IMPEDANCE BEHAVIOUR AND THE TEMPERATURE DEPENDENCE OF RESISTIVITY OF PAN-BASED CARBON FIBERS

M.M. Abdul-Gader, M.S. Ahmad, R.N. Ahmad-Bitar,
and A.M. Zihlif

Department of Physics, University of Jordan,
Amman, Jordan.

Abstract:

The electrical resistivity measured at temperatures from 300 K to 10 K and the impedance at 300 K and up to several MHz for as-spun high strength PAN-Based Carbon fibers were found to show some interesting behaviour. A maximum at 35 K was observed in the resistivity which decreases with temperature on either side, in good agreement with the results reported for heat-treated carbon fibers. The ac impedance measurements allowed finding of the real part of the dielectric constant which was found to vary with frequency, f, nearly as $f^{-0.7}$ *at* $f \leqslant 500$ *KHz and to be almost constant at higher frequencies (*$f < 10$ *MHz). The imaginary part of the dielectric constant was found to change as 1/f up to 9 MHz suggesting that the ac conductivity is frequency-independent consistent with theoretical predictions.*

Introduction

Numerous models based on the X-ray diffraction and transmission electron microscopy were proposed for the micro structure of carbon fibers [1-4]. A carbon fiber consists of graphite structural units or crystallites with preferred orientation to the fiber axis. Other crystallites are slightly misaligned relative to the fiber axis with a misorientation angle of 20°-23°, and hence a porous structure is established. The proposed micro structure for carbon fibers were used successfully to explain the mechanical properties and the electrical resistivity behaviour under heat treatment. A correlation between elastic moduli and resistivity was established from the variations in the crystallite size and orientation under heat treatment [5-8]. Recently, few studies have been reported on the electrical properties of PAN-based carbon fibers as a function of various conditions [5, 9, 10]. Guigon et al. [6] concluded that the observed electrical resistivity for a family of PAN-based carbon fibers correlates well with the diameter of the microstructural units extended parallel to the fiber axis. Spain et al. [10] observed that the low temperature resistivity showed a maximum for PAN-based Celion fibers heat-treated to ~1300°C. Bright and Singer [9] have studied the electronic properties of mesophase Pitch-based carbon fibers heat-treated at various temperatures and Rappeneau et al. [11] investigated heat-treated Rigilor Ac and AG carbon fibers. Those authors found that the electrical resistivity of their fibers decreases, in general, with increasing temperature, but no maximum in the resistivity was observed.

It is therefore interesting to investigate the temperature behaviour of resistivity for as-spun (not heat-treated) PAN-based carbon fibers not only to compare with that reported for heat-treated carbon fibers but also to see if it is a common property for all carbon fibers. This is the purpose of the present communication. Also, good insight into the conduction mechanisms of carbon fibers may be achieved by studying their dielectric properties. These can be obtained from ac impedance measurements. In this study the ac impedance was only measured at room temperature and as a function of frequency up to f = 12 MHz.

Experimental:

Material

High strength as-spun PAN-based Celion 6000 carbon fibers obtained from Celanese corporation in U.S.A. were used in this study. Fibers are 7 μm in diameter and posses high strain-to-failure. The tensile strength and modulus for these fibers are 2.73 and 230 GPa, respectively, and the predicted misorientation angle of the crystallite is 22° [4-6].

Resistivity measurements

Measurements of longitudinal resistance were made on a single carbon filament using the ac-four probe method. This method has the advantage of minimizing the noise and pick-up signals and of high precision. A single fiber of about 20 mm long was mounted on a quartz plate using copper clamps. The electrical contacts to the sample were made by using silver dag and the electrical leads were then soldered to the copper clamps. Measurements were carried out with a current of about 1 μA passing through the filament. Such a low current value is important to prevent self-heating effects [10]. The voltage drop across the filament was measured directly using a frequency lock analyzer. The temperature of the quartz plate, which was attached to the head of a closed-cycle cryogenic refrigerator, was varied continuously from 300 K to 10 K with uncertainty of ± 0.5 K.

