JOURNAL OF MATERIALS SCIENCE 25 (1990) 3061–3066

D.c. electrical conduction phenomena between two non-contacting stainless steel fibres in a polycarbonate matrix

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Model two-fibre devices have been constructed to simulate the local electrical environment between neighbouring fibres in stainless steel fibre polycarbonate composites. The voltage–current characteristics of the device have been studied as a function of the shortest distance (gap length) between the fibres, arranged in T-configurations. From the device behaviour it is concluded that to explain the observed levels of resistivity in bulk composites (as low as a few ohms centimetres for 1% volume fraction of metal) gap levels must be <1 nm. Whilst the device resistance for larger gaps of several micrometres is too large to explain bulk resistivities of a few ohms centimetres in composites, it is nevertheless six orders of magnitude lower than one would expect if tabulated bulk resistivities of polycarbonate ($2 \times 10^6\,\Omega$cm) obtained in the gap between fibres. Furthermore the lowest experimental estimate of the dielectric strength of the polycarbonate in the gaps, exceeds by a factor of ten or more the tabulated value for bulk polycarbonate. In the conclusion some tentative suggestions on the origin of these device "size effects" are presented. This involves consideration of the length and orientation of polymer chains in relation to the gaps and cross-linking effects.

1. Introduction

Currently there is much interest in conductive polymer composites using short metal fibres as the filler, rather than metal flakes or carbon particles. The most obvious reasons for using fibrous fillers are the improved mechanical properties, but what is becoming increasingly apparent is that for many applications they also produce the required electrical performance more cost effectively. As an example, resistivities of a few ohms centimetres can easily be produced using only 1% volume fraction of metal fibres [1] and straightforward moulding and extrusion technology. Far higher volume fractions of conducting particles are required to achieve useful resistivities by such technology [2], although percolation conductions at about 5% volume fraction can be achieved by hot pressing mixtures of polymer granules with much smaller metal particles [3].

It is advantageous to be able to predict the electrical behaviour of a composite from the physical properties of the fibres and matrix. In principle, if the conductivity between two neighbouring fibres is known as a function of the separation and orientation of the fibres, the electrical performance of a fibre loaded polymer composite can be modelled. For this reason the authors have been measuring the voltage–current characteristics of two-fibre devices of various geometries. In a composite, fibres are not straight but describe complex trajectories. However, the voltage drop along a fibre is negligible compared with the drop between neighbouring fibres. For this reason the use of model devices consisting of two straight wires with various relative orientations and separations should give a reasonable simulation of the electrical environment of two nearest neighbour fibres in a composite. In fact, statistically, the use of a T-configuration of wires will approximate to the usual environment whilst the use of parallel and end-on configurations will correspond to relatively infrequently occurring situations. In order to reduce still further the number of indeterminate variables it is desirable to employ a non-crystalline matrix. Indeed, in a previous study of a T-configuration two-fibre device reported by the authors [4], a polypropylene matrix was employed and the electrical behaviour was found to vary in a complicated manner with the size and distribution of spherulites. Therefore we used polycarbonate in the present study of the dependence of the voltage–current characteristic of a T-configuration of stainless steel fibres on the shortest fibre–fibre distance (gap length). An important range of stainless steel fibre-filled polycarbonate composites are manufactured by the Bekaert company (Belgium) for electromagnetic shielding applications. The model devices described here ought to provide a reasonable simulation of the local electrical environment in these materials.

2. Sample preparations

The polycarbonate used, which was in granular form was supplied by G. E. Plastics Ltd, U.K. and had a

