JOURNAL OF MATERIALS SCIENCE 23 (1988) 4121–4126

Conductive PE–carbon black composites by elongational flow injection moulding

Part 2 *Variation of the molecular weight of the matrix*

T. A. EZQUERRA, R. K. BAYER, F. J. BALTÁ CALLEJA
Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

A study of the distribution of electrical conductivity in elongational-flow injection-moulded high-density polyethylene materials containing carbon black is reported. Radial and axial conductivity profiles are discussed in terms of molecular orientation variations across the bars. It is shown that for low and intermediate molecular weight matrices the conductivity decreases after material orientation through injection moulding. For high molecular weight polyethylene, as demonstrated in Part 1 of this report, conductivity increases with orientation. The results are qualitatively explained in terms of three principal effects: (i) orientation of particle aggregates during injection moulding, (ii) degradation of the aggregates depending on molecular weight, and (iii) flow-induced segregation of additive particles. The variation of the percolation threshold for the composites is additionally discussed for isotropic and injection-moulded materials in terms of factors affecting the mixing efficiency between filler and molten polymer.

1. Introduction

The interest in composites made with carbon black has been increasing in recent years [1–5]. The origin of this interest is due to the fact that carbon black is nowadays the additive most widely used to make conducting polymer materials [6, 7]. Composites made with carbon black are not only replacing metals in several applications but also are industrially used in capacitative video discs and xerographic processes [8]. The applicability of carbon black–polymer composites depends on how well their properties can be manipulated. This, in turn, requires an understanding and controlling of the physical mechanism involved. The achievement of good electrical conductivity requires carbon loading near the limits of polymer processability. In these composites the structure of the polymer matrix plays only a secondary role on the carrier mobility [9, 10]. The conductivity primarily depends on the percolation threshold for the carbon black particles. Beyond the percolation threshold carriers are transported through the carbon three-dimensional network, mostly involving a tunnelling mechanism [11].

In Part 1 of this report [12] the preparation of carbon black–high molecular weight polyethylene (PE) composites was examined by means of elongational flow injection moulding [13]. The method was applied to these composites to give high mechanical strength materials combined with homogeneous conducting electrical properties. It was shown that the injection-moulded carbon composite material exhibits a lower percolation threshold and conductivities two to three orders of magnitude larger than for pressure-moulded samples. In addition, the variation of the conductivity profile within injection-moulded test bars was discussed in terms of molecular orientation across the injection-moulded sample. A segregation of filler particles during flow-induced orientation into axial channels was shown to explain the high conductivity levels reached in the injected mouldings. The present paper attempts to explain the influence of injection moulding on the electrical properties of carbon black–polymer composites. It will complement, as well, the results obtained in Part 1 [12] using a high molecular weight matrix. Two aspects are the object of the present study:

(i) To investigate the dependence of the molecular weight on the conductivity level of the injection-moulded composites. For this purpose several PE materials in a wide range of molecular weights (50 to 250 000) were used as matrices.

(ii) To examine to what extent the above segregation effect of additive particles may be influenced by the materials used.

2. Experimental procedure

Composite materials based on linear polyethylene with different molecular weights and varying amounts of carbon black were prepared (see Table I). The carbon black used was XE2 from Phillips Petroleum, showing a very high tendency to form aggregates with

TABLE I Density and molecular weight of the polyethylene matrices used

Matrix	Density (g cm^{-3})	M_η
Vestolen A 6017	0.966	51 000
Rigidex 006-60	0.962	115 000
Lupolen 6021D	0.962	161 000
Lupolen 5261Z	0.958	248 000

0022–2461/88 $03.00 + .12

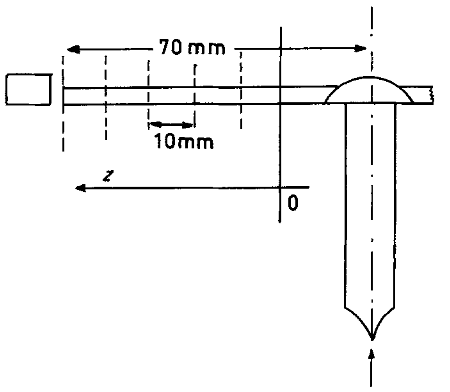

Figure 1 Mould geometry of injected bar. Arrow denotes injection direction. Only left half of the mould is represented. Overflow volume is shown on the left side. The central part is used for radial conductivity measurements in the z direction (see text).

