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DIELECTRIC AND AC CONDUCTIVITY OF POLYSTYRENE/OIL SHALE COMPOSITES

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ABSTRACT

The electrical properties of prepared polystyrene/oil shale composites with different concentration: 0, 5, 10, 20, 30 wt. % of oil shale were studied in this paper, under various measuring conditions including filler content and applied electric field frequency. The dependence of AC-electrical properties of polystyrene/oil shale composites on filler content and frequency were studied using the AC impedance technique. The impedance measurements were performed in the frequency range (100 kHz - 1.5 MHz) at room temperature (30°C). Impedance, dielectric constant and AC-conductivity showed frequency and filler content dependencies. The relaxation time was determined for different filler concentrations .The study includes application of some models to explain the observed results. The universal power law of the AC conductivity behaviour is satisfied for different concentration.

Keywords: oil shale, composites, impedance, dielectric constant, AC conductivity.

1. INTRODUCTION

Many of our modern technologies require materials with uncommon combination of properties that cannot be met by the conventional polymeric materials, metal alloys and ceramics. Material property combinations and ranges have been, and are yet being, extended by the development of composite materials [1].

Composite materials have been utilized to solve technological problems for a long time, but in the 1960s did these materials start draw attention of industries with the introduction of polymeric-based composites. Since then, 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 [2,3].

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 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 have 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) 450-550°C) in the absence of oxygen. The industrial procedure used to convert oil shale into useful hydrocarbons is called "retorting".

2. EXPERIMINTALWORK

2.1 Materials and composites films preparation

Polystyrene/oil shale composites with different filler concentrations (5, 10, 20, and 30wt% oil shale) and neat polystyrene were prepared. Oil shale rocks were obtained from El-Lajjun 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°C 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-1(a) and (b) shows 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.

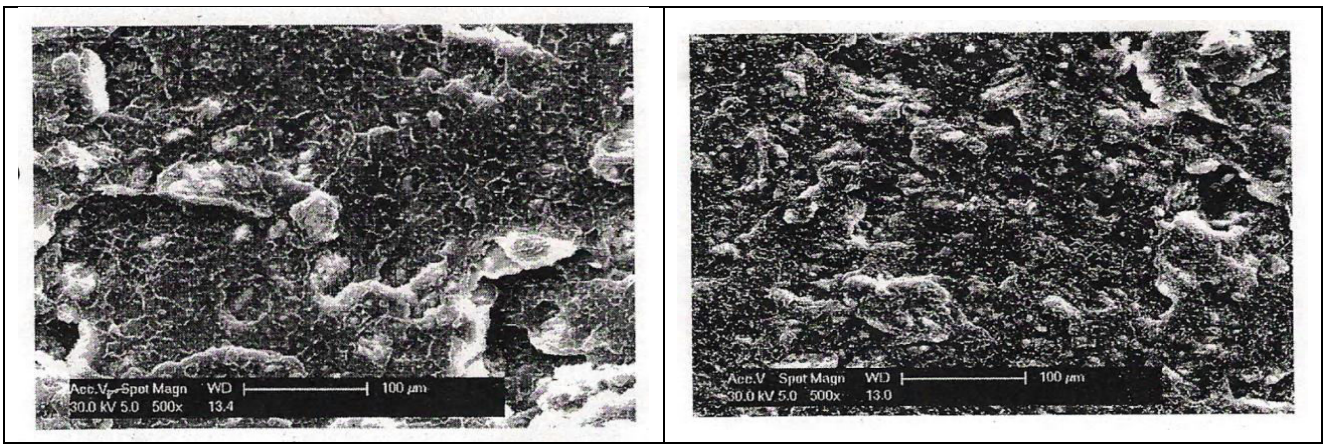

Figure-1. Scanning electron micrographs of PS/oil shale composites (a) 10 wt.% and (b) for 30 wt.% [8].

