Carbon Black-Filled PET/HDPE Blends: Effect of the CB Structure on Rheological and Electric Properties

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ABSTRACT: The rheological and electric properties of blends of poly(ethylene terephthalate) (PET) and high-density polyethylene (HDPE) filled with various types of carbon black (CB) were analyzed in detail in this project. Four types of CB samples with available values of surface area, particle size, porosity, density, and maximum packing fraction were considered. Blends were prepared using an internal mixing chamber at two different rotational speeds, prior to mold compression of the samples. The rheological properties of the blends with varying polymer composition and a constant amount of CB were recorded in terms of torque variation with time for two shear rates (in terms of rotational speed). Rheological data were related to the resistivity of blends. Results show that the CB structure (porosity, surface area, apparent bulk density, and particle size) largely determine the resulting equilibrium torque and electrical properties. Furthermore, since CB is preferentially located in the HDPE phase, higher conductivity is observed as the PET content decreases, since the relative CB content in this phase increases. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 562–569, 2001

Key words: immiscible polymer blends; carbon black structure; carbon black filled polymer blends; electrical and rheological properties; particle–filler interaction

INTRODUCTION

It is well known that the use of conducting particles in polymeric matrices increases the conductivity; however, these added fillers have the effect of increasing the blend viscosity, leading to a more difficult processability. To obtain electroconductive systems with high conductive values and acceptable processing properties, a blend of immiscible thermoplastics with only a small concentration of conductive fillers is required. In these systems, it is possible to obtain low percolation thresholds if a double percolation is present, that is, both particle and phase percolation. This may be observed when the conductive particles, localized preferentially in one polymer phase, have a concentration equal to or larger than the electric percolation threshold and when the host polymer phase is the matrix or the continuous phase of the polymer blend.[1–8]

The conductivity level of electroconductive polymer systems is essentially controlled by the properties of the filler: type, form, concentration, structure, surface properties, and conductivity. In addition, there are other factors such as the properties of the matrix, distribution of particles in the matrix, contacts between particles, and particle orientation. It is well known that carbon

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black (CB) particles with a larger structure may render a relative high conductivity.[9]

There are several models that describe the electroconductivity of these systems: the effective medium theory, the onset for percolation theory, and thermodynamic models. Sumita′s model considers the formation of chainlike conductive structures.[10,11]

The study of electroconductive polymer systems based on conductive particles and polymer blends has been quite intensive during the last 10 years. Gubbels et al.[3] studied the selective localization of CB particles in multiphase polymeric materials. According to these results, the percolation threshold may be reduced by the selective localization of CB. Minimum resistivity was obtained when double percolation (phase and particle percolation) exists in polystyrene–polyethylene (PS/PE) blends. In addition, it was found that the percolation threshold may be obtained at very low CB concentrations, provided that CB is selectively localized at the interface of the blend components. Soares et al.[12] found that the type of CB (i.e., different surface areas) did not affect the conductivity of a blend with a 45/55 polystyrene/polyisoprene (PS/PIP) composition.

Blends of poly(ethylene terephthalate)/high-density polyethylene (PET/HDPE) have been treated previously in the literature.[13–16] These are immiscible, but the addition of compatibilizers improves the mechanical properties of the *blends*, such as SEBS and EPDM,[13] maleic anhydride,[14] EGMA,[15] polyethylene–acrylic acid,[16] and maleated copolymers of SEBSX, HDPE, and EPX. The addition of compatibilizers modifies the rheological properties of blends of PET with HDPE. In this polymer blend, the viscosity increase is monitored as the component interaction increases. Changes in the crystallization of PET were evaluated in its blends with poly(phenylene sulfide) (PPS), poly(methyl methacrylate) (PMMA), HDPE, aromatic polyamides, and copolyesters.[17]

CB has become one of the more preferred conductive fillers, due to an easy mixing with elastomers and thermoplastics.[18,19] It is made of colloidal-size particles that provide a good dispersion in the matrix and also good mechanical properties.[20–23] The manufacturing process of CB[21,23] involves the thermal decomposition of petroleum or natural gas. The product leaves the oven at high temperature in the form of agglomerates with a high surface area and a quasi-graphite conformation. The most important properties of CB are the structure and surface area. The structure involves the arrangement, distribution, and ordering of the particles, which in itself is a function of the surface area and the number of particles in each aggregate. The structure is characterized by the value of the absorption of dibutyl phthalate (DBP).

