JOURNAL OF MATERIALS SCIENCE 24 (1989) 1309–1315

Mechanical and electrical behaviour of "Magnex DC" conductive polymer composite

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Mechanical and electrical behaviour of the "Magnex DC" conductive polymer composite is reported. X-ray diffraction patterns and scanning electron microscopy (SEM) show that the composite has a semicrystalline, isotropic, and defected structure. It was found that both the elastic modulus and yield stress increase with decreasing temperature; the yield stress increases nonlinearly with increasing strain rate due to the voids in the composite. In addition, the activation energy and the activation volume of a single rate-activated process observed at relatively high strain rates are determined. The dependence of the impedance behaviour on frequency is investigated. It was observed that the a.c. conductivity is almost independent of frequency below 10 kHz and increases with frequency above this range. The values obtained for the conductivity indicate that the composite has a relatively small electrical conduction which is rather less than that for the pure semiconductors.

1. Introduction

Recently, much progress has been made in the development of reinforced composite materials because they have an outstanding combination of mechanical and physical properties. These composites, which include carbon, steel, and glass fibres embedded in a resin matrix, are currently playing a leading role in many advanced technological and constructional applications [1–3]. A type of fibre composite material called "Magnex DC" has attracted our attention [4]. The interest in this conductive polymer composite lies in the utilization of its mechanical and electrical properties such as the elastic–plastic deformation behaviour and its electrical conduction. In previous studies [5, 6], we have shown that the microwave properties of this composite depend on its structure and the possible use of this material in electromagnetic shielding is also considered. It was found that the equivalent impedance of this composite decreases as the frequency increases in the X-band microwave frequency range (8 to 12 GHz) and the insertion loss of a 1.4 mm thick specimen is greater than 9 dB over the whole band. The present study is concentrated on the mechanical and a.c. impedance behaviour in the low frequency range for this composite material.

2. Experimental work

2.1. Material

The material used in this work, "Magnex DC", is produced by Diamond Shamrock Corp., Ohio, USA in the form of pellets. This composite is an acetylonitrile–butadiene–styrene (ABS) polymer matrix with stainless steel fibres as conductive fillers or reinforcement elements [4]. Examination of this composite material parallel and normal to the pellet axis, using the SEM, reveals that the texture contains many voids around short discontinuous steel fibres of about 10 μm diameter as shown in Fig. 1. The X-ray diffraction pattern given in Fig. 2 shows clearly that the "Magnex DC" composite is a semicrystalline material with isotropic structure. Furthermore, the observed glass transition temperature [5] is about 110° C. Sheets of 1.4 mm thickness are prepared from the pellets by a hot-pressing technique at 180° C. These sheets contain randomly distributed steel fibres which vary from one sheet to another.

2.2. Dynamic mechanical measurements

The dynamic mechanical behaviour was investigated by using a dynamic mechanical thermal analyser (PL-DMTA) manufactured by Polymer Laboratories Ltd. The DMTA technique detects the variations of the dynamic storage modulus (E') and the damping factor ($\tan \delta$) with temperature. Dynamic measurements were carried out on flat strips of 10.3 mm × 2.5 mm × 1.4 mm cut from the composite sheet. The dynamic modulus and damping loss factor were measured at three decades of frequencies over a temperature range from -80 to 175° C with an ascending rate of 5° C min^{-1}, where liquid nitrogen was used as a coolent at low temperature.

