Kinetic and Thermodynamic Control of the Selective Localization of Carbon Black at the Interface of Immiscible Polymer Blends

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Several strategies are reported that allow carbon black (CB) particles to be selectively localized at the interface of polyethylene/polystyrene (PE/PS) blends used as models of two-phase polyblends. A first general approach relies upon a kinetic control, i.e., the choice of such processing conditions that the CB particles are "immobilized" at the polyblend interface at least for a workable period of time. The dry premixing of the two powdery polymers and CB particles followed by compression molding is the first valuable kinetic control. A second one can be implemented during the melt blending of the immiscible polymers, which makes this strategy more attractive. Actually, CB is first dispersed in the melted polymer with which it less strongly interacts. Upon the addition and melting of the second polymer, CB particles are thermodynamically driven to this second polymer phase. The conducting particles are observed to accumulate at the polyblend interface at a rate and for a period of time that depend on the rheology of the polyblend under the processing conditions. The thermodynamically controlled localization of the CB particles at the two-phase polyblend interface is certainly the most efficient strategy, even though it is not the most general one. In this respect, CB particles have been oxidized in such a way that they cover a large range of pH. Depending on this surface property, the CB particles are spontaneously localized either in one polymer phase or at the interface. Actually, the selective localization of the CB particles changes from the PS phase to the interface and finally to the PE phase, when the pH of these particles is increased from 2.4 to 7.0. The selective localization of the CB particles at the polyblend interface is most interesting when the polymer phases are co-continuous, since then the conducting particles can percolate at a volume fraction as small as 0.002−0.003. Furthermore, this selective modification of the polyblend interface improves the stability of the phase morphology against coalescence when the material is annealed.

Introduction

Although most of the world production (90%) of carbon black (CB) is intended for the rubber industry as a reinforcing additive,[1] at least some grades of this particulate material are used for their intrisic electrical conductivity. The role of CB is then to provide synthetic polymers, which are commonly insulating, with anti-static properties,[2−7] which is a prerequisite for the production of, for example, electrical wires and pipe- lines. A critical amount of the electrically conductive filler, known as the percolation threshold, must however be used for imparting conductivity to the polymer.[8−10] This critical weight or volume percentage of CB particles required for building up a continuous electrically con-ducitve network throughout the polymer matrix actually depends on the aggregation,[11−13] structure, porosity, average size, and size distribution of the conducting

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Table 1. Characteristic Features of Polymers and Carbon Black

polymers	Mn	Mw	density	melt index	crystallinity
polyethylene, PE (Solvay Eltex B3925)	8500	265 000	0.96	<0.1	semicrystalline (50% crystallinity)
polystyrene PS (BASF 158 K)	100 000	280 000	1.05	0.39	amorphous

carbon black, CB	specific area		apparent density	pH (ASTM D1512−90)[a]
	BET (m²/g)	DBP (mL/100 g)		
Degussa Printex XE-2	1000	400	0.120	7
Cabot BP1000	343	104	0.26	2.5
Cabot BP2000	1475			

[a] CB had been washed several times with toluene and then with distilled water.

particles,[14,15] and on the polymer rheology[12,13] and processing conditions as well.

There are technical and economical incentives for decreasing the CB percolation threshold as much as possible. Indeed, dispersion of increasing amounts of CB particles commonly has a detrimental effect on the mechanical properties of thermoplastics, on polymer processing, and last but not least on the final cost of the composite material. A few papers coauthored by some of us have shown that the selective localization of conducting particles in one phase or best at the interface of a co-continuous two-phase polyblend is a very efficient strategy to decrease the CB percolation threshold, since 0.003 volume fraction of CB was found to percolate in the continuous interfacial region of a polyethylene/polystyrene (PE/PS) blend and to induce electrical conductivity.[17−19] It is worth pointing out that a double percolation is at the origin of this very unusual situation: (i) percolation of the polymer phases and thus of their interface and (ii) percolation of the conducting particles at the interface, thus ideally in a two-dimensional (2D) space. The beneficial effect of the annealing of these ternary systems on the CB percolation threshold has also been reported and accounted for by a decrease of the interfacial area, as will be confirmed in this study by the image analysis of the phase morphology.

This paper mainly aims at investigating the possible strategies for achieving this unique situation of double percolation in the case of a model system consisting of conducting CB particles and two traditionally immiscible polymers, PE and PS. The issue of the phase co-continuity in polymer blends is beyond the scope of this paper, the interested reader being referred to a few and certainly not all pertinent papers.[20,21] Sumita et al.[22] have previously shown that the CB distribution in a binary polyblend is controlled by the balance of the interactions of the filler with each constitutive polymeric component. Although this thermodynamic control is the best one, since it operates spontaneously and becomes effective at thermodynamic equilibrium, each ternary conducting particle/polymer1/polymer2 is a case in itself that requires a specific optimization. This aspect will be discussed in the second part of this paper. It is thus highly desirable to exercise a kinetic control on the CB localization at the interface of a co-continuous polyblend during the processing of this ternary system particularly by molding of a powdery preblend and melt blending in an internal mixer. Any valuable emerging strategies might deserve interest in several fields of applications,

such as antistatics, sensors,[23] autoregulating resistors,[24,25] electrodes, electromagnetic interference shielding,[26] and polymer pigmentation.

Experimental Section

The main characteristic features of the polymers and CB grades used in this study are listed in Table 1.

CB Oxidation. Twenty grams of CB (Cabot BP2000; Degussa Printex XE-2) were poured into a 500 mL beaker containing 100 mL of distilled water. This mixture was heated to the boiling temperature, and then 100 mL of HNO₃ was added. In addition to the HNO₃ concentration (*x* wt %, Table 2), the reaction time at 100 °C (*y* min, Table 2) was changed, so as to change the oxidation degree and thus the final pH of the particles. After reaction, the particles were washed with distilled water until a neutral pH was maintained and then dried at 100 °C for 24 h in vacuo. The pH of the CB particles was measured according to the ASTM D1512-90 method.

