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Design of Electrical Conductive Composites: Key Role of the Morphology on the Electrical Properties of Carbon Black Filled Polymer Blends

F. Gubbels,[†] **S. Blacher,**[‡] **E. Vanlathem,**[§] **R. Jérôme,**[*,†] **R. Deltour,**[§]
F. Brouers,[‡] **and Ph. Teyssié**[†]

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman B6, B-4000 Liège, Belgium, Génie Chimique, University of Liège, Sart-Tilman B6, B-4000 Liège, Belgium, and Physique des Solides, Université Libre de Bruxelles, CP 233, Boulevard du Triomphe, 1050 Brussels, Belgium

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ABSTRACT: Effect of carbon black (CB) on the morphology of filled polyethylene (PE)/polystyrene (PS) blends has been investigated by image analysis of optical micrographs (2-D analysis) and by the selective extraction of one phase of the binary blends (3-D analysis). The macroscopic electrical resistivity of the filled polyblends strongly depends on the selective localization of CB in one phase or at the interface and above all on the double percolation, i.e. percolation of the polymer phases and percolation of the CB particles. The selective localization of CB in the PE phase has remarkable effects on the polyblend phase morphology. The phase cocontinuity is indeed extended over a much larger composition range, and the phase morphology is stabilized toward post-thermal treatment at 200 °C. In the case of double percolation and selective localization of CB at the polyblend interface, electrical conductivity is observed at a CB content as low as 0.4 wt %.

Introduction

Conducting polymer composite materials (CPCM),[1] that consist of a random distribution of a conducting filler throughout an insulating polymer, deserve interest in several application fields. They are used as antistatic materials and low-temperature heaters, and they are very promising for electromagnetic radiation shielding.

The choice of the filler–polymer pair is crucial in the production of CPCM. Indeed, there must be a good balance between the filler–filler and the filler–polymer interactions. If the filler self-interactions dominate, then the filler particles tend to stick together and to form aggregates rather than particle-contacting chains. Conversely, an exceedingly good adhesion of the polymer to the filler results in an insulating layer around the particles and prevents the formation of current-conducting chains. In this respect, the lasting use of carbon black (CB) in CPCM makes it appear as the most universal conducting filler. Another major problem in the production of CPCM is the filler content, that must be as low as possible, otherwise the mixture processing becomes difficult, the mechanical properties of the composites are poor, and the final cost is high. High-grade conductive CB is indeed expensive.

The percolation theory is the most adequate for modeling conductivity of CPCM.[2] It involves convergence of particles to distances at which the probability of transfer of current carriers between them becomes higher than zero. The so-called percolation threshold, i.e. the lowest concentration of conducting particles at which continuous conducting chains are formed, is easily determined from the experimental dependence of conductivity on the filler concentration. It is a very useful tool to probe the filler distribution within a polymer matrix.

The only way to reduce the CB content in CPCM is to favor inhomogeneities in the material.[3–5] For instance, CB particles are rejected from crystal regions in semicrystalline polymers, which accordingly decreases the percolation threshold. Using a two-phase polymer blend as the polymer matrix in CPCM is an alternative which is receiving increased attention. Two requirements must however be fulfilled for the polymer blend composite to be conductive at a lower CB content. One of these requirements concerns the phase morphology of the polyblend and the other has to do with the heterogeneous distribution of the filler within the polyblend. Two situations may actually be envisaged. Either one of the two polymer phases is continuous and CB particles must be localized in the continuous phase, or the two phases are cocontinuous and the filler has preferably to be in the minor phase or still better at the interface.[6,7] These situations of dual continuity or double percolation have already been reported in the scientific literature.[8,9]

The aim of this paper is to focus on the selective localization of CB particles in one of the phases of polyblends displaying a cocontinuous two-phase morphology. It is essential to know what effect the CB particles can have on the phase morphology of the polyblend, and this question will also be addressed in the particular and most interesting case of the selective localization of CB particles at the polyblend interface. Is an originally cocontinuous two-phase morphology preserved? Is it stabilized or not against a post-thermal treatment? Is it possible to decrease the interfacial area while preserving the cocontinuity of the phases and, as a result, to decrease the percolation threshold? The phase cocontinuity of polyethylene (PE)/polystyrene (PS) blends has been studied in the presence of various amounts of CB by selective extraction of one polymeric component, followed by microscopy and image analysis. Electrical conductivity has also been measured in order to draw a relationship between the morphology of the polymer composites and their electrical properties.

[†] CERM.
[‡] Génie Chimique.
[§] Physique des Solides.
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Experimental Section

1. Mixing Procedure. High-density polyethylene (SOLVAY Eltex B3925: M_n = 8500, M_w = 265 000, density 0.96, melt index <0.1), polystyrene (BASF Polystyrol 158K: M_n = 100 000, M_w = 280 000, density 1.05, melt index 0.39), and CB (DEGUSSA Printex XE-2) were introduced in an internal mixer (BRABENDER Rheomixer) at 200 °C. The initial mixing rate was 25 rpm. Two minutes later, it was increased to 64 rpm for 10 min. Blends were then compression molded at 200 °C for 10 min under a 0.25 kg/mm^2 pressure, as sheets suited for electrical resistance measurements. Phase morphology was usually investigated immediately after melt mixing and rapid cooling of the samples in liquid nitrogen. Melt viscosity and melt elasticity were measured with a dynamic mechanical analyzer (Rheometrics RDA-700) at 200 °C.