2.3. Compression tests

To study the deformation behaviour of this composite material, specimens for compression tests were machined from the pellets. The test specimens were in the form of cylinders of 5 mm diameter and 4 mm long. Compression tests were performed on an Instron testing machine provided with an oven chamber and compression jigs and over strain rates from 2.06×10^{-3} to 2.1 sec^{-1} and over a range of temperature from -80 to 120° C. The chamber was cooled by pumping liquid

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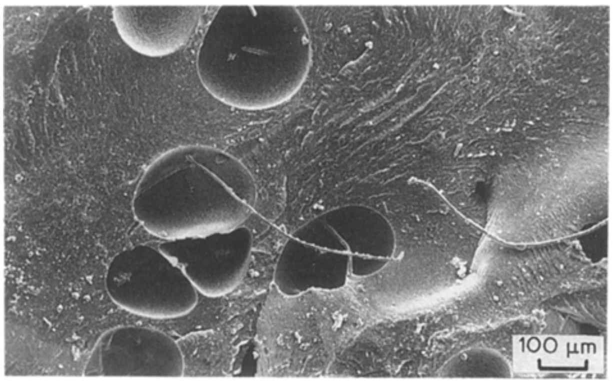

Figure 1 Scanning electron micrograph of "Magnex DC".

nitrogen, and the temperature readings were taken by placing a thermometer near the test specimen.

2.4. Impedance measurements

For impedance measurements, a disc-shaped sample of 10 mm diameter and 0.25 mm thick was machined from the composite sheet. Two copper electrodes, about 300 nm thick, were vaporized under vacuum on each surface. Then two fine copper wires were soldered to the electrodes by silver dag. The sample was shielded and connected to an a.c. electronic bridge described elsewhere [7, 8]. The gain-phase meter was used to measure the amplitude and the phase of the ratio of the input to the output signal for this sample. Measurements were performed as a function of frequency in the range 0.5 Hz to 100 kHz. The uncertainty in the measured values was approximately less than ±5%.

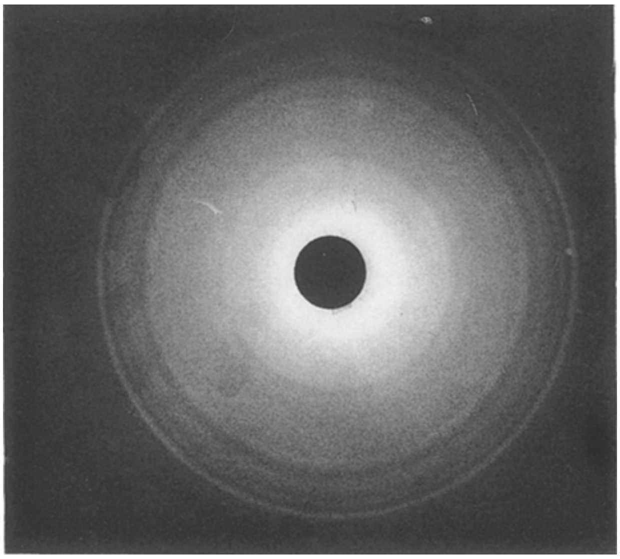

Figure 2 Wide-angle X-ray diffraction patterns.

3. Results and discussion

The results obtained using both the SEM and X-ray diffraction show that the "Magnex DC" composite has an isotropic and defected structure with small pores in the ABS polymer matrix with cylindrical voids around the fibre fillers. Fig. 3 shows the variation of the real component of the complex modulus, E', for the ABS polymeric composite. The general feature of the $\log E'$–T curve is similar to those reported for many polymers [9, 10]. The variation of the dynamic loss factor, tan δ, with temperature is also shown in Fig. 3. A strong relaxation transition takes place at about 105° C which is identified as the glass transition temperature (T_g). This value of T_g is the same value obtained recently from the measurement of the relative dielectric constant as a function of temperature [5]. Fig. 3 also shows a weak relaxation transition at about 150° C.

Fig. 4 shows the variation of the Young's elastic modulus measured, along the pellet axis or the steel fibres direction, as a function of temperature. It can be seen that the modulus decreases parabolically with temperature. Similar behaviour has been observed for the compressive yield stress as a function of temperature shown in Fig. 5. The calculated ratio of the yield stress of the composite was found to be around 0.075 which is greater than the reported value ($\simeq 0.02$) for the ABS polymers [11, 12]. The excess in the value of this ratio is accounted for by the existence of the steel fibres as filler elements.

