

STRUCTURE, AC CONDUCTIVITY AND POWER LOSS IN PVC AND PMMA POLYMERS

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Abstract

Frequency and temperature dependence of AC-conductivity (σ_{AC}) and power loss (W) for polyvinyl chloride (PVC) and poly (methyl methacrylate) (PMMA) were studied (in the frequency range 1KHz-1MHz and in the temperature range 20-100°C). It has been found that the AC-conductivity increases with increasing frequency and temperature for both samples. The value of the exponent S is less than 1 for both samples as determined experimentally. The power loss which is in the form of heat, is increased for both samples with increasing frequency and temperature. The IR spectra shows the presence of C-Cl and C=O bond, which are the main sources for power loss.

التركيب والتوصيلية المتناوبة و فقد القدرة للبوليمرين PVC, PMMA.

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الخلاصة

تم دراسة تأثير التردد و درجة الحرارة على التوصيلية المتناوبة (σ_{ac}) و فقد القدرة (W) لمادة بولي ميثاكريلات المثل PMMA وكذلك مادة بولي كلورايد الفايثيل PVC لمدى من التردد 1 كيلو هرتز الى 1 ميكا هرتز ودرجة حرارة من 20 الى 100 درجة مئوية. من خلال الدراسة تبين ان التوصيلية المتناوبة تزداد بزيادة التردد ودرجة الحرارة لكلا المادتين. لقد وجدت قيمة الاكسبوننت (S) اقل من واحد لكلا المادتين من خلال التجربة. اما فقد القدرة والتي هي بشكل حرارة تزداد بزيادة التردد ودرجة الحرارة. لقد اظهرت دراسة الاشعه تحت الحمراء الاواصر (C-Cl) و (C=O) والتي تعتبر المصدر الرئيسي لفقد القدرة.

1. Introduction

The literature on AC conductivity in disorder solids and its scaling properties with temperature and composition is expensive although experiments have been performed on a wide range of semiconducting and insulating materials. In general the frequency dependent conductivity is characterized by an approximate power law behavior $\sigma \propto \omega^S$ [1]. Even today it remains surprisingly difficult to unambiguously determine all of the important features of

electrical conduction in polymers, due to several of the solid state theories that have been useful in establishing the properties of crystalline semiconductors and insulators give predictions that are not sufficiently unique when applied to data for polymers. Another very real source of difficulty is the great morphological complexity of most polymer systems [2]. In polymers as a class of materials both electrons and ions contribute to the total conductivity,

however in a given case it is likely that one type of conductivity will predominant [2].

The power loss of polymeric materials heavily influenced by factors such as ionic conduction and structural heterogeneities, which will generate flow of charges and result in thermal dissipations [3].

2. Experimental Method

The polymer samples are commercial polyvinyl chloride (PVC) and poly (methyl methacrylate) (PMMA). Extrusion molding process was used for making these samples. The samples were prepared in circular shape with 6 cm diameters and of thicknesses of 2 and 2.6mm respectively. The thickness was carefully measured with a micrometer for each sample within ± 0.01 mm. The polymer sample was inserted between two identical circular smooth and cleaned aluminum electrodes.

Specimens were prepared as a mixture of KBr and polymer sample and then compressed at 10 tones to form 1mm thick disks. The IR spectra of PVC and PMMA were obtained at room temperature in the wave number ($450\text{-}4000\text{cm}^{-1}$) with a double beam recording IR spectrometer (Perkin Elmer).

The dielectric loss cell was locally designed. The heating coil was made from a resistive wire in the form of circular coil arranged symmetrically in the chamber. The resistance coil is connected to an A.C. source variac transformer. The current through this heater could be adjusted to optimal. To eliminate temperature gradient we heated the system for several hours to attain thermal equilibrium (a pre experiment was performed in which two identical thermocouples was attached to each disc it was found that at thermal equilibrium they record the same temperature). Also we switched off the power supply during the taking of the measurement, otherwise A.C. current passed through the electrical heater around the sample cell; this would produce a magnetic field which could have a bad effect on the results.

The sample holders which were two identical discs of 1cm thickness made from aluminium was set at the centre of the circular coil and at the high of 7cm. The lower plate is fixed, while the upper is movable by using a screw to ensure good electrical contacts between the electrodes and the sample; this enables us to avoid the parasite capacitance induced by the presence of air interstices at the interfaces between the sample and the electrodes. The thermocouples

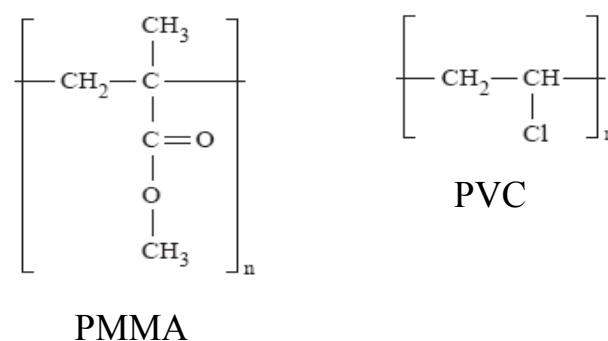
were not being attached to the capacitor plates directly because it produce leak which in turn could changes the value of the capacitance, therefore it was set as close to the capacitor plate as the thickness of one mica sheet.

