the present study, the conduction process by ion exchange in a solid PVC/$MnCl_2$ membrane is investigated as a function of applied frequency and temperature. The main object of this study is to give information concerning the electrical behavior of PVC/$MnCl_2$ composite by using the impedance spectroscopy which is one of the powerful techniques to characterize the dielectric properties as we reported in several previous publications (20,22).Therefore, thin films based on PVC with $MnCl_2$ salt as a reinforcement filler were used in the present study .We believe that this study is of a great interest for some applications in the electrical industry by using some blended polymeric membranes and in semiconducting composites.

Experimental

In this work, the electrical behavior of the prepared membrane is examined at different temperatures (27, 35, 45 and 55 ^{o}C) for 20 wt.% $MnCl_2$ composite in the frequency range 10 Hz -13 MHz.

Composite Preparation

The PVC polymer was obtained from Sigma while $MnCl_2$ salt was obtained from Merck and the solvent tetrahydrofuran (THF) was obtained from J.T. Baker. Ordinarily, the salt $MnCl_2$ was grounded into a fine powder by agate mortar and sieved by a U.S. standard sieve of size (63 µm).

The required weights of PVC and $MnCl_2$ were dissolved in a suitable solvent THF (Tetrahydrofuran) at (45) ^{o}C, PVC powder was dissolved in (THF) also at the same time the salt ($MnCl_2$) was dissolved in (THF) in the same temperature. All the polymer composite films were prepared by casting from solution (casting method). Later, the solution of $MnCl_2$ was added to the dissolved polymer at a suitable viscosity. The solutions were mixed thoroughly for (4-6) hours by using a magnetic stirrer at that temperature until the mixture appeared to be homogeneous.

Then the mixture was cast into a stainless steel ring resting on Teflon substratum and waiting for a few days until the solvents have evaporated. All the samples were dried in a vacuum oven at 40^{o}C for two days. The drying process was repeated until prepared membranes have fixed weight to ensure the removal of solvent traces. Polymeric thin films of thickness range (60-140) µm. The PVC and $MnCl_2$ weight ratio were maintained at 80:20 and the amount of $MnCl_2$ dispersed was expressed as a weight percent (wt. %) with respect to the total weight present in the system i.e. ;

wt. % = (wt. $MnCl_2$) / (wt. PVC + wt. $MnCl_2$) x 100.

Impedance Measurements:

Impedance measurements were carried out by using HP 4192A impedance analyzer. The real and imaginary parts of the complex dielectric constant were calculated from:

$$\varepsilon` = \frac{Z_i}{2\pi f C_o (Z_r^2 + Z_i^2)} \qquad [1]$$

$$\varepsilon`` = \frac{Z_r}{2\pi f C_o (Z_r^2 + Z_i^2)} \qquad [2]$$

Where f is the frequency, Co = (ε_o A/T) is the electrodes capacitance, A is the area of the disk electrode, ε_o is the permittivity of the free space, and T is the specimen thickness of the membrane. The impedance Z is given by ($Z=Z_r-jZ_i$), where Z_r, Z_i are the real and the imaginary of the impedance, respectively. The AC electrical conductivity (σ_{AC}) was calculated from the relation:

$\sigma_{AC}=2\pi f \varepsilon_o \varepsilon``$ [3]

The activation energies (E_a) were calculated by using the Arhenius Equation:

σ□ = σ_o □exp ($-E_a/kT$) [4]

Where σ □□is the conductivity, σ_o is the material constant, k is Boltzman constant and E_a is the activation energy.

Results and Discussion

The variation of phase angle (Φ) with the frequency at different temperatures is shown in Figure (1). It was found that the negative values of phase angle decreases with the increase of the temperature, i.e., the membrane becomes less capacitive at the increase of the temperature, and it is very clear at high temperature at (55°C). The behavior of impedance with temperature at different frequency is shown in Figure (2). Temperature strongly affects the impedance values especially at low frequencies, i.e., it was found that the impedance decreases with the increase of the temperature, and the impedance curve of composite specimens of different frequencies show, in general, a similar behavior resulting in a negative temperature coefficient of resistance similar to semiconductor (23). This may be explained in terms of certain events such as charge carrier generation, increasing of ionic mobility, closing up the energy gap, and mobility development of a band overlap due to structure changes. These processes strongly affect the charge carrier transport in the composite bulk. Generally, the total observed current may be assumed as a superposition of polarization current and conduction current. The polarization current depends on temperature, where the decay time of the polarization is shortened by increasing the temperature (24, 25). This behavior proves that for a strong polar polymer, the conductivity increases as the temperature increases, or the temperature enhances the conduction process.