Mixing Techniques. *(1) Compression Molding of the Preblended Powdery Constitutive Components*. The two pellet-shaped polymers were ground to a powder of ca. 1 mm and 100 μm diameter, respectively. PE and PS powders were then mixed in a 45/55 (wt/wt) ratio and added with the required amount of CB. The final dry preblend was compression molded between aluminum sheets at 200 °C for 10 min and then cooled to 25 °C under pressure for 1 min.

(2) Conventional Melt Blending (or the experimental conditions used when the "thermodynamic" localization of CB at the interface is concerned). PE and PS were mixed in an

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Table 2. Oxidation of CB Particles

sample reference	CB grade	HNO$_3$ concn x (wt %)	reaction time y (min)	pH measured
CB 0	BP2000	10	1620	2.4
BP1000				2.5
CB1	BP2000	5	30	2.8
CB2	XE-2	0.25	1440	3.2
CB3	BP2000	1	120	3.4
CB4	BP2000	0.25	240	4.2
CB5	BP2000	0.25	120	4.7
CB6	BP2000	0.25	60	5.0
CB7	BP2000	0.25	30	5.4
CB8	XE-2	0.5	240	5.4
CB9	BP2000	0.25	30	5.9
CB10	BP2000	0.025	120	6.5
CB11	BP2000	0.025	1080	6.5
XE-2				7.0
BP2000				7.0

internal mixer (Brabender Plasticorder; 50 cm^2) at 200 °C for 1 min, the screw rotating speed being 25 rpm. CB was then added, and 1 min later the mixing rate was increased up to 64 rpm and maintained for 10 min. The final blend was compression molded as previously mentioned. Samples filled with the series of CB of different pH (Table 2) were, however, molded at 260 °C for 40 min. Phase morphology was currently analyzed immediately after melt blending and rapid cooling in liquid nitrogen.

(3) Thermodynamically Driven CB Migration in Polyblends during Melt Blending (or the experimental conditions used when the "kinetic" control of the CB localization at the interface is concerned). PS (or PE) was first added into the 50 cm^3 chamber of the Brabender internal mixer, whose screws were rotating at 25 rpm. XE-2 (BP1000) was then added to the completely melted PS(PE), and the rotating speed was increased up to 64 rpm for 3 min. PE(PS) was rapidly added and the mixing time was recorded from the very early addition of the second polymer. The final blends were compression molded between Al sheets at 200 °C for 240 min before analysis.

Sample Characterization. The electrical conductivity of filled polyblends was measured with the four-probe technique so that they were free from resistance of the sample/electrode contacts.

Reflectivity was measured with a L$_{ab}$ apparatus (Instrumental Color Systems) and expressed as the ratio of intensity reflected at 10° with respect to the incident intensity (%).

One micrometer thick sections were observed by optical microscopy. If required, the PS phase of polyblends was indentified (if free from CB) by selective staining with an organic dye. Image treatment and image statistical analysis were performed using the Noesis software "visilog". The images were first digitized and then binarized, and the binarized images were treated by statistical analysis. Samples were assumed to be isotropic, so that images associated with different section planes were statistically equivalent. To account for statistical fluctuations in relation to the sampling, thin sections in various locations were analyzed. A total of five images per blend were analyzed. The procedure used for the calculation of the mean size and the specific interfacial area was detailed in a previous paper.[18]

Results and Discussion

Interfacial Localization of CB by Compression Molding of a Preblend of the Powdery Constitutive Components. The compression molding of polymers is a processing technique which is conducted in the absence of shear stress so that the opportunity for the CB particles to penetrate the viscous polymer phases is severely restricted. The filler particles are then expected to remain localized at the frontier of the original polymer grains and thus to percolate along this
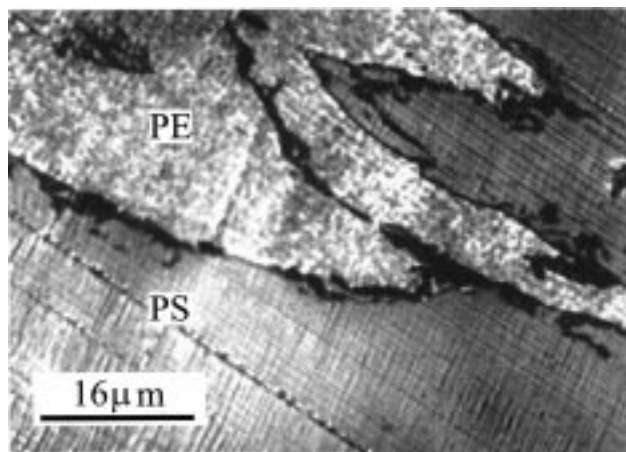

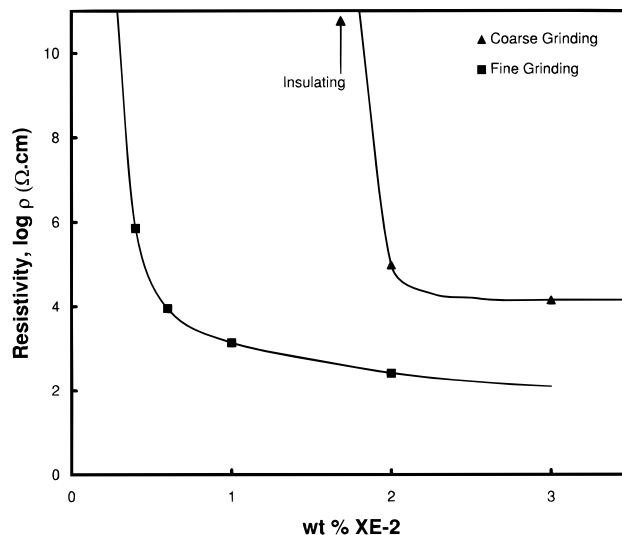**Figure 1.** Optical micrographs of 1 wt % XE-2 filled PE/PS 45/55 blend.

