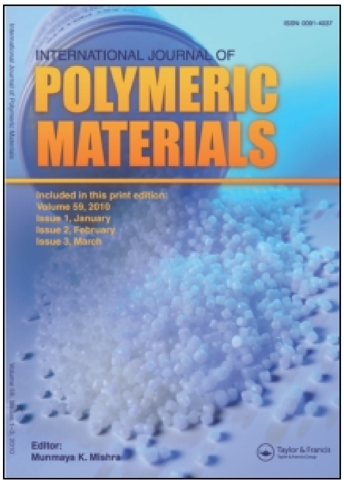

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Influence of Anisotropy on the PTC Effect in Injection Moulded Samples of CB-filled Polyethylene and Polystyrene

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Influence of Anisotropy on the PTC Effect in Injection Moulded Samples of CB-filled Polyethylene and Polystyrene

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This paper reports on measurements of the temperature dependence of resistivity, ρ, in injection moulded samples of LDPE, HDPE, and PS filled with two grades of carbon black (CB). The CB concentration was adjusted to give a relatively small PTC-effect in isotropic (annealed) samples. It was found that the orientation of the matrix polymer that occurred during the injection moulding process highly enhanced the PTC-efficiency of all the compounds used. The magnitude of this effect and the level of RT resistivity were orientation dependent. Upon annealing (second heating run) the behaviour of the isotropic samples was recovered.

In general, ρ increased with the degree of orientation in a fashion similar to the effects associated with lowering the CB content. One of the effects observed in highly oriented samples was a pronounced frequency-dependence of the resistivity (ρ decreasing at higher frequencies), and a non-ohmic I-V-behaviour. The ρ-data relate to d.c. and 1 kHz. Samples with higher and lower orientation were obtained by microtoming the surface and core portions of the injection moulded test bars.

INTRODUCTION

Within certain ranges of concentration, carbon black (CB)-containing polymers exhibit a positive temperature coefficient of electrical resistivity (PTC-effect). The increase in the resistivity level (ρ) may amount to several decades, allowing devices based on such compounds to be used as self-limiting heating elements. Primarily, crystalline polymers are used for this purpose, since they produce a time independent PTC-effect.

The nature of the PTC-effect has been the subject of numerous investigations concerned mainly with analyses of the influence of the composition of the filled systems.[1-9] There appear, however, to be no reports on the variation of this effect with the anisotropy of the material used.

The present paper reports on measurements of the PTC-effect in low and high density polyethylene (LDPE, HDPE), and polystyrene (PS) samples (test bars) produced by injection moulding. The results relate to samples taken from the surface and the core of the central portion of the test bars, characterized by higher and lower orientation, respectively. The magnitude of the PTC-effect appeared to increase significantly with anisotropy; the effect was also direction dependent. The PTC-effect in the corresponding isotropic (annealed) samples was relatively small, due to a relatively high CB-content. The increase in the PTC-efficiency with orientation brought about during the mould filling process is probably associated with effects equivalent to a reduced CB-content (disruption of the CB-network). This is in agreement with the finding that the ρ-level increases with orientation, at the same time as the ρ-values become frequency dependent. Due to the complexity of the systems used we do not analyze the results in terms of current theoretical concepts, particularly as these do not treat anisotropic conduction.[10-13]

Similarly, the relatively large number of papers dealing with the influence of deformation on the electrical properties of CB filled elastomers appear to be of little value in the present context, mainly because of lack of consistency of the various results.[14] Furthermore, the results cannot be simply transferred to thermoplastic systems like CB filled polyolefines that undergo complicated deformations during the injection moulding step. In contrast to rubbers, the influence of deformation on the electrical properties of CB filled thermoplastics has not been investigated. Only a few reports are available on the anisotropy of parts produced by injection moulding or extrusion.[15,16]

EXPERIMENTAL

Materials used

The properties of the polymer grades used were as follows:
LDPE, density 917 kg/m^3, melt flow index 7 (ICI type 017040);
HDPE, density 953 kg/m^3, melt flow index 0.1 (Unifos DMDS 2215);
PS, density 1040 kg/m^3, M_w 227000, $M_w/M_n = 3.07$ (Poly Science, USA).

Two CB types were used, both highly conducting, i.e. Ketjenblack EC and Vulcan XC, the former producing a conducting network at about half the concentration required for the latter. The CB concentrations used for PE were 10% and 20%, respectively, giving a resistivity (ρ) level of c. 10^3 ohmcm in isotropic samples. For PS 12% and 22.5%, resp., were needed in order to obtain c. 10^3 ohmcm. The resistivity vs. concentration curves are shown in Figure 1. As can be seen, the three polymers used, i.e. LDPE, HDPE, and PS produce rather similar results when filled with the same CB grade. A fact not always noted in reported data is the