Resilience [3, 13], which is often considered as the inverse measure of damping or the capacity of the material to absorb energy in mechanical deformation, was investigated. The modulus of resilience, which is

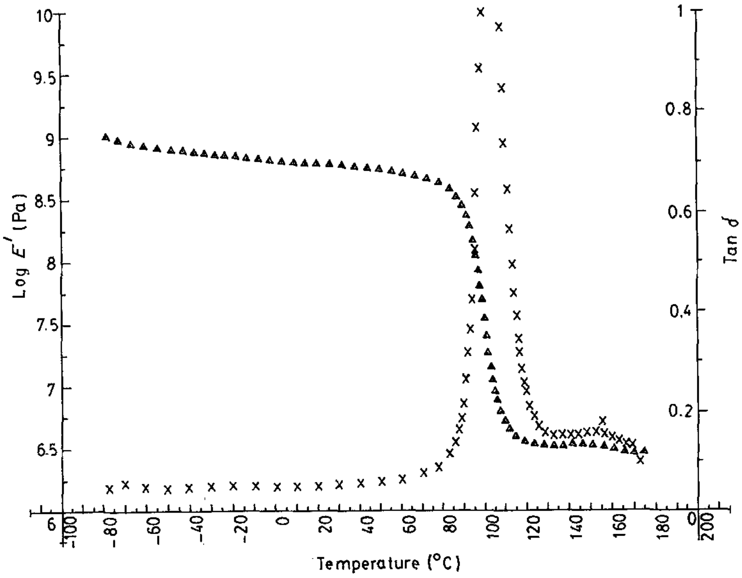

Figure 3 The logarithm of the dynamic Young's modulus and the dynamic loss factor of "Magnex DC" as a function of temperature.

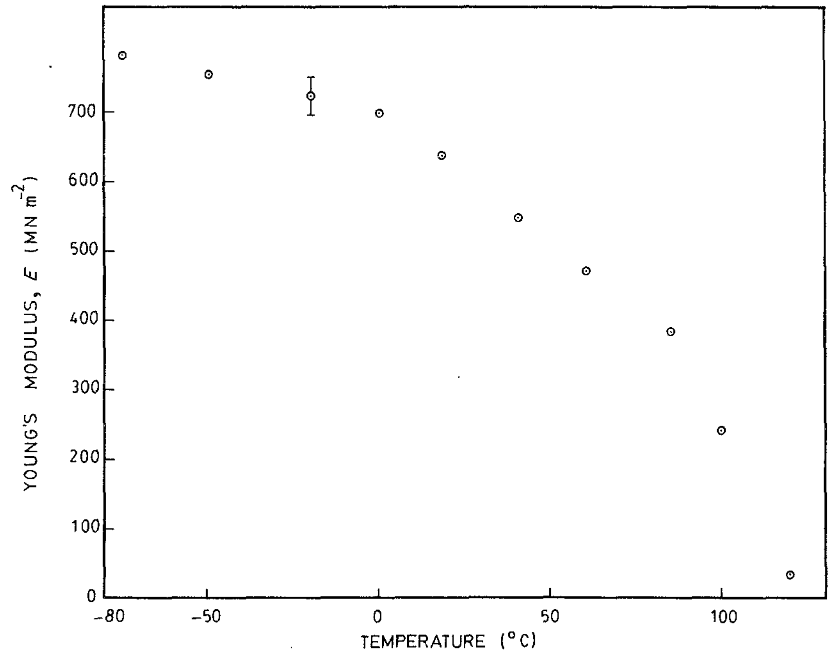

Figure 4 The static Young's modulus of "Magnex DC" as a function of temperature.

defined as the greatest amount of strain energy per unit volume that a material can absorb at the yield point, is calculated over a temperature range −75 to 120° C. The resilience, R, is calculated from Figs 4 and 5 using the following equation [3]

$$R = \sigma_y^2/2E \quad (1)$$

where σ_y is the yield stress and E is the Young's modulus. Fig. 6 represents a plot of resilience against temperature. Resilience value is greater than unity below 50 and it decreases rapidly to a very small value above 100 when the polymer is in the leathery state near T_g.