Impedance measurements:

Carbon fiber strands were crushed to powder and pressed into disc-shaped samples of 2 cm in diameter and about 1.2 mm in thickness. Electrical contacts were made by using silver dag and two leads connected to the sample, which was palced inside a shielded metallic box. Since the apparent resistance of the sample was found to be about 4 ohms and the apparent capacitance was of the order of 1 nf, very high frequencies in the MHz range were used to obtain appreciable and meaningful measurements. A hp-3575A Gain-phase meter was used to measure the sample impedance and phase angle at room temperature in the frequency region 50 KHz to 12 MHz.

Results and Discussions

Resistivity results *

When the organic polyacrylonitrite (PAN) is converted to carbon fibers, a fibril structure is produced with interesting orientational and electrical properties. Graphite crystallites are oriented nearly with their basal planes parallel to the fiber axis. The reported average value of the electrical resistivity of PAN-based carbon fibers is $10^{-5}\Omega$.m parallel to the fiber axis and it is high compared to that of the graphite single crystals parallel to the based plane [7]. The mean values of the dimensions of the crystallite size in high modulus and strength fibers are L_c = 50 A° (prependicular to the fiber axis) and L_a = 450 A° (parallel to the fiber axis). Furthermore, it was found [6-9] that the electrical resistance is related to some fiber properties such as orientation of the structural units, interlayer spacing, degree of lattice ordering, and the charge carriers.

Fig. 1 shows the temperature variation of the resistance, R, of the as-spun PAN-based carbon fibers investigated in this work. It can be seen from Fig. 1 that the observed resistance-temperature data can be reasonably represented by a mathematical fitting-curve of the form

$$\frac{1}{R} = \frac{1}{a_1 + a_2 T + a_3 T^2} + \frac{1}{a_4 \exp(a_5 T)}$$

where a_1, a_2, etc. are constants.

Nevertheless, there is no theoretical or physical grounds on which such a fitting curve is based. A plot of the resistivity of the fiber versus the temperature may be more informative and this is depicted in Fig. 2. The resistivity increases with decreasing temperature, displays a slight hump (maximum) at about 35 K, and then decreases upon further lowering the temperature. Similar behaviour of the resistivity of PAN-based carbon fibers of about 10 µm in diameter and heat-treated to 1300°C was observed by Spain et al. [10]. These authors have found also that similar resistivity maximum and behaviour occurs in other PAN-based fibers (Magnamite), whereas the maximum is exhibited at lower temperatures (25 K) in others such as Thornel 300.

---

* Resistivity data was collected two years ago and a maximum was observed on the resistance-temperature curve. Similar maximum has been observed earlier by Spain et al. [10] on a PAN-based Celion fibers heat-treated to 1300°C. Professor Spain sent us kindly his solid state communication after a first draft of this article was written.

The increase of the resistivity as the temperature is decreased, but with no maximum at low temperatures, was found also by Robson et al. [8] for PAN-based carbon fibers, Bright [9] for mesophase pitch-based carbon fibers, Herinckx [12] for rayon-based carbon fibers and Rappeneau et al. [11] for Rigilor AC and AG carbon fibers. All these carbon fibers were heat-treated to very high temperatures ($<$ 3000°C). These authors have discussed the resistivity variation with temperature in terms of semiconductive behaviour. Such a model, however, would lead to a further increase in the resistivity as the temperature is continuously decreased. Therefore, this model might not be applied successfully to our findings though the as-spun PAN-based carbon fibers investigated in this work contain considerable amount of metallic impurities [5, 13] which may effect the resistivity behaviour of these Celion fibers at low temperatures. A correlation between the crystallite size and the resistivity ratio ρ_{77}/ρ_{300} (or the relative graphitic order parameter) may be found from the results of Robson et al. [8] on PAN-based carbon fibers. Fig. 2 yields a resistivity ratio of 1.07 which corresponds to a crystallite size of about 40°A for our Celion PAN-based fibers. The graphitic order parameter, and hence the imperfections, defect levels, crystalline boundaries and the like, govern the behaviour of resistivity and its variation with temperature. The observed decrease in resistivity with increasing temperature seems difficult to interpret in terms of electron-phonon interactions.