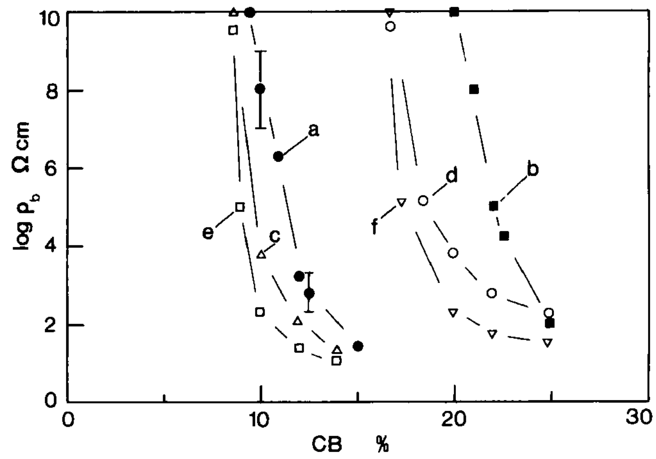

FIGURE 1 Conductivity vs. CB-concentration at 10 V for LDPE, HDPE, and PS containing KBEC and VXC. Sample dimensions 10 × 10 × 3.5 mm; the samples were cut from injection moulded test bars heated to 180°C for 15 min in order to restore isotropy, and cooled at 10°C/h. PS with KBEC (a) and VXC (b); LDPE with KBEC (c) and VXC (d); HDPE with KBEC (e) and VXC (f).

frequency dependence of the ρ (concentration) curves, which may be different at different ρ-levels. There is also a time dependence (physical ageing), the ρ-values decreasing with increasing storage time. In the present case, the data of Figure 1 were obtained from measurements made at 10 V (d.c.) on injection moulded samples (see below) which had been treated at 180°C for 15 min in order to restore an isotropic structure.

Mixing and injection moulding

The mixtures were compounded twice at 200°C for 4 min (residence time c. 2 min) on a Buss Kneader (mixing extruder) with a vented screw (Type PR 46, $D = 46$ mm, $L/D = 11$). The extrudate was granulated and dried at 105°C for 12 h prior to injection moulding. Repeating the compounding step produced a reproducible resistivity level. On the whole, variations in the compounding procedure (two-roll mill, Brabender Mixer) gave rise to minor variations in the ρ-level only. With KBEC, such changes were less pronounced than with VXC.

Injection moulded samples (test bars, DIN, $10 \times 3.5 \times 150$ mm) were produced on a conventional machine (Arburg 221 E/170 R) using two settings, one for normal injection, and one giving samples with an enhanced anisotropy level (low melt and mould temperature, low injection speed).

Orientation measurements (heat shrinkage)

Longitudinal and transversal heat shrinkage values, S_L and S_T, were used as a measure of the orientation of the samples cut from the central portion of the injection moulded test bars.[17] Two levels of orientation were used, i.e. samples from the surface and the core of the bars, giving a higher and lower orientation degree, respectively. The samples had the dimensions 5×5 mm, thickness 0.5 mm. With PS/CB a closer examination of the orientation distribution across the sample was also carried out to supplement the data given for PE/CB.[17] These measurements were performed on microtome cuts with the dimensions 15×4 mm, thickness 30 μm, taken from the central part of the test bars. Details of the shrinkage method are given in Ref.[17] These S-values are corrected for lateral shrinkage effects. Low S-values refer to low orientation. The temperature used during the shrinkage test was 120°C for 10 min for the PS samples; for LDPE and HDPE 120° and 140°C, resp., were used.

Electrical measurements

The resistivity vs. temperature data relate to measurements of bulk resistivity on samples with the dimensions $5 \times 5 \times 0.5$ mm, that is the same samples as those used for the determination of S_L and S_T. The resistivity was measured in the three main directions of anisotropy, x denoting the flow (longitudinal) direction, y the lateral, and z the thickness directions. Also here, two kinds of samples with different orientation were used (surface and core of the test bars, cf. above under Shrinkage).

With PS/CB the surface resistivity of the central portion of the bars was also determined at varying distance from the surface (successive microtoming of 30 μm thick cuttings). This was done in order to obtain a supplement to the corresponding data measured on PE/CB,[17] where details of the resistivity measurements may also be found (both surface and bulk resistivity).

During the determination of ρ (bulk) the samples were embedded in a silicon preparation which prevented their shrinkage during the heating procedure.

RESULTS

The resistivity vs. temperature data presented in this section relate to injection moulded samples with two different degrees of anisotropy as obtained by an appropriate adjustment of the setting of the moulding machinery. As a measure of orientation we used the shrinkage values (see Experimental).