Stress–strain curves of "Magnex DC" were obtained at different strain rates. The compressive yield stress measured at room temperature is plotted as a function of the logarithmic strain rate in Fig. 7. The data show a departure from the commonly observed linear relation beween the yield stress and the strain rate at constant temperature, as is expected from a single activated rate process which can be described by the Eyring theory [14, 15]. However, the data still show that the yield stress increases as a function of strain rate as for most polymeric materials. The equivalence between increasing the yield stress with increasing strain rate and with decreasing temperature can be drawn from Figs 4 and 5. The overall effect of the strain rate on the yielding behaviour, shown in Fig. 7, can be described from the defect structure of the given composite. It is well established [13–16] that the dependence of the yield stress on the strain rate for most isotropic and even oriented polymers is linear. The yield stress always increases linearly with the applied strain rate. The type of yielding behaviour observed for "Magnex DC" composite is expected to be due to its defect structure and the effect of gases and voids around the steel fibres. At low strain rates, the gas bubbles will have a good chance of emerging easily from these cavities and leave the structure, which is highly defected, with low values of yield stress. However, the observed rapid increase of σ_y with log E' at low strain rates (or high temperatures) can be

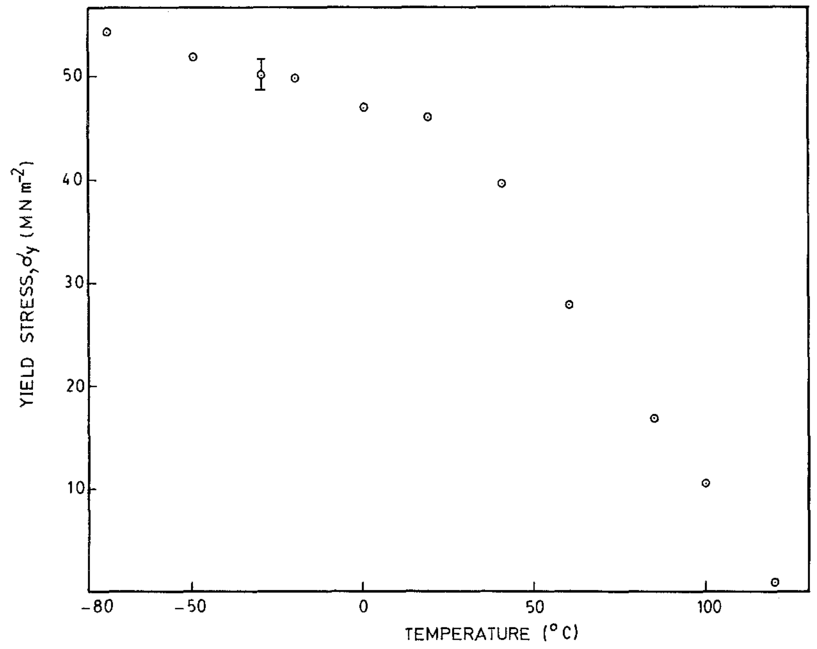

Figure 5 The yield stress of "Magnex DC" as a function of temperature.

