JOURNAL OF MATERIALS SCIENCE 28 (1993) 117–120

I–V characteristics of carbon black-loaded crystalline polyethylene

H. M. AL-ALLAK, A. W. BRINKMAN, J. WOODS
Physics Department, University of Durham, South Road, Durham DH1 3LE, UK

The I–V characteristics of carbon black-loaded crystalline polyethylene were investigated at room temperature and at few degrees above the melting temperature, T_m. The material was chemically cross-linked using silane. It had a large carbon black content of 28 parts per hundred by weight and displayed a strong positive temperature coefficient of resistance (PTCR) effect with a resistivity jump of four orders of magnitude. Logarithmic current–voltage plots were found to be linear with unity slopes at temperatures above and below T_m, indicating good ohmic behaviour. This is in contrast with previous theories which explain the PTCR effect on the basis of electron tunnelling as the current conduction mechanism. A new model capable of explaining both the PTCR effect and the steep reduction in resistance above T_m is presented, according to which the PTCR effect is the result of the co-operative effect of changes in crystallinity and volume expansion.

1. Introduction

The resistivity of some carbon black-loaded polymers is found to increase sharply as the composite is heated towards its melting point, T_m. This effect, which was first observed by Frydman [1], is commonly referred to as the positive temperature coefficient of resistance (PTCR). In crystalline polymers the resistivity jump is normally observed within few degrees below T_m, and can be very large (many orders of magnitude) depending on a number of factors such as the degree of crystallinity [2], the type of carbon black used and the degree of cross-linking [3]. However, with amorphous polymers, the PTCR effect is very much smaller and is observed only over a wide temperature range when very high levels of conductive fillers are used [2]. Unlike ceramic $BaTiO_3$ PTCR materials, non-cross-linked crystalline polymers show a very sharp decrease in resistivity (NTCR effect) immediately above the melting point. Such devices show poor reproducibility with thermal cycling [3]. However, cross-linking the PTCR polymers, using either physical or chemical techniques, eliminates the NTCR effect and results in more reproducible behaviour [3].

Although polymer PTCR materials have been known for some time, the exact mechanism behind the anomalous jump in resistivity is not well understood. Kohler [4] suggested that the conductive filler forms a network of conductive chains at temperatures below T_m. As the polymer is heated, the sudden expansion which takes place at the crystalline melting point results in the break-up of the conducting chains with a consequent anomalous increase in resistance. However, Kohler was not able to explain the steep decrease in the resistance above the melting point, when the volume of the polymer continues to increase with temperature.

In contrast, Ohe and Natio [5] suggested that the PTCR jump is due to the increased difficulty electrons find in tunnelling through intergrain gaps separating the particles of the carbon filler. Below T_m the distribution of the intergrain gaps is assumed to be comparatively uniform and the gap width is small enough to allow intensive tunnelling to take place. At temperatures near T_m the intergrain gap distribution becomes more random due to thermal expansion leading to a significant number of interparticle gaps too large to allow appreciable electron tunnelling (overall, the average increase in gap width was considered to be too small to eliminate tunnelling completely) with a consequent rise in resistance. No reason was given to explain why the distribution of the intergranular gaps should become more random on approaching T_m, nor was the impact of any change in crystallinity on the PTCR behaviour considered. The NTCR behaviour above T_m also remained unexplained.

The tunnelling model of Ohe and Natio was later modified by Meyer [2, 6] to take account of the effects of changes in crystallinity on the PTCR behaviour. Meyer's model depends on the assumption that thin (300 nm) crystalline films of polymer are significantly better conductors (due to tunnelling) than amorphous films of polymer. Having observed experimentally that the carbon black particles are present only in the amorphous regions between the crystallites (i.e. that they are excluded from the crystallites themselves), Meyer suggested that the high conductivity below T_m was due to tunnelling through the thin crystallites. The anomalous rise in resistivity near the T_m point was attributed to the phase change of these crystallites. Meyer also observed that as the polymer softened up above T_m, the compressed carbon black particles

0022–2461 © *1993 Chapman & Hall*

in the original amorphous region start to migrate to the new amorphous areas with the result that NTCR behaviour is observed following the formation of new continuous chains of conductive particles. However, as Meyer acknowledges, the model relies on a single, experimentally debatable, fact that thin films of crystalline polymers are highly conductive. It should also be noted that a thickness of the crystallites of 300 nm appears to be too large for effective tunnelling to occur.

In 1978, Klason and Kubat [7] explained the PTCR effect on the basis of changes taking place in the carbon structure with temperature. However, Voet [8] disagreed with this model because similar effects also occur in the absence of crystallinity. Instead, Voet attributed the PTCR effect to the large volume expansion of the polymer in the melting range, as well as to the migration of the carbon black to the previously carbon black-free crystalline regions as explained above, which further dilutes the concentration of the conductive filler in the polymer and increases the resistance.