Figure 2. Percolation threshold of 45/55 PE/PS blends filled with XE-2. The samples were prepared by mixing technique 1 (see Experimental Section).

specific area, depending on the ternary blend composition and fineness of dispersion. Figure 1 is a typical optical micrograph of PE/PS (45/55,wt/wt) blend filled with 1 wt % XE-2. CB particles are clearly concentrated at the PE/PS interface but also at the frontier between PE/PE (as shown in Figure 1) and PS/PS grains that have not succeeded in merging during molding at 200 °C.

As expected, the electrical resistivity of the 45/55 PE/PS blends depends on the CB content as illustrated by Figure 2. In the case of polymer grains of ca. 100 μm diameter, a low percolation threshold is observed, i.e., 0.4 wt % (or 0.002 vol fraction), which is a dramatically low value compared to the percolation threshold of XE-2 in PE (5 wt %) and PS (8 wt %).[17] It is, however, surprising that the XE-2 particles start to percolate at a five times higher content when the constitutive polymers are ground more coarsely, i.e., an average diameter of 1 mm instead of 100 μm. Indeed, the intergrain area must decrease when the grain diameter is increased, and less XE-2 particles should be required for building up a continuous conductive path. The origin for this abnormality might be found in phases that have sizes comparable to the electrode used for the measurement of the electrical conductivity.

Equation 1 is the well-known dependence of the conductivity σ of a polymer filled with conducting particles on the particle content (p wt %) in excess with respect to the percolation threshold (p_c).[27-29]

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

According to the universal percolation theory, t is a critical exponent related to the dimensionality of the percolating system. Predicted values of t are 1.9 and 1.3 for 3D and 2D systems, respectively.[30] The experimental dependence observed in Figure 2 is best fitted by eq 1 in the case of $t = 1.5 \pm 0.1$, which suggests that XE-2 percolates in the compression molded samples in a 2D rather than in a 3D space, which is qualitively consistent with the interfacial localization of the conducting particles.

Although this compression molding technique is very straightforward and provides exceptionally low percolation thresholds, it is not well-suited to the production of materials with high mechanical performances as a result of a poor intergrain adhesion.

Thermodynamically Driven Migration of CB Particles from One Polymer Phase to the Second One during Melt Blending. It is a preliminary observation that XE-2, which is a nonoxidized CB with a nonpolar surface, spontaneously migrates and accumulates in the less polar PE phase of melt blended PE/PS mixtures. Conversely, the surface of BP 1000 is polar as result of strong oxidation, and this conducting CB is observed in the more polar PS phase of the same polymer blends. The question is to know whether advantage may be taken of this clear-cut thermodynamic control to drive the CB particles to the interface. Indeed, what may happen if XE-2 is previously dispersed in melted PS before the addition of PE, for which XE-2 has a marked preference? The whole procedure has to be carried out in the melt under continuous shearing, so that the system can rapidly respond to the thermodynamic incentives.

In a series of experiments, 1, 3, and 10 wt % XE-2 (with respect to the final PE/PS blend) have been premixed with PS at 200 °C for 3 min, followed by the addition and melt blending of such an amount of PE that the PE/PS weight composition is 45/55 and the two-phase morphology is co-continuous.[18]

The mixing time dependence of the electrical resistivity is shown in Figure 3. At short mixing times (<1 min) and low XE-2 content (1 wt %), the high resistivity indicates that the conductivity particles are still essentially in the PS phase, in which their nominal concentration (1.8 wt %) is far below the percolation threshold (8 wt %).[17] The question of the time required for the two-phase morphology to be co-continuous may also be addressed. However, upon increasing mixing times at high temperature, the filled polyblend becomes increasingly conductive. This observation is consistent with the setting up of the polymer phase co-continuity
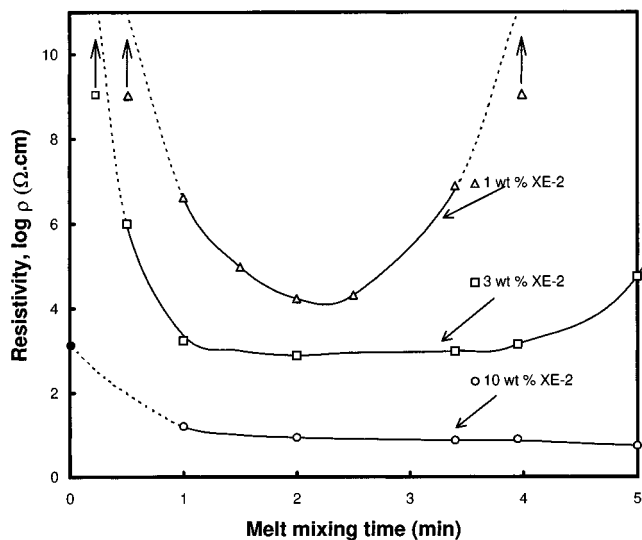

Figure 3. Influence of the melt mixing time on the resistivity of 45/55 PE/PS blends loaded with different amounts of XE-2 (Samples prepared by mixing technique 3; see Experimental Section). ● refers to homo PS loaded with 10 wt % XE-2.

and the migration of the XE-2 particles from the PS phase to the PE phase through the interface. The electrical resistivity passes through a minimum when most the conducting particles are concentrated in this restricted interfacial region. Beyond 4 min of mixing, the polyblend is again highly insulating as result of the complete transfer of the XE-2 filler into the PE phase, in which the XE-2 percolation threshold (5 wt %)[17] is at least two times higher than the nominal content (2.2 wt %). When the XE-2 content is increased from 1 to 3 wt %, the minimum in resistivity is more rapidly observed: it is decreased by ca. 1.5 order of magnitude, and it is rapidly flattening in agreement with a nominal content in the PE phase (6.6 wt %) close to the percolation threshold (5 wt %) in the case of complete transfer in that phase. Finally, when the XE-2 content in the final polyblend is 10 wt %, the nominal content in each phase—in the case of selective localization in each of them—largely exceeds the percolation threshold, which explains that a plateau in the electrical resistivity is observed at a comparatively low value as soon as the co-continuous two-phase morphology is set up.