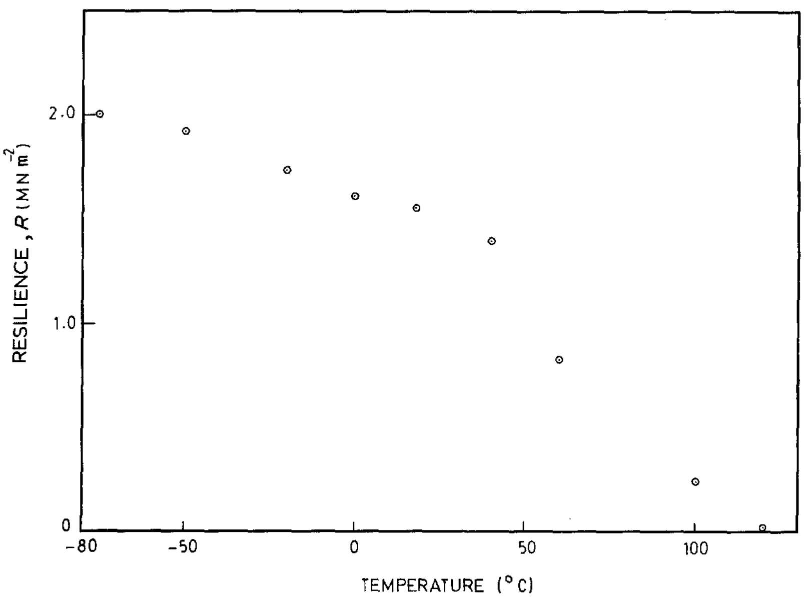

Figure 6 Resilience of "Magnex DC" as a function of temperature.

understood from the fact that yielding of the composite is dominated by the yield behaviour of steel fibres, which strongly increase with strain rate [17]. At high strain rates, the yielding mechanism is dominated by the yield behaviour of the polymer matrix in the composite, where a linear dependence is observed as in most polymers. This is supported from the calculated values of the activation energy and stress activation volume by using the Eyring equation [14, 15] for an activated rate process, which can be written in terms of strain rate, $\dot{E}$, and the absolute temperature, T, as

$$\dot{E} \;=\; \dot{E}_0 \exp\{-[(\Delta U - \sigma_y V^*)/kT]\} \qquad (2)$$

where $\dot{E}_0$ is constant, ΔU is the activation energy for an activated rate process, σ_y is the yield stress, V^* is the stress activation volume, k is the Boltzmann constant, and T is the absolute temperature. This equation implies that the stress at yield and the logarithm of strain rate have a linear relation with a slope given by

$$\partial\sigma_y/(\partial \ln \dot{E})_T \;=\; kT/V^* \qquad (3)$$

Values for the activation energy and the activation volume are calculated from the observed linear dependence of Fig. 7 at high strain rates. The values obtained at room temperature are $\Delta U = 2.5 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$, and $V^* = 2.156\,\mathrm{nm^3}$. This low value of the activation energy for a conductive polymer composite is expected and consistent with the predicted a.c. conductivity given in this paper.

Because the embedded stainless steel fibres in the polymer matrix are short and randomly distributed, their contribution to the d.c. conductivity is expected to be small. However, studying the a.c. electrical characteristics may provide valuable information about the electrical conduction mechanisms occurring in the specimen, which may be in the form of electronic, ionic, orientation, and space charge polarization. The magnitude of these effects can be understood from the behaviour of the impedance (Z) and the phase angle (ϕ) with frequency. The dielectric constant, ε, related to Z and ϕ is given elsewhere [18–20]. The data presented in Figs 8 to 10 are calculated from the following equations

$$\varepsilon \;=\; \varepsilon' + j\varepsilon'' \qquad (4)$$

where ε' and ε'' are the real and imaginary parts of the complex dielectric constant, respectively, and $j = (-1)^{1/2}$,