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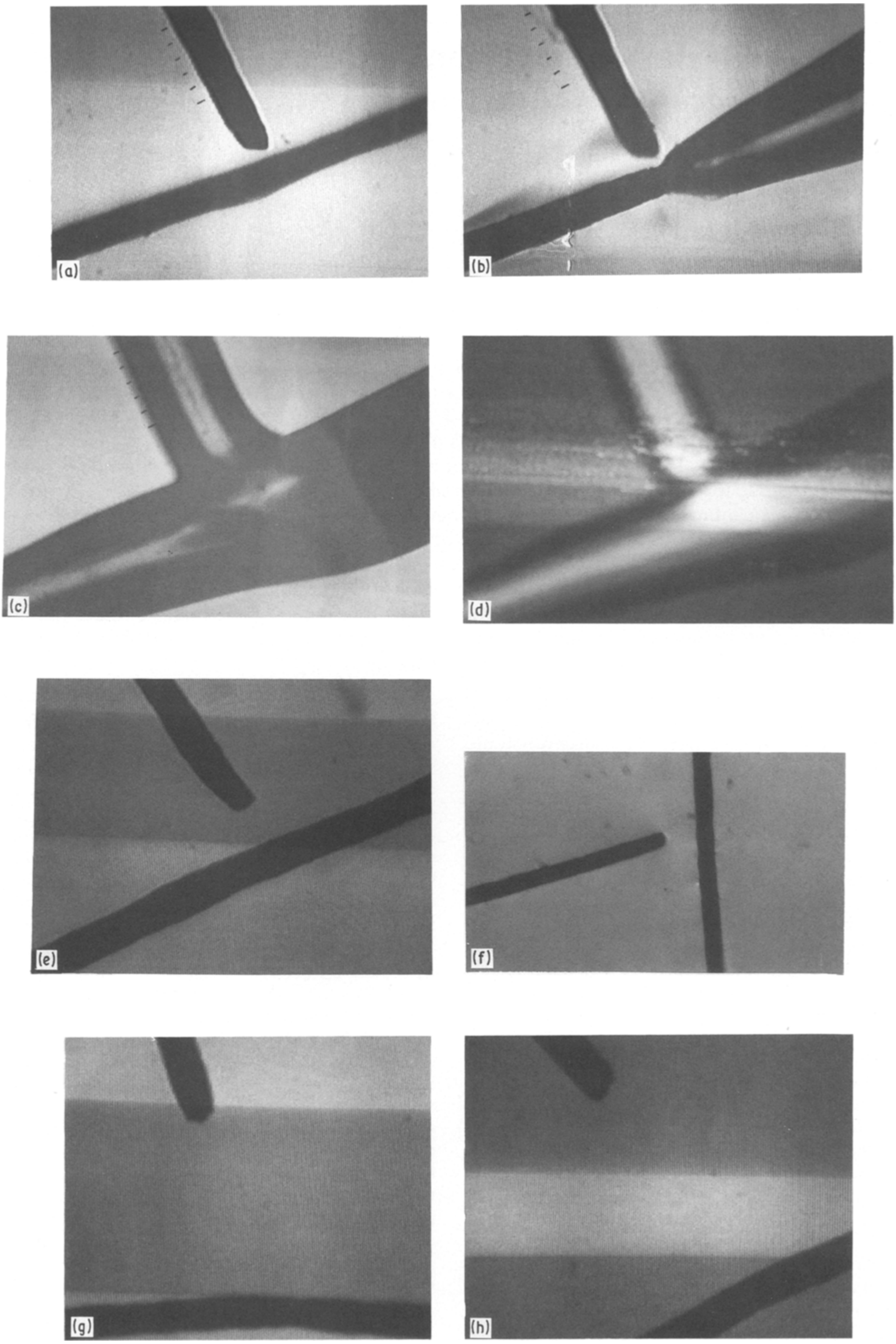

Figure 1 Microscope photographs of two-fibre devices in T-configurations. (a) $5\,\mu$m gap 0 V; (b) $5\,\mu$m gap 1100 V, 2.85×10^{-10} A local melting; (c) $5\,\mu$m gap, 1300 V, 5×10^{-10}, A further melting; (d) $5\,\mu$m gap, 1500 V, breakdown; (e) $20\,\mu$m gap; (f) $30\,\mu$m gap; (g) $120\,\mu$m gap; (h) $145\,\mu$m gap. No visible changes occur in cases (e) to (h) throughout the voltage range investigated, 10 V – 3 kV.

product Code 141-111-Co3927, LEXAN polycarbonate. The fibres used were kindly supplied by Bekaert Steel and Wire Ltd, and had product Code BEKINOX VS22/250/1000CR, a diameter of 22 μm and in addition a size coating of the order of a micrometre.

The first stage of specimen preparation was the pre-drying of the polycarbonate. To obtain an extruded product with good appearance pre-drying is essential, to produce a moisture content of ideally less than 0.02%. The drying time carried out in a vacuum oven was 3 h at a temperature of 120° C.

