

Effect of the Mold Temperature on the Electrical Properties of Carbon-Black-Loaded Polystyrene/SB Block Copolymer Blends

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ABSTRACT: The electrical resistivities of a carbon-black-filled styrene–butadiene block copolymer (SB) and their blends with polystyrene were measured as a function of carbon content for specimens compression-molded at 200 and 250°C. The insulator–conductor point transition was greatly influenced by the mold temperature. This behavior associated to the scanning electronic microscopy investigations suggests the presence of some amount of the filler at the interface. A strong interaction between the filler and the polymer was also observed. The formation of bound rubber and a coherent rubber–filler gel depend on the molding conditions and the carbon black content in the composites. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 825–833, 1998

Key words: polymer blend; carbon black; electrical conductivity, styrene–butadiene block copolymer

INTRODUCTION

There is an increasing interest in developing conducting polymer composite systems filled with carbon black (CB) in a concentration as low as possible to minimize processing problems and the depletion of the mechanical properties. The critical concentration of the conducting filler necessary to form continuous conducting chains through the polymer matrix is referred to as the percolation threshold point and may be decreased

by several orders of magnitude by optimizing the processing conditions. For example, composites melt-blended followed by compression molding exhibit lower conductivity than those formed by direct compression molding of the powder mixture.¹ On the other hand, compression-molded composites display higher conductivity than does an injection-molded one.¹ Furthermore, increase of the mold time,^{2,3} mold temperature,³ and mold pressure⁴ was reported to increase the conductivity of the system.

In addition to the processing conditions, the characteristics of the polymer matrix play an important role in the critical filler concentration. A less viscous polymer matrix normally displays a lower percolation threshold point.² The chemical nature of the polymer also affects the conductivity of the composite. Polymers with high polarity and high surface tension require a higher amount of

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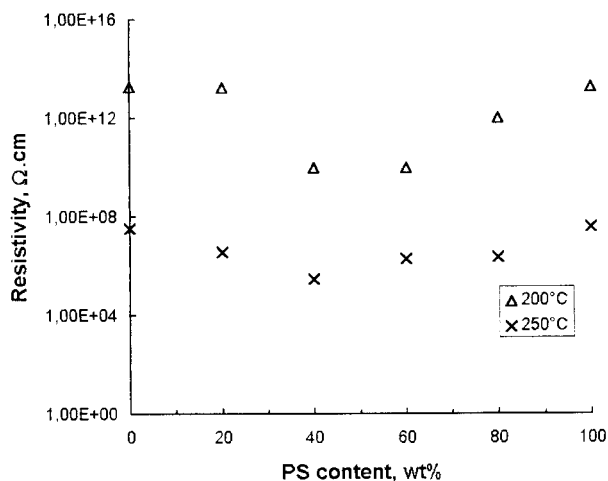


Figure 1 Volume resistivity of PS/SB blends filled with 3 wt % CB as a function of blend composition and mold temperature.

CB to present an insulator–conductor transition.⁵ Semicrystalline polymers display a lower percolation threshold because of the inhomogeneity in the system.⁶ The filler prefers to be located in the amorphous region. As a consequence, a lesser amount of the filler is necessary to form continuous conducting chains. The heterogeneous distribution of CB is also observed in several heterogeneous polymer blends.^{3,7–10} In these cases, the insulator–conductor transition with the lowest amount of CB may be achieved if the two phases are cocontinuous and the filler is located inside the minor phase or preferentially at the interface.

Recently, we reported that the insulator–conductor transition with a relatively low amount of CB can also take place in compatible multiphase polymer systems.¹¹ Indeed, the styrene–butadiene block copolymer (SB) and its blend with polystyrene (PS) loaded with CB presented a percolation threshold point lower than that of the PS homopolymer. These results suggest a heterogeneity in the system and an uneven distribution of the filler. The critical CB concentration in the PS/SB blends was even lower than that in the PS/polybutadiene (PBD) incompatible blend at the same amount of PBD. In addition, the mechanical properties of the PS/SB blends, mainly the elongation at break, were hardly influenced by the addition of as low as 3 wt % CB. Based on these electrical and mechanical behaviors, we supposed that the CB particles could be acting at the interface of the PS/SB blends, thus disturbing the interfacial situation required for a good mechanical performance. According to the literature,³ when the filler is located at the interface of a cocontin-

ous two-phase polymer system, the electrical conductivity is strongly dependent on the compression-molding time or temperature. In this article, we discuss how the mold temperature affects the electrical conductivity, morphology, and polymer–filler gel formation in SB and PS/SB multiphase polymer systems filled with extraconductive CB.

