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DC electrical conduction phenomena in fibre reinforced composites

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ABSTRACT: A programme of experiments designed to examine several aspects of the DC conduction properties of metal fibre filled thermoplastics, is described. It is shown that the inclusion of less than 1% volume fraction of stainless steel fibres in a polypropylene matrix is sufficient to realise volume resistivities of less than 1Ω cm. The application of percolation models of conductivity based on the assumption of kinked or curved fibre trajectories are considered, and it is shown that non-uniform sample heating caused by poor particle dispersion can be readily identified by infrared imaging. Model samples consisting of two fibres embedded in a thin layer of polypropylene were subjected to simultaneous electrical measurements, thermal imaging, and optical microscopy. The data suggested that spherulite boundaries constitute the most likely path of charge transfer between the fibres and that the dielectric strength of a spherulite is many times that of the bulk polymer.

1. INTRODUCTION

The incorporation of short, electrically conducting fibres into thermoplastics to provide enhanced levels of conductivity in the resulting composite is an area of growing industrial importance (Bigg 1977, Bigg 1979, Wehrenberg 1982, Bigg and Stutz 1983, McCullough 1985). Even at concentrations as low as 0.5% volume fraction, it is known that stainless steel fibres for example, can be used in thermoplastics to give a range of moulding compounds having useful levels of DC conductivity and electromagnetic shielding properties. As such they are widely used, especially for business machine housings and other applications where sensitive microelectronic circuits must be protected from stray electric fields. Of special note we may cite the deployment of these materials in the shielding of defence installations against electromagnetic pulses and their use in stealth technology, i.e. the provision of minimal radar profiles for military aircraft and naval vessels.

Our studies have been concerned with developing a fundamental understanding of the conduction process in stainless steel fibre, reinforced polypropylene and polycarbonate. Ideally a theoretical model should allow one to predict what combination of fibre properties (e.g. length, aspect ratio, volume fraction) and polymer morphology, will produce the desired perfomance in a specified application, at the least cost. The realisation of

2. OVERALL STRUCTURE OF THE PROGRAMME

The approach adopted in tackling this multi-variable problem has been to separate the variables as much as possible and then to study systematically the effect of each variable in turn. The obvious first step is to limit observations to measurements of DC conductivity as a function of the structural variables. To a first approximation AC behaviour can then be predicted by substitution of the DC conductivity into Maxwell's electromagnetic field equations. However this approximation may fail dramatically at high frequencies where fibre dimensions and gaps may no longer be negligible compared with the electromagnetic field wavelength. At lower frequencies too, significant deviations in behavour from the predictions of the first order approximation may occur for two reasons. Firstly, the fibres will form a complex network of inductors and capacitors, thus producting a reactive component to the sample impedance across two given terminals. Secondly the dielectric constant and loss tangents of the polymer matrix will be frequency dependent and may vary locally with the polymer morphology. For this reason in the later stages of our programme AC impedance measurements will be carried out in the range 4 HZ - 120 MHz using automatic swept frequency impedance analysers.

Our present discussion will subsequently be restricted to reports on the progress of DC measurements to date on polypropylene based specimens. Summaries of several experiments (B Bridge et al 1987a - 1987d) are described, using injection-moulded samples in the form of rectangular 80 mm x 80 mm x 3 mm thick plaques, and idealised devices consisting of just two fibres embedded in a thin layer of thermoplastic. The only possible variable affecting the voltage-current characteristic of a 2-fibre device is the polymer microstructure. Thus the use of these devices has proved to be an elegant method of isolating the effects of polymer morphology from those of the fibre properties, in the study of the mechanism of charge transfer from one fibre to another.

3. INFRARED IMAGING OF CURRENT DISTRIBUTIONS IN NON-UNIFORM COMPOSITES

The production of completely uniform bulk samples of fibre filled composites is a major problem. Whilst the processing variables can be optimised to produce mouldings which are mostly uniform, random local fluctuations of fibre concentration are still likely to occur, if only infrequently. Often non-uniform dispersions will not prejudice the attainment of a desired level of volume resistivity in the sample as a whole, and furthermore high frequency shielding performance will be unaffected if the wavelength is long compared with the spatial period of the fluctuations in fibre concentration. However poor dispersion is disadvantageous in that locally high Joule heating may arise even when the overall power input into the sample is within normal operating limits, at which the mean rise in sample temperature is considered acceptable. Local hot spots are serious in that irreversible changes in the electrical performance of the sample may be caused either by structural changes in the polymer matrix, changes in the fibre-matrix interfacial bonding by differential expansion, or changes in the fibre trajectories caused by the same.

