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Polystyrene + Styrene-Butadiene Blends: Mechanical and Morphological Properties

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Blends of 3, 5 and 10 weight % of styrene-butadiene rubber (SBR) embedded in a rigid polystyrene matrix were first mixed in a co-rotating twin screw extruder and then injection molded. The blends were characterized in terms of: tensile strength, flexural strength and Izod impact and morphology by scanning electron microscopy (SEM). The addition of SBRs improves impact strength but lowers tensile and flexural modulae. Homogeneous distribution of the reinforcing phase enhances the impact strength. Best results are obtained for linear SBRs.

Keywords: polymer blends, polystyrene, styrene-butadiene, Izod impact, scanning electron microscopy.

1. INTRODUCTION

In a number of cases blending has been shown as a way to enhance impact strength of polymers [1 – 3]. This applies also to reinforcement of polystyrene by styrene-butadiene rubbers (SBRs) [4].

Depending of synthesis either by anionic or free radical polymerization [5] the SBRs can have semi-spherical, spherical [6] or elongated shapes up to the diameter of 10 μm on the average [7, 8]; star, linear, block or random macrostructures; trans-, or cis- configurations; as well as a certain vinyl percentage. The blend properties depend on these factors, as well as the interfacial adhesion between polystyrene and the elastomer [9].

Several techniques has been used for the morphology characterization, such as: digital image processing [2], nuclear magnetic resonance (NMR) and ultrasonic degradation. These provide data on particles morphology, particle size distribution and concentration of the elastomeric phase [10].

By using scanning electron microscopy (SEM) it is possible to identify a variety of structures on surfaces such as: particles (spherical, elongated, etc.), voids, crazes and shear bands formation. These factors either enhance or deteriorate the performance [4, 11].

Unfortunately, our understanding of the mechanics so as to control the crazes and thus the mechanical properties is insufficient. We do know that the craze formation depends on the applied stress, molecular-weight and content of the elastomeric phase [11] as well as on the particle diameter [12].

We have used earlier work on nylon blends as a guidance on effects of the particle size in high impact polystyrene [13, 14]; apparently particles with diameter below 2 μm are not effective in impact resistance improvement [1]. Nevertheless, there exist a controversy on increasing the rubber particle diameter because the impact resistance can go either way [14]. As a consequence, in the present work we have varied the SBR content as well as its chemical structure to elucidate the connection between morphological structure and mechanical properties of the polystyrene + styrene-butadiene blends.

2. EXPERIMENTAL

Blend Preparation. 18 blends of polystyrene and styrene-butadiene rubber (SBR) were prepared. 3, 5 or 10 wt.% of SBR (Industrias Negromex S.A., Lerma, Mexico) were embedded in polystyrene matrices (Resirene S.A., Tlaxcala, Mexico). The SBRs had different structural properties as shown in Table 1.

Each blend was first blended in a Haake-Büchler model 600 co-rotating twin screw extruder. The extruder conditions were 75 rpm and the temperature sections: zone 1: solids transport (190 °C), zone 2: melt (200 °C), zone 3: pumping (200 °C) and zone 4: die (200 °C). Afterwards, the blends were injected in a Negri-Bossi model NB-90 injector with the following specifications: injection pressure 140 psi, planar profile of temperature 200 °C; and the cycle time 70 s.

The additives employed for all blends were BHT and IRGANOX to prevent oxidation and Loxamide and magnesium stereate as lubricants. BHT = butylated hydroxytoluene = 2,6-di-tert-butyl-para-cresol; IRGANOX 1076 = octadecyl-3,5-di-tert-butyl-4-hydroxyhydro cinnamate, from Ciba Specialty Chemicals, Tarrytown, NY, USA. Loxamide = cis-13-docosenoic amide, Fisher Scientific Ltd., Ottawa, Ontario, Canada. Magnesium stereate was used as a lubricant.

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Table 1. Characteristics of the SBRs

SBR Type	Styrene Content	Butadiene Content	Structure	Isomers /(%)			Molecular weight	
				1,4-trans	1,4-cis	1,2 vinyl	M_w	M_n
1	30	70	Star	53	34	13	210,000	183,000
2	40	60	Star	53	32	15	330,000	287,000
3	25	75	Linear	53	37	10	110,000	98,000
4	30	70	Linear	53	38	9	220,000	207,000
5	40	60	Linear	53	38	9	330,000	313,000
6	43	57	Multiblock	53	34	13	180,000	162,000

Mechanical Tests. The tensile and flexural tests were carried out in a Zwick dynamometer according to ASTM D638 and D790 standards, respectively.