TABLE II Processing procedure of composites*

Mixing of the components [12]
↓
Extrusion
↓
Grinding
↓ ↗ *oriented bar*
Injection moulding → unoriented part → *compression moulding*

*Final processed materials are italicized.

a very well-developed agglomerate structure (DBP absorption = $4\,\mathrm{cm^3\,g^{-1}}$). The filler concentration was varied from 1 to 5 vol %. The mixing process was the same for all the materials, i.e. the mixing time was kept constant, and the processing procedure was described in detail in Part 1 [12]. Summarizing, the homogenized material was successively injection-moulded, using the same mould geometry and injection conditions as those quoted in Part 1. In this way highly oriented bars were obtained. This is due to a strong component of elongational flow that arises from the narrowing of the flow cross-section at the transition from the inlet into the mould [12] (Fig. 1). The overflow volume represents the part of the injected moulding with lowest orientation. This part was sawn off and thereafter compression-moulded to a plate with a thickness of approximately 1 mm. In this process the melt temperature was kept constant at 150° C for 20 min under a pressure of 40 bar before cooling down at a rate of $4°\mathrm{C\,min^{-1}}$ to room temperature. Table II shows schematically the preparation process. Conductivity measurements in the parallel direction to the injection flow (axial σ_z) were carried out in cuts of 1 cm length (Fig. 1). In order to investigate the variation of σ_z radially across the cross-section, injection flow sections of different diameters were produced in the central part of the injected bar. In this case the conductivity was calculated according to

$$\sigma_z = [(R_s - 4R_a/5)r^2\pi]^{-1} \qquad (1)$$

where R_s is the resistance of the bar with the central reduced section and R_a is the resistance of the initially unmodified bar. The electrical field was applied by using a Keithley power source. The voltage drop and the intensity current were measured with a voltmeter and an ammeter from Data Precision, respectively. The electrodes were prepared by painting the end cross-sections with a silver paint (Demetron) from Degussa.

The injection-moulding procedure itself changes the state of aggregation and homogenization of the carbon black aggregates within the matrix. In order to obtain an equivalent PE–carbon black system for injected and compression-moulded samples, injection moulding was carried out first, and compression mouldings were produced thereafter from the overflow volume. It is not expected that the low deformation of the melt by compression moulding may have caused any appreciable change of the filler system.

3. Results

3.1. Conductivity of compression- and injection-moulded samples

Fig. 2 shows the dependence of $\log\sigma_z$ for the compression-moulded (unoriented) PE–carbon black composites as a function of filler concentration for various PE matrices. Independently of molecular weight, σ_z increases at first rapidly above a percolation threshold for low additive concentrations