The second stage of the specimen preparation involved the production of a thin tape of polycarbonate using a single screw extruder. The equipment used was a Betol model 2520 and the temperature of the three extrusion zones were set at 225, 240 and 265° C. The screw speed was 60 r.p.m. and the roller speed was 3 m min^{-1}. The fish-tail die was set to operate at 280° C. The last stage of specimen preparation involved the careful alignment of two fibres on a microscope slide with a configuration as shown in Fig. 1a to h. In the repeated manufacture of this configuration the gap between the end of one fibre and the surface of another was varied from 5 to 145 μm, the former figure representing the smallest non-zero gap length that could be obtained. The fibres were held temporarily in place using small pieces of insulating tape, while a small piece of the polycarbonate tape was laid over the two fibres. A cover slip was then placed on the polymer and then the whole assembly clamped together. This was then heated for 30 min at temperatures of 200° C, following which the sample was allowed to cool slowly to room temperature. At this stage, the specimen was examined to check the alignments of the fibres and for the presence of any air bubbles that would otherwise affect our electrical data. Silver clay was added to the ends of the fibres to ensure good electrical contact with our test equipment. Specimens were stored in a desiccator to prevent long-term modification of electrical properties due to humidity.

3. Electrical measurements

Following the specimen preparation, the current–voltage characteristic of the device was measured using a 5 V–5% kV, d.c. power supply, (Brandenburg Alpha Series II, 5MA, I 5% V measurement precision) and a sensitive electrometer (Keithley model 614, 20PA ± 10FA to 2 mA ± 1 μA). A resistance of 1 MΩ was always maintained in series with the device to protect the power supply against overload from devices breakdown. During the electrical measurements, simultaneous observations of changes in the micro-structure of the specimens were made by the use of a transmission optical microscope (Leitz model Laborlux) and a video camera. Fig. 1a to h shows the alignment of fibres. For the smallest gap employed (5 μm), the appearance of the polycarbonate started to change due to joule heating effects, at about 1100 V, when the current was 2.8×10^{-10} A (Fig. 1b). At 1300 V the melted area had increased substantially (Fig. 1c) and finally breakdown occurred at 1500 V (Fig. 1d). (The bright area which was blue in the original colour presentation, shows the actual spark.)

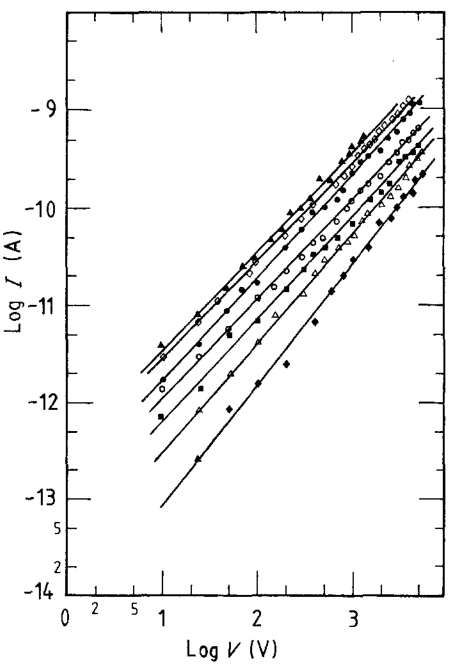

Figure 2 Voltage–current characteristics of the devices. (▲) 5 μm; (◇) 10 μm; (●) 20 μm; (○) 30 μm; (■) 100 μm; (△) 120 μm; (◆) 145 μm.

Figure 2 shows that linear behaviour was exhibited closely throughout the whole range of applied voltage and gap lengths employed. Therefore it is reasonable to conclude that the device is ohmic because at low voltages, the sample temperature will be reasonably constant and close to ambient. Figure 3 shows that to have a reasonable approximation, the current flow at constant voltage and therefore the conductance of the device, is inversely proportional to the gap length.