Izod groove impact testing was performed in a Tinius-Olsen model 66 impactometer (Olsen, Shakopee, MN, USA) following the ASTM D256. Five samples of each composition were studied. Resulting averages are reported below as impact strength.

Morphological characterization by scanning electron microscopy (SEM). The materials were submerged in OsO_4 for 48 hours and cooled in liquid nitrogen for 0.5 hours. They were cut into pyramidal shapes with a RMC model MT 6000-XL micrometer that produces very thin and uniform cuts with diamond knives and then vacuum-coated with carbon (shells between 3 to 10 nm) in a vacuum pump (E.F. Fullam) at 50 militorrs [15]. Finally, the surfaces were analyzed by SEM in a JEOL model JSM-5200 machine, in the secondary-electron mode at 25 keV.

3. RESULTS AND DISCUSSIONS

3.1 Tensile Behavior. The tensile, flexural and impact performance of the blends were evaluated by varying the following parameters: a) SBR content in the blends; b) butadiene content in the SBRs; and c) molecular weight of the SBRs.

For all blends, when increasing the SBR content the values of the tensile stress at yield point decrease, reaching the value 42.2 % lower (23.8 MPa) than that for the polystyrene matrix (41.2 MPa) (Fig. 1).

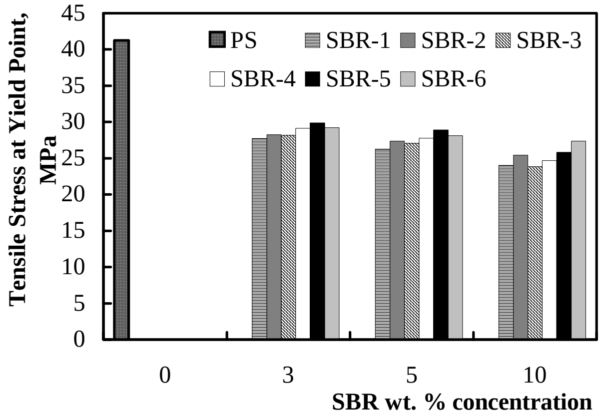
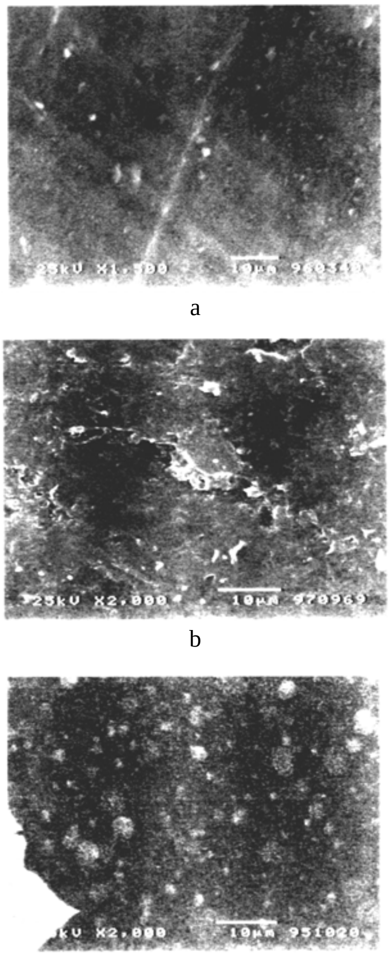


Fig. 1. Tensile stress at yield point vs SBR wt.% concentration

Addition of SBR results in a decrease of the tensile stress at yield point. This can be related to increment of the quantity of SBR particles as seen in SEM in Fig. 2. Moreover, when increasing the SBR content a more uniform distribution of particles is obtained (Fig. 2c).