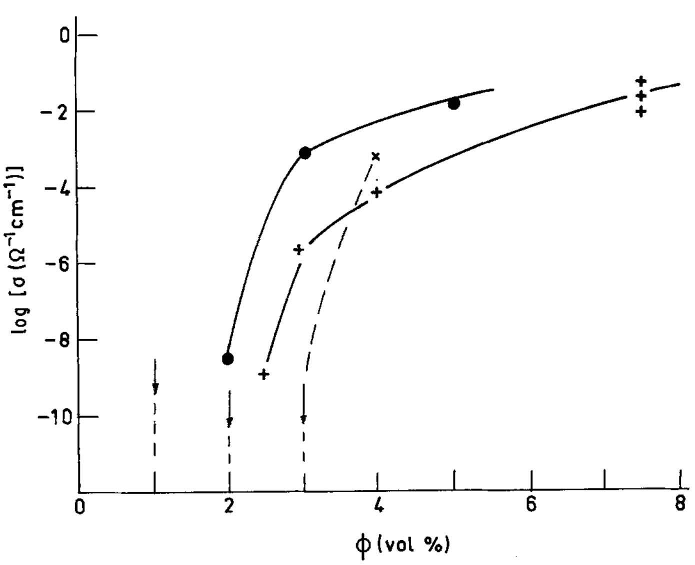

Figure 2 Electrical conductivity of compression moulded polyethylene–carbon black composites as a function of filler concentration. The data show the influence of molecular weight of PE matrices. Arrows indicate the percolation thresholds. M_η = (●) 51 000, (x) 161 000, (+) 248 000.

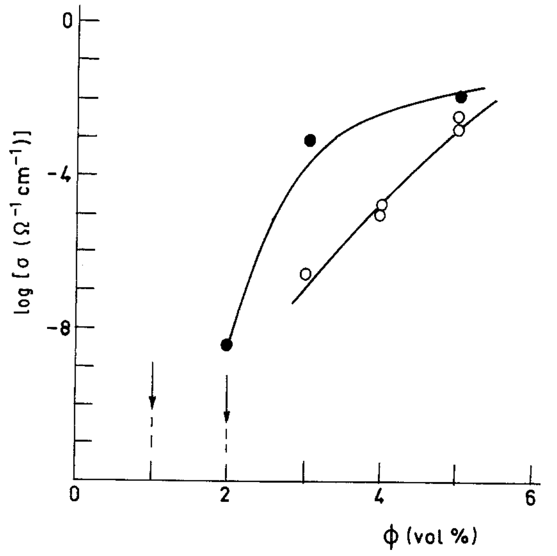

Figure 3 Conductivity of (○) injection-moulded and (●) compression-moulded (unoriented) PE–carbon black composites as a function of filler concentration. Matrix used: low molecular weight grade PE (Vestolen A 6017).

($\phi < 3$ vol%) while it rises at a much lower rate for higher carbon black concentrations. Furthermore the σ value at a given concentration decreases by two to three decades with increasing viscosity of the matrix (which is proportional to molecular weight). This means that the highest conductivity values are obtained for the low molecular material (Vestolen A 6017) while the lowest conductivities result for the higher molecular weight matrix (Lupolen 5261Z). The effect of injection moulding on conductivity is shown in Fig. 3 for the composite containing the low molecular weight matrix. After injection moulding the oriented materials show lower σ values than those for compression-moulded samples. A similar σ decrease in σ on orientation of carbon-black filled PE has been previously-reported [14]. However, the opposite behaviour, i.e. an increase in σ after injection moulding, was obtained in composites with high molecular weight matrices [12].

Fig. 4 shows the percolation threshold ϕ_c for unoriented and for injection-moulded composites as a function of $\log M_\eta$. Despite the error involved a maximum at about $\log M_\eta \approx 5.2$ is observed for both composite types. It is noteworthy that the lower σ level in Fig. 3 for the injection-moulded low molecular weight matrix material (as compared with the compression-moulded composite) corresponds in Fig. 4 to a higher value of ϕ_c for the injection-moulded in contrast to the compression-moulded composite. The opposite result is obtained for composites with a high molecular weight PE matrix [12]. Indeed, injection-moulded materials give rise to an increased conductivity level and to a concurrent low percolation threshold (Fig. 4). The above behaviour points out the conspicuous role played by flow in injection-moulded composites, increasing the orientation and leading to a distinct shift of the percolation threshold towards lower carbon black concentration.

