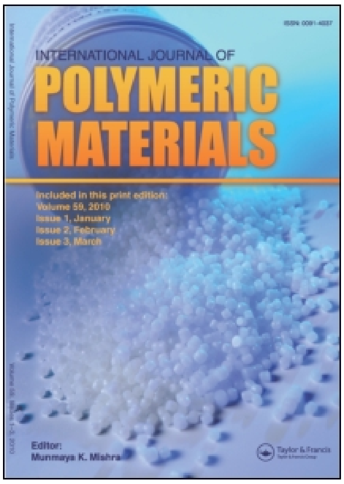

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About Some D-C Conduction Processes in Carbon Black Filled Polymers

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The conductive properties of carbon black filled polymers have already found many qualitative applications while quantitative ones remain infrequent because of the number of unexpected parameters which influence the conductance of samples of the material. We have tried to connect the anomalous electrical behaviour of such materials with three particular phenomena which influence d-c conduction:

—Percolation, which is a process expected to occur in mixtures of conducting and insulating solids.

—Volumic polarization and ionic heterocharge near the electrodes which supply a new explanation for the variable contact resistance.

—Filamentary conduction and localized thermal effects which produce under some conditions, regions of negative resistance in the current-voltage characteristics of samples.

Possible electrical applications for filled polymers are deduced from this analysis.

Les propriétés conductrices des polymères chargés de noir de carbone trouvent actuellement des utilisations beaucoup plus qualitatives que quantitatives: les variations inattendues de la conductance des échantillons, en fonction des paramètres les plus divers, en sont la cause. Aussi nous avons essayé de relier les anomalies de conduction de ces matériaux à trois types de phénomène:

—La percolation qui est un processus propre aux solides hétérogènes constitués d'une phase isolante et d'une phase conductrice.

—L'apparition, près des électrodes, d'une densité volumique de charge créant une polarisation spatiale qui pourrait faire intervenir des ions et qui expliquerait les inévitables et imprévisibles résistances de contact.

—La conduction filamentaire et les effets thermiques localisés responsables de phénomènes de résistance différentielle négative observés sur les caractéristiques courant–tension de certains échantillons.

Quelques reflexions concernant les extensions possibles des applications électriques des polyméres chargés sont déduites de cette étude.

I INTRODUCTION

The fact that polymeric materials are usually very good electrical insulators has been appreciated for a long time. However, while this makes them very suitable for many applications, for others, it has many drawbacks. In particular, in these insulating materials, static electricity formed by involuntary rubbing cannot flow and the consequences are dust attraction, disagreeable electrical discharge when touched and incendiary sparks when in the vicinity of inflammable gas, liquid or dust. Besides, considering the many useful physical and chemical properties of polymeric materials (lightness, easy fabrication, resistance to corrosion and chemical products) it would be interesting to extend their use to other kinds of materials than just insulators.

In fact, non-insulating polymeric mixtures are already employed as antistatic materials while semiconducting polymeric mixtures now find an application in high-voltage coil technology. It has been noted, that breakdown in high voltage coils is connected with the accidental separation of the conductor from the insulator which occurs when the coil experiences mechanical strains. In the interstice so formed, the electric field initiates Corona discharges which cause the deterioration of the insulator.

To prevent this, the insulating polymer of the coaxial coil is embedded in a layer of semiconducting polymeric mixture before it is wrapped by the copper tress. In this way, no electric field appears in the space between the polymer surface and copper tress which are therefore at the same potential.

Since, non-insulating polymeric materials are of interest for many electrical applications, this paper is concerned with d-c conduction processes in carbon black filled polymers which present many anomalous and as yet incompletely explained properties.

In Section II, we recall how the conductance of filled polymers increases with the concentration of conductive filler and how an explanation for this may be provided by percolation theory. In Section III, we present voltage distribution measurements obtained along samples of filled PVC and rubber which provide evidence for a volumic charge distribution, near the electrodes, which increases the apparent resistance of the material. Section IV deals with localized thermal effects and with the current controlled negative resistance observed in filled PVC. Finally, the conclusion presented in Section V deduces from this study the conditions which must be satisfied to make, from carbon black filled polymeric materials, linear components with a constant and reproducible conductance.