Polyethylene

Figure 2 shows the $\rho(T)$-curves for a LDPE/20% VXC sample, thickness 0.5 mm (length × width 5×5 mm), taken from the central part of a tensile test bar injection moulded to a normal degree of orientation. The position of the sample in the test bar is evident

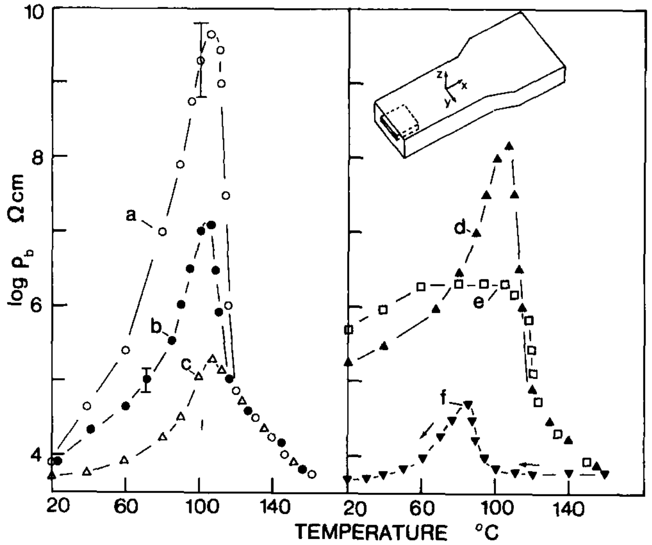

FIGURE 2 Resistivity (bulk) vs. temperature for a 0.5 mm thick sample cut from the central portion of an injection moulded test bar. LDPE with 20% VXC. Heating rate 0.5°C/min. Normal orientation, $S_L = 0.35$, $S_T = 0.20$. Left: flow (x) direction; curve (a) d.c. and (b) 1 kHz at 1st heating: curve (c) 2nd–4th heating, d.c. and 1 kHz. right: curve (d) y-direction and (e) z-direction at 1st heating, 1 kHz, curve (f) cooling from 160°C, 1 kHz, 10°C/min.

from the insert in Figure 2. Normally, the orientation in the central part of injection moulded parts is rather low. This was also reflected in the relatively low shrinkage values, $S_L = 0.35$, and $S_T = 0.20$.

Figure 2a (left) relates to the longitudinal direction of the test bar (flow direction). As can be seen, the PTC-effect is significantly larger at d.c. that at 1 kHz. This difference disappears, however, at the second and subsequent heating cycles. At the same time, the height of the $\rho(T)$-peak is markedly reduced, while the temperature, defining the position of this peak, remains largely unchanged.

There was no measurable hysteresis between the second and subsequent cycles with regard to the $\rho(T)$-behaviour.

The behaviour of the same sample in the other two main directions of anisotropy is shown in Figure 2b (right). As d.c. measurements did not produce reproducible results in these two directions, only the curves relating to a measuring frequency of 1 kHz are shown. As can be seen, the y-direction peak in $\rho(T)$ is largely similar to the peak measured along the flow direction (x). In contrast, the PTC-effect is only weakly developed when measured perpendicular to the plane of the test bar (z-direction).

Upon repeated heating, the differences between the three directions of anisotropy disappear entirely, as does also the frequency dependence of the $\rho(T)$-curves. Thus, the curve in Figure 2a, relating to the behaviour in the flow (x) direction during the 2nd, 3rd, and 4th heating is also valid for both the other directions and for d.c. as well as 1 kHz.

For samples which regained their isotropy after the 1st heating cycle, there was no measurable hysteresis between the ρ-values obtained during heating and cooling. To illustrate the effect of rapid cooling, a $\rho(T)$-curve obtained at 10°C/min has been inserted into Figure 2b (right), showing a shift of the PTC peak towards lower temperatures, and a reduction of its height. Upon subsequent heating at 0.5°C/min the normal behaviour according to the 2nd–4th heating curve was recovered (see curve (c), left).

Figure 3 shows $\rho(T)$ data for LDPE filled with 10% KBEC, a grade known to produce relatively weak PTC-effects. Such a behaviour is also reflected by the data of Figure 3. As in Figure 2, the results relate to normally oriented samples, In this case, however, the height of the PTC-peak does not follow the pattern of Figure 2, the flow direction (x) exhibiting the lowest PTC-effect. The highest peak was measured perpendicular to the plane of the test bar. Again, there is a dramatic drop in the height of the PTC-peak between the first and second heating run, due to the loss of orientation. The second run did not show any dependence on the measuring direction (isotropy). The character of the rapid cooling run (10°C/min) was similar to that shown in Figure 2.

The differences between the $\rho(T)$ curves for the three directions are significantly smaller than in the case of LDPE/20% VXC. This applies also the values of ρ at RT. A particular feature of the data of Figure 3 was their independence of the measuring frequency (d.c. to 10 kHz). The orientation as measured by heat shrinkage was the same as in the LDPE/20% VXC samples, i.e. $S_L = 0.35$, $S_T = 0.20$.

