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Electrical and morphological studies of polymeric composites based on carbon black

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Conventional polymers, polypropylene and polystyrene, containing carbon black as conductor additive, were prepared. Impedance complex-plane analysis is used in order to characterize the composites obtained. Microstructure studies indicate that carbon black affects the size but not the geometrical morphology. The electrical conductivity of polypropylene composites is higher than polystyrene, and is correlated to the microstructural and wettability properties of these polymer matrices.

1. Introduction

A number of authors [1–5] describe the obtention and electrical characterization of polymeric extrinsic conducting systems (conventional polymers containing conductor additives such as powders or fibres). But there are no reports in the literature related to the preparation of polymeric systems based on polypropylene or polystyrene and carbon black as conductor additives, despite their great interest for industrial applications as conductors, taking into account the easy production and low cost of these polymers.

In the present work, the preparation of a series of extrinsic conducting polymers based on polypropylene and polystyrene with carbon black was carried out: the microstructure and electrical characteristics of the composites were investigated by isothermal crystallization, SEM and electrical measurements.

2. Experimental procedure

All the composites were prepared by mixing the components (polypropylene (PP) and carbon black (N) or polystyrene (PS) and carbon black) in a brabender-type torque rheometer with a mixing chamber for thermoplastics W-60, heated at 200 °C. The torque speed was 60 r.p.m. Blends were retained in the mixing chamber for 15 min to achieve a homogeneous blend and then composites were pulled out, cooled and processed. The isothermal crystallization from the melt was studied by using a Perkin Elmer DSC 7 differential scanning calorimeter operating under N_2 atmosphere.

Electron microscope observations were carried out on a Zeiss SEM model DMS 950. Impedance and inductance complex-plane analyses were performed with an impedance analyser (Hewlett-Packard model 4192 A) with computer assistance (model 9000-216) in the frequency range of 10 to 10^7 Hz at room temperature.

3. Results and discussion

To discover the effect of carbon black on the polypropylene microstructure, the kinetics of the isothermal crystallization from the melt of polypropylene composites were analysed on the basis of the Avrami equation [6]:

$$\chi_T = 1 - \exp(-Kt^n)$$

where χ_T is the weight fraction of crystallized material at time t; K is the overall kinetic rate constant; and n is the Avrami exponent which depends on the type of nucleation and on the geometry of the growing crystals.

In Table I are listed the starting composition of the composites, the chosen crystallization temperature and the kinetic parameters obtained in the isothermal crystallization of the polypropylene–carbon black system. The values of K and n have been derived for each T_c, from the intercept and the slope of straight lines respectively, obtained by plotting $\{\log[-\ln(1-\chi_T)]\}$ against $\log t$ (Fig. 1) for each sample and crystallization temperature (T_c).

From these data it can be deduced that the crystallization rate of polypropylene increases as the carbon black concentration increases for each crystallization temperature, and diminishes when crystallization temperature is raised, as illustrated in Fig. 2; this fact confirms the nucleant character of the carbon black during the polypropylene crystallization.

The carbon black hardly affects the spherulitic growing geometry, in agreement with the constant value of n, as a function of the carbon black concentration in the composite (Fig. 3); in all cases the growth geometry is two-dimensional ($n = 3$) and athermic, that is to say, independent of crystallization temperature.

From the above, it is concluded that the incorporation of carbon black only affects the size of the spherulites, but not their geometry.

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TABLE I Isothermal crystallization: melting and kinetic parameters of the polypropylene (PP) and polypropylene–carbon black (PP/N) systems

Samples	PP/N (wt %)	T_c (°C)	T_m (°C)	log K_n (min)	n	$t^{1/2}$ (min)
PP	100/0	124	163.1	0.976	2.45	5.90
		126	163.9	− 1.761	2.75	9.86
		128	164.7	− 2.429	2.77	18.46
		130	165.5	− 3.367	2.95	29.87
PN-5	95/10	128	–	0.967	3.02	5.00
		130	165.2	− 1.699	3.09	7.70
		132	165.8	− 2.389	3.08	9.65
		134	166.4	− 3.056	3.05	20.16
		136	167.1	− 3.658	3.00	33.58
PN-15	85/15	130	165.5	− 0.871	2.92	4.16
		132	166.1	− 1.580	2.97	7.71
		134	166.6	− 2.285	3.10	11.61
		136	166.6	− 2.991	3.14	19.41
PN-30	70/30	130	165.0	0.527	2.54	4.16
		132	165.4	− 1.258	2.91	6.33
		134	165.4	− 1.948	2.97	8.88
		136	165.5	− 2.474	2.93	14.73

