

Carbon Black Filled PET/PMMA Blends: Electrical and Morphological Studies

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In this work, the electrical and morphological properties of blends of poly(ethylene terephthalate) (PET), poly(methyl methacrylate) (PMMA), and carbon black (CB) were analyzed. Resistivity decreases similarly in both PET and PMMA with CB concentration. Similarly in the PET/PMMA blend, extensive modification to this behavior occurs, since resistivity becomes a function of morphology and specific location of CB in the polymers. A minimum in the resistivity of the blend with 5% CB (PET basis) is observed at 100% PET, whereas with an increase in the CB content to 20%, the minimum in the resistivity shifts to 60% PET. High conductivity is observed when PET is the continuous phase (having the larger viscosity). Large stresses lead to a large dispersion of CB and a high deformation and rupture of the dispersed PMMA phase. This situation itself promotes an increase of surface area of droplets and high CB concentrations at the interface. Consideration is given to models that predict a selective location of conductive particles in the PET matrix based on its lower interfacial tension with CB.

INTRODUCTION

The electrical properties of an insulating polymer may be modified when it is mixed with conductive particles such as metal powder, carbon black, graphite or an intrinsically conducting polymer. Among the available fillers, the most popular is carbon black (CB).

The selective localization of CB particles in multiphase polymeric materials is a favorable condition for obtaining heterogeneous microdispersion of CB (1–10). It is found that CB distributes unevenly in each component of the immiscible polymer blend. Two

types of distribution are observed: in the first, CB is distributed predominantly in one phase of the blend homogeneously (1–7, 10). In the second, the conductive particles concentrate at the interface of the two phases (1, 2, 4, 5, 7, 8, 10). The conductivity of these composites is determined by two factors: the preferential concentration of CB in one phase, and the structural continuity of this phase. This double percolation, i.e., percolation of the polymer phases and percolation of the CB particles, or co-continuous phase morphology, depicts especially low resistivity values (1, 3–7, 10). Interfacial free energies, mixing kinetics and viscosities, and polymer polarity and crystallinity are important factors governing the selective localization of CB (1, 2, 5, 10).

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The production of low conductive materials with permanent antistatic properties using polymeric alloys has been given attention by Lee (11). In his work, the use of conductive alloying polymeric additives with a resistivity in the range of 10^5 and 10^{12} ohm-cm was proposed. From the blend of an intrinsically conductive polyether copolymer of high molecular weight and a glycol modified poly(ethylene terephthalate) (PETG), a composite with a resistivity of 10^{10} to 10^{12} ohm-cm is obtained. This polymer blend is highly suitable for a precise adjustment of conductivity values in the required conductivity region for antistatic applications.

PET is widely used as an engineering thermoplastic for packing, electronic, automotive, and other applications. Nowadays, there is a tendency to alloy PET urban plastic waste with other polymers to improve their properties, mostly with high density polyethylene (HDPE) and others such as polypropylene (PP), polyphenylene sulfide (PPS), polycarbonate (PC), and liquid crystalline polymers (LCP) (12-18). Most of these polymer blends are incompatible and the studies are focused on compatibilization techniques. In the present work, we have selected PMMA, which is immiscible with PET (19, 20).

The main objective of this work is the description of the electroconductive properties of an immiscible polymer blend filled with CB and the relations with its morphological and thermal properties. To properly analyze the results obtained, models that predict the selective location of CB in the blend are considered.

EXPERIMENTAL

Recycled PET was blended with PMMA at different concentrations. A local recollection company, Mayan Recycles International, which collects PET from commercial bottles, provided cleaned and crushed PET. A thermoplastic resin, PMMA, commercially designated as H12, was used. The main characteristics of this polymer are shown in Table 1. PMMA was selected because its adequate processing, good mechanical properties, and immiscibility with PET (19, 20). Sumita *et al.* (1-3) studied the interactions and affinity of the components of various immiscible blends, providing criteria to obtain highly conductive systems. In the present work, we use carbon black (CB) as conductive filler, BP 2000, supplied by Cabot, with a surface area of $1500 \text{ m}^2/\text{g}$ (N_2) and a plasticizer absorption value, DBP (dibutyl phthalate), of $330\text{cc}/100\text{g}$.