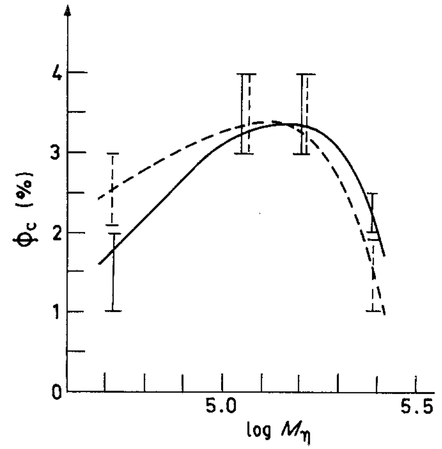

Figure 4 Volume concentration of carbon black at the percolation threshold, ϕ_c, as a function of molecular weight of the matrix for (——) compression-moulded (unoriented) and (- - -) injection-moulded samples. Large error bars are caused by the stepwise variation of carbon black concentration.

3.2. Radial conductivity and birefringence profiles in injection-moulded bars

In order to compare the conductivity behaviour between injection-moulded and compression-moulded carbon composites, with high and low molecular weight matrices, radial conductivity profiles were measured. Birefringence measurements of the unfilled matrix processed under the same injection conditions were also carried out as described in Part 1 [12]. Fig. 5 illustrates the parallel behaviour of birefringence Δn and relative axial conductivity σ_z/σ across the radial direction (r) in the centre of the bar ($z = 35$ mm) for Vestolen A 6017 filled with $\phi = 4$ vol% of carbon black. Both quantities Δn and σ_z show maxima near the walls (shear zones), and in the centre (elongational zone) of the injection-moulded bar. The outer orientation zones as revealed by σ_z and Δn for the low molecular weight matrix are much smaller than in

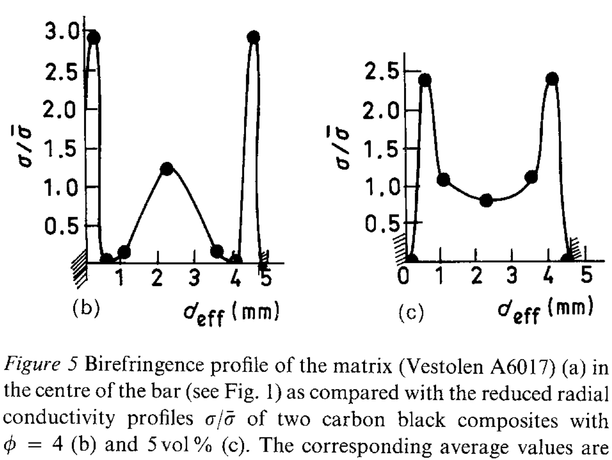

Figure 5 Birefringence profile of the matrix (Vestolen A6017) (a) in the centre of the bar (see Fig. 1) as compared with the reduced radial conductivity profiles $\sigma/\bar{\sigma}$ of two carbon black composites with $\phi = 4$ (b) and 5 vol% (c). The corresponding average values are $\bar{\sigma} = 2.2 \times 10^{-5}$ (b) and $4.5 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (c). The effective diameter is $d_{eff} = 2\pi(A/\pi)^{1/2}$ where A = area of rectangular cross-section (see Part 1 [12]). Shaded zones indicate bar diameter.

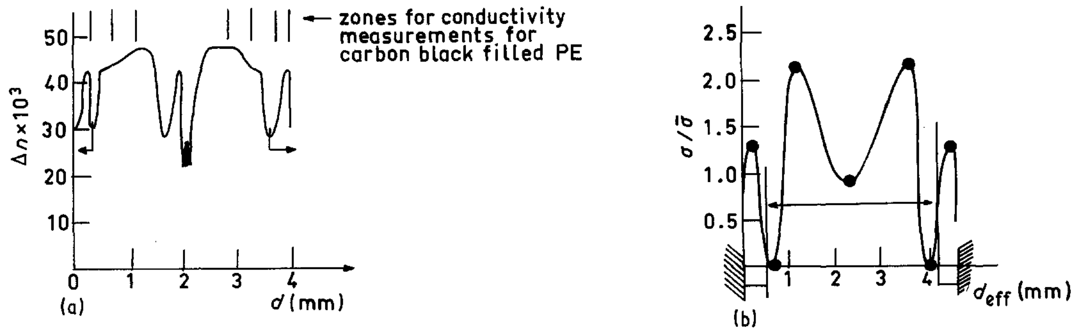

Figure 6 Parallel behaviour of (a) birefringence for the Rigidex 006-60 matrix ($M_\eta = 115\,000$) and (b) radial reduced conductivity for the composite with $\phi = 4$ vol % measured in the centre of the bar ($\sigma = 10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$).