The explanation proposed for accounting for the experimental data in Figure 3 has been confirmed by the fracture surfaces of the 45/55 PE/PS blend filled with 1 wt % XE-2, observed at different mixing times by scanning electron microscopy (Figure 4). It is indeed known that the fracture in a multiphase system preferably propagates along the paths of smaller resistance, thus along the interface in a blend of highly immiscible polymers, such as PE and PS. There is a remarkable parallelism between the electrical resistivity of the polyblend (Figure 3) and the situation at the interface (Figure 4). Indeed, after 1 min of mixing, a few XE-2 particles are observed at the interface and the resistivity is as high as 10^6 Ω cm. One minute later, the interface appears to be completely invaded by the conducting particles and the minimum in resistivity is reached. For a longer mixing (3 min), the interfacial situation observed after 1 min is more or less restored after 3 min, although more particles are left in the interfacial region consistently with a smaller resistivity (10^5 Ω cm).

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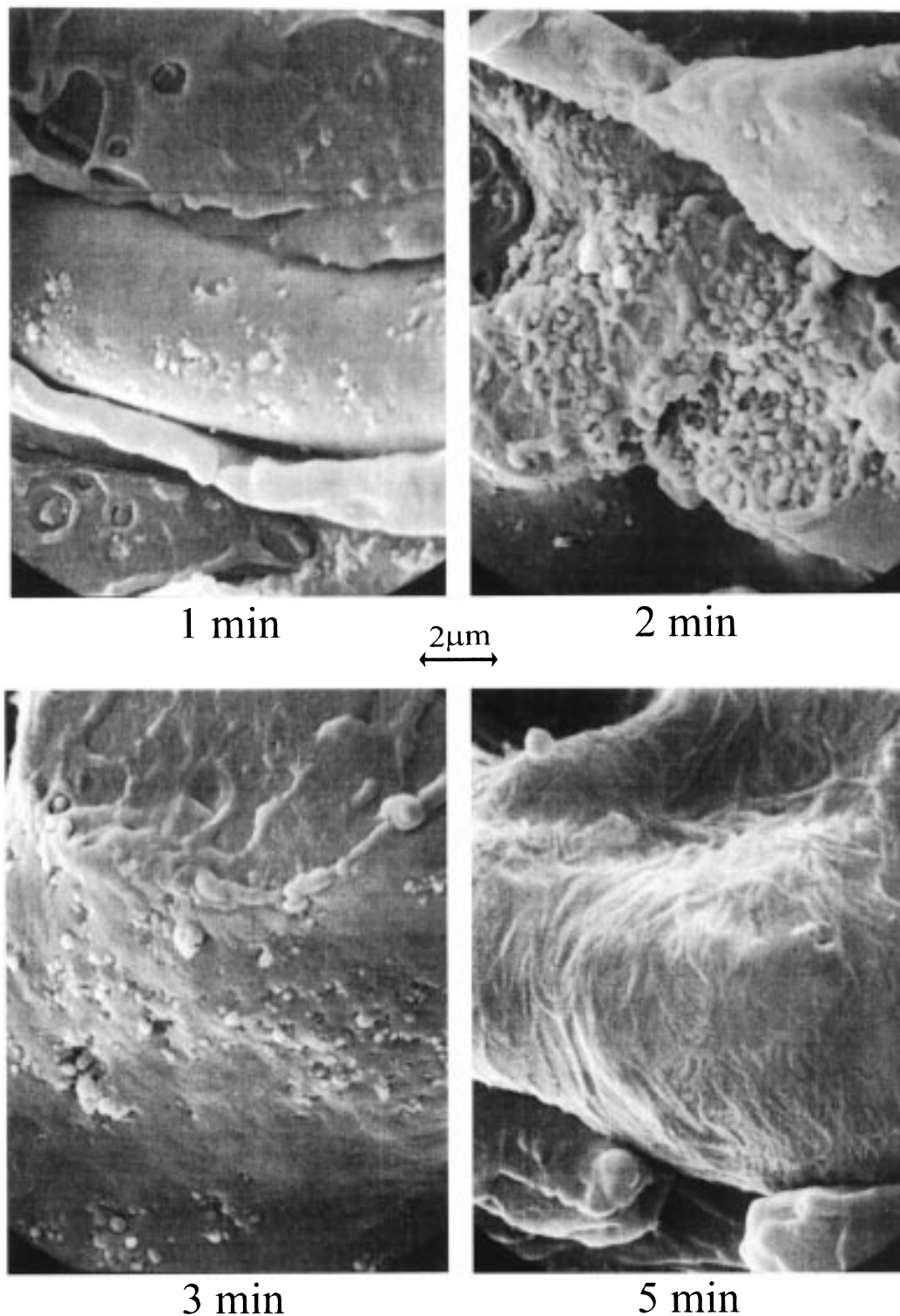
Figure 4. Scanning electron micrographs of 45/55 PE/PS blends filled with 1 wt % XE-2 at different melt mixing times (samples prepared by mixing technique 3; see Experimental Section).

Finally, the fracture surface is essentially free from filler particles after 5 min, thus when the polyblend is an insulating material. More convincing evidence for this transfer of XE-2 particles from PS to PE through the interface has been found in the observation of the same polyblends by transmission electron microscopy (Figure 5). Originally, the conducting particles are dispersed in the PS phase, and they tend to move to the interface after 0.5 min of mixing. After 2 min, these particles have essentially accumulated in the interfacial region.

Finally, they succeeed in crossing the interface, and they are selectively dispersed in the PE phase after 6 min, which corresponds to the most favorable thermodynamic situation. We thus have to do with a mixed thermody-namic−kinetic control of the CB interfacial localization, since this unique situation may result from the kinetic control of the thermodynamically driven migration of CB from one polymer phase to the second one.

