Conductive PE–carbon composites by elongation flow injection moulding

Part 1 *Flow-induced conductivity profile–high molecular weight matrix*

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In Part 1 and Part 2 of this paper the preparation of linear polyethylene(PE)–carbon black processed composites with conducting electrical properties was examined by means of elongation flow injection moulding. Mould geometry was optimized in the form of oriented double-armed bars so as to give enhanced mechanical properties combined with a high degree of electrical homogeneity. The present paper deals with composites using a high molecular weight PE matrix. It is shown that the injection-moulded composite material exhibits not only a lower percolation threshold, ϕ_c, than the conventionally pressure-moulded isotropic sample, but also conductivities two to three orders of magnitude larger than the latter. The radial and axial conductivity profiles, for concentrations well above ϕ_c, are discussed in the light of the molecular orientation variations across the bars as determined by birefringence. A segregation of primary filler particles, during flow-induced orientation, into axial channels has been shown to explain the enhancement of conductivity detected in the injected mouldings. In addition, for filler concentrations near 7%, σ-profile analysis indicates the development of a uniform conductive-stiff inner cylinder, several millimetres wide, homogeneously extending along the full length of the injected material.

1. Introduction

The investigation of electrically conducting composites consisting of a polymer insulating matrix and a conductive microadditive has been a topic of increasing attraction in recent years [1–8]. Among the various possible composite combinations, those based upon carbon-black as a filler are acquiring special interest because they combine the inherent properties of polymers (toughness, processability, low density) with a relatively high conductivity ($\sigma \sim 10^0$ to $10^1\,\Omega^{-1}\,cm^{-1}$). It is now well established that these solid polymer–carbon black mixtures show a discontinuous sudden insulator–conductor transition at a critical percolation volume of microadditive [1]. The low concentration of additive (a few per cent) required to form a conducting network is an additionally attractive feature of these light composites. The transport mechanism near the percolation limit is based upon electron tunnelling between microadditive particles [9]. We have recently verified that the percolation threshold for polycarbonate–carbon black composites depends on the structure level (aggregation and agglomeration of the basic 50 to 60 nm diameter particles) of the microadditive [10]. Further, we have reported the conductivity behaviour for low-density polyethylene–carbon black composites [11] as a function of temperature. Here the contact resistance developed during metal coating was discussed in the light of fluctuation-induced electron tunnelling across the surface of the metal–polymer interphase [11]. The above studies shed light on basic questions of carrier transport in composites and may lead to the development of novel light processable materials amenable to conduct electricity. Memory and switching electrical properties have, likewise, been reported for polycarbonate–graphite composites [12].

From the viewpoint of immediate applicability, the major problems arising in composites are concerned with the control and reproducibility of the conducting features, the stability and, most importantly, the processability of the composite material. In this sense, we extend in the present study the above mentioned investigations to the case of high-density PE–carbon black composites processed by injection moulding. It is known that processing variables in injection moulding induce substantial changes in the orientation and microstructure of the moulded material [13, 14] and, consequently, may enhance properties such as

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toughness, strength, elastic modulus, hardness, etc. [14, 15]. Elongational flow injection moulding (EFIM) [16–18] offers, in addition, the advantage of producing polymer materials having a tensile stress about four times larger than conventionally processed ones. The purpose of this work is to attempt to develop a route for processing stiff materials, concurrently exhibiting enhanced electrical properties.

In the present papers such an attempt is substantiated by EFIM of PE previously mixed with carbon black. The subject is divided in two papers according mainly to the materials used. Part 1 deals with high molecular weight PE as a matrix. The changes of the flow-induced conductivity profile along the radial and axial cross-section of the mouldings will be first discussed. Special emphasis on the influence of the injection-moulding processability upon the percolation threshold will be made.

Part 2 [19] will be concerned with the influence of molecular weight as a parameter on EFI moulded polyethylene–carbon black composites, covering a wide range of materials, including some very low ones.