2. Microscopy and Image Treatment. Sections 1 μm thick were observed by optical microscopy. In the absence of CB, the PS phase of polyblends was selectively stained by an organic dye in order to ascertain the phase assignment.[10]

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 treated by statistical analysis. Samples were assumed to be isotropic, so that images associated with different section planes were statistically equivalent. In order 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.

3. Electrical Measurements. Electrical measurements were performed with the four-probe technique, so that they were free from resistance of the sample/electrode contacts.

Results and Discussion

1. Morphological Analysis. Polymeric materials with a cocontinuous two-phase structure, i.e. a morphology with a dual phase continuity, are receiving increasing attention and are extensively discussed in reference to the percolation theory.[11] Percolation of CB particles in one continuous phase or at the interface of a cocontinuous binary polyblend is a more complex but also a much more attractive situation, since a double percolation phenomenon can provide the polymeric material with electrical conductivity at a very low CB content.

The composition range in which the phases of a melt-processed binary polyblend are continuous is basically governed by the relative melt viscosities of the two components 1 and 2. According to Paul and Barlow,[12] the condition for phase inversion is expressed by eq 1,where φ_i and η_i are the volume fraction and melt

$$\varphi_1/\varphi_2 = \eta_1/\eta_2 \tag{1}$$

viscosity of component *i*. Equation 1 has been corroborated by several authors,[13-15] although some deviations have also been reported.[16,17] On the basis of the analysis of phase unstability by Tomotika,[18] Metelkin and Blekht[19] have proposed a theoretical background for eq 1 and come to the conclusion that the critical volume fraction for a cocontinuous two-phase morphology is a function of the viscosity ratio (eq 2). The

$$\varphi_1 = [1 + F[\eta_1/\eta_2]]^{-1} \tag{2}$$

function *F* has to be extracted from experiments. Equations 1 and 2 have been discussed by Utracki and found to be in reasonable agreement.[20] More recently, this author has proposed eq 3 based on an emulsion model.[21]

$$\lambda = \left(\frac{\varphi_m - \varphi_{2i}}{\varphi_m - \varphi_{1i}}\right)^{[\eta]\varphi_m} \tag{3}$$

φ_{1i} and φ_{2i} are the volume fractions of the continuous phase (1) and the dispersed phase (2), respectively, at the phase inversion (i). λ is the viscosity ratio (η_2/η_1); $[\eta]$ is the intrinsic viscosity approximated to 1.9.[21] Actually, φ_{cr} is defined by the percolation theory as being the critical value of φ_1 at which monodisperse spheres (spherical particles or domains) form a three-dimensional percolation structure. Since, φ_{cr} is 0.156 according to this theory, $\varphi_m = 0.844$ is nothing but the critical value of φ_2.[22]

The three-dimensional continuity of PE and PS phases in the parent polyblends has been analyzed by the selective extraction of the PS phase with THF. As far as the extraction leaves the sample compact (no fragmentation into smaller pieces), PE is considered as 100% continuous, whereas continuity of PS is quantified as the weight fraction of PS which is extracted. Conversely, when the sample falls apart, PS is 100% continuous and the PE continuity is estimated as the weight fraction of the big compact piece of PE released by the extraction process. Although contaminated by small fragments of PE, this big piece is thought to be representative of the infinite clusters defined by the percolation theory.

Figure 1a shows that the phase cocontinuity extends over a composition range of ca. 15 wt % (i.e. from 30 up to 45 wt % PE). These figures are in complete disagreement with values predicted by eqs 1−3 (Table 1). Indeed, all the theoretical values are in a composition range exceeding 50 wt % PE. Compared to the upper PE/PS composition for the experimentally observed cocontinuity, eq 3 provides the most acceptable prediction in contrast to eq 2, which predicts a value 50% in excess. It may however be argued that the value of the viscosity ratio used in eqs 1−3 (1.59) relies upon the double approximation that the torque (*T*) measured with the Brabender rheometer is linearly proportional to melt viscosity (η) (eq 4)[23]and that *k* is independent of the

$$\eta = kT \tag{4}$$

polymer structure (PE or PS), which results in the currently used eq 5.

$$\eta_1/\eta_2 = T_1/T_2 \tag{5}$$

Although this approximation might explain systematically higher theoretical values compared to experiment, it cannot explain the magnitude of the disagreement and why eq 2, which is a refined version of eq 1, leads to the worst prediction. All the theoretical models actually assume that the phase morphology is dictated by a sole characteristic feature, i.e. the melt viscosity of the phases. They ignore the possible role played by the relative melt elasticities of the phases and the interfacial tension, respectively. It is worth pointing out that PE is not only more viscous but also more elastic than PS (Figure 2). Although the more viscous component of a binary blend tends to form the dispersed phase, the more elastic one has the opposite tendency.[24] This duality of behavior for PE might explain why models based on only one parameter fail in predicting acceptable values. Deviation from theorical predictions is actually in line with the argument according to which the more elastic PE phase tends to form the matrix, thus at a smaller PE content than expected from eq 1.

