

# CARBON BLACK-FILLED POLYMER BLENDS: A SCANNING PROBE MICROSCOPY CHARACTERIZATION

Ph. LECLÈRE<sup>1</sup>, R. LAZZARONI<sup>1</sup>, F. GUBBELS<sup>2</sup>, C. CALBERG<sup>2</sup>, Ph. DUBOIS<sup>2</sup>,  
R. JÉRÔME<sup>2</sup>, and J.L. BRÉDAS<sup>1</sup>

<sup>1</sup> Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et  
Photonique Moléculaires, Université de Mons-Hainaut,  
B-7000 Mons, Belgium

<sup>2</sup> Centre d'Etude et de Recherche sur les Macromolécules (CERM)  
Université de Liège, Institut de Chimie, B-4000 Sart-Tilman, Belgium

## ABSTRACT

Conducting polymer composites, that consist of a conducting filler randomly distributed throughout an insulating polymer or polymer blend, attract interest in several application fields such as sensors or electromagnetic radiation shielding. The macroscopic electrical resistivity of the filled polyblend strongly depends on the localization of the filler. Here, we investigate the morphology of Carbon Black (CB)-filled polymer blends in order to determine the parameters governing the selective localization of CB in one phase of the blend components or at the interface between the components. The dispersion of the CB particles in the polymer blend is observed by means of Lateral Force Microscopy (LFM) as a function of the blend composition and the load in CB. The selective localization of CB at the interface enables the reduction of the percolation threshold down to 0.5 wt%; as a result, the mechanical properties of the polymer blend can be fully retained. Different techniques can be used to locate the CB at the interface; we compare their efficiency experimentally.

## INTRODUCTION

Polymers made electrically conductive by loading with a conductive filler have been known and used for decades [1, 2]. For instance, we can cite their use as antistatic or electromagnetic shielding materials as well as piezoresistive materials [3] (pressure sensors, switches electrical safety devices, and self-regulated heaters [4]).

A better knowledge is still required of the actual structure of the clustered particles, the structure formation during material processing, and its relationship with the macroscopic properties. Tools such as electronic microscopes and scanning probe microscopes (Scanning Tunneling Microscopy and Atomic Force Microscopy) can therefore be of major help. In this context, scanning probe potentiometers [5, 6] have been used to examine electrostatic forces on the surface, however with a low lateral resolution. Recently, Electric Force Microscopy (EFM) has been proposed [7] as a new type of scanning probe microscopy that is able to measure electric field gradients near the surface of a sample when using a sharp conductive tip.

Note that a major problem in the production of such composites is the filler content. This must be kept as low as possible since otherwise processing becomes difficult, the mechanical properties of the composites are poor, and the final cost is high (high-grade conductive fillers are indeed expensive). In this context, our aim is to set up a strategy to

decrease the filler content by *combining the advantages of composites* (polymer/filler combinations) and *polymerblends* (polymer/polymer combinations). Polymer blends with a co-continuous two-phase structure, *i.e.*, a morphology with a dual phase continuity, have been extensively discussed in relation to percolation theory [8-10]; percolation of the filler particles in one of the continuous phases or at the interface of a co-continuous binary polyblend is a complex but very attractive situation, since a double percolation (one for the polymer phase and one for the filler in this phase or at the interface) phenomenon results in significant electrical conductivity at a very low filler content.

## EXPERIMENTS

High-density polyethylene (PE) (Solvay Eltex B3925:  $M_n = 8,500$ ,  $M_w = 265,000$ , density 0.96, melt index  $< 0.1$ ), polystyrene (PS) (BASF Polystyrol 158K:  $M_n = 100,000$ ,  $M_w = 280,000$ , density 1.05, melt index 0.39) and carbon black particles (CB) (Degussa Printex XE-2 (XE) or Cabbot Black Pearls BP-1000 (BP)) are introduced in an internal mixer (Brabender Rheomixer) at 200°C. Electrical measurements are performed with the four-probe technique (to prevent resistance from the sample/electrode contacts). Atomic Force Microscopy (height and friction) images are recorded with a Digital Instruments Nanoscope III microscope, operated in contact mode at room temperature in air, using a 100  $\mu\text{m}$  triangular cantilever (spring constant of 0.58  $\text{Nm}^{-1}$ ).