The difficulties encountered in the determination of the ρ-value at d.c. for the samples referred to in Figure 2b (right) and Figure 4 are probably due to effects associated with contact resistance at high ρ-levels.[18]

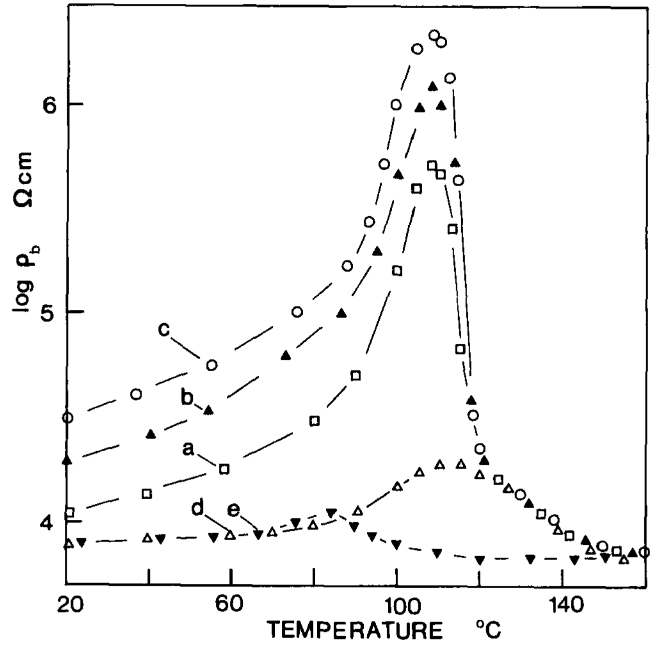

FIGURE 3 Resistivity (bulk) vs. temperature curves for LDPE/10% KBEC with normal orientation, $S_L = 0.35$, $S_T = 0.20$. Samples 0.5 mm thick cut from the central portion (core) of tensile test bars. Curve (a): x-direction, (b): y-direction, (c): z-direction at 1st heating. The $\rho(T)$-curve obtained at 2nd and subsequent heating seems independent of orientation, curve (d). Curve (e): cooling at 10°C/min. No frequency dependence (d.c. to 10 kHz).

The results reproduced in Figures 2 and 3 relate to LDPE samples cut from the central portion (core) of the injection moulded test bars where the orientation is known to be relatively low. When cutting the sample from the surface of the bars, samples with a substantially higher level of orientation are obtained. Figure 4 illustrates the corresponding $\rho(T)$-behaviour for 0.5 mm thick samples of LDPE/20% VXC. The heat shrinkage values defining the degree of orientation in the x- and y-directions were $S_L = 0.6$ and $S_T = 0.3$, i.e. significantly higher than in the samples taken from the core, cf. Figure 2. As d.c. measurements did not produce repeatable data, especially at $T > 60°C$, only results relating to 1 kHz are shown in Figure 4. The d.c. values of ρ were typically of the order

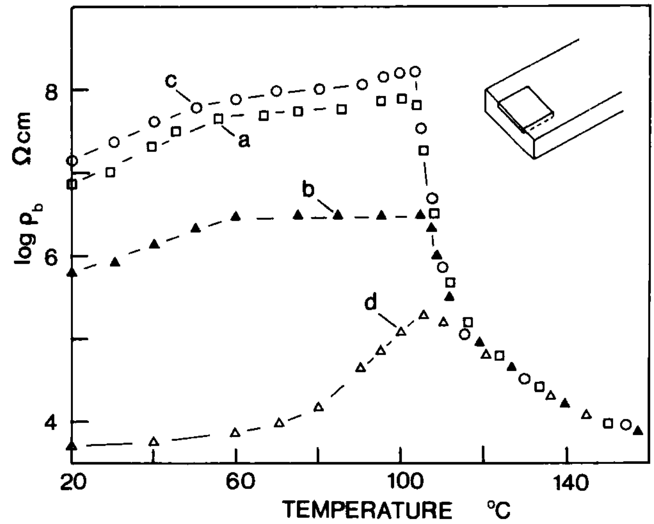

FIGURE 4 Resistivity (bulk) vs. temperature for an LDPE/20% VXC sample 0.5 mm thick, cut from the surface of an injection moulded test bar (higher orientation, $S_L = 0.6$, $S_T = 0.3$). Curve (a): x-direction, (b): y-direction, and (c): z-direction at 1st heating, 1 kHz. Second heating, curve (d), produced $\rho(T)$-curve independent of direction and frequency.

10^9 ohmcm at RT, and highly frequency dependent. To be noted among the features exhibited by the data of Figure 4 are the high ρ-levels at RT, 10^6–10^7 ohmcm, depending on the measuring direction, and further an only weakly developed PTC-effect. There is also an unusually sharp drop in the ρ-value at the melting point of LDPE. The $\rho(T)$-curves obtained after a second heating were identical with the curve shown in Figure 2 for the sample which had recovered its isotropy. As in Figure 2, the ρ values were orientation and frequency independent once the isotropic state had been restored, i.e. from the 2nd heating run onwards (curve (d)).

