Conductive Polymer Composites: Influence of Extrusion Conditions on Positive Temperature Coefficient Effect of Poly(butylene terephthalate)/Poly(olefin)–Carbon Black Blends

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ABSTRACT: Processing conditions determine both the morphology and the carbon black (CB) distribution in conductive polymer composites (CPCs). Good control of these parameters is essential to obtain reproducible electrical properties. We found that for extruded tapes of poly(butylene terephthalate) (PBT)/poly(olefin) (OLE)–CB blends, an increase of both processing temperature and screw speed leads to a significant decrease of resistivity. This shift factor, more important with PBT/poly(ethylene)–CB than with PBT/poly(ethylene-*co*-ethyl acrylate)–CB, is attributed to viscosity variations of all compounds. A decrease of viscosity promotes CB aggregation at the PBT/OLE interface and creates larger conductive channels by coalescence. Nevertheless, the CB concentration effect appears predominant compared to the morphology effect to explain resistivity variations. This interesting finding can be used either to improve reproducibility of electrical properties or to adjust electrical properties without changing CPC formulation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2151–2157, 2004

Key words: conducting polymers; blends; processing; shear; electrical properties

INTRODUCTION

Blends of poly(butylene terephthalate) (PBT)/poly(olefin)–carbon black (PBT/OLE–CB) lead to conductive polymer composites (CPCs) with smart properties for heating applications. CB is initially dispersed in the olefin to constitute the conductive phase, whereas PBT provides the system with both thermal stability and mechanical properties. Although the positive temperature coefficient (PTC) is lowered by PBT thermal expansion, no negative temperature coefficient (NTC) can be observed up to 200°C, the temperature beyond which PBT begins to melt. To guarantee the reproducibility of electrical properties of such materials, it is necessary to control every influential parameter. We previously investigated the role of CB during poly(ethylene-*co*-alkyl acrylate) crystallization[1] and the influence of composition on electrical properties.[2,3] Because processing conditions determine both morphology and carbon black distribution, their control is essential to obtain reproducible electrical properties. In most works reported in the literature, electrical properties of CPC are measured from samples obtained by compression molding after mixing (i.e., rarely by a process close to industrial conditions as extrusion or injection).[4–6] It is therefore difficult to find unique interpretation of the influence of processing temperature, screw speed, and blending time, which broadly depend on the considered techniques and polymer systems.

Nevertheless, it seems that for monophase systems, increasing mixing time or mixing speed increases resistivity of the CPC as a result of the dispersion of better conducting particles and aggregate destruction.[4,7,8]

For multiphase systems contradictory behaviors can be found and no general statement can be made, thus showing the necessity for a finer analysis of experimental conditions. Increasing shear rate can either promote migration of conducting particles to the interface (viscosity decrease effect) leading to a decrease of resistivity[9,10] or degrade CB aggregates (shearing effect), thus increasing resistivity.[4,5] This latter phenomenon is especially sensitive in the case of low CB contents. The shear rate range must also be considered because any apparatus able to reach high shear rate will also create peculiar morphologies.

However, for all CPC, the effect of an increase of blending temperature is generally to favor particle aggregation in the melt and thus to decrease resistivity. CB aggregation in the melt (Fig. 1) is a key factor
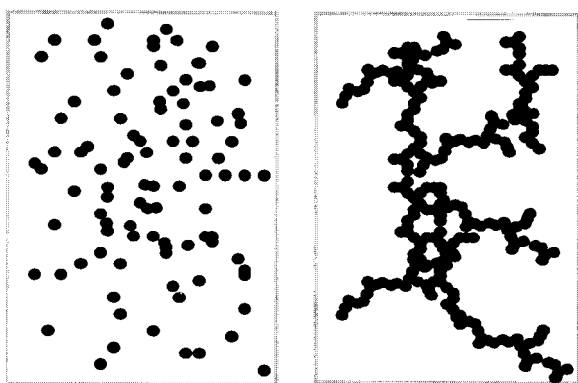
Figure 1 Aggregation of carbon black in the melt: dynamic percolation from left to right.

that has been studied in isothermal conditions for several monophase systems.[11–14] This phenomenon, called dynamic percolation, is characterized by a retardation time of percolation decreasing with both increasing temperature and carbon black content. Close relations exist between dynamic percolation times, terminal relaxation time, and interfacial tension.