What is true for the migration of XE-2 from PS to PE should also hold when BP 1000 is originally dispersed
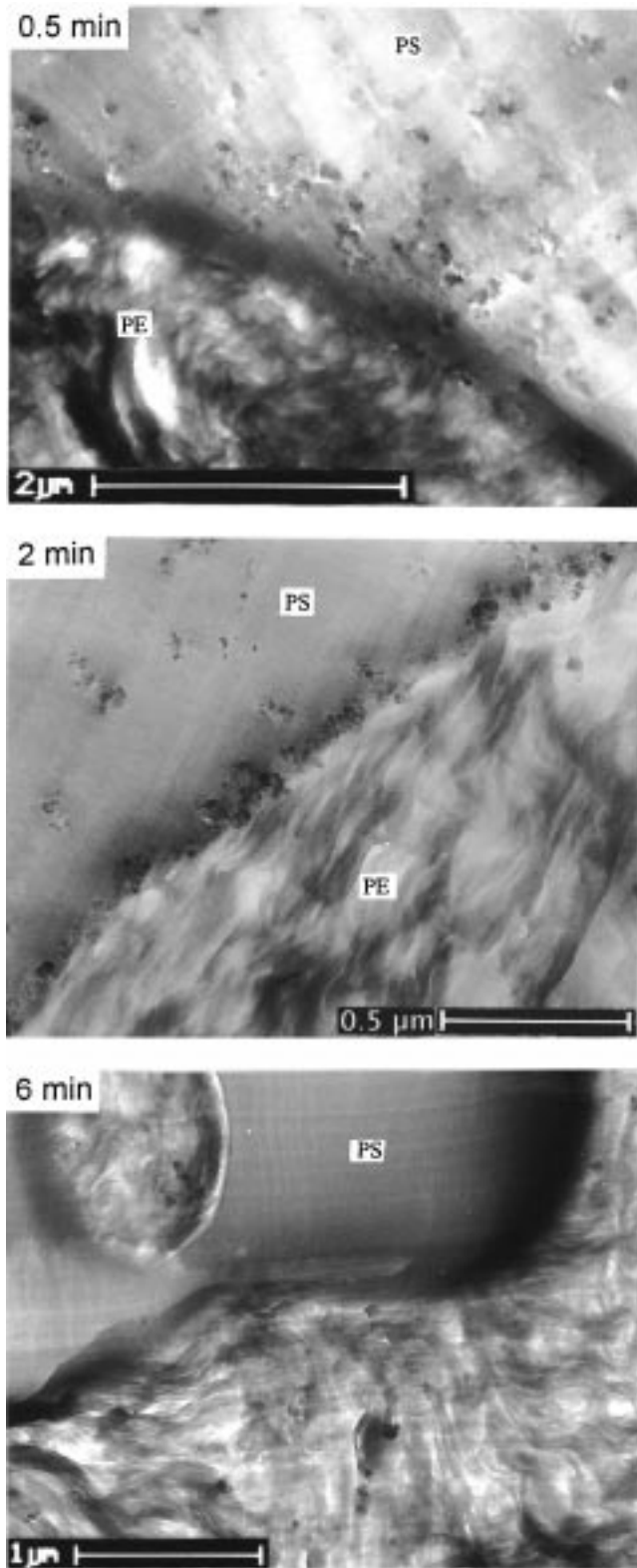
Figure 5. Transmission electron micrographs of 45/55 PE/ PS blends filled with 1 wt % XE-2 at different melt mixing times (samples prepared by the mixing technique 3; see Experimental Section).

in melted PE and then added with PS, which is more strongly interacting with BP 1000 than PE. Figure 6 completely confirms this expectation, since the resistivity curve also shows a minimum when the melt mixing time is increased. Although the ternary blend composition is the same (45/55 PE/PS loaded by 1 wt % CB),
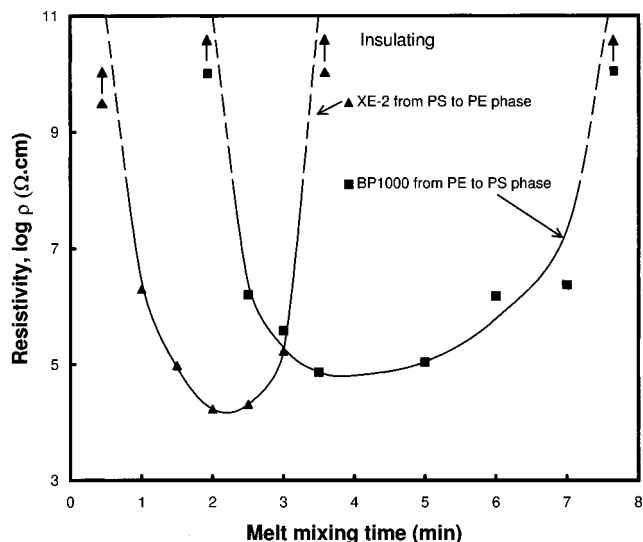
Figure 6. Influence of the melt mixing time on the resistivity of 45/55 PE/PS blends loaded with 1 wt % XE-2 and BP1000 (samples prepared by mixing technique 3; see Experimental Section).

the minimum in resistivity is reached after a longer mixing time, and it is much flatter and the value higher when the CB particles are originally in the PE phase (BP 1000) than in the PS one (XE-2). This observation indicates that the transfer of BP 1000 from PE to PS is much slower, which may be related to the much higher melt viscosity of PE compared to PS (Table 1), thus of the phase in which the CB particles are originally dispersed. A broader concentration gradient of these particles between the two phases is accordingly expected to set up in the course of mixing, which explains a delay in the resistivity decrease, a less efficient CB percolation in the interfacial region, and the occupation of this region for a longer period of time. Some difference in the balance of thermodynamic interactions (CB/PE vs CB/PS) could also contribute to change the resistivity vs mixing time curves (Figure 6), when BP 1000 is substituted for XE-2 and all the other conditions being the same.