When the effect of localized energy states in the energy band associated with impurities and/or other defects are assumed to exist in carbon fibers [9, 14], some sort of activation energy would be deduced from the variation of resistivity, ρ, with temperature [4]. This activation energy may be due to charge carrier activation and/or mobility activation. Impurity scattering processes, which are usually dominant at temperatures lower than those at which electron-phonon interactions are important, would lead to an increase in mobility μ, and hence a decrease in resistivity, with increasing temperature (i.e., $\mu \propto T^{3/2}$). Our resistivity results do not follow this latter mobility behaviour, but showed an activated conduction process on the $\ln \rho$ versus $1/T$ plot over a narrow range on the high temperature side.

It is noteworthy that more measurements (including Hall effect data, thermopower, magnetoresistance) might reveal the actual conduction mechanisms occuring in carbon fibers as these measurements usually give complementary informative results to those of resistivity.

A fairly successful and physically acceptable interpretation of the observed resistivity behaviour over the whole temperature range studied may be achieved if one consider that localization effects are responsible for this behaviour as was argued by Spain et al. [10]. These authors have qualitatively discussed such a behaviour in terms of localization of electrons at high temperatures due to thermal disorder and delocalization as well as lowering effective mass of electron at low temperatures. They also pointed out that electron-spin interactions would account

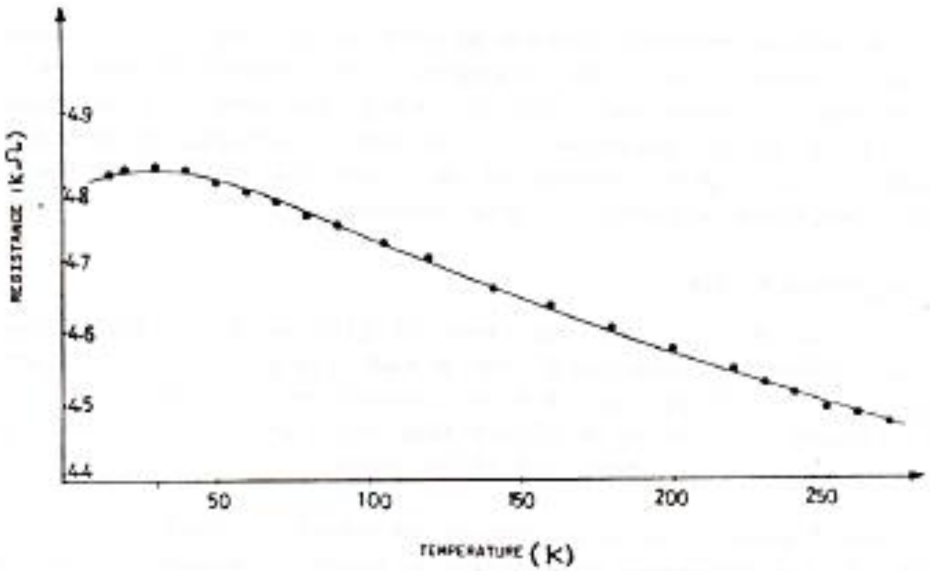

Fig.1: Temperature variation of resistance of as-spun PAN-based carbon fiber.