a

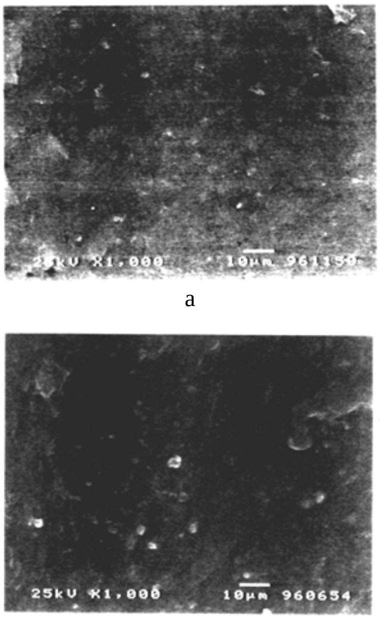
b

c

Fig. 2. Blends containing linear SBR-4: a – 3 wt.%, b – 5 wt.%, c – 10 wt.%

Refer now to the structural properties of SBRs (Table 1). For blends containing star or linear SBRs, when the butadiene content increases (or molecular weight decreases) the values of the tensile stress at yield point decrease. Moreover, blends containing multiblock-SBRs (lowest butadiene content 57 %) have higher values than blends containing linear-SBRs or star-SBRs (60 wt.% of butadiene).

The highest values of the tensile stress at yield point are obtained in blends with 3 wt.% and SBR-5. By contrast, the lowest values are those for 10 wt.% and SBR-3. High values are related to surface homogeneity, that is for a smoother phase dispersion of elastomeric particles. This is the case of blends containing star-SBRs and 3 wt.% of SBR (Fig. 3).



a

b

Fig. 3. Blends containing 3 wt.% of star SBRs: a – SBR-1, b – SBR-2

When increasing the SBR content, the values of the tensile modulae decrease (Fig. 4). This occurs down to values 36.9 % lower ($2.23 \cdot 10^3$ MPa) with respect to the polystyrene matrix.

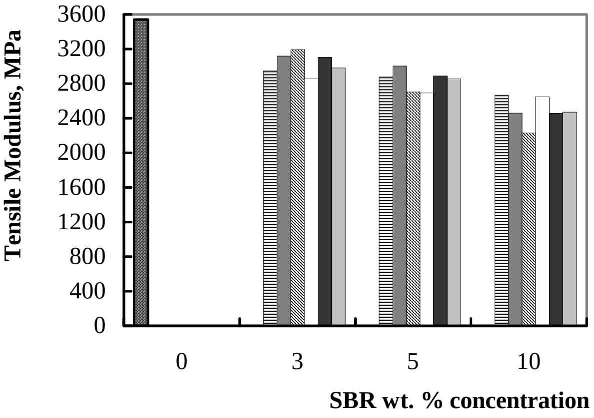
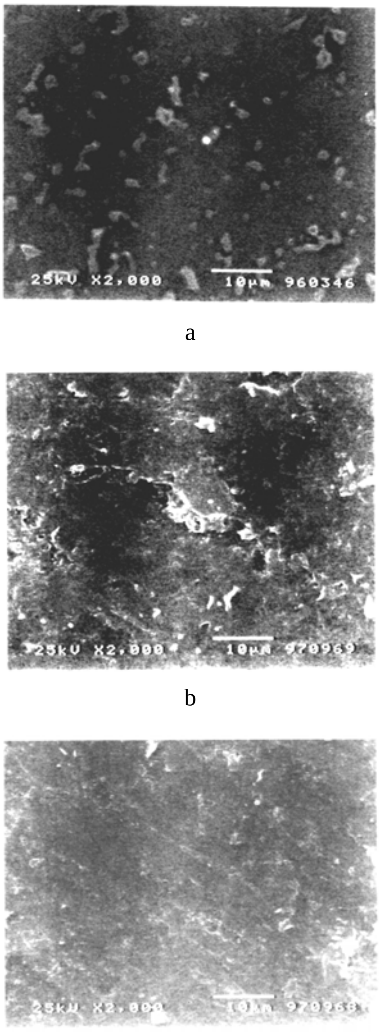


Fig. 4. Tensile modulus vs SBR wt.% concentration (marked as in Fig. 1)

According to butadiene content in the SBRs, for blends containing star-SBRs the values diminish when increasing the butadiene content from 60 % (SBR-2) to 70 % (SBR-1). For blends containing linear-SBRs, there exist a minimum value for tensile modulus with 70 % of butadiene content (SBR-4). This can be related to non-homogeneous surfaces (Fig. 5b) with the presence of particles of different shapes and sizes. In general, the increment of butadiene content in the SBRs when blending with polystyrene first generates polydispersity of particle sizes and then smooth surfaces.

