Polymer Bulletin 38, 95-100 (1997)

Polymer Bulletin

Electrical conductivity of polystyrene/styrene-butadiene block copolymer blends containing carbon black

K. M. N. Gamboa[1], **A. J. B. Ferreira**[1], **S. S. Camargo Jr.**[2], **B. G. Soares**[1,*]

[1] Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro,
Centro de Tecnologia, P.O. Box 68525, RJ, Brazil, 21945-970
[2] Departamento de Engenharia Metalúrgica e de Materiais, Escola de Engenharia,
UFRJ, P.O. Box 68505, Brazil

Received: 28 July 1996/Revised version: 1 October 1996/Accepted: 3 October 1996

Abstract

The electrical resistivity and mechanical properties of carbon black (CB)-filled polystyrene (PS)/styrene-butadiene block copolymer (SB) blends have been studied. Good electrical performance was achieved with pure SB and PS/SB blends indicating an inhomogeneity of these materials and the heterogeneous micro-dispersion of the CB particles. The percolation threshold of the filler inside SB or PS/SB blends is around 3.6wt%, which is lower than that expected for incompatible PS/PBD blend. The addition of small amount CB decreases the elongation at break of PS/SB blends indicating some disturbance at the interface of these compatible material.

Introduction

The addition of a particulate electrical conducting filler into a nonconducting polymer matrix causes a sharp transition from insulator to conductor system at a critical volume percent of the filler.(1-5) This "critical volume concentration", called percolation threshold, depends upon several parameters: the physical properties of the polymer matrix and the filler, the filler-polymer interactions and the processing conditions. Among the available conducting fillers, carbon black (CB) has been extensively studied because of its good interaction with some polymers and relatively low cost. In addition, the development of extra-conductive CB made possible to impart high conductivities in polymer composites at comparatively low degree of loading.

The necessary amount of CB to achieve the percolation threshold, C*, must be as low as possible to preserve the mechanical performance of the polymer and to avoid or minimize problems during processing. For this purpose, several authors have been studying the electrical behavior of CB-loaded multiphase polymer blends.(2,6-9) These systems normally display higher electrical conductivity than their pure components as a consequence of the uneven distribution of the filler into the polymer phases.(9-10) The heterogeneous distribution of CB should concentrate the filler inside one continuous phase or at the interface of two co-continuous phases. Therefore, a lower amount of CB is enough to reach the percolation threshold point.

Polystyrene/styrene-butadiene block copolymer blends (PS/SB) may be used to obtain multiphase systems with outstanding properties. The micro-heterogeneity of these blends is a function of the molecular weight of the components and the proportion of these components in the blend.(11-12)

---

[*] Corresponding author

In this communication we investigate the electrical conductivity of the SB block copolymer and the PS/SB blends loaded with CB as a function of the blend composition and CB content. The mechanical and electrical properties of these blends were also compared to polystyrene/polybutadiene (PS/PBD) blends of similar composition.

Experimental

Materials. Polystyrene (PS) (EDN-89G: M_n = 95800, M_w = 210800, density = 1.05, melt index (160°C/15Kg) = 0.55 g/10min from EDN - Poliestireno do Sul Ltda., Brazil), styrene-butadiene block copolymer (SB) (BASF Styrolux-656C: M_n = 102100, M_w = 143000, PS/PBD = 83:17 wt%, M_n of PS segment in the block copolymer = 84200, melt index (160°C/15Kg) = 4.60 g/10min) and carbon black (CB) (DEGUSSA Printex XE-2: DBP = 370 ml/100g, BET = 1000 m^2/g) were dried at 60°C in a vacuum oven for 24 hr. Polybutadiene (PBD) (Coperbo, M_n=200000, M_w=410000) was also employed in blends without purification.

Blend Preparation. PS and SB or PBD were first introduced into an internal mixer (Brabender Plasticorder) at 160°C and 20 rpm. After one minute, the CB was added and the rotor speed was increased to 60 rpm for 10 min. Blends were then compression molded at 200°C for 10 min, under 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 sandwich configuration. The electrode area was 9 cm^2. Silver paint was used between samples and electrodes so as to minimize the contact resistance.

