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Time-dependent resistivity in carbon fibre sheets

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The electrical properties of sheets of short carbon fibres in resin, glass-fibre and wood-pulp materials have been investigated. For carbon fibre in wood-pulp, a conductor-to-insulator transition was observed at 3 wt% (0.6 vol%) carbon fibre above which conductivity varied linearly with weight fraction. This result is interpreted in terms of a percolation threshold in a system of high aspect ratio. The data agree well with previous measurements on carbon-fibre in polymer composites, and satisfactorily with two-dimensional Monte Carlo calculations. At high concentrations of carbon fibre in all materials, the in-plane resistivity was found to be strongly time-dependent, the fractional change being proportional to $\ln t$. A theoretical model is presented which assumes a continuous increase in the number of interconnecting pathways as fibres physically move together under electrostatic attractive forces. Thermal activation over a continous spectrum of energy barriers leads to logarithmic time dependence as observed experimentally. Studies of the effect of external compression support the model for the time dependence.

1. Introduction

Over the past few years there has been a growing interest in the use of conducting polymer composites for electromagnetic shielding. Conducting fillers used include carbon black, metal flakes, metal-coated glass fibres and carbon fibres. All show an insulator-to-conductor transition characteristic of a percolation threshold at a critical volume fraction of filler. The properties of the various composites have been reviewed by Bigg and Stutz [1]. Carbon fibres have an attraction in that they enhance the mechanical strength of the composite, and for high fibre aspect ratio only a very small volume fraction of filler is needed to produce a resistivity below 100 Ω cm.

Recently composite materials of carbon fibre in resin, fibreglass and wood-pulp have been manufactured by modifications of existing paper-making technologies. These composite materials take the form of thin sheets, typically 0.5 to 2 mm in thickness, containing short lengths of carbon fibre dispersed in the matrix material. Except at very high fibre concentrations in some early formulations, these sheets have excellent handling characteristics and a number of applications for these paper-like materials can be envisaged.

This paper reports the first measurements of the room-temperature d.c. electrical properties of these materials. An unexpected time dependence in the resistivity is shown to be analagous to the time dependence of the relaxation kinetics of metallic glasses [2, 3], remanence magnetism in metallic fine particle systems [4–7] and susceptibility of spin glasses [8].

2. Compositional variation of conductivity

In low carbon-fibre concentration sheets no appreciable time dependence was found for the in-plane conductivity. The conductivity within

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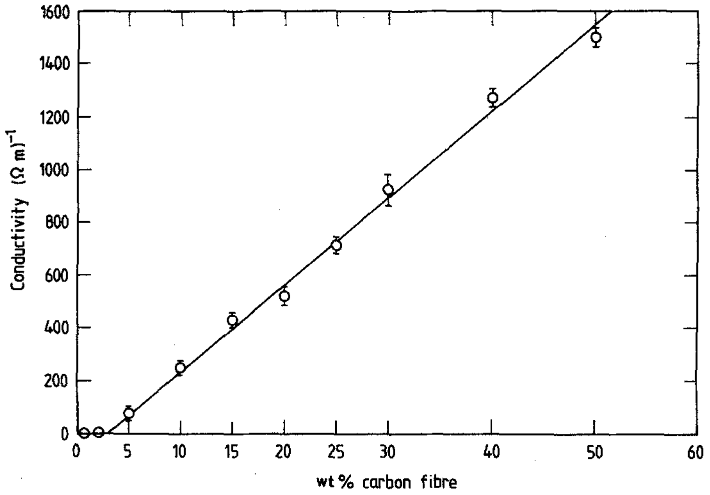

Figure 1 In-plane conductivity against mass fraction of carbon fibre in a wood-pulp matrix.

the plane of the sheet varied widely depending on the type of carbon fibre, the matrix material and manufacturing technique employed. This result is not surprising as it is known that individual carbon fibres exhibit a variation in resistivity of several orders of magnitude depending on the precursor material and the pyrolysis and graphitization steps in the manufacture [9].

For a given class of composite materials containing the same type of carbon fibre in wood-pulp a linear variation in conductivity was observed above the insulator-to-conductor threshold, deduced by extrapolation to be at 3 wt % carbon fibre. (Fig. 1). For all samples below 2 wt %, the conductivity was found to be less than 2×10^{-5} $(\Omega\ \mathrm{cm})^{-1}$.