Table 1. Properties of the PMMA Resin.

Property	Value
Melt flow index (g/10 min)	7.0
Deflection temperature ($^{\circ}\text{C}$)	95
Tensile strength (MPa)	26
Density (g/cm^3)	1.19

supplier: Plastiglas de México, S.A.

Blends with the compositions indicated in Table 2 were prepared in a Brabender internal mixer, with roller blades, at a blade speed of 30 rpm. The polymers were first melted, and then CB was added in a period of 2-3 min. After CB addition, the rotor speed was increased to 60 rpm. The mixing stage was carried out during 10 min at 245°C to disperse the CB particles.

With this material, 100×100 mm sheets were compression molded at 250°C at a pressure of 2.67 MPa for 15 min. Subsequently, the sheets were cooled under pressure to 50°C . The blend resistivity at room temperature was measured on 30×30 mm squares, using a Keithley multimeter, model 6517A. Silver conductive paste was used to reduce the contact resistance.

To evaluate the phase morphology, several samples were treated with CHCl_3 to extract the PMMA phase from the surface. The resulting PMMA-chloroform solutions remained clear with negligible CB presence, implying that CB is preferentially located in the PET matrix. Subsequently, they were observed by scanning electron microscopy, using a JEOL microscope, model JSM-35C (we have developed a system for SEM control, scanning and data acquisition based on an IBM PC with Windows 3.1). The SEM images were obtained at 25 kV.

Calorimetric measurements were performed to evaluate thermal transitions of blends in a Perkin Elmer DSC 7. All the samples were scanned from 30°C to 280°C at a heating rate of $10^{\circ}\text{C min}^{-1}$. After scanning, the samples were quickly quenched to room temperature and reheated using the same conditions.

Infrared measurements were made using Nicolet 460 FTIR spectrometer. 100 scans at a resolution of 8 cm^{-1} were carried out to produce a spectrum. These tests were performed on samples mixed with potassium bromide using the transmittance mode with a sample concentration of 5% w/w.

RESULTS

The internal mixer (torque rheometer) was used to study the effect of CB on the rheological behavior of the blends under processing conditions. Torque is proportional to the blend viscosity and may explain the effect of CB inclusion. When the CB content is

Table 2. Blends Made in a Brabender Mixer Chamber at 245°C , 30 rpm.

PET (% w/w)	PMMA (% w/w)	CB (% w/w)*
0	~100	0, 1.25, 2.5, 5, 10, 20
20	80	0, 1.04, 4.76, 5
40	60	0, 2.06, 5, 9.09
60	40	0, 3.06, 5, 13.04
80	20	0, 4.04, 5, 20
100	0	0, 1.25, 2.5, 5, 10, 20

*CB is a conductive carbon black "BP 2000" from CABOT de México, and weighed over the 100% of polymer blend.

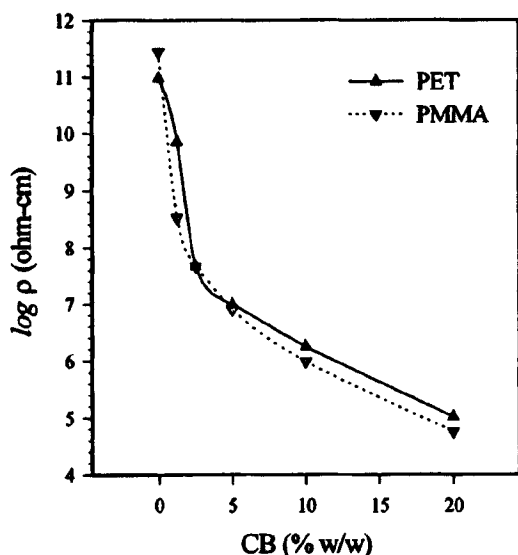


Fig 1. Resistivity of each polymer with different CB contents.