$$\cot\phi \;=\; \varepsilon''/\varepsilon' \;=\; Z_R/Z_C \qquad (5)$$

where Z_R and Z_C are the real and the imaginary parts

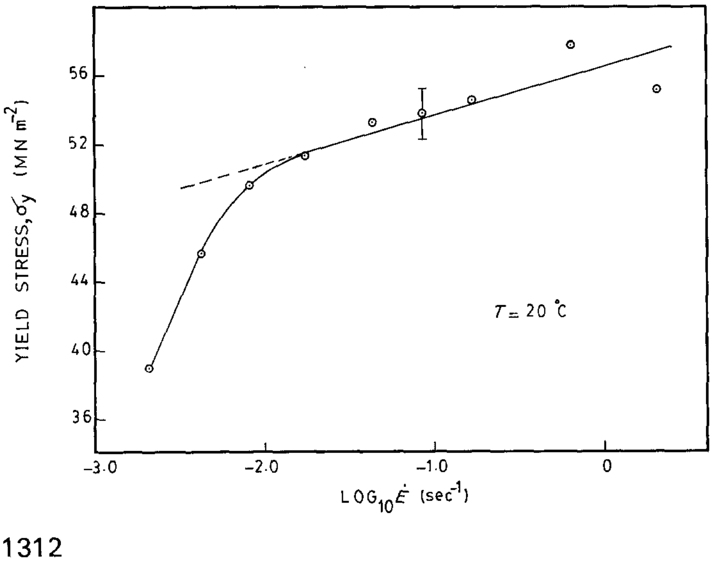

Figure 7 The yield stress of "Magnex DC" as a function of log strain rate at room temperature.

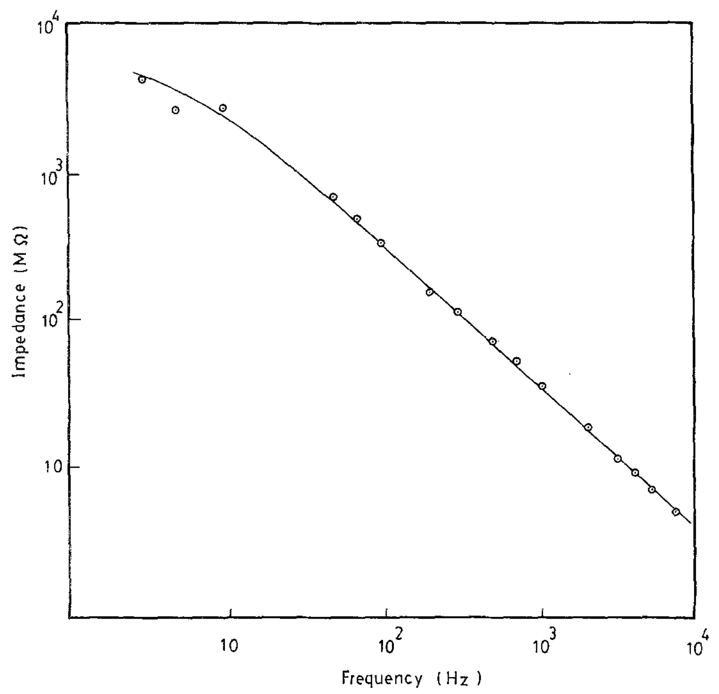

Figure 8 The impedance as a function of frequency for "Magnex DC".

of the impedance, Z, which is given by

$$Z = Z_R - jZ_C = 1/\{j2\pi f C_0 \varepsilon\} \quad (6)$$

where C_0 ($=2.25\,\text{pF}$) is the capacitance of the electrodes, and f is the frequency.

The relationship between ε and Z is given by

$$\varepsilon' = Z_C/[2\pi f C_0(Z_R^2 + Z_C^2)] \quad (7)$$

and

$$\varepsilon'' = Z_R/[2\pi f C_0(Z_R^2 + Z_C^2)] = \sigma/2\pi f \varepsilon_0 \quad (8)$$

where σ is the a.c. conductivity and ε_0 is the permittivity of the free space.

Impedance measurements have been carried out at room temperature in the frequency range 0.5 Hz to 100 kHz. The amplitude of the applied electric field was kept as low as possible ($2\,\text{kV}\,\text{m}^{-1}$) in order to avoid any perturbation in the specimen itself. The results obtained are shown in Fig. 8. The curve indicates, in general, that the impedance decreases continuously with frequency as observed for many polymeric materials [21–23]. This suggests that the specimen and the electrodes operate as a pure capacitive element, where the phase angle was always about 90° at low frequencies. This may be due to the existence of space charge polarization in the polymer matrix and on the void walls surrounding the steel fibres. These space charges cause some potential barriers which, in turn, increase the impedance [21, 22].