composites with a high molecular weight matrix [12]. This result is connected with the difference in viscosity of the molten material. Indeed, high molecular weight melt viscosities yield wider outer shear zones [15]. Hence, with increasing carbon black concentration a widening of the outer shear zones is revealed by the conductivity profiles (Fig. 5c). Here, though the inner conductivity maximum disappears, the level of conductivity at the centre of the cross-section is maintained. Fig. 6 depicts the parallel results of Δn and $\sigma_z/\bar{\sigma}$ for the carbon composite with the PE matrix having an intermediate molecular weight ($M_\eta = 115\,000$). In this case a more complicated orientation pattern paralleled by a similar conductivity profile is obtained. The elongational flow, as revealed by the inner well-developed maximum, is more pronounced for this material. In summary, the examples of Figs 5 and 6 highlight the parallel behaviour between birefringence and conductivity within the injection moulds investigated.

3.3. Axial conductivity profiles

Fig. 7 illustrates the conductivity profile along the injection direction z, using now the values averaged over the bar cross-section for composites with the different polyethylene matrices used and carbon black concentration $\phi = 4$ vol %. Broad maxima of σ_z near $z \approx 30$ mm are obtained for composites with the high and low molecular weight matrices. In the case of composites showing a pronounced elongational flow (Lupolen 6021D and Rigidex 006-60) only a steady increase in σ_z along the flow direction is detected.

4. Discussion

4.1. Conductivity of compression-moulded samples

Compression-moulded composites can be regarded as thermoplastic materials exhibiting a low orientation. Only a negligible flow is required here to form a plate from the molten overflow volume (see Fig. 1). In order to account for the electrical conductivity of the compression-moulded composite, particle orientation can thus be neglected. Only the mixing process used may explain, in this case, the level of conductivity reached for composites with the different polyethylene matrices investigated (Fig. 2). It is known that the porous structure of carbon black in which particles are arranged in weakly bounded agglomerates of several micrometres is destroyed during the mixing process [5, 16]. The remaining fragments – aggregates of primary carbon black particles of several hundred nanometres – are surrounded by the molten polymer matrix. Since the mixing procedure and mixing time were the same in all cases, different matrix viscosities leading also to different shearing forces are assumed to be responsible for the various conductivities obtained. Thus, for the composite having the low molecular weight PE matrix one would expect the lowest acting shearing forces and consequently the lowest level of destruction of the carbon black structure (degradation effect). On the other hand, the composite with the high molecular weight matrix should yield the largest additive degradation. It is, further, known that carbon black degradation at sufficiently long mixing times results in a conductivity decrease [16]. Hence this effect can explain that (i) the composite containing the low molecular weight matrix (low viscosity) in Fig. 2