2.3. Electrical measurements

The AC electric properties of the PS/oil shale composite were studied through measurements of the impedance (Z), and the phase shift angle (φ) by using LF Impedance Analyzer (HP model 4192). Impedance measurements were done at different temperatures and applied field frequency range from 100 kHz to 1.5MHz at temperature 30ºC. The test specimens were placed firmly between two copper electrodes in a sample holder. 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%).

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

$$Z' = Z \cos \varphi \quad (1)$$

$$Z'' = Z \sin \varphi \quad (2)$$

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 Co is the capacitance of the two plates of the cell (capacitor) without the sample (dielectric), and is given by:

$$Co = \varepsilon o A / d \quad (5)$$

Here A is the area, and d is the thickness of the test specimen.

where εo is the electrical permittivity of free space {εo = 8.854 x 10-12 F.m-1}.

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

$$\sigma AC = 2\pi f \varepsilon 0 \varepsilon'' \quad (6)$$

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, relaxation time were determined.

3.1 Dependence of electrical properties on the applied field frequency

Impedance measurements have been performed on the PS/oil shale composites in the frequency range from 100 kHz up to 1.5 MHz.

Figure-2 shows the dependence of phase angle (φ) on frequency of the applied field for specimens of different oil shale concentration and neat PS. The phase angle is always negative, and is close to - 87.5°C. The negative values of phase angle for samples of different concentration indicate that this behavior can be represented by capacitive and resistive networks and that the composites are still capacitive [11]. The change of phase angle towards higher negative values, with increasing frequency, shows that the materials become more capacitive than resistive. The shift of phase angle towards low negative values with decreasing the oil shale concentration in PS/oil shale composites indicates that the samples become more resistive than capacitive. This behavior may result from the existence of leakage current

at the grain boundaries, which is more effective than the leakage current in the bulk of oil shale grains, and to more oxides impurities in the oil shale deposit.

The AC-conductivity (σAC) was calculated from the equation (6), and plotted versus frequency for the specimens as shown in Figure-3 the figure shows clearly that the σAC value increases with increasing the applied frequency and oil shale concentration. This result supports the well-known fact that the bulk AC conductivity is induced at high frequency range. This enhanced conductivity may be due to the increase of the electronic and ionic mobility of the existing impurities [12,13].

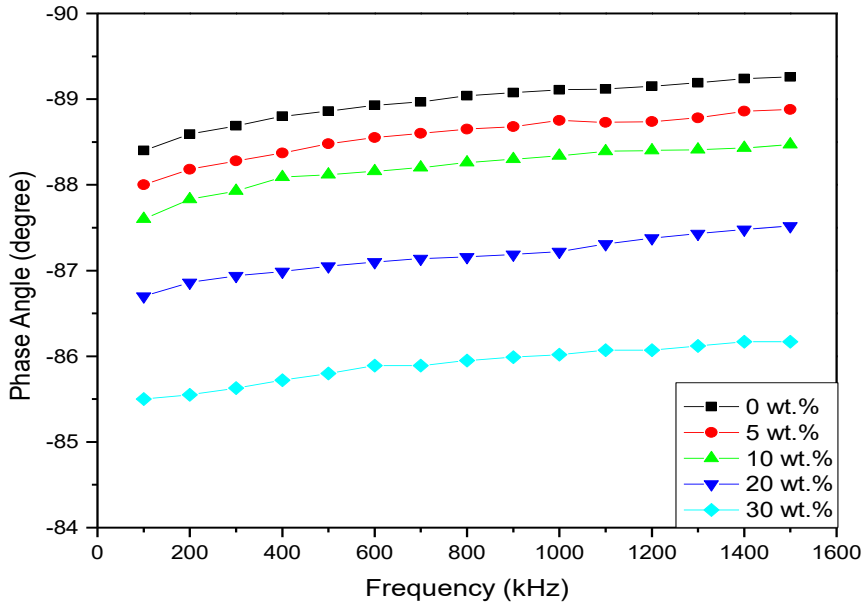

Figure-2. Variation of phase angle with frequency.