On the basis of the information collected in Figure 3, increasing amounts of XE-2 have been first dispersed in melted PS, before being added with PE (45/55 (wt/ wt) PE/PS) and melt blended for 2 min at 200 °C. The plot of the electrical resistivity vs XE-2 content can accordingly make the percolation threshold available, the percolation being expected to occur in the interfacial region. Figure 7 points out the critical effect that the thermal posttreatment of the polyblends has on the percolation of the XE-2 particles. Indeed, when the filled polyblends are compression molded at 200 °C for 10 min, a percolation threshold of ca. 3 wt % is observed, which is comparable to the value reported for the selective localization of XE-2 in the PE phase of the 45/ 55 PE/PS blend.[17] However, when the compression time at 200 °C is increased up to 150 min, or alternatively when both compression time (10 to 40 min) and temperature (200 °C to 260 °C) are increased, the phase morphology has the opportunity to reorganize in such a way that the percolation threshold is dramatically decreased down to 0.4−0.6 wt % (i.e., 0.002−0.003 vol fraction) XE-2. This very beneficial effect indicates an increase in the local XE-2 concentration as result of a
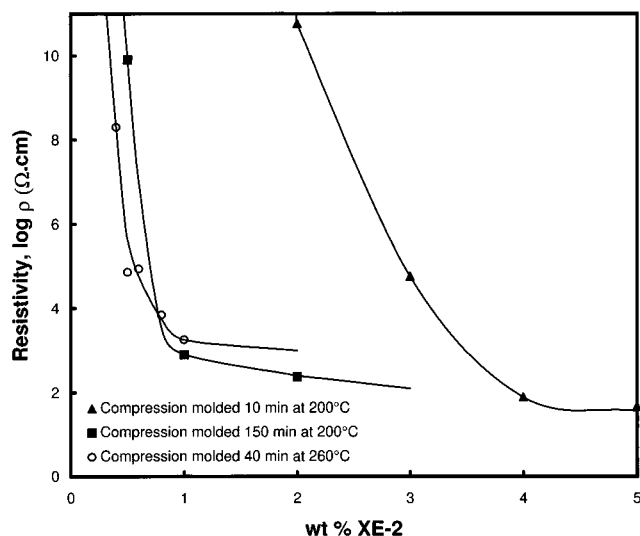
Figure 7. Percolation threshold of 45/55 blends filled with XE-2 melt mixed during 2 min at 200 °C and compression molded under different conditions (samples prepared by mixing technique 3; see Experimental Section). The XE-2 batch is different from (and apparently less conductive than) the batch used in Figure 3.

decreased interfacial area, which is the spontaneous tendency of an immiscible polymer blend in the melt in absence of shear forces. It is also clear that the CB particles do not leave the interface under conditions of zero shear but rather concentrate more uniformly in this region. This conclusion is supported by the values calculated for the critical exponent t in eq 1. Indeed, $t = 1.5$ in the case of compression molding at 200 °C for 10 min, which suggests that the conducting particles percolate in a space intermediate between 2D and 3D. When the thermal posttreatment is more severe, t is found in the $1.2-1.3$ range, which is the signature for a 2D percolation, thus for a much more selective interfacial localization of XE-2.

In addition to electrical conductivity, the selective localization of CB particles at the binary polyblend interface can also affect other physical properties, and particularly optical properties such as reflectivity. Interestingly enough, the mixing time dependence of the reflectivity (Figure 8) is quite comparable to that of the electrical resistivity (Figure 3) in the case of the 45/55 PE/PS blend loaded by 1 wt % XE-2. The initial decrease in reflectivity is followed by a minimum at the same mixing time as that required for observing the minimum in resistivity and finally by a rapid increase at longer mixing times. The important conclusion is that light is most efficiently absorbed by the filler when it selectively percolates along the continuous interface of a binary polyblend. Thus, the strategy proposed for optimizing the electrical conductivity of original polymers could also be helpful for improving other physical properties in relation to the intrinsic characteristics of the filler.

Thermodynamically Driven Localization of CB Particles at the Interface of PE/PS Blends. The data discussed in the previous section have emphasized the role played by thermodynamics in the localization of CB particles in PE/PS blends. It may thus be predicted that CB particles will spontaneously accumulate at the interface, provided that the CB/PE and
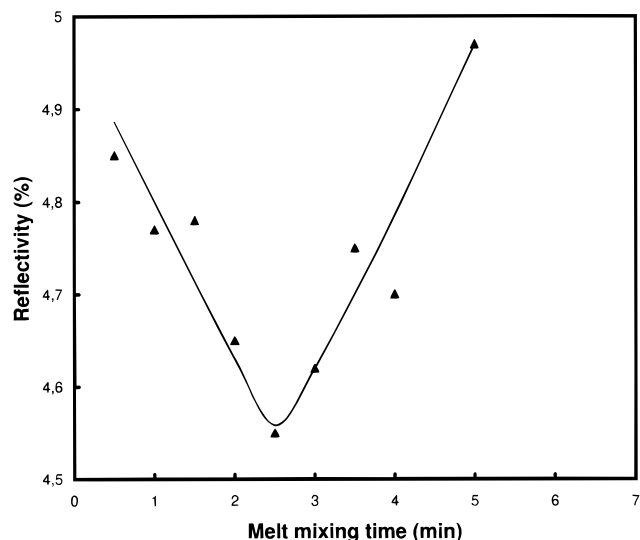

Figure 8. Influence of the melt mixing on the reflectivity of 45/55 PE/PS blends loaded with 1 wt % XE-2 (samples prepared by mixing technique 3; see Experimental Section).

