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### The Influence of Chemical Topology on Morphology, Elastic and Rheological Properties of Rubber-Reinforced Polymer Blends

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# The Influence of Chemical Topology on Morphology, Elastic and Rheological Properties of Rubber-Reinforced Polymer Blends

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Blends of random polystyrene-SBR were prepared first in a co-rotating twin screw extruder and then injected for being used as impact modifiers. Several experiments were realized, changing the chemical composition of SBR. The blends were made with 5% of SBR in a rigid matrix of polystyrene and the SBRs had different compositions. The samples were characterized by different techniques and compared to a sample with 0% SBR content. The tests performed were: a) mechanical: tensile strength, flexion and Izod impact; b) rheological: melt index flow and melt index razor-sharp at 205 °C and c) morphology: studied by scanning electron microscopy (SEM). The results show that the morphology of surfaces and the mechanical and rheological properties of these blends depend on the relation Styrene/Butadiene and on the structure of the SBRs.

*Keywords:* Polystyrene-styrene-butadiene rubber; blends; impact modifier; morphology

## INTRODUCTION

In recent years, applied and pure scientists have dedicated increasing effort to the study of polymer blends, particularly rubber-reinforced

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polymers such as rubber-styrene, to the extent that it has become one of the most active areas of research and development in polymer science and technology, with a wide range of industrial applications such as automotive bumpers and helmets [1]. These materials combine more than one desired property not found in single polymer system. Moreover, the materials that form the composites are specifically chosen in order to achieve a set of properties that are required for specific purposes.

Natural and synthetic elastomers are of special interest as modifiers for many engineering plastics, particularly SBR (styrene-butadiene rubber) [2]. In fact, one of the most important artificially produced composites is the so-called high-impact polystyrene (HIPS), where the impact properties depend on parameters like : the content and particle size distribution of the rubbery phase, the morphology of the rubber particles, the chemical structure of rubber phase, the phase volume fractions and the adhesion between the two phases. Therefore, it is extremely relevant to find out the morphology and particles size distribution of rubber phase, if a full understanding of the properties of these materials is to be achieved.

The discrete rubber phases in HIPS are formed with particles of very complicated structures, generally solid particles with a size in the range from 0.5 to 10  $\mu\text{m}$ . The essential features of this type of composites is the improvement on fracture strength especially, because the matrix polymer is brittle, even when there is a limited reduction in their stiffness, yield stress and creep resistance.

Conventional scanning electron microscopy (SEM) shows a homogeneous morphology of the rubber particles. However, to obtain a quantitative picture, more sophisticated tools such as digital image processing [3] and the measurement of NMR (nuclear magnetic resonance) and ultrasonic degradation have been employed. These alternative techniques provide valuable data on particles morphology: particle size distribution and percentage of rubber [4]. Also, it has been found that the molecular weight of the rubber embedded affect the rheological properties such as melt index flow (MIF) [5].

In the present work, polystyrene-SBR blends with different chemical structure, i.e. different topologies, from linear to star-shaped, of the SBR phase were synthesized by non-reactive extrusion and injection. The mechanical testing of the resulting materials was carried out by using a Zwick dynamometer in the case of tension and flexion; for Izod

groove impact test an Impactometer was used. Melt Index Flow was evaluated in a rheometer and the razor-sharp viscosity in a Zwick dinamometer. All test were realized according to ASTM standards. Finally, the morphology was analyzed by SEM.

## EXPERIMENTAL

### a) Blend Preparation

Six blends of polystyrene 95% with 5% of SBR (Hules INSA) with different chemical composition and structures, identified by the numbers 1 through 6, and also a blend of 0% content of rubber, were studied. The SBR characteristics are described in Table I.

Each blend was first prepared in a Haake-Büchler co-rotating twin screw extruder model 600. The conditions of extruder were 75 rpm and the following 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 injector model NB-90 with the following specifications : injection pressure : 140 PSI, plane profile of temperature : 200 °C, charge speed of material : 150 rpm, injection speed : arbitrary scale B-O, cycle time : 70 seconds.

The additives employed for all blends were : BHT and IRGANOX to prevent oxidation and loxamide and magnesium stearate as lubricants.

### b) Mechanical and Rheological Testing

The tensile strength and flexion tests were performed in a Zwick dinamometer according to the ASTM procedures D638 and D790, respectively.