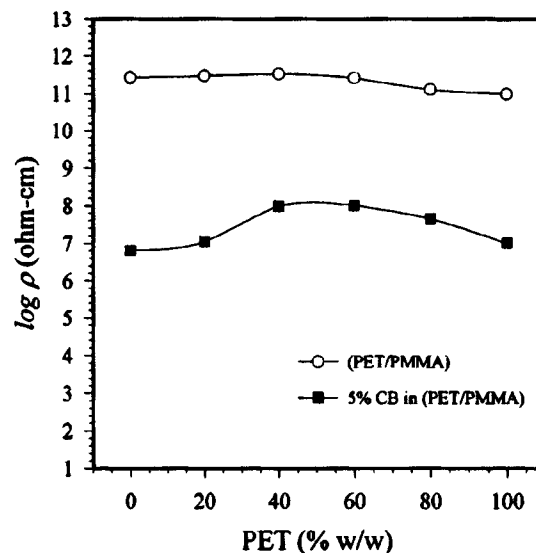


Fig. 2. Resistivity of PET/PMMA blends without and with 5% w/w CB (blend basis).

20%, samples achieve high torque values for concentrations higher than 40% PET, which indicates a high viscosity and substantial viscous dissipation. The peak in the torque, resulting from the incorporation of CB in the blend, may be related to the energy needed to incorporate the CB to the blend. This energy rises as PET content and CB concentration increase.

The change in resistivity as the CB content increases is shown in Fig. 1, evidencing that conductivity increases with CB concentration in a similar way for both polymers. A drop at 2.5% CB is followed by a more gradual decrease up to 20% CB. Here the resistivity decreases from 10^{11} to 10^5 ohm-cm over the whole CB concentration range considered.

The inclusion of CB in PET/PMMA blends shows a large decrease in blend resistivity. Five percent (5%) CB (blend basis) in PET/PMMA may produce an average resistivity value of $\approx 2.6 \times 10^7$ ohm-cm, Fig. 2. As was mentioned, there is preferential location of CB in PET phase; therefore the CB concentration in PET is not constant. For example, in 20/80 and 80/20 PET/PMMA blends the relative concentration of CB is 20.83% and 6.17% respectively. The effect of constant CB/PET ratios over PET/PMMA blends resistivity is shown in Fig. 3. Here, two CB/PET ratios were used: 0.05 and 0.25 related to the inclusion of 5% and 20% CB in PET, respectively. It is observed that the resistivity decreases very steeply as the CB content increases. For a 0.25 CB/PET ratio, the drop in resistivity lies within 0%–60%. In blends with a 0.05 CB/PET ratio, the resistivity steeply descends for CB/PET concentrations higher than 40%.

To observe the blend's morphology after the CB incorporation and processing, PMMA was extracted from the surface of samples with chloroform. Then the samples were observed by SEM. Figure 4a–j shows

micrographs taken at the center of samples for various PET contents without and with 5% CB (blend basis). All images have $600 \times 350 \mu\text{m}$ size for comparison. In Fig. 4a and 4b, pure PET with and without CB does not show special features of interest. As PMMA is incorporated, the 20% PMMA sample with 5% CB shows slightly elongated PMMA particles embedded in the PET matrix, with a mean size of $18 \mu\text{m}$ and 2.3 aspect ratio (Fig. 4d). Also, an important CB concentration (white zones) on the PET/PMMA interface is observed. On the other hand, in Fig. 4c particles are smaller, $7 \mu\text{m}$, with circular cross section. It