## RESULTS

### Electrical and morphological characterization of CB-filled homopolymers

For low CB concentrations, the resistivity is close to that of the polymer matrix, on the order of  $10^{11}$  to  $10^{16}$   $\Omega\cdot\text{cm}$  [11]. When the CB concentration increases, the resistivity undergoes a fast decrease by several decades over a narrow concentration range corresponding to the percolation threshold; it then decreases more slowly towards the limiting resistivity of the compressed filler powder of order  $10^4$  to  $1$   $\Omega\cdot\text{cm}$ . The resistivity [12] of the composites obeys a power law of the form  $\rho = (p - p_c)^{-t}$  near the transition, where  $\rho$  is the bulk resistivity of the composite,  $p$  is the concentration of the conductive component,  $p_c$  is the percolation threshold concentration, and  $t$  is a universal exponent. Prediction of the exact percolation threshold remains difficult, as the critical volume concentration value can be observed in the 5-30 % range [8-13]; understanding such a broad range of critical concentrations is not easy since the main results of percolation theory is that the threshold should be close to 20% [13]. For XE, the values of  $p_c$  are 5% and 8% in PE and PS, respectively; for BP, the corresponding values are 12% and 25% [11]. From these results and for a given type of CB, it is seen that substitution of a monophasic polystyrene by a two-phase semicrystalline polyethylene favors a decrease in the percolation threshold (*i.e.* from 8% and 25% down to 5% and 12%, for PS and PE respectively). This is consistent with the selective localization of CB particles in the amorphous phase of PE; increasing the degree of crystallinity would thus be a potential way of decreasing further the percolation threshold.

## Characterization of the CB-filled polymer blends

These systems can be characterized in direct space at the nanometer scale by using Lateral Force Microscopy (or Friction Force Microscopy) [11]. Since their friction coefficients  $\mu$  are different, it is possible to distinguish PE, PS, and CB particles (Figure 1). It appears from the collected images that PE is characterized by a higher value of  $\mu$ , which translates on the image to a lighter color on the gray-scale; CB appears in black, since there is almost no interaction between the tip and the CB particles; the  $\mu$  value for PS is intermediate and PS therefore appears in dark gray on the image. The black spots attributed to CB particles are observed to be dispersed only in the PE phase of a PE/PS polymer blend. This indicates that in these experimental conditions (45% PE, 55% PS, and 1% XE), CB prefers to localize in the PE phase. For this system, the percolation threshold is about 2.9%. In the case of BP-type CB, the CB particles then localize exclusively in the PS phase and the percolation threshold is about 10.9%.