TABLE I Compositions of SBRs

<i>SBR</i>	<i>Styrene</i>	<i>Butadiene</i>	<i>Chemical Structure</i>
1	30	70	Linear
2	30	70	Star
3	43	57	Multiblock
4	40	60	Linear
5	30	70	Linear
6	25	75	Linear

Izod groove impact was evaluated in a Impactometer Tinius-Olsen model 66, according to ASTM procedure D256; Melt Index Flow (MIF) in a rheometer Tinius-Olsen at 200 °C and 5.0 kg according to ASTM procedure D1238 and razor-sharp viscosity at 205 °C and speed of 0.1 in/min was studied in a Zwick dinamometer.

### c) Morphology Characterization

The resulting materials were prepared by ultramicrotomy in a microtome model MT 600-XL (RMC) which produces very thin and uniform cuts with diamond knives. The pyramid-shaped cuts were vacuum-coated with carbon to diminish charging effects [6] and the surfaces were observed by scanning electron microscopy (SEM) in a JEOL-JSM-5200 machine, in secondary electrons' mode at 25 KeV.

## RESULTS AND DISCUSSION

The results of the mechanical testing are summarized in Tables I through IV. As known, tensile test provide the stress that each sample can endure when the material is subjected to an external force. In Table II the stress at : initial deformation (F-S), yield (F-B) and rupture (F-R) is shown. For each stress, the corresponding elongations recorded were : initial deformation (L-S), yield (L-B) and rupture (L-R). Finally, the elastic modulus in tension (E-modulus-T) for all blends, were obtained.

In Table III, the flexion tests of samples prepared are summarized. The maximum force at yield point (F-B) allowed to obtain the maxi-

TABLE II Tensile properties of blends

<i>Exp</i>	<i>F-S</i> (KPSI)	<i>F-B</i> (KPSI)	<i>F-R</i> (KPSI)	<i>L-S</i> (%)	<i>L-B</i> (%)	<i>L-R</i> (%)	<i>E-Modu.</i> (KPSI)
0	3.835	3.969	3.954	1.452	41.941	42.158	340.842
1	3.416	3.608	3.596	1.391	<b>50.349</b>	<b>50.694</b>	309.862
2	3.544	3.712	3.690	1.449	46.447	47.004	344.044
3	3.689	<b>3.828</b>	<b>3.794</b>	1.470	43.631	43.690	348.52
4	3.610	3.735	3.706	1.465	44.566	42.436	343.533
5	3.558	3.665	3.632	1.454	49.145	49.805	340.066
6	<b>3.726</b>	3.796	3.730	<b>1.608</b>	41.265	41.739	<b>289.155</b>

TABLE III Flexural properties of blends

<i>Exp</i>	<i>F-bB</i> ( <i>KPSI</i> )	<i>F-B</i> ( <i>Lb<sub>f</sub></i> )	<i>L-bB</i> (%)	<i>L-bR</i> (%)	<i>f-B</i> ( <i>in.</i> )	<i>f-R</i> ( <i>in.</i> )	<i>E-Modu.</i> ( <i>KPSI</i> )
0	9.064	<b>21.970</b>	5.338	9.013	0.299	0.501	331.094
1	8.159	19.817	5.728	9.017	0.318	0.501	300.265
2	8.143	19.777	<b>5.932</b>	9.012	<b>0.329</b>	0.501	299.897
3	<b>8.427</b>	20.428	5.654	9.014	0.314	0.501	302.962
4	8.204	19.830	5.366	9.011	0.301	0.501	299.098
5	7.861	19.055	4.273	9.011	0.237	0.501	299.561
6	8.058	20.415	4.874	<b>9.162</b>		0.501	273.623

mum stress at yield (*F-bB*). Values for elongation at yield (*L-bB*) and rupture (*L-bR*) are given. The elastic modulus in flexion (*E-modulus-F*) is obtained.

The path to rupture (*f-R*) for this sort of materials overcomes the capacity of the instrument. So, it was necessary to fix it at 0.500 inch. The values obtained at this point are taken as the rupture point of the material.

In Table IV, the energy that the material can endure until fracture is calculated by Izod groove impact. The data are expressed in  $Lb_f$ -ft/in.

The Melt Index Flow (MIF) data are shown in Table V. The MIF gives information on the molecular weight of the molecule of the investigated polymer. To carry out this test the conditions of analysis such as temperature and weight, must be established choosing similar conditions as the injection or extrusion industrially used for preparing these materials. Finally Table VI contains data over Razor-sharp viscosity. Both tables permits to know the processability of the materials.