Finally, blends containing multiblock-SBRs have higher tensile modulae values than blends containing linear-SBRs (see again Fig. 1). The highest values are obtained in the presence of wide distributions of particles with different shapes and sizes (Fig. 6b). These conditions generate non-homogeneous surfaces.



a

b

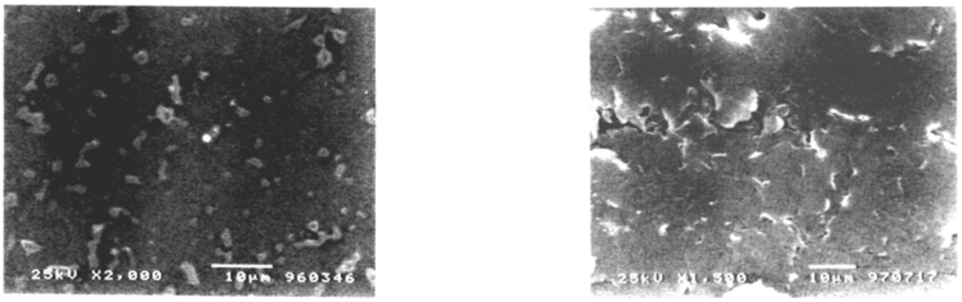
c

Fig. 5. Blends containing 5 wt.% of linear SBRs: a – SBR-3, b – SBR-4, c – SBR-5

3.2 Flexural Behavior. The flexural stress at yield point values decrease when increasing the SBR content, independently of the kind of SBR (Fig. 7), with respect to the polystyrene value of 90.7 MPa. As for tensile behavior, the highest values are obtained for 3 wt.% of SBR and SBR-3. Conversely, the lowest values are obtained for 10 wt.% of SBR and SBR-3. In general, for all blends the flexural stress values are larger than tensile values. Moreover, the values diminish until 40.4 % on average, comparable to tensile values with 42.2 %.

The increment of SBR content generate lowering of the flexural stress at yield point and non-homogeneous surfaces, with a distribution of particles with different shapes and sizes. As seen in Fig. 7, these factors produce less flexion resistant materials. The SEM surfaces are shown in Fig. 8.

In terms of characteristics of SBRs, for blends containing star-SBRs, when increasing the butadiene content in the SBRs the flexural stress at yield point increases – a similar behavior as for tensile modulus.



95 % PS + 5 % SBR-3 95 % PS + 5 % SBR-6

Fig. 6. Blends containing 5 wt.% of SBR: a – linear: SBR-3, b – multiblock: SBR-6

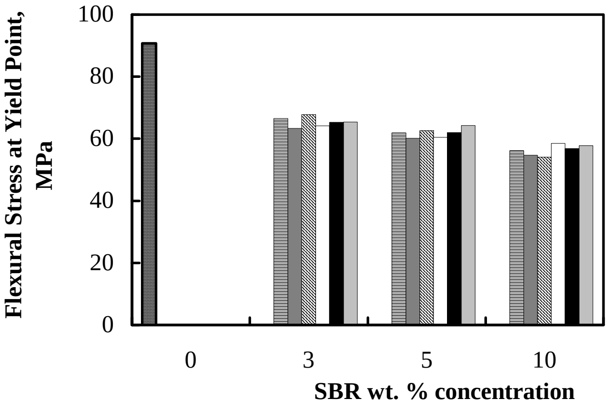
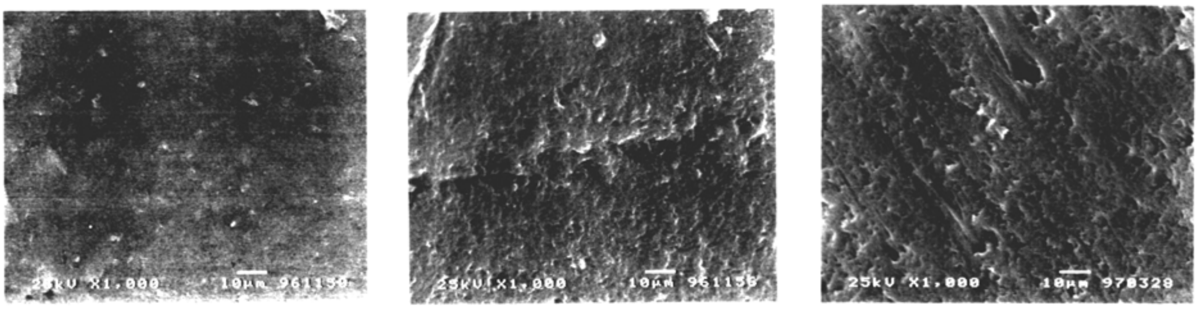