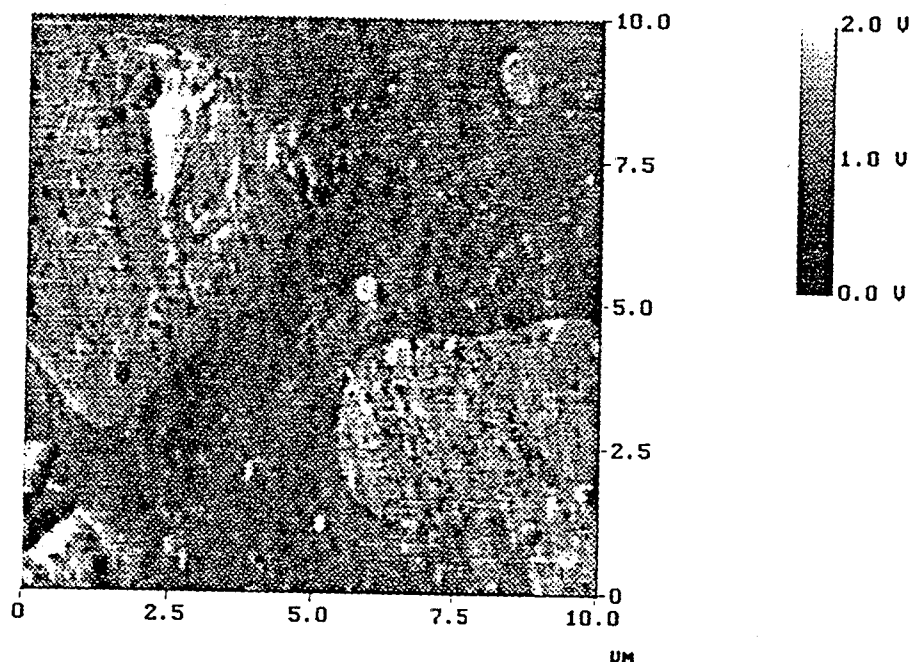


Figure 1. Detailed LFM image of a PE/PS/XE (45/55/1) sample. PE is brighter and PS darker; black spots in PE phase correspond to CB aggregates.

The percolation threshold can be decreased by selective localization of CB in the smaller phase of a co-continuous PE/PS blend [14, 15]. To further decrease the value of  $p_c$ , one can exploit topology arguments that indicate that the interface of a co-continuous morphology is continuous through the volume: localization of the CB particles at the PE/PS interface should thus drastically reduce the  $p_c$  value. We describe below two ways to achieve such a localization via either a kinetic or thermodynamic process.

**Kinetic localization of CB at the PE/PS interface.** The idea, previously proposed by Gubbels (16), is to mix first the CB particles with the less preferred phase (for instance XE with PS or BP with PE) and thereafter to add the second polymer. The CB particles then tend to

migrate slowly from the first polymer to the more "attractive" one. By stopping the mixing at regular time intervals and recording an LFM image, we can determine the optimal time when the CB particles are mainly located at the PE/PS interface. Figure 2 gives the corresponding LFM image for the optimized mixing time for the system (45% PE, 55% PS and 1% of BP-CB): there clearly appears to be a CB layer between PE and PS. The thickness of this layer is about 100 nm. For this system, the percolation threshold value is as low as 0.60%.

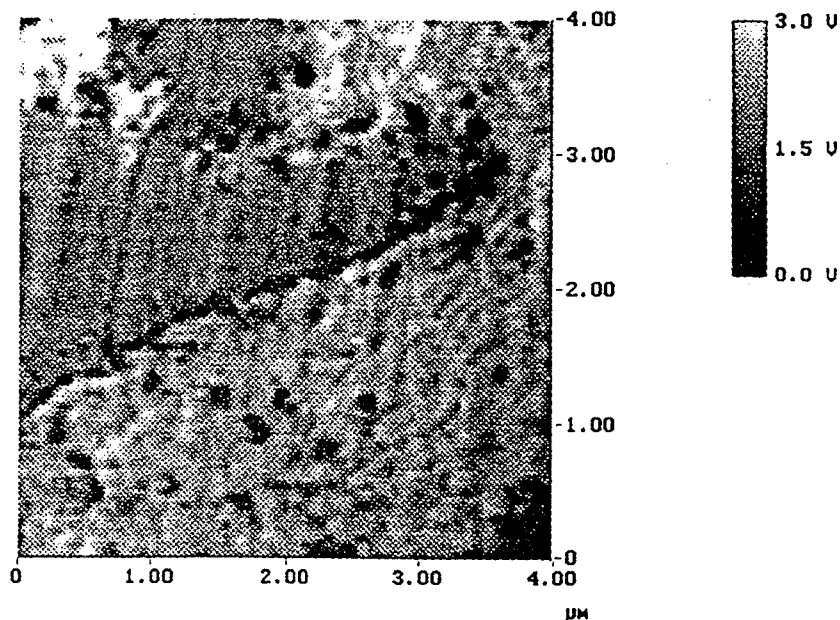


Figure 2. LFM characterization of the localization of CB at the PE/PS interface by a kinetic process (PE/PS/CB-BP = 45/55/1).