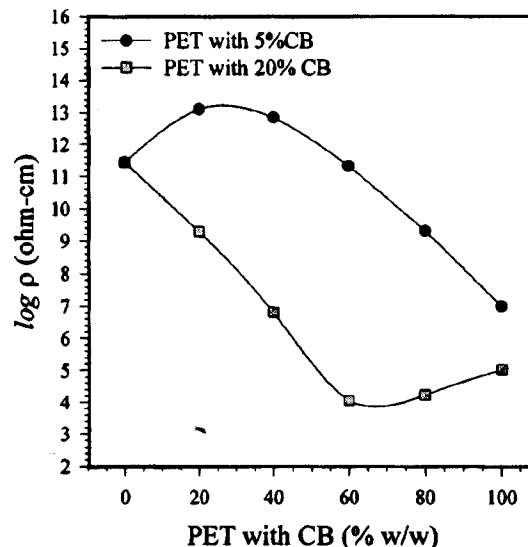


Fig 3. Resistivity of PET/PMMA blends with 5 and 20% w/w CB (PET basis).

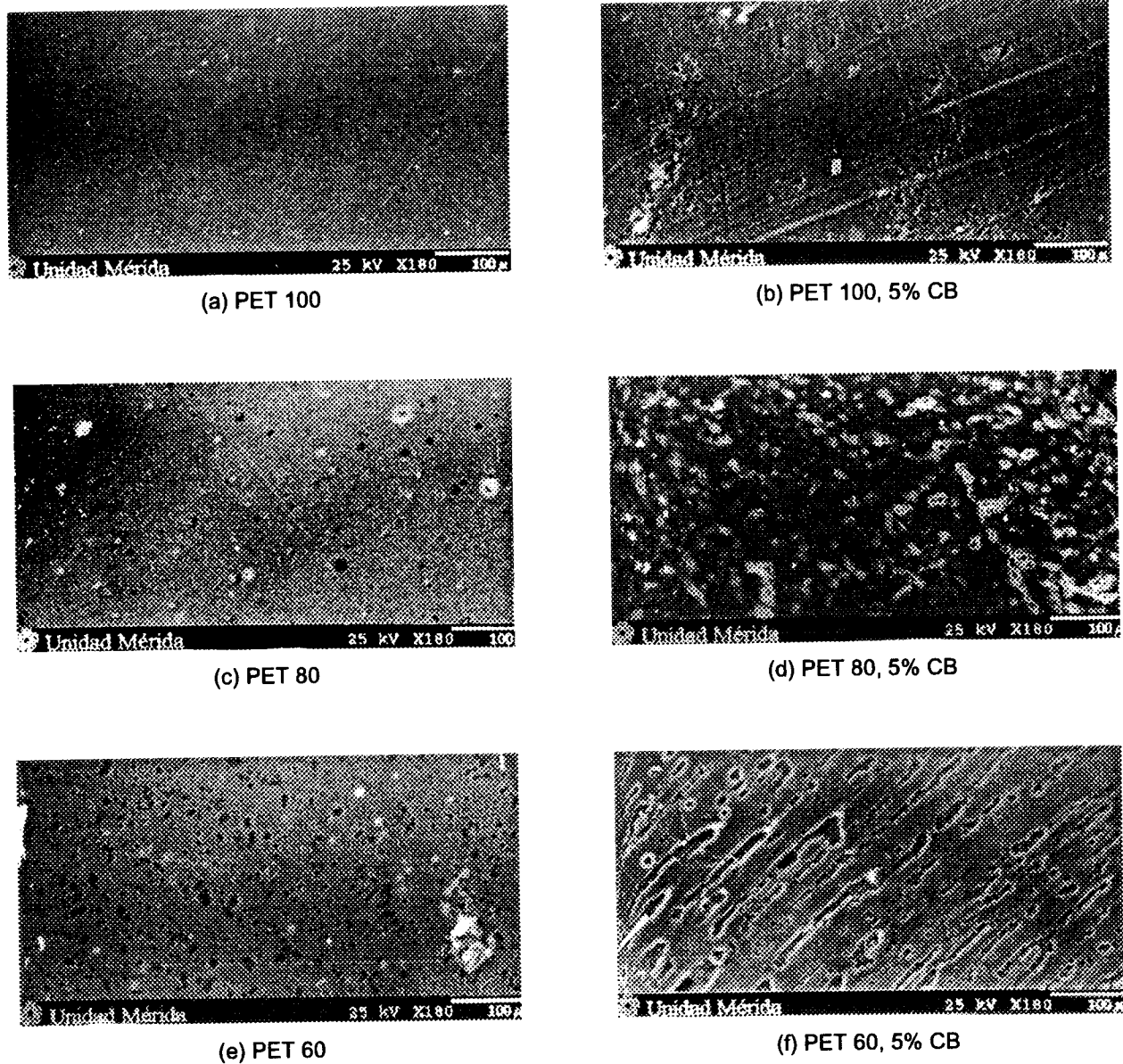


Fig 4. SEM photographs of PET/PMMA blends without CB and with 5% w/w CB (blend basts).

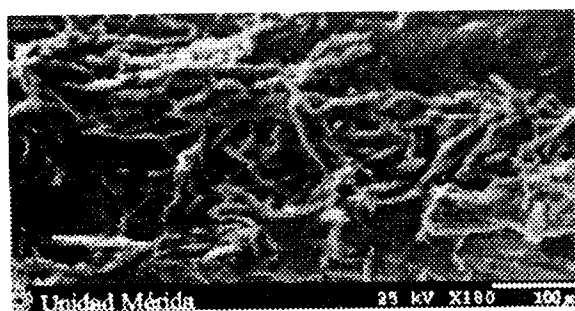
is important to point out that after PMMA extraction the resulting PMMA-chloroform solutions remained clear with negligible CB presence, implying that CB is preferentially located in the PET matrix.

In Fig. 4f the PMMA content is 40%, blended to the CB. A fibrillar structure is observed in the PMMA phase, with a breadth of $33\ \mu\text{m}$ and average aspect ratio of 3.75. Also, it is noted that the CB is not so concentrated in the interface as in the previous case; however, the chloroform extracted solutions remain clear. In contrast, in Fig. 4e, the PET/PMMA blend without CB presents circular particles of $12\ \mu\text{m}$ mean size. As the PMMA content increases to 60% in the