2. Experimental details

2.1. Materials and processing conditions

Composite samples were prepared by mixing linear polyethylene (Lupolen 5261-Z) with carbon black XE2 from Phillips Petroleum. Lupolen 5261-Z is a high molecular weight grade (M_w 450 000) material and the XE2 carbon black shows a well-developed structure favouring the formation of particle aggregates [10]. The above two components were mixed with the aid of an extruder at 160° C following the scheme of Fig. 1. The filler concentration was varied from 1 to 7.5 vol %. The mixture of Lupolen 5261–Z with $\phi = 7.5\%$ carbon black was prepared by Zipperling and Kessler, Ahrensburg. The samples were: (a) moulded into isotropic 1 mm thick plates of 30 mm diameter at 40 MPa and 150° C, and (b) prepared in the form of oriented double-armed bars (gauge length 70 mm, thickness 4 mm, width 4.2 mm) (Fig. 2), using a Krauss Maffei Monomat 80 injection moulder. Fig. 3 depicts the relation between the shape of the bar and the injection direction, Z. Injection of the melt through a 15 mm wide inlet into the comparatively thin mould cavity contributes not only to shearing flow zones near the cavity walls but also to elongation flow at the centre of the cavity cross-section (elongational flow injection process) [20]. Bayer *et al.* [16] have investigated the processing conditions for which the polymeric material exhibits optimum mechanical properties. The injection conditions adopted in this study were: melt temperature 148° C, mould cavity temperature 20° C, injection pressure 2 kbar, injection speed 3.5 cm sec^{-1}, time of cavity under pressure 50 sec.

2.2. Techniques

The conductivity, σ, of the moulded bars was measured in axial direction (injection direction Z). To measure σ as a function of Z each bar was cut into 10 mm long segments. Electrodes were prepared by painting with silver the cut surfaces perpendicular to the Z direction. Electrical properties were measured along the Z direction using a Keithly potential source of 3 kV. The voltage and current were measured with a Data

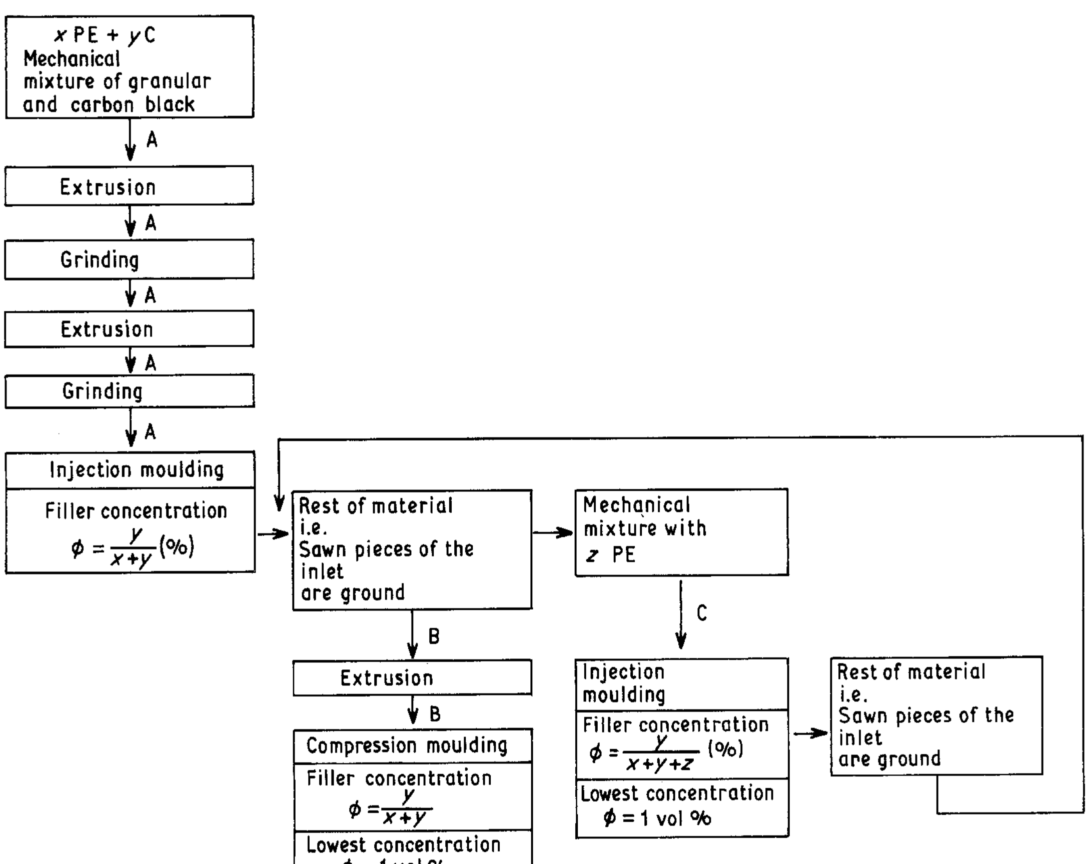


Figure 1 Processing and mixing procedure.

