Mechanical and Processing Properties of Polystyrene-(Styrene Butadiene) Blends

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Blends of Polystyrene-(Styrene Butadiene) rubber copolymers were prepared in a twin screw extruder and then injected. The samples were characterized by various techniques and their properties compared to those of a sample with 0% rubber content. The results show that the morphology of the segregated phases in the blends as well as the chemical architecture of the rubber phase have a definite influence on the mechanical and rheological properties of these materials.

Keywords: Polystyrene-(Styrene Butadiene); copolymers; blends; morphology; mechanical properties; rheological properties

1. INTRODUCTION

It is well known that the impact properties of brittle polymers can be markedly improved by the addition of a dispersed rubber phase [1]. These materials tend to fail by crazing or shear yielding depending on the matrix nature [2, 3]. Polystyrene (PS), polystyrene-acrylonitrile

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(SAN) and poly(methylmethacrylate) (PMMA) are typical polymers which fracture by a crazing initiation mechanism [4, 5]. On the other hand, the toughening of rubber-reinforced thermoplastics depends on many factors, including size and morphology of the rubber inclusions, rubber phase volume, interfacial adhesion between the rubber and the matrix, relaxation behavior of the rubber (modulus and Tg) and composition of the matrix [6, 7].

In the case of the so-called High Impact Polystyrenes (HIPS), which are typically fabricated by polymerization of a polybutadiene-in-styrene solution, the final engineering product is a toughened polymer with rubber inclusions containing polystyrene regions. The improved toughness of HIPS is caused by the grafted polybutadiene particles acting as both craze initiator and terminators [8].

An alternative method to prepare HIPS is the dispersion of copolymers of butadiene (B) and styrene (S) in a PS matrix by mechanical blending. In this case the composition of the SB rubber copolymer determine strongly the size of the rubber inclusions and the interfacial adhesion between SB particles and the PS matrix [9, 10]. In spite of the known role of the microstructure of the phases formed on the final properties of these materials, scarce work has been dedicated to establish a clear relation between the macroscopic properties and the detailed spatial structure of the different phases of these polymeric systems. Accordingly, the aim of the present research is to study the blending of PS with a SB rubber copolymer and the mechanical properties of the obtained blends. A series of copolymers of styrene and butadiene, with different chemical architecture (i.e., linear, star and multiblock) and S/B ratios were employed as impact modifiers.

2. EXPERIMENTAL

Materials

A series of Styrene Butadiene rubbers (SBR) with different structures and compositions were kindly furnished by Hules INSA. Some of their properties are summarized below in Table I. Polystyrene (PS, RESIRENE) with a molecular weight $MW_v = 180\,000$ g/mole was used as matrix.

TABLE I   Characteristics of Styrene Butadiene rubbers employed

SBR (code)	Structure	Styrene content (% wt.)	Butadiene content (% wt.)	M_n (g/mole)	M_w (g/mole)
S3070 (SSBR)	Star	30	70	272000	313 000
MB4357 (MBSBR)	Multi block	43	57	117000	130000
L4060 (LSBR)	Linear	40	60	285000	300000
L3070 (LSBR)	Linear	30	70	207000	220000
L2575 (LSBR)	Linear	25	75	101000	113000

Blending Procedure

Blends of PS and SBR were compounded at two weight ratios (95/5 and 90/10) by melt extrusion using a Haake-Büchler co-rotating twin screw extruder, Model 600. The rotational speed in the extruder was fixed at 75 mrp's. The temperature profile in the extruder is summarized in Table II. Then, the blends were injected in a Negri-Bossi injector model NB-90 with the following specifications: injection pressure = 0.97 MPa, temperature plane profile = 200°C and cycle time = 70 s.

Two antioxidants were introduced in the blends: BHT (Dresen) and IRGANOX (CIBA). Loxamide and Magnesium stereate of Aldrich were used as lubricants.

Mechanical and Rheological Testing

The tensile strength and flex tests were performed in a Zwick dynamometer according to ASTM D638 and D790 standards, respectively. Izod groove impact was evaluated in a Tinius-Olsen Impactometer, Model 66, according to ASTM D256. The Melt Flow

TABLE II   Temperature profile of Haake-Buchler twin screw extruder utilized for blend preparation

Zone 1 (solid transport)	Zone 2 (melting)	Zone 3 (pumping)	Zone 4 (die)
190°C	200°C	200°C	200°C

Index (MFI) was measured in a Tinius-Olsen Rheometer at 200°C and 5.0 kg (ASTM D1238 norm).