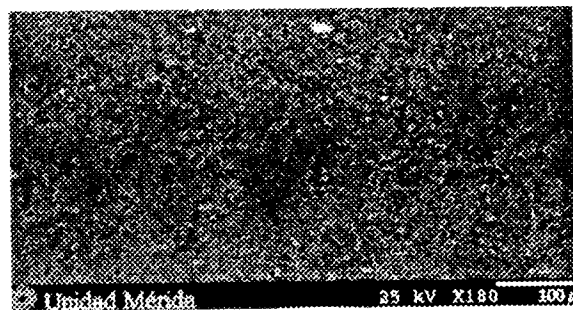
blend with CB, shown in Fig. 4h, finely dispersed PET particles of $3\text{--}5\ \mu\text{m}$ size are observed. In the blend without CB, Fig. 4g shows a fibrillar structure in the PET phase with $34\ \mu\text{m}$ breadth.

In Fig. 4j, PET agglomerates of $10\text{--}30\ \mu\text{m}$ size are formed in the 80% PMMA blend with 5% CB. The blend without CB, Fig. 4i, shows larger PET agglomerates. Even in these cases, the extracted solutions remain clear, implying a higher CB content in the PET phase.

For the blends with and without CB, thermal properties are shown in Fig. 5. PMMA glass transition temperature increases from 100.7°C to 107.2°C as the



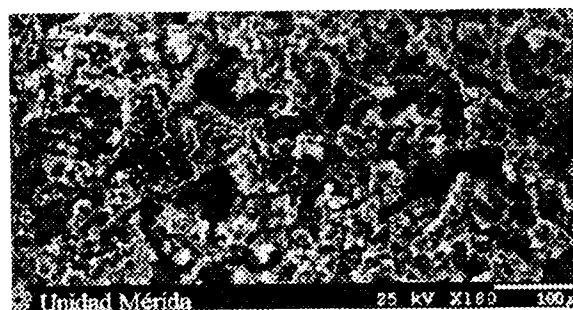
(g) PET 40



(h) PET 40, 5% CB



(i) PET 20



(j) PET 20, 5% CB

Fig 4. Continued.