Very strong anisotropy was found between in-plane and transverse conductivities, the ratio being approximately 2000:1 for the 50 wt % sheet. This quasi-two-dimensional conducting behaviour is not surprising in view of the nearly 550:1 aspect ratio of the fibres which are oriented predominantly in the plane of the sheet, where thickness is typically 1/4 to 2/3 of the fibre length. On the other hand, whilst variations of up to 20% were found for the in-plane conductivity as a function of orientation within individual sheets, no systematic variation with angle was found.

The principal reason for the 20% variation noted above was found to be the small area of contact between the probe and the material surface. This is especially noticeable in low carbon-fibre concentration materials, as here the limited number of fibres protruding from the surface is small and ensuring good electrical contact correspondingly difficult, a feature noted by workers on other conducting composites [1]. Care was necessary to ensure that the contact geometry was kept constant in any one set of comparative studies.

Effective medium theory (EMT) [10], such as developed by Bruggeman [11], predicts that the conductivity σ_t of a multi-phase medium is given by the identity

$$\sum_i \varepsilon_i(\sigma_i - \sigma_t)/[\sigma_i + (n-1)\sigma_t] = 0 \qquad (1)$$

where ε_i and σ_i are the volumetric packing fraction and conductivity of the ith constituent and n is the dimensionality of the system, i.e. $n = 3$ for a three-dimensional system. As the ratio of the conductivity of carbon fibres to dry wood-pulp is $\sim 10^{10}$ we simplify Equation 1 to the form applicable to a two-phase conductor–insulator medium

$$\sigma_t = \frac{\sigma}{(n-1)}(n\varepsilon - 1) \qquad (2)$$

where it is noted that the conductor–insulator transition is given by $n\varepsilon - 1 = 0$. That is, the percolation threshold P_c for a three-dimensional system is anticipated at

$$\varepsilon = \varepsilon(P_c) = \tfrac{1}{3}$$

This is indeed very close to the volume fraction at which the conductor-to-insulator transition occurs in equiaxed carbon fibres in a polymer composite (see Fig. 5 of [1]). However, our

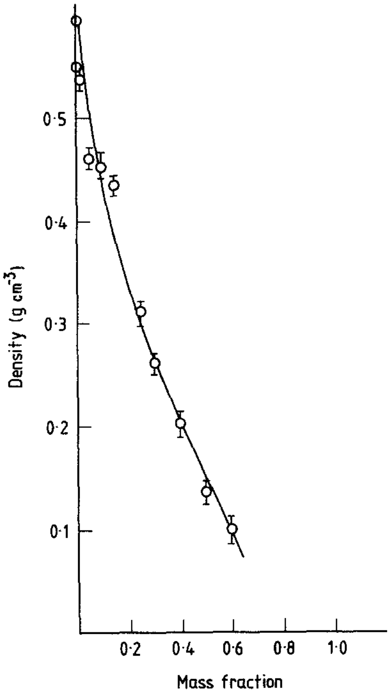

Figure 2 Sheet density against mass fraction of carbon fibre in wood-pulp.

experimental data show that the conductivity varies linearly with mass, not volume as predicted by Equation 2. For an inhomogeneous medium of constant density, mass and volume cannot be proportional.

The densities of the composite carbon-fibre in wood-pulp sheets were determined from their mass, area and thickness. Determination of sheet thickness required that the sheets be placed between light flat plates before measurement with a micrometer to ensure that the fibre sheets were subjected to a minimal, uniform pressure during measurement, as the compressibility of sheets containing a high carbon fibre concentration is large. Sheet densities are presented in Fig. 2. It is seen that nowhere is the total density ϱ_t independent of fibre mass concentration ϕ_c; rather it is a smoothly varying function of ϕ_c, approximately inversely proportional to ϕ_c at high and low concentration and linear in ϕ_c at medium carbon-fibre concentrations. The densities of other fibre sheets manufactured from a different batch of fibre and pulp were also determined and found to lie on a similar but different $\varrho_t : \phi_c$ curve, presumably related to subtle differences in the preparative conditions. We note that the densities shown in Fig. 2 are typically ten to twenty times smaller than that of either carbon fibre or wood-pulp, a direct result of the air voids in the fibrous sheets.

