EFFECT OF OIL SHALE PARTICLES ON THE ACTIVATION ENERGY OF POLYSTYRENE SHEETS

Husam Miqdad and Abeer Adaileh
Department of Basic Science, Applied Science Private University, Amman, Jordan
E-Mail: hmiqdad@hotmail.com

ABSTRACT

Electrical properties of hybrid polymer sheets, made of Polystyrene filled with oil shale particles, have been investigated. The observed physical constants of the sheets like activation energy were determined. The present study has focused on the variation of activation energy with frequency in the range (200-1000 kHz) and temperature in the range (30 ºC-90 ºC) for composites as compared to that case of neat polystyrene sample. The observed values of the activation energy (Ea) showed frequency and temperature. It was found that the activation energy of the prepared sheets decreases with oil shale concentration in the composite and that it decreases with temperature according to polarization processes. The activation energy of the prepared sheets increases with frequency.

Keywords: polystyrene, oil shale, activation energy, frequency, temperature.

INTRODUCTION

Most polymeric materials are poor conductors of electricity because of the unavailability of large numbers of free electrons to participate in the conduction process. So focused on enhancing their electrical conduction and improving their properties. As is the case with semiconductors, these polymers may be made either n type (i.e., free electron dominant) or p type (i.e., hole dominant) depending on the dopant [1]. Polymers exhibit a variety of electrical properties reflecting their structures and molecular motion. Electrical properties can be tailored to a specific requirement by the addition of suitable dopant materials.

Polymer composites are materials in which a second component with very different properties is added to the polymer so that both components contribute to the properties of the product. The second component often increases the strength or stiffness of the product and is said to reinforce it [2]. composite materials have become common technical materials that are designed and manufactured for several applications. Today, it appears that composites are the materials of choice for many engineering and sciences applications. The most advanced composites are polymer matrix composites. They are characterized by relatively low costs, simple manufacturing and high strength. In general, added to the matrix to improve or alter the matrix properties. The reinforcement forms a discontinuous phase that is dispersed uniformly throughout the matrix [3].

Polystyrene (PS) is a polymer which finds widespread use in the developed world due to its desirable properties, combined with its relative cheapness. Among its features are excellent color range, transparency, rigidity, and low water absorption. Polystyrene can be polymerized with butadiene to make high impact polystyrene (HIPS) or expanded with pentane to make plastic foam, which is made in the form of foam packaging and insulation (Styrofoam is one brand of polystyrene foam). Also, it can be transparent or can be made to take on various colors [4]. The monomer styrene is a derivative of benzene, vinyl benzene (Figure-1). It is a colorless mobile liquid that polymerizes readily. The polymer is based on a simple head-to-tail arrangement of monomer units. Since the specific position of the benzene ring is somewhat variable this inhibits crystallization, hence the polystyrene is amorphous.

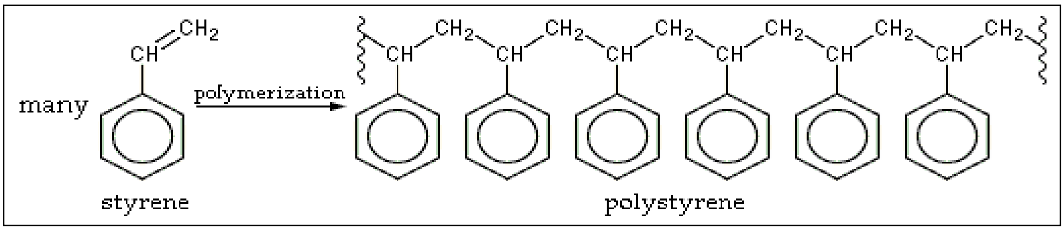

Figure-1. structure of polystyrene.