4. Results and discussion in relation to the conductivity of composites

It will be interesting to work out the electrical resistivity of a composite consisting of a regular array of

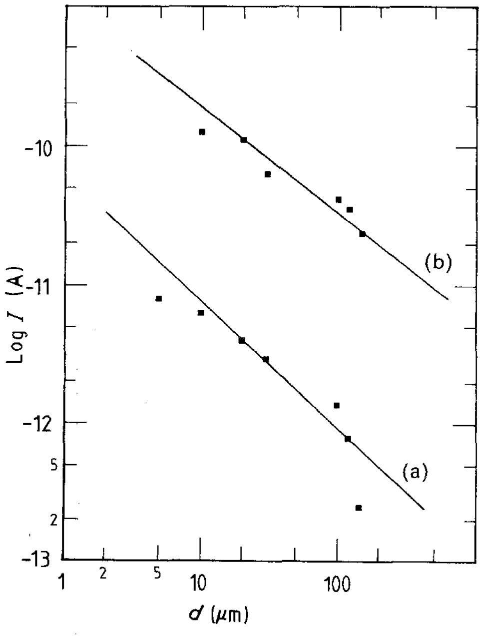

Figure 3 Variations of device current with gap length at constant voltage (a) 10 V, (b) 3 kV.

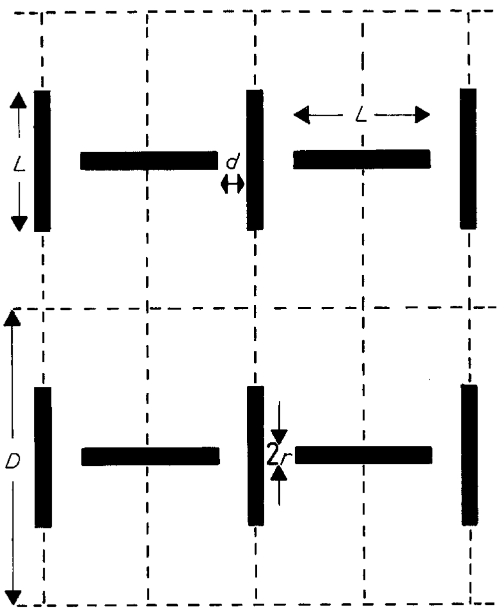

Figure 4 Simulation of a conductive composite by a regular array of straight metal fibres in T-configurations. Illustrating one of the many parallel planes separated by uniform distance of D.

T-configurations, as illustrated in Fig. 4. If R is the resistance of one T-configuration, the resistance of a unit cube of the material, i.e. the resistivity of the composite, measured parallel to L, is given by

$$\varrho^{-1} = (L/2 + d + r)/R + (L/2 + d + r)/R + \ldots + \ldots +$$

where there are $1/D^2$ terms in the sum and r is the fibre radius. Thus

$$\varrho = RD^2/(L/2 + d + r) \qquad (1)$$

Now if v is the volume fraction of fibres in the composite,

$$v = \pi r^2 L/(L/2 + d + r)D^2 \qquad (2)$$

The factor 1.5 rather than 2 arises because one wire of each T-configuration is shared between two neighbouring rectangles (dotted lines in Fig. 5). From Equations 1 and 2

$$\varrho = \pi R r^2 L/(L/2 + d + r)^2 v \qquad (3)$$

It should be appreciated that R may be an implicit function of r, d and L through the effect of these quantities on the electrostatic field distribution around the T-configuration.

The polycarbonate composites of Beakart have resistivities of the order of $10\,\Omega$cm for $v = 0.01$, and $r = 5\,\mu$m. The present devices contain fibres of twice this radius, which is not an important difference with respect to the present order of magnitude calculation. Substituting the above value for ϱ, $L \approx 500\,\mu$m, $v = 0.01$, and $r = 11\,\mu$m into Equation 3, and neglecting d in comparison with L, we obtain

$$R \approx 360\,\Omega \qquad (4)$$

This is the resistance required between two neighbouring fibres to explain the observed bulk sample resistivity. From inspection of Figs 3 and 4 it is obvious at once that values of d far less than the range investigated are required to account for this situation. Assuming that the straight line drawn through the log (I) against log (d) data for $V = 12$ V is extrapolatable, the resistance of the two fibre devices is given, experimentally, by the relation.

