

# Preparation and Characterization of High-Impact Polystyrene Using Different Types of Polybutadiene

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**ABSTRACT:** The mechanical, morphological, and rheological properties of polymer blends based on polystyrene (PS) and three different types of polybutadiene (PB) were studied. The polymer blends containing 20% of PB were processed in a Haake mixer at 180°C and 60 rpm for 6 min. The materials exhibited impact strength superior to that of the PS. An increase was observed in the impact strength of 138, 208, and 823%, when low-*cis* polybutadiene (PB<sub>l</sub>), high-*cis* polybutadiene (PB<sub>h</sub>), and styrene-butadiene block copolymer (PB<sub>co</sub>), were respectively used. The materials presented dispersed morphology with polybutadiene do-

mains, with sizes inferior to 1 μm, randomly distributed in the PS matrix. The viscous and storage moduli increased as the applied frequency increased. The flow activation energy, calculated by Arrhenius equation, varied from 34 to 71 kJ/mol. In the rheological experiments all polymer blends presented pseudoplastic behavior, showing decreasing viscosities as the shear rate increased. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 406–413, 2008

**Key words:** toughening; polystyrene; polybutadiene; polymer blends; rheology

## INTRODUCTION

Polystyrene (PS) is a thermoplastic, easily synthesized, conveniently processed, and recycled; it is relatively resistant to thermal degradation, however, its impact resistance is not good. For certain applications it needs to be toughened.<sup>1</sup>

The toughness determines if a certain polymer can be used as an engineering material. In thermoplastic blends toughened with elastomer when a load is applied, the dispersed particles concentrate and absorb that stress provoking an alteration in the stress state of the matrix phase and an intense plastic deformation. The absorption–dissipation of energy by the dispersed particles occurs by different mechanisms, such as, cavitation, plastic deformation (yielding), and by deformation-cavitation.<sup>2–4</sup>

High-impact polystyrene (HIPS) is a material produced by combination of PS and an elastomer by two different processes, graft polymerization or melt-blending. The resultant material is an elastomer-modified thermoplastic that presents a good balance between rigidity and elasticity. The toughening of PS has been made by incorporating about 20%

of low-*cis* polybutadiene (PB) (40% *cis* 1,4; 50% *trans* 1,4; and 10% vinyl units).<sup>5–12</sup>

The factors affecting impact performance of these polymer blends include the volume fraction of elastomer, size, distribution and morphology of elastomer particles, degree of adhesion of the elastomer to the matrix, and interparticle spacing.<sup>13–14</sup> In the physical compatibilization process, a third component (compatibilizer) can be added into the polymer to improve the polymer/polymer interface. In the case of copolymers, they nicely organize at the interface and modify the properties of the heterogeneous systems. It is expected to observe a decrease in the phase separation and in the size of the dispersed phase.<sup>15–17</sup>

The PS blends produced with high-*cis* PB is a material of commercial importance. However, the literature relative to the study of blends based on that elastomer is still scarce.<sup>18–20</sup> Therefore, in this work a comparative study on the effect of three different types of PBs [low-*cis* polybutadiene (PB<sub>l</sub>), high-*cis* polybutadiene (PB<sub>h</sub>), and styrene-butadiene block copolymer (PB<sub>co</sub>)] on the mechanical, morphological, and rheological properties of polystyrene (HIPS) produced by melt-blending was carried out.

## EXPERIMENTAL

### Material and blend preparation

#### Materials

The materials used in this work are detailed in Table I.

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**TABLE I**  
**Polymer Specifications**

Specification	PS	PB <sub>h</sub>	PB <sub>l</sub>	PB <sub>co</sub> <sup>a</sup>
Supplier	EDN/Brazil	Petroflex/Brazil	Petroflex/Brazil	Petroflex/Brazil
Density (g/cm <sup>3</sup> )	1.05	1.00	0.89	0.4
MFI (g/10 min)	3	–	–	7.7
Mooney Viscosity	–	42.0	47.0	–
Percentage of 1,4- <i>cis</i> repeating units	–	97.21	36.0	–

<sup>a</sup> Styrene–butadiene–styrene block copolymer (31% styrene and 69% butadiene).

The materials (blends and PS) were processed in a HAAKE Rheomix 600 mixer at 180°C, 60 rpm for 6 min, with volume fraction of 20% of PBs.

### Mechanical properties

#### Hardness

The hardness was measured by penetration depth of an indenter. The specimens with thickness between 6 and 10 mm were prepared by compression molding, and evaluated in a Shore-Durometer Hardness Type “D”, according to ASTM D2240. The values were the average of at least five measurements.

#### Tensile properties

The tensile properties of samples prepared by compression molding (100 mm × 5.20 mm × 2.30 mm) were evaluated in a Universal Mechanical Testing Machine (Emic DL 10000) at room temperature (23.8°C and 58% of relative humidity) at crosshead speed of 3 mm/min, according to ASTM D 638-II. Ten specimens for each sample were prepared.