Morphology Characterization

The resulting materials were prepared by ultramicrotomy in a micro-tome model MT-600-XL (RMC), which produces very thin and uni-form cuts with diamond knives. The pyramid-shaped cuts were vacuum-coated with carbon to diminish charge effects and the surface were observed by scanning electron microscopy (SEM) in a JEOL-JSM-5200 microscope, in secondary electrons mode at 25 keV.

3. RESULTS AND DISCUSSION

Results of mechanical testing for a series of polystyrenes reinforced with different rubbers, as described above are summarized in Figures 1 through 3. The incorporation of SB rubbers produced a fall of the tensile strength of the PS matrix. This decrease depends specially on the rubber content (lower values of τ_r were measured at a rubber content of 10% wt., as it is shown in Fig. 1). However, an important
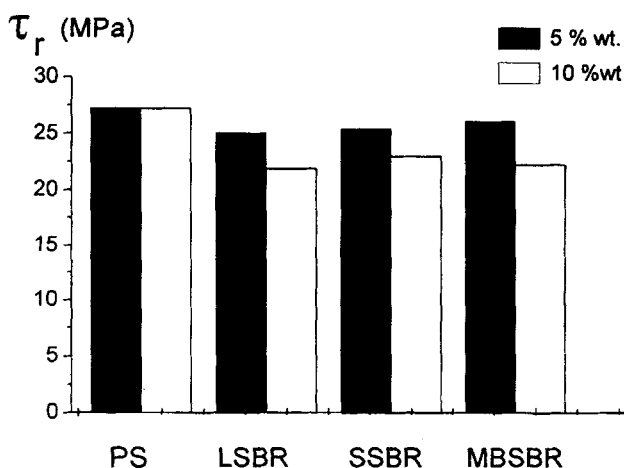
FIGURE 1   Tensile strength as a function of the different SB rubbers utilized. Linear (LSBR); star (SSBR) and multiblock (MBSBR).

increase of the elongation at rupture was detected for all the blends (see Fig. 2). Blends with star and multiblock SB rubbers showed higher values of ε_r than PS reinforced with a linear SB rubber. In the case of the star shaped SBR, the improved value of ε_r may be explained by the formation of a greater number of chain entanglements, which contribute to increase the elastic resistance to breakage. The multi-block SB chains, formed by sequences of polystyrene and polybuta-diene, may act as a sort of tensoactive and induce an improved interfacial adhesion. Therefore, the addition of this multiblock co-polymer into PS must increase the breakage resistance. The Elastic Modulus of blends with a low content of SB rubbers (5% wt.) was not affected, as can be observed in Figure 3. However, this value was con-siderably diminished when the elastomer content was increased up to 10% wt. Also, considerable decrease of the elastic modulus was detected in PS blended with star shaped and multiblock copolymers.

A noticeable improvement of the impact resistance of the PS blend-ed with the three SB rubbers was observed (see Fig. 4). This is more evident at a rubber content of 10% wt. The PS blended with a linear SBR showed the highest reinforcement. In fact, linear SBR inclu-sions initiate a greater number of crazes, which contribute to absorb more efficiently the fracture energy during impact. SEM micro-graphs (Figs. 5a, b and c) confirmed this, since a higher number of
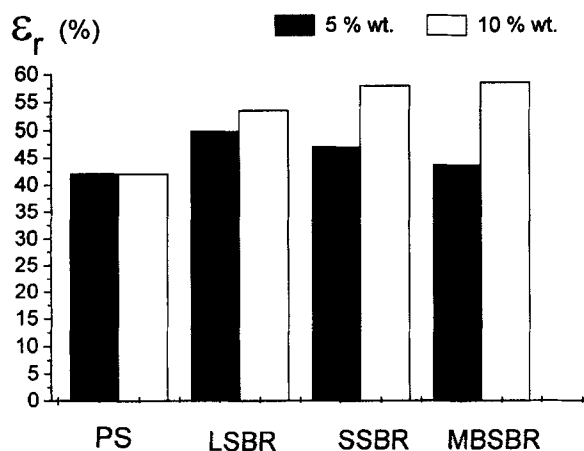