$$R = 12\,[\text{anti log}\,(-0.917 \log d - 10.25)]^{-1}\,\Omega \qquad (5)$$

Rearranging in the form

$$d = \text{anti log}\,\{[\log (R/12) - 10.25]/0.917\} \qquad (6)$$

the value of d required to achieve a device resistance of $360\,\Omega$, is ≈ 0.27 nm, i.e. a few atomic spacings. The extrapolation will not, in fact, be valid at such small d values as quantum mechanical tunnelling will cause R to rise rather more rapidly with decreasing d, for $d < 1$ nm. Using Fig. 3 of the paper by Simmons [5], for convenience reproduced here in Fig. 5, taking the work function of the wires to be about 4 eV, [6], and the relative dielectric constant of polycarbonate to be ≈ 3 [7], the device resistance would be $26\,\Omega$ for $d = 0.7$ nm and $900\,\Omega$ for $d = 0.9$ nm, i.e. when d is increased to ≈ 1 nm, the quantum mechanical estimate

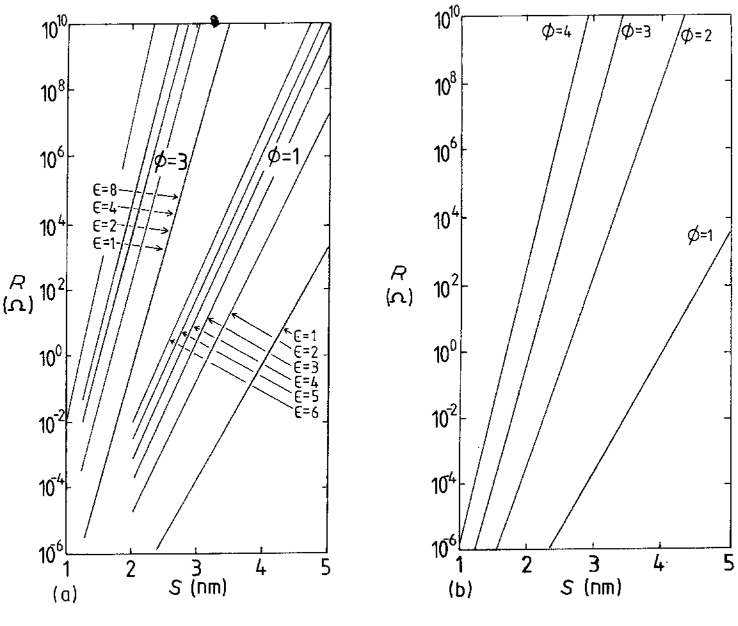

Figure 5 Quantum tunnelling current between planar electrodes separating a thin insulating film. ϕ is the work function in eV, ε is the relative permittivity (the dielectric constant), S is the film thickness (nm), and R is the device resistance for electrodes of $1\,\text{cm}^2$ area at low voltages, and image forces have been allowed for (after [5]): (a) $\varepsilon = 1$, (b) effect of ε.

of R exceeds that of Equation 6 by a factor of 2. Thus for $d \gtrsim 1$ nm the device resistance is determined principally by the resistivity of the matrix rather than by quantum mechanical tunnelling. In applying Simmon's data the effective electrode area is taken to be the cross-sectional area of a fibre tip, i.e. about $3.8 \times 10^{-6}\,\text{cm}^2$.

From the above considerations there can be little doubt that the levels of resistivity encountered in stainless steel fibre filled polymer composites require continous chains of fibres either in contact, or separated by gaps of < 1 nm, in which case quantum tunnelling is a significant contributory factor in the observed conductivity. Now, as in our twin-fibre models, the Beakart fibres in the composites under discussion were coated with a size of thickness of $\sim 1\,\mu$m or more. Thus we conclude that partial stripping of the coating must occur during extrusion and moulding to explain the occurrence of metal–metal contacts or quantum-tunnelling gaps.