Another example of a sample with a relatively high orientation is given in Figure 5, this time relating to HDPE/20% VXC (lower) and HDPE/10% KBEC (upper). This figure shows the behaviour of a 0.5 mm thick sample cut from the surface of a test bar, curves (a)–(b). The heat shrinkage values characterizing the degree of orientation of the surface sample are $S_L = 0.6$ and $S_T = 0.3$. The $\rho(T)$-data for this sample are compared with the corresponding data

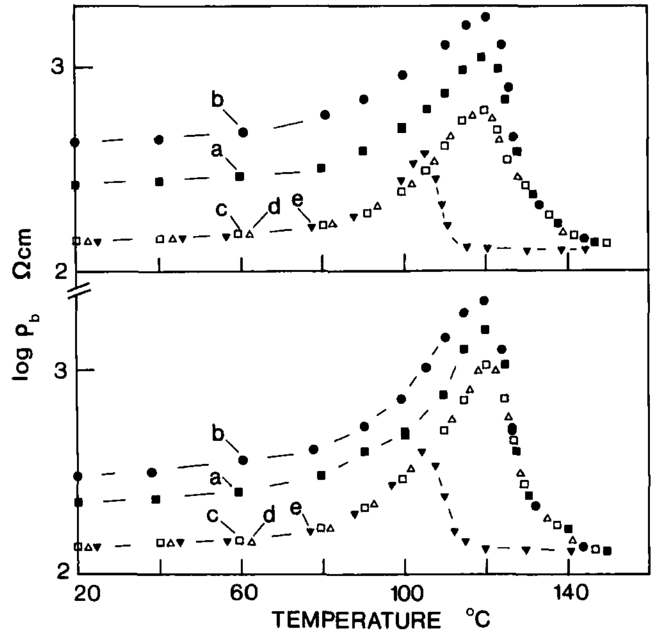

FIGURE 5 Temperature dependence of ρ_b for HDPE/20% VXC (lower) and HDPE/10% KBEC (upper). Samples taken from the surface (higher orientation) and the core (lower orientation) of injection moulded samples. Orientation given as heat shrinkage for both CB-grades: surface, $S_L = 0.6$, $S_T = 0.3$; core, $S_L = 0.4$, $S_T = 0.2$. Surface: curve (a): *x*-direction, (b): *y*- and *z*-directions at 1st heating, d.c. −10 kHz. 2nd–4th heating represented by curve (d). Core: curve (c) *x*-, *y*- and *z*-directions, d.c. −10 kHz. Cooling represented by curve (e).

obtained with a sample cut from the core of the test bar (lower orientation, curve (c)), with $S_L = 0.4$ and $S_T = 0.2$. The sample with the higher degree of anisotropy shows only a limited dependence of $\rho(T)$ on the measuring direction. Also the PTC-effect is relatively small. The sample taken from the core did not show any orientation dependence of $\rho(T)$. The results of Figure 5 relate to d.c., 1 kHz and 10 kHz (i.e. there was no frequency dependence). Upon reheating, curve (d), a $\rho(T)$-curve identical with curve (c) (core, 1st heating) was found.

The corresponding data for HDPE/10% KBEC with two degrees of orientation are shown in Figure 5 (upper). The sample from the surface of the test bar shows a limited orientation dependence of

$\rho(T)$, curve (a)–(b), while there is no such dependence for the sample cut from the core (lower orientation), curve (c). Furthermore, there was no difference between the 1st and subsequent heating runs, curve (d) for the latter sample. The cooling curve (e) represents cooling from 160°C (KBEC and VXC, upper and lower resp.).

The RT-values of ρ for all the HDPE samples were relatively low, $1\text{–}5 \times 10^2$ ohmcm, for both CB-grades used. The PTC-peak in the flow (x) direction was lower than in the other two directions for the oriented samples. Renewed heating produced in all cases $\rho(T)$-curves identical with those obtained with samples taken from the core. There was no frequency dependence of $\rho(T)$ in any of the samples.

Polystyrene

In this section, the above results obtained with LD and HDPE are compared with shrinkage and resistivity data for polystyrene compounded with 22.5% VXC and 12% KBEC. As the orientation distribution of the PE samples has been reported in detail previously,[17] only the S_L and S_T shrinkage values have been given in the preceding section. The orientation of the injection moulded PS bars measured as thermal shrinkage on 0.03 mm thick microtome slices is shown in Figure 6. On the whole, the anisotropy changes with the distance from the surface in a fashion normally found in injection moulded parts, that is to say, the orientation corresponds to a layered structure, consisting of a surface layer, a shear zone, and the core. In general, the degree of orientation in the flow direction (x) decreases from the surface to the centre. In the present case, there were some minor differences between the two CB-grades near the surface. No such difference was noted for the core. The lateral (y-direction) shrinkage, S_T, was also independent of the CB-grade. In contrast to S_L, the S_T values fell sharply with the distance from the surface; at around 0.2 mm, they reached a constant level. The maximum in the S_L values at around 0.4–0.5 mm from the surface (test bar thickness 3.5 mm) was not found with the HDPE/CB compounds analyzed and corresponds to the shear zone.[17]

Figure 7 shows the surface resistivity values, ρ_s, as measured during the successive microtoming of the 0.03 mm slices for the heat

