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Electrical conductivity of polyethylene–carbon-fibre composites mixed with carbon black

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The study of electrical conductivity of high-density polyethylene–carbon-fibre composites mixed with different concentrations of carbon black is reported. The influence of the mixing procedure of the additives and material preparation is examined with regard to the conductivity values. The use of these two filler types in polyethylene composites combines the conducting features of both. Thus, while fibres provide charge transport over large distances (several millimetres), carbon black particles improve the interfibre contacts. Results are discussed with reference to simple electrical models. It is shown that for composites in which the segregated carbon black–polyethylene component lies above the percolation threshold the electrical interfibre contacts are activated through carbon black particle bridges, leading to a conductivity rise. This effect is more relevant in the case of shorter fibres. Processing of the material involving fibre orientation, such as in injection-moulding, decreases drastically the conductivity level reached.

1. Introduction

One of the additives most widely used to make conducting plastic materials is carbon black. Besides providing mechanical reinforcement by mixing and adhering to the matrix efficiently, carbon black does not change substantially the overall density of the material. In addition, owing to its high specific surface area, only 2 to 3 vol % of carbon black is required to form a conductive network [1–3]. The transport mechanism near the critical concentration is governed by the tunnelling of electrons from one particle to the next one across gaps of a few nanometres [4]. Reports have appeared recently suggesting that conducting particles will be efficiently deployed if they are distributed in such a way that sufficiently large interconnected chains of particles prevail, after processing, throughout the polymer matrix [3, 5]. One immediate approach to this idea is to start with a conductor which is already in fibrillar form. Conductive carbon fibres can be used in this way. If the fibre content is sufficiently high, interfibre contacts will arise and conductive paths can be obtained within the polymer matrix. As the fibre concentration is increased the conductivity remains low until a three-dimensional network is established, when it suddenly increases by several orders of magnitude. The electrical resistance of the fibre aggregates is lower than the resistance of paths of carbon black particles. Consequently, the addition of carbon fibres to a polymer matrix leads, in principle, to composites of higher conductivity.

This paper presents the results of an experimental study on the variation of electrical conductivity of polyethylene composites when using mixtures of carbon fibres and carbon black within the polymer matrix. The aim of this study is to examine whether the electrical interfibre contacts can be activated by the formation of additional conduction bridges through carbon black particles. It is shown that the resulting structures are largely affected by the mixing process of the additives into the polymer. The results obtained are discussed in the light of various electrical models.

2. Experimental procedure

Various types of composite material were prepared by mixing a polyethylene (PE) matrix (Lupolen 5261Z, $M_w = 450\,000$) with the two following conducting microadditives: (a) carbon black XE2 from Phillips Petroleum, and (b) carbon fibres Tenax HTA C6-S from Enka. The carbon black XE2 consists of primary particles of 60 to 70 nm [3] with a specific surface of about $100\,\mu\text{m}^{-1}$ which agglomerate to form well-developed chain-like structures [6]. The carbon fibres are characterized by a uniform length of $6000\,\mu$m, a diameter of $7\,\mu$m and a specific surface of $0.6\,\mu\text{m}^{-1}$. The additive concentrations used for the composites investigated are shown in Table I. The concentrations in Table I are given in volume percentages and are just referred to the PE phase and not to the three-component system. The composites were prepared in three different ways (Table II). The different components were first mixed in the proportions of Table I using a plastograph. The mixture was stirred until a homogeneous composite was achieved. The system prepared in this way was subsequently compression-moulded at 150° C (Composite A in Table II). No degradation of the original fibre length was induced by this method. This was confirmed by optical

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TABLE I Additive concentrations used in polyethylene composites

Additive	Concentration (vol %)	
	Carbon black	Carbon fibres
F1	0	8.3
F2	0	14.1
CF1	1.7	8.3

microscopy observations. Samples with a reduced length of carbon fibre were prepared by milling the solid mixture prior to an extrusion. Extrusion was carried out to homogenize the distribution of the cut fibres. After this, the material was compression-moulded (Composite B). Finally, injection mouldings directly from the milled granular material were produced, using the mould as described elsewhere [7] (Composite C).

Conductivity measurements are carried out on compression-moulded discs of 35 mm diameter and 3 mm thickness using a Fluke ohmmeter. The disc surfaces were painted with silver paint to measure the conductivity across the materials' surface. The conductivity in the direction parallel to the surface was measured on 30mm × 10 mm parallelepipedic pieces. The conductivity of the injection mouldings was measured in the flow direction by contacting the cross-sectional surfaces of a cut piece of the bar.