In the present work the I–V characteristics of a carbon black-loaded crystalline polyethylene showing a normal PTCR effect are discussed. A new model capable of explaining both the PTCR and the NTCR behaviour is suggested.

2. Experimental procedure

The composite materials were prepared using commercially available high-density polyethylene and partially conductive carbon black. These two materials were mixed for about 30 min using a Brabender cavity mixer at a temperature of about 155 °C. A number of different composites were made using different filler contents ranging from 18–24 parts per hundred by weight (p.p.h.). All samples were silane cross-linked. The investigated specimens, which were about 0.15 cm thick and 0.5 cm^2 in area, were obtained by compression moulding using a hydraulic press at about 155 °C.

Silver paint was applied to the opposite large area surfaces for electrical contacts. Samples were placed in a controlled oven, while making resistivity measurements. The temperature was maintained for about 5 min before each reading was taken to ensure that the specimens were heated homogeneously.

In order to avoid self-heating effects, the I–V measurements were carried out using a pulsed voltage technique. Single pulses of short duration (60 µs) were applied to the specimen. The voltage drop across a known resistor connected in series with the sample was recorded on a digital storage oscilloscope to obtain the current value.

3. Results and discussion

Fig. 1 shows the dependence of the room-temperature resistivity on the carbon black content. There is a dramatic drop in resistivity with filler content up to about 24 p.p.h. (corresponding to the percolation threshold) as the conductive pathways throughout the polymer are being established. The result is in agreement with previously published data [3, 8].

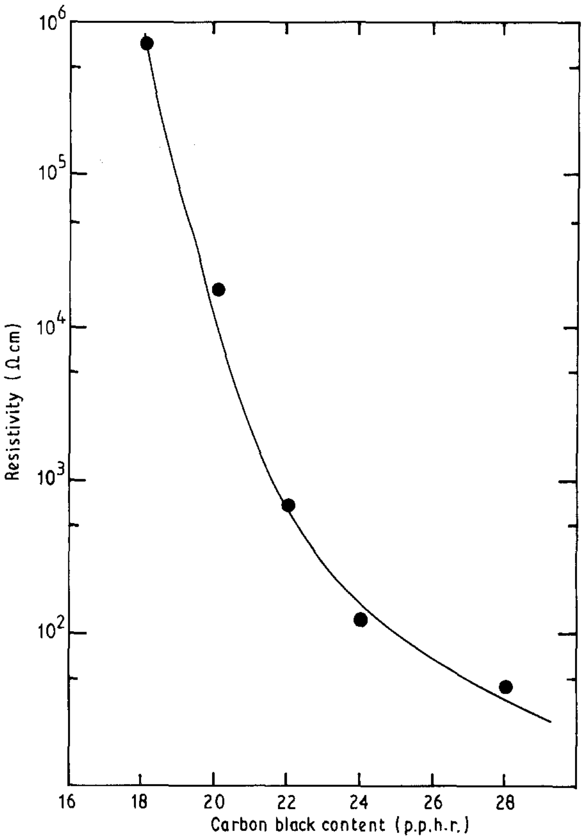

Figure 1 Dependence of room-temperature resistivity on carbon black content.

The material with the lowest resistivity, corresponding to the highest content of carbon black of 28 p.p.h., was chosen for the I–V investigation. This was to render the current contribution arising from any space charge (which may be present in the polymer matrix) negligible compared with the d.c. current due to the applied voltage. This material was found to show a normal PTCR effect, Fig. 2, with a resistivity jump of around four orders of magnitude. The resistivity above T_m did not show a steep reduction with temperature. This is thought to be due to the fact that the carbon black particles become strongly attached to the cross-linked networks thus reducing their freedom of movement at high temperatures, including the melting region, where the NTCR phenomenon occurs [3].

I–V characteristics measured at 136 °C and room temperature are shown in Fig. 3. The high-temperature measurements were carried out a few degrees above T_m where the dependence of the resistance on temperature is very small. The plots at room temperature and 136 °C are both linear with slopes of about unity clearly showing good ohmic behaviour. These results conflict with the electron tunnelling theories of Ohe and Natio and of Meyer which require an exponential dependence of I on V. However, ohmic conduction at room temperature has also been reported by Burton [9] and Reboul [10] using carbon–rubber and carbon–PVC composites, respectively. Reboul concluded that most of the deviations from Ohm's law observed in carbon black-filled poly-

