JOURNAL OF MATERIALS SCIENCE **23** (1988) 1955–1960

Electrical conduction phenomena between adjacent stainless steel fibres in a thermoplastic matrix

B. BRIDGE*, M. J. FOLKES‡, H. JAHANKHANI‡
**Department of Physics and ‡Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

In a programme designed to elucidate the fundamental mechanisms involved in electrical conduction through a polypropylene matrix filled with non-contacting stainless steel fibres, the current flow between two individual fibres orientated perpendicularly in a polypropylene bead has been studied. The fibre diameter was 22 μm and the gap length was 100 μm. The resistance at low voltages was five orders of magnitude lower than could be accounted for by assuming that homogeneous conduction had taken place with tabulated values of the volume resistivity of the matrix obtaining. Transmission optical microscopy revealed that during current flow, the greatest heating and degradation of the polymer did not take place along the shortest path between the fibres. It is argued that this heterogeneous conduction process may be preferentially located at the boundaries of spherulites and that low molecular weight residues, additives etc., are at least partially responsible for the enhanced conductivity levels.

1. Introduction

Electrically conducting composites based on polymeric matrix systems are now being used in many applications ranging from resistive heating tapes to business-machine housings having electromagnetic interference shielding properties. Some of the earliest conducting composites were formulated using carbon black as the filler, but latterly it has been found that higher composite conductivities can be obtained, for the same volume fraction, by using conducting flakes or fibres, e.g. carbon or stainless steel. A considerable amount of effort has been devoted both to establishing processing–property relationships in injection-moulded conducting composites and in the theoretical modelling of the conduction process [1–9]. It has been proposed [1] that the onset of electrical conduction occurs when a conductive path forms through the composite by a sequence of touching fibres; a process referred to as a percolation mechanism [10, 11]. It is suggested that this provides one explanation for the rapid change in composite resistivity at a critical volume fraction of filler, corresponding to the generation of a statistically significant number of contacting fibres. However, this cannot provide a complete description of the conduction process as it occurs in practice, since the fibres used in these composites will have a "size" applied to them to promote adhesion with the matrix and so true electrical contact between adjacent fibres cannot occur. This implies that some other conduction mechanism is locally operative between fibres. Due to the lack of long-range periodicity in the structure of bulk polymers, there is no regular band structure and hence it is unlikely that there is one dominant conduction process. The high electric field strengths between fibres may promote quantum-mechanical tunnelling or complete breakdown of the matrix or "size" applied to the fibres. Impurities in the resins, e.g. unpolymerized material, additives etc., may well assist the conduction process. Hence, the overall composite conductivity levels may depend critically on the purity of the resins.

In a crystallizable thermoplastic, the process of spherulite growth is known to lead to a rejection of low molecular weight species and impurities to the spherulite boundaries. Hence, the detailed microstructure of the resin close to the fibres will have a major effect on the conduction processes between fibres, either through the provision of direct conducting paths around the spherulites or by the presence of adventitious chain orientation between fibres leading to the increased prospect of intramolecular hopping mechanisms.

Accordingly, with a view to seeking a more fundamental understanding of the conduction processes in reinforced thermoplastics, we are currently studying a series of model systems composed of two stainless steel fibres embedded in a polypropylene matrix. The reasoning behind this approach is as follows: progress is best made by minimizing the number of variables affecting the conduction process being studied at one time. Thus a sensible starting point is to remove all factors associated with the statistics of fibre distributions. In principle, if for a given matrix the conductivity between two fibres is determined as a function of gap length and fibre orientation, the conductivity of a macroscopic composite sample can be computed from network theory combined with fibre orientation and distribution statistics.

0022–2461/88 \$03.00 + .12

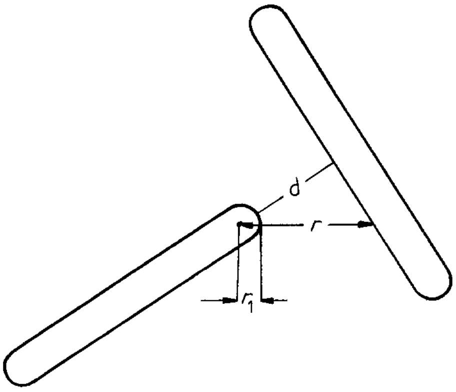

Figure 1 Configuration of fibres and notation used in Section 5.