3. Results

3.1. Conductivity of polyethylene–carbon-fibre systems

Fig. 1 shows the conductivity values of PE–carbon-fibre composites containing 8.3 and 14.1 vol % of carbon fibres. High conductivities were only obtained in the case of compression-moulded samples of Composite A. Here it is seen that the conductivity perpendicular to the compression-moulded plates is higher than that measured parallel to the plate surface. This can be explained in terms of the conductivity anisotropy within the samples, due to the fact that the length of the carbon fibres (6 mm) is larger than the thickness of the plate (3 mm). The carbon fibres have to be consequently inclined by at least 60° or more with respect to the normal to the plate surface. Thus, a preferential orientation of fibres parallel to the plate surface arises. The conductivity is lower in the direction parallel to the carbon fibres than in the direction perpendicular to the fibre orientation because the number of interfibre contacts decreases with orientation [8]. The conductivity value might, however, be influenced not only by orientation, but also by a fraction of fibres traversing the whole moulding (Fig. 2). In order to examine the possible influence of fibre traversing on the conductivity level, measurements were carried out parallel to the plate surface on 2 mm wide cuts (see Fig. 2). No differences with respect to the overall conductivity along the whole plate were detected. Hence, the contribution to conductivity of direct electrical fibre connections across the thickness of the plates seems to be negligible in contrast to the contribution of the great many interfibre contacts. One may conclude that the fibres themselves are not the main charge-carrying elements through the plate thickness. Only fibre segments between contact points through neighbouring fibres contribute to the zigzag path of electrical flow, which is formed by many fibres. The above experiment suggests that the electrically active fibre segments are less than 2 mm in length. This magnitude will depend, of course, on the fibre concentration within the composite. Here the concentration was 14.1 vol %. Owing to the good contact between the carbon fibres and the matrix the fibres are completely coated at the surface. Experiments were also carried out perpendicular to the plate surface by removing the skin before measuring the conductivity. A slight but nevertheless detectable increase of conductivity. A slight but nevertheless detectable increase of conductivity was observed when the insulating polymer skin was removed.

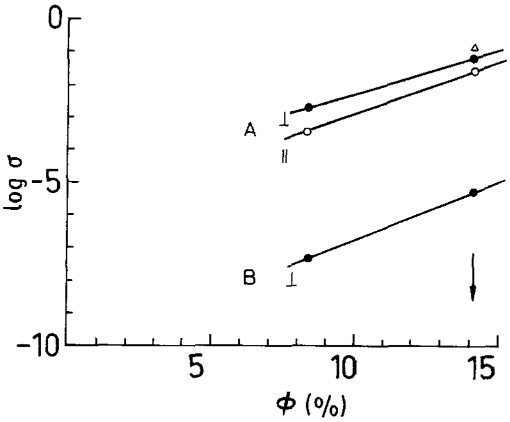

Figure 1 Variation of log [$\sigma(\Omega^{-1}\,\mathrm{cm}^{-1})$] against volume percentage of carbon fibres (Additives F1 and F2) for compression-moulded Composites A and B (see Tables I and II). Measurements were carried out perpendicular and parallel to the surface of the moulded plates. The arrow denotes the measurement of an injection-moulded sample falling below the measuring range used ($< 10^{-10}\,\Omega^{-1}\,\mathrm{cm}^{-1}$).

Conductivity values of composites with the same additives (F1 and F2) after milling, subsequent

TABLE II Mixing procedure and sample preparation

Composite	Procedure			Result
A	Mixture of matrix and additives in a plastograph	⟶	Compression moulding	Long fibres
B	↓ Milling ⟶ Extrusion	⟶	Compression moulding	Short fibres
C	└	⟶	Injection moulding	Short fibres

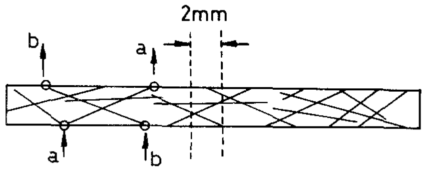

Figure 2 Schematic diagram of moulded composite section showing (a–a and b–b) carbon fibres traversing the thickness of sample and possible paths of electrical conduction through interfibre contacts.

extrusion and final moulding with the same geometry (Composites B) are also given in Fig. 1. After this preparation mode the fibres are cut to the dimensions of the milled granulates (0.5 to 2 mm). The observed decrease of conductivity can, thus, be interpreted in terms of a decrease of fibre length. The average mesh size of the conducting network of zigzag paths, assuming a constant number of contacts per unit volume, can now be thought as substantially widened. Due to the reduced length of the fibres the number of contacts between neighbouring fibres contributing to the percolation system decreases, and leads consequently to conductivity values that are various orders of magnitude lower (Fig. 1).