In this work, attention to rheological and electroconductive properties of the PET/HDPE blends filled with CB is given. Particular emphasis is made on the effect of CBs, comprising different types of CB and different surface areas and structure, upon the resulting rheological and electric properties of the blends.

EXPERIMENTAL

Blends of PET and HDPE were prepared in several proportions. The CB proportion for each blend was 5% w/w (95% w/w PET/HDPE blend). Various types of CB were used: Printex, Ketjenblack, BP-2000, and Vulcan. These types are all highly structured, except for the latter one. Characteristics of the particles are shown in Tables I and II. The PET sample was prepared from clear bottle scrap, characterized to have a density of 1.35 g/cm and an intrinsic viscosity of 0.75 (dL/g). HDPE (Padmex 60003, from PEMEX, Veracruz, Mexico) had a density of 0.96 g/cm and a melt flow index of 0.3 g/10 min.

Blends were prepared in an internal mixing chamber (Brabender EPL-V5501), with roller rotors. The chamber was filled at 70% of its volume capacity (following the equipment's manufacturer recommendation). Crushed PET was dried at 110°C for 3 h. The chamber temperature was fixed at 270°C. The procedure to prepare the samples begins with the addition of PET, HDPE, and CB at 10 rpm using a nitrogen atmosphere. Subsequently, the mixing speed was increased to 60 rpm. Mixing time for CB was 10 min. Torque was recorded for the rheological analysis of the data.

A Carver press at 250°C with a constant pressure of 4.9 MPa for 2 min was used to shape the samples for the electric studies, which included electric resistivity measurements using a Keithley electrometer Model 6517A, with 7.6-cm electrodes. Samples were cleaned with ethyl ether and dried at 110°C for 3 h. Resistivity measurements were performed at 20°C under a relative humidity of 80%. Measurements were taken after a time of electrification of 1 min. The resulting resistivity was calculated according to the following relation:

Table I CB Characteristics

Carbon Black (CB)	Supplier	Surface Area, N_2 (m^2/g)	Particle Size (nm)	Porosity (DBP) ($cm^3/100$ g)
Black Pearls 2000	Cabot Mexico D.F., Mexico)	1435[12] 1475[9] 1500[22]	12[22]	330[12,19,22]
Printex XE-2	Degussa (Mexico D.F., Mexico)	1000[7,12]	70[26]	370[7] 400[12]
Ketjenblack EC	Akzo (Los Reyes La Paz, Edo. de Mexico, Mexico)	929[4] 950[24]	30[4,27]	310–345[28] 340[29] 350[27] 360[4]
Vulcan XC72	Cabot	254[22] 257[25]	18[25] 30[22]	174[22]

$$\rho_v = R(a/L) \tag{1}$$

where ρ_v is the volume resistivity of the sample in ohm cm; R, the resistance in ohms; L, the thickness in centimeters; and a, the electrode area in cm^2.

Localization of CB in the samples was evaluated through solubility tests using 80/20/5- and 20/80/5-composition PET/HDPE/CB samples. A solution of 60/40 phenol/tetrachloroethane, which is a selective solvent for PET, was added to the sample with 80/20/5 PET/HDPE/CB at ambient temperature and left for 48 h. To the sample with composition 20/80/5 PET/HDPE/CB, xylene was added, a selective solvent for HDPE, at 120°C for 20 h.

The CB structure was observed with an optical microscope in transmitted light using CB samples dispersed in ethyl alcohol. This liquid was selected since it has lower surface tension than that of CB, which allows one to observe the arrangement of agglomerates and aggregates of CB particles, directly as they were received.

RESULTS

Rheological Properties

Initially, the torque was recorded as a function of time to observe its variation due to the incorporation of the ingredients of the mixture. Figure 1 shows the data of sample with a 80/20/5 PET/HDPE/CB composition. The observed peaks correspond to the different stages of the mixing process, and the area under the curves corresponds to the power consumption during the melting and blending process. The first two peaks correspond to the polymer addition and the third is identified with the CB addition. The last peak is due to the increase in the rotational speed, from 10 to 60 rpm. After the initial transients, a stable torque is observed, which is related to the end of the incorporation stage of the ingredients of the mixture. Similar curves were obtained for the other types of CB. It is interesting to observe that the melting of PET presents a large peak (about 32.5 N m) as compared to that of HDPE (around 10 N m). After 6 min, CB is added and leads to an increase in the

Table II True Bulk Density and Apparent Bulk Density of CBs

CB	Supplier	True Bulk Density (g/cm^3)	Apparent Bulk Density (g/cm^3)	Maximum Packing Fraction (ϕ_m)
BP2000	Cabot	1.90	0.146[a]	0.138
Printex XE-2	Degussa	1.94	—	0.114
Ketjenblack EC	Akzo	1.92	0.125[a]	0.126
Vulcan XC72	Cabot	1.92	0.259[a]	0.230

[a] From refs. 22 and 30.