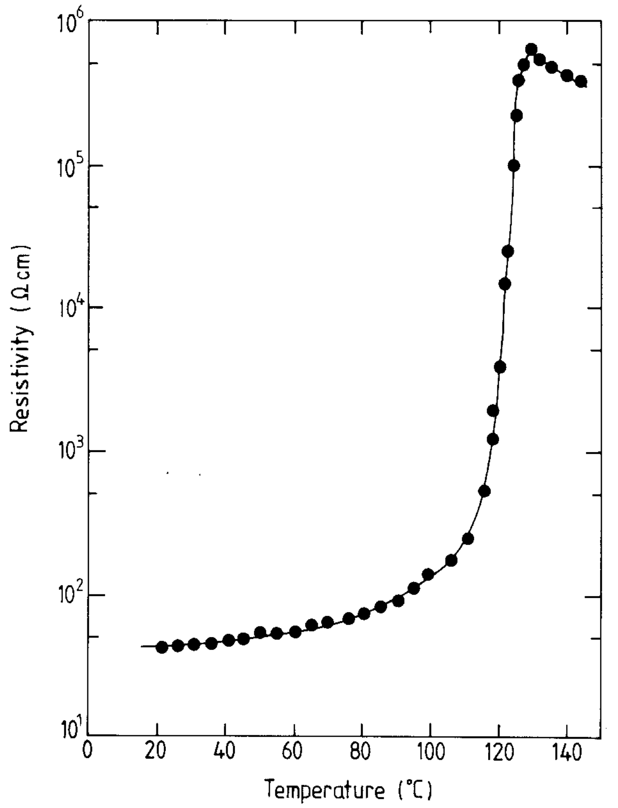

Figure 2 Showing the behaviour of resistivity with temperature of materials containing 28 p.p.h. carbon black.

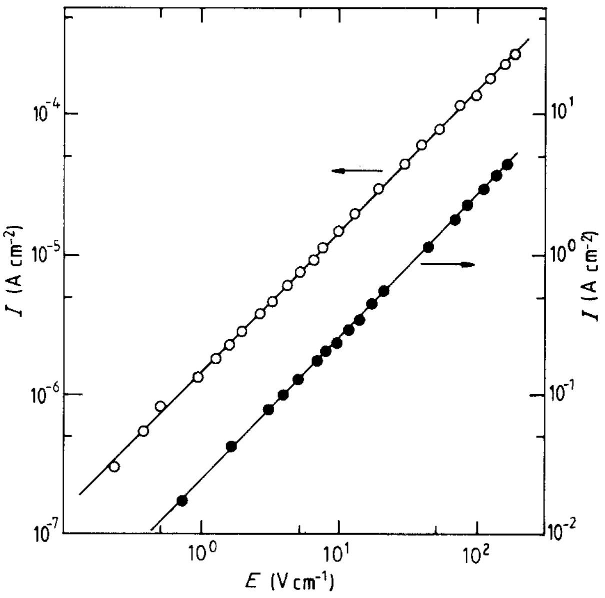

Figure 3 I–V characteristics of materials having 28 p.p.h. carbon black, at (●) room temperature and (○) 136 °C.

mers are associated with space charge phenomena in the contact region.

4. A new model for the PTCR effect in crystalline polymers

As discussed above, none of the models proposed so far is able to account accurately for the PTCR behaviour in carbon black-loaded crystalline polymers. A more comprehensive model that can explain both the PTCR and the NTCR (above T_m) effects, taking into account the influence of both the crystallinity and the volume expansion, is clearly necessary.

Crystalline polymers, such as polyethylene, consist of a crystalline phase embedded in an amorphous phase. As mentioned earlier, when carbon black is incorporated in such materials it is found to reside in the amorphous phase, and is excluded from the crystalline regions. It is assumed here that the amorphous regions, interspersed between the crystallites, form a continuous open network, Fig. 4a. Thus the carbon black compressed in the amorphous phase can easily establish conductive chains throughout the material giving rise to the observed low resistivity of the material. This is in contrast with Meyer's model which invokes conduction through the crystallites by tunnelling as a prerequisite for the formation of conductive chains.

As the temperature of the crystalline polymer approaches T_m, the crystallites start to become amorphous. This process is also accompanied by a sudden and large increase in their volume. (With high-density polyethylene an overall increase in the specific volume of about 20% has been reported by Chiang and Flory