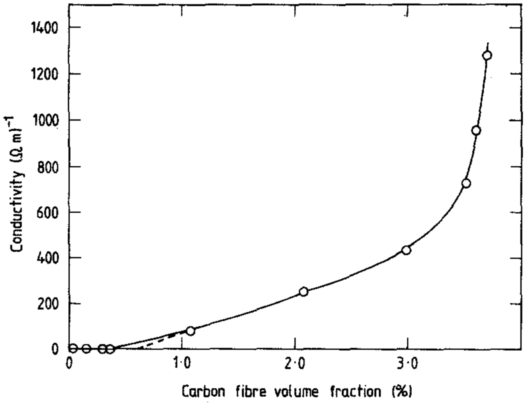

Figure 3 In-plane conductivity against volume fraction of carbon fibre in wood-pulp.

Fig. 3 shows the variation of conductivity as a function of carbon-fibre volume fraction. While there is a temptation to fit a straight line to the three higher data points, it is clear that when error bars are regarded the conductivity varies monotonically, but non-linearly with volume fraction. Further the conductor-to-insulator transition lies at a very small value of volume fraction, definitely above 0.4% and between this value and about 0.6% depending on the exact extrapolation technique used.

In order to explain the onset of conduction at this small volume fraction, bond percolation theories must be used [10]. The problem of conduction in a system of rods arranged at random has been treated in two dimensions by Pike and Seager [12, 13] using Monte Carlo methods. They found that, assuming conduction to take place by physical contact between rods, percolation occurred when

$$L(\pi N_s)^{\frac{1}{2}} \geqslant 4.236 \tag{3}$$

where L is the length of the rod and N_s is the density of rod sites, assumed random. There was, in contrast to similar calculations for circles or squares, no critical area fraction as the rods used in the model were infinitely thin. However, for a high ratio of the length L to the width D, the result still holds valid for rods of non-zero area. Here a critical area fraction exists. The area fraction A is given by

$$A = L\,D\,N_s \tag{4}$$

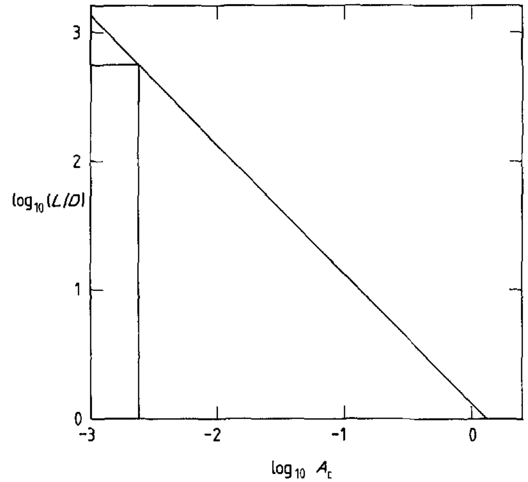

Figure 4 Critical area fraction against aspect ratio for two-dimensional rods with non-zero area oriented at random.

and percolation occurs above a critical area fraction A_c given by substitution of Equation 4 into Equation 3. Thus

$$(L/D)\,A_c = 1.35 \qquad (5)$$

at the percolation threshold.

This result is represented graphically in Fig. 4 and we note the resemblance to the curve given in [1]. The fibres used in the materials studied by us had an aspect ratio of 550:1 and we see that the model predicts a critical area fraction of 0.25%. If we assume that the sheets are made up of a series of equivalent non-connected sheets of thickness D then the critical volume fraction is 0.25%, in reasonable agreement with our measured value. While the two-dimensional approximation inevitably breaks down at low fibre aspect ratios (see Fig. 4 and compare with EMT results) the high anisotropy of conductivity measured in these sheets suggests that it is a very reasonable approximation. Seager and Pike [13] also point out that the percolation threshold is critically dependent on the degree of randomness of the rods. If one has a system of aligned, high aspect ratio rods, the percolation threshold will be very much higher than that of an identical system with rods oriented in random directions. The lack of a systematic variation in conductivity with in-plane orientation suggests that the fibres in the present samples are close to the random orientation condition.