EXPERIMENTAL

Materials

Polystyrene [PS; EDN-89G; $M_n = 95800$, $M_w = 210,800$, density = 1.05, melt index (160°C/15 kg) = 0.55 g/10 min] was kindly supplied by Poliestireno do Sul (Rio Grande do Sul, Brazil). The styrene–butadiene block copolymer [SB; Styrolux-656C; $M_n = 102,100$, $M_w = 143,000$, PS/PBD = 83 : 17 wt %, M_n of PS segment in the block copolymer = 84200, melt index (160°C/15 kg) = 4.60 g/10 min] was kindly supplied by BASF (Ludwigshafen, Germany). Carbon black [CB; Printex XE-2; DBP = 370 mL/100 g, BET = 1000 m²/g] was kindly supplied by Degussa (Frankfurt, Germany). All components were dried at 60°C in a vacuum oven for 24 h.

Blend Preparation

PS and SB were first introduced into an internal mixer (Brabender plasticorder) at 160°C and 20 rpm. After 1 min, the CB was added and the rotor speed was increased to 60 rpm for 10 min. Blends were then compression-molded at variable temperatures for 10 min, under a 6.7-MPa pressure into sheets about 1-mm thick.

Testing and Characterization

The electrical conductivity was measured with a Keithley electrometer 617 using contacts in a sandwich configuration. The electrode area was 9 cm². Silver paint was used between the samples and electrodes so as to minimize the contact resistance.

The polymer–filler gel formation measurements were made by dissolving small samples of known mass (about 0.4 g) in dry toluene. After 2 days in contact with the solvent, the formed emulsion was submitted to centrifugation at 7000 rpm for 2 h. The toluene layer containing the free-unbound material and filler particles with the adsorbed polymer were separated. Then, a fresh