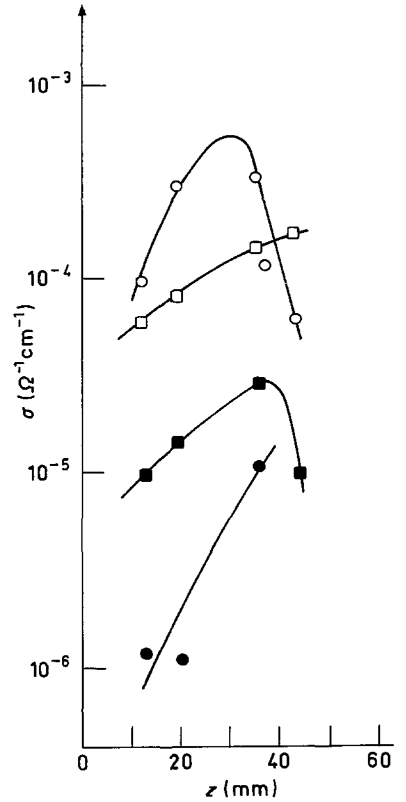

Figure 7 Conductivity profiles along the flow direction (z-axis) for different matrices: (○) $M_\eta = 245\,000$, (□) $M_\eta = 115\,000$, (■) $M_\eta = 51\,000$ and (●) $M_\eta = 161\,000$ with $\phi = 4$ vol %. Values of σ are averaged over the whole cross-section.

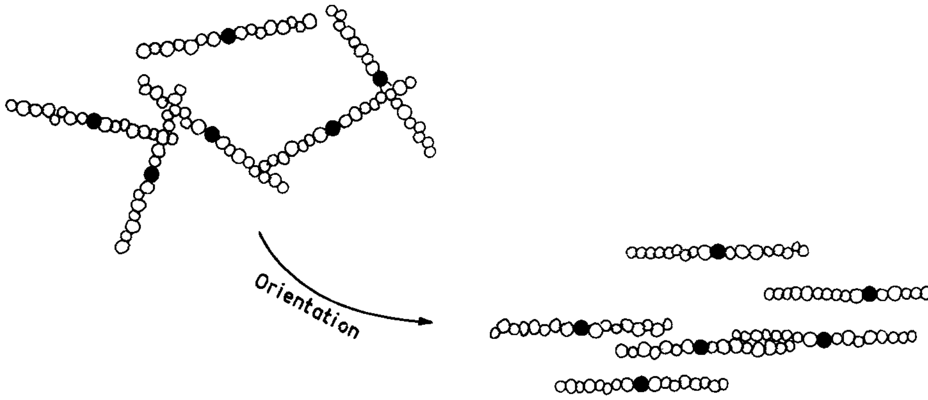

Figure 8 Schematic diagram showing the orientation of anisotropic particle aggregates when dispersed in an injection-moulded matrix.

shows the highest σ values (i.e. the lowest carbon black structure degradation), and (ii) σ decreases with increasing molecular weight, implying that the structure of carbon black is increasingly degraded.

An even more complex behaviour is revealed when examining the critical carbon black concentration at which percolation is achieved (Fig. 4). It is known that the percolation threshold ϕ_c is very sensitive to the homogenization of the microadditive particles within the matrix [11]. Thus, the better is the homogenization of the mixture of the particles, the higher will be ϕ_c. Conversely, an inhomogeneous mixture of the additive with the polymer involves for the same concentration a low percolation volume. We have detected essential differences in the mixing of the four different molecular weight grade PEs (Table I) with carbon black in the molten state. Miscibility is, in fact, not only influenced by the amount of shearing stress of the melt, but also by the degree of physical contact between carbon black particles and the molten polymer. The contact efficiency of carbon black decreases markedly with molecular weight. For instance, molten Lupolen 5261Z ($M_\eta = 245\,000$) behaves more like a rubber than like a liquid. Thus the contact efficiency of this matrix with carbon black is worse than with molten low molecular weight PE. On the other hand, the effect of low shearing stresses is best illustrated in case of Vestolen A 6017, where the low viscosity melt leaves regions of unperturbed original carbon black agglomerates when passing through the extruder for the first time [12]. From the foregoing, we invoke a superposition of two effects to explain the data of Fig. 4: (i) a shear stress contribution of the melt increasing with molecular weight, and (ii) a contact efficiency between particles and matrix at low molecular weights which decreases with increasing molecular weight.

The superposition of both effects with increasing molecular weight of the matrix could explain a maximum value of miscibility in the intermediate molecular weight range. For the intermediate molecular weights (Lupolen 6021D and Rigidex 006-60) we observe, indeed, a perfect mixture already at the first extrusion of the mixing process (Table I). Thus the predicted maximum of miscibility as a function of molecular weight explains satisfactorily the maximum value obtained for the percolation threshold in Fig. 4.