It is interesting to note that close to the percolation threshold spatial fluctuations in local conductivity may be observed directly. Central to the "bond" percolation model of two-phase conductor–insulator media is the percolation probability. This is the probability that a given conducting region is connected to the main network of conducting paths, and it may or may not be itself part of the current-carrying path. That is, it may be on a dead-end branch. Thus just below the critical volume fraction large areas of conducting material may be connected, without there actually existing a conducting path through the whole sample. This is observable for fraction $\phi_c = 2\%$ which, whilst non-conducting over a length of 140 mm, has a variable local conductivity below lengths of 10 mm.

3. Time dependence of the resistivity

3.1. Experimental observations

Samples containing more than 60 wt % of carbon fibre exhibited a decrease of the in-plane resistivity as a function of measurement time. The fractional variation was found to be proportional to the logarithm of the measurement time. An example of data taken over a four-minute period is shown in Fig. 5. The gradient of the $\Delta\varrho/\varrho$ against $\ln t$ plot was found to be approximately independent of current.

As electrical contact with the carbon-fibre–glass-fibre sheet was made with spring-loaded contacts a variety of contact types and geometries were investigated. Increase of contact area did lead to a modest decrease in absolute sample resistance, but logarithmic time decay continued.

Samples exhibited a curious "memory effect" when the current was intermittently broken. Fig. 6 shows that on re-connecting the circuit, the resistivity was found to have the same value as it would have had if the circuit had not been broken and current had continued to flow uninterruptedly. Similarly on reversal of the current, the magnitude of the voltage continued to decay logarithmically, independent of direction of current flow. Periodic reversal gave a voltage–time trace in which the current-reversed section was a mirror image of what it would have been if current reversal had not occurred.

3.2. Theoretical model

Whatever mechanism is responsible for the time dependence of the resistivity, it must continue to be effective when the circuit is broken; it must

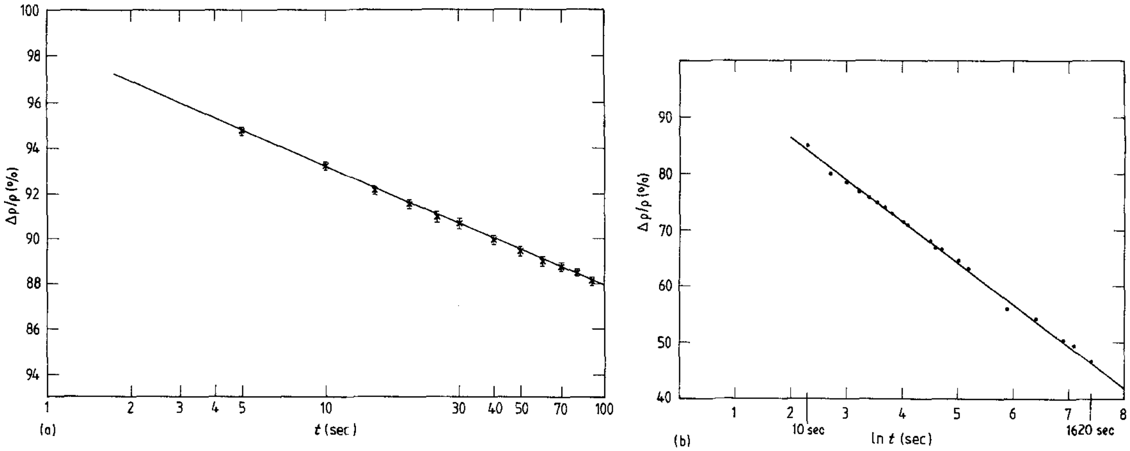

Figure 5 Fractional variation in resistivity as a function of the logarithm of time since current was first passed: (a) carbon fibre in resin binder, (b) stainless steel fibre in binder.

operate independently of the direction of current flow and give a logarithmic decay of resistivity with time. The latter can be explained in a perfectly general manner and is observed whenever a distribution of energy barriers is swept out by thermal activation [2]. While we suggest here a specific mechanism for the time dependence, it should be noted that the arguments for the ln$t$ decay are quite general.

We propose that the decreasing resistivity (increasing conductivity) arises due to the gradual increase in the number of connecting pathways through the material arising from touching of adjacent carbon fibres. Our model for the time dependence is one in which new conduction paths are formed by the formation of new links due to the attractive electrostatic force arising from opposite charge on adjacent non-touching elements. As time dependence of the in-plane resistivity is not observed for medium and low fibre-concentration composites, we may exclude consideration of the intrinsic resistivity of the fibres themselves.