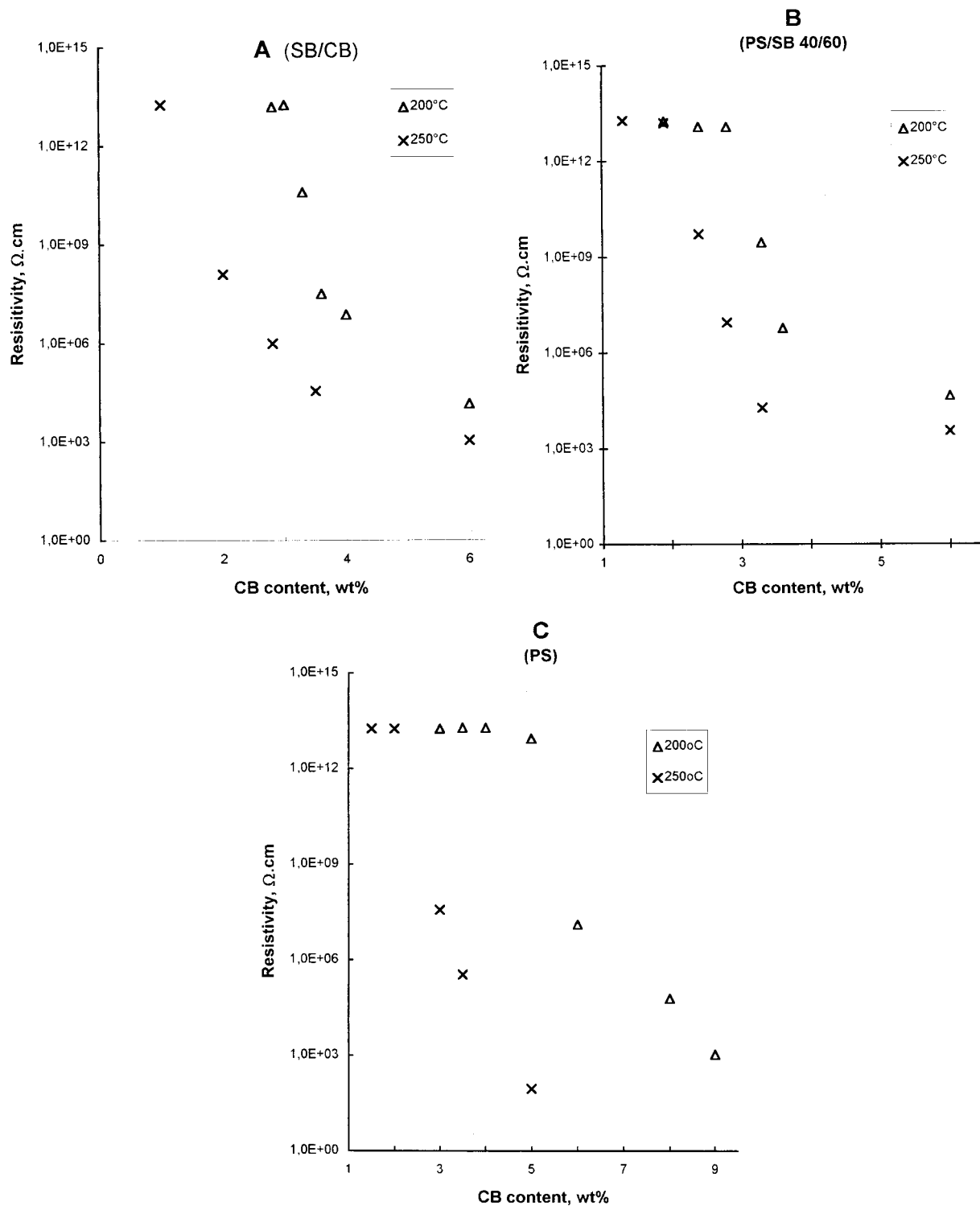


Figure 2 Volume resistivity of (A) SB, (B) PS/SB (40 : 60 wt %), and (C) PS composites as a function of CB content and mold temperature.

amount of toluene was introduced into the tube containing the nonextracted material and the operation was repeated three times until a clear toluene layer was obtained. The polymer–filler gel

swollen with toluene was then dried and weighed. The polymer–filler ratio in the gel was determined by thermogravimetric analysis according to the literature.¹² For these analysis, a Perkin–

Elmer TGA-7 was employed. The samples were heated in nitrogen at $20^{\circ}\text{C min}^{-1}$ to 750°C .

For scanning electronic microscopy analysis, the samples were fractured under liquid nitrogen and the surface coated with a gold vapor. Micrographs were taken by a JEOL 5300 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Electrical Conductivity of PS/SB Blends as a Function of the Mold Temperature

The effect of the mold temperature on the volume resistivity was studied for the PS/SB blends loaded with 3 wt % CB. Figure 1 illustrates the dependence of the resistivity versus the blend composition for specimens compression-molded at 200 and 250°C . Both curves present a minimum in resistivity, suggesting a phase-separation morphology and an uneven distribution of the filler. The resistivity is also strongly influenced by the mold temperature. This effect is better demonstrated in experiments performed with different amounts of CB. As indicated in Figure 2, the insulator–conductor transition (percolation threshold of CB) in pure SB [Fig. 2(A)] and PS/SB (40 : 60 wt %) blends [Fig. 2(B)] decreases when the specimens are compression-molded at a higher temperature. According to the literature,³ this behavior is an indication that some amount of the CB particles should be located at the interface. The higher mold temperature increases the size of the polymer phases, thus decreasing the interfacial area. When the CB particles are preferentially located at the interface, the chance of these particles touching each other increases, giving rise to the current-conducting chains. The decrease of the width of the interface between the microdomains related to the size of the microdomains was reported for block copolymers when the blocks are highly incompatible.^{13,14}

It is important to point out, however, that the reduction in the percolation threshold by increasing the mold temperature cannot be considered a definitive criteria for supporting the hypothesis of the CB location at the interface of immiscible polymer blends, as suggested by Gubbels et al.³ Indeed, as observed in Figure 2(C), the percolation threshold of CB in the amorphous polystyrene matrix decreases as the mold temperature increases. These results may be related to the decrease of the melt viscosity of the PS matrix at higher temperature. The mobility of the filler par-

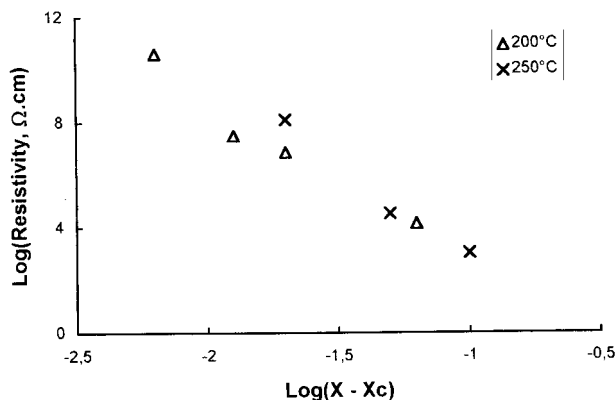


Figure 3 Electrical resistivity as a function of excess concentration of CB ($x - x_c$) for SB/CB composites compression-molded at 200 and 250°C .

ticles inside the less viscous matrix is favored, resulting in flocculation of the CB aggregates, which contributes to the formation of the continuous conducting pathway.