In this work we investigated the influence of extrusion temperature and screw speed on electrical properties of extruded PBT/OLE–CB blends.

EXPERIMENTAL

Materials

The poly(butylene terephtalate) (PBT) used in this investigation was Vestodur 3000 from Degussa-Huels (Europe); carbon black–filled poly(ethylene-*co*-ethyl acrylate) (EEA–37%m/m CB) was LE 7704 from Borealis (Europe). The characteristics of these materials are listed in a previous work[1] but some of them are recalled in Table I. The low-density polyethylene (LDPE) was Escorene MP654 from ExxonMobil (Europe), with 30% of Elftex 430 carbon black from Cabot (Europe).

Preparation of samples

The poly(olefin)–27.75%CB conductive phase was obtained by dilution of commercial master batches (EEA with 37% w/w CB and LDPE with 30% w/w CB) in a twin-screw Brabender extruder ($L = 400$ mm, $\Phi = 16$ mm) with the following temperature profile (from first zone to die): 220/240/250/260°C. In a second step PBT was blended with poly(olefin)–27.75% w/w CB in a single-screw Fairex extruder ($L = 600$ mm, $\Phi = 30$ mm) with three temperature profiles (from feeding zone to die): 220/240/240/240, 240/260/260/260, and 260/280/280/280°C, corresponding to processing temperatures of, respectively, 240, 260, and 280°C. All samples were cut from extruded tapes. We used 2

$\times$ 10 $\times$ 70-mm^3 samples for electrical measurements. In this study, all formulations were obtained by blending 60% w/w PBT with 40% w/w poly(olefin) containing 27.75% w/w of carbon black blends.

Characterization

Electrical resistivity was measured by a four-probe technique described in a previous work.[3] Collection and processing of data were done by an acquisition program developed with Visual Designer 4.0 (current is automatically adjusted for measurements under 2 V DC voltage). Silver paint was used to ensure good electrical contacts. Cycles were applied in loops to samples (heating from 30 to 170°C at 0.6°C/min and cooling from 170 to 30°C at 0.6°C/min). To eliminate the thermomechanical history of the poly(olefin) phase and the PBT amorphous phase, only the second heating/cooling cycles were used.

Rheological properties of neat polymers were obtained with a ThermoHaake RheoStress 1 rheometer with both cone/plate geometry in steady-state conditions and plate/plate geometry in dynamical mode. *In situ* measurements were done during extrusion of the blends with an instrumented die [0.004 $\times$ 0.05 $\times$ 0.06 m (height $\times$ width $\times$ length)].

Morphologies were observed with a JEOL JSM-6031 scanning electron microscope (SEM; JEOL, Peabody, MA) after fracture of the samples in liquid nitrogen followed by extraction of the poly(olefin) phase by toluene for 12 h in a Kumagawa apparatus. The etched surfaces were then coated under vacuum by a thin gold layer.

RESULTS AND DISCUSSION

Figure 2 shows the percolation curves of EEA–CB and PE–CB. The classical percolation law [eq. (1)] was used to predict the theoretical threshold V^* and the values obtained for PE and EEA, 11.2 and 11.5% v/v, respectively, are realistic. Nevertheless the values obtained for t (2 and 2.59, respectively) are larger than 1.9, the critical exponent predicted for spherical particles associated in a three-dimensional system. This may be explained by the anisotropy generated by the extru-