Figure (3) shows the Cole-Cole plot of the imaginary component Z_i versus the real component Z_r for the specimen 20 wt.% $MnCl_2$ content at different temperatures. The construction plots are greatly distorted semicircles exhibiting different electrical conduction processes with relaxation time spectrum. The figure shows that the impedance real component (Zr) or the bulk resistance of the films decreases with the increase of temperature, i.e., the membrane becomes less resistive or more conductive (26).

The relaxation time (τ) was determined by approximating these Cole-Cole plots to semicircles by using the relation $\omega_{max} \cdot \tau = 1$, where ω_{max} is the angular frequency at maximum values of Z_i observed on the constructed plots. Table (1) shows that the calculated relaxation time (τ) decreases with the increase of temperature. This may be attributed to the ionic mobility, which increases as temperature increases in the PVC phase or from impurities existing in the commercial resins(26), i.e., this might be due to the fact that the dipole rotation is facilitated when the temperature rises since the dipoles have higher thermal energy (27).

The temperature dependence of the dielectric constant (ε`) is shown in Figure (4) where it increases with temperature. This suggests that when temperature raises, the orientation of dipoles is facilitated, this can be explained in terms of a large number of dipole which is blocked at low temperature will be relaxed at high temperature, and this increases the dielectric constant (28). This is similar to what is normally observed in polar polymer as (PEO). However, since the specific volume of the polymer is temperature dependent, i.e., it increases with the increase of the temperature (30), and it can be seen that for all temperatures, the dielectric constant decreases as the frequency increases below 10^3 Hz, while above this frequency value, (ε`) remains nearly constant. Also, it was found that the increase in ($\varepsilon$`) value is more pronounced especially at lower frequencies, and may be due to the increase of the total polarization in polar dielectrics (dipolar, interfacial/Max-Wag., and ionic polarization) (29). The dielectric dispersion in (ε`) becomes stronger at low-frequency as the temperature increases. Outside the region of the dispersion, the dependence of the ($\varepsilon$`) on temperature for polar molecules is like that for non polar molecules as polystyrene, i.e., the temperature does not affect the polarization anymore, or (ε`) is independent of temperature.

The temperature dependence of the dielectric loss (ε``) is shown in Figure (5). It was found that the dielectric loss increases with the increase of temperature, especially at low frequencies. The observed increase in ($\varepsilon$``) is due to the enhancement of the ionic conductivity with the increase of temperature by the addition of ($MnCl_2$). A similar effect in PVC doped with Dioctylphthalate was observed by Bishai et al (31). In addition, the increase of temperature will increase the energy of the dipole so the dipole rapidly responds to the external electric field, i.e., the increase of temperature decreases the relaxation time of the dipole. The same is observed by Aihara et al. (32) and Eid et al. (13).

Figure (6) represents the AC conductivity ($\sigma_{A.C}$) versus temperatures at different frequencies. It was found that the ($\sigma_{A.C}$) values are very small and remain nearly constant below 10 kHz. But above 10 kHz up to 100 kHz, the ($\sigma_{A.C}$) increases slowly at temperatures (27, 35, 45 and 55^{o}C). At higher frequency above 100 kHz and up to 10 MHz, the conductivity increases rapidly indicating a break-down of the dielectric. It was found that $\sigma_{A.C}$ increases with the increase of temperature due to the electron activation that increases rapidly with temperature, and due to ionic and molecular mobility stimulated at high temperature, i.e., the flow of electrons or charged ions is established between the electrodes with the high relative motion of polymer chains and thus leading to a higher conduction (26,13).