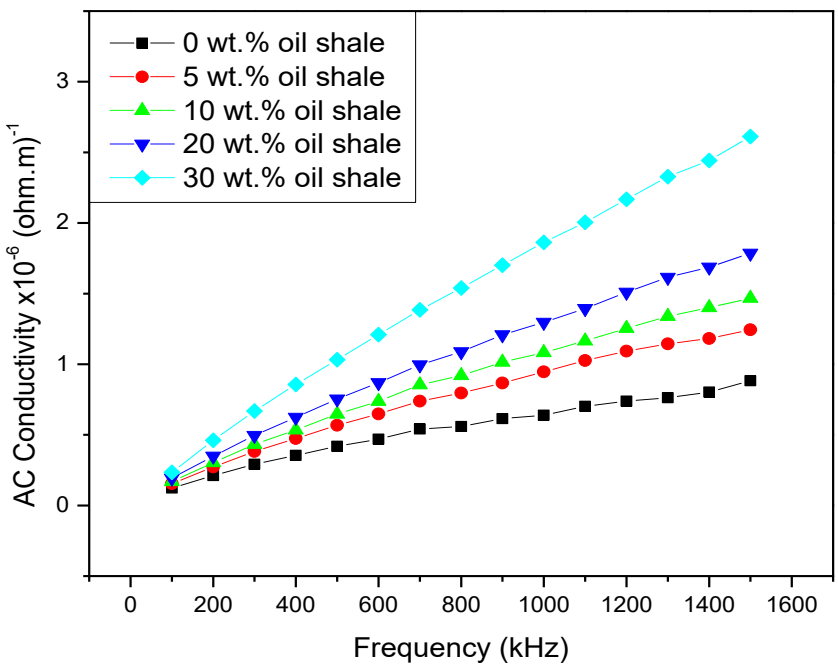

Figure-3. The AC conductivity of composites as a function of frequency.

3.2 AC conductivity model for different concentrations in PS/Oil shale composite

It is generally thought that the AC conductivity corresponding to the universal relation is given by the power law [14]:

$$\sigma AC\ (f) = \sigma DC + A\ f\ n \quad (7)$$

where A and n are coefficients, f is the frequency of the applied field (Hz), σDC is the dc conductivity of the material and σAC is the AC conductivity of the material in (Ω.m)-1. At higher frequencies the conductivity increases

as a power of frequency with exponent 0< n < 1. In this case A and n are oil shale concentration dependents. At low frequencies, the conductivity is almost constant, and is equivalent to the DC conductivity of the materials. When the exponent n is found to be very close to unity, the AC conductivity is said to have the universal behavior.

We will analyze the observed AC conductivity behavior of the five samples presented in Figure-4 by plotting the common logarithms Log (AC conductivity) versus Log (frequency) for each sample as shown in Figure-4. From equation (7), and then the equation writes as [15]:

$$\sigma AC \approx A\, f\, n \qquad (8)$$

From the figure, A and n values were found and tabulated in Table-1. These coefficients show changes due to the change of oil shale concentration, and (n ≈ 1, the universal behavior) is satisfied.

Table-1. Estimated A and n coefficients at T=30°C for all samples.

Composites	A x10^{-11} (Ω.m)-1 (Hz)-m	n
neat PS	10.3	0.604
5 wt.% oil shale	2.34	0.768
10 wt.% oil shale	1.94	0.792
20 wt.% oil shale	1.65	0.816
30 wt.% oil shale	1.04	0.875