TABLE I
Characteristics of Polymers

| Property	PBT	LDPE	EEA
Alkyl acrylate content (mol %)	0	0	15
T_g (°C)	50 ± 3		−33 ± 3
T_m (°C)	223 ± 3	101.7	99.5
$T_{c,n}$ (°C)	185	86.1	83
ΔH_m (J g^{-1})	140	90	63
Density (25°C)	1.310	0.930	0.925
Melt flow index (dg min^{-1})	7.7	—	6.9 ± 0.1
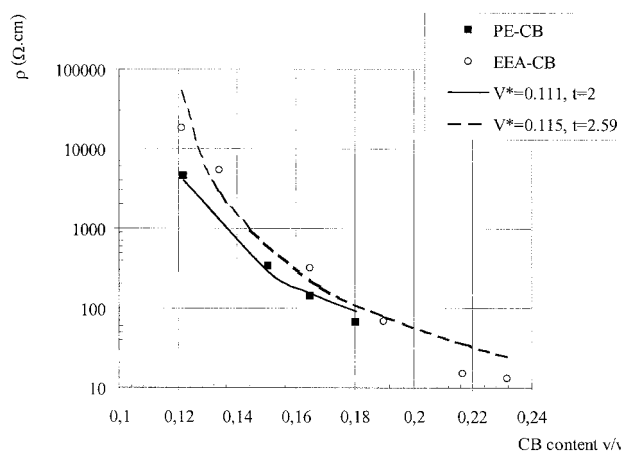
Figure 2 Percolation curves of poly(ethylene-*co*-ethyl acrylate)–CB and high-density poly(ethylene)–CB, experimental points, and fitted curves (solid lines).

Figure 3 Magnification of PTC effect encountered with PBT/EEA–CB CPC.

sion process, given that overestimated values of t were already found for conductive carbon fibers.[15,19] (1)

$$\rho = \rho_0(V - V^*)^{-t} \qquad (1)$$

where ρ is the resistivity (Ω cm^{-1}), ρ_0 is a constant, V is the volume fraction, V^* is the volume fraction at the percolation threshold, and t is the critical exponent.

A CB content of 16.48% v/v (27.75% w/w) in the poly(olefin) phase was chosen because it is somewhat over the percolation threshold (V^*) for both PE and EEA (Fig. 2). In such conditions the conductive pathways in the sample are dense enough to prevent resistivity fluctuations attributed to parasite solicitations. The lower percolation threshold obtained for PE–CB suggests a more important dispersion of CB in the amorphous phase of EEA attributed to either its lower crystallinity or higher level of interactions with CB. In such CPCs with conductive particles content over the percolation threshold, a more or less sharp conductor to insulator transition is observed, called PTC (positive temperature coefficient) effect. This nonlinear evolution of resistivity with temperature corresponds to the disconnection of carbon black particles attributed to the polymer matrix expansion. Many parameters can influence PTC effect characteristics, among which are crystallinity, thermal expansion coefficient, reticulation, and composition, as discussed in a previous work[20]; nevertheless, the exact origin of the PTC effect is not yet fully understood. Figure 3 illustrates the typical electrical behavior obtained with PBT/EEA–CB CPC during the second heating/cooling cycle. The first cycle is generally different from the others and acts as an annealing treatment to eliminate the thermomechanical history of the poly(olefin) phase. The PTC amplitude corresponds to the resistivity difference between room temperature and temperature over PTC transition. It may be seen
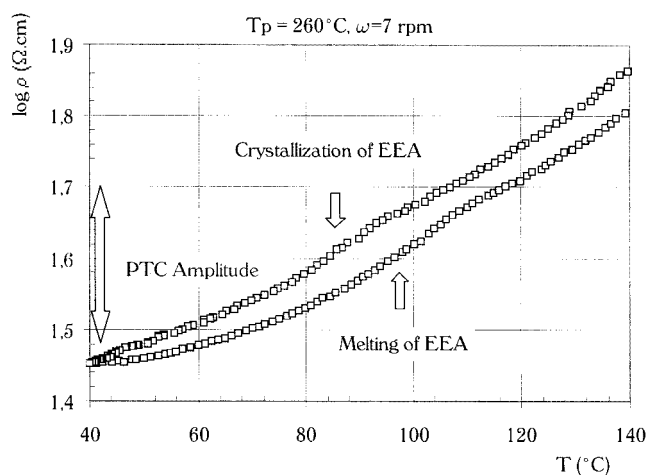
that the curves are not necessarily superimposable during heating and cooling. This hysteresis phenomenon can have several origins and proves quite sensitive to processing conditions. One of them is that destruction of conductive pathways during melting does not occur at the same temperature as that of structuring during crystallization. This is clearly shown in the example of Figure 3, where PTC transition is shifted by about 10°C; however, because in diphasic systems the morphology of PBT matrix and CB localization are influential parameters, processing conditions may also make an important contribution to the hysteresis.