#### Impact strength

The impact strength of nine specimens measuring 12 mm × 6 mm × 3 mm, were prepared by compression molding and measured in a Resil Impactor Ceast SPA Impact Tester at the V-notched Izod mode, according to ASTM D 256.

#### Morphology

The morphology of the polymer blends were examined in a Jeol scanning electron microscope (SEM), model JSM 6460LV at operating voltage of 15 kV. The samples were cryogenically fractured in liquid nitrogen and etched with hexane/heptane (1 : 1) and HCl (20%) at room temperature to extract the elastomer phase. The samples were dried and then coated with a layer of gold prior to their SEM observations.

The fracture surfaces of the samples after the impact test were also coated with a thin layer of

gold and observed in a SEM, model JSM 6460LV at operating voltage of 15 kV.

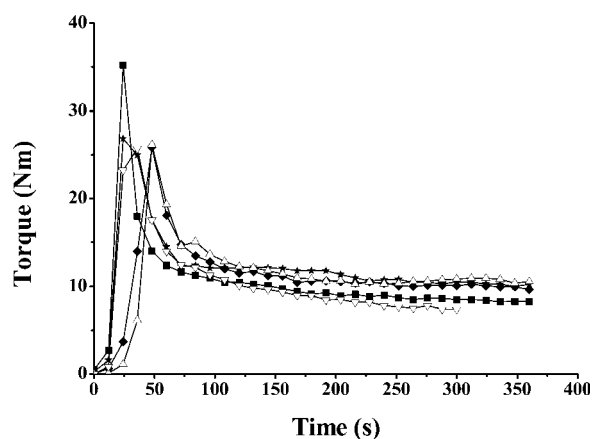
#### Rheological behavior

The viscoelastic properties were evaluated in a tension controlled dynamic rheometer, Anton Paar Physica MCR 301, using plate–plate geometry at 190, 200, and 210°C. The complex viscosity ( $\eta^*$ ), the storage modulus ( $G'$ ), and the loss modulus ( $G''$ ) were determined in the frequency range from 10<sup>-1</sup> to 10<sup>2</sup> rad/s under nitrogen atmosphere. All rheological measurements were carried out in the linear viscoelastic region.

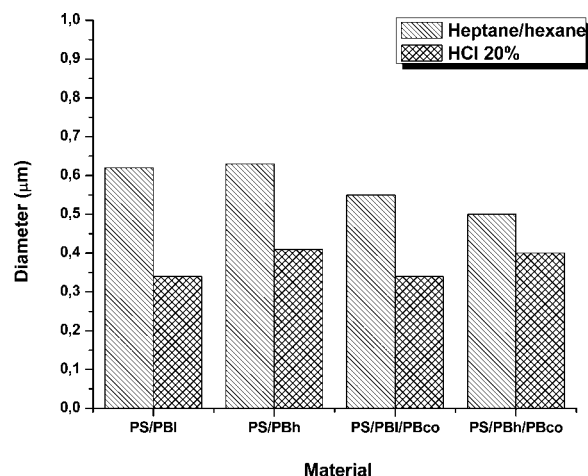
## RESULTS AND DISCUSSION

### Blends preparation

It was observed that the conditions of processing have a remarkable effect on the quality of the material produced. Temperatures superior to 180°C provoked the degradation of the material. The incorporation of an elastomeric phase in the PS matrix produced opaque materials. Figure 1 shows the curves of processing for the polymer blends



**Figure 1** Curves of torque versus time. PS (■); PS/PB<sub>l</sub> (★); PS/PB<sub>h</sub> (◆); PS/PB<sub>h</sub>/PB<sub>co</sub> (△); PS/PB<sub>co</sub> (▽).



