Communications to the Editor

Selective Localization of Carbon Black in Immiscible Polymer Blends: A Useful Tool To Design Electrical Conductive Composites

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Introduction. It is well-known that the electrical resistivity of insulating polymers can be decreased by dispersing a conductive filler, e.g., carbon black (CB) throughout the polymer matrix.[1–7] The critical amount of filler necessary to build up a continuous conductive network and accordingly to make the material conductive is referred to as the percolation threshold.

CB-filled polymers have great potential as antistatic materials. However, it is a problem to reach a suitable conductivity by the addition of an amount of CB small enough to preserve the mechanical properties of the polymer and to reduce as much as possible the cost of the final composite. Conductive CB are indeed expensive fillers.

There are several ways to decrease the percolation threshold of CB particles in polymers. They are mainly based on the use of additives, the optimization of processing conditions, and the size distribution and porosity of CB particles.[8,9] This paper focuses on a completely different approach which relies upon the selective localization of CB particles in multiphase polymeric materials. This approach has already been considered by some authors, who reported very encouraging results.[10–16] One of the most remarkable data corresponds to a percolation threshold of 0.005 volume fraction of CB.[14] This result has been obtained by the compression molding of a mixture of CB and polystyrene (PS) powders. In the absence of any shear, the CB particles do not penetrate the PS phase and remain essentially located at the interface between PS particles. This method has however several drawbacks as far as the mechanical properties and the reproducibility of the process are concerned. Furthermore, its scaling up to the industrial production is not realistic. In this respect, the lower percolation thresholds reported in the scientific literature by conventional techniques are in the range of 2–3 wt % of CB. The purpose of this paper is to show how efficiently the percolation threshold can be decreased by the selective localization of CB (DEGUSSA PRINTEX XE-2) particles in multiphase polymeric materials, i.e., in one phase or better at the interface of binary polyblends.

Results and Discussion. Electrical resistivity of an amorphous polymeric matrix, such as polystyrene, shows that the percolation threshold is close to 8 wt %, when CB is dispersed by melt blending in a Brabender internal mixer. Substitution of the monophase PS by a two-phase semicrystalline polyethylene (PE) favors a decrease in the percolation threshold down to 5 wt %, in agreement with the selective localization of CB particles in the amorphous phase of PE. Increasing the degree of crystallinity of PE is a potential way of decreasing further the percolation threshold. Since this approach is not straightforward, an alternative might be found in mixing PE with a nonmiscible polymer, e.g., PS, in which CB has no tendency to accumulate. It is, of course, crucial that PE forms a continuous phase throughout the polyblend, so as to reach the double percolation,[16,26] i.e., CB and phase percolation. In the PE/PS blend considered in this study, the cocontinuity of the phases occurs at a PE/PS weight composition of 45/55. At a lower PE composition, the PE phase is no longer continuous. Figure 1 illustrates the selective distribution of CB within the PE phase. According to Figure 2, the percolation threshold has decreased by a factor of $^5/_3$, which is consistent with the reduction of the material volume in which CB is now dispersed.

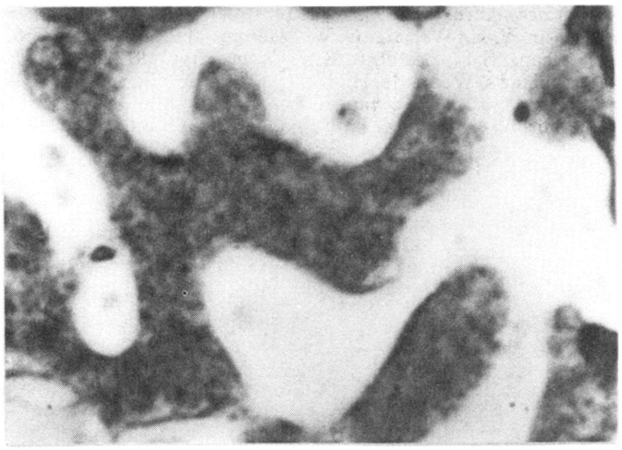

Figure 1. Optical microscopy of a 45/55 PE/PS blend filled with 1% CB. CB is localized in the PE phase (dark phase). 1 cm = 6 μm.