Influence of processing temperature and screw speed on resistivity

The curves of Figure 4 show the evolution of resistivity with temperature of PBT/EEA–CB for several temperatures constituting the processing window of PBT.
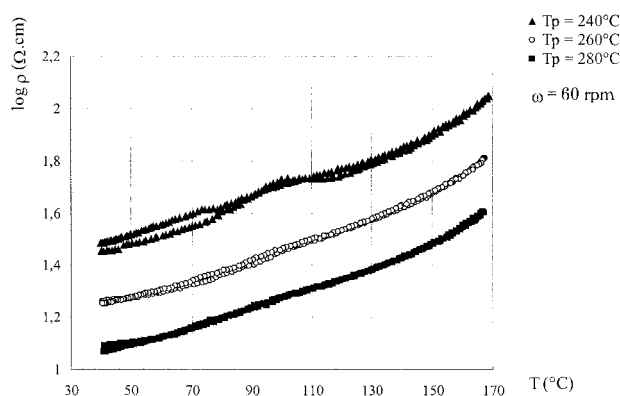
Figure 4 Resistivity versus temperature as a function of processing temperature for a screw speed of $\omega = 60$ rpm (PBT/EEA–CB).
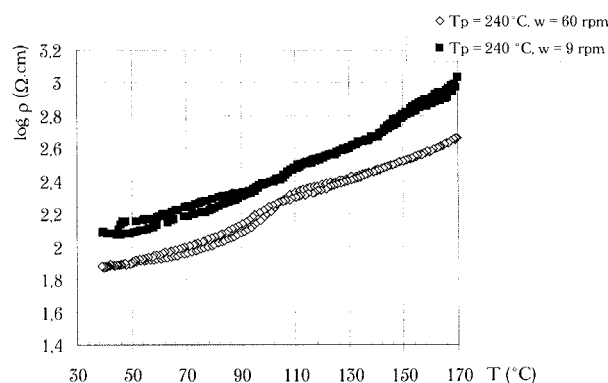
Figure 5 Resistivity versus temperature as a function of screw speed for a processing temperature of $T_p = 240°C$ (PBT/PE–CB).

TABLE II
Rheological Measurements Evaluated by Instrumented Extruder Die

	$T = 260°C$			
Variable	PBT60/(EEA27.75NC)40		PBT60/(PE27.75NC)40	
ω (rpm)	7.1	56.1	9.2	60.4
β	1.649		1.485	
$\dot{\gamma}_{cor}$ (s^{-1})	3.6	19.7	3.51	18.9
η (Pa.s)	618	402	452	260
E_a (kJ mol^{-1})	12.2	21.1	16.6	28.4