Fig. 7. Flexural Stress at Yield Point vs SBR wt.% concentration (marked as in Fig. 1)



a b c

Fig. 8. Blends containing star SBR-2: a – 3wt. %, b – 5 wt.%, c – 10 wt.%

Consider now blends containing linear-SBRs, confronting again stress values in Fig. 7 with SEM micrographs. First, when increasing the butadiene content (from Fig. 5a to Fig. 5b) the values increase, passing through a maximum value (Fig. 5b), then decreasing for a further increase of the butadiene content (Fig. 5c).

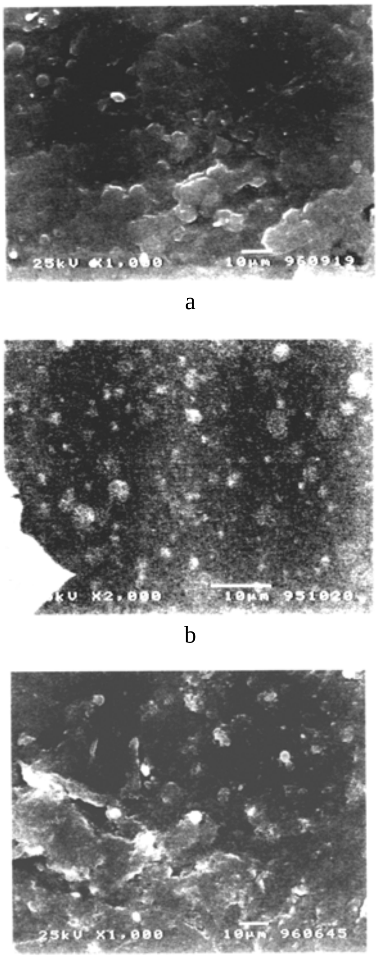
The highest values of flexural stress at yield point are obtained for surfaces with a distribution of particles of similar size without voids or elongated structures (Fig. 9b). The morphology changes for blends containing 60 wt.% of butadiene where agglomerate particles are visible (Fig. 9a). For 75 wt.% of butadiene, the morphology becomes less homogeneous with a wide distribution of particle sizes and substantially deformed particles (Fig. 9c). This lowers values of the flexural stress at yield point. Finally, blends containing multiblock-SBRs have higher values than blends containing linear-SBRs or star-SBRs, with both kinds of blends containing more butadiene.

Consider now modulae results. When increasing the SBR content, the modulae go down (Fig. 10) with respect to the polystyrene value of $2.82 \cdot 10^3$ MPa. Similar behavior is observed for tensile modulae. The lowest values for flexural modulae (19.4 % lower on the average with respect to the polystyrene matrix) are obtained for blends with 10 wt.% of SBR and SBR-3. In general, the values of the flexural modulae are lower than in tension by 36.9 %).

As for morphologies created in tensile modulus determination, an increase in the SBR content results in less homogeneous surfaces - as shown in Fig. 11.

According to characteristics of SBRs, for blends containing either star-SBRs or multiblock-SBRs the flexural modulae values vary, either decrease or increase when increasing the butadiene content. For blends containing linear-SBRs, the values decrease when increasing the butadiene content (or lowering the molecular weight).

3.3 Impact Behavior. In general, when increasing the SBR content the impact strength increases independently of the kind of SBR (Fig. 12). The highest values are obtained for blends containing linear-SBRs, either SBR-4



a

b

c

Fig. 9. Blends containing 10 wt.% of linear SBRs: a – SBR-5, b – SBR-4, c – SBR-3