The behavior of loss tangent (tanδ) versus frequency at different temperatures is shown in Figure (7). The relaxation peak is observed due to the dipole relaxation. The observed relaxation peak of the tan loss in this plot is shifted to a higher frequency as the temperature increases. The side group rotation and the main chain motion should be accelerated with the increase of temperature. Taking into consideration the rate of side group rotation associated with the main chain motion, one can expect the peak frequency (f_{max}) to become higher when the side group rotation becomes faster, which mean the increase of temperature will decrease the relaxation time of the dipole and increases the conductivity of the sample. In other words, this shift is due to facilitating the dipoles rotation under thermal effects as the frequency is increased (32).

The activation energies (E_a) were calculated from the slopes of the approximated straight lines obtained by plotting the natural logarithm of the conductivity versus (1000/T) (35) shown in Figure(8) at different frequencies. The mean value of the activation energy is about (1.08) eV. The decrease of activation energy shown in table (2) is consistent with the decrease in the relaxation time of the ionic conduction mechanism. It was found that the calculated activation energy decreases with the increase of the frequency as shown in Figure(9). The decrease in the (E_a) reflects a higher ionic conduction process, i.e., which corresponds to the increase in the AC conductivity of the tested PVC/$MnCl_2$ thin membranes.

Conclusion

The research work presented in this study deals with the dielectric properties of (PVC/ 20%$MnCl_2$) composite. The dielectric and impedance of this polymeric membrane were studied as a function of the applied electrical field frequency, and temperature by impedance technique. From the obtained results the following conclusions are drawn:

1. Temperature, frequency affects the electrical and dialectical behavior of the composite membranes.
2. The dielectric constant and dielectric loss of the composite membrane increase with temperature.
3. The peak value of (tan loss) is shifted to a higher frequency at higher temperature.
4. The phase angle takes always negative values for all samples at different frequencies and temperatures, which indicates that the specimens can be represented by (RC) networks.
5. Both the impedance and the dielectric behavior showed frequency dependence, explained on the basis of the interfacial (space charge) polarization, dipolar polarization and on the decrease of the hindrance of the polymer matrix. This filled PVC polymer could be good for low cost semiconducting composites.
6. The complex impedance plots exhibit different mechanisms operating in the bulk related to the relaxation times of the relaxations influenced by the temperature.
7. The AC conductivity increases and the activation energy decreases with the increase of frequency and temperature due to enhancement of ionic conduction in the membrane bulk.

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Table (1) : Relaxation time as a function of temperature for PVC/$MnCl_2$

Temperature (^oC)	$\tau \times 10^{-6}$ (sec.)
27	1.873
35	0.721
45	0.385
55	0.084

Table (2) : The activation energy for PVC/$MnCl_2$ composite

F(Hz)	t=1/F (sec)	Slope	E_a (ev)
400	2.5 E-03	15.412	1.329
1000	1.0 E-03	14.963	1.290
10000	1.0 E-04	13.824	1.192
30000	3.3 E-05	12.954	1.117
50000	2.0 E-05	12.374	1.067
100000	1.0 E-05	11.516	0.993
150000	6.6 E-06	10.893	0.938
200000	5.0 E-06	10.448	0.901