We have shown that local variations in sample temperature caused by non-uniform dispersions can be detected directly by non-contact infrared

allowed electrodes to be applied to two opposite end faces of the plaques with a controllable contact pressure. The end faces were also coated with a thin layer of conducting paint. Images obtained during simultaneous passage of current through the plaques, were displayed as computer print-outs with a 16 tone colour scale (black through to pale yellow), spanning a temperature difference of approximately 3.2°C in 0.2°C intervals. Figure 1 gives a monotone reproduction of a thermal image in a case where a pronounced hot spot with dimensions of a few mm, was obtained. The interesting feature of this hot spot is that it did not correlate with extremes in fibre concentrations. Thus it would be difficult to predict temperature variations from direct measurements of fibre distributions, for example by optical methods if the samples are transparent, or by radiographic methods. Therefore it seems that the infrared technique is the best method of diagnosing problems that may arise from non-uniform sample heating.

We have devised an idealised electric network (Figure 2) which contains the minimum number of resistances required to simulate approximately the electrical behaviour of a composite consisting of a uniform fibre distribution, apart from a central region. Network analysis shows that a central cold spot will exist if the fibre loading there is abnormally high or low, but a hot spot will exist if the fibre concentration is slightly less than normal. The network model can be improved by increasing the number of elements to the extent that the physical size of the mesh is comparable with the spatial period of any fluctuations in fibre distribution. Computer techniques could then be employed to solve the network equations.

4. LOW VOLTAGE CHARACTERISTICS

By the use of very low power inputs to eliminate all possibilities of local temperature changes caused by non-uniform fibre distributions, a set of plaques have been established to be ohmic conductors (Bridge et al 1987c). Using fibres supplied by BEKAERT (Beki-shield product code 1/4B/e9/6), with nominal lengths and diameter of 6 mm and 6.5 μm respectively, resistivities ranging from 12 to 0.6 Ω cm were obtained for fibre volume fractions ranging from 1 to 3%. A programmable voltage source controllable in intervals of 1 μV down to a level of 50 μV (KEITHLEY instruments model 230), was employed for these low level measurements. The result is of note because it is not obvious that Ohm's law should be obeyed. A completely uniform material can be described as a simple thermodynamical system which is specified by just two independent variables and such a system obeys Ohm's law. However the composites under consideration by us do not even approximate to such a system. Mechanisms by which non-ohmic conductivity could have taken place are quantum mechanical tunnelling between fibres almost in contact (Simmons 1963, Simmons 1964, Sheng 1980, Sherman et al 1983, Soukoulis et al, 1983), and field emission from individual fibres into the matrix. Plausibly these processes may make a significant contribution to the current flow between fibres if very intense local electric fields are present round rough fibre surfaces. However, clearly these mechanisms were of little importance in the samples considered by us.

5. PERCOLATION MODEL OF SAMPLE CONDUCTIVITY

A sharp change in the dependence of the resistivity of the plaques on fibre volume fraction occurs when the volume fraction is about 1%. A

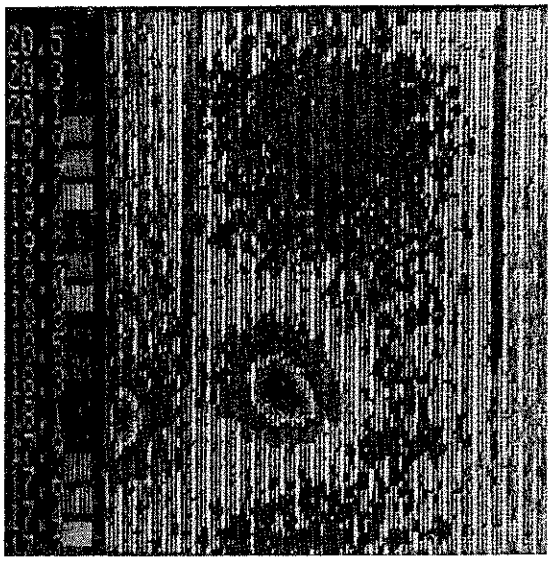

Fig. 1 Infrared image of an 80mmx80mmx 3mm polypropylene plaque containing 1% volume fraction of steel fibre, current = 6mA, resistivity 88 Ωcm.