In order to obtain a better understanding of the nature of the interactions between carbon black and PE or PS, we have undertaken a series of theoretical calculations based, on the one hand, on quantum-chemical approaches (post-Hartree–Fock *ab initio* technique including electron correlation via second-order perturbation theory[17] and density-functional theory technique[18]) and, on the other hand, on empirical molecular mechanics techniques.[19] Details of these calculations will be reported in a forthcoming paper. It is important to stress that all the methods lead to very similar conclusions. The most significant results are that the interactions between the carbon surface and the polymers are weak (on the order of a few kilocalories per mole per polymer unit) and nearly identical for both polymers; this points out the possibility of locating the carbon particles at the interfaces between the two polymers. We note that the weak binding between the carbon surface and the polymers originates (i) in dispersion forces, as could be expected, and (ii) in the formation of hydrogen-type bonds whereby the protons on methylene

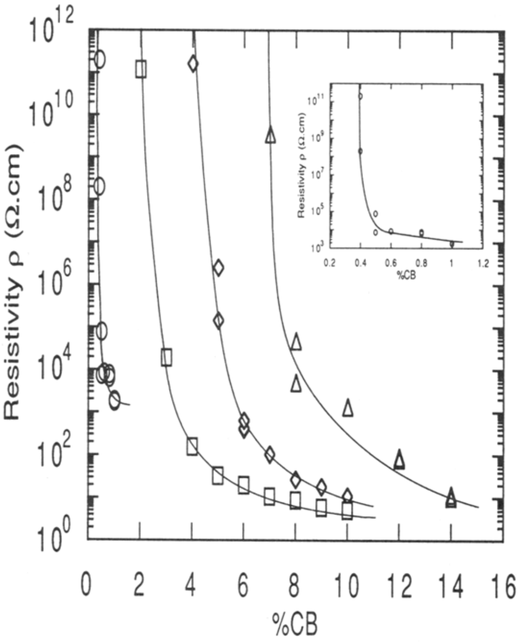

Figure 2. Resistivity vs wt % CB. (△) CB is dispersed in an amorphous PS matrix. (◇) CB is dispersed in a semicrystalline PE matrix. (□) CB is dispersed in the PE phase of a cocontinuous 45/55 PE/PS blend. (○) CB is localized at the interface of a cocontinuous 45/55 PE/PS blend. This plot (○) has been magnified for the sake of clarity.

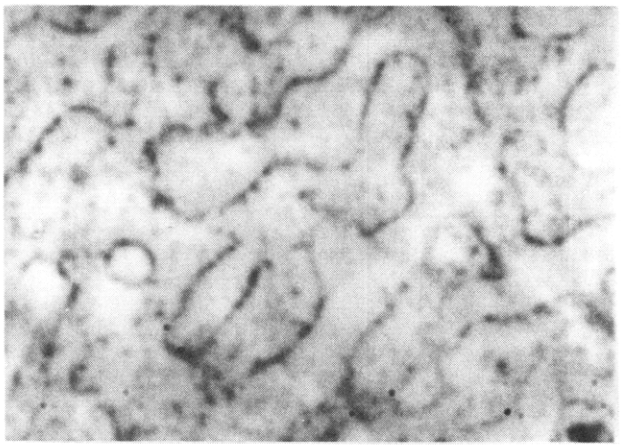

Figure 3. Optical micrograph of a 45/55 PE/PS blend filled with 1% CB. CB is localized at the interface of the blend (both phases are white). 1 cm = 6 μm.

or phenyl groups along the polymer backbones point toward the center of graphite-type hexagons on the CB surface. Such interactions have already been described previously in the case of the benzene dimer (in a T-perpendicular conformation) or the methane–benzene complex.[20,21]