The term oil shale refers to a class of fine-grained sedimentary rocks containing high concentrations of organic material, called kerogen, that can be a source of petroleum upon extensive heating and processing. Like other hydrocarbon source-rocks, oil shale originates from accumulations of sediments and organic matter deposited in anoxic environments. As the deposits are buried by additional sediment, high temperature and pressure remove water and enable chemical reactions that transform the organic matter into kerogen. These reactions can proceed at greater temperatures to produce oil, but oil shale has not been buried to sufficient depths to allow this further conversion [5]. Oil shale typically contains enough hydrocarbons to burn in raw form and can be used directly as a solid fuel. However, producing oil from kerogen requires pyrolysis, an energy intensive process in which the rock is heated to (45 ºC-55 ºC) in the absence of oxygen. The industrial procedure used to convert oil shale into useful hydrocarbons is called "retorting".

2. EXPERIMINTAL WORK

2.1 Materials and Composites Films Preparation

Polystyrene/oil shale composites with different filler concentrations (5, 10, 20, and 30 wt% oil shale) and neat polystyrene were prepared. Oil shale rocks were obtained from area located in Jordan and embedded at about 10m depth in the ground. The deposit filler was grinded into powder and chemically purified. A summary of chemical, physical property, and morphology of the oil shale deposits were reported previously [6, 7]. Polystyrene resin and oil shale powder with grain size of about 63 mm were thermally mixed in a Brabender-like apparatus at a temperature of 180 ºC and a pressure of 150 bar in a heat press. The compressed molded composite sheets were about 1.3mm thick.

2.2 SEM Microscopy

Fracture surfaces of notched composite specimens were examined by scanning electron microscopy (SEM). Figure-2(a) and Figure-2 (b) show two micrographs of the fractured surfaces of 10 and 30 wt% oil shale composite specimens. The micrographs exhibit good distribution and strong adhesion of the oil shale particles within the polymer matrix [8].