Tensile testing was performed on an Instron apparatus 4204 in accordance with ASTM D882-83, using a crosshead speed of 10 mm min^{-1}. All tests were carried out on samples conditioned for 2 days at room conditions (25°C and 60% relative humidity). All results were the averages of at least five measurements.

Results and Discussion

The volume resistivity of PS/SB blends loaded with 3.0 and 3.6wt% of CB as a function of the blend composition is shown in Fig.1. A minimum in resistivity, lower than the resistivity of each blend constituent, was observed when 3.0wt% of CB was employed. This feature is normally found in heterogeneous binary blends and attributed to the uneven distribution of the filler.(6-9) It was reported in the literature that blends of block copolymer with one of the corresponding homopolymer may display a phase-separation morphology when the molecular weight of the added homopolymer is larger than that of the corresponding segments in the block copolymer.(11-14) As described in the experimental part, the molecular weight of the PS homopolymer used in our work is larger than the PS segments in the SB block copolymer and may also exhibit phase-separation morphology which could be responsible for the observed electrical behavior. In spite of the blend imiscibility, the block copolymer may act as a surface active material anchoring in the PS homopolymer phase.

At a little higher CB concentration (3.6 wt%), the electrical conductivity of all blends is similar to the one of the pure SB block copolymer and lower than the pure PS homopolymer. These results suggest heterogeneous micro-dispersion of CB in the pure SB and their blends with PS. In addition, the electrical conductivity does not depend on the PBD amount, as it is normally found in heterogeneous incompatible polymer blends.(15)

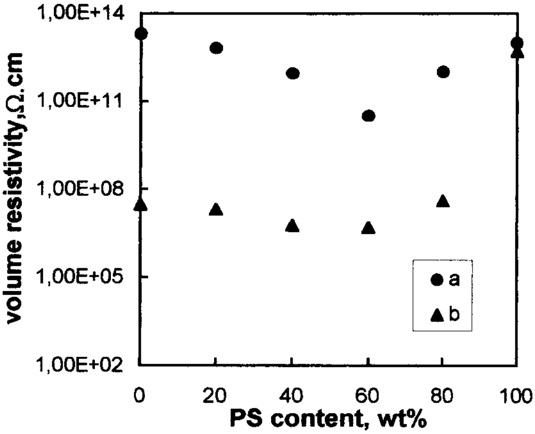

Fig.1. Volume resistivity (ρ) of PS/SB blends filled with (a) 3wt% and (b) 3.6wt% of CB Printex XE2

Figure 2 shows the electrical resistivity of PS, SB and the PS/SB (40:60 and 80:20wt%) blends as a function of the CB content. A percolation threshold (discontinuity in the curve) at around 3.5wt% of CB was observed for both pure SB block copolymer and the PS/SB blends. This value is significantly inferior to that one observed for CB-loaded polystyrene, which displays a percolation threshold at around 6.0wt%. These results are in agreement with the heterogeneous micro-dispersion of CB in the SB and PS/SB polymer blends.

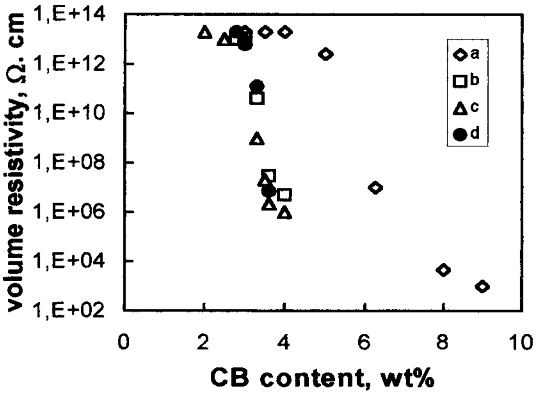

Fig.2. Volume resistivity (ρ) of (a)PS, (b)SB, (c) PS/SB (40:60wt%) and (d) PS/SB (80:20wt%) blends as a function of CB content.