Under 240°C the high viscosity of PBT imposes an important torque to the extruder and over 280°C the CPC is too fluid to be processed. For a screw speed of $\omega = 60$ rpm, increasing the processing temperature from 240 to 280°C decreases both room-temperature resistivity and PTC amplitude. The decrease in resistivity is about 0.2 orders of magnitude for an increase of processing temperature of 20°C, which is rather significant. The same shift in temperature is observed with PBT/PE–CB, showing that the nature of the interactions between the poly(olefin) and carbon black is not a determining parameter in this case. The fact that the resistivity shift is the same before and after PTC transition, whatever the processing temperature, confirms that the PBT matrix controls the expansion of the conductive phase during the thermal cycles. The origin of the decrease in both resistivity and PTC amplitude corresponds quite well to a densification of the carbon black network favored by a larger mobility of macromolecules in the conductive phase. However, the effect of extrusion temperature could also come from the cooling process that begins just after the material has left the die into ambient air. Actually, higher temperatures also increase the time allowed to CB to structure into dense pathways during crystallization.

Figure 5 provides an example of the influence of screw speed on resistivity evolution with temperature for PBT/PE–CB at a processing temperature of 240°C. In the screw speed range accessible on the extruder ($\omega = 7$–60 rpm) resistivity decreases by about 0.2 orders of magnitude with an increase of speed. Shear rate in the die $\dot{\gamma}$ and viscosity η, corresponding to these screw speeds, can be evaluated from eqs. (2) and (3), respectively, for rheothinning flows. Results of rheological measurements made *in situ* with an instrumented extruder are presented in Table II.

$$\dot{\gamma}_{cor} = \left(\frac{2 + \beta}{3}\right) \frac{6Q_v}{Wh^2} \text{ with } \beta \equiv \frac{d\left(\log \frac{6Q_v}{Wh^2}\right)}{d\left(\frac{\Delta P}{L}\frac{h}{2}\right)} \quad (2)$$

where W, h, and L are the width, height, and length of the die (m), respectively; Q_v is the volume flow (m^3/s); and ΔP is the pressure drop in the die (Pa).

$$\eta = \frac{\tau_w}{\dot{\gamma}_{cor}} \text{ and } \tau_w = \frac{\Delta P}{L}\frac{h}{2} \quad (3)$$

The values of $\dot{\gamma}_{cor}$ and η obtained for the blends are compared to rheological curves of pure polymers in Figure 6. Highly CB loaded EEA and PE have a pronounced non-Newtonian behavior, which is often the case,[16] whereas in the same shear rate range PBT is rather Newtonian and the viscosity decrease begins only for $\dot{\gamma}_{cor} > 10$ s^{-1}. It is quite surprising to find that the viscosity of the blends is weaker than that of either pure polymer, but this fact has also been observed by some investigators[17] in an analogous case with immiscible polymer blends when flow curves cross, which is the case here. It must also be emphasized that mea-
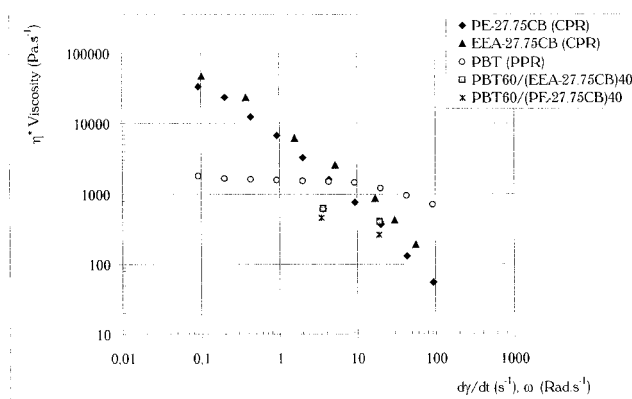
Figure 6 Viscosity versus shear rate for PBT, EEA–CB, and PE–CB measured by plate/plate rheometry (PPR), cone/plate rheometry (CPR), or on extruder for $0.01 < \dot{\gamma} < 100$ s^{-1} at 260°C.
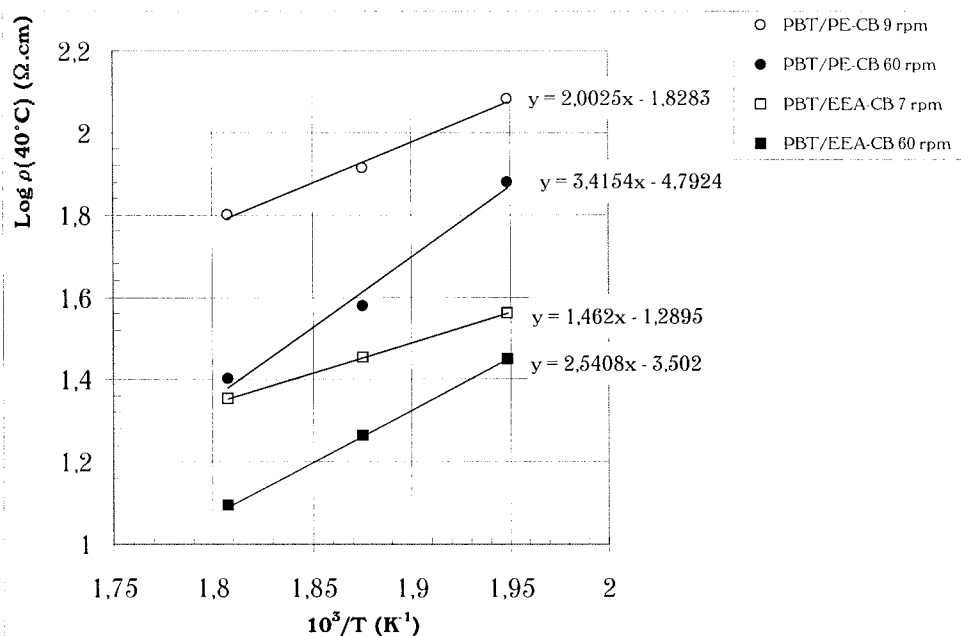
Figure 7 Arrhenius plots of resistivity versus extrusion temperature and screw speed for PBT/EEA–CB and PBT/PE–CB.