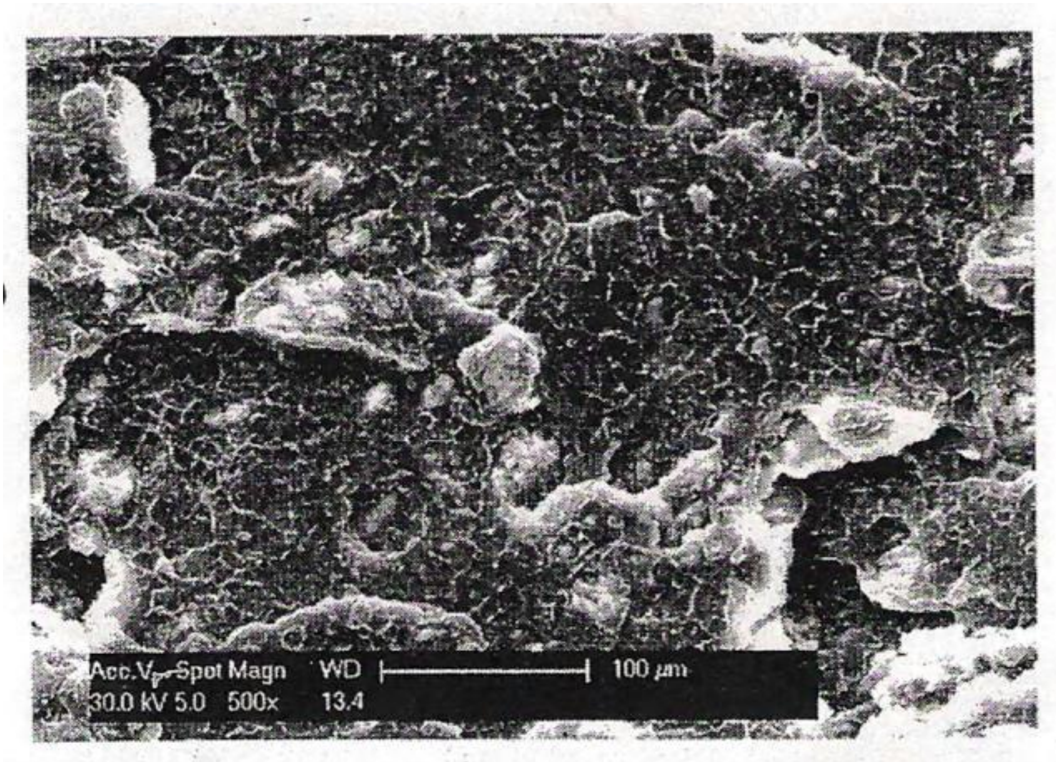

Figure-2.a. Scanning electron micrographs of polystyrene/oil shale composites for 10 wt.%.

VOL. 16, NO. 16, AUGUST 2021 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

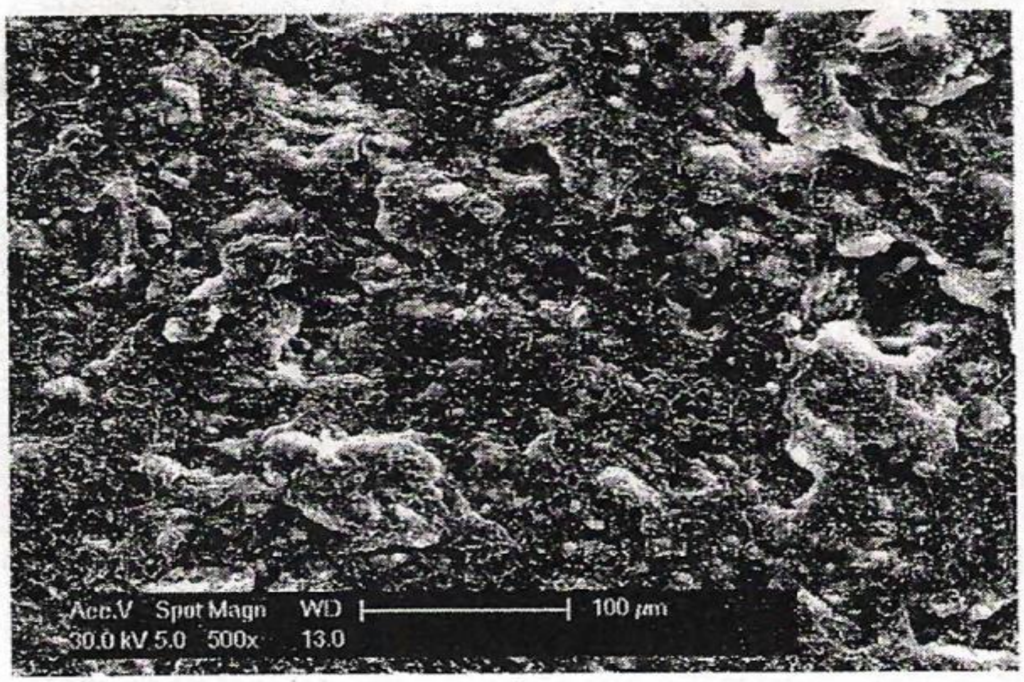

Figure-2.b. Scanning electron micrographs of polystyrene/oil shale composites for 30 wt.%.

2.3 Electrical Measurements

The AC electric properties of the Polystyrene/oil shale composite were studied through measurements of the impedance (Z), and the phase shift angle (φ) by using LF Impedance Analyzer. Impedance measurements were done at different temperatures and applied field frequency range from 5 Hz up to 13 MHz. The test specimens were placed firmly between two copper electrodes in a sample holder shown in Figure-3. These electrodes were connected through cables to the impedance analyzer. Disk-shaped specimens with 2cm diameter and 1.3mm thick were cut from the prepared sheets. The test specimens were placed firmly in a cell between two copper electrodes connected through cables to the impedance analyzer. The cell was placed in an oven and the temperature was measured by thermocouple wires. A period of about 20 min was maintained between successive impedance measurements to allow a steady state of temperature to be reached. The impedance analyzer reads values of impedance and phase angle of the specimen by varying the applied frequency. The mean and standard deviations were estimated with average error of about (3-5 %). Impedance measurements were performed in a frequency range from about (200-1000 kHz) over a temperature range (30 ºC - 90 ºC) with steps of 15 ºC. Since the glass transition temperature (Tg) for Polystyrene is about 100 ºC, no higher temperature measurements were conducted. Temperature readings were taken in a steady state condition.