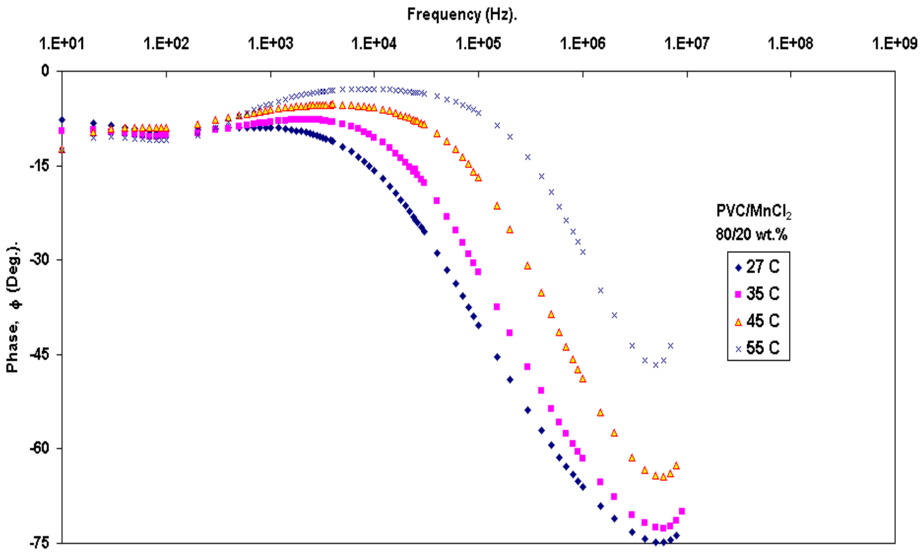

Fig. (1): Phase Angle Dependence on Frequency for PVC/MnCl$_2$ (20wt. %) Composite at Different Temperatures.

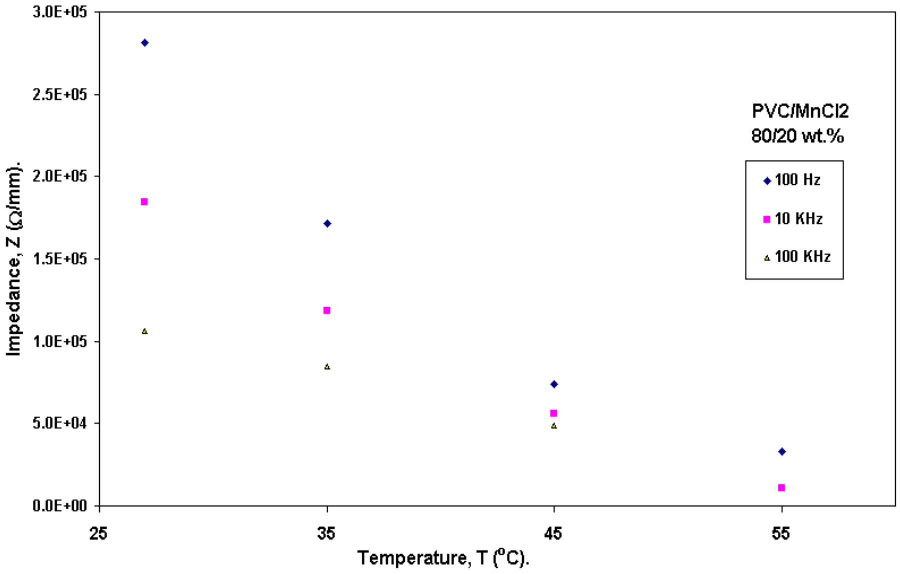

Fig.(2): Dependence of Impedance on Temperature.

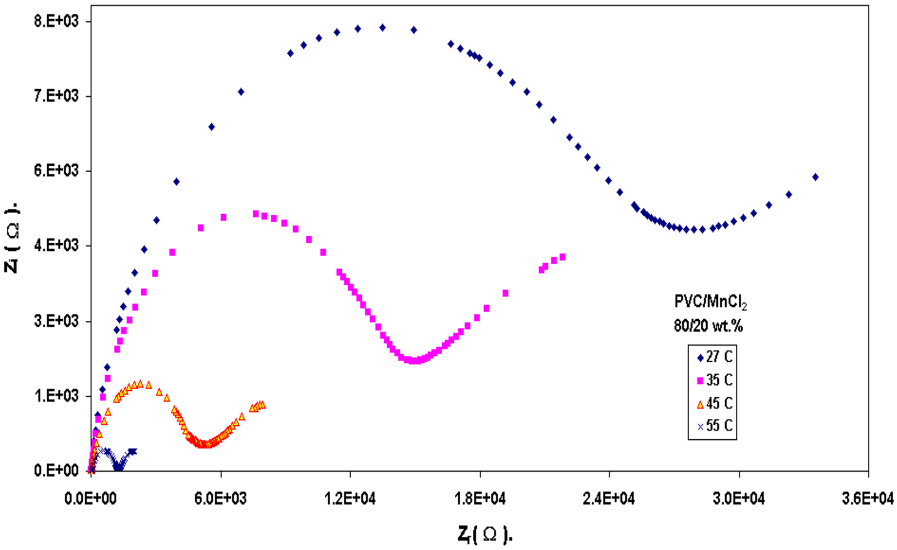

Fig. (3): Complex Impedance Plots for PVC/$MnCl_2$(20wt.%) Composite at Different Temperatures.