Figure 1b shows that the composition range in which phase cocontinuity is observed is shifted toward higher PE/PS percentages (i.e. in the range from 37/63 to 50/

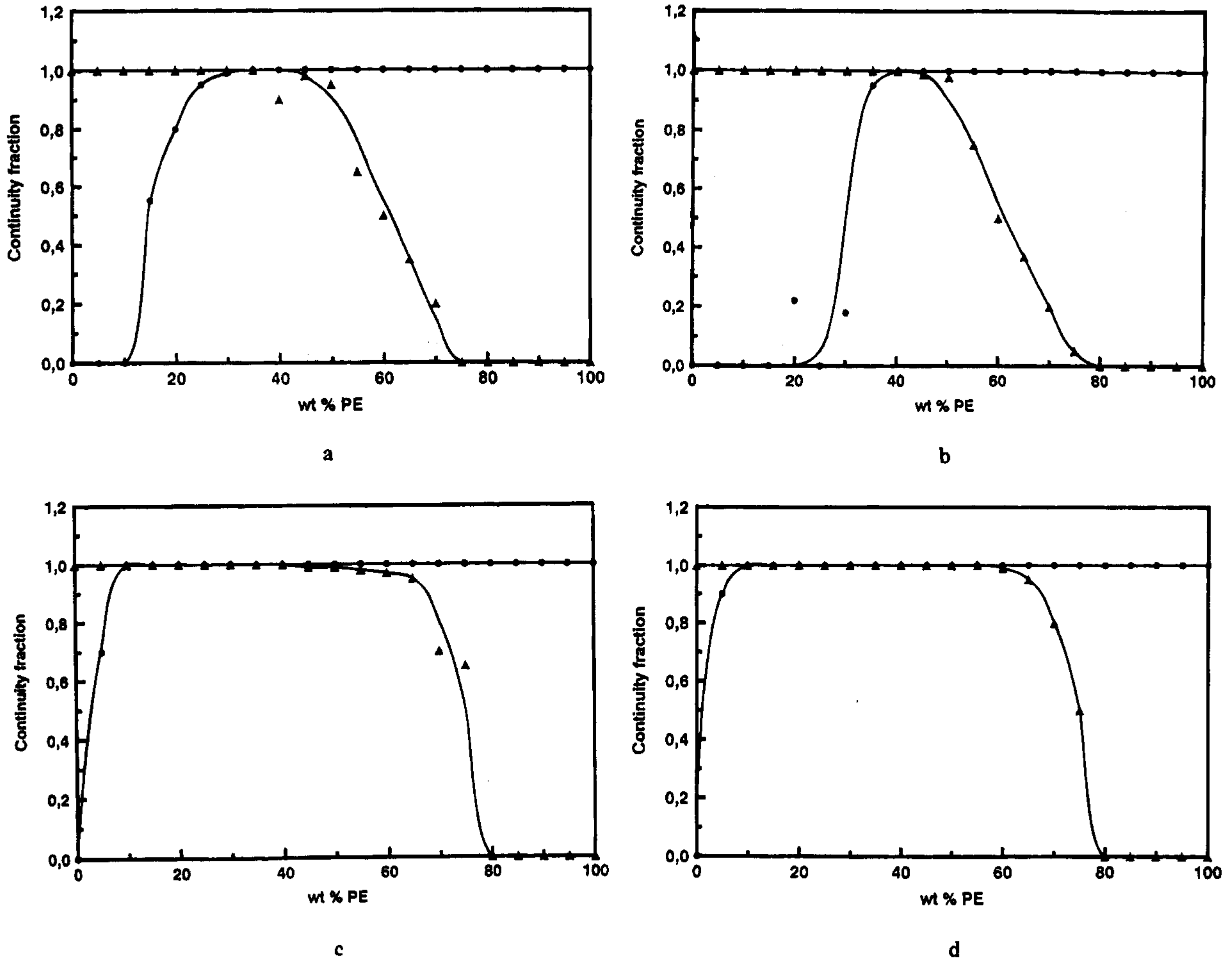

Figure 1. Dependence of the PE (●) and PS (▲) continuity fraction on the PE/PS blend composition: (a) PE/PS blends without CB; (b) PE/PS blends, without CB, but compression molded for 10 min at 200 °C; (c) PE/PS blends containing 4 wt % CB; (d) PE/PS blends containing 4 wt % CB and compression molded for 10 min at 200 °C.

Table 1. Composition of PE/PS Blends at the Phase Inversion (Melt Blending at 200 °C)

η_{PE}/η_{PS}	eq 1	eq 2	eq 3	PS extraction	optical microscopy
1.59	58/42	67/33	53/47	from 30/70 to 45/55	45/55

50) upon compression molding at 200 °C for 10 min. This observation may be explained in reference to Figure 2. Indeed, compression molding is similar to a zero-shear stress process, and Figure 2 shows that the PE/PS viscosity ratio, at low shear rates, is higher than at the mixing shear rate (arrow). Furthermore, the melt elasticity of both PE and PS is decreased by 1 order of magnitude, in contrast to the melt viscosity that increases by the same magnitude when the shear rate is decreased over 3 decades. Thus melt viscosity at low shear is expected to have a more decisive effect than elasticity on the phase morphology, so that the morphological characteristics become in better agreement with predictions based on eqs 1−3.