From Table II, it can be observed that the blend with **SBR-3** has the best properties in tension followed by blend with SBR-6.

TABLE IV Izod impact properties of blends

<i>Experiment</i>	<i>Impact (ft-lb<sub>f</sub>/in)</i>	
	$1/2'' \times 1/2''$	$1/2'' \times 1/8''$
0	1.1787	1.3655
1	<b>1.6727</b>	<b>2.3047</b>
2	1.4211	1.8869
3	1.4518	1.7965
4	1.5016	1.7599
5	1.5458	2.0508
6	1.6235	1.9383

TABLE V Melt Index Flow of blends

<i>Experiment</i>	<i>MIF (g/10 min)</i>
0	3.3000
1	<b>1.8327</b>
2	2.4427
3	2.5607
4	2.4550
5	2.3892
6	<b>4.0817</b>

TABLE VI Razor-Sharp Viscosity of blends

<i>Experiment</i>	<i>Force (lb<sub>f</sub>)</i>	<i>Razor-Sharp Stress (PSI)</i>	<i>Razor-Sharp Viscosity (PSI)</i>	<i>Razor-Sharp Viscosity (Poises)</i>
0	148.267	8.364	0.5558	266.1360
1	<b>159.177</b>	<b>8.979</b>	<b>0.5967</b>	<b>285.7000</b>
2	147.763	8.335	0.5540	265.2550
3	150.257	8.476	0.5630	269.7240
4	149.873	8.454	0.5620	269.0860
5	150.161	8.471	0.5630	269.5640
6	158.979	8.968	0.5960	285.3648

According to the content of styrene/butadiene, SBR-3 has the highest content of Styrene (43%) and SBR-6 the smallest (25%). Moreover, the morphology of blend with **SBR-3** showed greater homogeneity (micrograph of Fig. 1) with a smoother and better phase dispersion which can be compared with the micrograph correspond to blend with 100% polystyrene where exists lower homogeneity and voids (see micrograph 2). Also, it was observed that the tensile properties decrease respect to blend with 0% of SBR, in approximately 3.5%.

The elongation at yield point (L-B) is bigger in blend with **SBR-1** followed by blend with SBR-5. According with the chemical structure of SBR's, SBR-1 is linear, whereas SBR-5 is linear. The morphology of blend with **SBR-1** showed lower homogeneity (Fig. 3). The elongation of blends change up to 16.38% with respect to the sample with 0% of SBR.

Also, according to Table II, the blend with more elongation is the blend with **SBR-6** followed by the blend with SBR-1. The blend with **SBR-6** presents lower content of styrene (25%) with linear structure. The micrographs showed irregular shapes of the SBR's phase (Fig. 4).

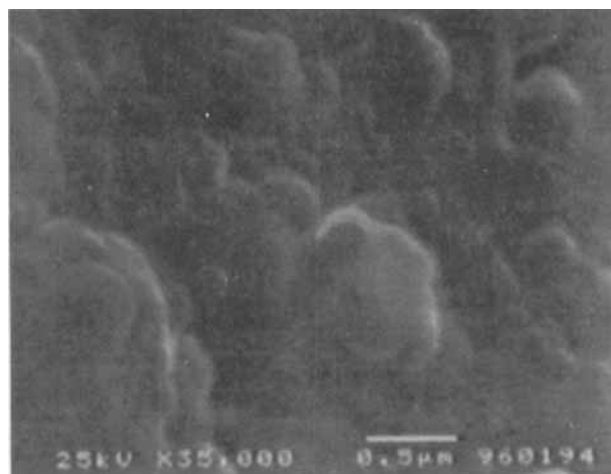


FIGURE 1 SEM micrograph of 43/57 Styrene/Butadiene in linear SBR.

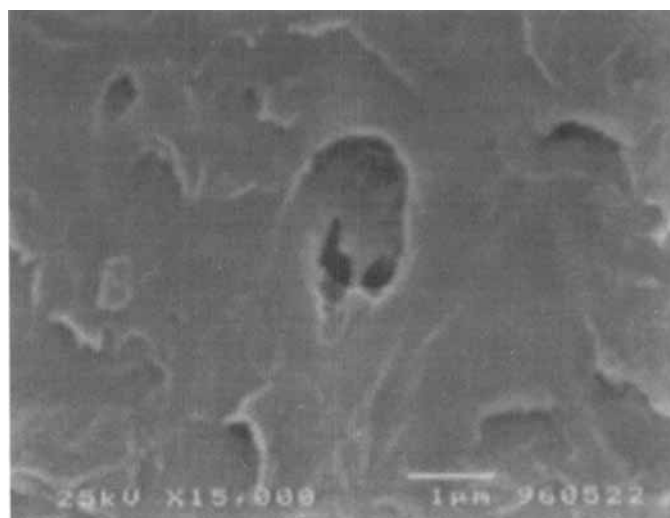


FIGURE 2 SEM micrograph of 100% Polystyrene.