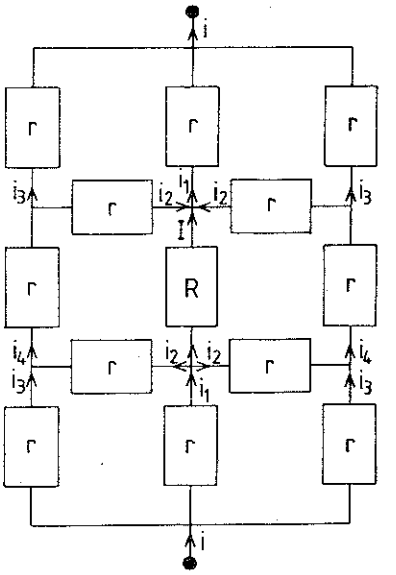

Fig. 2 Simple network simulating the electrical behaviour of a composite with a local variation in an otherwise uniform fibre distribution

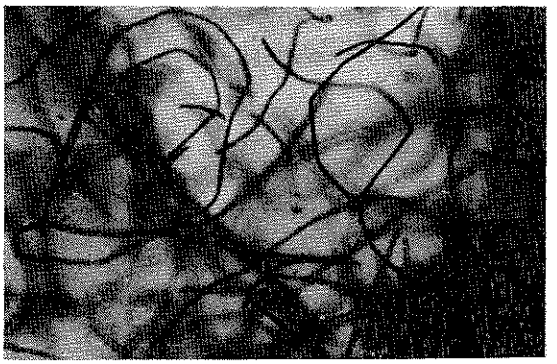

Fig. 3 Typical fibre trajectories in a 1000μm wide section of the composite illustrated in Fig. 1

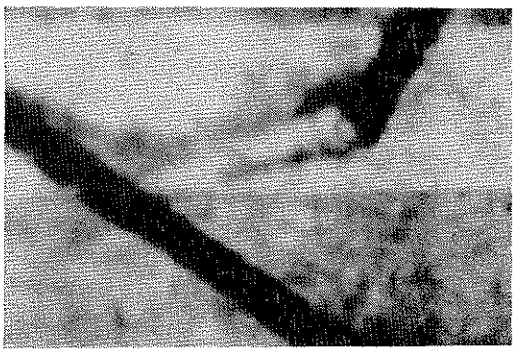

Fig. 4 Heterogeneous conduction phenomena between two fibres embedded in a polypropylene bead. Fibre diameter 22μm, potential difference = 1250V, current = 10^{-8}A.

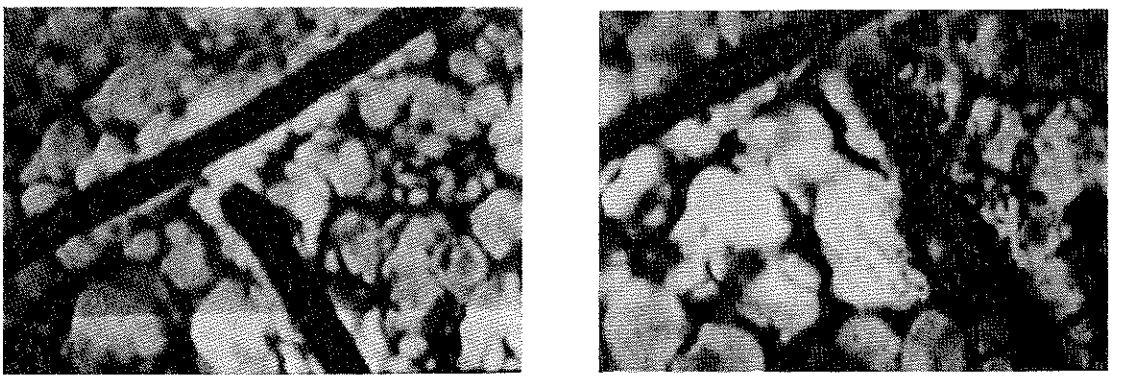

Fig. 5 Two fibre device in which the polypropylene morphology has been controlled so that a spherulite fills the entire fibre - fibre gap of 20um.