**Figure 2** Particle diameter of elastomeric domains of PS/PB blends.

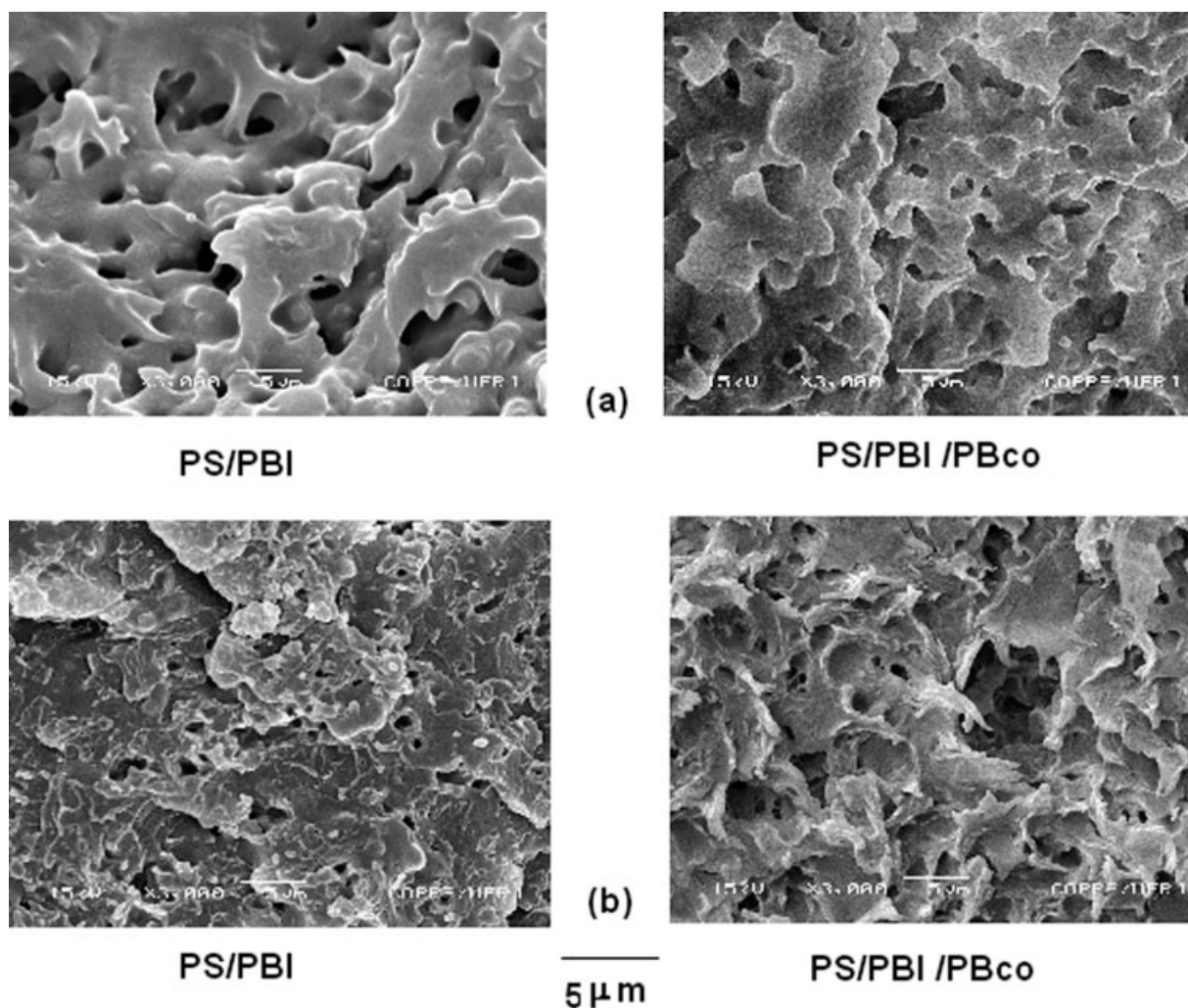
produced with different types of PB. Neat PS exhibited a superior torque, in the first stage of the processing, than the blends. This fact is because of

the uncompleted melting and the higher stiffness of the PS. The incorporation of an elastomer phase in the PS matrix makes the material easier to be processed, as can be seen in the Figure 1. After 120 s a steady condition was reached indicating that all the materials were completely melted and homogeneous.

### Morphology analysis

The morphology of a polymer blend is governed by its rheological characteristics, processing conditions, and composition of the blend. The morphological stability depends on the interfacial stress between the phases and the thermodynamic of the system.

Blends produced with different types of PB presented two-phase morphology with elastomeric domains with sizes inferior to 1 µm, randomly dispersed in the PS matrix (Fig. 2). The Figures 3 and 4 display the SEM of the blends prepared with PB<sub>i</sub>, PB<sub>h</sub>, and a blend with 2.5% of triblock copolymer (PB<sub>co</sub>).