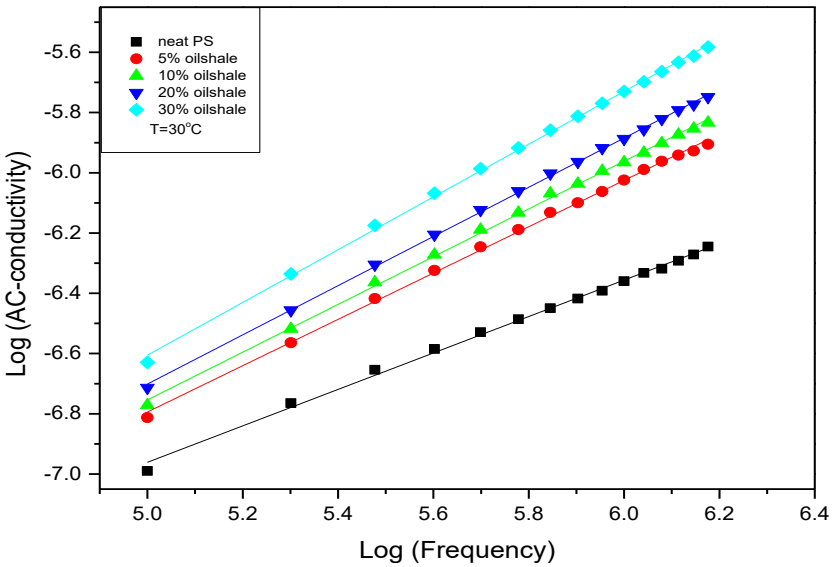

Figure-4. Log s AC versus Log (f) for oil shal/PS composites at T=30°C.

3.3 Dependence of electrical properties on oil shale concentration

Figure-5 shows the dependence of the AC impedance (per unit length) on the oil shale concentration at different frequencies (200 kHz, 400 kHz, 600 kHz, 800 kHz, and 1000 kHz) at room temperature for the prepared composite. When the filler content increases, Z decreases slowly. This decrease in impedance is due to both the increase of oil shale concentration and the decrease of impediment of polymer matrix.

The behavior of dielectric constant (ε') and dielectric loss (ε"), calculated from Equations (3) and (4), respectively, versus oil shale concentration at different frequencies (200 kHz; 400 kHz; 600 kHz, 800 kHz, and1000 kHz) at room temperature is shown in Figure-6 and Figure-7. The dielectric constant (ε') is increasing with increasing oil shale concentration. This was attributed to some ionic and conducting elements and oxides existing in the filler. The increase in ε "indicates more energy dissipation from higher filler concentration composite [16].

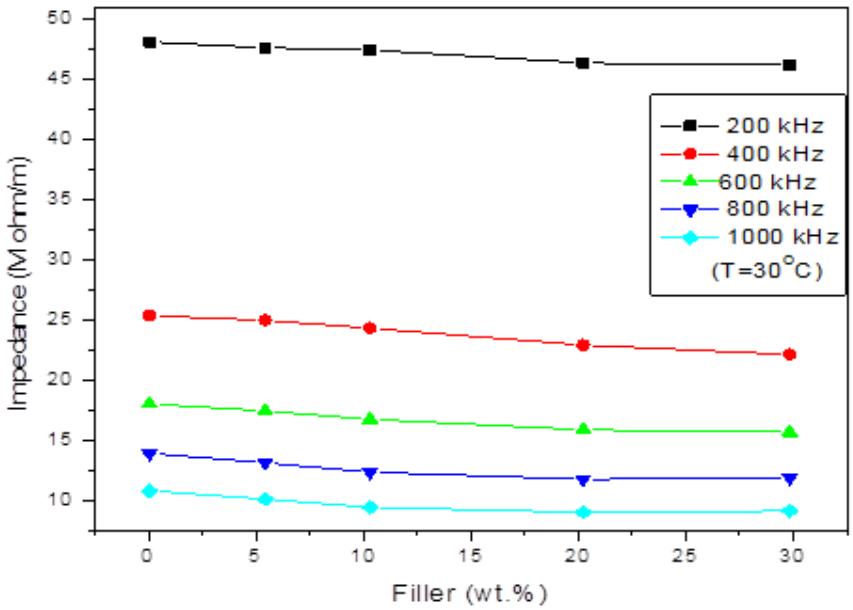

Figure-5. Variation of impedance with oil shale concentrations.