Finally, injection moulding of the milled granular material into bar-shaped samples leads to high orientation [9] of the short fibres parallel to the flow direction (Composites C). As a consequence, the conductivity falls below the measuring range of our apparatus ($\sigma < 10^{-10}\,\Omega^{-1}\,\text{cm}^{-1}$) (arrow in Fig. 1). As mentioned above, the orientation of anisotropic filler particles worsens the percolation [8] and the conductivity rapidly decreases.

3.2. Conductivity of polyethylene–carbon-fibre–carbon-black composites

Fig. 3 shows conductivities of the carbon fibre composites (Table I) after the addition of 1.7 and 2.2 vol % carbon black (CF1 and CF2, respectively). In the case of both Composites A and B (Table II) the addition of 1.7% carbon black leads to a decrease in σ, whereas the addition of 2.2% leads to an increase. These changes are more drastic for the B composites. The above changes are probably related to the fact that 1.7% carbon black in these materials lies still below the critical volume for percolation which would lead to low conductivity values, whereas 2.2% lies just above the critical volume giving rise to high σ values [10].

4. Maximum conductivity of the composite

The upper limit to the conductivity that can be reached for a composite with a volume fraction ϕ of an additive with conductivity σ_{add} is given [11] by

$$\sigma_{\max} = \phi\sigma_{\text{add}} \tag{1}$$

However, for a composite containing randomly distributed fibres, orientation of fibres out of the field direction reduces the conductivity from the maximum. Thus, the conductivity of a composite containing randomly oriented fibres becomes [11]

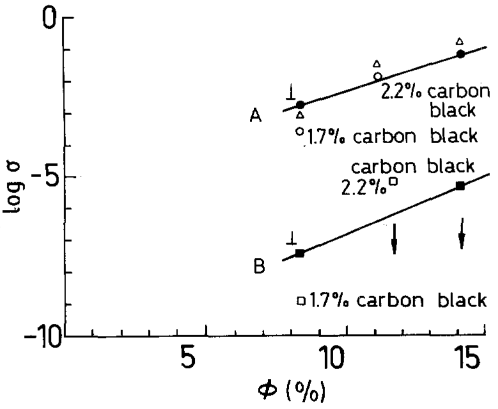

Figure 3 Dependence of $\log[\sigma(\Omega^{-1}\,\text{cm}^{-1})]$ against volume percentage of carbon fibres for PE Composites A and B mixed with various percentages of carbon black (○, □). Measurements carried out after removing the outer skin of the composite (△) and data from PE-carbon fibre mixtures (○, ■) are also indicated.

$$\sigma_{\max} \sim \frac{2}{3\pi}\phi\sigma_{\text{fibre}} \tag{2}$$

Since in our case $\sigma_{\text{fibre}} \geqslant 10^3\,\Omega^{-1}\,\text{cm}^{-1}$ [12], for the composite with $\phi \sim 14\%$ (Additive F1 in Table I) the maximum conductivity of the composite would be $\sigma_{\max} \sim 10^2\,\Omega^{-1}\,\text{cm}^{-1}$. This maximum value assumes that all fibres are electrically active along their length and connect directly across the distance between the two electrodes. However, owing to the fact that a fraction of the fibres does not contribute to the electrical conduction and due to the contact resistance arising between fibres, the experimental conductivity value found is various orders of magnitude lower than $\sigma_{\max}$. Indeed, in the case of the composites with $\phi \sim 14\%$, $\sigma \sim 10^{-1}\,\Omega^{-1}\,\text{cm}^{-1}$ (see Fig. 1). In order to reduce the large difference between $\sigma_{\max}$ and the experimental σ value one may attempt to introduce additional "bridges" between carbon fibres by means of the addition of carbon black particles. Tunnelling between fibres and carbon black particles may contribute to improving the conductive paths and hence the level of conductivity. However, if the mixture is not homogeneous and segregation effects of particles and/or fibres take place an efficient "bridging" of carbon fibres may not occur.

