

# Use of Recycled Polystyrene with Polyurethane in Polymer Network Compositions

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**ABSTRACT:** Postconsumer polymer recycling is a technology that involves many fields of science. The production of plastics has increased in recent years, and the products have many applications. Because of this, waste plastics are also increasing, causing many environmental problems due to the slow rate of natural decomposition of synthetic polymers. Polymer chemistry and process engineering are good tools for decreasing the problems caused by inappropriate polymer disposal. The subject of this work was the preparation of polymer networks based on recycled polystyrene (in the crystal form, PS; or in the expanded form, EPS) and polyurethane. The compositions were prepared by reaction between the polyurethanes (PU) components in the presence of recycled PS or EPS dissolved in the styrene monomer con-

taining benzoyl peroxide as a free radical initiator. 1,4-butanediol (BDO) was used as chain extender for PU network. The compositions were characterized by the evaluation of mechanical properties, thermogravimetric analysis, and morphological analysis. The PS or EPS concentration used in the mixtures was in the 1–5 wt % range. The addition of PS or EPS changed the mechanical behavior as well as the final morphology of the compositions. The use of the PS/PU or EPS/PU network systems is a way of decreasing PS or EPS discards decreasing this environmental problem. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2714–2719, 2007

**Key words:** polystyrene; polyurethanes; interpenetrating networks; mechanical properties; morphology

## INTRODUCTION

Polyurethanes (PU) can be applied in many technological sectors. The correct choice of the PU compounds leads to the perfect combination between hard and soft segments. This fact and the possibility of obtaining different crosslinking degrees play an important role in the resulting properties and final applications of the polymer. PU synthesis is based on the reaction between isocyanate and hydroxyl groups resulting in the characteristic urethanic link. The crosslinking structure is obtained using a trifunctional alcohol, for instance. The reaction is shown in Figure 1.<sup>1–4</sup>

PU is considered as a segmented copolymer. The flexible segment is constituted by a terminated hydroxyl group polymer ( $f \geq 2,0$ ) called polyol. In general the polyol has a lower glass transition temperature ( $T_g$ ) that imposes an elastomeric characteristic on PU. The rigid segments contain polar urethane links typically with higher  $T_g$ .<sup>4,5</sup>

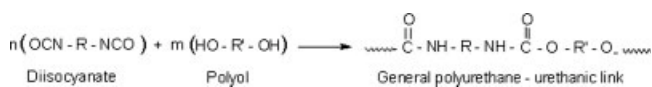
PU are used to produce foams (rigid or flexible) but can be also used to make elastomeric polymers, inks, fibers, textiles, and adhesives.<sup>4–6</sup>

On the other hand, polystyrene (PS) is broadly used in the industry and it can be used in many forms, mainly in crystal or in expanded forms (EPS) among others. Irregular PS waste has been causing serious problems for the environment and re-use has been identified as an economical and interesting alternative for solving this problem.<sup>7</sup>

In some situations it is interesting to have new properties to allow a specific use of a material. Thus it was observed that polymer combination constituted an important way of reaching this particular application. The combination of two or more different polymeric matrices is an alternative for producing new compositions with specific and better properties, which are not available from any of the mixture components. Most of the combinations are obtained by the use of two polymers producing the so-called binary mixtures. The final properties depend on the components, but also on the way in which the mixture is produced.<sup>4</sup>

Among the various combination methods involving polymers we can call attention to: mechanical mixtures or blends; chemical compositions (they are

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**Figure 1** Polyurethane chemical structure representation.

copolymers in the block or the graft forms); composites and interpenetration polymer networks (IPN).<sup>4,8–13</sup> PU and PS (or EPS) can be combined to produce different and new materials.<sup>14,15</sup>

The objective of the present work was the preparation of PU/PS and PU/EPS mixtures in the IPN form in an attempt to minimize the abusive problem of PS or EPS discards. The compositions were prepared with a larger amount of PS or EPS in the PU elastomeric matrix. The evaluation of compositions was done through determination of mechanical properties, thermal stability, and morphological analysis.