**Figure 3** SEM micrographs of PS/PB<sub>i</sub> (a) etched with heptane/hexane, (b) etched with HCl.

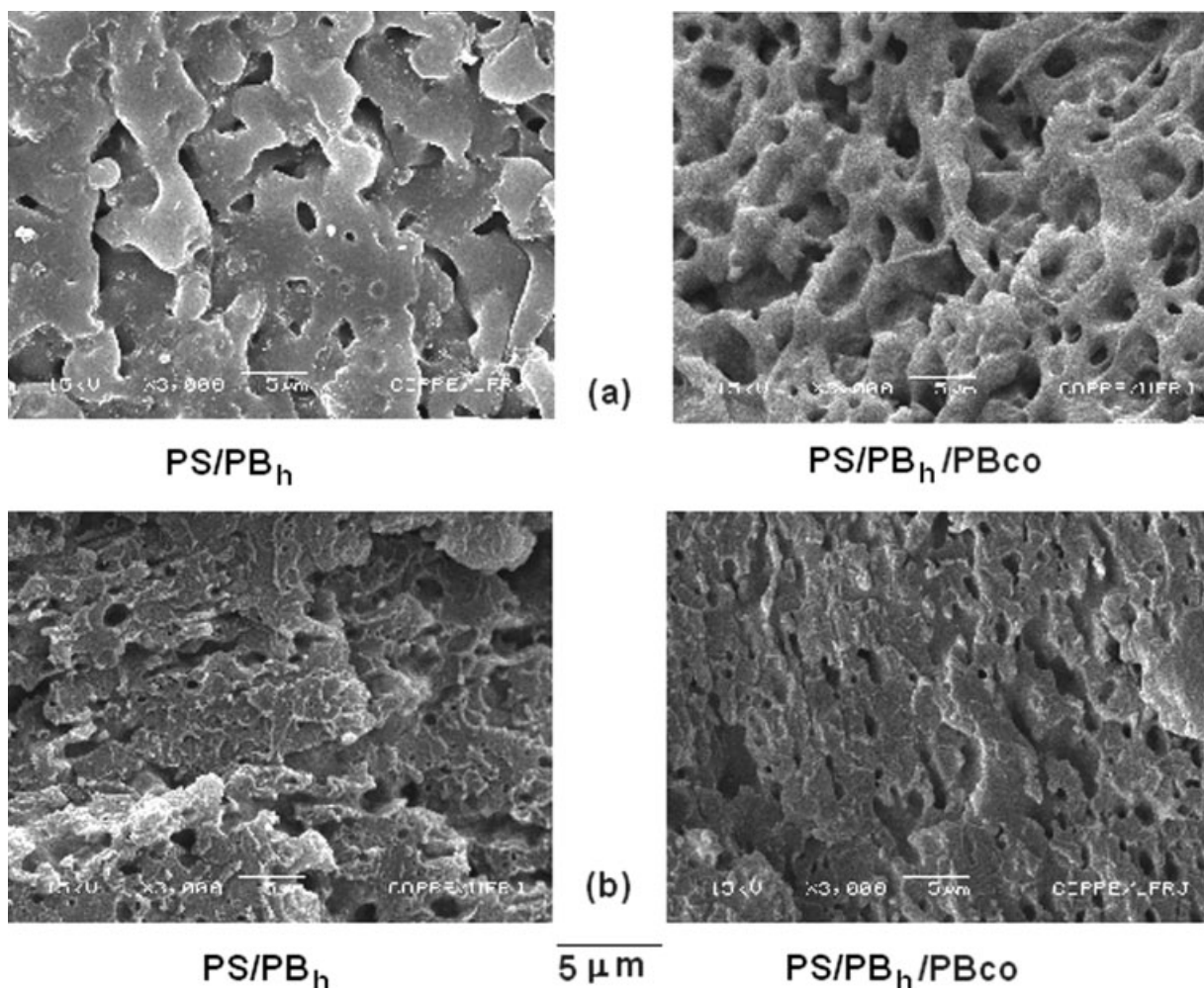


Figure 4 SEM micrographs of PS/PB<sub>h</sub> (a) etched with heptane/hexane, (b) etched with HCl.

The type etching agent had a significant influence on the elastomeric domains size. The elastomeric domains were larger in all blends etched with heptane/hexane (1 : 1) mixture than when HCl (20%) was used. This fact can be attributed to a certain swelling level of the PS matrix in the presence heptane/hexane mixture. The addition of a triblock copolymer (PB<sub>co</sub>) had only a slight influence on the particle size of the elastomeric domains.

**Mechanical properties**

The mechanical behavior of the polymeric materials is based on the deformations provoked by application of external forces. The nature of these forces change according with the type of stress that is being applied on the material and the final application is mainly governed by its mechanical properties. These properties are accentuatedly dependent on the homogeneity level, compatibility, and interfacial adhesion of the phases.<sup>21,22</sup>

The blends presented lower hardness values when compared with pure PS (Fig. 5). That behavior is because of the incorporation of the elastomer in PS matrix. The hardness values obtained for PS/PB