With mixing time, electrical resistivity decreases to reach a value of  $2.3 \times 10^4 \Omega \cdot \text{cm}$  at the optimized mixing time  $t_c$  for which CB is located at the PE/PS interface. For mixing times longer than  $t_c$ , resistivity starts going up again with time, due to dilution of CB in the PE phase. When using BP instead of XE, the same behavior is found for the resistivity evolution as a function of mixing time. The optimized values for locating CB at the interface is in a narrow range and must be optimized for a given system. For potential applications, it is thus preferable to rely on another process that avoids this problem.

**Thermodynamic localization of CB at the PE/PS interface.** We have indicated above that BP prefers to be located in the PS phase and XE in the PE phase. Since XE is more graphitic and the BP particles present a larger number of irregularities (such as holes and steps) and a higher oxidation rate due to the presence of oxygen-rich functional groups at the surface, the particle pH appears to be a good parameter to characterize the behavior of the CB particles. The idea proposed by Gubbels [16] is to slowly increase the CB particle pH. We then examine the corresponding resistivity evolution and the LFM images [11]. We observe the migration of CB particles from the PS phase (at low pH) to PE phase (at high pH). For intermediate values of pH, we can expect to locate the CB particles at the PE/PS interface independently from the mixing time. Figure 3 corresponds to a CB particle characterized by an intermediate pH. In this

case, a CB layer about 120 nm thick (appearing in black on the LFM image) is clearly seen at the PE/PS interface. The percolation threshold in this system is 0.46%, a remarkably low value.

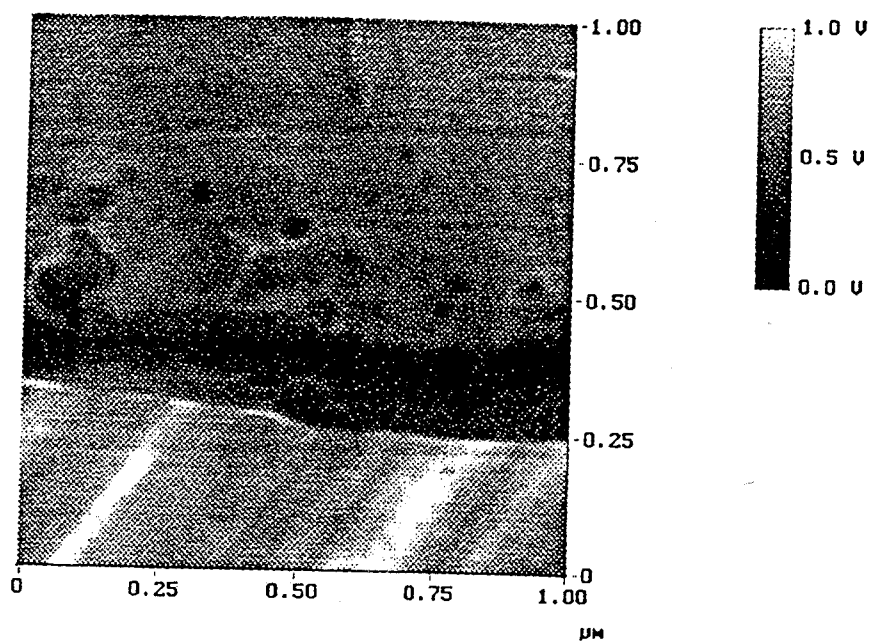


Figure 3. LFM image of a PE/PS/CB polymer blend for which the CB particle pH is intermediate.