The AC conductivity and power loss were measured as a function of temperature and frequency. The resistance of polymer samples was measured by using Programmable Automatic Precision RCL meter type PM6036. The sample temperature was measured by Chromel-Alumel thermocouple set as close as possible to one of the electrodes, which was accurate to $\pm 1^\circ\text{C}$, with digital thermometer TM-914C ($40\text{-}1200^\circ\text{C}$).

3. Results and Discussion

3.1 IR characterization

IR spectroscopy is a popular method for characterizing polymers. This technique is based on the vibrations of the atoms of the molecule [4]. In Figure .1 the peak at 2919cm^{-1} is attributed to the stretching of CH and CH_2 bonds of PVC and the peaks at 1390cm^{-1} , 1470cm^{-1} attributed to the CH and CH_2 bending. The absorption bands at 610, 680 and 710cm^{-1} corresponds to C-Cl groups. In Figure.2 the peak at 1732cm^{-1} is due to C=O bond, and the peak at 1385cm^{-1} is due to CH and CH_3 bending in PMMA. A broad absorption band around 3250cm^{-1} were observed in PVC and PMMA which can be ascribed to both OH groups and water absorbed by the KBr [5]. The general structure of PMMA and PVC are given below:



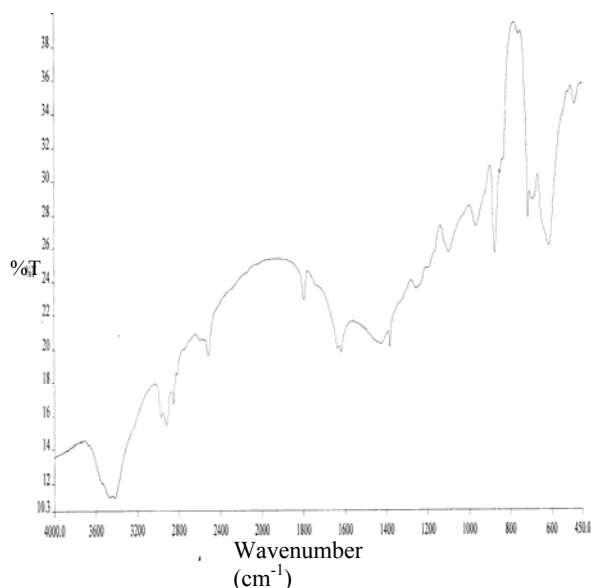


Figure 1: IR spectra for PVC

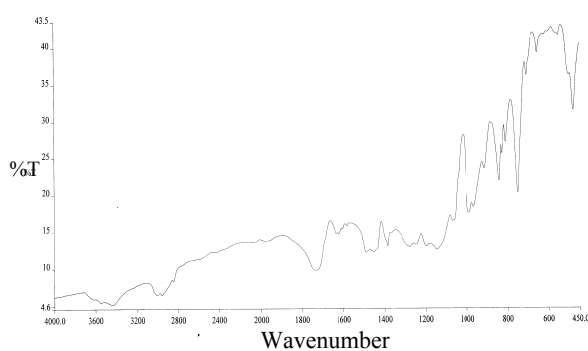


Figure 2: IR spectra for PMMA

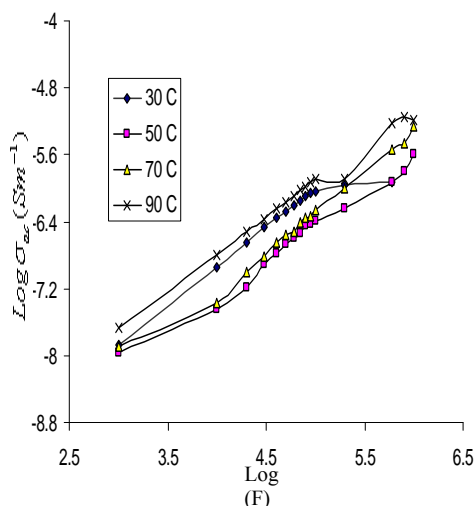


Figure 3: AC conductivity as a function of frequency for PVC

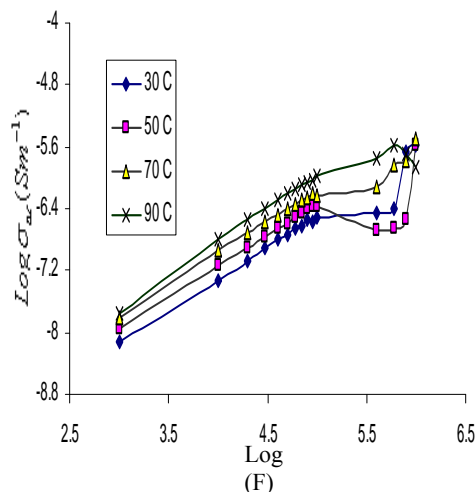


Figure 4: AC conductivity as a function of frequency for PMMA

3.2 AC Conductivity

The AC-conductivity (σ_{AC}) was estimated using the following relationship:

$$\sigma_{AC} = \frac{L}{RA} \text{ ----- (1)}$$