II CONDUCTION AND PERCOLATION

The method currently used to increase the electrical conductivity of polymers, is to fill them with conductive powders, such as metallic powders and carbon black. However, a high concentration of filler is necessary to obtain an appreciable increase in conduction and a transition from insulating to non-insulating behaviour is generally observed when the volumic concentration of conductive filler in the mixture reaches a threshold of about 25%. Such a value indicates that, to first approximation, the electrical properties of semi-conducting filled polymers are connected with theories of mixtures of two passive conducting and insulating solids rather than with the phenomena occurring in doped crystalline semiconductors where one is dealing with impurities concentrations of only a few p.p.m.

In fact, in an insulating matrix containing randomly dispersed conductive particles, probability calculations predict a sharp change in conductance when the volume of the conductive particles reaches a critical value called the percolation threshold. This theoretical value depends on the hypothetical shape and distribution of the particles; therefore real mixtures are often different from models utilized in calculations. Moreover, after Kirkpatrick,[1] in real mixtures, if insulating and conducting regions have on average a similar shape, the critical volume is 0.25.

In polymers filled with metallic powders, a percolation threshold is experimentally confirmed by a sharp change in resistivity close to a critical volume of metal. Such an observation was made by Gurland[2] on bakelite silver mixtures; Kusy and Turner[3] have also obtained a threshold on PVC filled with nickel or copper powders but the critical volume of fillers is lowered by means of a segregating process in the distribution of metallic particles.

Another illustration of this percolation threshold is provided by some PTC materials[4] (Positive Temperature Coefficient) which are insulating materials characterized by a high thermal expansion and filled with a concentration of conductive particles close to the critical volume. When the temperature is raised the volume of insulator increases while the volume of conductor remains nearly unchanged. The relative volume of the conductive phase, initially above the percolation threshold, falls below the critical value and the conductance of the mixture decreases. Carbon black filled waxes exhibiting such properties have been made and studied by Bueche.[5]

In carbon black filled polymers, in particular polyvinylchloride (PVC) and cis-polyisoprene (which is a natural rubber) which we have studied, the change in resistivity when increasing the volume of carbon is not as sudden as in metal filled polymers; it is spread over a relative volume range of 15 to 35%. Norman's data[6] on rubber filled with different types of carbon black lead to the same conclusions. The formation of special bonds between the carbon filler and the polymeric matrix is probably responsible for this difference; such an interpretation has, at least, been proposed in order to explain the considerable mechanical reinforcement of rubber by carbon black.[7] The formation, in the material, of a vitreous layer around each carbon particle has also been envisaged.[8] According to this assumption, the electrical behaviour of the mixture would be similar to that of a polymer filled with semiconducting particles more voluminous than the carbon particles themselves. Thus, with these equivalent *semiconducting fillers, a first percolation threshold would be reached while the* relative carbon black volume is still lower than the critical value; so, the succession of two percolation thresholds could explain the relatively gradual change in resistivity of these mixtures as the carbon black concentration is increased. Hence, it would not be surprising to find in polymeric materials filled with carbon black, other properties differing from those expected in a simple mixture of two passive conducting and insulating solids.

III HETEROCHARGES AND POLARIZATION

Because of the relatively gradual change in resistivity when increasing the volume of carbon black, it seems that a resistor of any desired value can be made from such filled polymeric materials. In fact, although the resistance of a sample certainly depends on the volume of carbon, it also depends on many other parameters.