The electrical behavior in these systems follows a percolation process with a relatively sharp insulator–conductor transition. According to the percolation theory,^{15,16} the resistivity of the composite (ρ) is related to the volume fraction of the CB by the following expression:

$$\rho(x) = K_0(x - x_c)^{-p}$$

where $\rho(x)$ is the resistivity of the composite sample; K_0 , a constant; x , the volume fraction of CB; x_c , the volume fraction of CB at the percolation threshold; and p , the critical exponent which represents the average number of contacts per particle at the critical concentration. A value about 1.5–2.0 for the exponent p is normally expected from the theory.^{15,16}

Figure 3 illustrates the dependence of the electrical resistivity against the excess of CB concentration above the percolation for SB–CB composites. The observed straight line indicates that the system obeys the percolation model. The values of x_c and p related to our systems are summarized in Table I. The values of the exponent p are unexpectedly high (in modulus) and increase for specimens compression-molded at a higher temperature (250°C). High values of p have also been found by Karásek et al.¹² for CB-loaded SBR rubber and by Abo-Hashem et al.¹⁷ for butyl rubber–CB systems. The authors suggested that occluded rubber trapped inside the voids of the filler could be responsible for

Table I Parameters of the Percolation Model Equation for CB-Loaded PS, SB, and PS/SB (40 : 60 wt %) Composites

| Polymer System | Mold Temperature (°C) | x_c | p | Linear Correlation Coefficient |
|-----------------|-----------------------|-------|--------|--------------------------------|
| SB | 200 | 0.064 | -6.35 | -0.981 |
| SB | 250 | 0.022 | -7.88 | -0.991 |
| PS/SB (40 : 60) | 200 | 0.06 | -4.57 | -0.961 |
| PS/SB (40 : 60) | 250 | 0.04 | -10.36 | -0.995 |
| PS | 200 | 0.087 | -6.61 | -0.971 |
| PS | 250 | 0.040 | -10.86 | -0.999 |

these high p values. The high effective conductivity exponent in conducting polymer blends was also explained by Levon et al.¹⁸ as a multiple percolation phenomenon.

Polymer–Carbon Black Gel Formation

When unsaturated rubbers are blended with fine particles of CB, a fraction of rubber can be adsorbed on the filler in such a way that the extraction by a solvent is not possible. The filler-insolubilized rubber is usually referred to as bound rub-

ber.^{19,20} Recently, Karásek et al.¹² published an interesting article comparing the phenomenon of rubber–filler gel formation with the electrical behavior of SBR–CB composites. They observed that the CB concentration necessary to achieve the insulator–conductor transition also corresponds to the point of coherent gel formation. According to the authors,¹² at this critical point, there are no filler particles dispersed in the solvent. All CB particles form with the polymer chains a coherent three-dimensional gel structure.

Table II Polymer–CB Gel Formation as a Function of CB Content and Mold Temperature for SB/CB and PS/SB/CB Composites

| | System | | | |
|---|-------------------------------|--------------------|--------------------|-----------------|
| | SB/CB Composites | | | |
| | CB Content | | | |
| | 1 wt % | | 3 wt % | |
| Mold temperature (°C) | 200 | 250 | 200 | 250 |
| Electrical resistivity (Ω , cm) | 1×10^{13} | 1×10^{13} | 1×10^{13} | 3×10^7 |
| R_b (%) | 0.76 | 2.07 | 5.04 | 3.10 |
| CB _{gel} (%) | 1.00 | 0.02 | 0.05 | 3.00 |
| CB _{disp} (%) | 0.00 | 0.98 | 2.95 | 0.00 |
| | System | | | |
| | PS (40)/SB (60)/CB Composites | | | |
| | CB Content | | | |
| | 1 wt % | | 3 wt % | |
| Mold temperature (°C) | 200 | 250 | 200 | 250 |
| Electrical resistivity (Ω cm) | 1×10^{13} | 1×10^{13} | 1×10^{13} | 1×10^7 |
| R_b (%) | 1.50 | 4.20 | 2.00 | 3.20 |
| CB _{gel} (%) | 1.00 | 0.44 | 1.66 | 1.93 |
| CB _{disp} (%) | 0.00 | 0.56 | 1.34 | 1.07 |