FIGURE 2   Maximum elongation as a function of the different SB rubbers utilized. Linear (LSBR); star (SSBR) and multiblock (MBSBR).
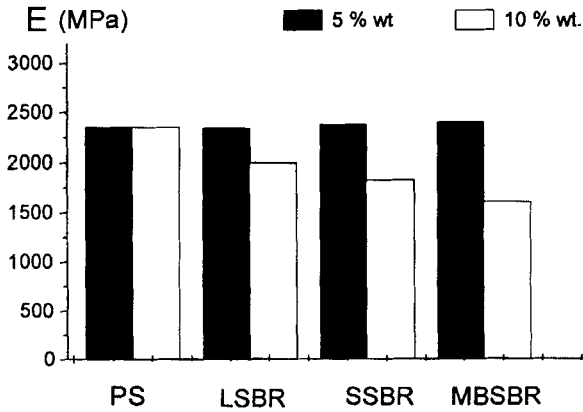
E (MPa)   ■ 5 % wt   □ 10 % wt.

FIGURE 3   Elastic modulus as a function of the different SB rubbers utilized. Linear (LSBR); star (SSBR) and multiblock (MBSBR).

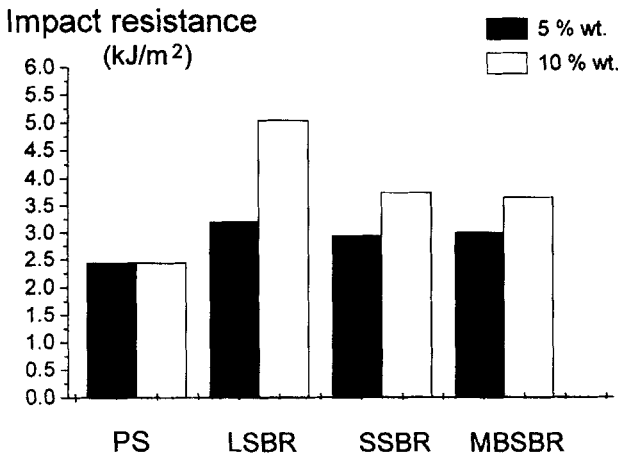Impact resistance (kJ/m^2)   ■ 5 % wt.   □ 10 % wt.

FIGURE 4   Impact strength as a function of the different SB rubbers utilized. Linear (LSBR); star (SSBR) and multiblock (MBSBR).

damaged regions were observed in the fracture surfaces of PS reinforced with linear SB rubber as compared to those of blends containing star and multiblock copolymers.

The addition of SBR inclusions into the PS matrix produced also a decrease of the Melt Flow Index (MFI), as can be observed in Figure 6.
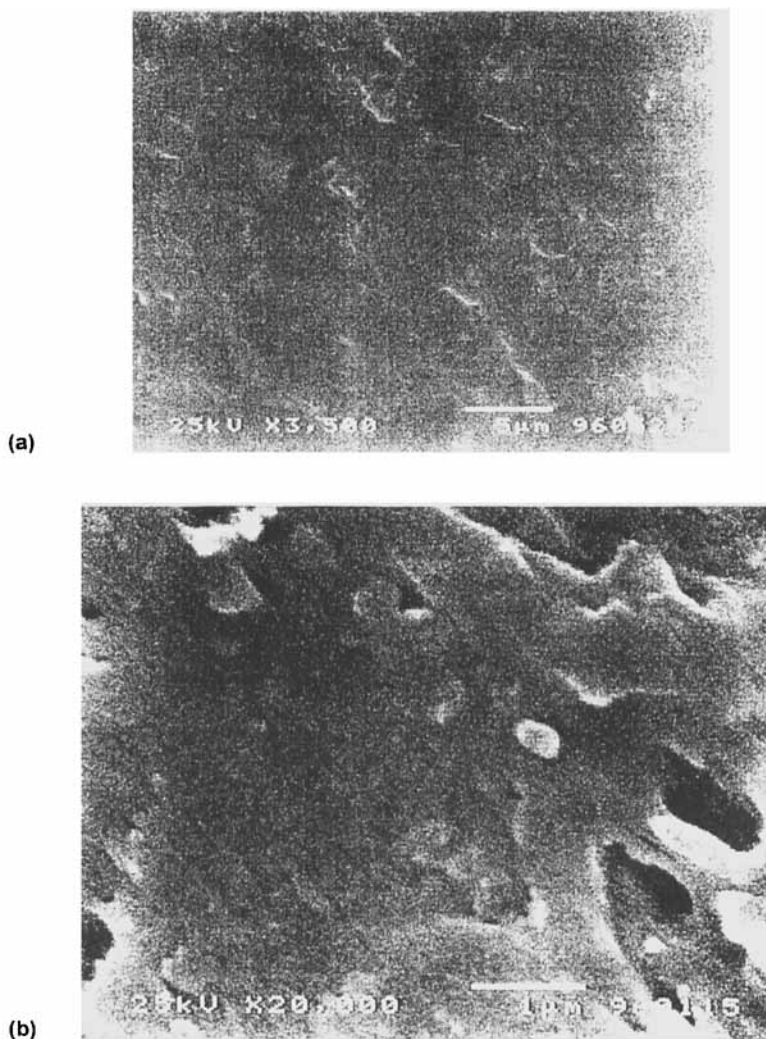
FIGURE 5   SEM micrographs of fractured surfaces of: (a) linear (LSBR); (b) star (SSBR) and (c) multiblock (MBSBR).