## EXPERIMENTAL

### Materials

Toluene 2,6-diisocyanate (TDI) was obtained from Bayer do Brasil S.A. (Rio de Janeiro, Brazil); 1,4-butanediol (BDO) was obtained from Aldrich (Milwaukee, EUA) and was distilled under reduced pressure (82–83°C; 10 mmHg)<sup>16</sup>; hydroxyl terminated polybutadiene (HTPB),  $M_n = 2700$  g/mol,  $[\text{OH}] = 0.785$  meq OH/g was supplied by Nitriflex (Rio de Janeiro, Brazil) and was dried under vacuum for 4 h, 100°C; styrene (Sty) was obtained from Arofibra (Curitiba, Brazil) and was treated to remove the inhibitor traces by washing with NaOH,<sup>17</sup> the Sty was distilled under reduced pressure (50°C; 50 mmHg);<sup>17,18</sup> benzoyl peroxide (PB) was obtained from Aldrich (Milwaukee, EUA), tetrahydrofuran (THF); dimethylbenzene; and antracene were used as received. Crystal polystyrene (PS) ( $M_n$  135,500;  $M_n/M_w$  5.6) was supplied by INNOVA (Porto Alegre, Brazil) and recycled polystyrene (EPS with  $M_n$ ; 156,700  $M_n/M_w$  4.3) was collected from domestic waste.

### Procedures

#### Pure polyurethane (PU) preparation

The PU was synthesized by reaction between TDI and HTPB. The NCO/OH index used was 1.1 and the free NCO content was 2% and the hard segment content was 11.92%. The compounds were added to a reactor and the reaction was kept under nitrogen with mechanical stirring (1 h, 60°C and atmospheric pressure). After this the system was submitted to vacuum (10 mmHg) for 10 min. This material is called prepolymer. In a second stage BDO was added to promote the chain extension. The reaction was kept under inert atmosphere with mechanical stirring (80°C, and

atmospheric pressure). After the mixing of the components, the solution was poured into a warm horizontal mold (20 × 20 × 0.2 cm<sup>3</sup>). The final stage was the thermal treatment for the pure PU cure (100°C; 24 h).

#### Interpenetrated polymer networks (IPN) preparation

IPN preparation was performed in four stages. The first one was obtaining the PU prepolymer (reaction between TDI and HTPB). The second stage was the addition of a recently prepared solution (0.1 g PS or EPS/3 mL Sty) prepared using powdered PS. For this solution, EPS or Crystal PS was used (with 100 mesh particle size) in styrene monomer containing 2 wt % of initiator (PB). The third stage was the polyurethane chain extension using BDO. These stages were conducted at 60°C, for 1 h under mechanical stirring. The homogeneous solution obtained was cast in a horizontal mold and put in a controlled temperature oven. The fourth stage was the thermal treatment of the composition (100°C, 24 h). This procedure was used to prepare the compositions containing from 1 to 5 wt % for Crystal PS and from 2 to 5 wt % of EPS.