Fig. 9 is a complex plane impedance plot which shows a greatly distorted and inclined semicircle. The observed distortion may be due to the anomalous behaviour of ε at low frequencies. However, Jonscher and Reau [21] have shown that if there is a distribution of relaxation times due to some local micro-inhomogenities caused by the distribution of the potential barriers within the specimen bulk, then one may get a distorted semicircle, as it has been obtained

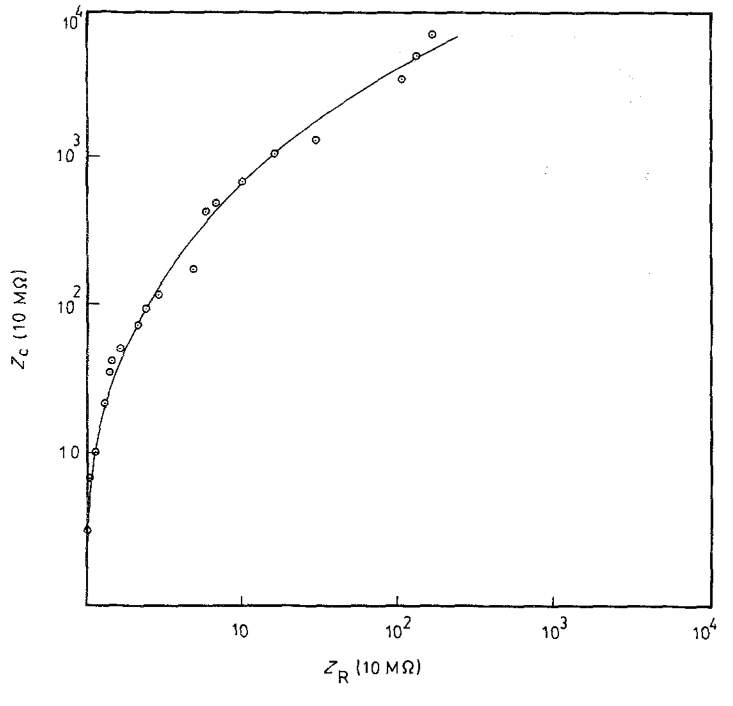

Figure 9 The Cole–Cole plot of the complex impedance for "Magnex DC".