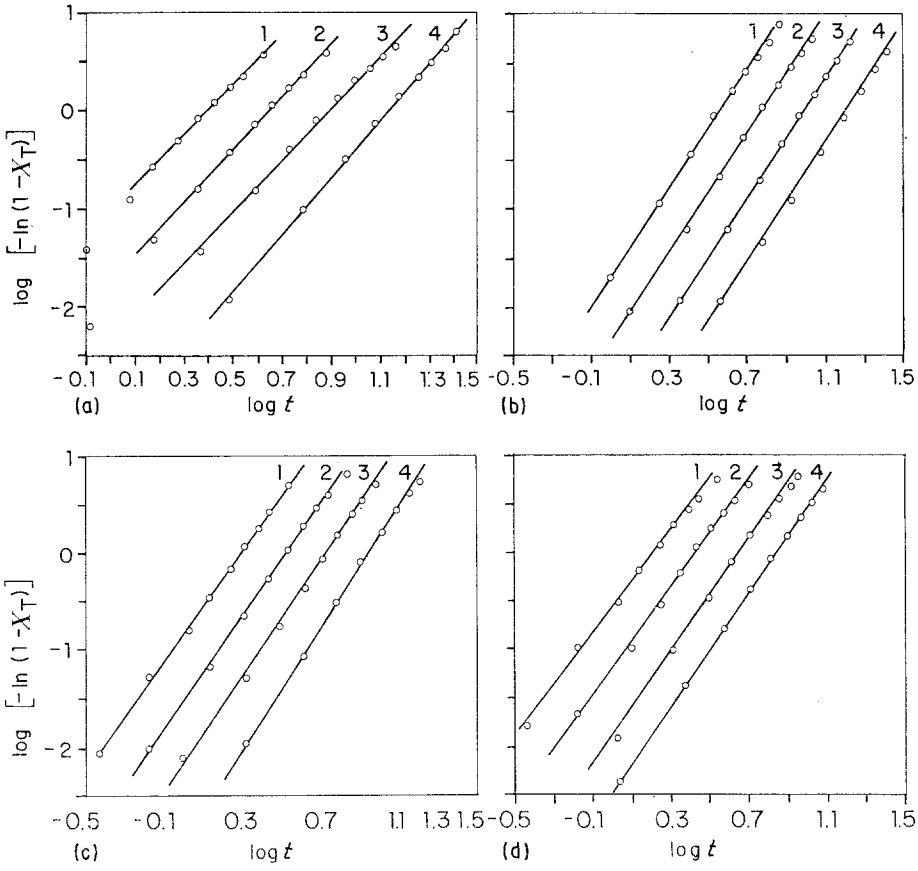

Figure 1 Isothermal crystallization of (a) polypropylene; (b) polypropylene–carbon black (95:5); (c) polypropylene–carbon black (85:15) and (d) polypropylene–carbon black (70:30) in Avrami coordinates at (1) 130, (2) 132, (3) 134 and (4) 136 °C.

The SEM observations of the polypropylene–carbon black (PN) samples (Figs 4 and 5), and polystyrene–carbon black (SN) for two carbon black concentrations (Figs 6 and 7), show a uniform microstructure of the matrix, where the carbon black spherical particles are distributed homogeneously and an interconnection framework takes place (particularly for composites prepared with polypropylene).

At 30 vol % carbon-black concentration, microstructural percolation (interconnectivity among carbon black particles within the polymer matrix) appears to take place. However ordering formation was not detected in all the samples investigated. Disc-shaped samples, electroded on to both surfaces with high-conducting silver paste, were used to determine the a.c. impedance spectra using the impedance

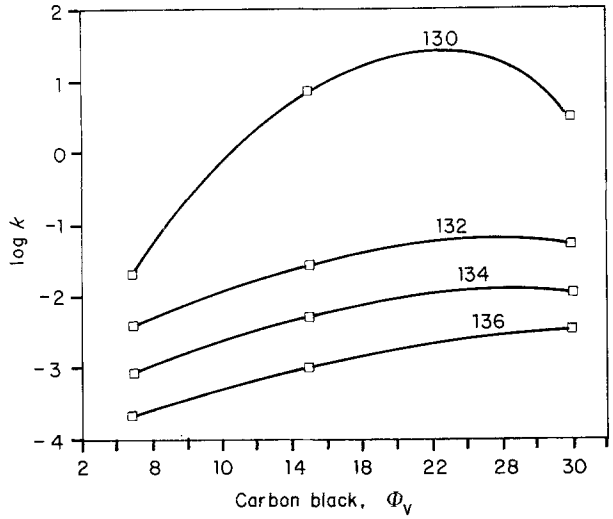

Figure 2 Variation of kinetic rate constant as a function of carbon black (N) content at the indicated crystallization temperature.