surements in the extrusion die are obtained in rather different conditions than those in the plate/plate rheometer (i.e., in the former, polymers have already been sheared in the screw). In our experimental conditions, it seems that shearing only induces a viscosity decrease instead of affecting CB aggregates, as observed by some researchers for higher solicitations.[4,5]

Results are synthesized in Figure 7, where the combination of temperature and shear effects appears clearly for PBT/EEA–CB and PBT/PE–CB. Coupling between these two parameters is evident and it may be noticed that for a screw speed of $\omega = 7$ rpm, the resistivity shift attributed to processing temperature is considerably less important (by a factor of 2) than that for $\omega = 60$ rpm. The same phenomenon is observed for the two CPCs despite their different nature, which suggests that the resistivity sensitivity to processing temperature may result from viscosity variations of both PBT and EEA according to the following equation:

$$\eta = \frac{c'}{\sqrt[3]{\bar{V}}}\, e^{E_a/RT} \tag{4}$$

where $\bar{V}$ is the specific volume, c' is a constant, R is the perfect gas constant, E_a is the activation energy for chain flow, and T is temperature in K.[18]

Consequently, a decrease in EEA viscosity will increase carbon black mobility and favor particle aggregation, which can also move to the interface leading to an increase in conductivity. Moreover, the change in viscosity ratio p induces shape modifications of EEA

channels, thus changing the CPC morphology (as discussed later). It may also be observed from Figure 7 that the shift in resistivity attributed to the variation of the screw speed is more sensitive at high temperature. The screw speed can act on both shear stress and residence time. An increase of shear stress has a cumulative effect with the increase of temperature on the viscosity decrease, whereas the effect of residence time in the extruder is difficult to evaluate independently from the other parameters, given that it could be done with an internal mixer. Therefore, the thinning effect resulting from an increase of screw speed is more important than the decrease of aggregation time. The activation energies (E_a) derived from the slopes of the plots of Figure 7 are reported in Table II. These results are consistent with the fact that the phenomenon of CB aggregation arising from the chain motion is favored by low viscosity coming from either high shear rate or high processing temperature or a low polymer molar mass.