This decrease of viscosity of the melt blends is more evident at a higher rubber content. The rubber chain structure has a considerable influence on the melt flow index values for the blends of PS and a linear SB rubber exhibited lower M7I than the PS reinforced with star and multiblock copolymers.
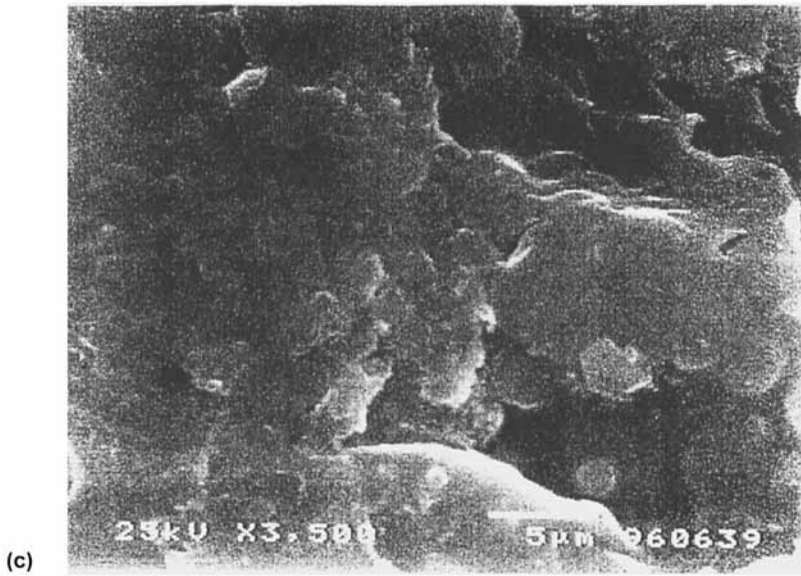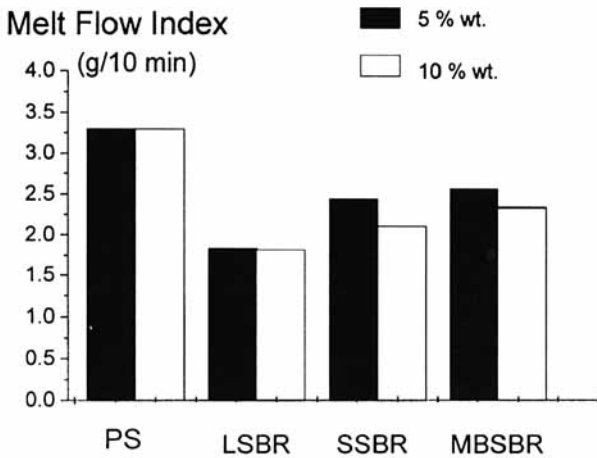
(c)

FIGURE 5 (Continued).

FIGURE 6 Melt flow index as a function of the different SB rubbers utilized. Linear (LSBR); star (SSBR) and multiblock (MBSBR).