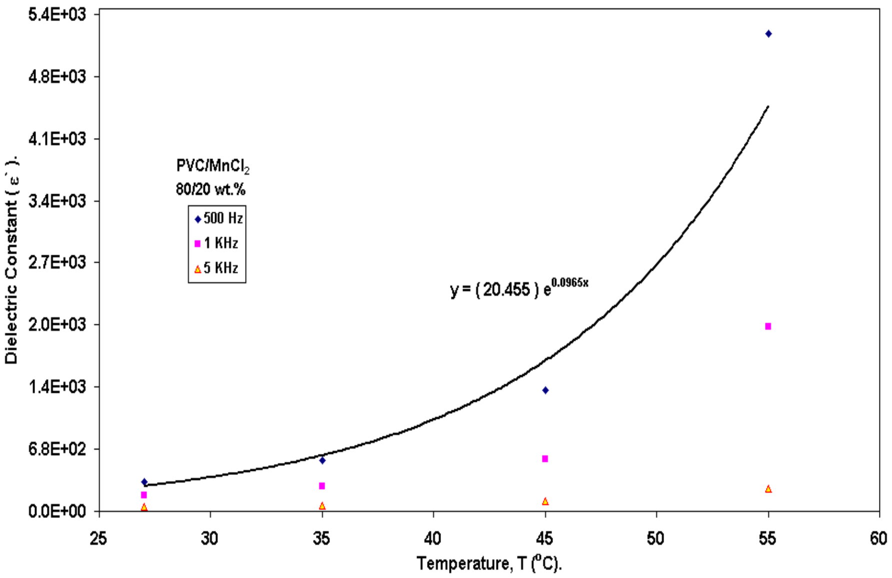

Fig. (4): The Dielectric Constant as a Function of Temperature.

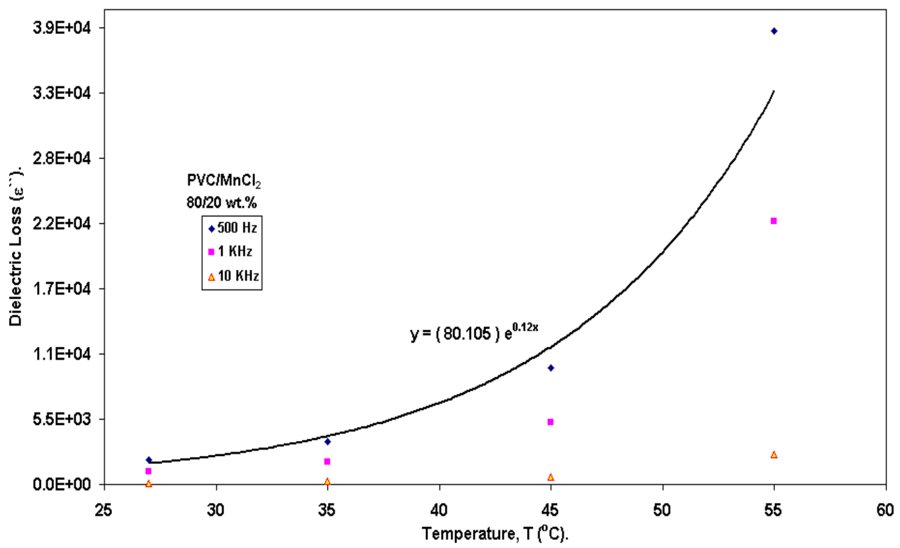

Fig. (5): The Dielectric Loss as a Function of Temperature.