4.2. Conductivity of injection-moulded composites

We have seen that σ values for the unoriented materials are characterized both by the degradation level of the carbon black structure and the degree of homogeneity of the carbon black particles within the PE matrices. We wish to discuss next the influence of flow by injection moulding on the value of σ. It is convenient to recall at this stage that the state of the filler is the same in the compression- and injection-moulded samples (see Section 2). The differences in σ shown in Fig. 3 can thus be directly related to flow effects of the polymer melt during injection moulding. The results of Fig. 3 showing lower σ values for the injection-moulded samples than for the compression moulded materials are apparently at variance with the data obtained for composites with high molecular weight PE [12]. However, the parallel behaviour of the radial σ_z and Δn profiles (Figs 5 and 6) suggests that flow-induced segregation of additive particles also takes place within the low molecular weight matrix. Consequently, we must seek an additional effect of the material flow capable of counterbalancing the segregation influence of additive particles.

It is known that carbon black aggregates exhibit geometrical anisotropy [17, 18]. Under very severe mixing conditions, however, primary carbon black isotropic spheres are observed [5]. We may, therefore, expect the anisotropy of carbon black aggregates to increase with decreasing molecular weight of the matrices. Particle aggregate orientation would only be expected in the case of lower molecular weight PE grades. Fig. 8 schematically illustrates the influence of orientation on anisotropic particle aggregates [19]. According to this concept, connectivity (percolation) is worsened on orientation and σ would decrease as observed in Fig. 3. This will be confirmed directly when experiments to observe particle morphology and segregation within the polymer matrix are completed.

5. Final remarks

In conclusion, the conductivity level observed in elongational flow injection-moulded carbon black–PE composites can be explained in terms of a combination of three major effects: (i) an orientation of anisotropic carbon black aggregates, (ii) a degradation effect of these aggregates during processing, increasing with molecular weight of the PE matrix, and (iii) a

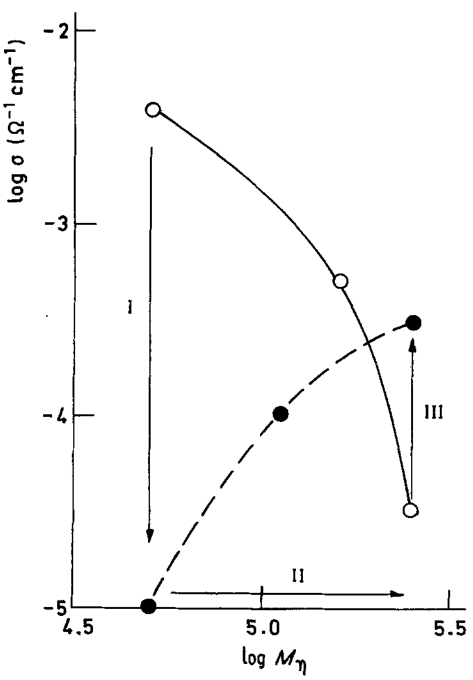

Figure 9 Variation of log σ with molecular weight for composites with ϕ = 4 vol %, highlighting the effects of (I) orientation, (II) degradation and (III) flow-induced segregation of carbon black aggregates: (●) injection-moulded, (○) unoriented.

flow-induced segregation of additive particles along conductive channels.

Fig. 9 summarizes the changes of σ with molecular weight for the isotropic (compression-moulded) and oriented (injection-moulded) composites at 4% filling level in the light of the three above-mentioned contributions. For low and intermediate molecular weights the conductivity decreases after material orientation (injection moulding) (I). We attribute the decrease in σ to an orientation of filler particles. With increasing molecular weight, degradation of the filler structure increases and consequently the anisotropy of the particles decreases (II). As a result σ for the isotropic samples decreases due to a less well-defined percolation conductive filler network. However, for injection-moulded materials a particle segregation prevails with increasing molecular weight (larger degradation). For the highest molecular weight matrix having a highly degraded filler the influence of particle segregation is dominant (III). Here the conductivity is larger than that obtained for the unoriented material with a nearly homogeneous particle distribution. Of course, the σ level for injection-moulded composites markedly increases with ϕ, reaching σ values near 1 Ω^{-1} cm^{-1} for filling levels near 7% [12].