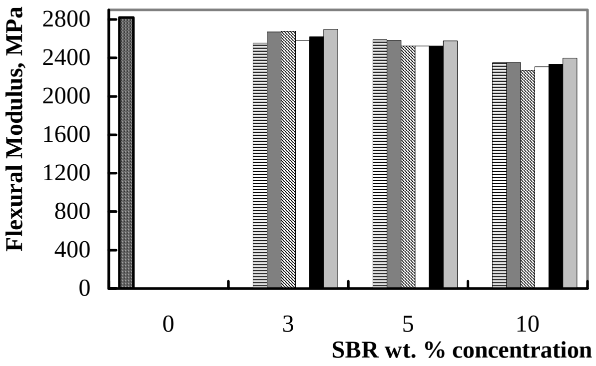
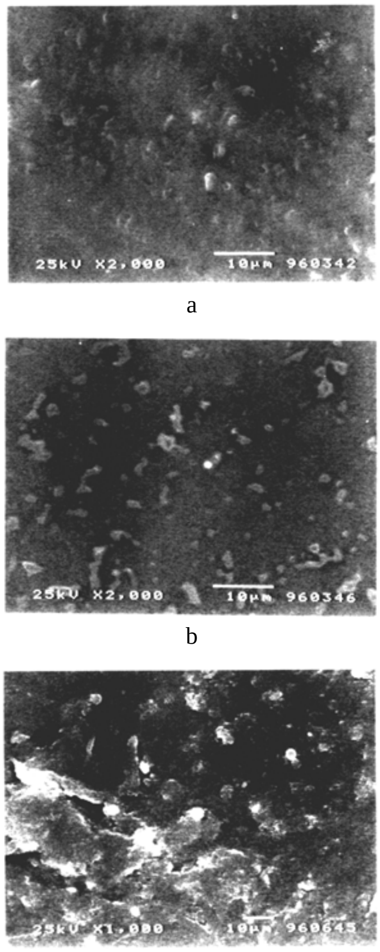


Fig. 10. Flexural modulus vs SBR wt.% concentration (marked as in Fig. 1)



a

b

c

Fig. 11. Blends containing linear SBR-3: a – 3 wt.%, b – 5 wt.%, c – 10 wt.%

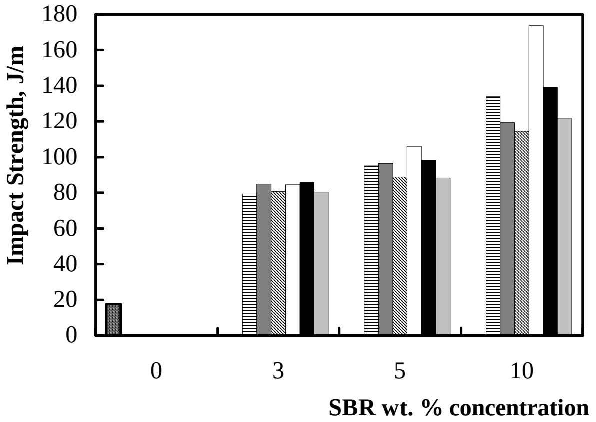


Fig. 12. Impact strength vs SBR wt.% concentration (marked as in Fig. 1)

or SBR-5; we see tenfold improvement with respect to the Izod impact strength for the pure polystyrene matrix (17.6 J/m). In contrast, the lowest values are obtained for blends containing SBR-3, with 450 % of improvement. It is important to mention that the SBR-4 and SBR-5 have the highest molecular weights: 220,000 and 330,000 respectively, and 53 % of trans-1,4-; 38 % of cis-1,4- and 9 % of vinyl-1,2- configurations.

It is possible to relate the impact strength results with the surface morphology and to evaluate the effects of the kind and content of SBR utilized. In general terms, when increasing the SBR content the blend surfaces are changing and the impact strength is improved. We can observe several behaviors: a) an increment of the quantity of particles when increasing the SBR content (Fig. 2); b) the morphology of the highest impact blend (Fig. 2) reveals fair homogeneity, with nearly-spherical elastomers dispersed in the matrix that act as in-situ reinforcing agents.

The sizes of the small particles are of the order of few microns, what agrees with earlier results [7]. The highest impact strength values are thus related to homogeneity in the surface morphology.