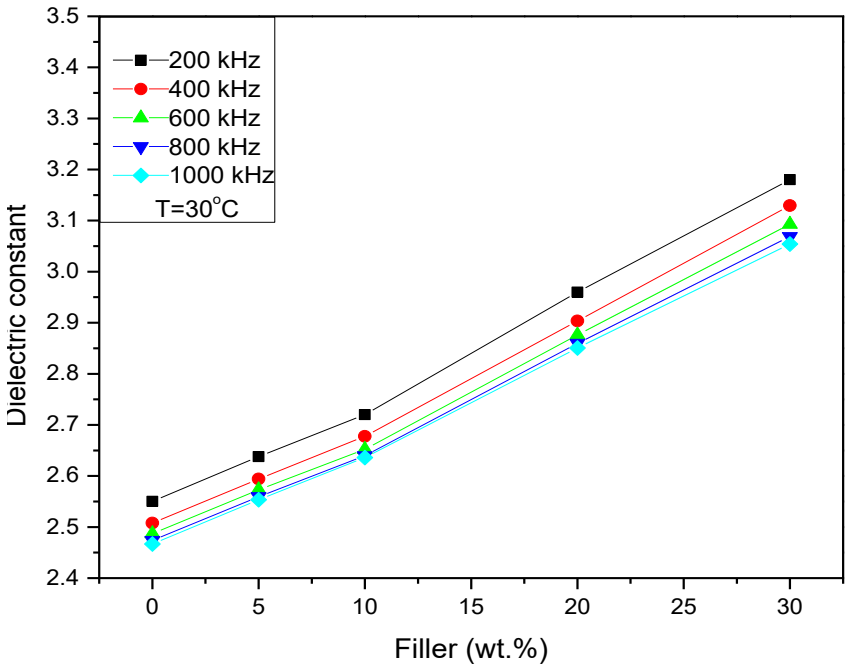

Figure-6. Variation of dielectric constant with oil shale concentrations.

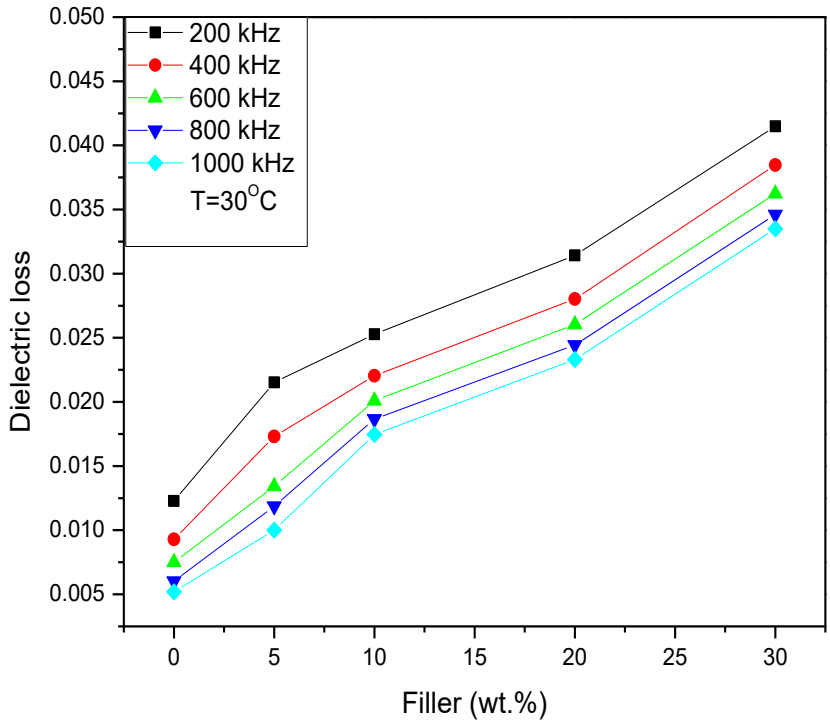

Figure-7. Variation of dielectric loss with oil shale concentrations.