common assumption in the literature is that such changes are caused by the onset of percolation conditions, i.e. the formation of continuous chains of contacting fibres running across the sample from one electrode to the other (Frisch et al, 1962, Sykes and Essam, 1964, Gurland 1966, Malliaris and Turner, 1971 Veda and Tays 1985, McCullough 1985). However it is easy to show that if the fibres remained straight, as they were prior to extrusion, the probabilities of such chain formation is infinitesimal at the low volume fractions under consideration. Detailed microscopic examination (Figure 3) of multiple planes in semi-transparent plaques showed, in fact, that the majority of the sample fibres followed curved or sharply kinked paths in three dimensions with radii of curvature typically much smaller than the mean fibre length, which was about 500 μm. A reasonable first order approximation for the description of the fibre trajectories is to assume them to be of helical form. The probability of contact between two helices with adjacent parallel axes separated by one helix diameter is quite high, even though the volume fraction occupied by the fibres remains small. Detailed calculations (Bridge et al 1987c) show that, for an assembly of helices of identical diameter and pitch (the pitch being equal to the diameter), a percolation threshold at 1% volume fraction could be explained by assuming a diameter of 145 μm. Correspondingly a sample resistivity of about 4×10^{-2} Ω cm would arise, assuming that each helix contact each of two neighbours in just one place. This theoretical resistivity is just two orders of magnitude less than the observed value. To explain the discrepancy we need only assume that only a small fraction of the contacts that are statistically possible on the above model, actually take place. This is easy to explain, for example, on the assumption that the size coating binding together the original fibre bundles, is still partly intact.

6. EXPERIMENTS ON TWO-FIBRE DEVICES : HETEROGENEOUS CONDUCTION PHENOMENA

The voltage-current characteristics of a number of twin-fibre devices were measured with the aid of a 5 - 5 KV power supply (BRANDENBURG Alpha Series II, 5 mA, ±5% measurement precision), and an electrometer (KEITHLEY model 614, 20 pA to 2 mA, corresponding measurement precision 10 fA to 1 μA). Simultaneous changes in the polymer microstructure were observed using a transmission optical microscope (LEITZ model Laborluz D) coupled to a large colour TV monitor and video recording facility. Results on fibres of 22 μm diameter (BEKAERT Bekinox VS 22/250/1000 CR) orientated perpendicularly in 'T' configurations, will be discussed here. In early experiments no special care to develop a specified morphology in the polypropylene, was exercised. The low voltage resistance of a device with a 100 μm fibre gap was found to be five orders of magnitude lower than the value calculated from electrostatic theory, using tabulated values of volume resistivity for polypropylene (Bridge et al 1987b). Furthermore, the spherically symmetric electric field assumed in this calculation, yielded a lower bound for the theoretically predicted resistivity. The conclusion was that non-uniform conduction must have been taking place, with specific paths between the fibres existing, along which local resistivity values much lower than accepted values for the bulk material, must exist. Support for this argument was found in the observation that at higher applied voltages the greatest heating and degradation of the polymer did not take place along the shortest path between the fibres where the electrostatic field was at its greatest (Figure 4). The [illegible]

such impurities may at least be partially responsible for the enhanced conductivity levels.

7. EFFECT OF CONTROLLING THE POLYMER MORPHOLOGY

To test these assumptions a new experiment was performed in which the polymer morphology was controlled so that a 20 μm gap between two fibres was completely filled with a spherulite (Bridge et al 1987d) (Figure 5), ie. almost pure polypropylene. For an applied potential difference of 1800 V, the first indications of local flow in the matrix due to Joule heating, became discernible, and this occurred to the side of one fibre, well away from the fibre - fibre gap. This mobile zone grew as the potential difference was increased to 3500 V, and the conclusion was that as in the earlier experiments, current flow took place predominantly, not along the shortest path, which was obstructed by a spherulite, but along a circuitous route defined by spherulite boundaries. Indeed the lack of structural changes in the fibre - fibre gap was striking, given that the field strength in the region of one fibre tip reached an estimated value of 5 MV cm^{-1}, some 18 times the tabulated value of the bulk dielectric strength of polypropylene. The interesting conclusion of this result is that the dielectric strength of a pure single crystal of polypropylene, exceeds 5 MV cm^{-1} and that breakdown in ordinary bulk polycrystalline polypropylene takes place by conduction round the grain boundaries. From this result possible device applications spring to mind. By ensuring that the ends of a two fibre device penetrate well into a single spherulite it should be possible to make resistors of high but controlled resistance values, small volume, and the ability to withstand unusually high voltages without breakdown.

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