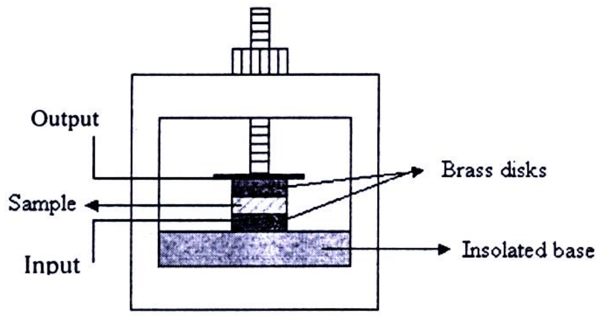

Figure-3. The sample holder diagram impedance analyzer.

Dielectric materials are a special class of substances that, under almost all conditions, are insulators. They have the interesting and useful property that their electrons, ions, or molecules may be polarized under the influence of an external electric field. When such materials are placed between charged plates as in capacitors, they increase the total capacity of these devices. This application constitutes one of the important applications of these materials [9].

The complex impedance of the sample with the real and imaginary components can be calculated by:

$$Z' = Z \cos \varphi \tag{1}$$

$$Z'' = Z \sin \varphi \tag{2}$$

ARPN Journal of Engineering and Applied Sciences

The dielectric constant ε' and the dielectric loss ε" of the sample are calculated from the following equations [9]:

$$\varepsilon' = \frac{Z''}{2\pi f C_o Z^2} \quad (3)$$

$$\varepsilon'' = \frac{Z'}{2\pi f C_o Z^2} \quad (4)$$

where f is the frequency of the applied AC electric field and C_o is the capacitance of the two plates of the cell (capacitor) without the sample (dielectric), and is given by:

$$C_o = \varepsilon_o A / d \quad (5)$$

Here A is the area, and d is the thickness of the test specimen.
where εo is the electrical permittivity of free space {ε_o = 8.854 x 10-12 F.m-1}.

The AC conductivity of the sample calculated from the following equation:[10]

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \quad (6)$$

The activation energy (Ea) of the conduction process is calculated by the Arrhenius equation, which is given by:

$$\sigma = \sigma_o \exp[-Ea / k_B T] \quad (7)$$

where σ is the conductivity, σ_o is the material constant conductivity, T is the temperature of the material in Kelvin, and k_B is the Boltzmann constant (k_B = 1.38 x 10-23 Joule / K) [11].

3. RESULTS AND DISCUSSIONS

The electrical properties of polystyrene/oil shale composite, containing 0, 5, 10, 20, and 30 % by weight oil shale were studied and some of their physical parameters such as the AC electrical conductivity and activation energy were determined. Oil shale appended to the matrix of polystyrene to compose sheets is being searched to evaluate the role of the Oil shale particles in the process of the activation energy when the electric field is affected. The objective of studying activation energy in polymers is to realize the type and nature of the charge transmission in conducting materials [12].

3.1 Activation Energy Determination

The minimum amount of thermal energy that is required to activate ions, atoms, and molecules to conduction in which they can undergo physical transport is known as activation energy (Ea). The values of activation energy were determined from the slopes of the straight lines obtained by drawing the natural logarithm of the conductivity (Ln σ_{AC}) versus (1000/T) for all thin films at the frequencies (200, 400, 600, 800 and 1000 kHz) as shown in Figures (4-8).