In the above arguments we have made the reasonable assumption that the resistivity of the size is within a few orders of magnitude of that of the polycarbonate matrix. If we make the alternative and unlikely assumption that the size coating had a relatively low resistance the extrapolation of Equation 5 to d values-coating thickness may be unreliable and the coating resistance could have a major influence on the bulk resistivity of the composites. For a fibre gap small enough for size coatings to make contact the field lines in the gap will be parallel. So with the size coatings making contact, the device resistance is given by

$$R = \varrho_s\, 2d_s \pi r^2 \qquad (7)$$

where ϱ_s and d_s are respectively the resistivity and thickness of the size coating. Taking $d_s = 1\,\mu$m, $r = 11\,\mu$m, to yield the value of R (900 Ω) required to account for the observed resistivity of a composite with $v \sim 0.01$, we require

$$\varrho_s = 1.7 \times 10^6\,\Omega\,\text{cm} \qquad (8)$$

This is ten orders of magnitude less than tabulated values of the resistivity of polycarbonate [7].

5. Results and discussion in relation to the conductivity of the matrix

The lower theoretical bound to the device resistance assuming that a homogeneous volume resistivity occurs, is given by assuming a spherically symmetric field distribution round the tip of the vertical fibre in the T-configuration (subsequently called the first fibre). Previously [4] we have shown that the device resistance is then

$$R = \varrho d / 2\pi r(r + d) \qquad (9)$$

where ϱ is the volume resistivity. Substituting $\varrho = 2 \times 10^{16}\,\Omega\,\text{cm}$, $d = 5\,\mu$m, $r = 11\,\mu$m, the device resistance for a $5\,\mu$m gap is $\approx 10^{18}\,\Omega$. The actual device resistance at 10 V is $2.6 \times 10^{12}\,\Omega$, almost six orders of magnitude lower. It is unlikely that surface conduction effects are the cause in view of the systematic way the device resistance decreases with increasing d. We must attribute the effect to enhanced conductivity within the amorphous matrix. Plausibly such enhanced conductivity in the matrix explains why the value of experimental device resistance extrapolated down to gap lengths of as small as 1 nm, exceeds the resistance predicted by quantum tunnelling theory which assumes the presence of a perfect dielectric. It will be observed that, as in previous experiments with a non-amorphous matrix [4] breakdown does not occur across the shortest path between the two electrodes (Fig. 3d) suggesting a highly inhomogeneous conduction process. Suggestions as to the cause of these novel effects are deferred until our conclusion section.

6. Breakdown effects

Assuming spherical symmetry as described in the preceding section the field strength (E) at a point r in the gap, measured from the tip of the first fibre (the tip being conveniently assumed to be hemispherical), is given by Equation 4.

$$E_r = Vr(r + d)/d\mathbf{r}^2 \qquad (10)$$

The smallest value of E_r occurs at the surface of the second fibre, where $\mathbf{r} = r + d$. When $V = 1400$ V (the breakdown voltage for) for $d = 5\,\mu$m,

$$E_r = 1925\,\text{kV}\,\text{cm}^{-1}$$

Alternatively, assuming parallel field lines in the gap a higher estimate of the breakdown field strength (dielectric strength), will be obtained, i.e.

$$E_r = 2800\,\text{kV}\,\text{cm}^{-1}$$

the tabulated value of dielectric strength applicable to bulk samples [8] is $150\,\text{kV}\,\text{cm}^{-1}$, thus the lowest conceivable experimental estimate for our device exceeds the bulk value by a factor of 13.

7. Conclusion

Our results suggest that the lowest values of resistivity observed in short steel fibre composites with $v \approx 0.01$ are caused by continuous chains of fibres which are contacting or separated by gaps of < 1 nm, on average. As for the low values of the matrix resistivity in the two fibre devices, compared with accepted bulk values, there are no grounds for supposing that the polymer tape employed contained more impurities than normal. The consistency of data taken on a number of devices is, in fact, suggestive of a sample "size" effect.

It seems unlikely that this size effect is related to the normal hopping conduction process obtained in polymers because the mean free path of carriers between localized states will be much shorter than the gap length. We might conjecture that the effect is associated with the traversal of a route between two electrodes by a single polymer chain, or with a specific orientation of chains in relation to the fibres. Plausibly the high dielectric strength of the device is also related to polymer chain geometry. Detailed microstructural studies will be required to test these proposals.

Acknowledgements

The authors would like to thank the SERC for their financial support for this work under the specially Promoted Programme on electroactive polymers, and to Dr Adriaensen of Bekaert Ltd, for helpful discussions and the supply of fibres.

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Received 28 October 1988
and accepted 14 April 198