Acknowledgements

We wish to thank Professors H. G. Zachmann and J. Petermann for the facilities given in their laboratories in Hamburg and Professor Meins, R. E. Diekow and P. Wiegel, Fachhochschule Hamburg for the possibility of preparing the samples in their laboratory as well as for their valuable advice. Grateful acknowledgement is due to Bundesministerium für Forschung und Technologie (FRG) and Ministerio de Asuntos Exteriores and CAICYT (Spain) for the generous support of this project. R. K. B. wishes to acknowledge the tenure of a Sabbatical grant (Ministerio de Educación y Ciencia) and T. A. E. that of a CSIC fellowship (Spain) during this work.

References

1. F. J. BALTÁ CALLEJA, T. A. EZQUERRA, D. R. RUEDA and J. A. LÓPEZ, *J. Mater. Sci. Lett.* **3** (1984) 165.
2. M. NARKIS and A. VAXMAN, *J. Appl. Polym. Sci.* **29** (1984) 1639.
3. M. HISHIMMA and T. YAMAMOTO, *J. Mater. Sci. Lett.* **3** (1984) 799.
4. S. RADHAKRISHNAN, *ibid.* **4** (1985) 1445.
5. T. A. EZQUERRA, J. MARTINEZ-SALAZAR, F. J. BALTA-CALLEJA, *ibid.* **5** (1986) 1065.
6. A. VOET, *Rubber. Chem. Tech.* **54** (1981) 42.
7. R. GILG, "Grundlagen und Anwendungen von Farbruss", Vol. 7, Russ für Leitfähige Kunststoffe, Schriftenreihe Pigmente Nr. 69 (Degussa, Frankfurt, 1982).
8. E. K. SICHEL (Ed.), "Carbon-black–Polymer Composites. The Physics of Electrically Conducting Composites" (Dekker, New York, 1982).
9. P. SHENG, *Phys. Rev.* **21** (1981) 2180.
10. M. KRYSZEWSKI, J. K. JEZZKA, J. VLANSKI and A. TRACZ, *J. Appl. Chem.* **56** (1984) 355.
11. T. A. EZQUERRA, F. J. BALTÁ CALLEJA and J. PLANS, *J. Mater. Res.* **1** (1986) 510.
12. R. K. BAYER, T. A. EZQUERRA, H. G. ZACHMANN, F. J. BALTÁ CALLEJA, J. MARTINEZ SALAZAR, W. MEINS, R. E. DIEKOW and P. WIEGEL, *J. Mater. Sci.* **23** (1988) 475.
13. R. K. BAYER, in Europhysics Conference Abstract Vol. 6G, 14th Europhysics Conference on Macromolecular Physics, Vilafranca del Penedés (European Physical Society, Geneva, 1982) p. 75.
14. C. KLASON and J. KUBAT, *Int. J. Polym. Mater.* **10** (1984) 259.
15. R. K. BAYER, E. LÓPEZ CABARCOS, F. J. BALTÁ CALLEJA and H. G. ZACHMANN, *J. Mater. Sci.* (1988) submitted.
16. D. J. SOMMERS, *Polym. Plast. Technol. Eng.* **23**(1) (1984) 83.
17. J. A. WENDORFF, private communication (1987).
18. J. BALBERG and S. BOZOWSKI, *Solid State Commun.* **44**(4) (1982) 551.
19. G. E. PIKE and C. H. SEAGER, *Phys. Rev. B.* **10** (1974) 1421.

Received 27 October 1987
and accepted 23 February 1988