CB/PS interactions are properly counterbalanced.[31,32] For this purpose, two nonoxidized CB samples (XE-2 and BP 2000) of pH = 7 have been oxidized by HNO_3 of various concentrations for different times (Table 2). The oxidation rate of BP 2000 is higher than XE-2, in agreement with a larger surface area (Table 1). Expectedly, pH decreases when the reaction time is increased at constant HNO_3 concentration (CB7 to CB4, Table 2) and conversely when HNO_3 is more concentrated and the reaction time kept unchanged (CB1 and CB7, Table 2). It also appears that when HNO_3 is diluted too much (CB10 and CB11, Table 2), the extent of the oxidation reaction becomes rapidly limited and the particle pH is only slightly decreased even though the reaction time is significantly increased. Although the samples CB7 and CB9 have been prepared under the same experimental conditions, their pH differs by ca. 0.5 units, which emphasizes the very difficult control of this heterogeneous reaction. The final pH reported in Table 2 is an average value which is supposed to hide a broad distribution of the particle surface properties.

The 45/55 PE/PS polyblend has been melt blended and systematically loaded with 2 wt % of each CB sample listed in Table 2. Although the co-continuity of the PE and PS phases was previously stated for this blend composition,[18] it has been confirmed by the selective extraction of the PS phase by tetrahydrofuran. PS is indeed quantitatively dissolved, leaving a porous PE block of the same shape as the original sample. It is worth recalling that the composition domain over which the PE and PS phases are co-continuous is basically increased by the addition of CB.[18]

Figure 9 shows that the electrical resistivity of the polyblend strongly depends on the acidity of CB. Indeed, the polyblend is insulating at pH < 2.8 and pH > 6.0 ($\rho > 10^{11}$ Ω cm), whereas in the intermediate range of pH, the resistivity is constantly close to 10^3 Ω cm.

(31) Asai, S.; Sakata, K.; Sumita, M.; Miyasaka, K. *Polym. J.* **1992**, *24*, 415.
(32) Sumita, M.; Sakata, K.; Hayakawa, Y.; Asai, S.; Miyasaka, K.; Tanemura, M. *Colloid Polym. Sci.* **1992**, *270*, 134.
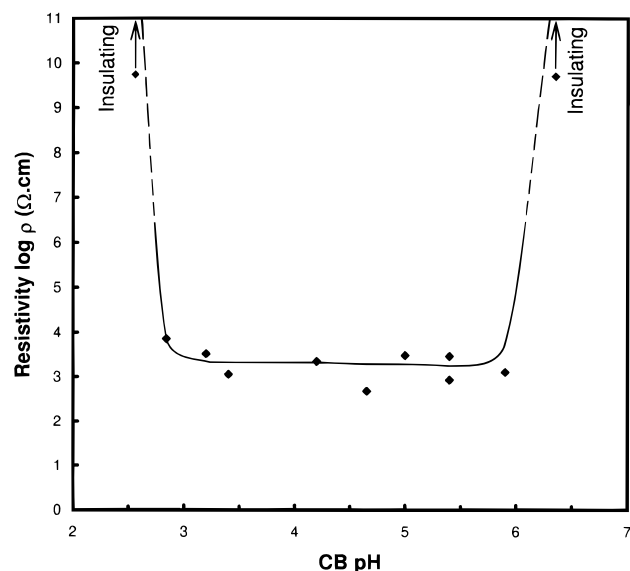(33) Calderone, A.; Parenté, V.; Brédas, J. L. *Synth. Metal* **1994**, *67*, 151.

Figure 9. Influence of the pH of CB on the resistivity of 45/55 blends filled with 2 wt % CB (samples prepared by mixing technique 2; see Experimental Section).
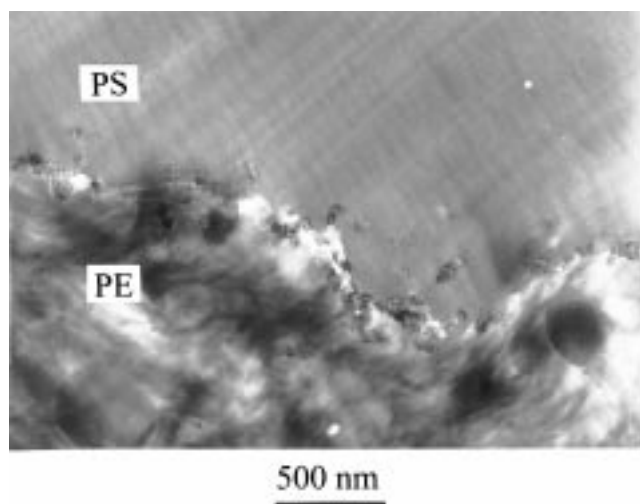

Figure 10. Transmission electron micrograph of 2 wt % CB5 filled 45/55 PE/PS blend prepared by mixing technique 2 (see Experimental Section).

This conductivity cannot be imparted to the polyblend by the selective localization of CB in one of the two phases, since XE-2, which is spontaneously localized in the PE phase of this polyblend, percolates in this phase at and above ca. 3 wt % (total content).[17] Similarly, BP1000 is spontaneously dispersed in PS, and the percolation threshold is 11 wt % (total content). Therefore, the 2 wt % CB used in this study cannot percolate in either polymer phase, and the observed conductivity can only be accounted for by a preferential localization of CB at the polyblend interface, when the particle pH is in the 2.8–6.0 range. Figure 10 illustrates this situation, since the CB5 particles (pH = 4.7) are concentrated in the interfacial region. The interfacial localization is, however, not 100% selective, as supported by the presence of conducting particles in each polymer phase. As a result, the percolation threshold (ca. 2 wt %) is by far higher than the 0.5 wt % observed when the strategy discussed in the previous section (the mixed thermodynamic–kinetic control) is used for driving CB to the interface.[17,18] This limited selectivity

Table 3. Resistivity of the 45/55 PE/PS Blend Filled with 1 wt % CB at the Interface