By using Arrhenius Equation (7), the activation energy values were calculated and summarized reported in Tables (1-5) which display the relation between activation energy and frequency for thermally activated conduction processes (ionic and electronic). It was observed that with increasing the frequency, the activation energy decreases for all tested composites. The decrease in activation energy reflects electronic mobility, higher ionic and increasing in electrical conduction in the samples membranes [10].

The values of activation energy for different composites, at frequency 400 kHz, are included in table 6 and drawn against the concentration in Figure-9 in order to study the effect of the oil shale concentration in the composites on their activation energy values. The highest conductivity value and the lowest activation energy values were observed at the 30 wt.% Polystyrene/oil shale sample (which has the largest oil shale concentration), where the lowest σ_{AC} value and the highest activation energy were those of the neat polystyrene sample. This observed behavior of oil shale composites seems to correlate with the Eopt and AC conductivity behavior. The low values of activation energies suggest the existence of localized energy levels in the forbidden energy gap in the examined composites which works as semiconducting material.

Table-1. The activation energy for neat PS.

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	0.173
400	0.189
600	0.209
800	0.226
1000	0.237

Table-2. The activation energy values for 5 wt. % composite.

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	0.147
400	0.157
600	0.161
800	0.168
1000	0.172

VOL. 16, NO. 16, AUGUST 2021 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Table-3. The activation energy values for 10 wt. % composite.

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	0.143
400	0.149
600	0.152
800	0.157
1000	0.161

Table-4. The activation energy values for 20wt. % composite.

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	0.139
400	0.144
600	0.148
800	0.153
1000	0.154

Table-5. The activation energy values for 30wt. % composite.

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	0.123
400	0.128
600	0.130
800	0.133
1000	0.135

Table-6. The activation energy values for composites at 400 kHz.

Samples	Activation Energy Ea $\times 10^{-2}$ (eV)
neat PS	0.189 ± 0.0041
5 wt.%	0.157 ± 0.0032
10 wt.%	0.149 ± 0.0030
20 wt.%	0.144 ± 0.0029
30 wt.%	0.128 ± 0.0026

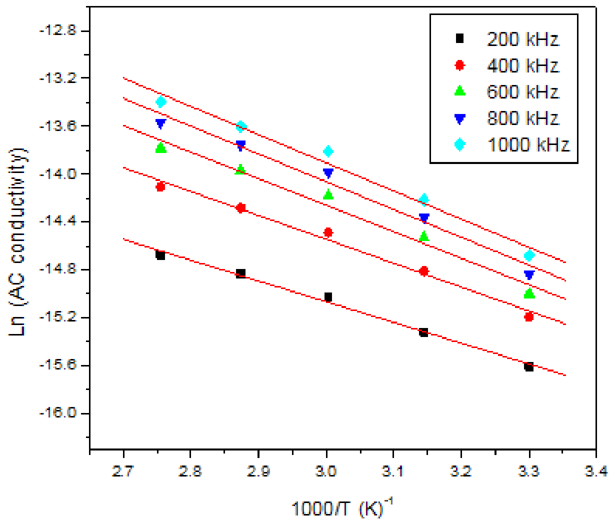

Figure-4. Ln (AC-conductivity) versus (1000/T) for neat PS.