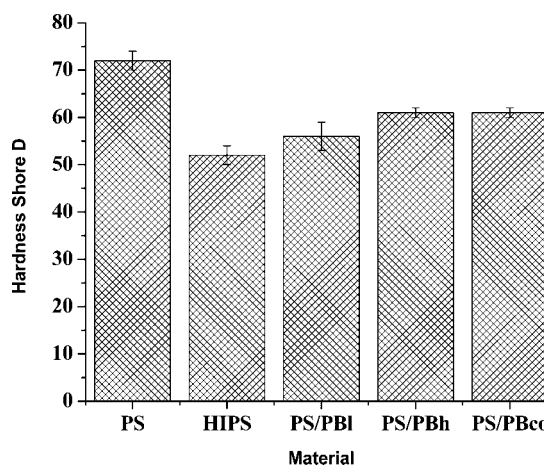
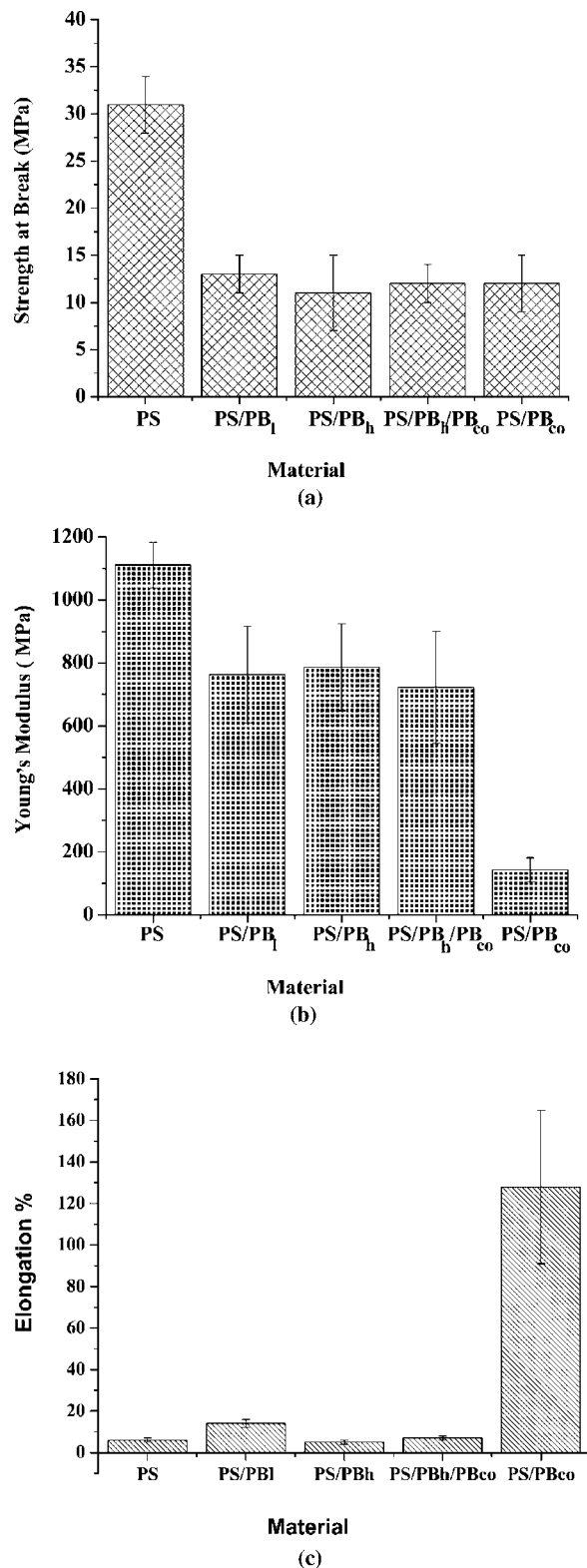


Figure 5 Hardness shore D for the PS/PB blends.



**Figure 6** Mechanical properties of PS/PB blends. (a) Strength at break; (b) Young's modulus; (c) Elongation.

blends are close to the hardness value of the commercial HIPS prepared by graft polymerization, that is 52 Shore D.

### Tensile test

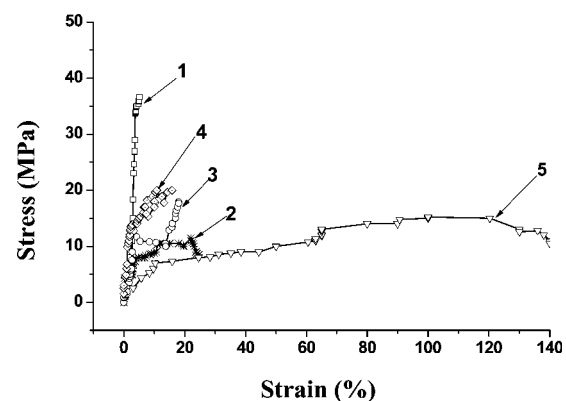
The strength and elongation at break, and the Young's modulus of the PS/PB blends are showed in Figure 6. The strength at break and the Young's modulus of the blends are lower than the ones for pure PS. However, the elongation at break had a slight increase when PB<sub>i</sub> was incorporated in the PS matrix. Otherwise, when styrene-butadiene triblock copolymer (20%) was incorporated in the PS matrix, an accentuated increase in the elongation at break was observed.

Figure 7 displays the characteristic features of stress-strain curves of the PS/PB blends. As can be seen, PS exhibited a hard and brittle behavior. When PB<sub>i</sub> and PB<sub>h</sub> were incorporated into the PS matrix a smooth transition from brittle to ductile was observed. Differently, the incorporation of PB<sub>co</sub> into the PS matrix provoked a modification in the mechanical behavior from brittle to tough. In the tensile tests, PS and its blends presented some whitening in the necked zone. The whitening of the materials during the deformation process is generally a manifestation of a fine-scale cavitation process, and suggests that both PS and PB can cavitate during the plastic flow under conditions used in the tests.<sup>23</sup>

### Impact test

The data of impact tests are displayed in Figure 8. An enhancement of 138, 208, 823%, on the impact strength was obtained when PB<sub>i</sub>, PB<sub>h</sub>, and PB<sub>co</sub> were respectively used. The addition of a block copolymer (SBS) increased the impact strength because of the increase of interfacial adhesion between the plastic and elastomeric phases, promoting a morphological stability. In the impact tests all samples also showed some whitening near the fractured surfaces.