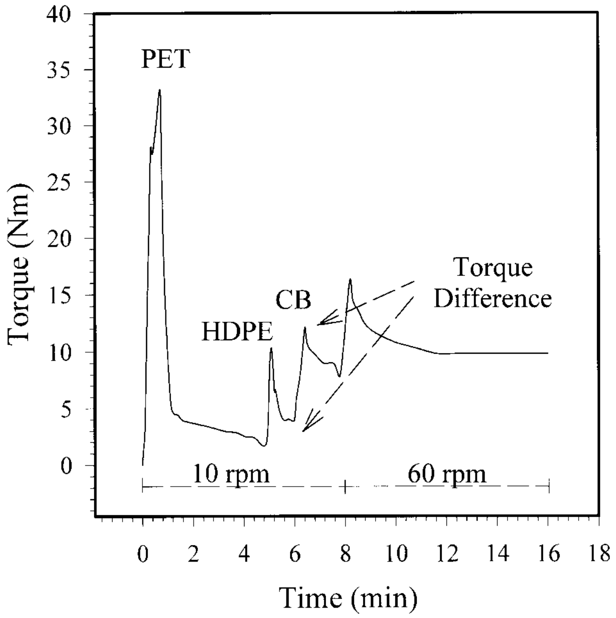


Figure 1 Typical curve of torque versus mixing time from PET/HDPE blends with 5% CB.

torque. The increase of equilibrium torque, produced by an increase of the rotational speed, is more notorious in HDPE due to its higher viscosity.

Figure 2(a,b) depicts the equilibrium torque as a function of composition for the PET/HDPE and PET/HDPE/CB blends at two rotational speeds (10 and 60 rpm). In Figure 2(a), the torque presents a maximum that shifts to higher PET contents for the more structured CBs. With no CB and with the less structured CB, the maximum is not clearly apparent and the torque is almost constant up to 40% PET. In general, the torque increases for the more structured samples, especially in those with a high porosity.

An increase in the rotational speed to 60 rpm leads to an increase in the torque but now the maximum is located at 20% PET, except for the sample with no CB. Again, the more structured CBs that possess the larger surface areas present the higher torque. According to Tables I and II, the Printex and Ketjenblack samples present larger porosities and lower maximum packing fractions than those of the other samples, and the BP-2000 and Printex samples possess the larger surface area.