Morphology of blends

Because resistivity variations often come from changes in conductive pathway characteristics, it is valuable to display CPC morphology as a function of processing conditions. SEM micrographs presented in Figures 8 and 9 show transversal cuts (perpendicular to extrusion direction) obtained, respectively, for low screw speed with low processing temperature and high screw speed with high processing temperature. These extreme conditions provide very different morpholo-
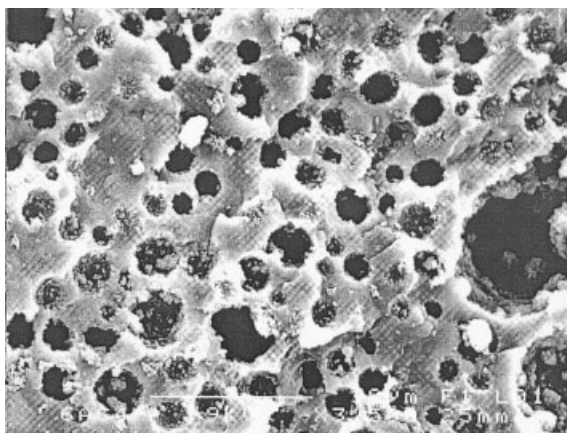
Figure 8 SEM micrograph of PBT60/(EEA27.75CB)40 with a screw speed of $\omega = 7$ rpm and a processing temperature of $T_p = 240°C$ (magnification ×3500).

gies corresponding to a resistivity shift of an order of magnitude of 0.6. The fact that cocontinuity of the two immiscible phases is achieved in both cases is obviously deduced from electrical measurements in the longitudinal direction. However, the morphology of the conducting tubes is more difficult to quantify in terms of tortuosity and connectivity. In a review, some authors proposed a model for phase cocontinuity prediction in polymer blends, based on geometrical requirements.[21] It emerges from this study that several parameters—p, the viscosity ratio; ϕ_{max}, the maximum packing density; and Ca, the capillary number—are useful for predicting morphological changes in immiscible blends [cf. eqs. (5), (6), and (7)]. Although these equations are difficult to apply rigorously to our systems because they are often restricted to the Newtonian case and to unfilled polymers, they nonetheless provide useful tools for analysis.
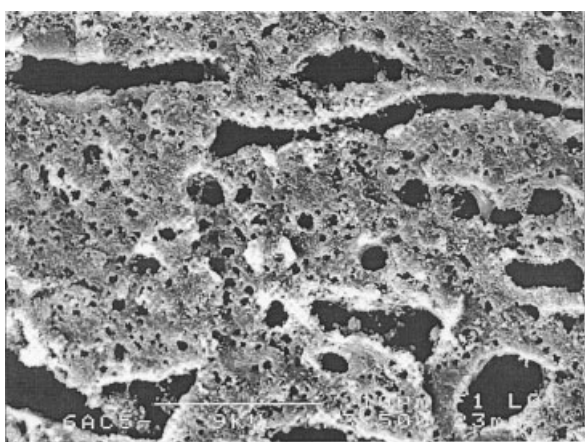
Figure 9 SEM micrograph of PBT60/(EEA27.75CB)40 with a screw speed of $\omega = 60$ rpm and a processing temperature of $T_p = 280°C$ (magnification ×3500).
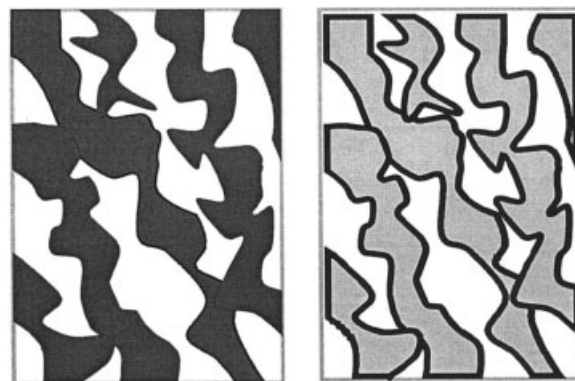
Figure 10 Migration of carbon black to the interface between PBT and poly(olefin), from left to right.