From Table III, it can be observed that the blend with **SBR-3** has the maximum flexural stress at point yield, followed by the blend with **SBR-4**. Again, the blend with **SBR-3** (43% Styrene) showed the best



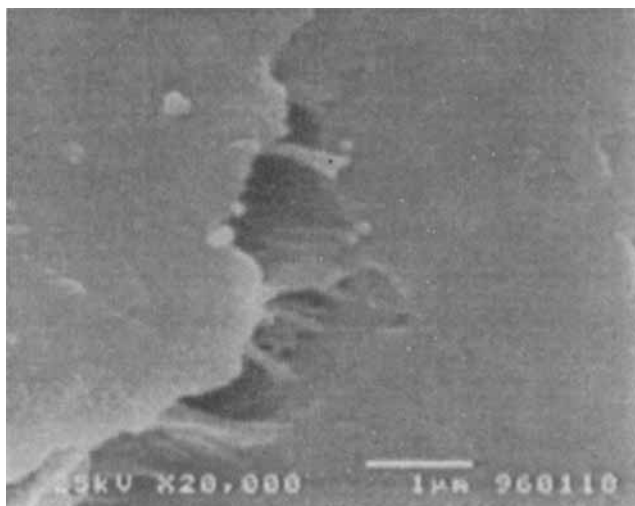


FIGURE 3 SEM micrograph of 30/70 Styrene-Butadiene in linear SBR.

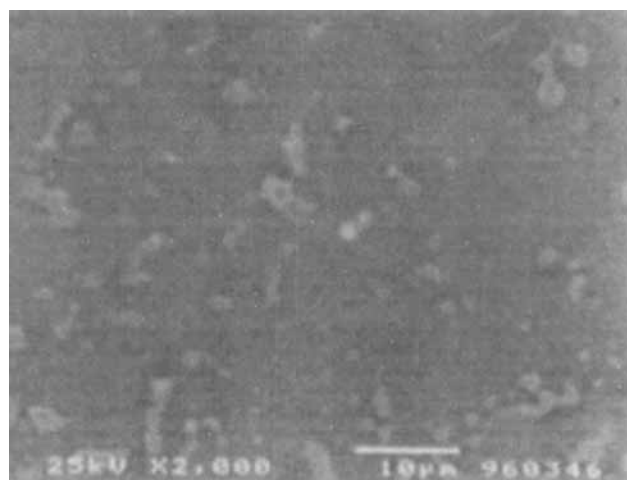


FIGURE 4 SEM micrograph of 25/75 Styrene-Butadiene in linear SBR.

properties when a stress is applied. It is very important to point out that the blend with SBR-4 has the best morphology (Fig. 5) as well as a favourable flexion behavior because it does not present voids or elongated structures in its morphology.

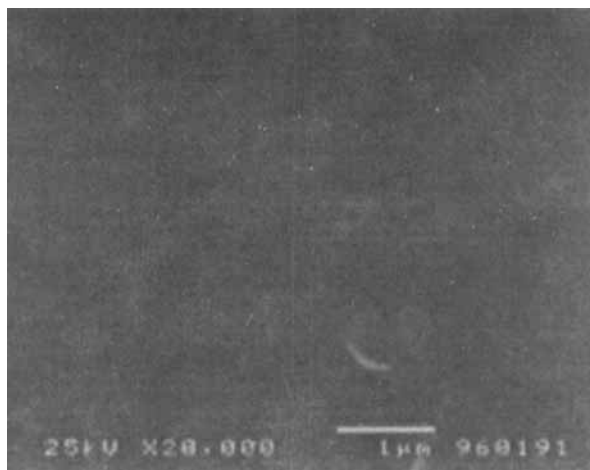


FIGURE 5 SEM micrograph of 40/60 Styrene/Butadiene in linear SBR.