The most interesting observation has to be found in Figures 1c and 1d, in relation to the effect of carbon black on the PE/PS phase morphology. Indeed, selective localization of 4 wt % CB in the PE phase is responsible for the extension of the dual phase morphology over a remarkably broader composition range. The upper limit of this range (i.e. a 45/55 PE/PS composition) is not significantly modified, although beyond that limit PS tends to be relatively more continuous than in the absence of CB. The remarkable effect is that the composition at which PE starts to be continuous drops from 30 down to 5 wt %, when filled with CB (Figures 1a and 1c). PE at 5% corresponds to a critical volume fraction of 0.075, which is 2 times smaller than the value of 0.156 predicted by percolation theory for the formation of an infinite cluster. This effect of CB cannot be attributed to an increase in the PE phase viscosity, since then the incipient continuity of PE should have to be

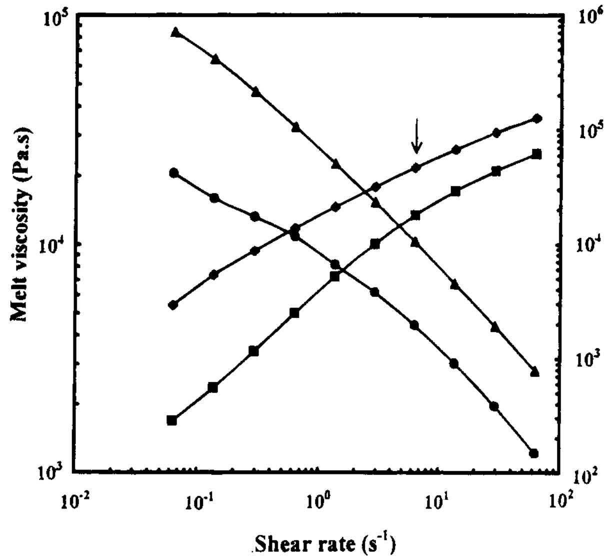

Figure 2. Shear rate dependence of melt viscosity (▲, PE; ●, PS) and melt elasticity (◆, PE; ■, PS) at 200 °C. The arrow shows the effective shear rate in the internal mixer.

delayed in agreement with, e.g., eq 1. Carbon black more likely has either an interfacial activity or a kinetic effect on the coalescence process, as supported by the stability of the phase morphology against thermal post-treatment (compression molding) at 200 °C for 10 min (Figures 1c and 1d).

2. Image Analysis. In order to improve our insight into the effect of CB on the PE/PS phase morphology, in the particular case where CB is selectively localized in the PE phase, the opening size distribution of the PE phase and the specific interfacial area of the PE/PS blends have been extracted from the optical micrographs. This type of analysis has recently proved to be very successful in highlighting the beneficial effect of interfacial agents on the polyblend morphology.[25] These mathematical tools used in the analysis of phase morphology will be discussed in a more intuitive than rigorous manner, in order to contribute to an easier physical understanding of the experimental results. A mathematical discussion can be found in the pertinent literature.[26]

2.1. Opening Size Granulometry Distribution. Standard granulometric analysis is currently dedicated to the size distribution of well-separated particles. In the particular case of dual phase connectivity in PE/PS blends, mathematical morphology concepts[26] have to be used in order to extend the standard granulometric method to interconnected systems.

Physical granulometric analysis relies upon classification of the objects in relation to a series of sieves of decreasing hole size. The opening transformation, which is a traditional tool of mathematical morphology, is used to simulate this physical procedure mathematically. Let X be a set of objects. When an opening transformation ($O^{\lambda B}(X)$) is performed, objects whose size is smaller than a convex structural element B of known size λ (noted λB), are removed. After a series of opening transformations with convex structural elements λB of increasing size λ, the filtering is carried out. This type of granulometric analysis can be applied to both semicontinuous and completely dispersed phases, although the ultimately found distribution must be carefully handled. As a result of an opening transformation, the analyzed phase appears more regular and less rich in details compared to the initial image: outlines are smoother, narrow isthmus are cutoff and small islands and narrow caps are suppressed. Therefore the average size distribution is narrower to an extent that depends on the initial complexity.

The opening size distribution $G(\lambda)$ can be calculated by using the following algorithm:

$$G(\lambda) = \frac{A(X) - A(O^{\lambda B}(X))}{A(X)} \qquad (7)$$

where $A(X)$ is the digital area of X, i.e. the number of pixels for the studied phase. For the sake of simplicity a circle has been chosen as the structural element (hexagon in the digitized image). $A(O^{\lambda B}(X))$ thus corresponds to the digital area formed by the elements of phase X in which a circle of radius λ or larger than λ can be inscribed.

The granulometry density $g(\lambda)$, which is the first derivative of the opening size distribution $G(\lambda)$, has been calculated for all the blends, togegher with the average value and dispersion of λ.