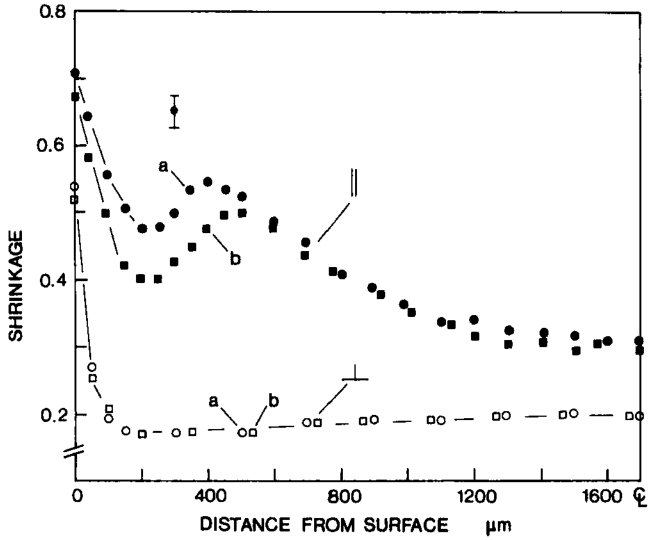

FIGURE 6 Heat shrinkage data, S_L and S_T, measured on 0.03 mm slices microtomed from injection moulded test bars of PS/22.5% VXC and PS/12% KBEC at varying distance from the surface.

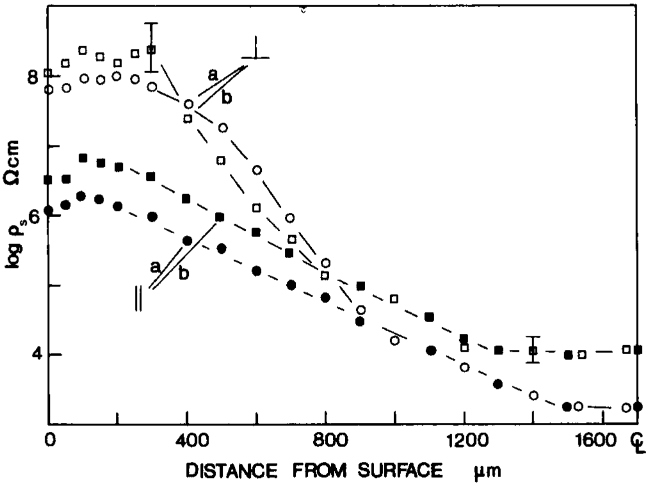

FIGURE 7 Surface resistivity measured on the remaining surface of injection moulded test bars of PS/22.5% VXC and PS/12% KBEC during successive microtoming of 0.03 mm thick slices. Measurements in x-(∥) and y-(⊥) directions. Curve (a): KBEC; (b): VXC.

shrinkage measurements, starting from the surface of the test bars. It may be noted that all the ρ-values of the preceding section related to bulk resistivity.

There is a pronounced difference between ρ_s-values measured in the flow direction (x) and perpendicular to it, the former values being more than a decade below the ρ_s-level measured laterally. After passing a weak maximum close to the surface, ρ_s falls monotonously, to level out eventually when reaching the central portion of the core, where the difference between the x- and y-direction disappears.

As shown for the PE-compounds,[17] the results of Figures 6 and 7 cannot be combined to give a simple relationship between orientation and ρ_s. This is shown for PS filled with the two CB grades in Figure 8. Despite the complicated shape of the $S_L - \rho_s$-curves, there is a general tendency for ρ_s to increase with orientation. Similar results were obtained for S_T.

The PTC-effect in the PS/12% KBEC compound was determined in the same way as in the preceding section, i.e. by determining the bulk resistivity, ρ, on 0.5 mm thick samples cut from the surface and from the central portion of the test bars.

The results are shown in Figure 9. As was found for PE, higher orientation enhances the PTC-efficiency, i.e. the increase in ρ with T

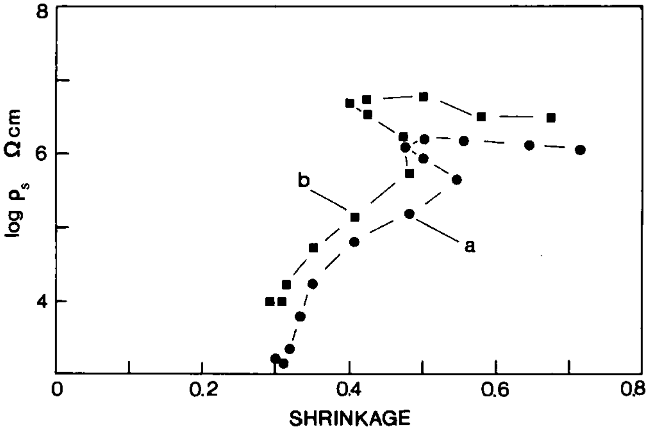

FIGURE 8 Surface resistivity, ρ_s, in flow direction vs. heat shrinkage, S_L for polystyrene with 12% KBEC (curve (a)) and 22.5% VXC (curve (b)). Cf. Figures 6 and 7.