First, it has been known for a long time that these materials are sensitive to pressure and exhibit, after deformation, relaxation phenomena responsible for a time dependent change in resistivity. Moreover, under the same conditions long samples and short samples are observed to behave differently. In particular the mixture seems to be more conductive in long devices than in short ones.[9] Light anisotropy can also be exhibited by the material due to the calendering process when manufactured. Each electrode type used introduces a different contact resistance as described by Norman.[6] Finally all the samples studied possess non-linear current–voltage characteristics like those drawn in Figures 1 to 4. These discrepancies from Ohm's law[10] remind us of the characteristics of space charge limited currents in amorphous semiconductors films;[11] however they do not seem to be much affected by the nature of the electrodes used which were vacuum deposited gold, colloidal graphite solution (aquagraph) and silver paint; so, in this study we have confined ourselves to the use of aquagraph electrodes.

As we can see it is difficult to predict the resistance of a sample even when the size and composition are known.

Because of the unusual number of parameters which influence the resistance of samples (length, orientation, voltage, temperature), *no significant value for*

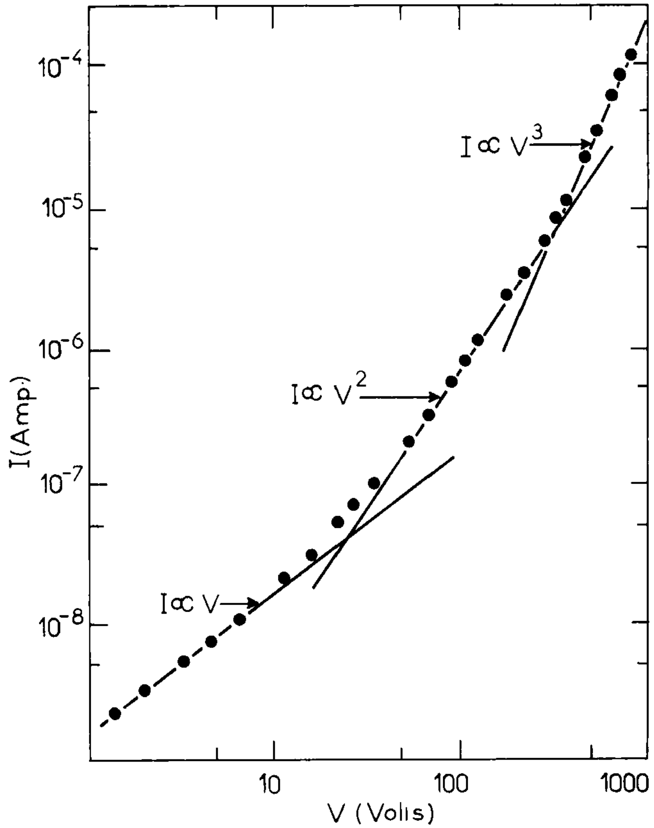

FIGURE 1 Current versus voltage in a sample of PVC filled with 20% carbon black (XC 72). Thickness: 2.3 mm. Section: 450 mm^2. Temperature: 23°C.

the conductivity of the material can be deduced from a single measurement of current and voltage. So it is necessary to distinguish between properties of the medium and properties of a particular sample with given shape, length and electrodes.

Therefore, we have determined with probes and a 610 C Keithley electrometer, voltage values at several points between the electrodes when a relatively conductive mixture is under an applied constant d-c voltage producing a constant d-c current. We have observed that the equipotential surfaces are planes parallel to the electrodes, but that the increase of the potential from cathode to anode is not regular. Figure 5 indicates the values of the potential as a function of distance from cathode, in a sample of PVC filled with 25% carbon black (Vulcan XC 72). The sample is 16 mm long and its cross-section