The PS was also blended with a series of elastomers with different composition. Results of tensile strength at rupture are reported in Figure 7. As it is shown, there was a decrease of τ_r by adding the
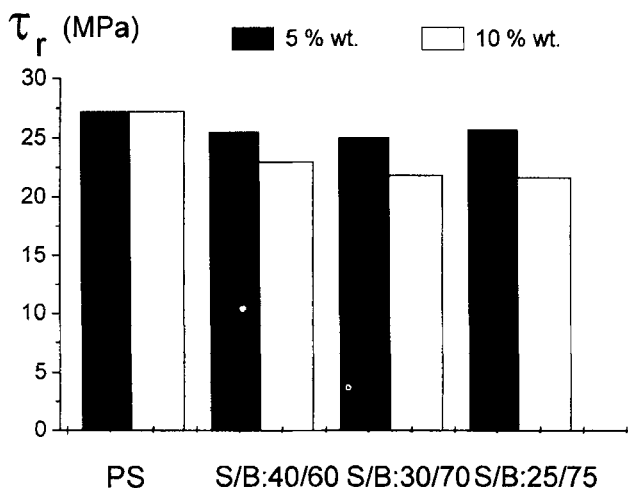
FIGURE 7   Tensile strength as a function of the SB rubber content.

rubbers, due to an earlier multiple craze initiation promoted by the elastomer nodules in the blend. A higher styrene content of the added copolymer produced a further decrease of tensile strength. This is not surprising, because an increase of the styrene content produces a fall of the glass transition temperature and of the rubbery character of the rubber. Elongation values, summarized in Figure 8, are similar for all the blends. This one may be due to a good adhesion among the copolymers caused by the presence of the styrene units in the chain. However, rubbers with a higher butadiene content show lightly improved values of ε_r because a lower glass transition of the rubber. On the other hand, a decrease of the elastic modulus was observed when rubbers with a high butadiene content were added (Fig. 9). This decrease of the modulus was specially evident at higher rubber contents.

Improved impact resistance values of the SB/PS blends are shown in Figure 10. The highest reinforcement are exhibited by blends containing a S/B ratio = 30/70. Probably an average inclusion size near to the optimal reinforcement size $(2-4\,\mu m)$ of PS is reached in this case. The elastomer nodule size depends strongly on the compatibility between the two components of a blend. A highest
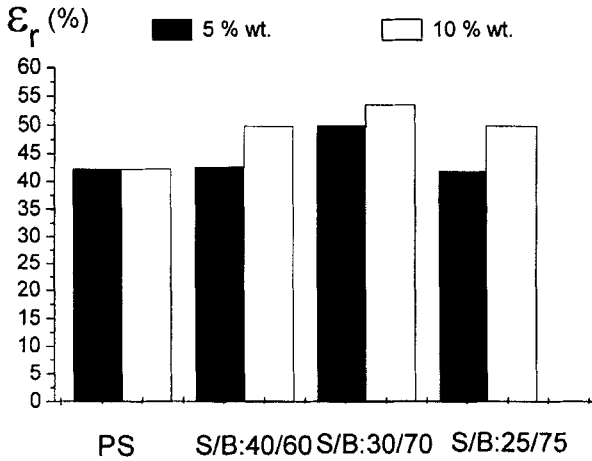
ε_r (%) ■ 5 % wt.   □ 10 % wt.

PS   S/B:40/60 S/B:30/70 S/B:25/75

FIGURE 8   Maximum elongation as a function of the SB rubber content.

E (MPa)   ■ 5 % wt.   □ 10 % wt.

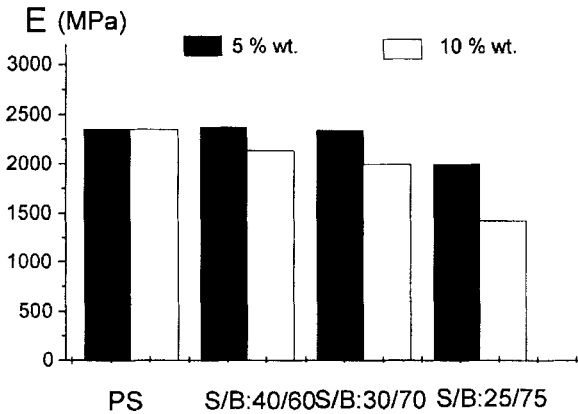PS   S/B:40/60 S/B:30/70 S/B:25/75

FIGURE 9   Elastic modulus as a function of the SB rubber content.