Figures (3 and 4) show the effect of frequency on AC conductivity for PVC and PMMA respectively at different temperatures.

It can be noticed that, AC conductivity increases with increasing frequency regularly at low frequency till $\text{Log}(F) = 5$ for both samples, but at high frequency there is a decrease in AC conductivity which is directly related to the mobility of charge carriers, because the mobility decreases with increasing frequency due to the laying of molecules towards alternating electric field [6]. Generally the electrical conductivity of polymer depends on the presence of free ions connected chemically with macromolecule. The molecular chain does not participate in the transfer of electrical charge [6]. The AC conductivity obeyed the empirical power law behavior such that [7, 8]:

$$\sigma_{AC} = A\omega^S \text{-----} (2)$$

Where ω is the angular frequency, A is the proportionality constant and S is the index which is characteristic of the type of conduction mechanism (relaxation mechanism dominant in amorphous materials). The exponent S is generally contained with the limits $0.5 < S < 1$ [1].

In the present study the value of S lies between 0.777 and 0.898 for PVC and 0.512 to 0.741 for PMMA which are in good agreement with the theoretical value given above as shown in Figures below

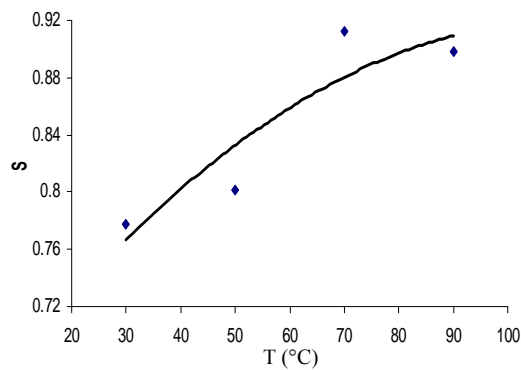


Figure 5: S versus temperature for PVC

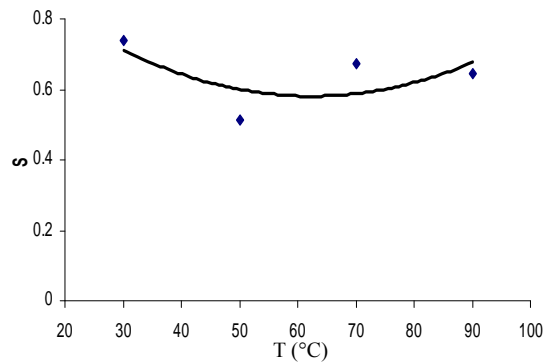


Figure 6: S versus temperature for PMMA

The variation of exponent S with temperature gives information about conduction mechanism involved. The value of S which is less 1 for PVC and PMMA samples characterizes the electronic conduction via hopping process [6]. The effect of temperature on AC conductivity for PVC and PMMA, are shown in Figures (7 and 8) respectively.