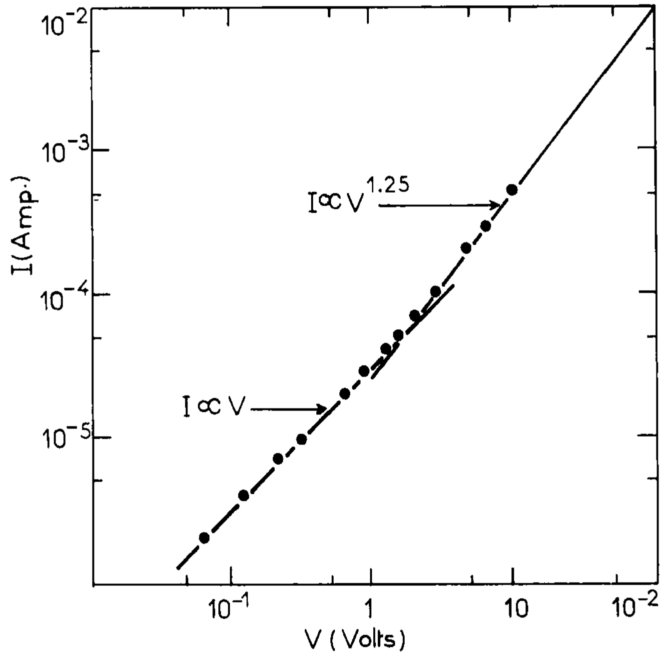

FIGURE 2 Current versus voltage in a sample of PVC filled with 30% carbon black (XC 72). Thickness: 2.3 mm. Section: 450 mm^2. Temperature: 23°C.

is 5.8 by 2.1 mm^2. The applied voltage is 46 volts (battery) producing a 8.2 μA current.

The bends in the voltage distribution curve, near the electrodes prove, from Poisson's law, that a volumic charge distribution appears in these regions. The sign of these charges is opposite to that of the adjacent electrode (heterocharges) as in dielectric polarization; so two important voltage drops occur in the vicinity of the electrodes and the apparent resistance of the sample is increased by the resulting screening.

Similar bends in the voltage distribution curves have been observed near the electrodes for different applied voltages (Figure 6). However, far from the cathode, all the voltage distribution curves are rectilinear which proves the existence of a constant electric field. Hence, we can deduce the conductivity in this region by writing $j = \sigma E$

with j: current density

σ: conductivity

E: electric field.

The value for the conductivity thus obtained is rigorously identical for each curve which means that Ohm's law is verified. In the sample used, for a tempera-

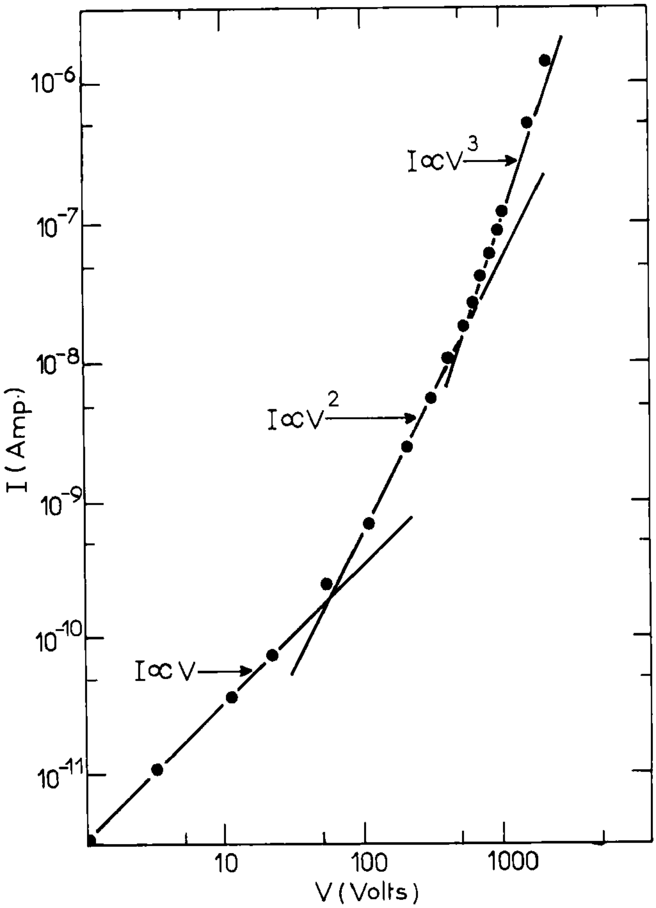

FIGURE 3 Current versus voltage in a sample of rubber filled with 20% carbon black (MPC). Thickness: 0.6 mm. Section: 324 mm². Temperature: 23°C.