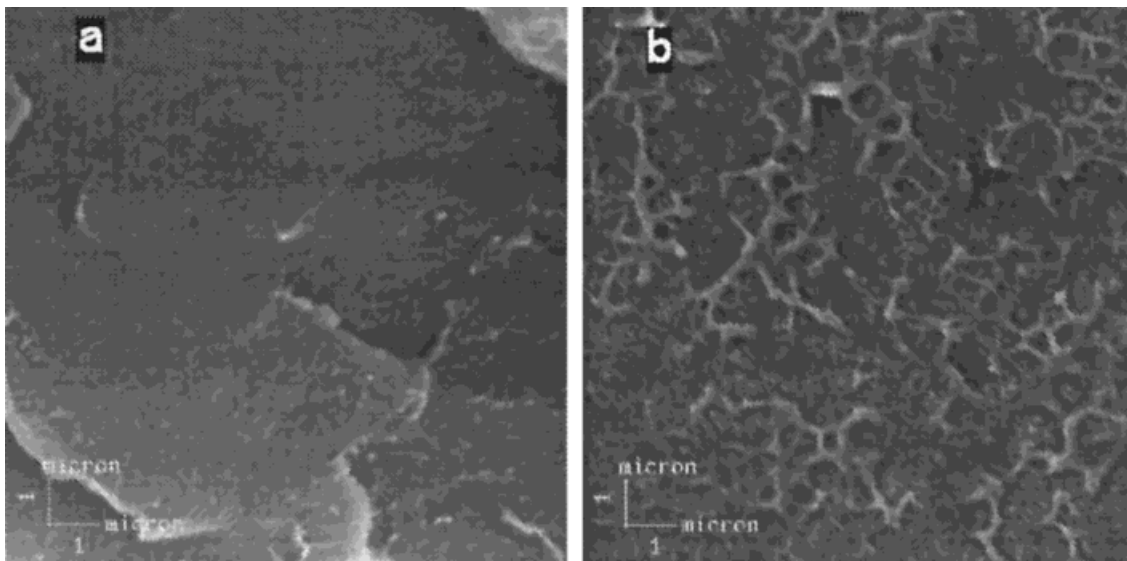


Figure 4 SEM micrographs of PS/SB (40 : 60 wt %) blends (a) without CB and (b) with 3 wt % of CB (10,000 \times).

In this article, we try to relate the electrical behavior of SB–CB and PS/SB–CB composites with the amount of bound rubber. As described in the literature¹² and summarized in the Experimental part, the samples were extracted with toluene in order to separate the free-unbound polymer. Besides unbound polymer, the toluene layer also contained CB particles well adhered to the polymer chains, as indicated by the black emulsion which remains intact after centrifuging the material at 7000 rpm for 2 h. The dry insoluble material was submitted to TGA analysis to determine the polymer–filler ratio in the gel. The results concerning the amount of bound rubber (nonextracted polymer, R_b), the amount of CB in the gel (CB_{gel}), and carbon black dispersed in the solvent (CB_{disp}) as functions of CB content and mold temperature are compared to the electrical behaviors in Table II. The absence of CB resulted in completely soluble materials in toluene, whatever the mold temperature employed. SB and PS/SB composites containing 1 wt % of CB and compression-molded at 200°C presented a small amount of bound rubber but no CB dispersed in the organic layer. These results seem to indicate that the filler is able to promote the crosslinking inside the rubber phase, but the molding conditions and the amount of CB are not enough to promote a substantial polymer–filler interaction. These samples also display higher electrical resistivity. When the material was compression-molded at 250°C, an increase of the amount of bound rubber and the presence of CB particles

dispersed in the toluene layer were observed, indicating an improved interaction between CB and the rubber phase at higher molding temperatures. Similar behaviors were also observed with composites compression-molded at 200°C but with higher CB content (3 wt %).