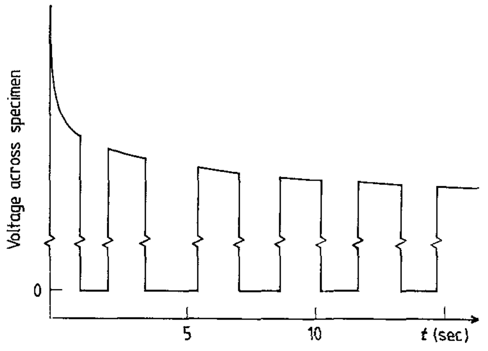

Figure 6 Voltage across sample (proportional to resistance) as a function of time with interruptions in the current supply.

Resistance to such fibre motion occurs due to the presence of resin, wood-pulp or glass fibres. The attractive force still exists if the current is interrupted and the sheet left in open circuit and is always attractive, irrespective of the sense of current flow. The general nature of the phenomenon is further demonstrated in the data of Fig. 5b. This shows ln$t$ kinetics in a sheet of stainless steel fibres in binder. The resistances of the carbon fibre and stainless steel sheets differed by several orders of magnitude, and the fractional change in the stainless steel sheet was very much larger than in the carbon fibre material. This may be due to the lower stiffness of the stainless steel fibres compared to the carbon fibres.

Following Gibbs and co-workers [2, 3] we assume that a broad range of energy barriers exists and that new links are made by thermal activation over these barriers. The change in resistivity associated with activation over an energy barrier of height between E and $E + \mathrm{d}E$ is denoted $\varrho(E)$. However only a macroscopic change in resistivity $\Delta\varrho$ can be measured, associated with excitation over *all* energy barriers up to an energy shown in [2] to be

$$E_0 = kT\ln(\nu_0 t) \qquad (6)$$

Here ν_0 is a characteristic frequency and t is the time from the beginning of the experiment. This abrupt cutoff in the energy spectrum is a valid approximation because of the very rapid variation in the time t for excitation over a barrier with the barrier height E_0. The excitation time is given by reorganization of Equation 6, i.e.

$$t = \tau_0 \exp(E_0/kT) \qquad (7)$$

from which it is seen that the characteristic time can vary by many orders of magnitude for a relatively small change in E. Since t defines the time of the experiment, and is restricted to a few orders of magnitude, the step function cutoff is usually valid. In contrast, an example where such an approximation is not valid for thermal excitation over an energy barrier is the dependence of the isothermal remanent magnetization of a fine particle system, examined, both experimentally and theoretically, by Chantrell, Hoon and Tanner [5]. Upon the basis of the step function cutoff model the macroscopic resistivity change $\Delta\varrho$ is given by

$$\Delta\varrho = \int_0^{E_0} \varrho(E)\mathrm{d}E \qquad (8)$$

and assuming that $\varrho(E)$ does not vary over the range of energy barriers swept out during the course of the experiment we have

$$\Delta\varrho = \varrho(E)kT \ln(\nu_0 t) \qquad (9)$$

This ln$t$ dependence is analogous to that found in the remanence magnetization of frozen ferrofluid systems [4]. As stated before, thermal activation over a broad spectrum of energy barriers leads quite generally to "ln$t$ kinetics" [2], regardless of the specific mechanism. The present experiments provide just one more example of a system obeying such a law.

4. Compression studies

If the time dependence of the resistivity has its origin in the movement of individual fibres, then the compression of the composite material by dead-weight loading should not only change the value of the resistivity due to the decrease in separation of fibres but also the time dependence. As the material creeps under the dead-weight pressure, so the resistivity will fall, but in a different way to the ln$t$ dependence associated with the thermal activation processes suggested above.

Experiments were performed using large-area electrodes to measure the out-of-plane (transverse) resistance as a function of time under various static loads. Despite the transverse resistivity being three orders of magnitude higher than the in-plane resistivity, due to the larger cross-section and much smaller separation of electrodes, the measured resistance was small. Significant time dependence was seen in the transverse resistance even at low carbon-fibre concentrations.