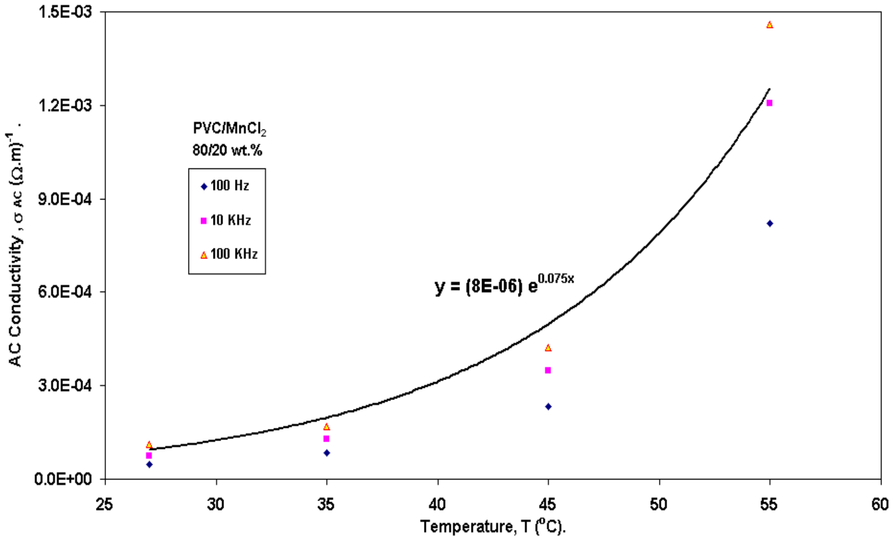

Fig. (6): The AC Conductivity as a Function of Temperature.

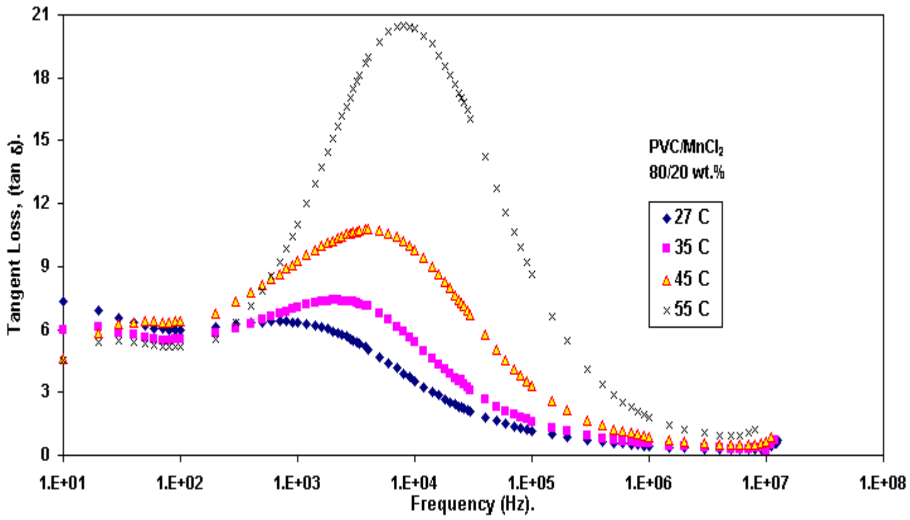

Fig. (7): The Variation of the Tangent Loss as a Function of the Frequency for PVC/MnCl$_2$(20wt.%) Composite at different