Composites containing a greater amount of CB and submitted to a higher mold temperature present increasing electrical conductivity by several orders. Such systems also display a high CB content in the insoluble fraction. The high CB_{gel} content associated to a relatively high amount of rubber bounded indicate the presence of a coherent three-dimensional gel structure constituted by almost all the CB particles and the polymer chains. As suggested in the literature,¹² this situation may be responsible for the higher electrical conductivity of these systems.

Morphological Analysis

The effect of the CB addition on the morphology of PS/SB blends was investigated by scanning electronic microscopy (SEM). Figure 4 displays SEM micrographs of the surface fracture related to the PS/SB (40 : 60 wt %) blends without CB and with 3 wt % CB compression-molded at 200°C. The filler is seen as the white points in the micrographs. There is no visible phase separation in the nonfilled blend [Fig. 4(a)]. The presence of a small amount of CB [Fig. 4(b)] promotes a phase separation, as indicated by the elongated and branched white chains at the fracture surface. As

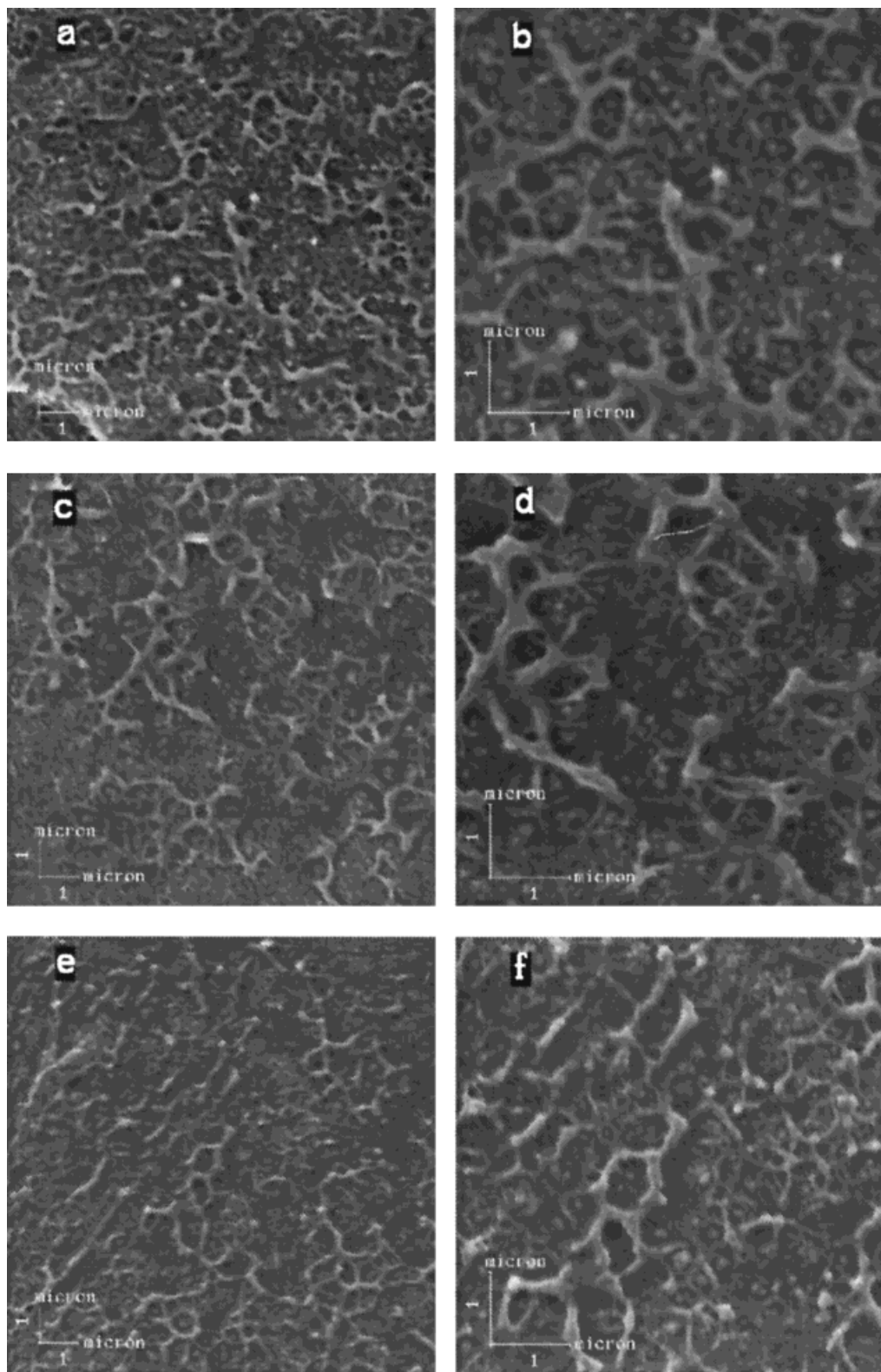


Figure 5 SEM micrographs of (a,b) SB, (c,d) PS/SB (40 : 60 wt %), and (e, f) PS/SB (80 : 20 wt %) composites loaded with 3 wt % CB and compression-molded at 200°C. The micrographs at the right side were taken at higher magnification.

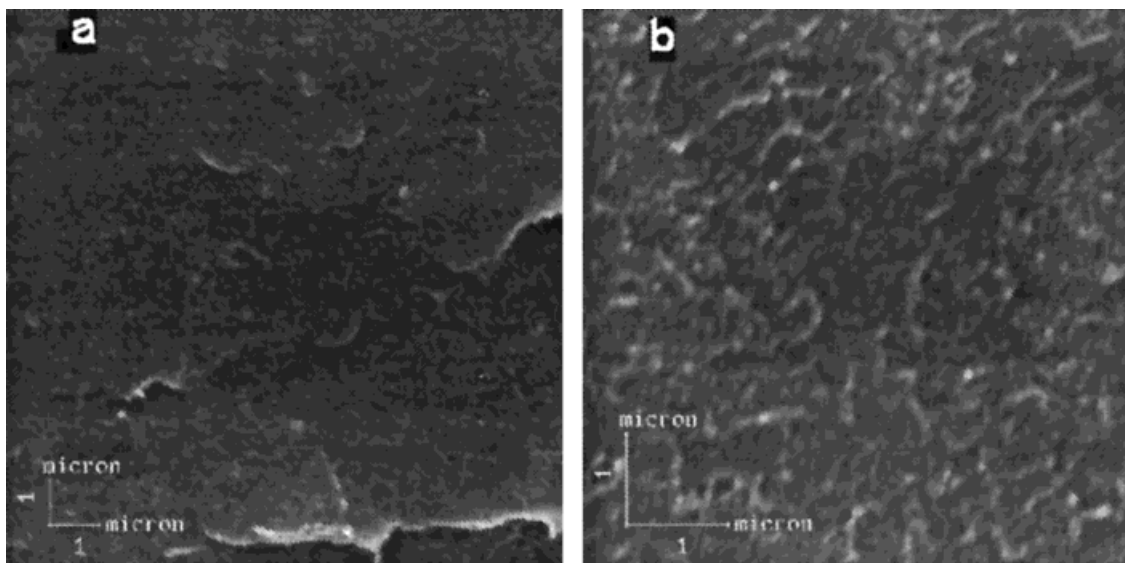


Figure 6 SEM micrographs of PS/SB (40 : 60 wt %) composite loaded with 3 wt % of CB and compression-molded at 250°C: (a) 10,000 \times ; (b) 20,000 \times .