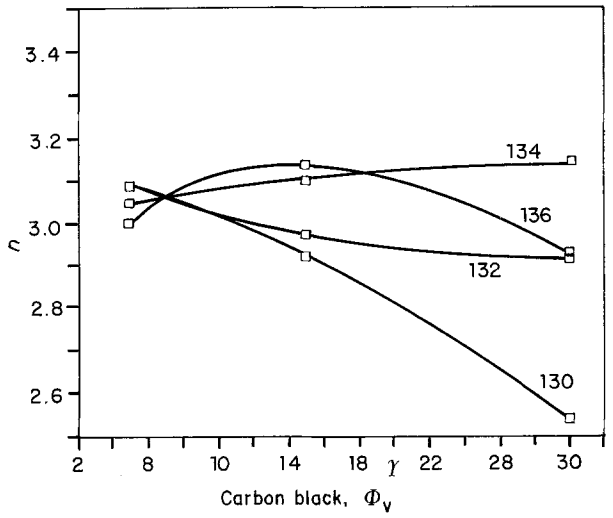

Figure 3 Variation of Avrami exponent *n* against carbon black (N) content at the indicated crystallization temperature.

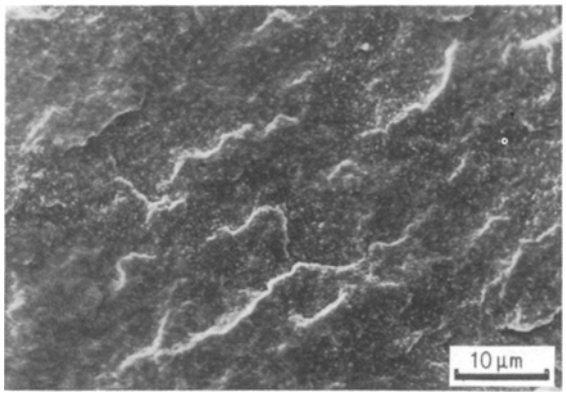

Figure 4 SEM micrograph of the fractured surface of the polypropylene–carbon black (80:20) system.

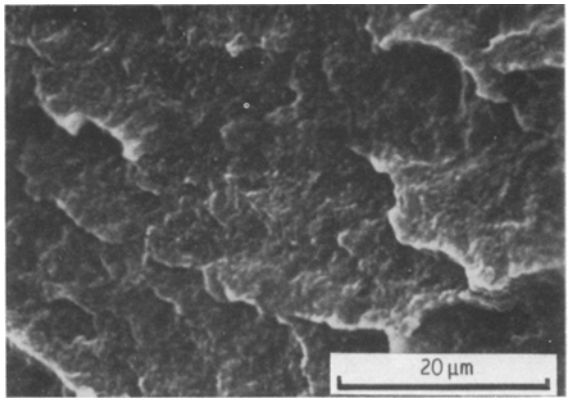

Figure 5 SEM micrograph of the fractured surface of the polypropylene–carbon black (70:30) system.

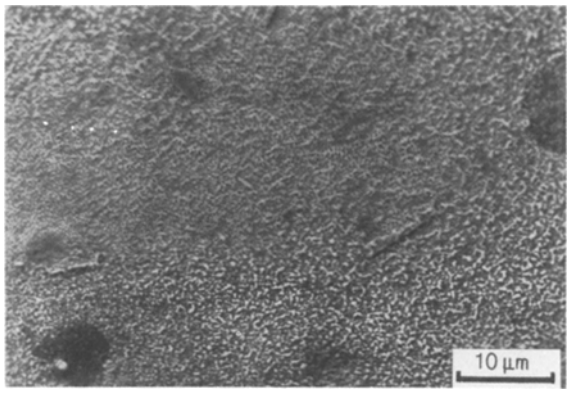

Figure 6 SEM micrograph of the fractured surface of the polystyrene–carbon black (80:20) system.

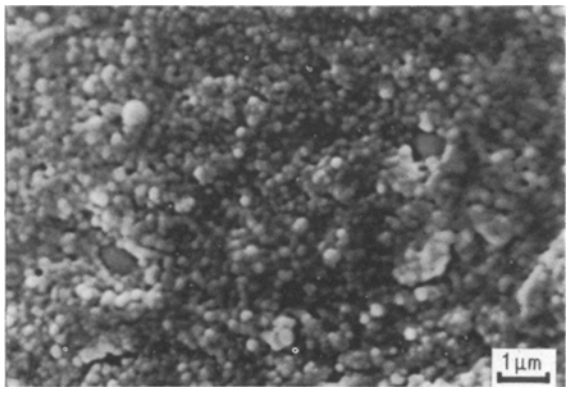

Figure 7 SEM micrograph of the fractured surface of the polystyrene–carbon black (70:30) system.