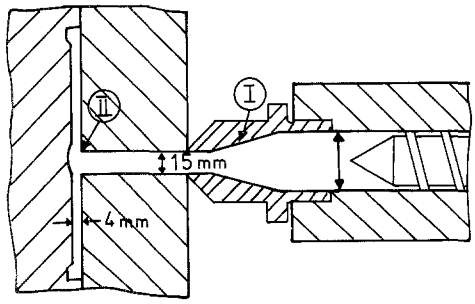


Figure 2 Schematic drawing of the elongational flow injection moulding (EFIM) used: wide inlet (15 mm) and small cross-sections (4 mm). Elongation flow zones: I, inlet zone of die; II, transition from wide inlet into opposite bars.

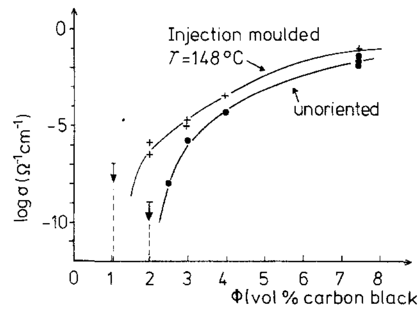


Figure 4 Dependence of log σ on concentration of carbon black for compression-moulded (unoriented) and elongational flow injection-moulded (oriented) samples. 10 mm long samples from the injected moulds were taken at $Z = 25$ mm (Fig. 2).

Precision voltmeter and a Leeds and Northrup current recorder, respectively. In order to investigate the axial conductivity profile, σ_Z, across the thickness of the moulded bars, coaxial cylindrical sections with varying radii were prepared (Fig. 3). Thus segments for $Z = 25$ mm from the inlet were machine reduced to cylinders of 4, 3 and 2 mm diameter, respectively. The average conductivity, $\bar{\sigma}$, here was derived according to: $\bar{\sigma} = 1/0.17\, R_a \Omega^{-1}\, \mathrm{cm}^{-1}$ where R_a is the electrical resistance of the cut. The value of σ_Z was examined as a function of the radial distance, r. The reported data of σ_Z represents an average of at least two or three measurements. For the birefringence study, additional 40 μm thin film cuts of the injection-moulded matrix were made with a microtome on the XY plane for $Z = 25$ mm. Birefringence, Δn was measured using a Leitz microscope with a white light source and the phase shift was calibrated by means of quartz and calcite compensators. The quantity Δn was investigated as a function of radial direction r, and Z was taken as a variable parameter.

3. Results

The dependence of log σ_Z against the volume per cent filler for PE Lupolen 5261-Z–XE2 carbon black composites prepared in the form of compression-moulded plates and injection-moulded bars is shown in Fig. 4. The dotted lines denote the percolation threshold for both materials. A similar step-like conductivity behaviour has recently been reported for LDPE–XE2 carbon black composites [11]. Most interesting is, however, the fact that the injection-moulded material shows not only a lower percolation volume, ϕ_c, but also notably larger σ values (one to three orders of magnitude) than the simply compression-moulded composite. The opposite behaviour is actually the normal case when using conventionally injection-moulding matrix grades, i.e. injection moulding of carbon black composites normally depresses the conductivity properties of the isotropic composite. Such an opposite behaviour will be discussed in detail in Part 2 [19]. Above ϕ_c, in Fig. 4, σ clearly tends towards metallic conduction levels reaching values in the vicinity of $10^{-1}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for $\phi \sim 7$ vol %. In order to explore the conductivity variation in the injection-moulded material with reference to the degree of orientation, concurrent measurements of birefringence and axial conductivity were performed across the injection direction. Fig. 5 offers evidence for the parallel behaviour of birefringence Δ_n of the polymer matrix and relative axial conductivity $\sigma_Z/\bar{\sigma}$ across the radial direction, r, for a filler concentration $\phi = 4$ vol %, well above the percolation level. In both cases Δ_n and σ_Z show minimum values at the walls and in the centre of the injection moulded oriented bar and broad maxima with a thickness of about $r \sim 1.5$ mm. With increasing filler concentration ($\phi \sim 7.5$ vol %) the profile σ_Z/σ across the radial direction becomes more uniform, showing just a distinct broad maximum in the central part of the section of the bar (Fig. 6). The variation of σ_Z along the axial direction for the composite bar with $\phi = 4$ vol % is shown in Fig. 7a. Here a broad maximum for σ_Z centred at $Z \sim 30$ mm emerges. The increase of filler concentration in the composite induces, as in the radial direction, a more uniform conductivity profile. Indeed, for 7.5 vol % a true constant σ_Z value along the axial direction is developed (Fig. 7b). Fig. 8 shows two birefringence profiles at varying values of Z. Together with Fig. 5a these profiles indicate that birefringence decreases with increasing coordinate Z in the flow direction.