ture of 20°C, the conductivity is:

$$\sigma = 5.12.10^{-4}\,\Omega^{-1}\,m^{-1}$$

From the form of the potential distribution between the electrodes we may conclude that a four electrode device is necessary to measure the electrical conductivity of such materials; a long sample will be chosen with current electrodes on the ends and two potential electrodes on the central part as in the BS 2044-2 method.[12]

Previous probe measurements are not available on samples of 25% carbon black filled rubber; this material is much too insulating and the potential

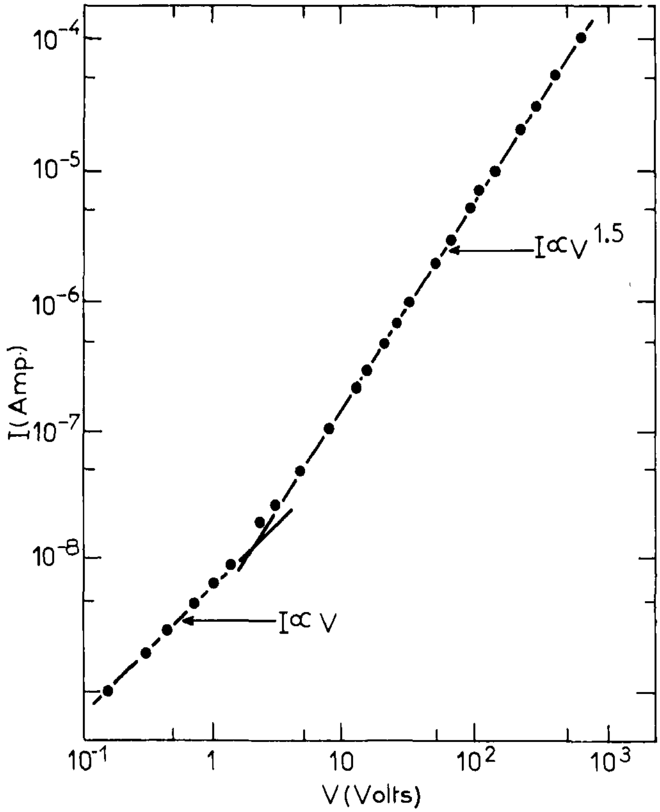

FIGURE 4 Current versus voltage in a sample of rubber filled with 30% carbon black (MPC). Thickness: 2.2 mm. Section: 450 mm^2. Temperature: 23°C.

distribution is perturbed by probes. However, on a sample of rubber filled with 40% carbon black (MPC), which is sufficiently conductive, it has been possible to observe the same important bends in the voltage distribution curves (Figure 7) and the conductivity may similarly be deduced from the rectilinear part of the curve. We obtained at 20°C:

$$\sigma = 0.67.10^{-6}\,\Omega^{-1}\,m^{-1}$$

To first approximation, far from the anode, the experimental voltage distribution curves of Figure 6 can be represented, as a function of the distance x from the cathode, by the expression