It is reported in the literature that CB has a good affinity with the PBD phase.(16-17) The preferential distribution of CB in the PBD phase decreases the volume of the material in which CB is dispersed thus increasing the probability of the CB particles of touching each other. Since the pure block copolymer has a higher PBD content, the percolation threshold should occur at higher CB concentration, as compared to

PS/SB blends, due to the dilution of the CB located in the PBD phase. It is intriguing that the values of the percolation threshold of CB found in both SB and PS/SB systems are the same, suggesting that the CB distribution in these systems is not dependent on the PBD concentration. This phenomenon may be associated with the morphological peculiarity of these blends. As previously discussed, such blends may be present as a multiphase system with good adhesion between the PS homopolymer and the PS in the block copolymer located at the interface. This interfacial situation is quite different from that found in truly incompatible heterogeneous binary systems. Therefore, we decided to compare the electrical behavior of CB-filled PS/SB and PS/PBD blends with the same amount of PBD. Figure 3 presents the effect of CB content on the resistivity of PS/SB and PS/PBD blends. The percolation threshold for PS/SB blends is lower than that for the incompatible PS/PBD blends. Indeed, PS/PBD blends exhibit insulating properties over the entire CB concentration range employed in this study (ca. up to 5wt% of CB)

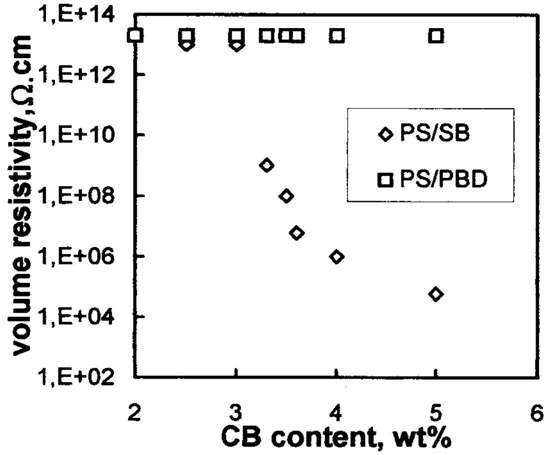

Fig.3. Volume resistivity (ρ) of PS/SB (40:60wt%) and PS/PBD (89:11wt%) blends as a function of the CB content.

It has been discussed in the literature that higher conductivity with lower amount of CB may be achieved in heterogeneous binary blends when the two phases are co-continuous and the CB is preferentially located in the minor phase or at the interface.(8) A dual-phase co-continuous morphology is considered when one phase is completely extracted without fragmentation of the sample into smaller pieces.(8) To investigate the continuity of the phases, the PS/PBD (89:11wt%) blend loaded with 3wt% of CB was submitted to selective extraction of the PS phase with methyl ethyl ketone (MEK) and the PBD phase with n-heptane. After this procedure the PS phase was completely extracted without fragmentation, indicating a two phase co-continuous morphology in this PS/PBD blend composition. The extraction of PBD phase was incomplete (only 6wt% was extracted) probably due to the bound rubber phenomenon in which part of the PBD phase becomes chemisorbed to the filler during processing.(18) Since the PBD minor phase forms a connected phase, the differences in the electrical behavior between PS/PBD and PS/SB blends may be attributed to the morphology of the PBD phase. Probably the size of the SB phase in PS/SB blends becomes thinner and elongated which helps to form current-conducting chains. In addition, one has also to account for the possibility of the filler to be located at the interface of the PS/SB system. This would favor the percolation threshold at lower amounts of filler.(8,19)

One of the great advantages of multiphase polymer systems for the development of conducting composites is the possibility of employing lower amounts of filler. These materials may display high electrical performance without substantial changes in other properties. The results concerning the mechanical properties of PS/SB and PS/PBD blends containing small amount of CB are summarized in Table 1. Incompatible PS/PBD blends display worse mechanical performance than PS/SB blends, as expected. The presence of a small amount of CB (3 wt%) has no discernible influence on the mechanical behavior of PS/PBD blends but affects substantially the properties of PS/SB blends. A substantial decrease on elongation (ε_B) was observed. The tensile strength (σ_B) and Young modulus showed a little increase with the addition of CB. The increase of ε_B and σ_B of OH- terminated PBD by adding small amount of high structure conductive CB has been described.(20) The decrease of ε_B observed in our work of PS/SB blends loaded with CB may be attributed to the filler location. Probably, a part of the CB may be located at the interface thus disturbing phase dispersion and interfacial adhesion. In the case of pure SB, there is no substantial influence of the filler on the mechanical properties of the composite.