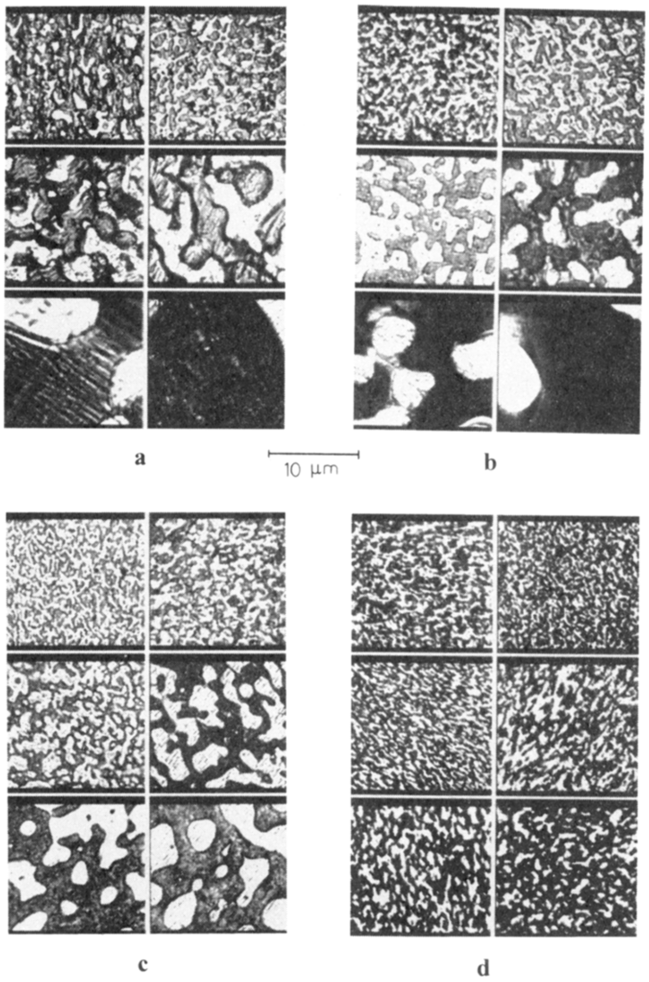

Figure 3. Optical micrographs of cocontinuous 45/55 PE/PS blends prepared (a) without CB (PS phase is dark), (b) with 1 wt % CB, (c) with 2 wt % CB, and (d) with 5 wt % CB. The PE phase is dark when CB is added. Compression molding times at 200 °C are increasing from left to right and up to down: 0, 1, 10, 30, 300, and 1400 min (1 cm = 10 μm).

2.2. Specific Interfacial Area. The effect of compression molding at 200 °C on the phase morphology of PE/PS blends has been analyzed in reference to the specific PE/PS interfacial area S_v. S_v is a stereological parameter, that has been extrapolated to a tridimensional space (R^3) from measurements on a two-dimensional image (R^2).[26] The Crofton relationship has been adapted to the situation where all of the studied phases are not included in one frame of measurements[27] and used to calculate the specific area S_v of a set X.

$$S_v(X) = 4N_L(X) \qquad (8)$$

$N_L(X)$ is the number of segments that enter (or leave) the analyzed phase per unity of length. From eq 8, S_v is clearly independent of the morphology or topology of the studied set X: it is always possible to cut segments on individual particles or interconnected systems.

2.3. Discussion of Image Analysis. Since Figure 1 has highlighted the decisive effect of CB on the phase morphology, the 45/55 PE/PS blend has been analyzed by image analysis in relation to compression molding time at 200 °C and the amount of CB (systematically localized in the PE phase). Thin sections of blends containing 0, 1, 2, and 5 wt % of CB have been observed by optical microscopy, as illustrated in Figure 3. Figure 4 shows that the average size of the PE phase dramatically increases with the molding time in the absence of CB. This is in complete agreement with the thermodynamic immiscibility of PE and PS. The interfacial

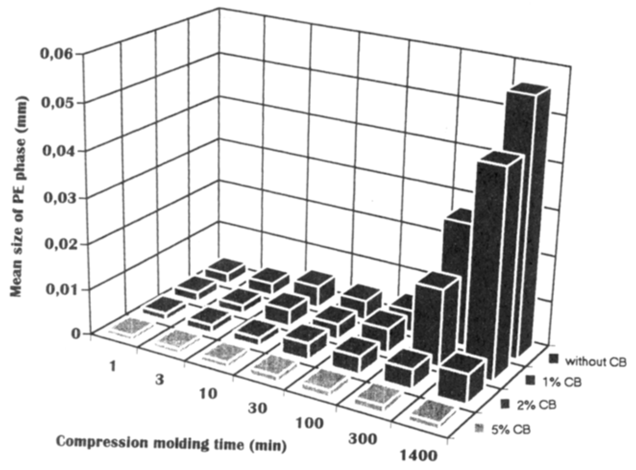

Figure 4. Dependence of the mean size of the PE phase on the compression molding time at 200 °C for 45/55 PE/PS blends filled with 0, 1, 2, and 5 wt %.

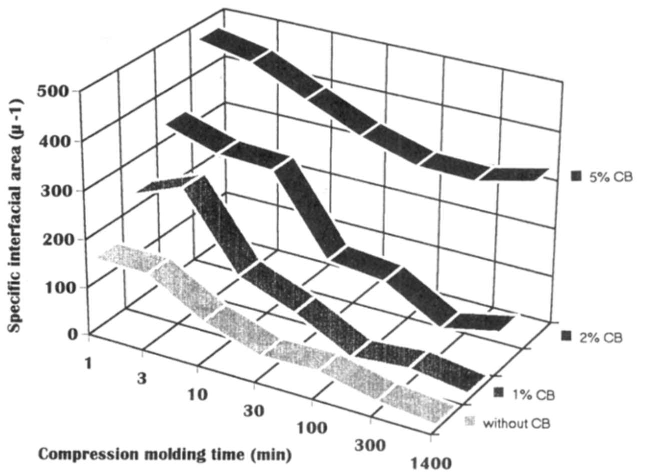

Figure 5. Dependence of the specific interfacial area on the compression molding time at 200 °C for 45/55 PE/PS blends filled with 0, 1, 2, and 5 wt % CB.

area tends to decrease in order to minimize the interfacial energy of the binary blend, resulting in phase coalescence and coarsening. The beneficial effect of the selective localization of CB in the PE phase on the thermal stability of the phase morphology is obvious. CB at 1% (i.e. 2.2% in PE) has a moderate stabilizing effect, in contrast to 2% that remarkably slows down the phase coalescence. When 5 wt % CB (i.e. 11% in PE) is used, then the average size of the PE phase remains constant even after 24 h at 200 °C (Figure 4). Two explanations might be proposed, either CB has an intrinsic interfacial activity responsible for a decrease in the PE/PS interfacial tension or CB increases the PE phase viscosity, thus slowing down the phase coalescence process. The first hypothesis may be disregarded, since an interface-active compound is expected to be preferentially localized at the interface. This situation, which should be most obvious when CB is used in low amounts, has not been observed with the CB used in this study.