Focusing on two-phase polyblends and by analogy with the aforementioned technique based on the compression molding of PS and CB particles, a very stimulating approach would consist of locating as selectively as possible CB at the interface of a polyblend with a dual-phase continuity. Compared to Figure 1, Figure 3 convincingly shows that CB can be essentially present at the interface of a cocontinuous PE/PS blend of 45/55 weight composition. To this particular situation corresponds a percolation threshold of 0.4 wt %, i.e., a CB volume fraction of 0.002, since CB density is in the range of 2.04–2.11 g/cm^3 (Figure 2).[27] This result is thus quite comparable to that published by Klason and Kubát (0.005 vol %).[14] The interesting point is that CB can be accumulated at the interface of a polyblend by a conventional melt blending technique. Conditions for the selective localization of CB in one phase or at the interface of two-phase polyblends will be discussed in a forthcoming paper. Nevertheless, and as an example, the sample shown in Figure 3 refers to a cocontinuous two-phase PE/PS blend in which CB is spontaneously located in the PE phase. On the basis of that tendency, CB has been first mixed with melted PS, which has been ultimately added with PE into the mixer. Obviously for accumulating in the PE phase from the PS phase, CB particles must come through the interface of the polyblend. This migration of CB particles is clearly highlighted in Figure 4, where resistivity of the CB-loaded polyblend goes through a minimum when the mixing time of the (PS + CB)/PE system is increased. This minimum in the curve corresponds to the preferential localization of CB at the interface.

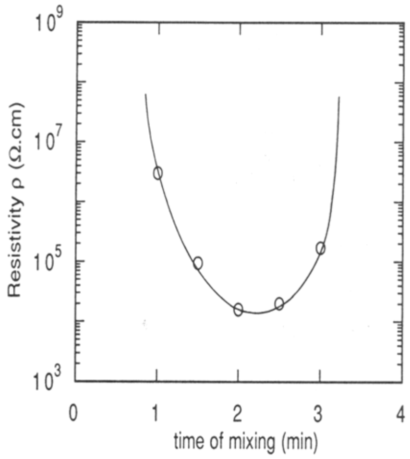

Figure 4. Resistivity vs mixing time. From left to right, CB (1%) is localized in the PS phase, then at the interface, and finally in the PE phase of the cocontinuous 45/55 PE/PS blend. The minimum of the curve corresponds to the crossing of the interface by CB.

Table 1

CB dispersed	percolation threshold (wt %)	critical exponent t
in a PE matrix	5	2.0 ± 0.2
in the PE phase of a 45/55 PE/PS blend	3	1.5 ± 0.2
at the interface of a 45/55 PE/PS blend	0.4	1.3 ± 0.2

Equation 1 relates the dc conductivity σ of a polymer filled with conductive particles to the weight amount p of the particles in the mixture above the percolation threshold p_c.[22–24] In "universal percolation theory", the value of "the critical exponent" t is only related to the dimensionality of the system, t being equal to 1.9 in 3D systems and 1.3 in 2D systems.[25] t and p_c have been estimated from the experimental data and eq 1, as shown in Table 1. t is found to be 2.0 when CB is dispersed within the amorphous phase of pure PE. When CB is at the interface of a PE/PS blend with dual-phase continuity, the critical exponent t is then equal to 1.3. This is consistent with the trend of a decreasing t-value in percolation theory when lowering the system dimensionality. This is a clear indication for the presence of CB in a two-dimensional space such as an interface. The intermediate situation would prevail when CB is located in the amorphous part of the PE phase of the cocontinuous PE/PS blend; t is then equal to 1.5. This

$$\sigma \approx \sigma_0(p - p_c)^t \qquad (1)$$

infers that the amorphous component of the continuous PE phase has a dimensionality in between 2 and 3.

Criteria for the controlled localization of solid particles within two-phase polyblends are essentially polymer/polymer interfacial tension and CB/polymers interfacial tensions.[11] The effect of these experimental parameters and how extensively they can be changed for a given ternary CB/polymer 1/polymer 2 system will be discussed in a forthcoming paper.

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