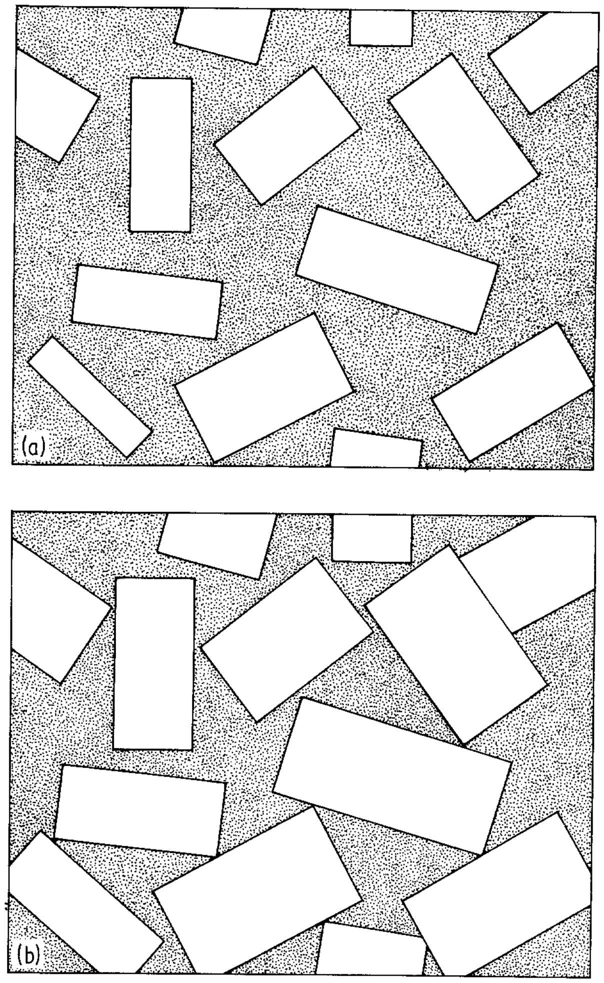

Figure 4 Schematic two-dimensional representation of crystalline polymer: showing (a) crystallites (clear rectangles) embedded in an amorphous region which forms continuous open network, (b) the reduction in the intergrannular gap width resulting from the increase in the volume of the crystallites after phase transformation near T_m.

[11].) Consequently, the width of the intergranular gaps between these newly formed and enlarged amorphous regions (which do not contain carbon black and are insulating) is expected to be considerably reduced. This will produce more resistive current pathways, and may even break up the conductive chains altogether as demonstrated in Fig. 4b, giving rise to the PTCR effect near T_m.

Above the melting point, the polymer becomes more fluid and the carbon black particles, which are compressed in the old amorphous region, begin to show considerable migration through the new amorphous region. This could well result in the re-establishment of the severed conductive links, possibly of the intergranular regions or across other short paths. Consequently, the resistance of the material will start to decrease giving rise to the NTCR effect. This is essentialy similar to the mechanism proposed previously by Meyer (Section 1) except that the manner in which the conductive chains are reformed is more clearly explained.

The main merit of this model is that it identifies both crystallinity and the volume expansion as the two necessary parameters for the occurrence of the PTCR effect. A higher degree of crystallinity implies more interruptions in the conductive chains on approaching T_m resulting in an enhanced PTCR effect, in agreement with the results of Meyer [2]. A higher volume expansion increases the probability of breaking up the conductive chains which again will intensify the resistivity anomaly near T_m. It is the co-operative effect of the volume expansion and change in crystallinity that ultimately defines the characteristics of the PTCR behaviour.

5. Conclusion

$I-V$ measurements (at room temperature and at a few degrees above the melting point) carried out on carbon black-loaded crystalline polyethylene, showing a normal PTCR effect, revealed good ohmic behaviour at both temperatures. The results are in contrast with the previous theories which assume that electron tunnelling processes dominate as the mechanisms responsible for the PTCR behaviour in these materials. A new model capable of explaining both the PTCR and the NTCR (above T_m) effects is proposed. This model invokes the co-operative effects of changes in crystallinity and volume expansion as the key factors responsible for this PTCR effect.

References

1. E. FRYDMAN, UK Pat. Spec. 604695, 8 July 1948.
2. J. MEYER, *Polym. Engng. Sci.* **3** (1973) 462.
3. M. NARKIS, A. RAM and Z. STEIN, *ibid.* **21** (1981) 1049.
4. F. KOHLER, US Pat. 3243753 29 March 1966.
5. K. OHE and Y. NATIO, *Jpn J. Appl. Phys.* **10** (1971) 99.
6. J. MEYER, *Polym. Engng. Sci.* **14** (1974) 706.
7. G. KLASON and J. KUBAT, *J. Appl. Polym. Sci.* **19** (1978) 831.
8. A. VOET, *Rubber Chem. Technol.* **54** (1981) 42.
9. L. C. BURTON, in "125th Meeting of the Rubber Division, American Chemical Society", Indianapolis, IN, 8–11 May 1984.
10. J. P. REBOUL, in "Carbon Black–Polymer Composites", edited by E. Keilsichel (Marcel Dekker, Waltham, 1982) p. 79.
11. R. CHIANG and R. J. FLORY, *J. Amer. Chem. Soc.* **83** (1961) 2857.

Received 17 October 1991
and accepted 7 April 1992