Figure-8 shows the variation of AC conductivity (σAC) with the concentration of oil shale. A slight increase in AC conductivity was observed as a function of filler content at different frequencies (200 kHz, 400 kHz, 600 kHz, 800 kHz, and 1000 kHz) as expected from the decrease of impedance with the filler content shown in Figure-5. The rate of increasing of σAC with the oil shale content is more rapid at higher oil shale content, especially above 10 wt.%. This is attributed to higher content of impurities and deposite oxides.

Figure-9 compares the oil shale composition dependence of the dielectric constant of PS/oil shale composites with some theoretical predictions about the dielectric constant of the composite materials. Van Beek reviewed the formulae that have been proposed to predict the dielectric constant of conductor-insulator systems. Some of them are Bruggman's formula:

$$\varepsilon_{oilshale\text{-}PS} = [\varepsilon_{PS}/(1 - \upsilon_{oilshale})\ 3] \quad (9)$$

and Botcher's formula: [17]

$$\varepsilon_{oilshale\text{-}PS} = \varepsilon_{PS}/(1 - 3\upsilon_{oilshale}) \quad (10)$$

where ε oilshale-PS and ε PS represent the dielectric constants of the composite and the matrix, respectively, and υoilshale denotes the volume fraction of the dispersed phase. These formulae were derived by taking the dielectric constant of the conducting phase to be infinite. In this work, the experimental value of the dielectric constant of PS matrix, εPS, was 2.6.
Figure-9 also compares the experimental values with an empirical power equation:

$$\varepsilon_{oilshale\text{-}PS} = \varepsilon_{PS}(1 + \upsilon_{oilshale})5 \quad (11)$$

Compared with various theoretical models, Bruggman's formula gives a better fit.

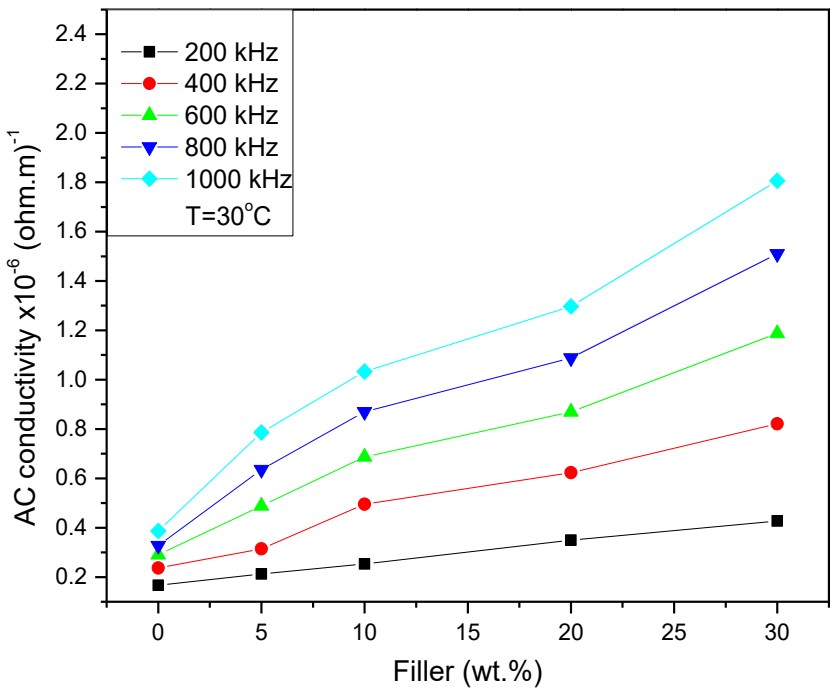

Figure-8. Variation of AC conductivity with oil shale concentrations at T=30 °C.