Figure 9 shows the SEM micrographs of the fractured surfaces of the PS/PB blends. All the blends



**Figure 7** Stress-strain curves of PS/PB blends. (1) PS; (2) PS/PB<sub>i</sub>; (3) PS/PB<sub>h</sub>; (4) PS/PB<sub>h</sub>/PB<sub>co</sub>; (5) PS/PB<sub>co</sub>.

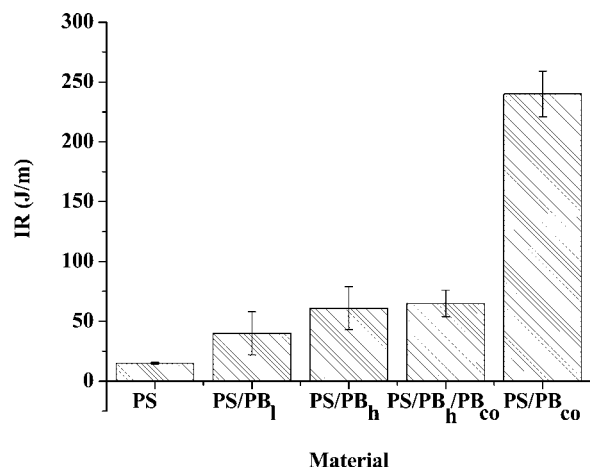


Figure 8 Impact resistance of PS/PB blends.

exhibited microfissuring and cavitation mechanisms of the elastomeric particles. The blends produced by mixing PS with the block copolymer presented only

microfissuring mechanism of the elastomeric phase. This result corroborated the high-impact resistance value (240 J/m) exhibited by this material.

**Rheological behavior**

It is very important to know the viscoelastic behavior of the polymeric blends, not only as a way to achieve good conditions of processing, but to get informations about the type of flowing and its effect on the morphology and final mechanical properties. The viscosity, fundamental rheological property of a fluid, is affected by the conditions of processing (shear rate, temperature, and pressure) and by the type of material (chemical structure, molecular weight, and polydispersion, presence of short and long chain branching), and presence of fillers and additives.<sup>24,25</sup>

Figure 10 shows the rheological curves of PS blends containing three types of PB.