On the other hand, the blend with **SBR-2** has the best elongation at yield point followed by the blend with **SBR-1**. At this point, it must be emphasized that, according to its morphology the blend with **SBR-2** (Fig. 6) is the less homogeneous morphology, since there are several voids and particle size polydispersity (sizes vary between 0.3 micron to about 4 microns), the larger particles are substantially deformed, and thus it is possible to assert that the method of manufacturing blend (extrusion) is not adequate to adequately disperse the rubber in the PS matrix when **SBR** have star structure and 30% of styrene. This produces segregation, which is detrimental to the mechanical properties.

From Table III, the blend with the best elastic modulus in flexion is that with **SBR-6** followed by blend with **SBR-4**. The flexural behavior in both blends perhaps is due to the highly homogeneous morphology (see the micrograph of Fig. 7) where polydispersity of particle **SBR** can be observed.

In Table IV, data on Izod impact reveals that the blend with **SBR-1** is the best impact-resistant material, followed by blend with **SBR-5**. It should be remembered that **SBR-1** is linear with 30% of styrene, its morphology (Fig. 8) showed lower homogeneity with several elongated features, irregular spherical rubber particles and several voids. The

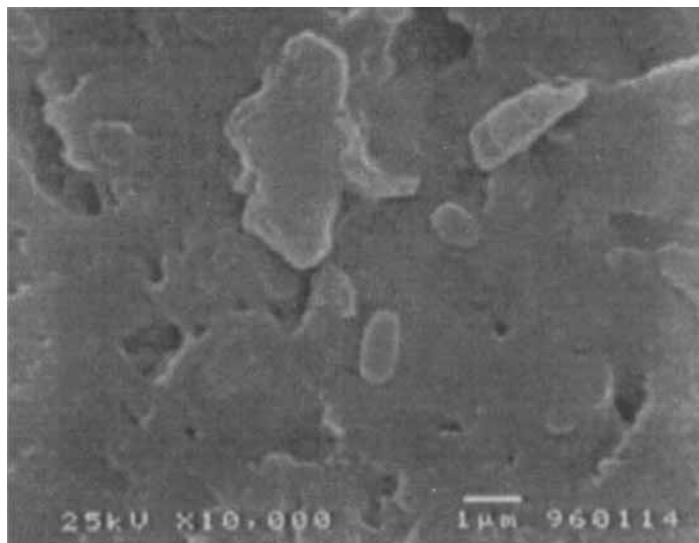


FIGURE 6 SEM micrograph of 30:70 Styrene/Butadiene in star SBR.

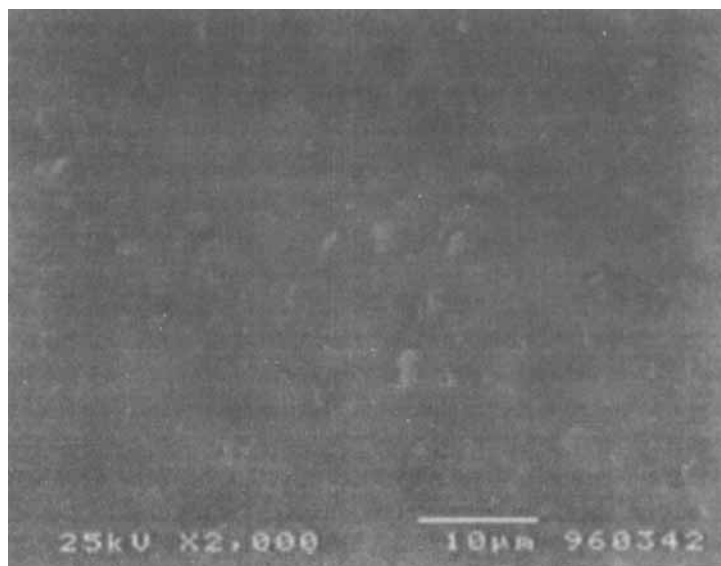


FIGURE 7 SEM micrograph of 25:75 Styrene/Butadiene in linear SBR.