5. Parallel and series models

One may think of two alternative extremes for non-homogeneous mixtures, characterized by parallel and series models respectively. Let us assume a segregation of carbon black–PE regions filling the fibre network within the composite leaving, however, the percolation through the fibre network undisturbed. No carbon black bridges between fibres are assumed. From an electrical conductivity viewpoint such a model essentially implies that the carbon black–PE (C–PE) and carbon fibre–PE (F–PE) regions are connected in parallel. The electrical resistance R of the composite can, thus, be written

$$\frac{1}{R} = \frac{1}{R_{\text{C-PE}}} + \frac{1}{R_{\text{F-PE}}} \tag{3}$$

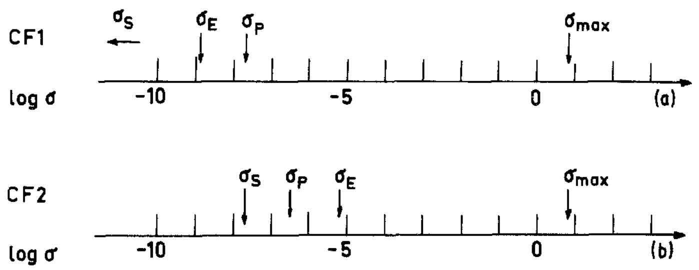

Figure 4 Experimental conductivity σ_E of short carbon fibres–PE–carbon black composites (B) for mixtures (a) below the percolation volume of carbon black (CF1), and (b) above the percolation volume of carbon black (CF2). Values of σ_S, σ_P and σ_{max} refer to the predictions given by Equations 2, 5 and 6.

where R_{C-PE} and R_{F-PE} are the resistances of the C–PE and F–PE components, respectively. If we assume that each component contributes to 50 vol % within the composite one can write

$$\sigma = w\sigma_{C-PE} + (1 - w)\sigma_{F-PE} \qquad (4)$$

where $w = 0.5$ and $(1 - w)$ represent the volume fractions of C–PE and F–PE, respectively. Since $\sigma_{C-PE} \ll \sigma_{F-PE}$, due to the low concentrations of carbon black used (see Fig. 1), for the parallel model we have

$$\sigma_{parallel} = \sigma_{F-PE}/2 \qquad (5)$$

Another extreme is to consider the C–PE regions as interrupting the three-dimensional network of carbon fibres within the composite volume. If the C–PE segregated regions extended through the whole cross-section of the composite as layers of resistance R_{C-PE}, the system could be simply described as a series connection of C–PE regions alternated by F–PE zones. According to this model the resistance of the composite is $R = R_{C-PE} + R_{F-PE}$. Again, since $\sigma_{C-PE} \ll \sigma_{F-PE}$ it results that

$$\sigma_{series} = 2\sigma_{C-PE} \qquad (6)$$

6. Discussion

6.1. Short carbon fibre–PE composites mixed with carbon black

The three extremes given by Equations 2, 5 and 6 can now be used to compare the experimental results with the above predictions. Fig. 4 shows the experimental conducting data σ_E of the composites consisting of (a) 8.3% short carbon fibres and 1.7% carbon black (CF1), and (b) 11% short carbon fibres and 2.2% carbon black (CF2) for B composites (Table II) and the calculated values σ_{max}, $\sigma_{parallel}$ and σ_{series}. In Fig. 4a, σ_E lies between σ_P and σ_S. In this case no carbon black bridges, enhancing σ to a value larger than σ_P, seem to exist. This is partly due to the fact that the C–PE component, for $\phi \sim 1.7\%$, lies below its percolation threshold. The above result suggests, in addition, that the segregated regions of C–PE and F–PE contribute to a nearly series microstructural arrangement. More precisely, the σ_E value can be explained in terms of a parallel arrangement of percolating regions of carbon fibre–PE with zones consisting of F–PE in series with C–PE regions. Such a model would give rise to $\sigma_E \sim \frac{1}{10}\sigma_P$, in accordance with the data obtained. In other words, for the CF1 samples only 10% of the carbon fibres are contributing to conduction across the sample.

For the CF2 samples having 2.2% carbon black, 11% carbon fibre–PE (Fig. 4b), σ_E is now larger than σ_P. Here the carbon black–PE component lies above its percolation threshold, i.e. an effect of carbon black particles bridging neighbouring carbon fibres seems to exist. Such an effect is so strong that the influence of segregation, giving rise to carbon fibre–PE islands within the composite, is now overcompensated by channels of carbon black particles joining adjacent fibres.