Furthermore, if CB is an interfacial agent, then the average size of the PE phases should dramatically decrease upon addition of increasing amounts of CB, which is not the case when the phase morphology is analyzed just after melt blending. It must also be mentioned that the surface tension of a traditional CB (42.5 dynes/cm) is much larger than that of PE (26.6 dynes/cm) and PS (27.8 dynes/cm). These characteristics are not in favor of an interfacial activity for CB in the PE/PS two-phase system. Therefore, CB more likely increases the PE melt viscosity and perturbs the kinetics of the phase coalescence. In this respect, dispersion of 4 wt % CB in PE increases the torque from 17.5 to 29 N·m at 200 °C.

Combination of the internal hard structure of CB with the substantial increase in the PE phase viscosity can account for a thinner dispersion of the phases (Figure 3) and the enlargement of the phase cocontinuity domain (Figure 1c). Furthermore, the higher melt viscosity imparted to the PE phase by CB particles is prone to stabilize the phase morphology in place (Figure 1d and 3d).

Change in the interfacial area of the blends as the annealing time is increased is illustrated in Figure 5. As a rule, the interfacial area, which is as large as the CB content is high, decreases when compression molding time is increased, in agreement with the thermodynamics of immiscible systems. Nevertheless, the relative change in the specific area of the interface is less pronounced, although not suppressed, when the CB content is high enough (5 wt %). Again, this observation is not consistent with an interfacial effect but rather with a kinetic one.

Special attention has been paid to the image analysis of the 5% CB filled 45/55 PE/PS blend. Indeed, the binary images have been treated according to the opening size granulometry distribution method, suited to cocontinuous two-phase systems. From Figures 4 and 5, the 2-D image analysis of the 5 wt % CB filled polyblend shows that the average size of the phases remains constant upon increasing annealing time, while the interfacial area decreases. This means that the phases participate in an increasingly more cocontinuous organization; i.e. the different convex structural elements tend to fuse together.

Moreover the 3-D analysis of the phase morphology by the selective extraction of one polymeric component confirms that the phase cocontinuity persists in all the investigated CB filled 45/55 PE/PS blends. Combined analysis of the 2-D and 3-D phase morphologies thus leads to the consistent conclusion that the degree of branching of the PE phase decreases upon increasing annealing time. This morphological evolution is obviously expected to affect the electrical properties of the polyblends.

3. Electrical Properties. Electrical resistivity has systematically been measured for compression molded samples (10 min at 200 °C). Figure 6 illustrates the resistivity dependence on the percentage of PE in the polyblend. Clearly a double percolation effect takes place in blends containing as low as 5 wt % PE when the total CB loading is 4 wt % in the polyblend. Thus, already at this extremely low PE composition, both the PE phase and the CB particles are continuous throughout the sample. This is in agreement with Figure 1d, that shows the dual polymer phase continuity when the 5/95 PE/PS blend is added with 4 wt % CB. The resistivity plot exhibits a very flat minimum in the vicinity of 20 wt % PE. Then above 30 wt % PE, the resistivity starts to increase with the PE content, due to the dilution of the constant amount of CB localized in the PE phase. Above 30 wt % PE, continuity of the PE phase is, of course, preserved, in contrast with the CB percolation that becomes looser and disappears beyond 65 wt % PE.

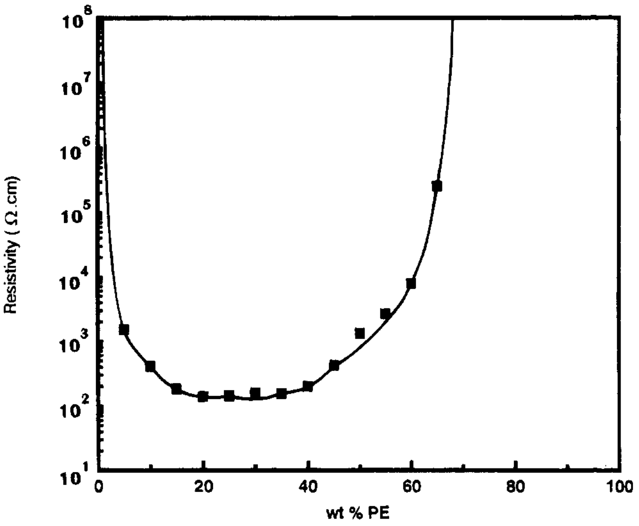

Figure 6. Dependence of resistivity on composition of PE/PS blends filled with 4 wt % CB (compression molding for 10 min at 200 °C).