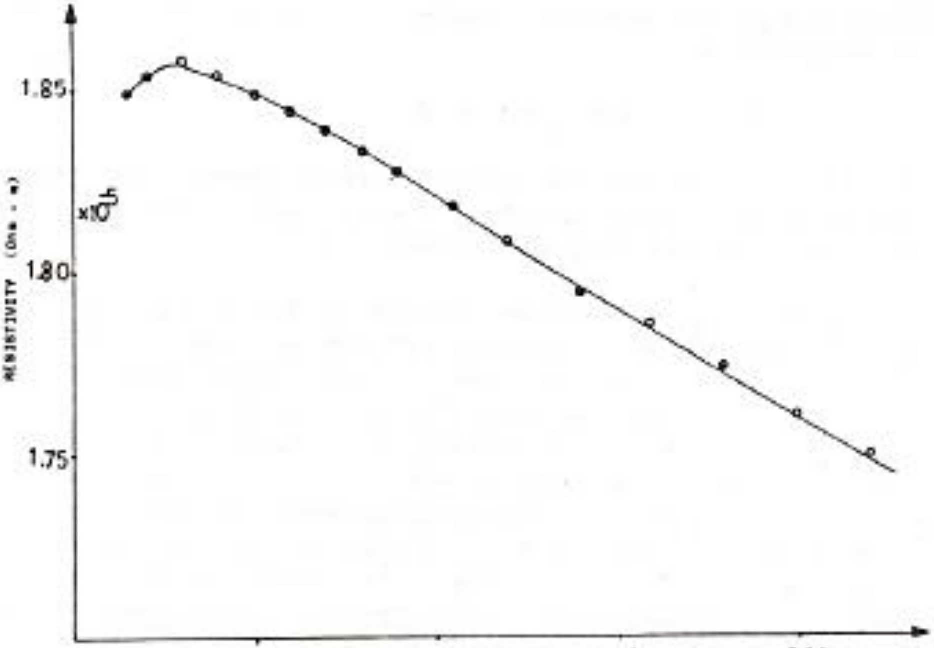

Fig.2: Resistivity of as-spun PAN based carbon fiber as a functio of temperature.

for the observed resistivity maximum as spins may be located at the edges of the ribbons in fibers. A quantitative description of the variation of resistivity, , with temperature, T, within the localization model [15] yields that the conductivity, $\sigma (=1/\rho)$, is linearly proportional to T at high temperatures. We believe that our experimental data of the resistivity of the as-spun PAN-based carbon fibers exhibits such a temperature-dependence of temperatures above 35 K.

AC Impedance Results:

An interest in our laboratory arose to study the ac impedance behaviour for as-spun PAN-based carbon fibers. Such a study may be useful for a better understanding of the electrical and dielectric properties of such carbon fibers. Impedance measurements were only made at room temperature and for pellet samples prepared from these fibers over a wide range of frequencies.

Fig. 3 shows a typical variation of the complex impedance, Z, and the phase angle, $\emptyset$, of a disc-shaped pellet sample as function of frequency, f. The measured impedance will be referred to as the apparent impedance since the sample is a porous one. It is clear from Fig. 3 that the apparent impedance remains constant ($\doteq 4\,\Omega$) up to $f \leq 5$ MHz, beyond which Z starts to increase monotonically with frequency. On the other hand, the phase angle begins to decrease with increasing frequency at $f \gtrsim 1$ MHz. Impedance components Z_R (real part) and Z_I (imaginary part) were calculated from

$$Z_R = Z \cos \emptyset; \; Z_I = Z \sin \emptyset$$

A plot of Z_I versus Z_R gives the so-called complex impedance plot shown in Fig. 4. This behaviour of conducting carbon fibers is dissimilar to the complex impedance plots observed in dielectric and other materials [16].

Detailed analysis of the complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$ showed [17] that the apparent real part, ', decreases with frequency nearly as $1/f^{0.7}$ up to $f \sim 5 \times 10^5$ Hz and then becomes almost constant at higher frequencies as clearly seen in Fig. 5 (a). On the other hand, the apparent imaginary part of the dielectric constant, ϵ'', was found to vary inversely with frequency in the frequency range 50 KHz to 8 MHz, beyond which a slight deviation from this relationship was observed as shown in Fig. 5 (b). Theoretical treatments [18] predicts that $\epsilon'' = \sigma/2\pi\epsilon_0 f$, where ϵ_0 is the permittivity of free space and σ is the ac conductivity of the material. The observed behaviour of ϵ'' with frequency suggests that the room-temperature ac conductivity of as-spun PAN-based carbon fibers is frequency-independent in the above mentioned frequency range. Such a conductivity behaviour is expected when electrical conduction occurs in extended (Bloch) energy states [19]. Nevertheless, we wish to point out that further intensive work is needed to measure the impedance of single Celion fibers parallel and perpendicular to the fiber axis and as a function of temperature. This type of study is in progress.