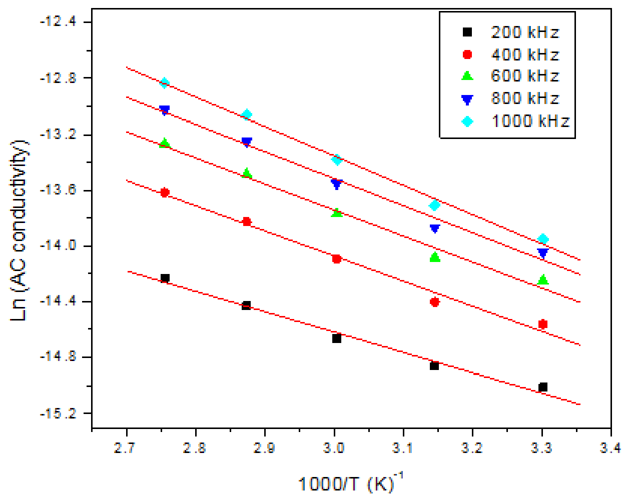

Figure-5. Ln (AC-conductivity) versus (1000/T) for 5wt.% composite

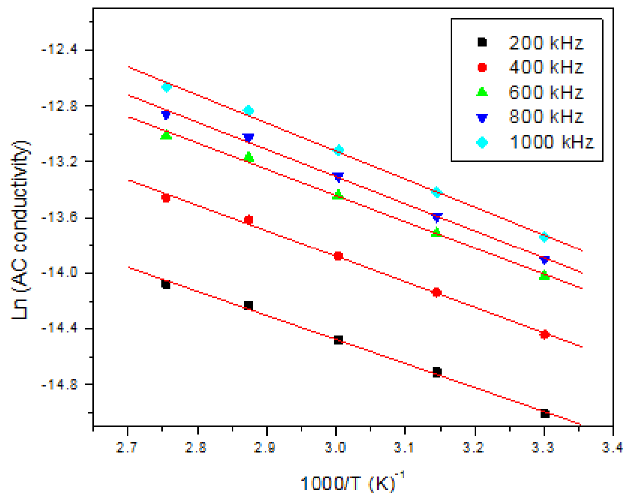

Figure-6. Ln (AC-conductivity) versus (1000/T) for 10wt.% composite.

ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

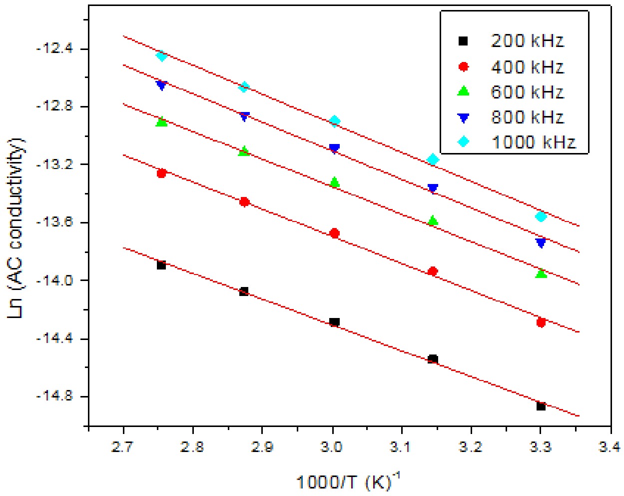

Figure-7. Ln (AC-conductivity) versus (1000/T) for 20wt.% composite.

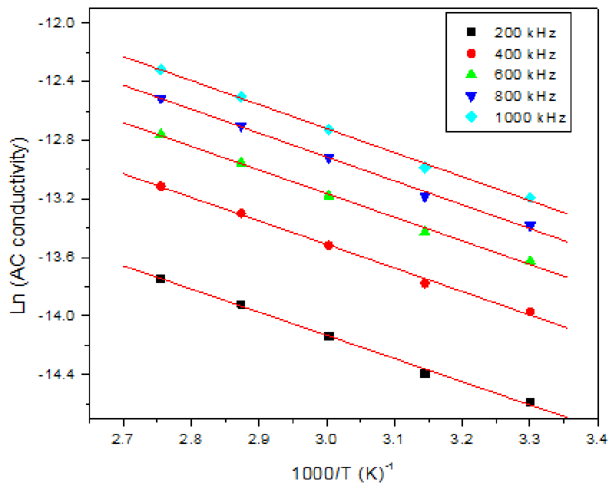

Figure-8. Ln (AC-conductivity) versus (1000/T) for 30wt.% composite.