pointed out in several articles, CB has a good affinity with polybutadiene.^{21,22} Therefore, the lighter phase in the micrograph of Figure 4(b) can be ascribed to the PBD phase containing CB.

The morphology of SB and PS/SB blends at different blend compositions is illustrated in Figure 5. All these blends are loaded with 3 wt % CB and compression-molded at 200°C. A heterogeneous morphology was observed in all the studied composites. The light phase (where the CB is supposed to be located) seems to be more continuous for SB and PS/SB (40 : 60 wt %) composites. As the PS homopolymer content increases, the white phase becomes smaller and less continuous, probably because of the decreasing amount of the PBD phase. The photographs of the same composites taken at higher magnification (Fig. 5 at the right side) indicate some amount of CB particles (white points) also located at the interface. This morphological feature may explain the decrease of the elongation at break in the CB-loaded blends reported in the previous article.¹¹ The presence of the filler at the interface is expected to disturb the good interfacial adhesion in the PS/SB systems.

The effect of the higher compression-molding temperature on the blend morphology is illustrated in Figure 6 for the PS/SB (40 : 60 wt %) blend. In this case, the white dispersed phase becomes thinner and more continuous than that observed for the same composite compression-molded at 200°C [see Fig. 5(c,d)]. The continuous pathway is so thin that it is only observable at higher magnification.

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