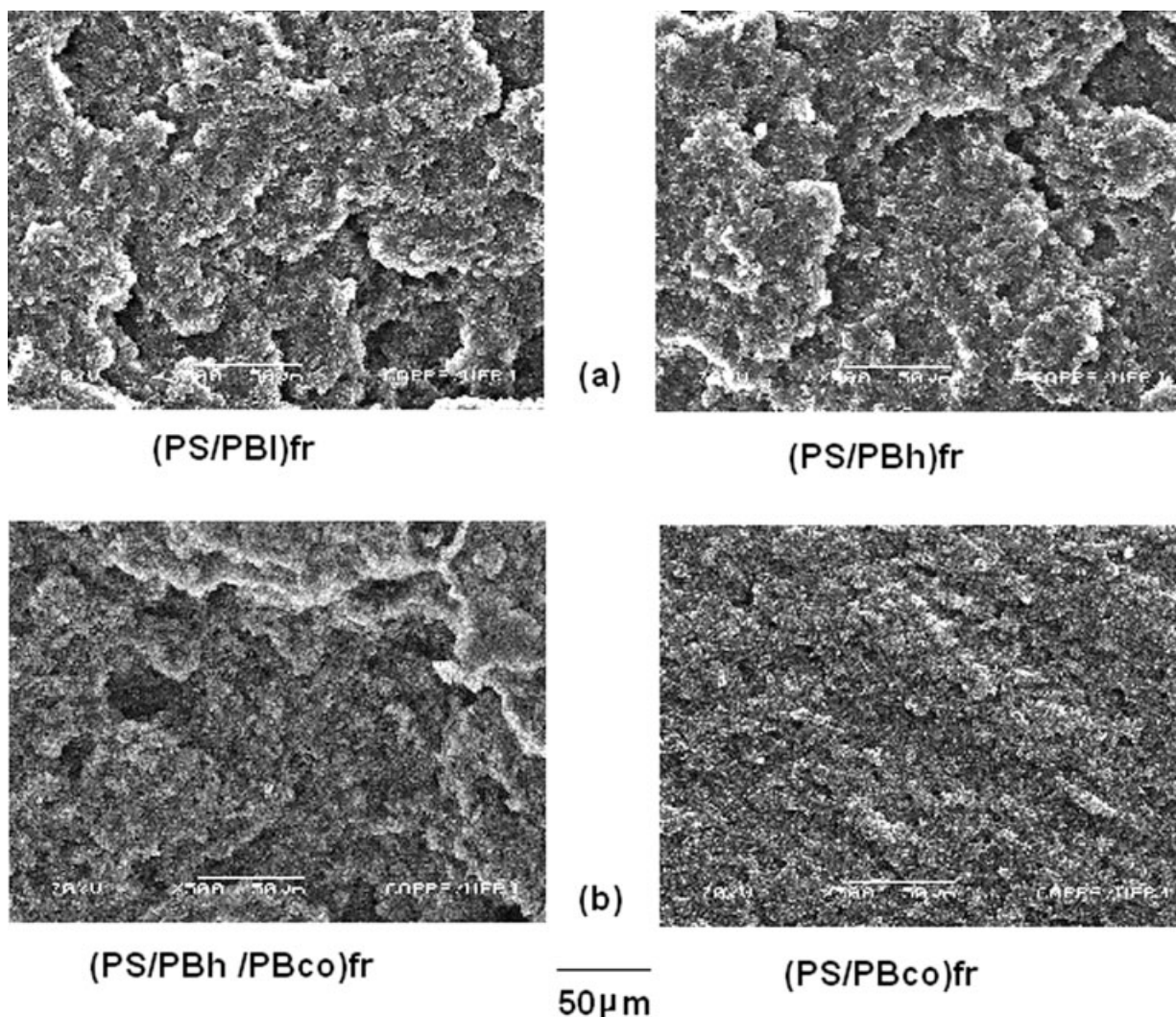
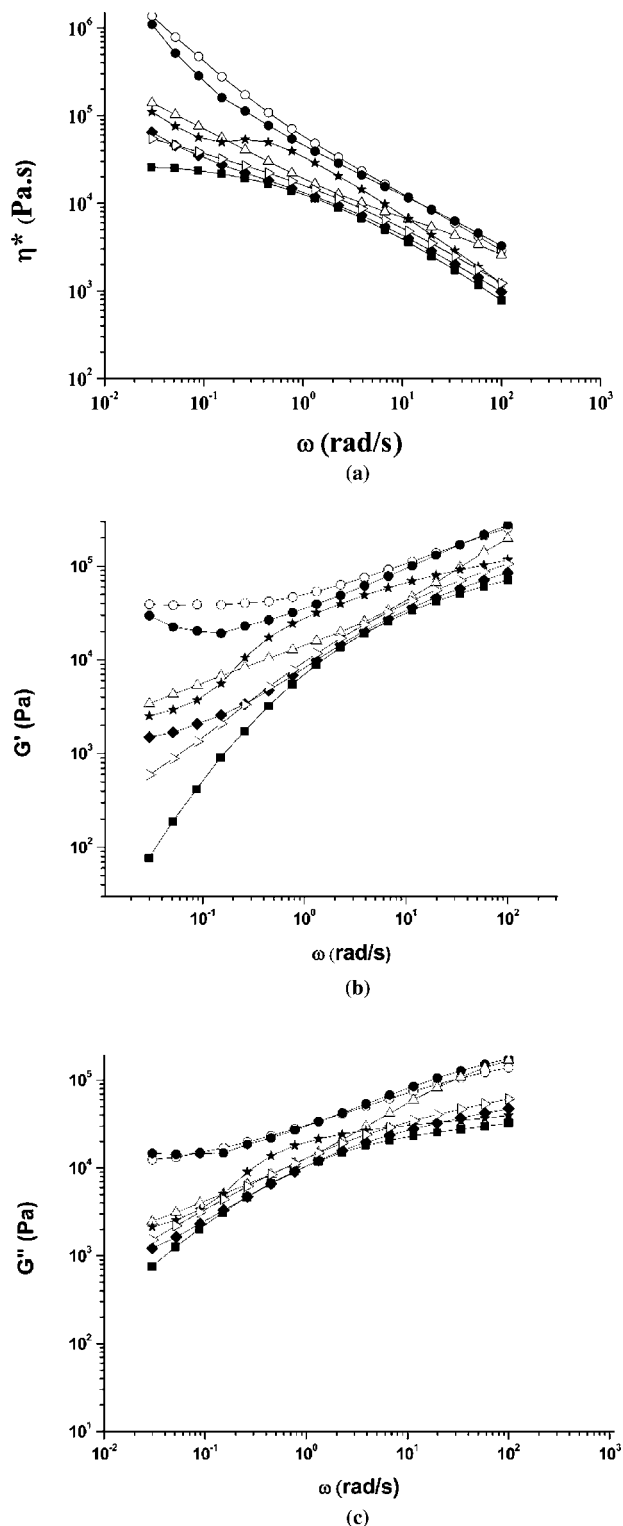
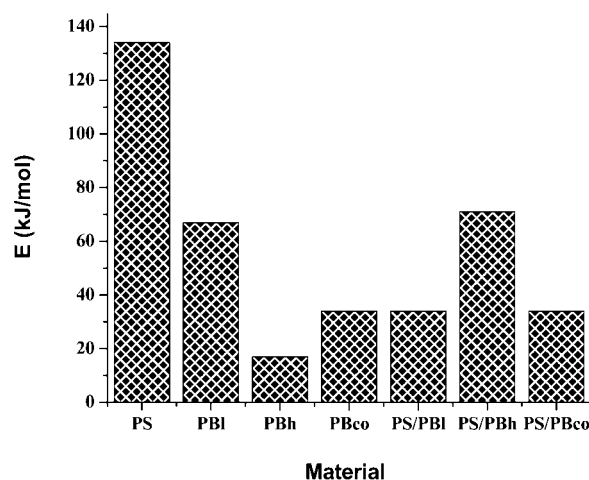


Figure 9 SEM micrographs of the fractured surface of PS/PB blends after impact test.