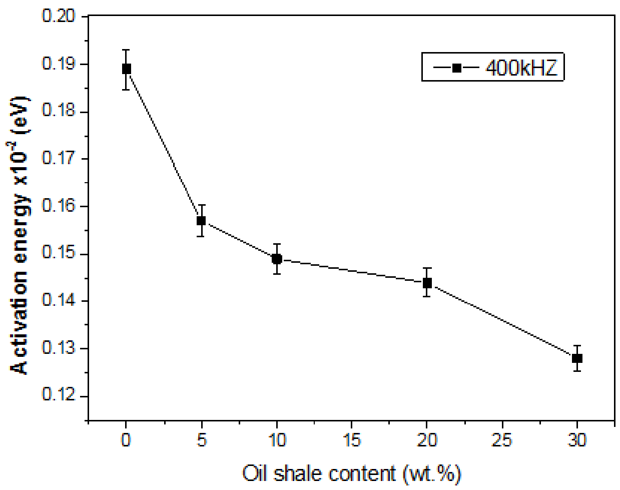

Figure-9. Variation of activation energy with oil shale concentration.

Figure-9 displays that the activation energy value decreases with the increase in the oil shale concentration, in a thermally activated process, the polymer sheets will have high conductivity as seen in Figure-12. This noticed decrease in activation energy value means that the Polystyrene/oil shale composites energy will be narrower, referring to production of localized energy states by heating, which increases the ability of the electron to tunnel or jump from the valence to conduction energy band and increases ion mobility. These events increase the amorphous region in the polymer Polystyrene and produce more active segmental motion which stimulates the electron hopping mechanism and thus the conductivity becomes higher. In our study, the noticed increase in conductivity and decreasing in the activation energy values with increasing temperature or the oil shale content could be controlled by the mobility in the localized positions bridged by the particles of oil shale in the amorphous regions present in the polymer electrolyte. The low activation energy for charges in the oil shale transition refers to the amorphous nature of polymer which simplifies the rapid ions and electrons movements in the polymer complex [13].

Figure-10 displays that with increasing the frequency the activation energy (Ea) increases because at higher field, less charges are moved, causing less participation of activated charges to conduction. It can be observed that activation energy is increasing at higher frequency and decreases with an increase in the oil shale concentration as shown in Figure-11.

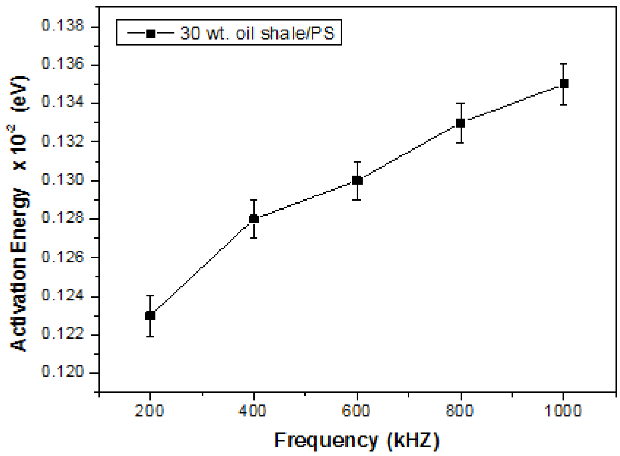

Figure-10. Variation of (Ea) values with frequency for for 30wt.% composite.

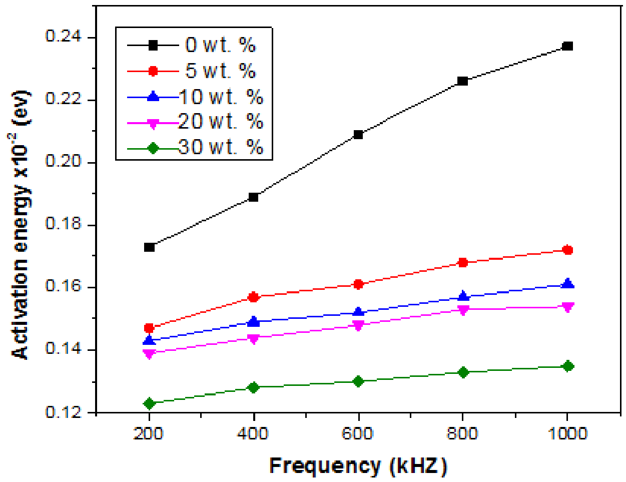

Figure-11. Variation of (Ea) values with frequency for 30wt.% composite.