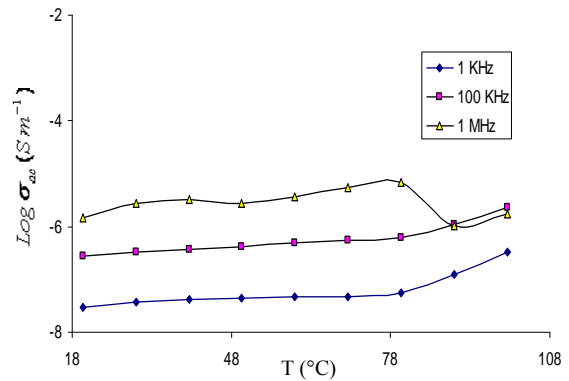


Figure 7: Temperature dependence of Ac conductivity for PVC

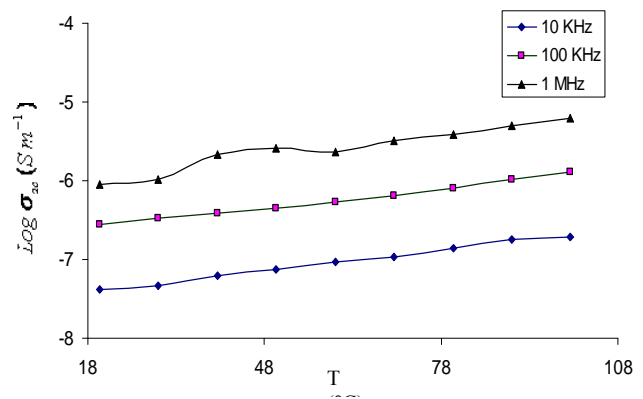


Figure 8: Temperature dependence of Ac conductivity for PMMA

As it can be observed that AC conductivity increases with increasing temperature and frequency. The influence of temperature on AC conductivity has been explained by considering the mobility of charge carriers responsible for hopping. As temperature increases the mobility of hopping carriers also increases thereby increasing conductivity. It is clear from Figure. 7 that the further increase of temperature reduces sharply the conductivity at 1 MHz. This decrease of AC conductivity at higher temperatures is due to thermal expansion of the polymer, which is directly related to the increase of free volume by increasing temperature, thus the density of the polymer is reduced which reduces the AC conductivity [9]. An increase in AC conductivity with frequency and temperature indicates the fact the charge carriers, are transported by hopping through the defect sites along the polymer chain [7].

3.3 Power Loss in AC Field:

In AC fields, the power loss per unit volume per unit time may be expressed as [10]:

$$W = \frac{E^2 \sigma_{AC}}{8\pi} \text{-----} (3)$$

Where E is the AC field and σ_{AC} is AC conductivity. The values of the power loss as functions of temperature were calculated at different frequencies are listed in Tables 1 and 2 for PVC and PMMA respectively as shown below.

Table 1: Power Loss (W) as a function of temperature for PVC

T(°C)	W(watt) at f=10KHz	W(watt) at f=100KHz	W(watt) at f=1MHz
20	2.72E-09	2.48E-08	1.31E-07
30	3.35E-09	2.91E-08	2.52E-07
40	3.67E-09	3.29E-08	2.98E-07
50	3.96E-09	3.77E-08	2.43E-07
60	4.15E-09	4.33E-08	3.25E-07
70	4.31E-09	4.82E-08	4.79E-07
80	5.02E-09	5.69E-08	6.01E-07
90	1.14E-08	9.93E-08	9.07E-08
100	2.92E-08	2.05E-07	1.55E-07

Table 2: Power Loss (W) as a function of temperature for PMMA

T(°C)	W(watt) at f=10KHz	W(watt) at f=100KHz	W(watt) at f=1MHz
20	3.72E-09	2.49E-08	8.11E-08
30	4.21E-09	2.99E-08	9.55E-08
40	5.67E-09	3.57E-08	1.93E-07
50	6.81E-09	4.03E-08	2.37E-07
60	8.21E-09	4.82E-08	2.09E-07
70	9.65E-09	5.99E-08	2.95E-07
80	1.23E-08	7.42E-08	3.50E-07
90	1.63E-08	9.45E-08	4.55E-07
100	1.75E-08	1.17E-07	5.59E-07

It can be seen from Tables 1 and 2 that the power loss which is the energy loss in the form of heat caused by internal friction of the molecular movements in the dielectric is increased with increasing of temperature and frequency [11], this increase of W is due to the presence of dipoles C-Cl in PVC and C=O in PMMA as indicated in IR characterization and a variety of polar additives and fillers which are also present. We note from Table 1 that there is anomaly in power loss at 1 MHz and at the temperature of 90°C, this is certainly can be attributed to the mechanism which cause the anomaly in AC conductivity at the same frequency and temperature.

The dipoles and many other charged particles can not keeping in phase with the field when the field is changes, this is leading to frictional damping mechanism that causes power loss and increase by increasing of temperature because the movability of charged particles increase which increase the internal friction.

5. Conclusion

The experimental results show that the AC-conductivity varied with frequency and temperatures. Increase of frequency increases AC-conductivity initially and at high frequencies $\text{Log}(f) = 5.5$ to $\text{Log}(f) = 6$, there was a decrease in conductivity which is due to the laying of dipole frequency and applied field frequency. The temperature dependence of the value of S indicates that, the conduction mechanism occurs via hopping process. The AC-conductivity decrease at high temperatures in polyvinyl chloride due to thermal expansion which reduces the polymer density. The increase of power loss value with increasing frequency and temperature can be ascribed to electrical conduction and internal friction.

Acknowledgment

We are grateful to thanks Dr. Emad A. Al-Khafagy for IR analysis and Mr. Luqman for IR measurement. Special thanks due to Dr. Omed G. Abdullah for computer knowledge. We are indebted to Salaadin University-Physics department for supplying as with LCR meter.

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