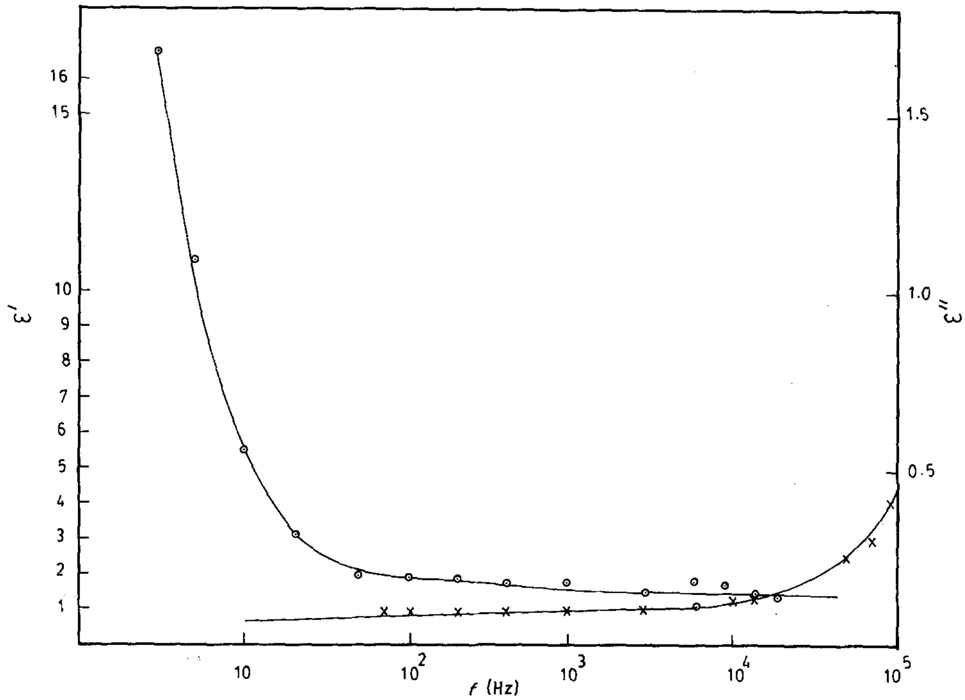

Figure 10 The real and imaginary parts of the dielectric constant as a function of frequency. (○) ε′, (x) ε″.

from the present data. Because the composite under study contains many voids, i.e. steel fibres and imperfections, the relaxation times are distributed over a wide range due to different polarization mechanisms existing in the specimen. Hence a particular relaxation time could not be found from the present data.

Fig. 10 represents the frequency response of the real part (ε') and the imaginary part (ε'') of the complex dielectric constant, ε. The ε' behaviour appears to have a regular curve which tends to have a ($1/2\pi f$) dependence at low frequencies ($f < 20$ Hz). At higher frequencies ($f > 20$ Hz), ε' decreases very slowly to attain a small constant value (~ 1.5) which is in agreement with the behaviour of pure dielectric materials. On the other hand, ε'' has a very small value ($\simeq 0.2$) at frequencies less than 10 kHz; but above this value it exhibits a relatively pronounced frequency dependence. It is possible that one can achieve a better clarity of the obtained results by utilizing the well-known fact that the variation of ε'' with frequency has an effect of enhancing the contribution of the bulk a.c. conductivity of the material [24]. The overall behaviour of ε observed at room temperature is consistent with the recently reported results measured at 1 kHz [5].

The values of a.c. conductivity (σ) calculated from Equation 8 has an almost constant value, $\simeq 1.1 \times 10^{-10}$ moho m^{-1}, at frequencies below 10 kHz. Above this frequency, σ becomes an increasing function of frequency and attains a value of $\simeq 2.8 \times 10^{-9}$ moho m^{-1} at 100 kHz. This calculated value is comparable to that reported recently for silver bromide ($\sim 10^{-10}$ moho m^{-1}) which is located between insulating materials and semiconductors [25].

4. Conclusions

The mechanical behaviour of the "Magnex DC" composite as a function of temperature and strain rate is considered, and the dielectric and a.c. conductivity are investigated through impedance measurements in the low frequency range (0.5 Hz to 100 kHz). From the data obtained the following conclusions are drawn.

1. The "Magnex DC" composite has a semicrystalline, isotropic, defect structure.
2. Both the elastic modulus and yield stress decrease with decreasing temperature. The yield stress increases nonlinearly with increasing strain rate due to the defect structure of the composite.
3. The variation of the yield stress with high strain rates reveals that a single activation process takes place and the activation energy and activation volume are determined.
4. The a.c. impedance and dielectric component show a frequency dependence which is discussed in terms of the polar and electronic polarization and the existence of space charges in the voids around the steel fibres.
5. The a.c. conductivity is almost independent of frequency below 10 kHz and increases parabolically up to 100 kHz. The calculated values for the conductivity indicate that the composite has a relatively small electrical conduction which is less than that for the semiconductor.

Acknowledgements

The authors thank Professor R. J. Farris, Polymer Science Department, University of Massachusetts, Amherst, USA, for providing the specimens and Dr S. Jawad, Physics Department, Al-Ain University, UAE, for taking X-ray diffraction patterns.

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Received 12 February
and accepted 14 June 1988