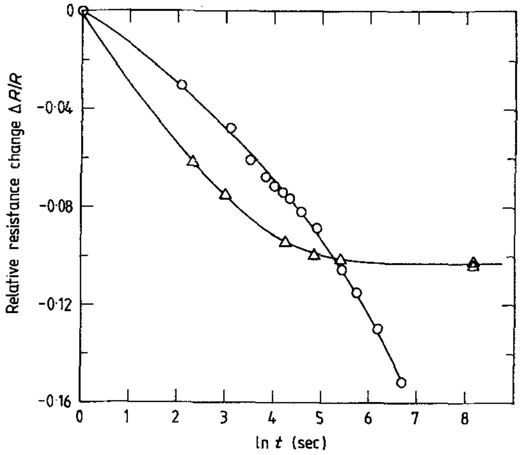

Figure 7 Relative change in transverse resistance as a function of the logarithm of time under 8.5 kPa pressure: ○ 5 wt %, △ 50 wt % carbon fibre in wood-pulp.

Fig. 7 shows the effect of 8.5 kPa pressure on 5 and 50 wt % carbon fibre in wood-pulp sheets. In both cases the time dependence now deviates from the "ln$t$ kinetics". For the 5 wt % sheet the deviation from linearity with ln$t$ is in the opposite sense to that of the 50 wt % sheet. Complete suppression of the time dependence of the transverse resistance occurred above 25 kPa for the 50 wt % sheet.

While it is clear in both cases that the ln$t$ kinetics are modified, the different curvature suggests that different processes are occurring in the low and high carbon-fibre content sheets. This was investigated by measuring the resistivity as a function of applied pressure at a well-defined time (one second) after the application of the pressure. Between pressure increments the pressure was reduced to zero. The 5 wt % sheet showed a monotonic decrease in the fractional change in transverse resistance $\Delta R/R$ as a function of pressure (Fig. 8). Changes were reversible. In contrast the 50 wt % sheet showed a marked hysteresis, though a similar monotonic decrease with pressure (Fig. 9). Pressure applied to the sheet had very little effect on the in-plane resistance, confirming the deductions about the quasi-two dimensional nature of the in-plane

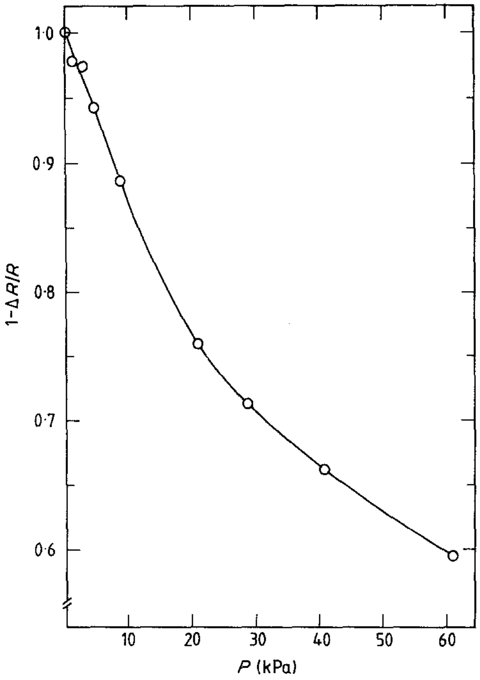

Figure 8 Fractional change in transverse resistance (measured one second after pressure application) as a function of pressure for 5 wt % carbon fibre in wood-pulp.

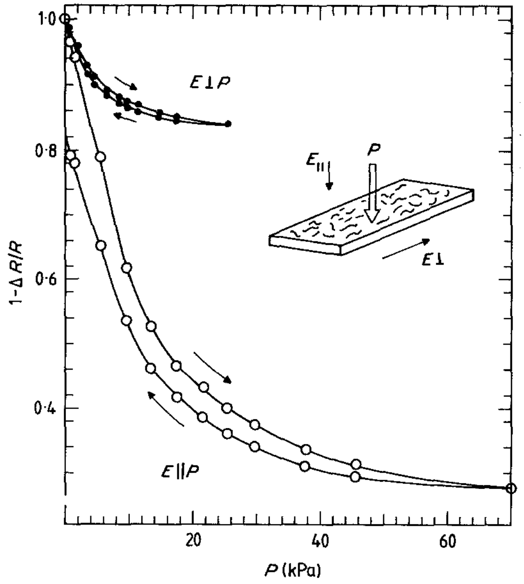

Figure 9 Fractional change in transverse and in-plane resistance of several sheets of 50 wt % carbon fibre in wood-pulp: ● in-plane, ○ transverse.

conduction process referred to earlier. We note that hysteresis again occurred for the in-plane resistance. In both cases the resistance on the return path was less than on the initial compression, indicating that inelastic compression of fibres had taken place.