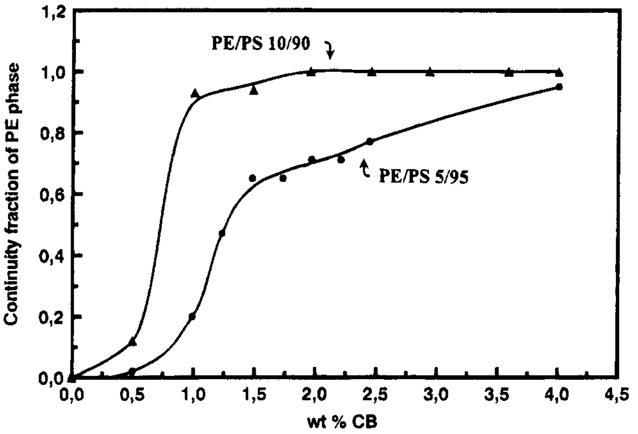

Figure 7. Dependence of the PE continuity fraction on the CB content in 5/95 (●) and 10/90 (▲) PE/PS blends (compression molding for 10 min at 200 °C).

Increasing amounts of CB have been added to the 5/95 and 10/90 PE/PS blends, respectively, in order to determine the percolation threshold in these two cases. Selective extraction of PS has been carried out as a way to probe the PE phase continuity in the polyblends. Figure 7 shows that PE is not perfectly continuous, even when 2.5 wt % of CB is added to the 5/95 PE/PS blend. Nevertheless 1 wt % of CB is enough to make the PE phase continuous in the 10/90 PE/PS blend, which is a very encouraging result for the production of electrically conductive composites with CB particles selectively dispersable in the PE phase. In line with the data of Figure 7, the 5/95 PE/PS blend loaded with 2.5 wt % of CB is not conductive. In contrast, the percolation threshold of CB in the PE phase of the 10/90 PE/PS blend is observed as soon as a total CB loading of 1.5 wt % is reached (Figure 8). The 10/90 PE/PS blend is thus a nice example of the advantage of a double percolation effect in decreasing the minimum amount of CB required to promote electrical conductivity. Indeed, the CB percolation threshold is 5 wt % in pure PE, compared to 1.5 wt % (Figure 8: percolation of CB) in a polyblend, the minor PE phase of which (10 wt %) selectively contains the CB particles and proves to be continuous. Phase percolation is illustrated by curve b and CB percolation by curve a in Figure 8.

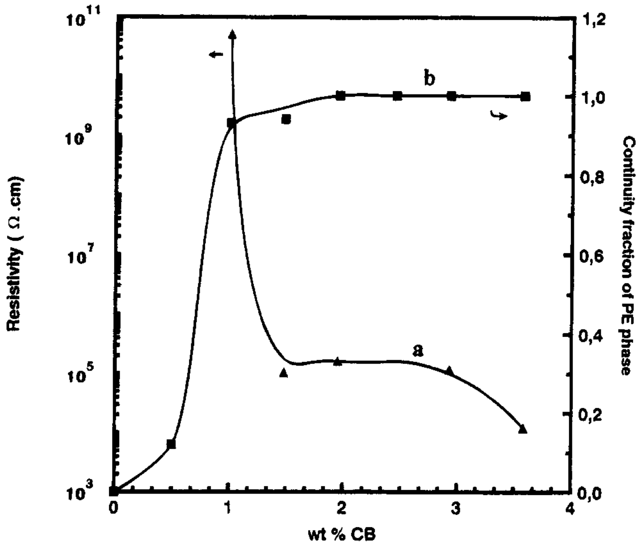

Figure 8. Resistivity (▲) and continuity fraction of the PE phase (■) versus the CB content in 10/90 PE/PS blends (compression molding for 10 min at 200 °C).

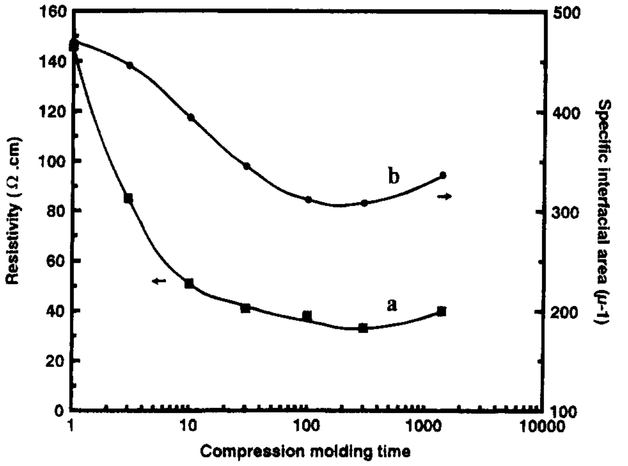

Figure 9. Resistivity (■) and specific interfacial area (●) versus the compression molding time at 200 °C, for 45/55 PE/PS blends filled with 5 wt % CB.

Resistivity of the cocontinuous 45/55 PE/PS blend containing 5 wt % CB dispersed in the blend and localized in the PE phase is plotted against the compression molding time at 200 °C in Figure 9. The decrease in the electrical resistivity parallels at least qualitatively the decrease in the interfacial area. The beneficial effect of annealing on the composite conductivity has thus to be related to a decrease in the branching degree of the PE phase, as already highlighted by image analysis. Indeed, when CB particles are percolating in the PE phase, the conductive pathway is as long as the branching of the PE phase is pronounced and resistivity accordingly increases. Conversely, when tortuosity of the PE phase decreases, the conductive pathway is shortened and the final resistivity is lower. Figure 9 thus illustrates the effect of the PE phase tortuosity on the composite resistivity. Clearly, special attention has to be paid to tortuosity of the double percolation phenomenon when conductivity of composite materials has to be optimized.