2. Sample preparation

The fibres used in the preparation of our specimens consisted of stainless steel fibres, type Bekinox VS 22/250/1000 CR, kindly supplied by Bekaert Ltd, Belgium, and having a diameter of 22 μm and a size coating. The polypropylene, which was in granular form, was supplied by ICI and had a product code GWM22. The first stage of the specimen preparation involved the production of a thin tape of polypropylene, using a single-screw extruder. The equipment used was a Betol model 2520, and the temperatures of the three extrusion zones were set at 150, 175 and 200° C. The screw speed was 90 r.p.m. and the fish-tail die was set at a temperature of 200° C. The second stage of specimen preparation involved the painstaking task of aligning two fibres on a microscope slide and with a configuration as shown in Fig. 1. The gap between the end of one fibre and the surface of the other was arranged to be about 100 μm. The fibres were held temporarily in place using small pieces of insulating tape, while a small piece of the polypropylene tape was laid over the two fibres. A cover slip was placed on the polymer and the whole assembly clamped together. This was then heated for 30 min at a temperature of 190° C, following which the sample was allowed to cool slowly to room temperature. The specimen thickness was about 200 μm. At this stage, the specimen was examined to check the alignment of the fibres and for the presence of any air bubbles that would otherwise affect our electrical data. Silver dag was applied to the ends of the fibres to ensure good electrical contact with our test equipment. For this particular study, no special care was taken to develop a specified morphology in the polypropylene; this aspect of our work is currently in progress and will be reported in a future publication.

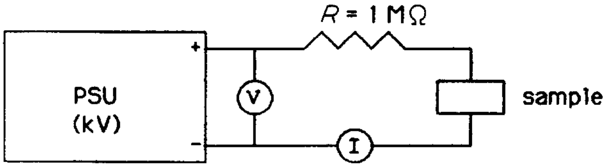

Figure 2 Circuit diagram.

3. Experimental procedure

Following specimen preparation, a potential difference was then applied between the fibres, using a 0 to 3 kV d.c. power supply (Model 3002, Canberra Packard Ltd.) and the resulting current was measured using a Keithley Model 610B electrometer. A circuit diagram is shown in Fig. 2. The current–voltage characteristic was recorded, commencing at low applied voltages up to sample breakdown. During the electrical measurements, we were able to observe any changes in the microstructure of the specimens using a Leitz transmission optical microscope (Figs. 3a to j). Additionally, possible temperature changes occurring in the polymer were detected [9] by the use of an Agema infrared (IR) thermovision camera (Figs. 4a and b). This was located about 75 cm from the specimen and received the IR radiation at an oblique angle to the specimen surface.

4. Results

Fig. 5 shows a plot of current I against potential difference V for the specimens. It appears that the resistivity is quite different above and below a potential difference of about 300 V. Indeed, it is possible to construct two straight lines through the data, indicating what appears to be a point of inflexion in the data. Using transmission microscopy, there seemed to be little change in the appearance of the specimen (Figs. 3a to c) until a potential difference of 1000 V had been applied. At this point, a darkened zone appeared in the gap between the fibres as shown in Fig. 3d. The material close to this zone appeared to be mobile, indicating that the polymer had locally melted.

It is interesting that the dark zone does not pass directly from one fibre to the other but takes a more tortuous route. This suggests that the heterogeneous microstructure of the polypropylene is playing an important role; in fact one explanation for such a phenomenon could be that the conduction process in the polymer is initiated by low molecular weight impurities, additives etc., swept to the spherulite boundaries during crystallization. As the applied potential difference was progressively increased, the dark zone continued to grow in a heterogeneous manner backwards along the first fibre and spreading sideways and forwards towards the second fibre in the form of tentacles. For an applied potential difference of 1250 V, when the current was 9×10^{-9} A, the tentacles have just traversed the gap between the two fibres (Fig. 3e), and with increasing voltage the area of contact between the tentacles and the second fibre grows (Figs. 3g to j). Two minutes after the application of 1750 V, breakdown took place, but it is worth noting that even at this point the shortest distance between the two fibres still passes through an undarkened and thus, presumably, relatively unaffected region. In Fig. 3j the final shape of the complete dark zone, after breakdown, is seen to take a cone-like shape with the base lying along the second fibre and the apex lying on the first fibre some 200 μm backwards from the tip. The anticipated Joule heating effect associated with the dark zone was confirmed by the thermovision image (Fig. 4b), which shows a hot zone for an applied potential difference of 1750 V, whereas the thermal image of the system at