$$V_{(x)} = U[1 - \exp(-x/D)] + Fx$$

where U, D and F are three parameters which can be determined for each

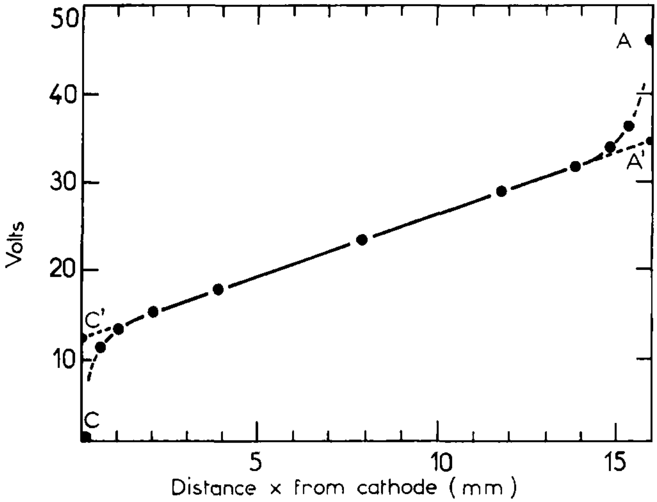

FIGURE 5 Voltage distribution along a sample of PVC filled with 25% carbon black (XC 72). Length: 16 mm. Section: 12 mm^2. Temperature: 23°C. Applied voltage: 46 volts. Resulting current: 8.2 μA. CC′ and A′A represent the voltage drops near the cathode and near the anode respectively.

curve. So the deduced expression for the electric field would be:

$$E(x) = -U/D \exp(-x/D) - F$$

and, from Poisson's law, the volumic charge density would be:

$$\rho(x) = \epsilon_o \epsilon_r U/D^2 \exp(-x/D)$$

where $\epsilon_o \epsilon_r = \epsilon$ is the dielectric constant.

Hence, the extrapolated values for the field and the charge density would be

$$E_{(o)} = -U/D - F$$

$$\rho_{(o)} = \epsilon_o \epsilon_r U/D^2$$

Integrating $\rho(x)$ we obtain the total polarization space charge spread through the material in the vicinity of the electrode per unit area

$$Q = \int_0^\infty \rho(x)\, dx = \epsilon_o \epsilon_r U/D$$

From these assumptions, values have been precisely calculated for three of the curves in Figure 6 and are listed in Table I.

It may be noted that the volumic charge density at the origin seems to remain constant, which would suggest a saturation effect; therefore, the total polarization space charge must extend further into the sample if it is to increase.

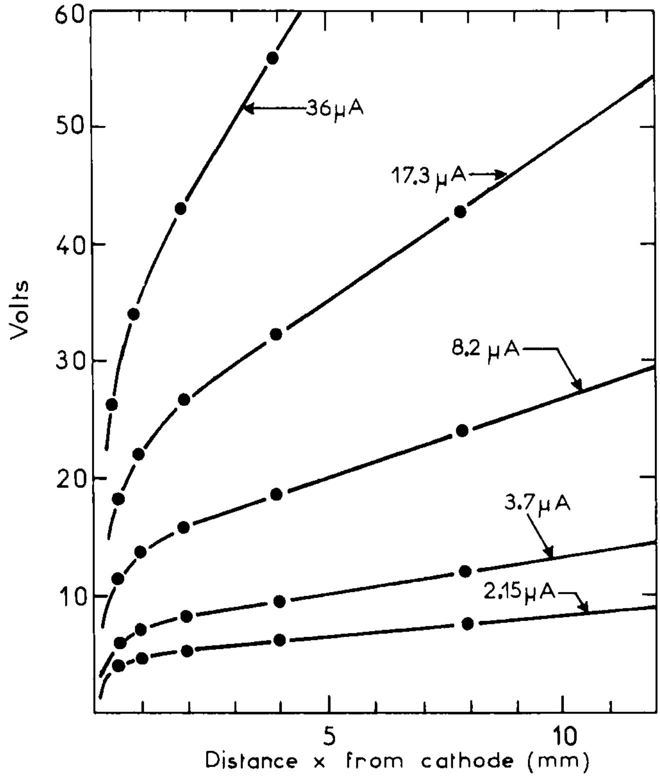

FIGURE 6 Voltage distribution near the cathode for different applied voltages and different resulting currents. Sample and temperature are those of Figure 5.