Table 1. Effect of the addition of 3wt% of CB on the mechanical properties of PS/SB and PS/PBD blends at different compositions.

	PS/SB blends (wt%)[a]					
Mechanical properties	without CB			with 3 wt% of CB		
	80:20	20:80	0:100	80:20	20:80	0:100
tensile strength, MPa	16.9±3	24.2±1	17.3±1	19.7±5	23.3±3	14.8±3
elongation, %	32±12	15±8	27±8	1±0.3	4±2	22±9
Young modulus, MPa	1240	1270	1160	1774	1371	1235

	PS/PBD blends (wt%)					
Mechanical properties	without CB			with 3 wt% of CB		
	96:4	89:11	82:18	96:4	89:11	82:18
tensile strength, MPa	17.1±4	24.4±3	20.5±2	12.2±3	24.8±2	16.6±3
elongation, %	1±0.1	2±0.1	2±0.5	1±0.1	2±0.6	2±0.5
Young modulus, MPa	1800	1500	1400	1800	1560	1200

a) the butadiene content in the PS/SB blends is comparable to those employed in PS/PBD blends

Conclusions

The results presented indicate a strong reduction of the electrical conductivity by the addition of small amounts of conductive CB in SB and PS/SB systems. The percolation threshold points of CB in SB and PS/SB blends are lower than that in CB-loaded PS suggesting that both SB and PS/SB systems are heterogeneous with a preferential location of CB inside the PBD minor phase or at the interface. In addition, the electrical behavior is not affected by the blend composition. In spite of the heterogeneity, these materials display a better mechanical performance than PS/PBD blends, as expected for block copolymers and compatible binary blends. The decrease of the ε_B by the addition of CB may be attributed to some disturbing at the interface of PS/SB blends. The effect of the CB on the morphology of these blends as well as the effect of molding conditions on electrical properties will be discussed in forthcoming papers.

Acknowledgments.

The authors would like to thank the financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq, Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior - CAPES, CEPG-UFRJ, PADCT-FINEP and Fundação do Estado do Rio de Janeiro (FAPERJ).

References

1. Bueche F-J, (1973) J. Appl. Phys. 44:532
2. Sircar AK (1981) Rub. Chem. Technol. 54, 820
3. Miyasaka K, Watanabe K, Jojima E, Aida H, Sumita M, Ishikawa K (1982) J. Mat. Sci. 17:1610
4. Sumita M, Abe H, Kayaki H, Miyasaka K (1986) J. Macromol. Sci.-Phys. B25:171
5. Medalia A I (1986) Rub. Chem. Technol. 59: 432
6. Lipatov S, Mamunya YP, Gladyreva NA, Lebedev V (1983) Polymer Sci. USSR 25:1714
7. Geuskens G, Kezel E, Blacher S, Brouers F (1991) Eur. Polym. J. 27:1261
8. Gubbels F, Blacher S, Vanlathem E, Jérôme R, Deltour R, Brouers F, Teyssié Ph (1995) Macromolecules 28:1559
9. Sumita M, Sakata K, Asai S, Miyasaka K, Nakagawa H (1991) Polym Bull 25:265
10. Asai S, Sakata K, Sumita M, Miyasaka K (1992) Polym Bull 24:415
11. Aggarwal SL, Livigni RA (1978) Rub. Chem. Technol. 51, 774
12. Berney CV, Cheng P, Cohen RE (1988) Macromolecules 21:2235
13. Inoue T, Soen T, Hashimoto T, Kawai H (1970) Macromolecules 3: 87
14. Löwenhaupt B, Steurer A, Hellmann GP (1994) Macromolecules 27:908
15. Geuskens G, Gielens JL, Geshef D, Deltour R (1987) Eur. Polym. J. 23:993
16. Wang M-J, Wolff S, Donnet J-B (1991) Rubber Chem. Technol 64:714
17. Dutta NK, Choudhury NR, Haidar B, Vidal A, Donnet J-B, Delmotte L, Chezeau JM (1994) Polymer 35:4293
18. Meissner B (1995) Rubber Chem. Technol. 68:297
19. Levon K, Margolina A, Patashinsky AZ (1993) Macromolecules 26:4061
20. Sandén R, Stenberg B (1996) J. Appl. Polym. Sci. 59:1195