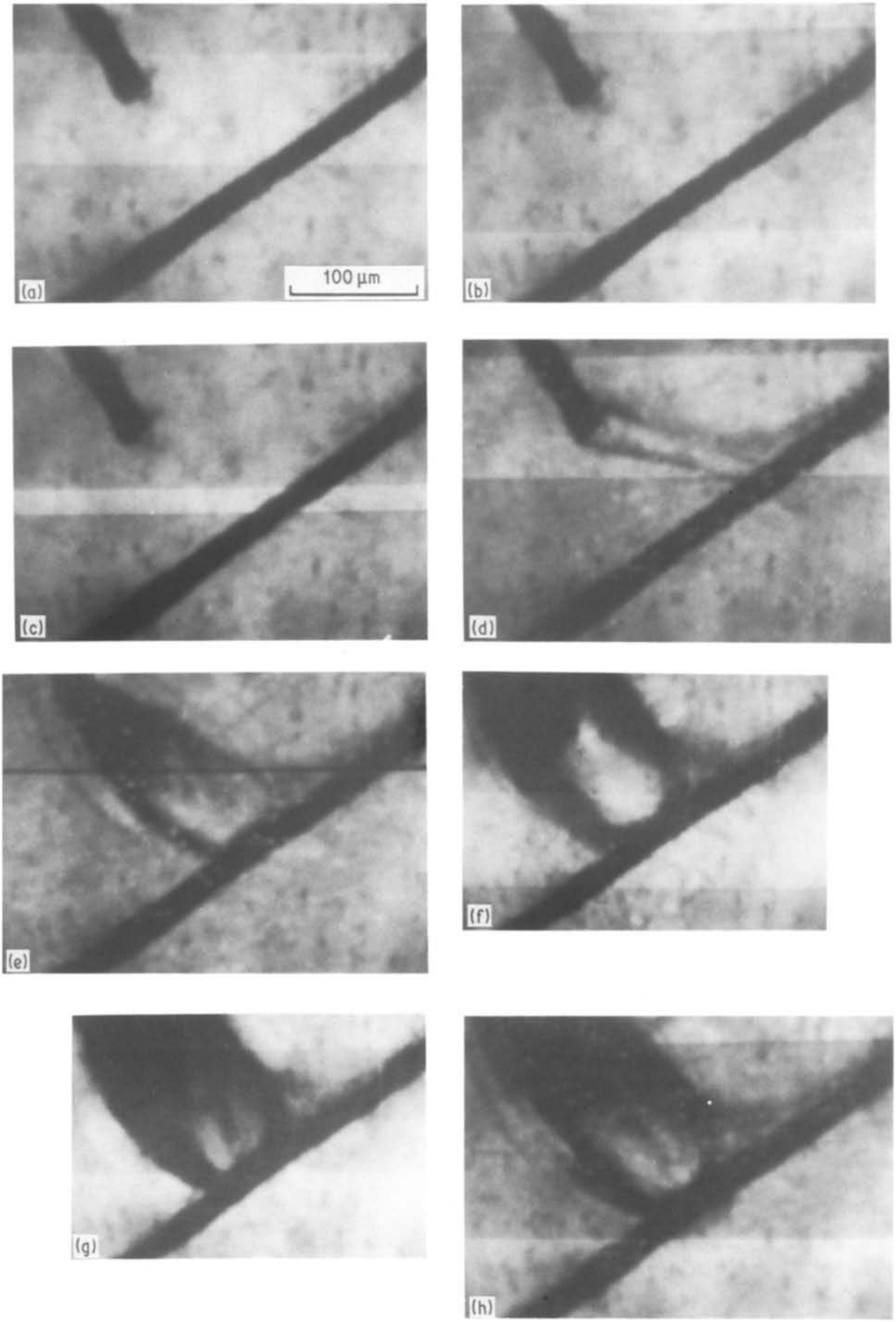

Figure 3 Transmission optical microscope views of the fibres when a potential difference is applied across them. (a) Zero volts; (b) 750 V, 4×10^{-9} A; (c) 1000 V, 7×10^{-9} A (instantaneously); (d) 1000 V, 7×10^{-9} A (after 1 min); (e) 1250 V, 9×10^{-9} A; (f) 1500 V, 1.1×10^{-8} A; (g) 1750 V, 1.4×10^{-8} A (instantaneously); (h) 1750 V, 1.4×10^{-8} A (after 1 min); (i) 1750 V (after about 2 min, current flow unstable indicating breakdown between the fibres); (j) several days after the removal of the breakdown potential difference. The arrow indicates the position of the tip of the first fibre.

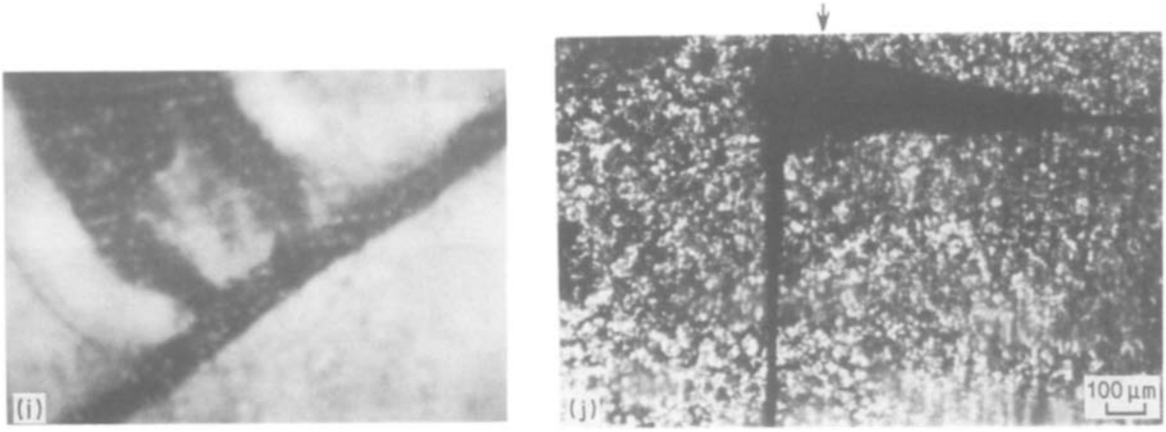

Figure 3 Continued.

zero volts and room temperature contains no such zone (Fig. 4a). Treating the gap between the fibres as a parallel-plate capacitor, breakdown occurs for a dielectric strength of $17.5\,\mathrm{kV\,mm^{-1}}$, which is close to the normally quoted figure of $24\,\mathrm{kV\,mm^{-1}}$ [12] for bulk polypropylene. The similarity of these two figures is very surprising at first sight, considering that no account has been taken either of the detailed field distribution between the fibres or the small radius of curvature of the fibre surface. Also, the fact that the darkened area within the polymer permanently remained after the voltage had been removed tends to suggest that a significant quantity of carbonaceous material was generated during the events leading to breakdown.

5. Discussion

From Fig. 5 the resistance of our two-fibre device is $10^{12}\,\Omega$ for an applied potential difference of $V < 300\,\mathrm{V}$, decreasing to $10^{11}\,\Omega$ for $V = 1750\,\mathrm{V}$, the breakdown potential difference. The following arguments show that it is impossible to explain these resistance levels simply in terms of electrostatic field distributions in a homogeneous polymer in which tabulated values of bulk resistivity obtain (homogeneous theory).