TABLE I

Parameters U, F and D in a representation of voltage distribution curves of Figure 6 by the function $V = U[1 - \exp(-x/D)] + Fx$. $E_{(o)}$, $\rho_{(o)}$ and Q are extrapolated values of field, density of charge and total heterocharge near the cathode

i (μA)	8.2	17.3	36
U (volts)	12.8	22	32
F (volts/m)	$1.31.10^3$	$2.67.10^3$	$5.70.10^3$
D (mm)	0.283	0.350	0.446
$E_{(o)}$ (volts/m)	$-4.6.10^4$	$-6.6.10^4$	$-7.8.10^4$
$\rho_{(o)}/\epsilon_r$(Cb/m^3)	$1.4.10^{-3}$	$1.6.10^{-3}$	$1.4.10^{-3}$
Q/ϵ_r (Cb/m^2)	4.10^{-7}	$5.5.10^{-7}$	$6.4.10^{-7}$

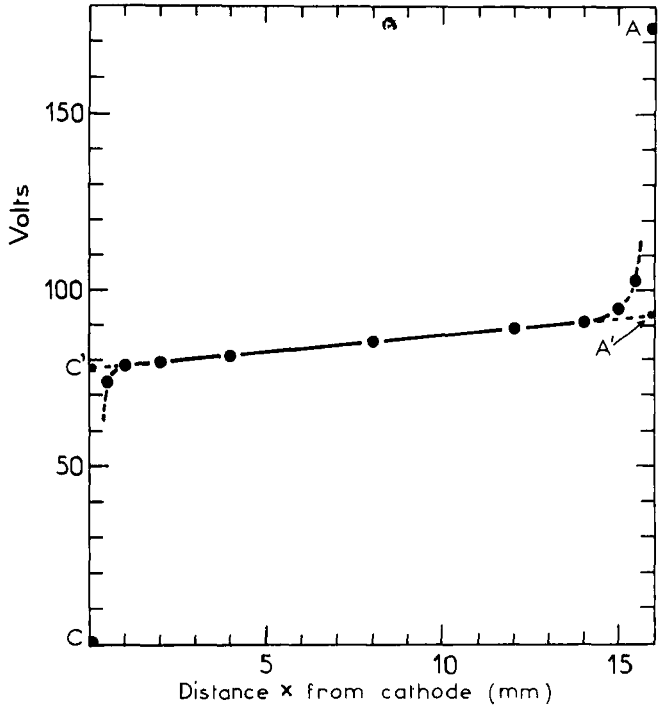

FIGURE 7 Voltage distribution along a sample of rubber filled with 40% MPC carbon black. Length: 16 mm. Section: 14 mm^2. Temperature: 23°C. Applied voltage: 173 volts; resulting current: 9.4 10^{-9} A. C C' and A'A represent the voltage drops near the cathode and near the anode respectively.

Because of the approximate symmetry of the voltage distribution, as seen in Figures 5 and 7, and according to the results we obtained on samples submitted to thermal sweeps,[13] we suppose that ions are responsible for this volumic heterocharge; we presume that the ions which cannot easily pass from material to electrodes tend to accumulate near the electrodes as in electrolytic polarization; thus the electric field inside the sample is reduced; as a consequence the current which is probably mainly electronic, decreases and Ohm's law remains verified in the body of the material.

IV FILAMENTARY CONDUCTION

If the electrical power dissipated in a sample is increased, the resulting rise in temperature generally leads to an irreversible deterioration of the polymeric material and eventually to its destruction. However, in PVC filled with 25% XC 72 carbon black, we observed a reversible rise in sample conductance when the current is increased.

Figure 8 is a current–voltage characteristic plotted point by point. It is S-shaped so that two current values are available for the same voltage. The measurements were made with a current controlled device which enables us to fix the current and read the resulting equilibrium voltage at the terminals of the component under test. For each value of the current in the region of the curve which exhibits a current controlled negative resistance (CCNR) the equilibrium voltage is only obtained after one or two seconds: a localized thermal effect therefore seems to be the cause of this phenomenon. For each value of the current, a temperature distribution depending on the area of the sample and the ambiant temperature probably exists in the material as is suggested by the shift of the curve when the ambiant temperature is changed (dotted curve of Figure 8).

Consequently, we may suppose that a conductive filamentary network is partially formed throughout the material so that the current preferentially flows in channels which are the first part to be heated and hence become more conductive above the transition temperature T_c of the polymer.