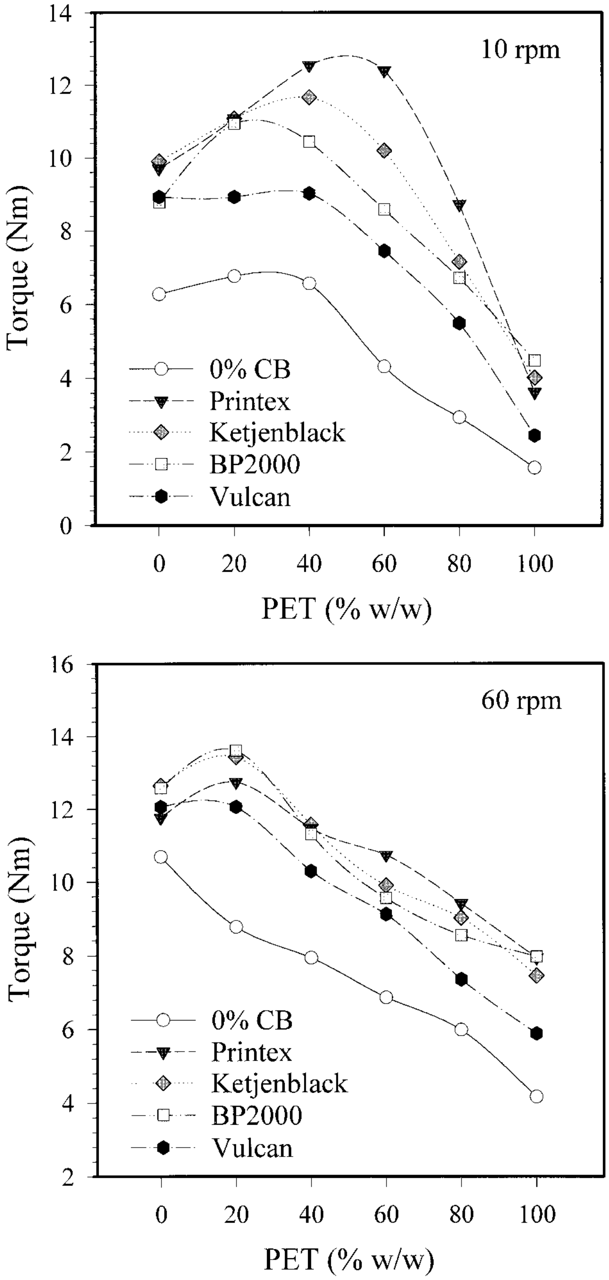


Figure 2 (a) Torque of PET/HDPE blends with 5% (w/w) CB at 10 rpm. (b) Torque of PET/HDPE blends with 5% (w/w) CB at 60 rpm.

Figure 3 shows the instantaneous increase in the torque due to CB incorporation in PET/HDPE blends, at 10 rpm. This instantaneous increase is also depicted in Figure 1 as the "CB torque difference." Here, the peak value was recorded with respect to the equilibrium torque existing prior to the addition. Maxima are observed in the 40–60% PET composition range, with larger magnitudes corresponding to the sample with the largest porosity value (Printex) and a high surface area.

Electrical Properties

The electrical properties of the samples are shown in Figure 4. Here, the resistivity of the system

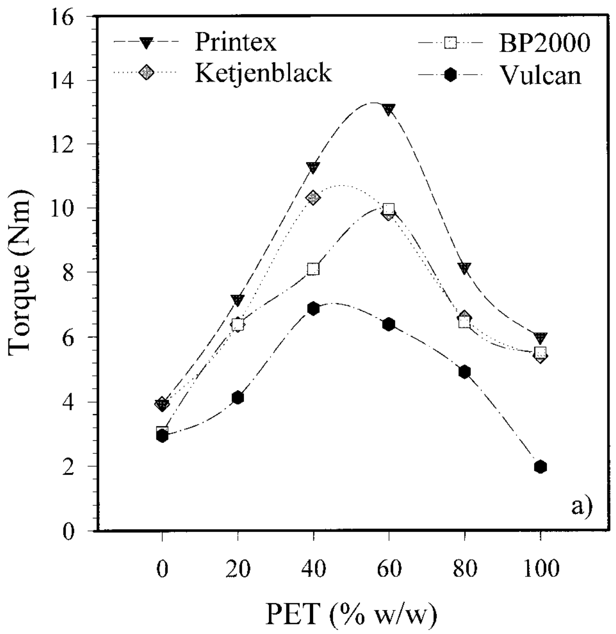


Figure 3 Torque difference during CB incorporation in PET/HDPE with 5% CB at 10 rpm.

PET/HDPE/CB is plotted against the PET content. Resistivity diminishes more than five decades as the PET content increases to 60%. The largest decrease at low PET contents corresponds to the Printex sample, and in the high PET content range, after phase inversion, the resistivity of the samples is almost constant.

Solubility Results

As previously mentioned, the localization of CB in the samples was evaluated through solubility tests using 80/20/5- and 20/80/5-composition PET/HDPE/CB samples. The sample with 80/20/5 PET/HDPE/CB, dissolved in phenol/tetrachloroethane, which is a selective solvent for PET, remained transparent, indicating that practically no CB was present in the PET phase. In contrast, when the sample with composition 20/80/5 PET/HDPE/CB was dissolved in xylene, a selective solvent for HDPE, it turned to black, since CB is preferentially located in HDPE.

DISCUSSION

CB Structure

The CB structure parameter, considered in this article, is a measure of the three-dimensional distribution of CB particles in the form of clusters, namely, aggregates, which may form agglomerates. In general, the cluster distribution determines the apparent bulk density of the samples. This density is the relationship between the actual mass of carbon particles and the apparent volume occupied by the clusters. A high apparent density corresponds to a lower structure. Highly structured CB samples normally possess a low apparent density (see Table II). The structure of CB may be evaluated by measurements of CB adsorption of DBP, which renders the main characteristics of the structure as the CB porosity, arrangement, and particle distribution.