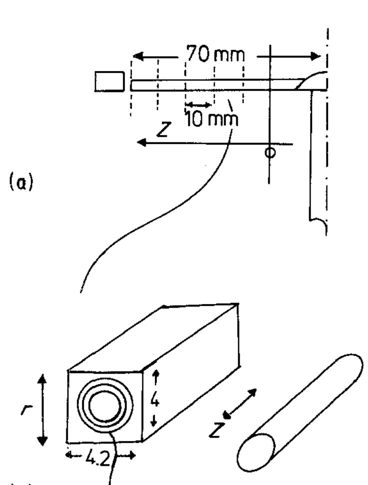


Figure 3 Schematic drawings of sample preparation from the injected moulds for conductivity measurements. (a) Longitudinal profile, (b) cross-sectional profile. The circles denote machined cross-sections of 4, 3 and 2 mm, respectively.

4. Discussion

4.1. Radial conductivity profile

It is known that the increased tensile mechanical properties in injection moulded polymer materials are related to the enhancement of flow induced molecular

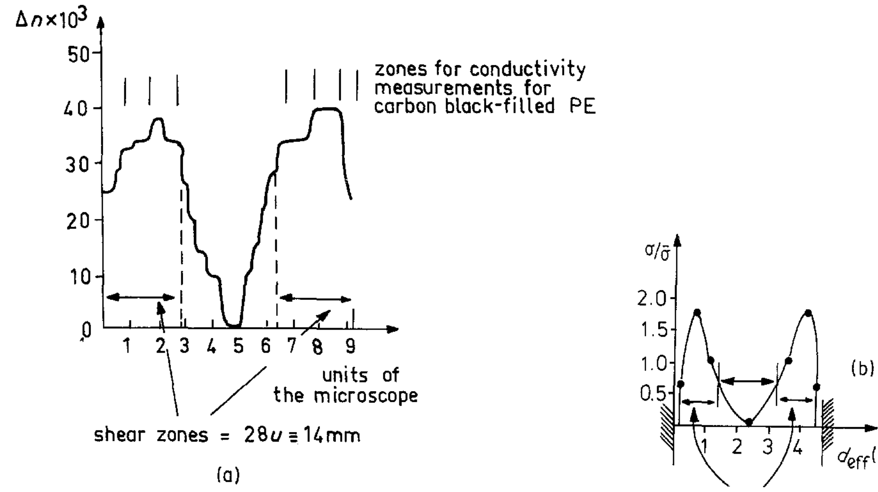


Figure 5 (a) Birefringence profile in the middle of the bar ($Z = 25$ mm). Measurements were carried out on a 40 μm thick film microtomed within the XZ plane from the middle of the cross-section. (b) Conductivity profile, $\sigma/\bar{\sigma}$ obtained from machined circular cross-sections according to Fig. 2 for $\phi = 4\%$ ($Z \cong 25$ mm, $\bar{\sigma} = 4 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$). To compare the conductivity of the circular cross-section with the original rectangular cross-section an effective diameter, $d_{\text{eff}} = 2\,(A/\pi)^{1/2}$ has been calculated (A = area of the rectangular cross-section). 1 unit of the microscope corresponds to 0.5 mm of d_{eff}. Arrows denote shear zones in Fig. 4a.

orientation under pressure [15–20]. Orientation arises, in fact, through flow elongation of the melt within the mould cavity. The orientation within the moulded bar is often not homogeneous, elongational flow developing mainly in the centre and shearing deformation zones arising on the vicinity of the cavity walls. The morphological feature of the injection moulded material has been shown to be a shish-kebab, fibre-like, structure oriented in axial direction [21]. Correlations between orientation and mechanical properties (modulus, yield strength, etc.) in the injection-moulded material are well established [13, 21]. The question arising in the present study is whether one can similarly attempt to explain the electrical conductivity profiles in terms of the orientation features of the injection-moulded sample. We shall confine our discussion to composite systems exhibiting electrical properties above the percolation threshold.