## CONCLUSIONS

In an amorphous homopolymer matrix, such as PS, the percolation threshold  $p_c$  is close to 8%. Substitution of a monophasic PS by a two-phase semicrystalline PE favors a decrease in  $p_c$  down to 5%, consistent with the selective localization of CB particles in the amorphous phase of PE. The experimental results reported here emphasize that co-continuous polymer alloys of insulating immiscible polymers (PE and PS) can be endowed with electrical conductivity at even smaller concentrations of conductive CB particles. The key tools in the design of such conducting polymer composites are: (i) polymer blend co-continuity and (ii) selective localization of CB at the interface. Since the components are characterized by different friction coefficients, LFM constitutes a useful technique for the morphology characterization of such systems at the nanometer scale. A double percolation is the basic requirement for electrical conductivity. Provided that CB is selectively localized at the polymer alloy interface, the CB percolation threshold  $p_c$  can be as low as 0.4 wt %, *i.e.*, a striking 0.002 volume fraction. This strategy is not restricted to the loading of polymer blends with carbon black fillers; particles of intrinsically conducting polymers could be used as well.

## ACKNOWLEDGEMENTS

The authors are grateful to R. Deltour and M. De Vos for some of the electrical measurements. The research in Mons is supported by the "Ministère de la Région Wallonne (DGTRE: Programme mobilisateur ALCOPO)", the Belgian Federal Government Office of Science Policy (SSTC) "Pôles d'Attraction Interuniversitaires en Chimie Supramoléculaire et

Catalyse", the Belgian National Fund for Scientific Research FNRS/FRFC, and an IBM Academic Joint Study. The research in Liège is supported by the SSTC "Pôles d'Attraction Interuniversitaires: Polymères". The collaboration between Mons and Liège is partially supported by the European Commission (Human Capital and Mobility Network: *Functionalized Materials Organized at Supramolecular Level*). RL and PhD are chercheurs qualifiés du Fonds National de la Recherche Scientifique (FNRS - Belgium).

## REFERENCES

- (1) R.M. Norman, *Conductive Rubbers and Plastics*; Elsevier: New-York, NY, 1970.
- (2) E. Sichel, *Carbon-Black Composites*, Eds.; Dekker: New-York, NY, 1982.
- (3) F. Carmona, *Ann de Chim. Fr.*, **13**, 395 (1988).
- (4) F. Carmona, R. Canet, P.J. Delhaes, *Appl. Phys.*, **61**, 2550 (1987).
- (5) Y. Martin, D.W. Abraham, H.K. Wickramasinghe, *Appl. Phys. Lett.*, **52**, 1103 (1988).
- (6) P. Murali, D. Pohl, *Appl. Phys. Lett.*, **48**, 514 (1986).
- (7) R. Viswanathan, M.B. Heaney, *Phys. Rev. B*, **75**, 4433 (1995).
- (8) G. Geuskens, J.L. Gielens, D. Geshef, R. Deltour, *Eur. Polym. J.*, **23**, 993 (1987).
- (9) S. Asai, K. Sakata, M. Sumita, K. Miyasaka, *Polym. J.*, **24**, 415 (1992).
- (10) C. Klason, J. Kubát, *J. Appl. Polym. Sci.*, **19**, 831 (1975).
- (11) Ph. Leclère, R. Lazzaroni, F. Gubbels, M. De Vos, R. Deltour, R. Jérôme, and J.L. Brédas, to be published in ACS Symposium Series "Scanning Probe Microscopy in Polymers", edited by V. Tsukruk and B. Ratner (1997).
- (12) S. Kirkpatrick, *Rev. Mod. Phys.*, **45**, 574 (1973).
- (13) J.P. Clerc, G. Giraud, J.M. Laugier, J.M. Luck, *Adv. Phys.*, **39**, 190 (1990).
- (14) F. Gubbels, R. Jérôme, Ph. Theyssié, E. Vanlathem, R. Deltour, A. Calderonc, V. Parente, J.L. Brédas, *Macromolecules*, **27**, 1972 (1994).
- (15) F. Gubbels, S. Blacher, E. Vanlathem, R. Jérôme, R. Deltour, F. Brouers, Ph. Theyssié, *Macromolecules*, **28**, 1559 (1995).
- (16) F. Gubbels, Ph. D. thesis, University of Liège, 1995.