6.2. Long carbon fibre–PE composites mixed with carbon black

Similar effects as in the case of milled fibres are observed for composites with 6 mm long fibres (Composites A). The conductivity changes are, however, not so pronounced. Owing to the increased length of the fibres a network with a higher density of contact paths is now expected. Segregated C–PE regions will not disturb so much the percolation of the fibre system. Generally the fibres are long enough to traverse the carbon black–PE regions. Thus, in the case of the non-percolating carbon black–PE component (1.7% carbon black, 8.3% carbon fibres) a σ_E value slightly below σ_P is obtained (Fig. 5a). As in Fig. 4a, this result suggests that no carbon bridges are built up between fibres. On the other hand, Fig. 5b shows for the percolating carbon black–PE system (2.2% carbon black, 11% carbon fibre–PE) that σ_E is slightly larger than σ_P. Due to an improved percolation through the fibres themselves the contribution of the carbon black bridges is not as strong as in Fig. 4b.

7. Conclusions

It is shown that for specific concentrations of carbon black (>2 vol %) of a given structure and carbon

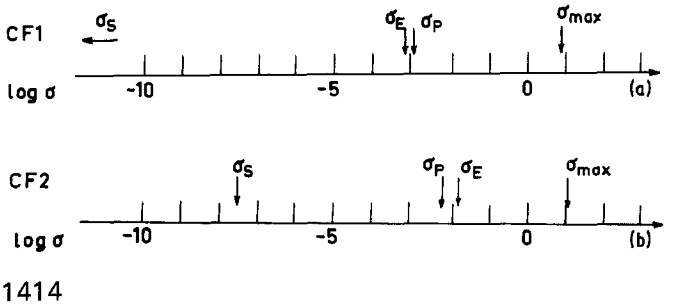

Figure 5 Measured conductivity σ_E of long carbon fibres–PE–carbon black composites (A) for mixtures (a) below the percolation volume of carbon black (CF1), and (b) above the percolation volume of carbon black (CF2). Values of σ_S, σ_P and σ_{max} refer to the predictions given by Equations 2, 5 and 6.

fibres (> 10 vol %) of a given length within a polymer matrix (PE) systems which can yield high conductivity values are obtained. The main idea is to partially replace carbon fibres, which are an expensive filler, by carbon black. On the one hand, the carbon black component is capable of forming a conducting network of filler particles at low concentrations. On the other hand, carbon fibres can transport electrical charges over large distances (corresponding to their length) without electrical losses. The use of the above two filler types in composites combines the advantages of both: i.e. while fibres are responsible for charge transport, carbon black improves the interfibre contacts. The practical application of the above concept requires a good mixture of the three components. However, we have shown that segregation of regions of carbon black–PE and carbon fibre–PE occurs when using normal mixing procedures. In addition, when producing granulates of carbon-fibre–polymer composite the fibres are cut, contributing to a substantial conductivity decrease. The above problems can be partially overcome by increasing the carbon black concentration. Finally, orientation by injection moulding decreases enormously the conductivity of the moulded material. The addition of sufficient amounts of carbon black may overcome this disadvantage.

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References

1. F. J. BALTÁ CALLEJA, T. A. EZQUERRA and D. R. RUEDA, *J. Mater. Res.* **3** (1984) 165.
2. T. A. EZQUERRA, F. J. BALTÁ CALLEJA and J. PLANS, *J. Mater. Res.* **3** (1986) 510.
3. T. A. EZQUERRA, J. MARTINEZ SALAZAR and F. J. BALTÁ CELLEJA, *J. Mater. Sci. Lett.* **5** (1986) 1065.
4. P. SCHENG, *Phys. Rev.* **21** (1981) 2180.
5. M. MEHBOB, R. DELTOUR and P. WYDER, in Conference Astracts of 7th Conference of Condensed Matter Division, E.P.S., Pisa, B152, April 1987, edited by G. Grosso, L. Martinelli and G. Pastori (Pisa) p. 266.
6. N. PROBST, *Eur. Rubb. J.* (November 1984) 25.
7. R. K. BAYER, A. E. ELIAH and J. C. SEFERIS, *Polym. Eng. Rev.* **4** (1984) 201.
8. G. E. PIKE and C. H. SEAGER, *Phys. Rev.* **B10** (1974) 1421.
9. R. K. BAYER and G. W. EHRENSTEIN, *Plastverarbeiter* **32** (1981) 1387.
10. R. K. BAYER, T. A. EZQUERRA, H. G. ZACHMANN, F. J. BALTÁ CELLEJA, J. MARTINEZ SALAZAR, W. MEINS, R. E. DIEKOW and P. WIEGEL, *J. Mater. Sci.* **23** (1988) 475.
11. A. R. BLYTHE, "Electrical Properties of Polymers" (Cambridge University Press, 1980) p. 126.
12. "Enka Hochleistungsfasern für Verbundstoffe" (Enka–Haus Kasinostr. Ressort Technische Gewebe, Postfach 100 149, 5600 Wuppertal 1).

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