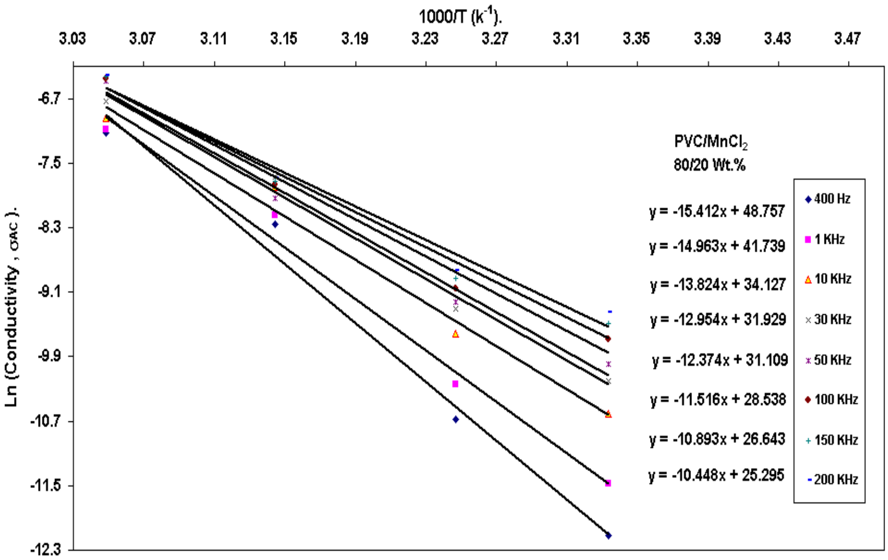

Fig. (8): Natural Logarithm of the AC Conductivity versus 1000/T.

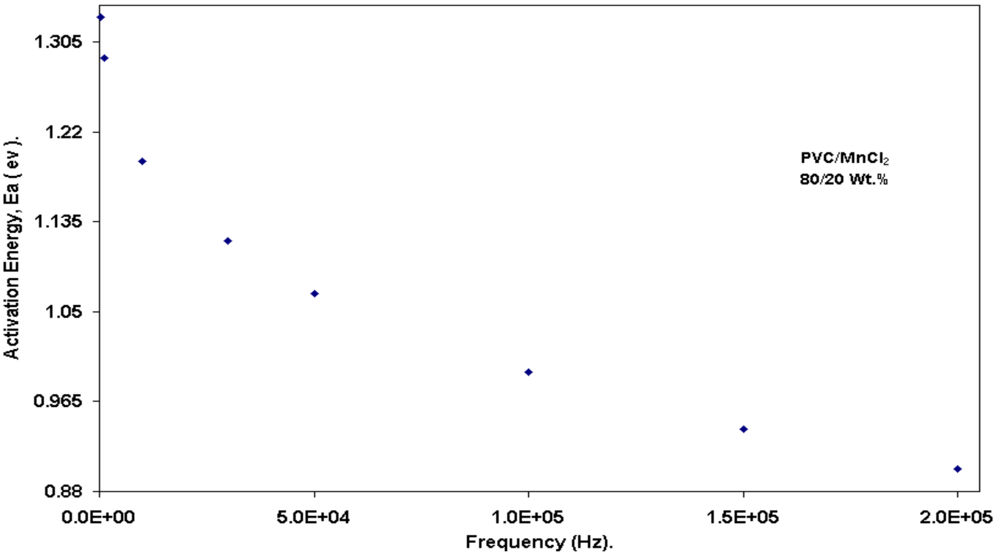

Fig. (9): The Activation Energy versus Frequency.

تأثير درجة الحرارة والتردد في الخصائص العزلية للمتراكب بولي كلوريد الفينيل مع ملح كلوريد المنغنيز

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الخلاصة

إن العمل المقدم في هذا البحث هو دراسة تأثير الحرارة في الخصائص العزلية لمتراكب من (بولي كلوريد الفينيل) مثل قالب وملح (كلوريد المنغنيز) حشوة بتركيز ٢٠% داخل القالب. تمت دراسة ثابت العزل الكهربائي ومعامل الفقد و زمن الاسترخاء المتراكب في نطاق التردد(١٠هرتز-١٣ ميكا هرتز)، وضمن تغيير مدى درجة الحرارة (٢٧ درجة مئوية – ٥٥ درجة مئوية) بتقانة الممانعة الكهربائية. وقد حُسِب تأثير زيادة درجة الحرارة وتردد المجال الكهربائي على الموصلية الكهربائية المتناوبة.

لقد وجد من النتائج أن زيادة درجة الحرارة تزيد التوصيلية الكهربائية وتخفض طاقة التنشيط ، وقد لوحظ إعتماد ثابتي العزل الكهربائي والممانعة الكهربائية على التردد المسلط و درجة الحرارة، وقد يعزى ذلك لبعض ظواهر الإستقطاب المعقدة وللقطبية العالية لهذا المتراكب. فزيادة درجة الحرارة والتردد المسلط على العينة يؤدي إلى نقصان زمن الإسترخاء للمتراكب المحضر مختبرياً لتأثير الحركة الأيونية و وجود الشوائب في المتراكب.