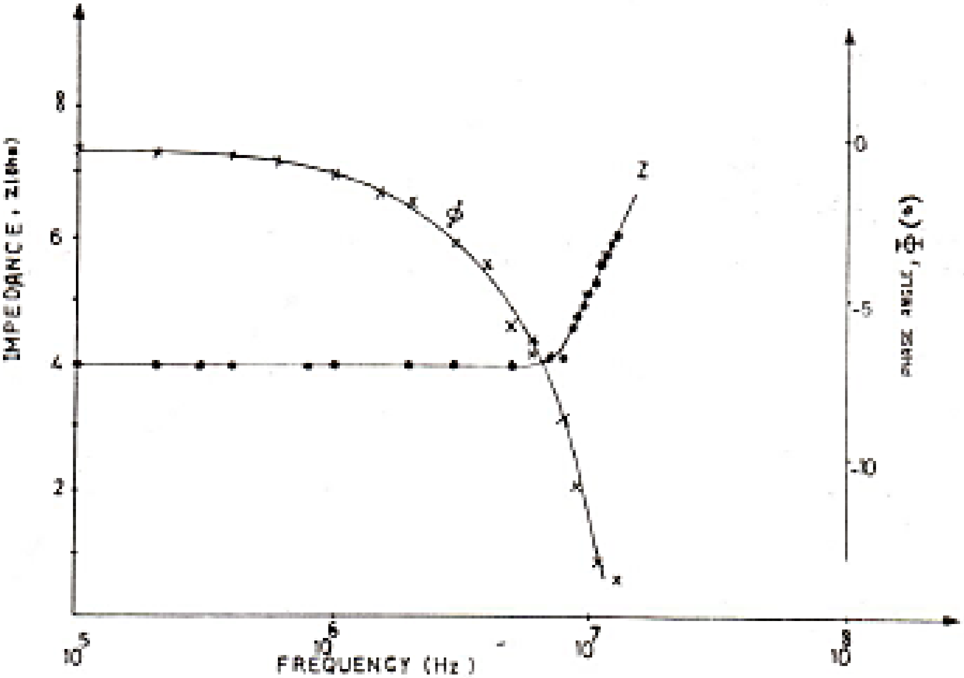

Fig.3: Frequency dependence of Complex impedance, Z, and phase angle, Φ, of as-spun based carbon fiber.

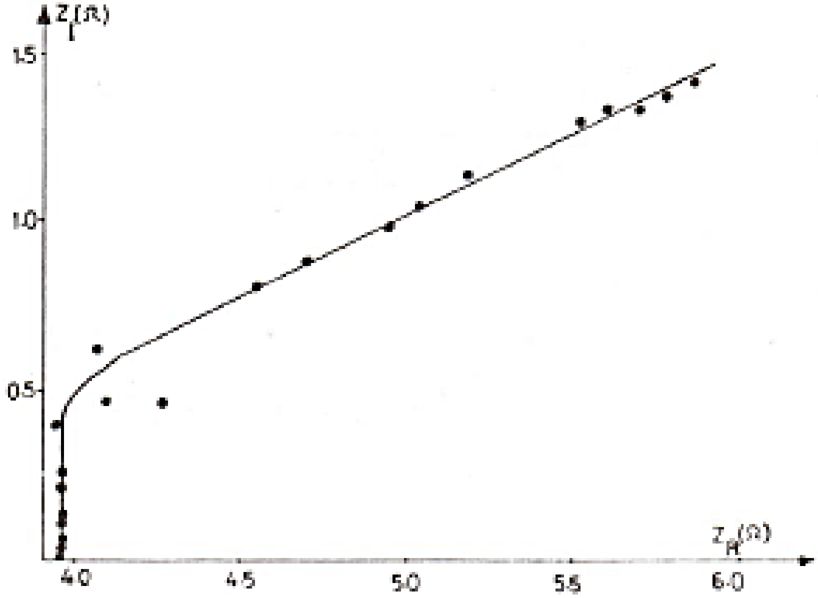

Fig.4: Complex impedance plot of Z_I versus Z_R for the as-spun PAN based carbon fiber.