A complete solution for the electric field distribution between the fibres would have to be a numerical one and has not been attempted at this stage. Indeed it would hardly be necessary, because an absolute lower limit to the resistance that could be achieved on a homogeneous theory can be obtained by assuming spherical symmetry for the field distribution about the centre of curvature of the radius r_1 of the tip of a fibre (Fig. 1) (we are further assuming that the fibre ends can be modelled as hemispheres). Thus the field strength E_r at a distance r measured from the centre of curvature towards the second fibre is given by $(\mathrm{const})r^{-2}$, where

$$\mathrm{const}\int_{r_1}^{r_1+d}(r^{-2})\,\mathrm{d}r = V$$

d being the gap (shortest distance) between the fibres. Thus

$$E_r = Vr_1(r_1 + d)/dr^2$$

The current flow across any hemisphere in the gap,

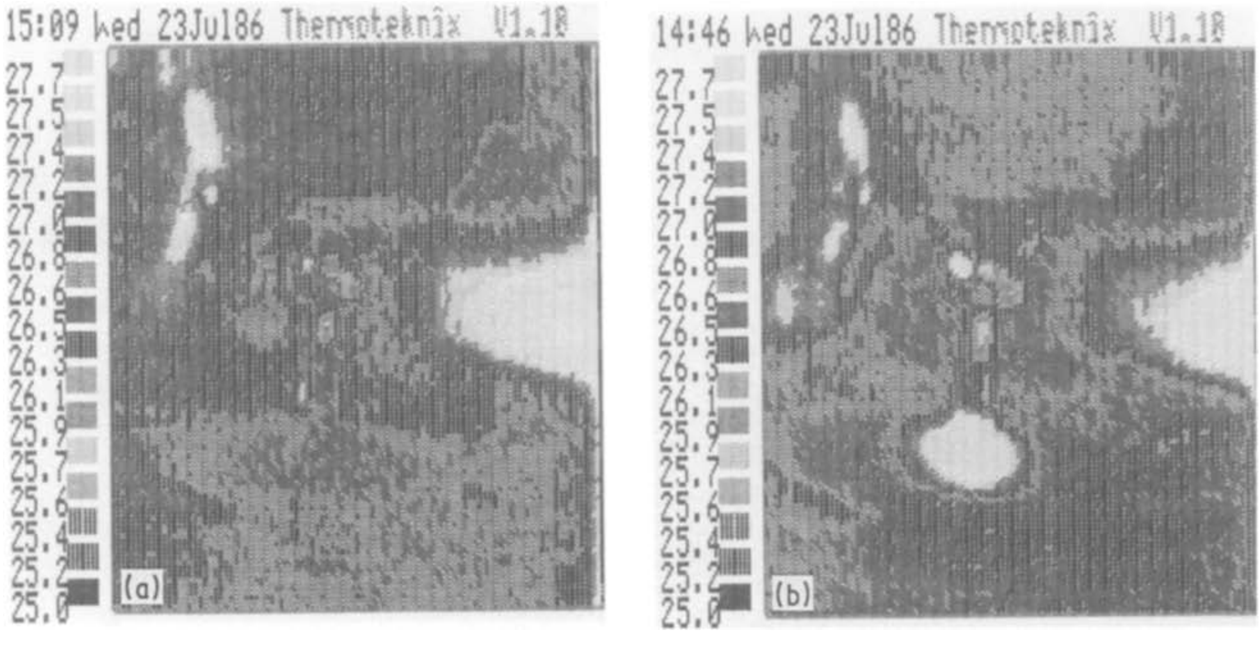

Figure 4 Infrared images of the two-fibre device: (a) with no applied voltage, (b) with 1750 V applied across them and a current flow of $1.4 \times 10^{-8}\,\mathrm{A}$.