Equation (5) predicts the range of volume fraction in which the two immiscible polymers form cocontinuous phases. The two limits of the domain can be obtained with eq. (5) stating successively that the matrix is PBT and poly(olefin). From data of Figure 6, cocontinuity values may be obtained for $30\% < \phi_{PBT} < 70$ and $10\% < \phi_{PBT} < 90\%$ for PBT/EEA–CB and PBT/PE–CB, respectively, which at least for the upper limit is in good agreement with our experimental results. Moreover, eq. (5) shows the dependency of morphology with viscosity ratio p. As the flow curves of PBT and poly(olefin)–CB cross in the shear rate range used for processing, the value of p will become less than unity with increasing shear rate. This variation of p can be invoked to explain the morphological changes in the CPC clearly visible from the comparison of Figures 8 and 9.

$$\frac{\phi_d}{\phi_m} = p\{1 + 2.25[\log(p)] + 1.81[\log(p)]^2\} \qquad (5)$$

where $p = \eta_d/\eta_m$, and η_d and η_m are the viscosity of dispersed phase and matrix, respectively.

In Figure 8, conductive channels have diameters that are between 2 and 4 μm and are of rather tubular shape. In Figure 9, three populations of channels can be identified considering their diameter and shape: $0.5 < \phi < 1.5$ μm tubular, $2 < \phi < 6$ μm tubular, and $\phi > 10$ μm lamellar. Equation (6) shows that connectivity of the system is obtained for lower content if inclusions have high aspect ratio. This could also justify the increase in resistivity observed with the conversion of tubes into lamella.

$$\frac{1}{\phi_{max}} = 1.38 + 0.0376\left(\frac{L}{B}\right)^{1.4} \qquad (6)$$

where L/B is the aspect ratio, L is the length, and B is the diameter of the dispersed particles; $\phi_{max} = 0.7$ for spheres and 0.31 for randomly oriented rods.

The capillary number Ca, eq. (7) expressing the competition between dispersion and coalescence of particles is often used to predict morphological changes in immiscible polymer blends. A value of Ca > 1 means an increase of the minor phase dispersion in the matrix, whereas if Ca < 1 the particles will coalesce. In our systems, coalescence of one part of the tubes into lamella and the spreading of the other part into smaller particles is in contradiction with eq. (7).

$$Ca = \frac{\eta_m \dot{\gamma} B}{2\sigma} \qquad (7)$$

where σ is the interfacial tension.

Thus the influence of morphological changes on resistivity is difficult to establish even if it seems that current circulation in the CPC is favored by an increase of the tubes section by a coalescence process.

CONCLUSIONS

Electrical properties of two CPCs blended by extrusion were investigated as a function of processing conditions. The main result is that CPC resistivity decreases regularly with increasing processing temperature and screw speed. Shift factors and activation energies were evaluated in each case and an interpretation of the phenomenon was proposed, based on viscosity variations during the process. The resistivity shift is observed with both EEA and PE in the conductive phase despite their different polarities, but the amplitude of the phenomenon is more important with PE, which is supposed to have fewer interactions with carbon black. The viscosity decrease changes both carbon black network structure and CPC morphology, but the main effect is a CB concentration at the interface by an aggregation process (Figure 10) which is consistent with the conclusions of a previous work.[20] The coalescence process of conductive tubes also observed has a weaker contribution to the resistivity decrease. These results confirm that small variations of processing temperature and screw speed have impor-

tant consequences on electrical properties of CPC. Thus, good control of these conditions is essential to obtain reproducibility. Moreover, this finding can also provide an interesting way to adjust the evolution of resistivity with temperature during heating/cooling cycles.

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