content in polystyrene contribute to improve the dispersion and to decrease the average size of the SBR nodules; large inclusions are obtained at low styrene contents of the copolymer, small inclusions are obtained at high styrene contents. These results indicate that the S/B ratio in a copolymer constitutes a way to control the average size of the inclusions in a PS blend. However, the efficiency to initiate
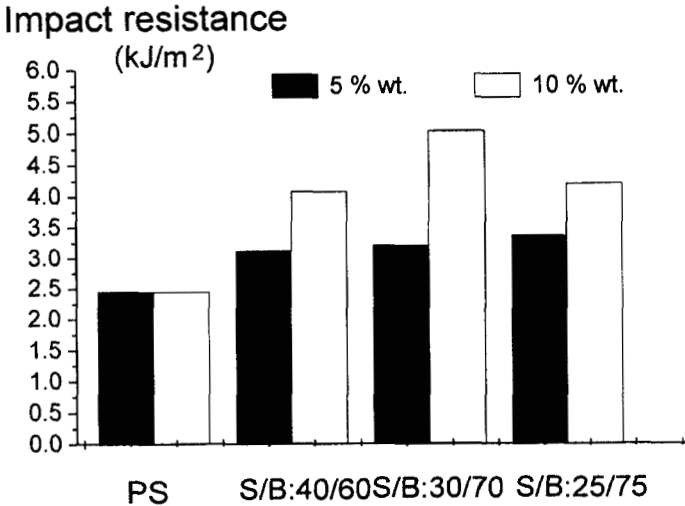
Impact resistance

FIGURE 10   Impact strength as a function of the SB rubber content.

multiple crazes diminishes with the styrene content in the rubber. This means that the reinforcement of these materials is the result of a balance between the component compatibility and the elastomer character of the impact modifier. Also, an increase of the impact resistance with the elastomer content was observed. This may be easily explained, since, when the content of rubber dispersed in the brittle matrix is increased, there will be a greater number of nodules available for craze initiation.

SEM images of fractured blends containing a rubber with a composition S/B:40/60 showed smooth fracture surfaces. It may be interpreted as a poor crazing initiation by the elastomer dispersed in the thermoplastic matrix (Fig. 11a). Blends of rubbers with a richer butadiene content exhibited more damaged surfaces with cavities (see Figs. 11b and c). The rubber-matrix lack of proper cohesion, produces these holes and it indicates that the rubber particles promote efficiently the crazing initiation.

Values of MFI as a function of the rubber composition and the rubber content show that blends of a rubber with the highest butadiene content (S/B:25/75) exhibited low viscosity values and
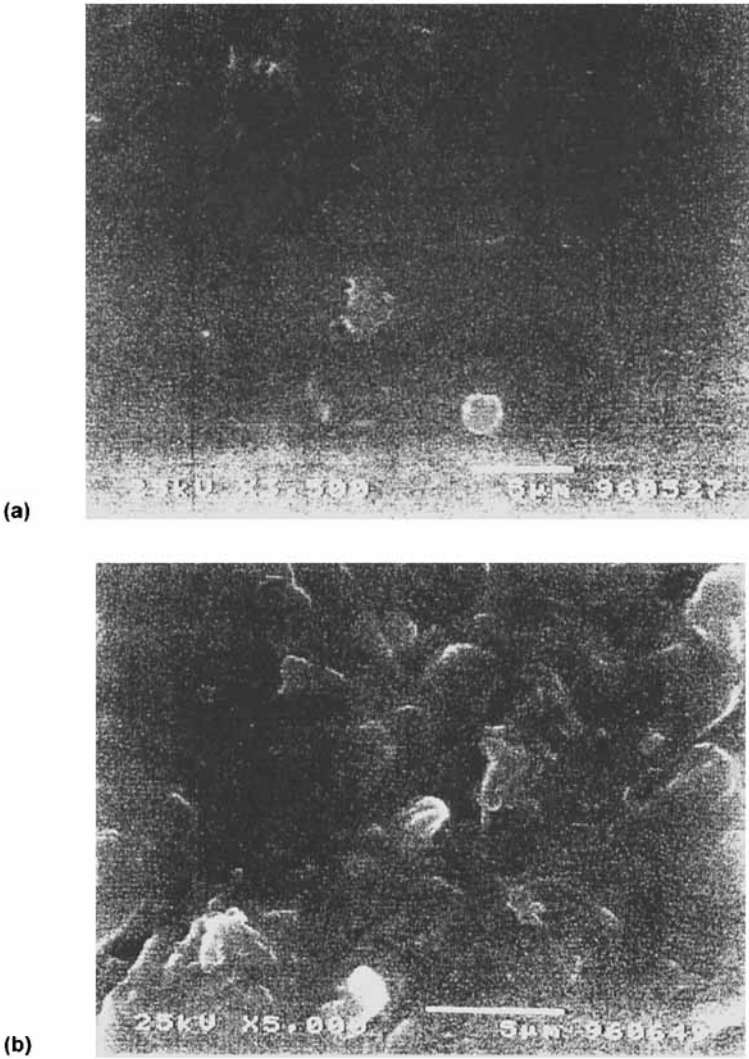
(a)