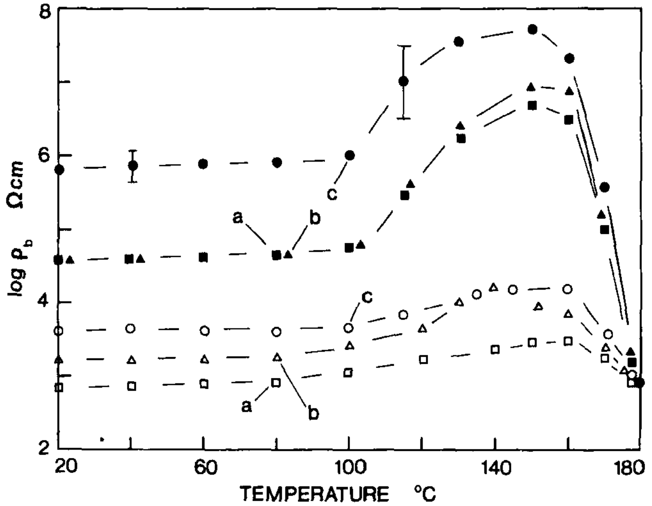

FIGURE 9 Bulk resistivity vs. temperature of a 0.5 mm thick sample (5 × 5 mm) cut from the surface ($S_L = 0.55$, $S_T = 0.2$; filled symbols) and the central portion of the core ($S_L = 0.3$, $S_T = 0.2$; open symbols) of injection moulded test bars of PS/12% KBEC. Curve (a): x-direction, (b): y-direction, and (c): z-direction.

in the surface region (filled symbols) is higher than in the core (open symbols). The shrinkage values were $S_L = 0.5$ and $S_T = 0.2$ in the surface. The corresponding values in the core part were $S_L = S_T = 0.3$. The x- and y-direction curves coincide for the surface sample. In the core, three directions produce separate curves; only a limited PTC-effect was recorded.

In contrast to the PE-samples, the width of the PTC-peak is rather broad starting just above T_g and ending about 80°C above that temperature. At 180°C the oriented samples have lost all orientation and the results from the surface and core sample coincide.

The behaviour of the PS samples during the second and subsequent heating runs was entirely different from that observed with PE, the height of the PTC-peak increasing with storage time prior to the measurement. Immediate reheating did not produce any PTC-peak at all, the $\rho(T)$ points forming a practically horizontal line. These phenomena typical of amorphous CB-containing systems have been treated in detail in previous publications.[19–20]

With regard to $\rho(f)$, the same behaviour was noted as with the PE/CB samples, high resistivity levels (orientation) being associated with a pronounced frequency dependence.

The bulk resistivity values measured over the whole cross-section of the PS-specimens used were as follows.

	ρ (kohmcm)	
Direction	KBEC	VXC
x	1.4	140
y	550	4000
z	95	800

The size of the samples was 10 × 10 × 3.5 mm.

Increasing the KBEC-content to 15% by weight produced a compound with a higher conductivity. Unlike the 12% compound, injection moulded samples of the new material were conductive also on the surface (ρ_s 1.0 kohmcm, x-direction; 1.6 kohmcm, y-direction, scatter ±20%). The ρ_B-value (10 × 10 × 3.5 mm sample from the central part of the test bar) was 12(x), 310(y), and 13 ohmcm (z) in the three main directions of anisotropy. Heat treatment at 180°C for 1 h gave ρ_s 20 ohmcm/cm, and ρ_B 12 ohmcm, both independent of direction. These values are qualitative illustrations only, since prolonging the duration of the treatment results in a further lowering of the resistivity level.

Thus increasing the CB-content produces a compound where the influence of orientation and processing conditions on the ρ-values is largely eliminated. As expected, such a compound exhibits practically no PTC-effect.

FINAL REMARKS

The main result of this investigation is the finding that the PTC-effect can be significantly enhanced by increasing the degree of orientation. In the present case, samples with varying orientation were obtained from the surface and the core of injection moulded test bars, utilizing the well-known difference in anisotropy found across the thickness of such parts.

The role of orientation is reminiscent of that played by the CB concentration. Apparently, optimal PTC-effects are obtained at CB contents corresponding to the inflexion of the sigmoid ρ (concentration) curve.[1,9] At higher concentrations, the PTC-effect disappears, as the sample becomes conductive within the entire temperature range of interest. At the other end of the CB concentration range, the resisitivity is too high to be of practical importance, and the PTC-effect is only weakly developed. Both these extremes can be found among the results presented above when analyzing the combined effect of CB concentration and orientation. On the whole, increasing the degree of orientation is equivalent to a reduction in the CB content. In samples having too high CB contents to produce any significant PTC-effect in the isotropic state, orientation creates a pronounced PTC-behaviour. This is especially true of the samples with a relatively low orientation, $S \approx 0.4$. Increasing the anisotropy still further, the equivalent decrease in the CB content reaches a level where the resistivity becomes too high.