4. Fine-Tuning of Conductive Composites. As published elsewhere,[7] selective localization of CB at the interface of a cocontinuous polymer blend is the most efficient strategy to reach an extremely small percolation threshold. Even in that extreme situation, the

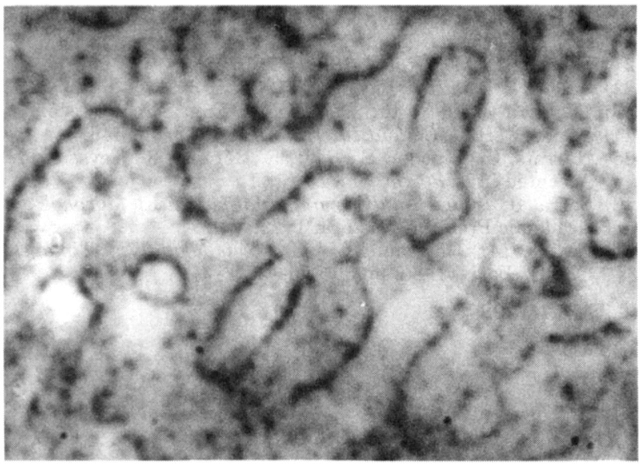

Figure 10. Optical micrograph of a 45/55 PE/PS blend filled with 1 wt % CB localized at the interface.

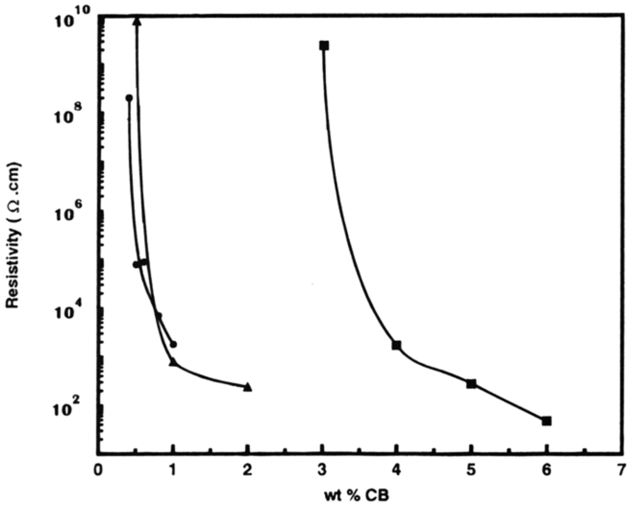

Figure 11. Dependence of resistivity on CB content for 45/55 PE/PS blends compression molded (■) for 10 min at 200 °C, (▲) for 150 min at 200 °C, and (●) for 40 min at 260 °C (CB localized at the polyblend interface).

critical role played by the size of the interfacial area may not be disregarded. Indeed, when CB particles are dispersed in a two-dimensional space, such as an interface (Figure 10), the interfacial area has to be decreased down to the point where CB particles are touching each other while preserving the interface continuity. The best way to reach this target is the annealing of a cocontinuous two-phase polyblend in which conductive particles are selectively localized at the interface. As shown in the previous sections of this paper, annealing of an immiscible polymer blend results in a reduction of the interfacial area, while preserving the cocontinuous phase morphology. Furthermore, the phases and thus the interface become less tortuous upon that annealing. As illustrated by Figure 11, the percolation threshold of CB selectively localized at the interface of the 45/55 PE/PS polyblend decreases upon that annealing. Indeed, a percolation threshold at 0.5 wt % CB is observed when the polymer blend is annealed at 200 °C for 150 min. Similarly, the percolation threshold is 0.4 wt % CB when the same polyblend is treated at 260 °C for 40 min, in sharp contrast to the 3 wt % CB needed when the thermal treatment is milder, i.e. 10 min at 200 °C. When CB particles are distributed throughout the PE phase, as opposed to being concentrated at the interface, this remarkable reduction in the percolation threshold is never observed upon the annealing of the polyblend.

Conclusions

The experimental results reported in this paper convincingly emphasize that blends of insulating immiscible polymers can be endowed with electrical conductivity by using very small amounts of conductive CB particles. In this respect, the appropriate control of the polyblend composition and morphology and the selective localization of CB particles in the multiphase material are key tools in the design of conducting polymer composites. A double percolation is the basic requirement for electrical conductivity, i.e. structural continuity of the 3D or 2D space in which the CB particles are selectively localized and percolation of these particles. Rheology of the polyblend as modified by the CB particles dictates the composition range in which electrical conductivity is imparted to the material. The required dual phase continuity can be reached with as small as 5 wt % PE for the investigated PE/PS polyblends. Then, provided that CB is selectively localized at the polyblend interface, the CB percolation threshold is as low as 0.4 wt %, i.e. a striking 0.002 volume fraction! The image analysis of optical micrographs has clearly shown the critical importance of properly annealing the melt-blended polymer composites. Such a post-treatment indeed decreases the tortuosity of the polymer phases and accordingly the interfacial area. It is responsible for a percolation threshold as small as 0.4 wt % CB particles, compared to 3 wt % if the annealing conditions have not been optimized. This general strategy is obviously not restricted to the loading of polyblends with inorganic conductive fillers. Particles of intrinsically conducting polymers might be used as well. Particulate pigments could also be considered, in the hope of improving the coloration efficiency by the selective localization of the pigment at the interface of a cocontinuous polyblend.

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