When the transition temperature T_c of a material is higher than its deterioration temperature, the characteristic clearly cannot be reversible which would explain why we have not observed such a phenomenon in rubber.

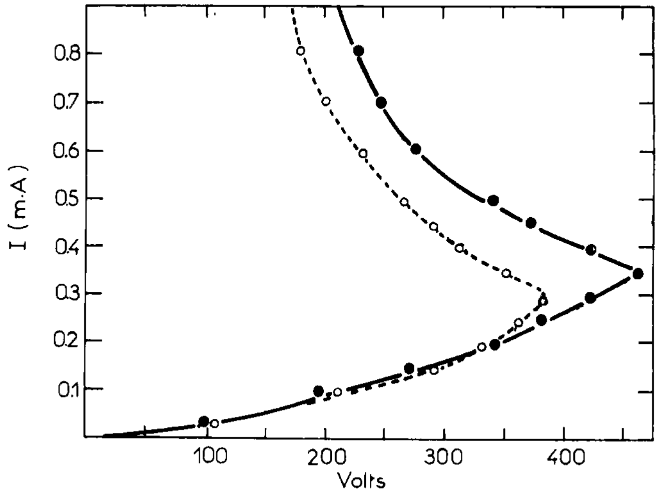

FIGURE 8 Current voltage characteristics obtained on a sample of PVC filled with 25% XC 72 carbon black. Thickness: 2.1 mm. Section: 72 mm^2. ● Ambiant temperature 26°C. ○ Ambiant temperature 52°C.

Theoretically, several calculations have predicted that a differential negative resistance can occur in a material when a current localization takes place and when the conductivity increases with temperature.

Let us consider the temperature of a conductive channel carrying a current flow; it obeys a heat equation which indicates that the temperature rise results from locally dissipated power and a change in the thermal flux that is:

$$\rho C\ \partial T/\partial t = P + \Delta\ .\ (K\ .\ \Delta\ .\ T)$$

with:

ρ = density
C = specific heat
P = power
K = thermal conductivity
T = absolute temperature

In this case replacing P by σE^2 and assuming a cylindrical channel, r being the radial distance, we obtain:

$$\rho C\ \partial T/\partial t = E^2 + K(\partial^2 T/\partial_r{}^2) + K/r\ \partial T/\partial r$$

This equation deals with the rate of change of temperature $\partial T/\partial t$ and is of interest for calculating the duration of switch phenomena as in the Ovshinsky[14] effect. On the contrary for our static current–voltage characteristics, each point corresponds to a thermal equilibrium and so we shall take:

$$\partial T/\partial t = 0$$

So the simplified equation is:

$$K(d^2T/dr^2) + K/r\ dT/dr + E^2 = 0$$

from which theoretical current–voltage characteristics showing a CCNR have been calculated by several authors[15–16] with the aid of computers, taking different boundary conditions and choosing different classical increasing functions of temperature for the conductivity.

Time constants, on the one hand, and agreement between experimental and theoretical characteristics, on the other hand, agree with the assumption of filamentary conduction and thermal effect.

V CONCLUSION

We may conclude that most of the discrepancies from Ohm's law observed in carbon black filled polymers are apparent properties since the conductivity of the bulk material is constant and perfectly accessible. Besides, the simple notion of contact resistance seems insufficient to explain the variable voltage drops which occur at the terminals of the samples. Volumic polarization caused by the accumulation of ionic heterocharge is probably the prevailing contact phenomenon.

To obtain linear resistors, all this suggests that the terminals should be made with a progressively increasing conductivity that is layers of polymer filled with a concentration of carbon black increasing towards the electrodes; such terminals should avoid charge accumulation. However, if polymeric materials are used to make linear power resistors it is recommended not to fill them near the percolation threshold because of filamentary conduction and CCNR. On the contrary if non-linear components are desired, it will be possible to adjust carbon black concentration and sample length to obtain wanted current voltage characteristics. Thus we believe that the electrical properties of filled polymers if better understood may lead to other important applications.

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