The first striking feature in the conductivity data measured across the injected composite bar is the existing parallelism between $\sigma_Z/\bar{\sigma}$ and Δ_n (Fig. 5). This correlation is strictly valid only at low concentrations of carbon black, because the filler may presumably influence the flow conditions and consequently can affect the birefringence profile. The results in Fig. 5 suggest that the σ_Z profile in radial direction is primarily induced by flow conditions. The variation of Δ_n with r indicates the presence of wide shearing zones, typical for high molecular weight materials in the elongational flow method. One may think that flow-induced orientation of the composite leads to a shish-

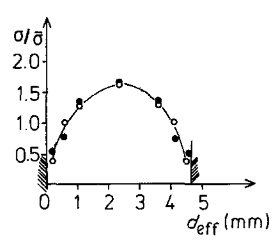
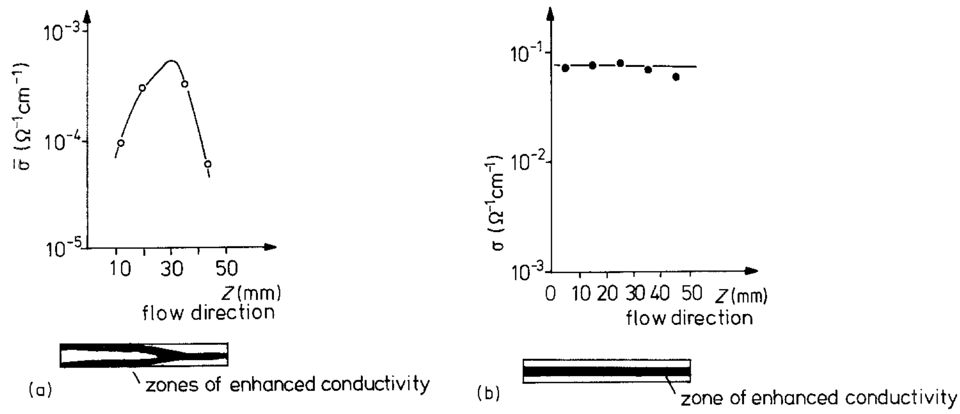


Figure 6 Conductivity profile as in Fig. 4b for $\phi = 7.5\%$ and $\bar{\sigma} = 8 \times 10^{-2}\,\Omega^{-1}\,\text{cm}^{-1}$. (●) $Z = 15$ mm, (○) $Z = 35$ mm.

kebab structure formation and to a concurrent segregation of primary particles into longitudinal regions. A replica of the etched surface [22] of the material shows, as expected, the existence of a shish-kebab structure of oriented polyethylene exhibiting segregated channels of conducting carbon black (Fig. 9). This result suggests that flow induces a segregation of carbon black particles which leads to the observed increase conductivity of the oriented structure. Further details relating to the interpenetrating structure of the carbon black within the matrix will be given in a forthcoming study [23]. Such an oriented shish-kebab structure filled with carbon black particles can be visualized as an electrical system of carbon black conducting channels in parallel with elongated insulators (polymer shish-kebabs) leading to the flow modulated σ-profile obtained (Fig. 5). One may expect that such a conductivity profile would give rise to a macroscopic electrical anisotropy. Indeed, while σ_Z (maximum) $\sim 8 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$ the $\sigma_\perp$ value normal to Z is about three orders of magnitude smaller.