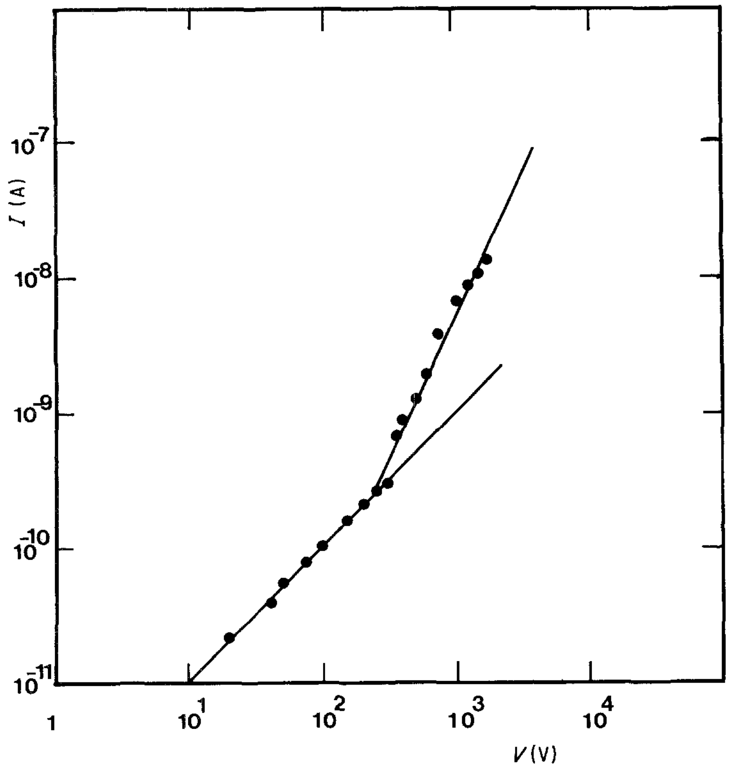

Figure 5 Voltage–current characteristic of the two-fibre device.

assuming a homogeneous volume conductivity σ, is

$$I = \sigma E_r(2\pi r^2) = 2\pi\sigma V r_1(r_1 + d)/d.$$

From the principle of continuity this is also the current leaving one fibre and entering the other; thus the resistance of the device is

$$R = V/I = \varrho d/2\pi r_1(r_1 + d) \qquad (1)$$

where ϱ is σ^{-1}, the volume resistivity.

The value of resistance that would have been obtained by assuming parallel field lines over a gap area of πr_1^2 only would be

$$R' = \varrho d/\pi r_1^2$$

Thus the assumption of spherical symmetry reduces the resistance by a factor of $2(r_1 + d)/r_1$. Taking $r_1 = 10\,\mu$m and $d = 100\,\mu$m for our two-fibre device, this factor ≈ 20. It is difficult to imagine how a more accurately determined field distribution could increase this factor any further.

Now the lowest quoted value of volume resistivity of polypropylene [13, 14] is $10^{15}\,\Omega$cm, so from Equation 1 the device resistance R falls in the range 10^{17} to $10^{18}\,\Omega$. This is about 10^5 orders of magnitude higher than the highest observed value. The discrepancy cannot be explained in terms of surface resistance effects since the surface resistance of polypropylene is said to be $10^{15}\,\Omega$ [14]. This calculation gives the clearest possible indication that the resistance of the two-fibre device cannot be explained in terms of a homogeneous bulk or surface resistivity for polypropylene (i.e. resistivity values measured over large volumes or areas of polymer).

The transmission optical microscopy revealed that during current flow, the greatest heating and degradation of the polymer did not take place along the shortest path between the fibres. It is argued that this heterogeneous conduction process may be preferentially located at the boundaries of spherulites and that low molecular weight residues, additives etc., which are swept to the spherulite boundaries during crystal growth, may be at least partially responsible for the enhanced conductivity levels. Clearly, this process could dominate in our system where fibre–fibre spacings become comparable to spherulite dimensions, so that small tunnelling or hopping gaps between spherulite boundaries and both electrodes, or even the occurrence of continuous paths along boundaries intersecting both electrodes, are highly probable. In a bulk specimen, the movement of charge carriers would necessitate a cooperative conduction process around a very large number of spherulites and other structural hierarchies. This will lead to much lower conductivity values, because across any path between two electrodes separating bulk material, the probability of occurrence of at least one large gap between adjacent spherulite boundaries will be very high.

When $V = 300$ V the value of E_r just surrounding the first fibre tip, assuming a hemispherical contour ($r = r_1$), would be 300 kV cm^{-1}, in rather good agreement with the tabulated figure [12] for the breakdown field strength in bulk polypropylene. Thus, plausibly, the inflexion in the V–I characteristic at 300 V could be indicating the onset of local breakdown in the vicinity of the first fibre tip. On this model, as the voltage increases, the region in which breakdown occurs grows from the first fibre, as indicated by the growth of the darkened zone of the matrix, until complete breakdown across the entire gap occurs for $V = 1750$ V, as mentioned earlier. However, the value of E_R for $r = r_1 + d$, obtained from Equation 1, is clearly substantially underestimated.