All samples presented pseudoplastic behavior and viscoelasticity in all range of frequency studied. The PBs presented the highest values of viscosity ( $\eta$ ), while the PS presented the smallest one.



**Figure 10** Rheological properties: (a) complex viscosity; (b) elastic modulus; (c) loss modulus. PS (■); PB<sub>1</sub> (●); PB<sub>h</sub> (○); PB<sub>co</sub> (△); PS/PB<sub>1</sub> (★); PS/PB<sub>h</sub> (◆); PS/PB<sub>co</sub> (▷).



**Figure 11** Activation energy for PS/PB blends.

The polymeric blends of PS with the three types of PBs presented viscoelastic behavior with the elastic and loss moduli increasing as the applied frequency increased. As expected, the rheological curves of the blends fell between the neat PS's and the neat elastomer's.

Figure 11 shows the flow activation energy values for the blends. The flow activation energy of the blends, calculated by Arrhenius equation, varied from 34 to 71 kJ/mol.

The flow activation energy for the blends is smaller than the pure PS. PS/PB<sub>1</sub> and PS/PB<sub>co</sub> blends presented the same activation energy. However, this value doubled when high-*cis* PB was used as toughening phase.

## CONCLUSIONS

The processing conditions influenced on the quality of the material obtained. Temperature of processing superior to 180°C provoked the degradation of the materials. The blends exhibited biphasic morphology with domains of PB dispersed heterogeneously on the PS matrix, with particle diameter inferior to 1 μm. These blends presented weak adhesion between the plastic and elastomeric phases and a high interfacial tension. The incorporation of an elastomer in the PS matrix produced opaque materials with high-impact resistance. The PS/PB<sub>h</sub> blends presented impact resistance higher than PS/PB<sub>1</sub> and smaller than PS/PB<sub>co</sub>. All materials produced in this work had impact resistance superior to the commercial HIPS.

All the blends exhibited thinning shear behavior, viscoelasticity, and different flow activation energies under shear conditions studied in this work.

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## References

1. Baltá-Calleja, F. J.; Cagio, M. E.; Adhikari, R.; Michler, G. H. *Polymer* 2004, 45, 247.
2. Lotti, C.; Correa, C. A.; Canevarolo, S. V. *Mater Res* 2000, 3, 37.
3. Jiang W.; An, L.; Jiang, B. *Polymer* 2001, 42, 4777.
4. Lung, H.; Jiang, W.; Zhang J.; Jiang, B. *J Appl Polym Sci* 1996, 59, 505.
5. Piorkowska, E.; Argon, A. S.; Cohen, E. R. *Polymer* 1993, 34, 4435.
6. Peng, M. F. *J Appl Polym Sci* 1990, 40, 1289.
7. Fisher, M.; Hellmann, G. P. *Macromolecules* 1996, 29, 2498.
8. Maestrini, C.; Monti, L.; Kausch, H. H. *Polymer* 1996, 37, 1607.
9. Maestrini, C.; Pisoni, K.; Kausch, H. H. *J Mater Sci* 1996, 31, 3249.
10. Alfarraj, A.; Nauman, E. B. *Polymer* 2004, 45, 8435.
11. Cavanaugh, T. J.; Buttle, K.; Turner, J. N.; Nauman, E. B. *Polymer* 1998, 39, 4191.
12. Dagli, G.; Argon, A. S.; Cohen, E. R. *Polymer* 1995, 36, 11, 2173.
13. Sundararaj, U.; Macosko, C. W.; Roland, R. J.; Chan, H. T. *Polym Eng Sci* 1992, 32, 1814.
14. Joseph, S.; Thomas, S. *Eur Polym J* 2003, 39, 115.
15. Silberg, J.; Han, C. D. *J Appl Polym Sci* 1978, 22, 599.
16. Mui, C. T. E.; Boating, B. V.; Fellers, F. J.; White, L. J. *J Appl Polym Sci* 1982, 27, 1395.
17. Joseph, S.; Lauprête, F.; Negrell, C.; Thomas, S. *Polymer* 2005, 46, 9385.
18. Joseph, S.; Oommen, Z.; Thomas, S. *Mater Lett* 2002, 53, 268.
19. La Mantia, F. P.; Acierno, D. *Eur Polym J* 1985, 21, 811.
20. Barlow, J. W.; Paul, D. R. *Polym Eng Sci* 1981, 21, 985.
21. Magalhães, A. M. L.; Borggreve, R. J. M. *Macromolecules* 1995, 28, 5841.
22. Bretas, R. E. S.; D'Avila, M. A. *Reologia de Polímeros Fundidos*; Editora UFScar: São Carlos, 2000.
23. Rohn, C. L. *Analytical Polymer Rheology: Structure-Processing-Properties Relationships*; Hans Publishers: New York, 1995.