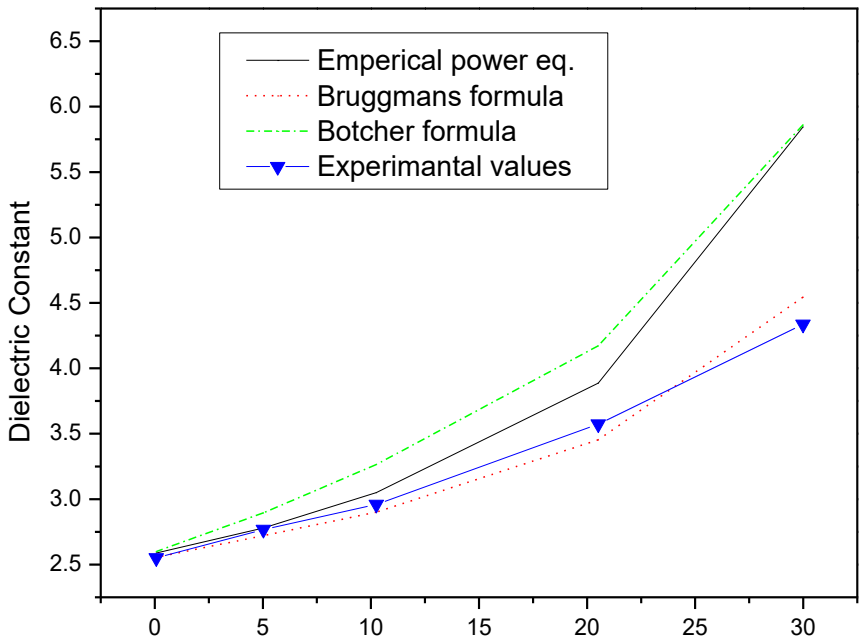

Figure-9. Comparison of the composition dependence of the dielectric constant of the composites with some theoretical predictions.

3.4 Cole-Cole plots and relaxation time

An important technique for the analysis the dielectric data of dielectric materials, is the Cole and Cole plots of ε' and ε'' of the dielectric systems in the complex plane [18]. A given point on this plot corresponds to a measurement of (ε') and (ε'') at a particular frequency. Plotting of (ε') and (ε'') for a normal dielectric material yields a semicircle according to the Debye frequency model. However, the geometry of the circle depends greatly on the polarity and structural uniformity of the dielectric materials [19,20]. We use it here to characterize the dielectric behavior of the PS/oil shale composites and find the relaxation time of these samples.

Figure-10 shows a plot for dielectric loss (ε'') against dielectric constant (ε') at room temperature (30oC). After extrapolating the arced lines to approximated semi-circles, the relaxation time (τ) was determined from the plot of (ε'') and (ε') using the relation (ωmaxτ=1), for

different filler concentrations, where ωmax is the angular velocity (or frequency) at maximum value of (ε") observed from Figure-10. The plots are shifted towards higher values of (ε'). Therefore, composites become more conductive since they show lower relaxation time of the electrical transport. The values of relaxation time (τ) for all samples are more than 1.59 × 10-6 (sec).

Figure-11 shows Cole-Cole plots for dielectric loss (ε") versus the dielectric constant (ε') for the composite sample of (30 wt. %) PS/oil shale at room temperature (30°C). The construction plane plots are distorted arcs exhibiting different electrical conduction processes with relaxation time spectrum.