PET content increases in the blends without CB. With CB, the PMMA T_g decreases as PET content rises. The melting endotherms of PET show a minimum when the percentage of the PET phase attains 60%. In contrast, in the blends without CB, a nearly constant T_g is observed.

Infrared spectra of the blends do not show evidence of thermo-oxidative degradation of PET, as no double carboxylic bonds present as vinyl (benzoate or benzene) end groups are observed (21).

Moreover, the torque measurements illustrate that blend viscosity is not substantially affected when the 0.05 CB/PET ratio is used. In contrast, the torque (and related blend viscosity) increases substantially with the 0.25 CB/PET ratio, Fig. 6. Finally, the energy needed to incorporate the CB in the blend increases more than seven times with rising PET content. This indicates that CB interacts more and is more compatible with PET than with PMMA.

DISCUSSION

Previous works on the electrical properties of immiscible blends with the inclusion of CB are numerous (1-10). These point out important factors that largely influence the final properties of the system: the preferential location of CB in one phase and the phase morphology (1, 3).

The location tendency of CB in either phase in a blend is influenced by the individual surface tensions, in such a way that CB is preferentially located in the phase having the lower interfacial tension, characterized by a larger wetting of the CB particles (5, 6, 10).

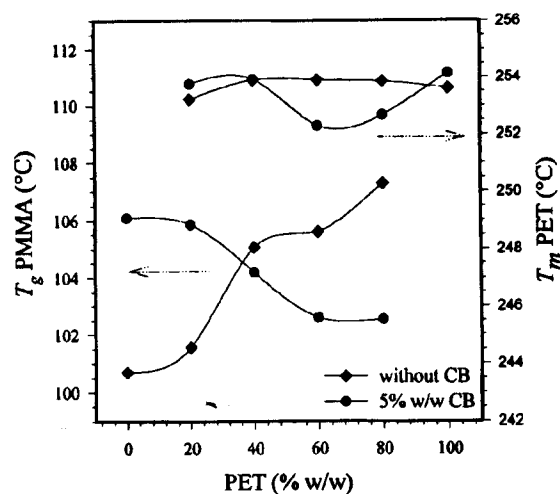


Fig 5. Variation of PMMA glass transition peak temperature and PET melting peak temperature with the blend composition and CB content (blend basis).

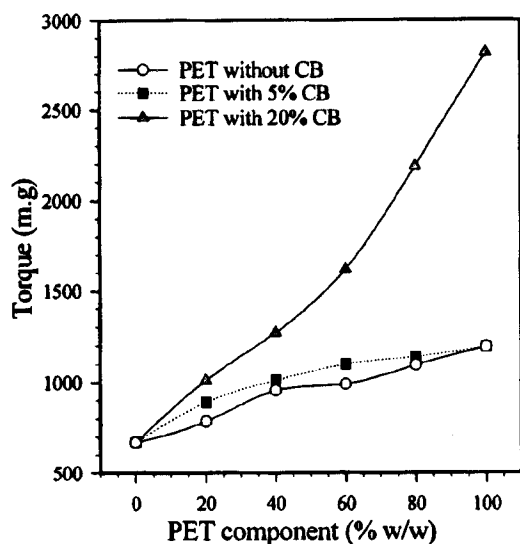


Fig 6. Equilibrium torque of PMMA/PET blends, where the second blend component can be: PET, PET with 5% CB, and PET with 20% CB.

Studies of immiscible blends have shown that the uneven distribution of fillers in a polymer blend is due to the differences in affinity of CB particles to each component of the blend (1-3). Hence, CB will locate in the PET phase rather than in the PMMA phase.