The CB structure may be related to the maximum packing fraction,[29] which is defined as the maximum fraction of particles that fill up a given matrix. Correspondingly, the DBP value allows one to calculate the maximum packing fraction (ϕ_m) in random media according to the following relation:

$$\phi_m = (1 + \rho \mathrm{DBP})^{-1} \qquad (2)$$

where ρ is the CB density. Maximum packing fraction data are shown in Table II, calculated from values given in Tables I and II.

Another method to evaluate the structure, in a qualitative fashion, is the optical microscopic observation of samples. The typical distribution of

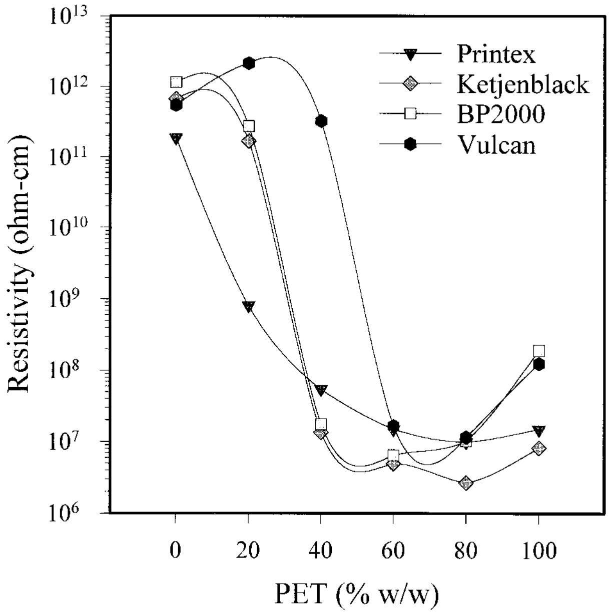
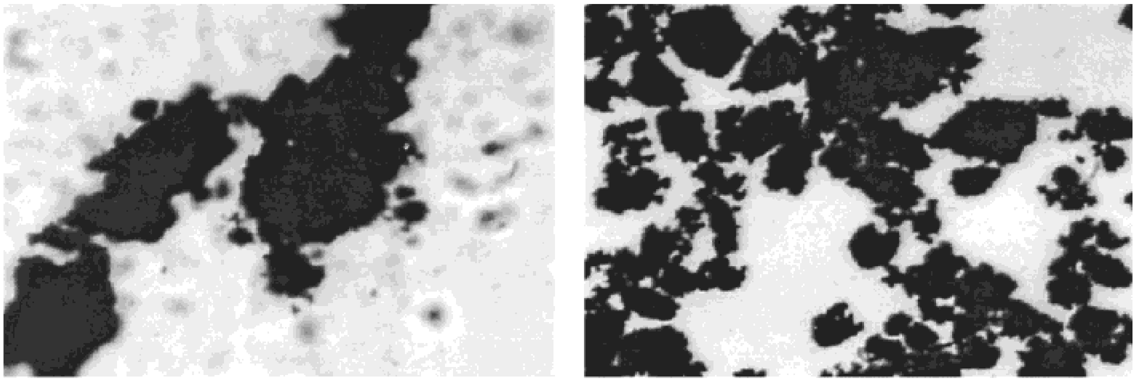
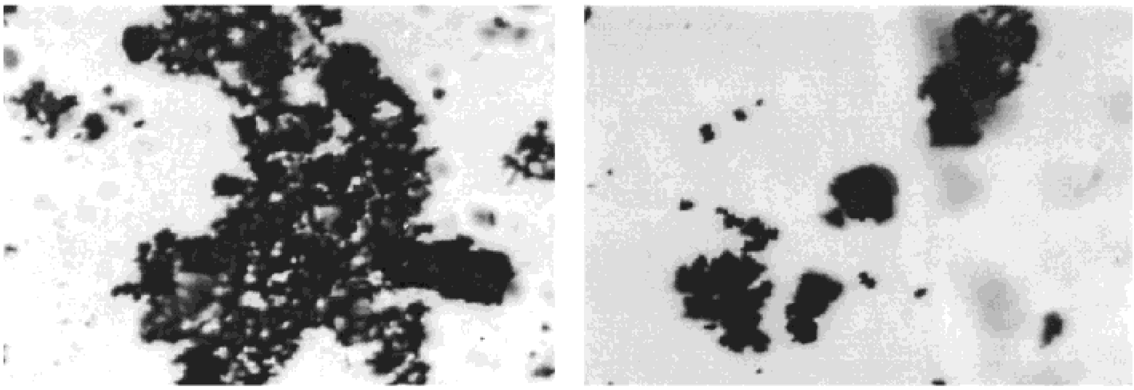


Figure 4 Resistivity of PET/HDPE blends with 5% CB.