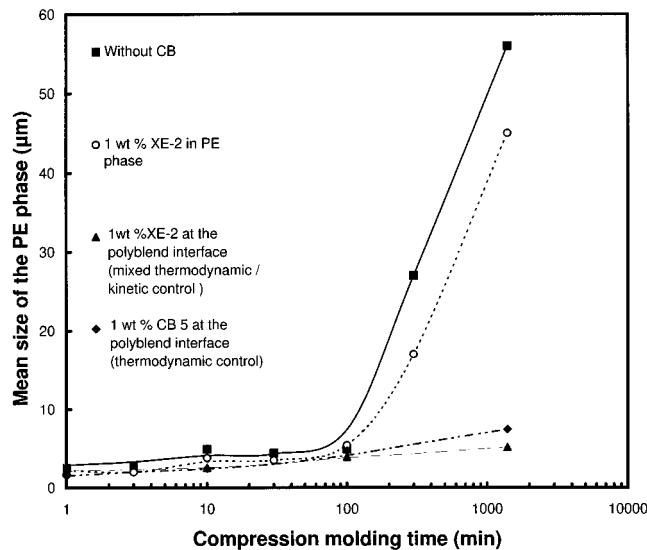| annealing time (min)	mixed thermodynamic–kinetic control (XE-2) (Ω cm)	thermodynamic control (CB5) (Ω cm)
1	$>10^{11}$	$> 10^{11}$
10	$>10^{11}$	$>10^{11}$
100	1.8×10^4	$> 10^{11}$
1000	494	2730

Figure 11. Influence of the compression molding time on the mean size of the PE phase for different localizations of CB (samples prepared by the mixing technique 2; see Experimental Section).

might be the consequence of the nonhomogeneous oxidation of the CB particles.

The thermal posttreatment of polyblends filled with CB localized at the interface has been shown to improve the electrical conductivity, which is again confirmed in Table 3. However, as a result of the more selective localization of CB in the interfacial region when the mixed thermodynamic–kinetic strategy is used, the electrical resistivity of the 1 wt % CB containing the 45/55 PE/PS blend decreases more rapidly and reaches a lower value upon increasing annealing times compared to the parent polyblend prepared according to the purely "thermodynamic" strategy.

The effect of (thermal) annealing of the filled polyblends on the PE/PS phase morphology has been studied by optical microscopy and image analysis of the micrographs. Figure 11 illustrates the phase coalescence that spontaneously occurs when the 45/55 PE/PS blend is annealed at 200 °C for increasing periods of time. The selective filling of the PE phase by 1 wt % (total loading) XE-2 does not perturb very significantly this behavior, in contrast to the CB localization at the interface which clearly slows the phase coalescence. The high local concentration of CB may explain this kinetic effect, which is also confirmed when the polymer blend interfacial area is measured (Figure 12) rather than the average size of the PE phase (Figure 11). The interfacial area appears to be more efficiently stabilized when the same amount of CB is driven to the interface by the mixed thermodynamic–kinetic strategy rather than by a purely thermodynamic incentive, more likely as result of some difference in the viscosity of the CB filled
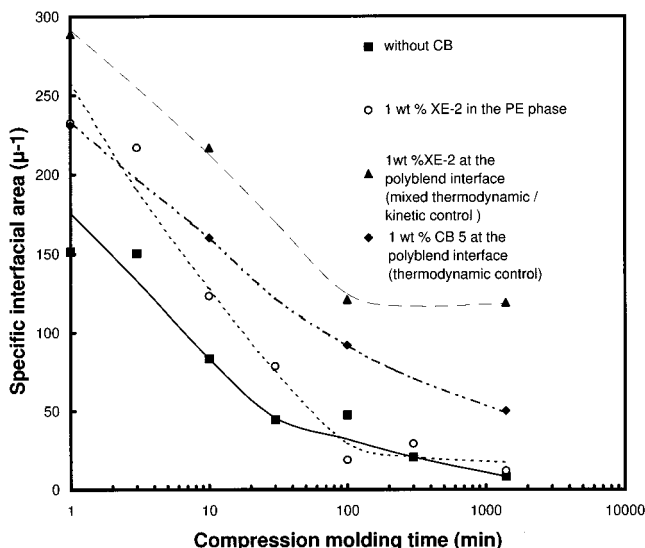
Figure 12. Influence of the compression molding time on the specific interfacial area (S/V) for different localizations of CB (samples prepared by mixing technique 2; see Experimental Section).

interfacial region. The slow phase reorganization when the interface is "lined" with CB allows the interfacial area to decrease safely and the electrical conductivity to improve rather than triggering a dramatic loss of phase continuity.

Conclusions

The most straightforward strategy for localizing a filler, such as CB particles, at the interface of an immiscible polymer blend consists of balancing properly the interactions of these particles with the constitutive components of the ternary system. When this thermodynamic control is effective, the particles will be found at the interface whatever the processing technique, provided that the thermodynamic control is reached. The major limitation to the application of this strategy is the availability of particles whose surface properties can fit the required balance of interactions.

It is a less specific requirement that the filler interacts more favorably with a polymer phase in a binary polymer blend, particularly if the polarity of these two polymers is different. Then, the kinetic control of the thermodynamically driven transfer of the filler from one phase (the less preferred one) to the second one allows one to stop the melt blending process when most of the particles have accumulated at the interface before being dispersed in the second phase. The kinetics of this transfer depends on the shear forces involved and the rheology of each polymer phase under the processing conditions. It is also clear that the interface tends to block the particle transfer, which makes their temporary accumulation possible in this specific region.

It must be noted that all these observations have been reported for particles of a very small size compared to the polymer phases. The stability of the polymer phase morphology is also remarkably improved when the filler particles occupy the interfacial region. This characteristic feature is very instrumental in decreasing the percolation threshold of the CB particles, since the major effect of the polyblend annealing is a decrease in the interfacial area while preserving an originally co-continuous two-phase morphology. This situation explains that a percolation threshold as small as 0.002– 0.003 volume fraction of CB can be reached by annealing co-continuous two-phase polyblends in which the conducting particles are concentrated at the interface.

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