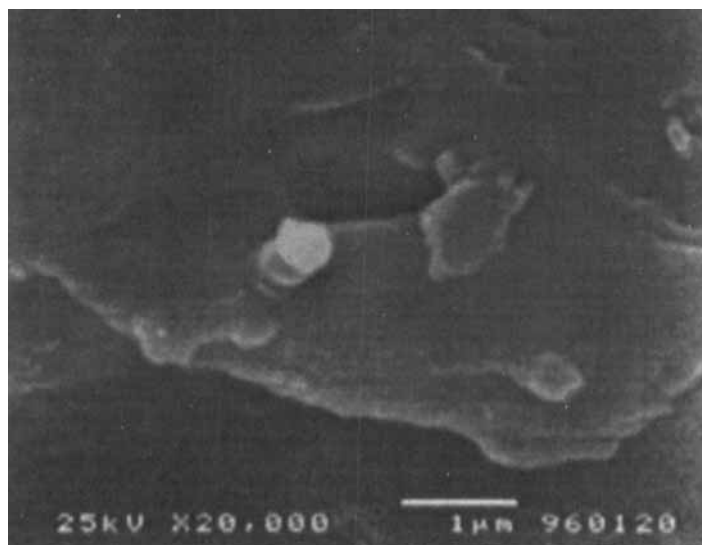


FIGURE 8 SEM micrograph of 30/70 Styrene/Butadiene in linear SBR.

impact characteristics of blends is due to its homogeneity. This is supported by observing Figure 9, corresponding to the blend with **SBR-5**, where exist elongated features that provide the blend higher elastic modulus, these acts as in-situ reinforcing agent. Both results can be compared to micrograph 2 corresponds to the blend of 100% polystyrene. It is important to mention that impact property is improved at maximum value of 40.75%.

In Table V, it can be observed that the material with lower viscosity (MIF) and therefore more difficult to process, is the blend with **SBR-1**, whereas the easiest material to process is the blend with **SBR-6**. The micrographs of blend with **SBR-1** (Fig. 8) and blend with **SBR-6** (Fig. 7) show that blend with **SBR-1** presents more nearly-spherical rubbers disperse in the matrix, the size of the small particles is, in accordance with previous reports in the literature [7], of the order of few microns and can be observed all over in the blend where also spherical rubbers of nearly 0.3 microns (Fig. 8) are observed. Finally, Table VI shows that the blend with the best Razor-sharp elastic modulus (MIR) is blend with **SBR-1** followed by blend with **SBR-6**.

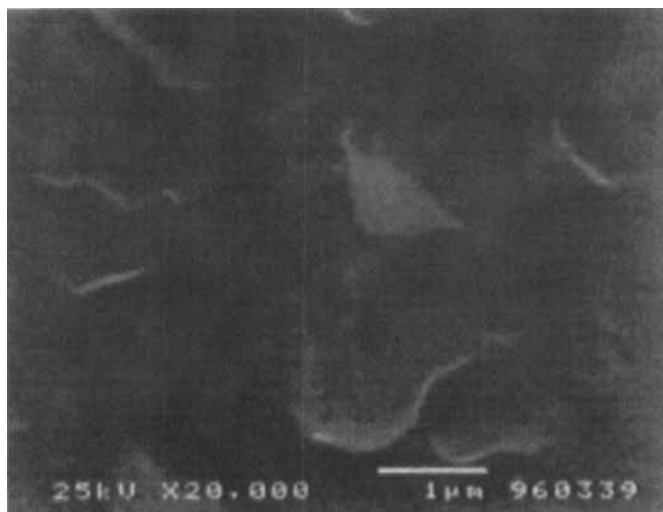


FIGURE 9 SEM micrograph of 30/70 Styrene/Butadiene in linear SBR.

## CONCLUSIONS

The influence of the relation Styrene/Butadiene content in SBRs on the mechanical and rheological properties of blends Polystyrene-SBR is very clear and relevant to find the adequate proportions of styrene and butadiene as well as the chemical structure appropriate for manufacturing good rubber-reinforced polymers.

The extreme cases where the content of styrene are (25%) and (43%) show improvement on mechanical properties of tensile and maximum flexural stress. According to SEM evidence, homogeneous morphology with few disperse particles is present, perhaps due to its linear macrostructure (25%) and multiblock (43%) of SBRs.

The major elongation was achieved when the samples had a 30/70 styrene/butadiene content. Morphology showed low homogeneity. More specifically, the star macrostructure showed polydispersity of irregular rubber particles and the linear macrostructure showed elongated features.

The blend with the best elastic modulus correspond to that the smallest content of Styrene (25%). The morphology present polydispersity of rubber particles of less to 1.0 microns, due to the linear macrostructure and its facility for processing.

Finally Izod impact was good in samples where the relation of content was 30/70 styrene/butadiene with lower homogeneity morphology and linear structure, but very difficult to process. Moreover, it is possible to obtain up to a until 40.75% improvement in impact.

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