BP2000

KETJENBLACK



PRINTEX

VULCAN

Figure 5 Arrangement of CB agglomerates and aggregates, taken from optical microscopy.

clusters of each kind of CB is depicted in Figure 5. Vulcan CB presents isolated compact structures of high apparent density without branches. This is characteristic of a less structured CB. On the other hand, Printex CB presents a structure formed by long branches of particles with a low apparent density and high porosity. BP-2000 CB possesses short branches with agglomerates and Ketjenblack CB presents larger branches with bigger agglomerates and with a smaller distance between agglomerates than that of BP-2000 CB.

CB Structure and Viscosity

Particle–particle interactions and polymer–particle interactions under shear stresses provided by the mixing device determine the viscosity of the system. In general, viscosity increases in the more structured samples, that is, those with high porosity and high surface area (see Fig. 3). As mentioned, the torque values obtained after CB addition clearly reflect high viscosity in the Printex sample and low viscosity in the Vulcan system. Shear stresses reflect the friction provided by surface forces on the particles. Printex CB has more than twice the DBP value and four times the surface area of the Vulcan CB, and, consequently, the torque increase (see Fig. 3) manifests a more than twice increase in the viscosity, which scales with the values of the porosity of both samples.

The viscosity of the system influences the dispersion of particles, in such a way that the shear stresses will be higher in a more viscous environment at a given shear rate. CB aggregates may be dispersed and broken to a larger extent with higher shear stresses.[25] CBs with higher porosity and long branches are more susceptible to be broken into finer particles, and the effect of the new structure is to provide a large surface area. As the surface area increases, the interaction polymer–particle increases, augmenting the viscosity of the system.

Viscosity, Interfacial Tension, and Resistivity

The selective location of CB in the polymer phases, the viscosity, and the structure of CB affect the conductivity of the system. In the PET/HDPE/CB system, CB is located in the HDPE phase, as shown by the solubility tests. This preferential localization of CB in the HDPE phase implies that the interfacial tension between PET and CB is larger than that existing between HDPE and CB. At 260°C, the interfacial tensions of the PET/HDPE, PET/CB, and HDPE/CB systems are 6.42, 6.04, and 3.35 mN/m, respectively. As observed in Figure 2, the compositions rich in HDPE are more viscous than are the compositions rich in PET. The maximum of the viscosity observed at intermediate compositions could be due to the combined effect of the two following phenomena: At these concentrations, after the phase inversion, the HDPE still dictates the blend flow, while the PET acts as a dispersed phase, and the preferential localization of CB in the HDPE phase that renders it very viscous. Then, as a result, the overall viscosity of the composite increases. The differences in the viscosity intensities are mainly due to the CB structure as it was explained above.

In Figure 4, the highest conductivity is observed when the HDPE concentration is lower than 40%, that is, after the phase inversion, when PET is the matrix. These results are similar to those of the ethylene–propylene copolymer (EPM) and PS.[3] CB, in this case, is preferentially located in the EPM phase, which is also the more viscous component. The explanation for this behavior is that the dispersed HDPE phase containing a higher concentration of well-dispersed CB particles is more conductive than when HDPE is the continuous phase (at lower concentrations). In the former case, it is more likely that CB forms conducting pathways either in the HDPE dispersed phase or at the interface. In Figure 4, the pronounced decrease in resistivity is observed before the phase inversion, when the proportion of HDPE in the blend is higher than that of PET. This may indicate that PET domains are deformed extensively in the more viscous HDPE matrix, and this situation promotes the formation of conducting pathways at the interface of the two polymers.

CONCLUSIONS

CB properties such as the particle structure, chemical properties of the surface, morphology of the surface, size, content, and orientation are important factors, besides the properties of the matrix formed by the blend of two immiscible polymers, determining the conductivity level of the blends. Higher viscosity during mixing is recorded in the systems with more structured CB samples, indicating higher particle–polymer interactions, affecting also the CB dispersion in the matrix. CB is preferentially located in HDPE phase, which presents a higher viscosity than that of the PET phase, due to the lower interfacial tension between them. High conductivities are reached when this polymer phase is dispersed in the PET matrix since its relative CB concentration is higher.

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