complex-plane analysis following the Bauerle criteria previously employed in ceramic electrolytes [7]. However, the capacitance values obtained in some composites, namely SN-30, PN-20 and PN-30, are negative, which implies that an inductance in parallel with resistance is the corresponding equivalent circuit. As a consequence of this it is no longer possible to use capacitance–resistance–impedance analysis, therefore a new inductance–resistance–impedance analysis which allows good characterization of samples is being developed in our laboratory. The composite SN-20 showed a capacitance component and therefore an impedance semicircle was observed (Fig. 8) whose arc has a depression angle of 25°. This fact indicates a strong contribution to the total conductivity of the

TABLE II Composition, conductivity and induction of the polypropylene–carbon black (PN) and polystyrene–carbon black (SN) systems

Samples	Composition, ϕ_v			Conductivity (σ) (Ω^{-1} cm^{-1})	Electrical inductance (L) (10^4 Hz)
	PS (wt %)	PP (wt %)	N (wt %)		
SN-20	80	–	20	3.4×10^{-3}	
SN-30	70	–	30	0.153 (10^4 Hz)	0.66×10^{-3}
PN-20	–	80	20	0.352 (10^4 Hz)	0.23×10^{-3}
PN-30	–	70	30	0.608 (10^4 Hz)	2.00×10^{-6}

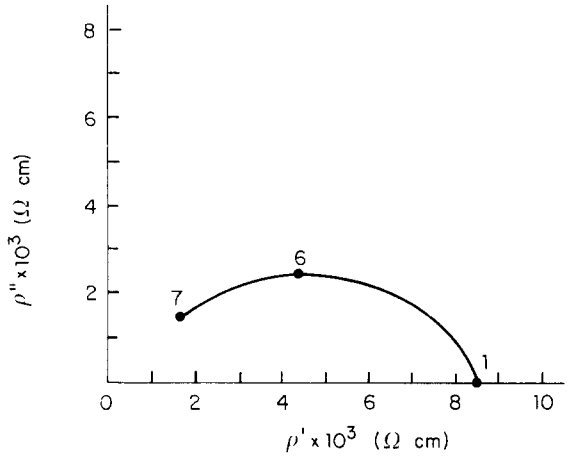

Figure 8 Capacitance–impedance spectrum of the polystyrene–carbon black (80:20) composite at 25 °C.

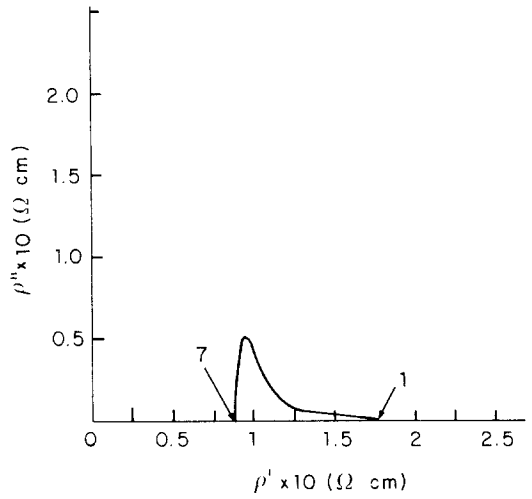

Figure 9 Inductive–impedance spectrum of the polypropylene–carbon black (70:30) composite at 25 °C.

interphase matrix–carbon black. The value of the conductivity was 1.26×10^{-4} (S cm^{-1}). In this case complete percolation is not achieved in the composite and a typical tunnelling effect is thought to take place, giving rise to semiconductor behaviour.

In the case of SN-30, PN-30 and PN-20 composites, it was observed that inductance decreases as the frequency increases, indicating a metallic behaviour. However, the conductance values of the composites are significantly smaller than those of the carbon black.

The conductivity values of the measured samples are shown in Table II. It seems that polypropylene composites have higher electrical conductivity than those of polystyrene; this can be explained taking into account both the different structural nature of the matrix and the wetting behaviour, which is better in the case of the polypropylene matrix. The inductive–impedance spectrum (Fig. 9) shows typical metallic behaviour and again the height of the impedance peak is higher for the polypropylene composites than those of polystyrene.

4. Conclusions

1. The microstructure of polypropylene was not significantly affected by the incorporation of carbon black.

2. A percolative effect was observed in samples with the highest content of carbon black (PN-30 and SN-30). At lower carbon black percentages, only the polypropylene samples showed percolation. This fact is related to the better wetting behaviour and microstructure of the polypropylene matrix.

3. The non-percolative samples seem to show a tunnelling effect as a conduction mechanism.

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