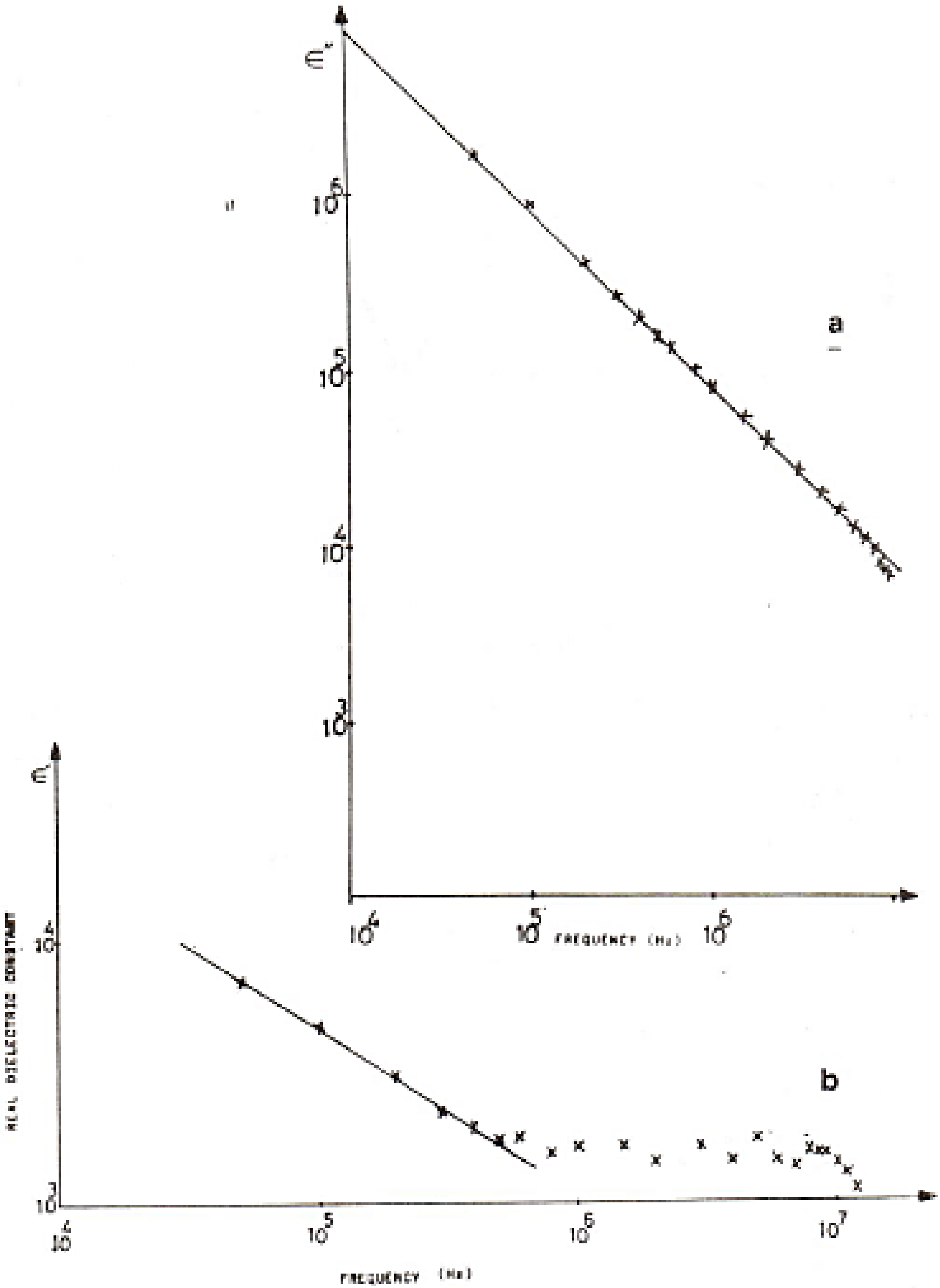

Fig.5: Frequency variation of the real part of thedielectric constant, ε', (5a) and imaginary part, ε'', (5b) of the as-spun PAN based carbon fiber.

Conclusion:

The electrical resistivity and the room temperature apparent impedance of high strength as-spun PAN-based carbon fibers were measured as a function of temperature and frequency, respectively. Several interesting results were observed.

The resistivity changes with temperature as 1/T for 35 K $\leq$ T $\leq$ 300 K. This behaviour isattributed to localization effects which are dominant at high temperatures. A maximum in the resistivity was observed at T$\sim$35 K, below which the resistivity seems to fall with further lowering temperature. This interesting feature was interpreted in terms of increasing delocalization of electrons and lowering their effective mass at low temperatures. It seems that such, resistivity behaviour with temperature occurs in PAN-based carbon fibers whether they are heat-treated or not.