On the other hand, in the outer zones and in the centre of the profile, $\Delta_n \sim 0$, i.e. the material is nearly isotropic. In this region shish-kebab formation is absent and the level of particle segregation hence decreases. Microscopy investigations on isotropic samples of polyethylene and polypropylene mixed with carbon black point to a preferential segregation of filler particles between spherulites [24]. The surface to volume ratio for spherulites (assuming spheres), available for filler segregation, is 30% smaller than for axial channels and leads consequently to a 30% larger percolation volume as obtained in Fig. 4. The conductivity value for isotropic samples of our Lupolen 5261–Z–4%. XE2 composite is equal to $\sigma_{\text{isotropic}} \simeq 5 \times 10^{-5}\,\Omega^{-1}\,\text{cm}^{-1}$ (see Fig. 4). Using now the value of σ_Z (max) $= 7.2 \times 10^{-4}\,\Omega^{-1}\text{cm}^{-1}$ for the intrinsic conductivity within the segregated carbon black oriented regions from Fig. 5, and the above $\sigma_{\text{isotropic}}$ value for the non-oriented regions, we can attempt to derive the average conductivity value, $\bar{\sigma}$, for the injection-



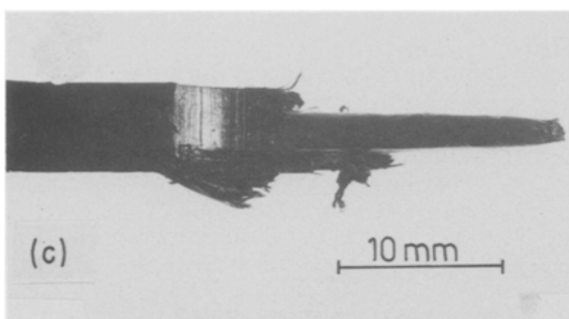


Figure 7 Conductivity profile along the flow direction (Z-axis). $\bar{\sigma}$ values are averaged over the whole cross-section. Measurements were taken on 10 mm long cuts (Fig. 2). (a) $\phi = 4\%$, (b) $\phi = 7.5\%$, (c) the fracture pattern of a notched sample of Lupolen 5261Z with $\phi = 4\%$. This fracture pattern corresponds to the schematic drawing of the shear zones of enhanced conductivity depicted in (a).

moulded bar:

$$\bar{\sigma} = \frac{\sigma_{\max} A_0 + \sigma_{\text{iso}} A_u}{A} \quad (1)$$

where A_0, A_u and A are, respectively, the cross-section areas for the oriented and less-oriented zones and A is the total cross-section of the bar.

Using the data of Fig. 5, $\bar{\sigma}$ turns out to be equal to $\bar{\sigma} = 4 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$, value which is in good agreement with the average data of Fig. 4 for $\phi = 4\%$. Summarizing, the larger σ value and lower ϕ_c threshold obtained for the injection-moulded bar in Fig. 4 can be understood in terms of the increased conductivity arising from the oriented regions, providing a more efficient inherent carbon particle segregation than in the isotropic material.

Typical conductivity profiles arising at higher filler concentrations ($\phi \sim 7.5$) can be explained as follows: because of the increased filler concentration, the reinforced melt exhibits a higher viscosity leading to a broadening of the shearing zones within the mould cavity, overlapping in the centre. The corresponding conductivity profile (Fig. 6) shows, as a result, a broad homogeneous maximum in the centre with a conductivity level of $\bar{\sigma}_Z \sim 10^{-1}\,\Omega^{-1}\,\text{cm}^{-1}$. Such a profile is evidence of the existence of a highly conducting cross-section in the centre of the injection-moulded bar.

4.2. Axial conductivity profile

The next question arises as to what extent the above conductivity profiles (Figs 5 and 6) are preserved along the axial direction Z. It is known that orientation gradually decreases along the injection direction [25, 26]. Fig. 8 illustrates the orientation decrease detected along the injection direction. Thus, in principle, a parallel decrease of σ with Z shoud be expected. Fig. 7a shows, however, for the composite with $\phi = 4\%$ an initial increase of σ along Z followed by a final decrease with a maximum σ value at $Z = 45$ mm. The mechanical fracture pattern of the composite with $\phi = 4\%$ (Fig. 7c) shows the presence of an inner core which is confined within the outer shearing zones in Fig. 5. Similar fracture patterns are also observed in the isolated matrix [16]. The preferential segregation of carbon black particles into these shearing zones activates the fracture mechanism in the injection-moulded composite. Nevertheless the strength at break of this composite exhibits values around $80\,\text{MN}\,\text{m}^{-2}$, still a factor of 3 larger than for conventionally injection-moulded materials. The conductivity increase with Z shown in Fig. 7a can now be