Under very high pressure, however, processes were observed where the hysteresis was in the opposite sense, i.e. the resistance increased on release of pressure. An example of this effect is given in Fig. 10, which shows the effect of compressing several sheets of 50 wt % composition, and total thickness 0.71 mm, between the jaws of a vice. The transverse resistance fell as expected but increased by 100% on release of the compressing jaws. When reduced to conductivity through the well-known relation $R = l/A\,\sigma_t$, we find that a broad maximum in conductivity occurs at a compression of about 0.2 mm (i.e. 30%). This is shown in Fig. 11.

The conductivity maximum cannot be explained in terms of effective medium theory. Because of the very large volume fraction which is air void, we can approximate Poisson's ratio to be zero in these materials. Then the volume fraction of conducting material ε in sample thickness l will be related to the critical volume fraction ε_i of uncompressed sample of thickness l_i by

$$\varepsilon l = \varepsilon_i l_i \tag{10}$$

Using Equation 2 we have

$$\sigma_t = \frac{\sigma}{(n-1)}\left(\frac{n\varepsilon_i l_i}{l} - 1\right) \tag{11}$$

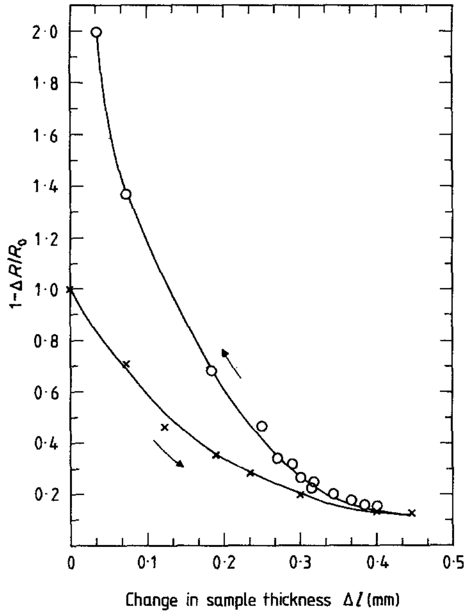

Figure 10 Fractional change in transverse resistance of several sheets of 50 wt % material as a function of decrease in thickness during compression.

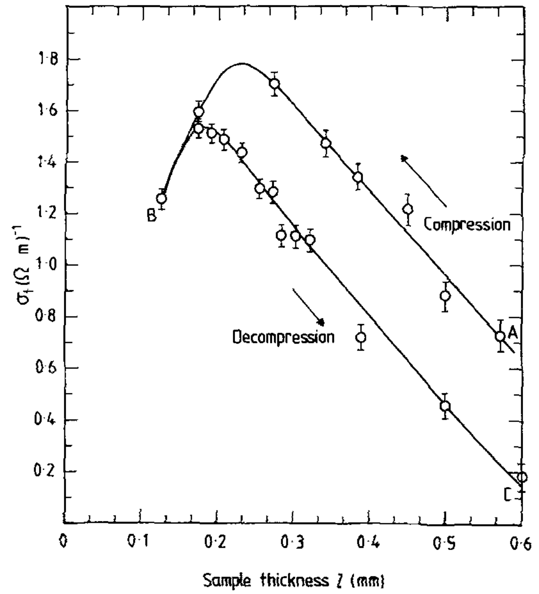

Figure 11 Conductivity as a function of the sample thickness taken from the data of Fig. 10. Compression sequence A to B, decompression B to C.

This is a monotonically varying function, with σ_t increasing as the specimen thickness is reduced. Plotted as a function of the reciprocal of the thickness (Fig. 12) a good linear fit is found only for the latter stages of the decompression sequence, labelled B′ to C in Fig. 12. We suggest that the conductivity fall at high compression arises from straightening of the out-of-plane fibres which link the quasi-two dimensional conducting sheets, which one can see from optical microscopy studies make up a large proportion of the material. As these out-of-plane fibres are compressed into the plane, the number of cross-links decreases, resulting in a fall in conductivity. On decompression due to a non-zero relaxation time for recovery, the conductivity σ of the decompression sequence is less than that observed initially. We note that irreversible breakage of fibres cannot be occurring, as after a period of about three hours the initial conductivity was regained, and on a subsequent compression the curve A to B was retraced.