The region over which the bulk of the current flows at the onset of complete breakdown is quite clearly defined optically and also by the thermal imaging camera. Calling the boundary area to this volume S, it will be interesting to estimate the order of magnitude of the matrix temperature T in the vicinity of the breakdown region from the formula

$$T - T_0 \approx (VI/S\sigma)^{1/4}$$

where T_0 is the temperature outside the volume S and σ is Stefan's constant, the heated volume being assumed to radiate as a black body. At final breakdown $V = 1750\,\mathrm{V}$, $I = 1.4 \times 10^{-8}\,\mathrm{A}$ and $S \approx 2.2 \times 10^{-7}\,\mathrm{m}^2$ (area of the cone in Fig. 3j which has a base diameter of $200\,\mu\mathrm{m}$ and a slanting edge of $700\,\mu\mathrm{m}$). So given that $\sigma = 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$, and taking T_0 to be room temperature $\approx 290\,\mathrm{K}$, $T \approx 500\,\mathrm{K}$, close to the softening point (475 K), consistent with the observation that local flow and melting appeared to have taken place.

6. Conclusion

The resistance of a two-fibre device with a polypropylene matrix has been found to be at least five orders of magnitude less than what would be expected from a homogeneous conduction mechanism relating to the bulk or surface resistivity of the polymer matrix. Heterogeneous conduction mechanisms enhanced by the proximity of the fibres are clearly operative and this, presumably, is the reason for the success of bulk fibre-filled composites in providing useful levels of resistivity. However, a $1\,\mathrm{cm}^2 \times 100\,\mu\mathrm{m}$ thick section of bulk polypropylene, with a loading of 5% volume fraction, could contain, at the most, 650 of the two-fibre devices, assuming 1 mm long fibres. Even if these all acted in parallel to minimize the resistance, the resistivity so obtained could not be less than $1.5 \times 10^7\,\Omega\,\mathrm{cm}$ measured across the faces. This is at least five orders of magnitude higher than what has been observed in bulk specimens, and it must be concluded that gaps far less than $100\,\mu\mathrm{m}$, or much smaller tip radii, and perhaps other fibre orientations, are instrumental in producing the observed volume resistivities. To test this reasoning, further efforts are being made to fabricate two-fibre devices with a range of gap lengths, fibre diameters and orientations.

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 Dr Adriaensen of Bekaert Ltd for helpful discussions and the supply of fibres.

References

1. J. GURLAND, *Trans. Met. Soc. AIME* **236** (1966) 642.
2. F. BUECHE, *J. Appl. Phys.* **43** (1972) 4837.
3. D. M. BIGG, *Polym. Eng. Sci.* **17** (12) (1977) 842.
4. *Idem, Compos. Sci. Tech.* **2** (1979) 95.
5. F. L. McCLOUGH, *ibid.* **22** (1985) 3.
6. D. M. BIGG and D. E. STUTZ, *Polym. Compos.* **4** (1983) 40.
7. D. BOTT, *Phys. Technol.* **16** (1985) 121.
8. N. UEDA and M. TAYA, in Proceedings of 5th International Conference on Composite Materials, ICC M-V (1985).
9. B. BRIDGE, M. J. FOLKES and H. JAHANKHANI, *J. Mater. Sci.*
10. H. L. FRISCH, J. M. HAMMERSLEY and J. A. WELSCH, *Phys. Rev.* **126** (1962) 949.
11. M. F. SYKES and J. W. ESSAM, *ibid.* **133** (1964) 310.
12. R. E. BOLZ and G. L. TUVE (eds.), "Handbook of Applied Engineering Science" 2nd Edn (CRC Press, Boca Raton, Florida, 1973) p. 152.
13. *Idem, ibid.* p. 152.
14. G. W. C. KAYE and T. H. LABY, "Handbook of Physical and Chemical Constants", 15th Edn (Longman, London, 1986), pp. 123 and 289.

Received 15 April
and accepted 6 July 1987