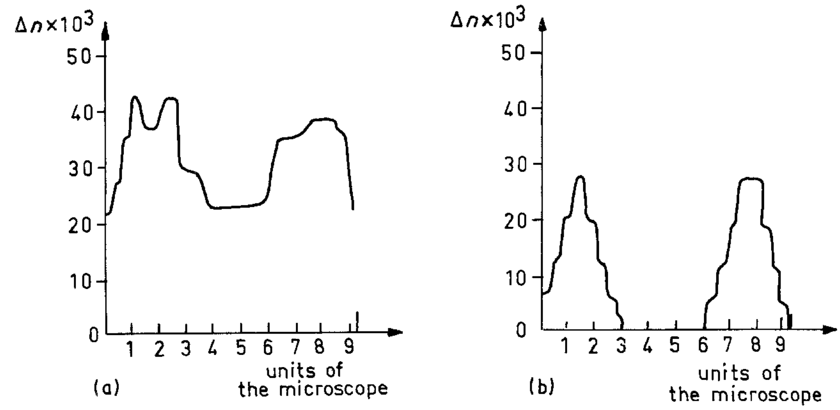


Figure 8 Birefringence profiles at (a) $Z = 5$ mm and (b) $Z = 45$ mm. Compare with Fig. 4a.

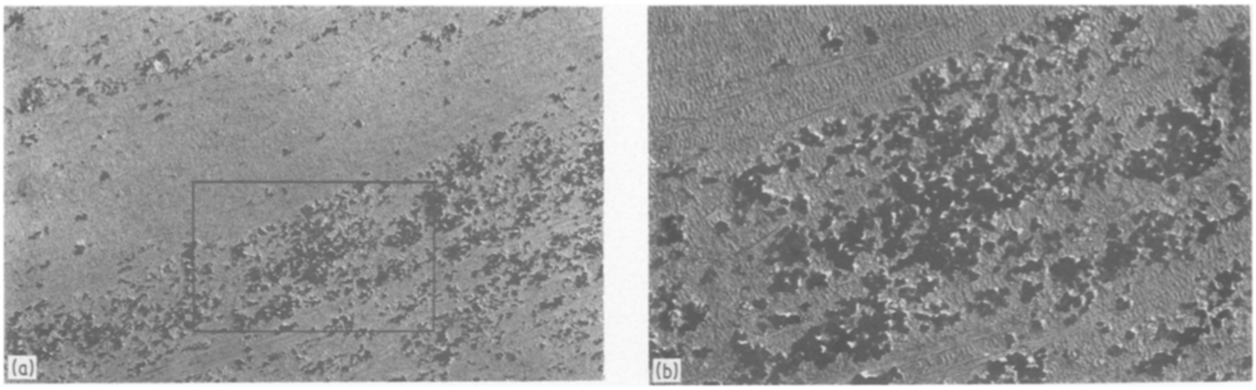


Figure 9 (a) Electron micrograph of a permanganic etched surface replica for the sample containing 4% carbon black. (b) Selected area of (a).

related to the fracture profile giving evidence for shearing zones of high conductivity. As the shearing zones in the Z direction approach each other, the value of σ increases. The tip of the inner core (maximum overlap of shearing zones) corresponds to the maximum obtained for $\log \sigma_Z$ at $Z = 30$ mm. For values of $Z > 30$ mm, σ decreases as a consequence of the overall orientation decrease along Z.

The increase of filler concentration up to 7.5% leads to a constant value, σ, along the axial direction of the composite bar. This means that the inner core is transformed, with increasing ϕ, into a true conductive cylinder along the full length of the injection-moulded bar (Fig. 7b). The result is supported by the data recorded in the profile of Fig. 6, showing that $\sigma_Z/\bar{\sigma}$ takes up identical values at two different Z positions. The above conductivity profiles for $\phi = 7.5\%$ give rise, in addition, to a very small electrical anisotropy arising from a $\sigma_\perp$ normal to Z one order of magnitude lower than σ_Z.

5. Conclusions

1. Elongational flow injection moulding of high molecular weight PE–carbon black composites of high filler concentration ($\phi \sim 7\%$) yields a novel class of processable light homogeneous materials with conductivity in the vicinity of $\sigma \sim 10^{-1}$ to $10^0\,\Omega^{-1}\,\text{cm}^{-1}$. The conductivity reached and the high degree of electrical homogeneity make these materials adequate candidates for the shielding of electromagnetic radiation [27].