Morphology of the blends with CB may be related with the increase in viscosity as PET content increases. Agglomerates observed at 20% PET content in a continuous PMMA phase represent the blend with relative low viscosity (see Fig. 4h and Fig. 6). The large surface area of the CB particle ($1500 \text{ m}^2/\text{g}$) promotes the formation of a PET layer in the form of small flakes. In the blend with 40% PET content, PET domains have decreased in size, showing a finely dispersed phase close to phase inversion. In Fig. 4f the continuous phase is now PET and the PMMA domains are highly distorted. Since the continuous phase corresponds to the phase of larger viscosity, high stresses are produced, which are able to deform the PMMA droplets extensively. As the viscosity of the blend increases with PET content, in the 80% PET blend the PMMA domains are broken and reduced in size, owing to the large shear stresses developed in the continuous PET phase.

The interfacial tensions were calculated using the harmonic equation to both polymers and the geometric equation to one polymer and carbon black (1, 2). The values obtained were 0.707 mN/m for PMMA-PET, 7.64 mN/m for PMMA-CB, and 5.89 mN/m for PET-CB, taking into account the data reported elsewhere (2, 22-24). A very high probability exists that CB is better adhered to PET than to PMMA because of its lower interfacial tension, or the larger affinity characterizing the system PET-CB.

The distribution of CB particles in the blend and the phase morphology determine the conductive properties of the blends, although both polymer components have very similar resistivity behavior when the CB concentration is increased, as observed in Fig. 1.

The initial increase in resistivity observed in the blend with 5% CB, shown in Fig. 2, may be ascribed to the presence of a microdispersion of PET particles in the PMMA matrix, in which contacts of the CB-rich PET aggregates are scarce, inhibiting the electric conductivity. After the phase inversion, the increase in conductivity may be due to the presence of more conductive pathways formed within the PET continuous phase. On the other hand, an increase in the PET-CB ratio to 20% results in a steep decrease in the resistivity for PET contents down to 60%, after which the resistivity increases slowly with rising PET concentration. In this case, the decrease in the resistivity when PET is the discrete phase may be ascribed to the formation of conduction pathways among the small domains. Because the CB concentration is high, it is likely that most particles may be located at the interface of the domains, which explains the percolation threshold. Beyond the phase inversion, PET is the continuous and highly viscous phase, which generates stresses that induce high deformations in the PMMA domains, producing a large dispersion of broken droplets. Morphological studies on the 20% CB samples (not shown) indicate that in the highly conducting blends, a continuous PET phase with broken PMMA domains, smaller than those with 5% CB, possesses a large dispersion of CB particles.

Morphology of the blends also influences the thermal properties. The minimum in the melting temperature of the PET crystals in the blend is located at about 65% with 5% CB content, Fig. 4. On the other hand, the glass transition temperature of PMMA increases in the PMMA-PET system as the PET content rises. This effect may be due to the increased crystallinity of the blend. However, with 5% CB content, the glass transition temperature diminishes as the PET content rises. This may be ascribed to the interaction of CB particles with PET crystals within the PMMA-PET interface (25).

CONCLUSIONS

The presence of CB modifies extensively the rheological and conductive properties of the blend. Resistivity decreases similarly in both PET and PMMA with CB concentration. But the immiscible polymer blend modifies extensively this behavior because resistivity becomes a function of morphology and location of CB in the polymers. The viscosity is observed to be a strong function of PET content at high CB concentrations. Indeed, resistivity decreases continuously (a drop of 7 decades) for 20% CB (PET basis) from 0% to 60% PET content. The same behavior (similar slope) is observed for 5% CB, but the conductivity curve is shifted to higher PET contents.

It was shown that the preferential CB location in the PET phase is explained on the basis of surface tension values. The polar groups of PET interact more strongly with the conductive CB particles, resulting in a relatively higher concentration of CB in PET.

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