The effects observed may be qualitatively understood in terms of a network of CB particles that is disrupted during the filling of the mould. Close to the surface, the disrupted state is preserved due to rapid cooling of the melt. On the other hand, the core portion reflects the behaviour of the corresponding isotropic material, since cooling is slower in the centre of the moulding, thus allowing the network, at least partly, to relax and reform its isotropic structure.

The difference between LDPE and HDPE demonstrated in Figures 2–4 and 5, resp., appears to be related to the different crystallinity of the two materials. In HDPE, the polymer exhibiting higher crystallinity, the space between the crystallites available to the CB particles is reduced, thus resulting in a higher local CB concentration and, consequently, higher conductivity. This, in turn, leads to a lower PTC-effect.

It is not possible to relate the ρ values given above to reported data on the changes of ρ during uniaxial deformation of CB filled elastomers.[21] The reasons for this is the more complicated orientation distribution encountered during the mould filling stage, and further the fact that shear forces affect the CB network in a more severe way than tensile forces.

Small but measurable degrees of orientation may leave the CB network unaffected. This is illustrated in Figure 5 for the sample taken in the core, curve (c); this anisotropic sample, $S_L = 0.4$,

$S_T = 0.2$, was completely isotropic when considering the resistivity. This also points at an important aspect of conductive systems consisting of two phases. It seems that, within certain limits, the matrix and the filler particle network do not follow each other's deformation pattern. This implies that the structure of the network may be different in samples with the same degree of orientation. Obviously, the state of a particle network cannot be described by a single parameter such as an orientation measure for the matrix polymer. Due to the dilution of the dispersant phase, the degree of aggregation of the particles may also show appreciable variation.

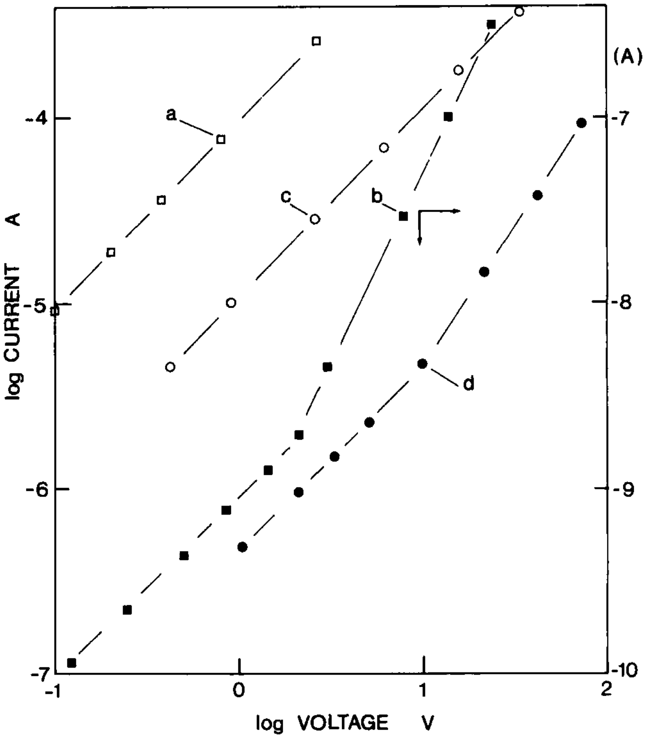

FIGURE 10 Current-voltage behaviour of samples with lower (ohmic) and higher (non-ohmic) orientation (resistivity), measured in x-direction. Curve (a): LDPE/10% KBEC ($S_L = 0.35$), (b): LDPE/10% KBEC ($S_L = 0.6$), (c): PS/12% KBEC ($S_L = 0.3$), (d): PS/12% KBEC ($S_L = 0.5$). Lower orientation, open symbols; higher orientation, filled symbols.

Such effects, elusive as they must be to an experimental observer, are of crucial importance for the process of electrical conduction.

Such a picture is consistent with other treatments of the electrical properties of CB-filled materials, the distance between the particles being the basis of theoretical treatment of such phenomena. The present work shows that orientation effects due to processing influence this distance in much the same way as the CB concentration. We illustrate this point in a qualitative fashion in Figure 10 which shows the I(V)-dependence for samples with low and high orientation. As already mentioned, higher orientation is equivalent to lower CB concentration, i.e. a larger particle distance. It is a well established fact that samples at the lower conductivity end show non-ohmic behaviour; at concentrations above the percolation threshold the conduction is ohmic. The data of Figure 10 show such a pattern for a flow-induced variation in particle distance. Although illustrated with a few examples only, the behaviour shown in Figure 10 was representative of all the results reproduced in the preceding sections.

The possibility of adjusting the magnitude of the PTC-effect to a desired level has an obvious practical significance. The reduction of the PTC-effect observed upon the second heating may appear to be a serious limitation. On the other hand, the results presented above do not represent a technical situation since the temperature range has been extended far above the maximum operating temperatures (relative to T_g or T_m) of normal PTC devices. In view of this, the orientation-induced PTC-effect may well represent a technically feasible solution.

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