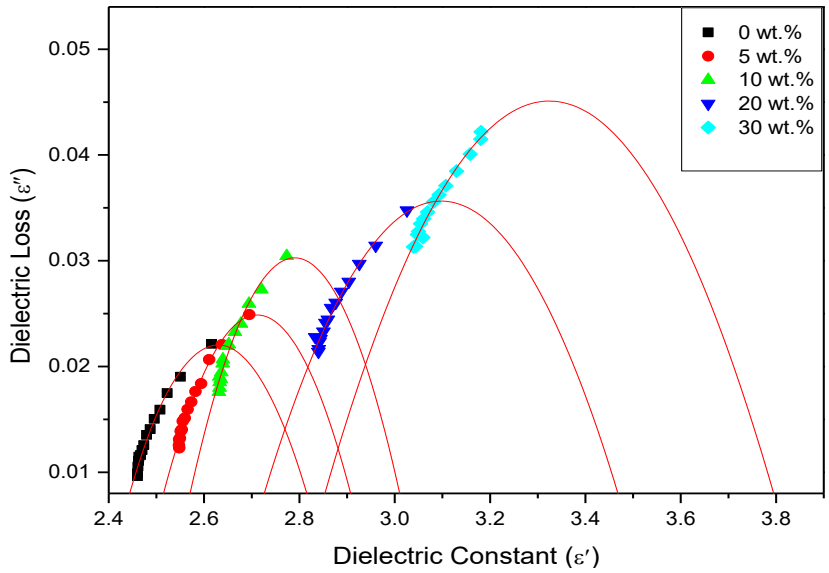

Figure-10. Cole-Cole plots for oil shale/ PS composites.

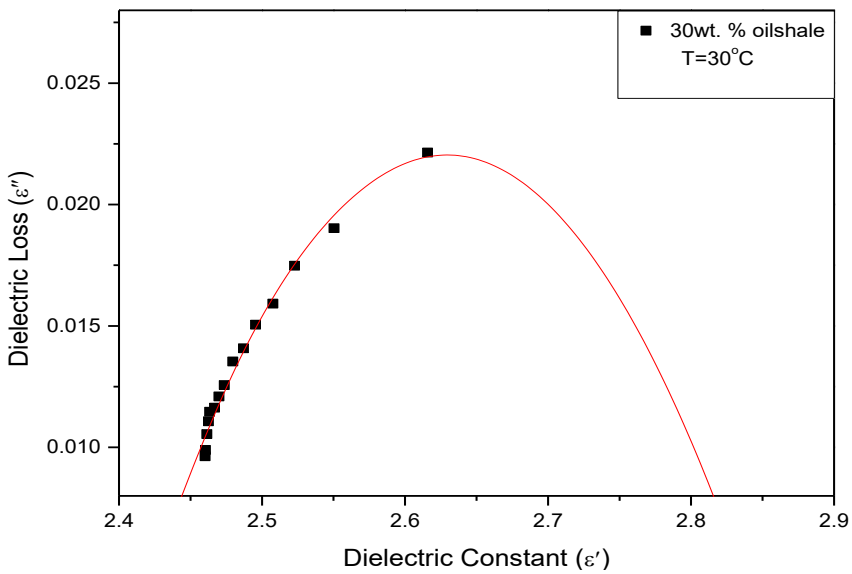

Figure-11. Cole-Cole plots for 30 wt.% PS/oil shale/PS composite at T=30°C.

4. CONCLUSIONS

The present study deals with the AC-electrical properties of polystyrene/oil shale composites with different filler concentration and applied frequency. The following conclusions can be drawn from the results obtained:

- The phase angle takes negative values for all prepared samples which indicate that the specimens can be represented by (RC) network.
- Impedance was found to decrease with increasing frequency and oil shale concentration.

- The dielectric constant (ε') and the dielectric loss (ε") of the composite samples increase with the oil shale concentration and decrease with applied frequency.
- The AC conductivity (σac) increases with frequency and oil shale concentration.
- The values of relaxation time (τ) for all samples are calculated. Composites become more conductive since they show lower relaxation time of the electrical transport.
- The Bruggman's formula gives a bitter fit of the observed dielectric data of the studied composites.
- The overall AC conduction taking place in the composites is attributed to some processes as transport of the charge carriers and polarization.
- The universal power law of the AC conductivity dependence on frequency is satisfied.

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