2. The processing parameters, mould geometry and filler concentration were chosen so as to reach a high degree of electrical homogeneity combined with acceptable mechanical properties.

3. Thinner mould geometries would require a lower filler concentration to obtain the merging effect of the shearing outer zones towards the centre required to produce a homogeneous conductivity profile.

Acknowledgements

We thank Bundesministerium für Forschung und Technologie (FRG) and Ministerio de Asuntos Exteriores (Spain) for the generous support of this project. R.K.B. wishes to acknowledge the tenure of a Deutschen Forschungsgemeinschaft Research grant during this work. Thanks are also due to Zipperling and Kessler, Ahrensburg, FGR, for kindly preparing the mixture of Lupolen 5261 Z with a 7.5% carbon black.

References

1. F. BUECHE, *J. Appl. Phys.* **43** (1972) 4837.
2. S. KIRKPATRICK, *Rev. Mod. Phys.* **45** (1973) 574.
3. M. NARKIS, A. RAM and Z. STEIN, *Polym. Eng. Sci.* **21** (1981) 1049.
4. R. B. SEYMOR (ed.), “Conductive Polymers” (Plenum, New York, 1981).
5. F. J. BALTÁ CALLEJA, T. A. EZQUERRA, D. R. RUEDA and J. ALONSO, *J. Mater. Sci. Lett.* **3** (1984) 165.
6. M. HISHINUMA and T. YAMAMOTO, *ibid.* **3** (1984) 799.
7. M. KRYSZEWSKI, J. K. JEZZKA, J. ULANSKI and A. TRACZ, *J. Appl. Chem.* **56** (1984) 355.
8. S. RADHAKRISHNAN, *J. Mater. Sci. Lett.* **4** (1985) 1445.
9. P. SHENG, *Phys. Rev.* **1321** (1980) 2180.
10. T. A. EZQUERRA, J. MARTINEZ SALAZAR and F. J. BALTÁ CALLEJA, *J. Mater. Sci. Lett.* **10** (1986) 1065.
11. T. A. EZQUERRA, F. J. BALTÁ CALLEJA and J. PLANS, *J. Mater. Res.* **1** (1986) 510.
12. T. A. EZQUERRA, F. J. BALTÁ CALLEJA, D. R. RUEDA and J. PLANS, *J. Appl. Phys.* **58** (2) (1985) 1061.
13. D. R. RUEDA, F. J. BALTÁ CALLEJA and R. K. BAYER, *J. Mater. Sci.* **16** (1981) 3371.
14. F. JOHANNABER, “Injection Molding Machines”, 2nd Edn (Hanser, New York, Toronto, 1985) p. 39.
15. R. K. BAYER and G. W. EHRENSTEIN, *Colloid Polym. Sci.* **259** (1981) 293.
16. R. K. BAYER, Europhys. Conference Abst. Vol 6G-75 “14 Europhysics Conference on Macromolecular Physics”, Vilafranca del Penedes (European Physical Society, Geneva, 1982) p. 75.
17. R. K. BAYER, A. E. ELIAH and J. C. SEFERIS, *Polym. Eng. Rev.* **4** (1984) 201.
18. G. W. EHRENSTEIN and C. MAERTIN, *Kunstoffe* **75** (2) (1985) 105.
19. F. J. BALTÁ CALLEJA, T. A. EZQUERRA and R. K. BAYER, *J. Mater. Sci.* in press.
20. E. LÓPEZ-CABARCOS and R. K. BAYER, unpublished results (1986).
21. W. HECKMANN, PhD Thesis, Technische Hochschule Darmstadt (1976).
22. D. C. BASSETT, “Principles of Polymer Morphology” (Cambridge University Press, 1981).
23. J. MARTINEZ SALAZAR, T. A. EZQUERRA, R. K. BAYER and F. J. BALTÁ CALLEJA, to be published.
24. R. BODE, *Kautsch. Gummi Kunstst.* **30** (1983) 660.
25. H. JANESCHITZ-KRIEGL, *Rheol. Acta* **18** (1979) 693.
26. J. L. S. WALES, I. V. LEEUWEN and R. V. D. VIJGH, *Polym. Eng. Sci.* **12** (1972) 358.
27. A. BLEDZKI and D. STANKOWSKA, *Kunstoffe* **74** (1984) 2.

Received 24 November 1986
and accepted 29 January 1987