Extrapolation of the curve of Fig. 12 to the intercept $\sigma_t = 0$ yields a thickness of approximately 0.83 mm at which the conductivity is zero. This thickness corresponds to that at which no interconnecting pathways occur on hypothetical *expansion* of the material. It is another type of percolation threshold.

5. Conclusions

The electrical properties of carbon fibre in wood-pulp composite materials have been seen to have a conductor-to-insulator transition at a critical volume fraction which is in reasonable agreement with that predicted from two-dimensional bond percolation calculations. In a survey of work on conducting polymer composites, Seager and Pike [13] note a wide range of critical volumes which are very sensitive to the exact material preparation conditions. In this context the present agreement is very good.

The appearance of ln$t$ kinetics in the time dependence of the resistivity is yet another example of what has now been recognized as a very widespread phenomenon. Although thermal activation over a spectrum of energy barriers

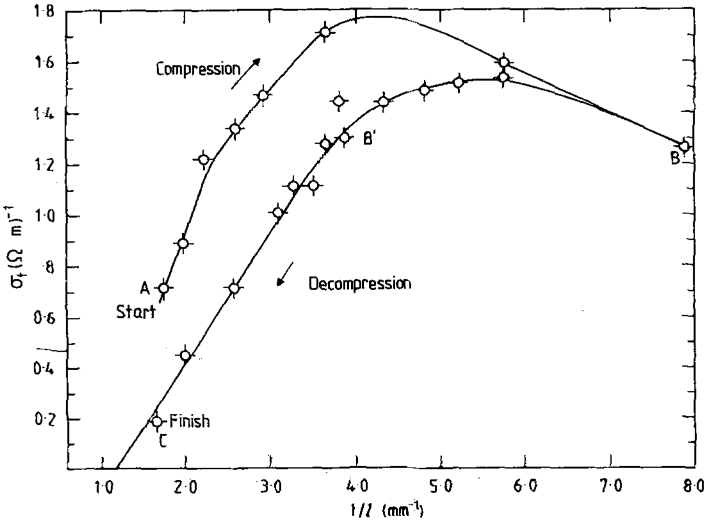

Figure 12 Conductivity against reciprocal of sample thickness.

caused by any mechanism would account for the ln t kinetics, our compression studies strongly support the concept of fibre movement under electrostatic forces leading to an increase in the number of percolation pathways through the material.

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References

1. D. M. BIGG and D. E. STUTZ, *Polym. Compos,* **4** (1983) 40.
2. M. R. J. GIBBS, J. E. EVETTS and J. A. LEAKE, *J. Mater. Sci.* **18** (1983) 278.
3. M. R. J. GIBBS and J. E. EVETTS, Proceedings of the 4th International Conference on Rapidly Quenched Metals, Sendai, 1981, Vol. 2, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, 1982) p. 479.
4. A. T. CAYLESS, S. R. HOON, B. K. TANNER, R. W. CHANTRELL and M. KILNER, *J. Magn. Mag. Mater* **30** (1983) 303.
5. R. W. CHANTRELL, S. R. HOON and B. K. TANNER, *ibid.* **38** (1983) 133.
6. G. E. FISH, V. R. V. RAMANAN, R. HASEGEWA and A. C. DIEBOLD, *IEEE Trans. Magn. MAG 19* (1983) 1937.
7. D. J. DUNLOP, *J. Geophys. Space Phys.* **40** (1974) 439.
8. C. N. GUY, *J. Phys. F* **7** (1977) 1505.
9. I. L. SPAIN, K. J. VOLIN, H. A. GOLDBERG and I. L. KALNIN. *Solid State Commun.* **45** (1983) 817.
10. R. LANDAUER, *AIP Conf. Proc.* **40** (1978) 2.
11. D. A. E. BRUGGEMAN, *Ann. Phys.* (*Leipz.*) **24** (1935) 636.
12. G. E. PIKE and C. H. SEAGAR, *Phys. Rev* **B 10** (1074) 1421.
13. C. H. SEAGAR and G. E. PIKE, *ibid.* **B 10** (1974) 1435.

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