Impedance behaviour of these carbon fibers is very dissimilar to that observed in dielectric and the like materials. The real part of the dielectric constant was found to vary as $f^{-0.7}$ below $f \sim 0.5$ MHz and being constant at higher frequencies. The observed behaviour of ϵ'', the imaginary part of dielectric constant, suggests that the conductivity of the carbon fiber is constant over the whole frequency range studied.

Acknowledgement:

The ahtours wish to thank professor R. Farris, Dr. J. Mayer, and Dr. N. Saleh for their cooperation. Celanese Research Company is gratefully acknowledged for providing us with high strength as-spun PAN-based carbon fibers investigated in this work.

References:

1. **R. Bacon,** "Chemistry and Physics of Carbon", Ed. P.L. Walker, Marcel Dekker, New York, Vol. 9, p 20 (1973).
2. **M. Guiqon, A. Oberlin and G. Desarmot,** Fibre Sci. and Tech., 20, 55 (1984).
3. **D.T. Johnson,** Chemistry and Industry, 18, 692 (1982).
4. **M.T. Yasin, M.Sc. thesis,** Physics Department, University of Jordan (1986); Materials Chem. Phys. (1986-In the Press).
5. **I. El-Rihail, M.J. Yasin, M.S. Ahmad and A.M. Zihlif,** Jordan Inter, Electrical and Electronic Eng. Cof., paper, (April-1985).
6. **M. Guigon, A. Oberlin and G. Desarmot,** Fibre Sci and Tech., 20, 177 (1984).
7. **G. Lubin,** "Handbook of Composites", Van Nostrand Reinhold Cop., London, Page 211 (1982).
8. **D. Robson, F.Y.I. Assabghy, E.G. Cooper and D.J.E. Ingram,** J. Phys. D: Appl. Phys., 6, 1822 (1973).

9. **A.A. Bright and L.S. Singer,** Carbon, 17, 59 (1979); 17, 259 (1979).

10. **J.L. Spain, K.J. Volin, H.A. Goldberg and J.L. Kalnin,** Solid State Comm. 45, 817 (1983); T. Phys. Chem. Solids, 44, 839 (1983).

11. **J. Rappeneau, G. Micand, A. Drout, A. Pacault, A. Marchand, and E. Dupart,** Carbon, 10, 455 (1972).

12. **C. Herinckx,** Carbon, 11, 199 (1973).

13. **W.N. Reynold and R. Moreton,** Phil. Trans. R. Soc. London, A 294, 451 (1980).

14. **C.E. Mostovoi, N.N. Dgunov, Yu. N. Rabotnov, and Yu. P. Anufriev,** Mekh. Polim., No. 4, 626 (1977).

15. **G.A. Thomas, Physica, 177BP 118B (1983); R. Mansfield, M. Abdul-Gader and P. Fozooni,** Solid-State Electronics, 28, 109 (1985); G.A. Thomas, A. Kawabata, Y. Ootuka, S. Katsumoto, S. Kobayashi, and W. Sasaki, Phy. Rev. B, 26, 2113 (1982).

16. **R.N. Ahmed-Bitar, M. Abdul-Gader, A.M. Zihlif, and A. Jaber,** J. Electronal. Chem. and Interfac. Electrochem., 143, 121 (1983); M.A. Abu-Samra, M.S. Ahmad and A.M. Zihlif, Egypt. J. Solids. 1, 165 (1985).

17. **J.L. Regolini and J.J. Saura,** Appli Phys., 54, 1528 (1983); M.M. Abdul-Gader, K.A. Wishah, Y.M. Mahmud, M. Al-Haj Abdallah, and R.N. Ahmed-Bitar (to be published).

18. **H.K. Welsh,** J. Phys., C18, 5641 (1985); L. Solymar and D. Walsh, Lectures on the electrical properties of Materials. 2nd ed. (Oxford Univ. Press, Oxford, 1979) Chapter 10.

19. **P. Nagles in Amorphous Semiconductors,** editor M.H. Brodsky (Springer-Verlag, Berlin 1979) p. 113.