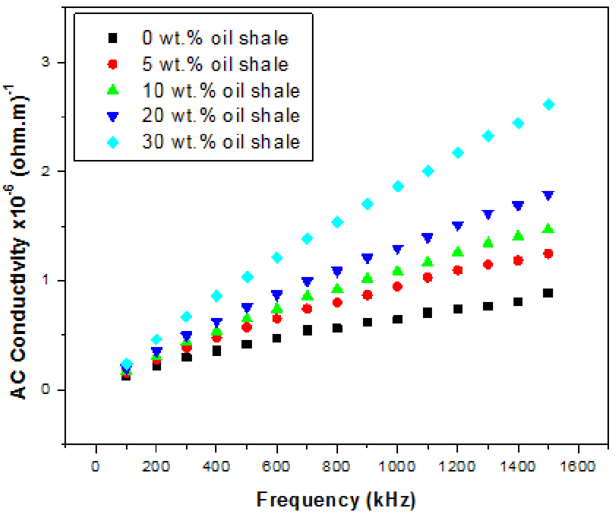

Figure-12. Dependence of AC conductivity as a function of frequency.

4. CONCLUSIONS

The activation energy of Polystyrene filled with oil shale particles was studied. By studying the results, we deduced that:

- The activation energy decreases with increase the oil shale concentration.
- The activation energy is decreased with increasing temperature.
- The activation energy is increased at higher frequency.

ACKNOWLEDGEMENTS

The author acknowledges Applied Science Private University, Amman, Jordan, for the fully financial support granted of this research article.

REFERENCES

[1] Callister William D. 1999. Materials Science and Eng ineering. An Introduction 5th edition. New York: John Wiley and sons.

[2] Bower David I. 2002. An introduction to Polymer Physics, London: Cambridge University press.

[3] Killops V. 2005. Introduction to Organic Geochemistry, (2nd). Blackwell Science Ltd. USA.

[4] Ahmad M, Abdallah M and Zihlif A . 1991. Electrical properties of oil shale rocks. J Mater Sci. 26: 203-207.

[5] Ahmad MS, Abdelazeez MK and Zihlif AM. 1990. Microwave measurements on oil shale rocks. J Mater Sci. 25: 5019-5024.

[6] Ragosta G. and Zihlif. 2009. Thermal Characterization of Oil Shale/PS Composites. (Private Communication).

[7] Ahmad MS, Abdelazeez MK and Zihlif AM. 1990. Microwave measurements on oil shale rocks. J Mater Sci. 25: 5019-5024.

[8] Ragosta G. and Zihlif. 2009. Thermal Characterization of Oil Shale/PS Composites. (Private Communication).

[9] Pollock D. 1993. Physical Properties of Materials for Engineers. (2nd ed.) CRC Press, Inc.

[10] Ahmad M.S, Haj Abdallah M., Zihlif A.M., Abdelazeez M.K.. 1991. Electrical Properties of Oilshale Rocks. Journal of Materials Science. 26: 203-207.

[11] Hummel R.E. 1993. Electronic Properties of Materials, (2nd ed.). Springer-Verlag, New York.

[12] Agrawal R. C., Pandey G. P. 2008. Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview, Journal of Application Physics. 41- 223001. p. 18.

[13] Sharma Rao, A., Bhargav P. and Mohan V. 2007. Structural, Electrical and optical characterization of PVA Polymer electrolyte films. International Journal of polymer Materials. 56: 579.