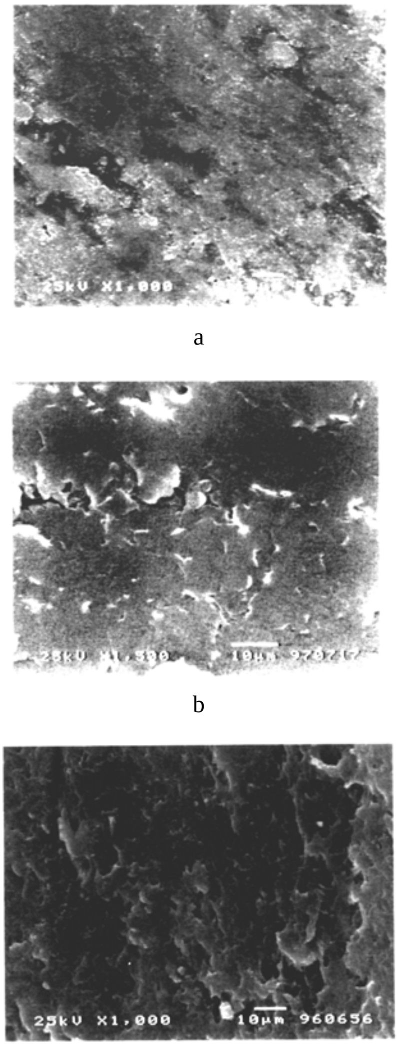


Fig. 13. Blends containing multiblock SBR: a – 3 wt.%, b – 5 wt.%, c – 10 wt.%

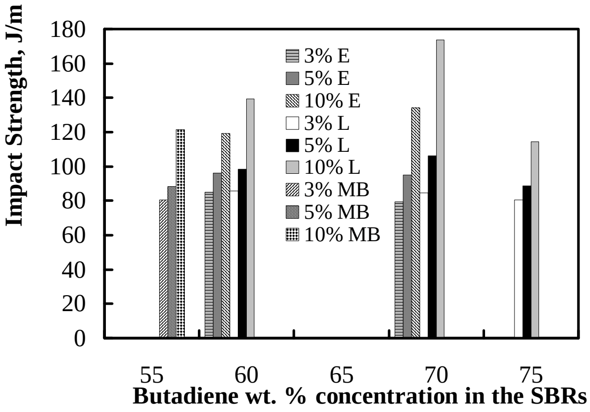


Fig. 14. Impact strength vs butadiene wt.% concentration in the SBRs

Nevertheless, the rule that an increase in the SBR content enhances the impact strength does not hold for blends containing SBR-1 or SBR-6. For the last one, surfaces corresponding to 5 wt.% of SBR are more homogeneous than for blends with 3 wt.% or 10 wt.% of SBR (Fig. 13). The blend homogeneity with 5 wt.% of SBR correspond to the high number of particles, a feature that allows the highest values of the impact strength.

According to butadiene content in the SBRs, the highest values are obtained for blends containing linear SBRs. In these kind of blends, first the impact strength increases, passes trough a maximum for 70 % of butadiene and decreases for higher butadiene content (Fig. 14).

For blends containing star-SBRs, when increasing the butadiene content, the impact strength values increase. Finally, blends containing multiblock-SBRs have the lowest impact strength values of all blends.

4. CONCLUSIONS

The mechanical properties improvement of polystyrene + styrene-butadiene rubber blends depends on structural characteristics and content of the SBRs employed. In general, increments of the SBR content produce impact strength improvement on one hand, and decrease of the tensile and flexural modulae on other. Moreover, the average impact strength values are comparable to the highest impacts values reported for various polymeric systems which are manufactured by sophisticated techniques. It is possible to propose the most adequate styrene/butadiene ratios, as well as the best chemical structure for manufacturing good impact materials.

According to the characteristics of the SBRs, when increasing the butadiene content or else lowering the molecular weight: 1) for blends containing star-SBRs the yield point and the elastic modulae values decrease (in tension and in flexion); 2) for blends containing linear SBRs, the yield point stress and the elastic modulae values have a maximum for 70 wt.% of butadiene in tension; but these values diminish in flexion; 3) for blends containing multiblock-SBRs the yield point and the elastic modulae values are higher than for blends containing star or linear-SBRs.

The highest impact values are obtained for blends with a homogeneous morphology of dispersed particles of similar size and without voids or elongated structures. Moreover, the morphology of blends containing star or multiblock-SBRs shows low surface homogeneity. More specifically, the star-SBRs show polydispersity of irregular elastomeric particles and the multiblocks show elongated structures.

Addition of a second phase is admittedly only one method of polymer reinforcement. A variety of such method exists [16]. Among others, material deformation - such as for instance by punching [17 – 19] – can also enhance (or otherwise) mechanical behavior.

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