(b)

FIGURE 11   SEM micrographs of fractured surfaces of samples with S/B ratios of: (a) 40/60; (b) 30/70 and (c) 25/75.

improved processing capability compared to pure PS. However, the blends with the other S/B rubbers showed a higher viscosity. The melt flow index increased with the rubber content in the matrix, as it is expected for a melt polymer suspension.

FIGURE 11   (Continued).

4. CONCLUSIONS

A series of S/B rubbers with different structure (linear, star and multiblock) and different S/B ratio were blended with PS. The rubbers were dispersed in the brittle matrix by continuous extrusion. The effects of the rubber structure and composition on the mechanical properties of the obtained materials were studied.

It was found that linear SB rubbers act as better impact modifiers in PS than star and multiblock SB rubbers. Although the latter contributed to increase elongation of PS, the most considerable improvement of the impact resistance of PS was obtained by addition of limited amounts of a linear SB rubber. SEM confirmed the efficiency of the linear rubber nodules as crazing initiators. Indeed, more damaged surfaces were found for blends containing linear SB rubber. Similar values of tensile strength and rupture were determined for all the blends containing a structured rubber. In the case of the flow melt index, blends with star and multiblock copolymers exhibited greater values (and a lightly improved processing capability) than that of PS blended with a linear SB rubber.

The S/B ratio in linear rubbers was also varied. Improved values of maximal elongation and impact resistance were found for PS reinforced with a rubber of a S/B ratio = 30/70 wt. In this material, the rubber nodules promote efficiently the initiation of crazes, as it has been shown by SEM micrographs of the fracture surfaces. The reinforcement of this kind of blends was evidenced at a rubber content of 10% wt. However, the reinforcement of this blend was accompanied by a fall of the elastic modulus. The blends of rubbers with a high styrene content exhibited also low values of the melt flow index. Blends of rubber with a S/B ratio = 25/75 showed a low melt flow index and an improved processing capability.

Acknowledgements

References

[1] Young, R. J. (1989). "Strength and Toughness" in Comprehensive Polymer Science, Allen G. G. and Bevington, J. C. (Eds.), Pergamon Press, 2, 527.
[2] Kramer, E. J. (1984). Polym. Eng. Sci., 24, 761.
[3] Henkee, C. S. and Kramer, E. J. (1984). J. Polym. Sci., Polym. Phys. Ed., 22, 721.
[4] Bucknall, C. B. (1987). "Toughened plastics", Appl. Sci. Publ., London.
[5] Vázquez, F., Schneider, M., Pith, T. and Lambla, M. (1996). Polym. Int., 41, 1.
[6] Bucknall, C. B., Cote, P. P. and Partridge, I. K. (1986). J. Mater. Sci., 21, 301.
[7] Bucknall, C. B., Davies, P. and Partridge, I. K. (1986). J. Mater. Sci., 21, 307.
[8] Michler, G. H. (1985). Acta Polymerica., 36, 285.
[9] Castaño, V. M., Velázquez, R., Rodríguez, R. and Monroy, V. M. (1991). Materials Letters, 12, 199.
[10] Rodríguez, R., Monroy, V. M. and Castaño, V. M. (1992). Materials Letters, 12, 448.