#### Materials characterization and evaluation

##### Numeric medium molecular weight of the PS and EPS samples

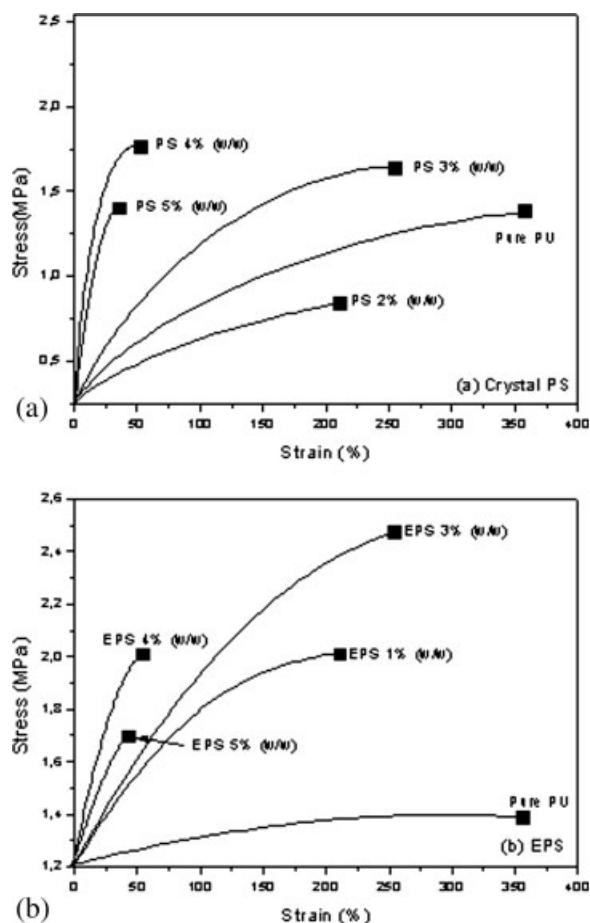
The evaluation of the numeric medium molecular weight ( $M_n$ ) was performed by size exclusion chromatography (SEC) in a Shimadzu LC10AD system equipped with a refraction index detector. For the analysis, two columns of Tosoh TSH-Gel were used in series with exclusion limits corresponding to 104 and 103 u.m.a. respectively. The analyses were done at 45°C in THF using the 1.0 mL/min flow. The injection procedure was accomplished through an automatic injection SIL-10A for which the injection volume was of 20  $\mu\text{L}$ . The apparent molecular weight was calculated from a PS standard, dimethylbenzene, and antracene, using the SEC module of the CLASS-LC10 software application.

##### Mechanical properties

The tensile properties were measured at room temperature in accordance with ASTM D638 M32 using an EMIC 10.000 testing machine at a crosshead speed of 10 mm/min.<sup>19</sup>

##### Thermal stability determination

The products were analyzed using a TA INSTRUMENTS thermal analysis apparatus (TGA) with an SDT 2960 heating model. The analyses were con-

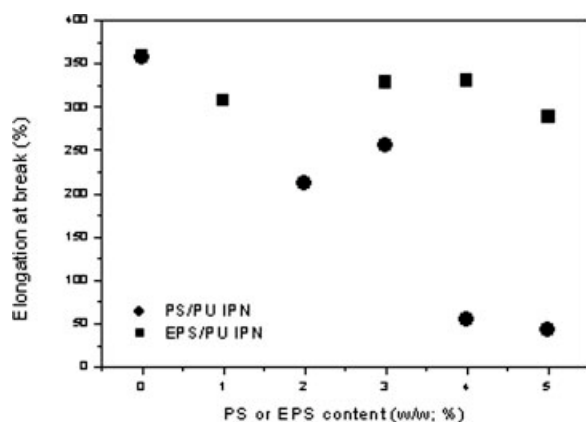


**Figure 2** Mechanical behavior of PU/PS and PU/EPS IPNs (a-PS and b-EPS compositions).

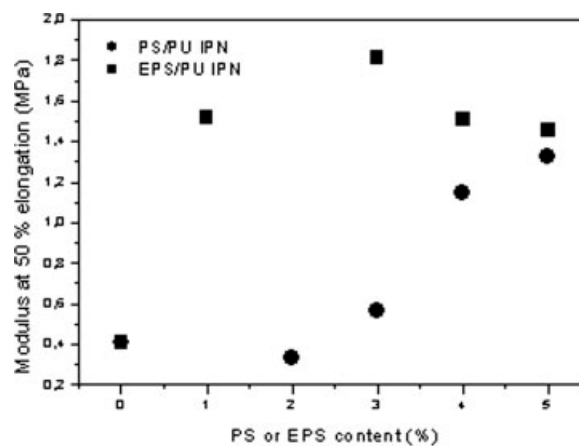
ducted in a nitrogen atmosphere, at a heating rate of 10°C/min, in the 25–800°C temperature range.

#### Evaluation of the surface morphology

The products were analyzed by scanning electronic microscopy (SEM) for the evaluation of the PS particle



**Figure 3** Dependence of the elongation at break with the PS or EPS content for the IPN.



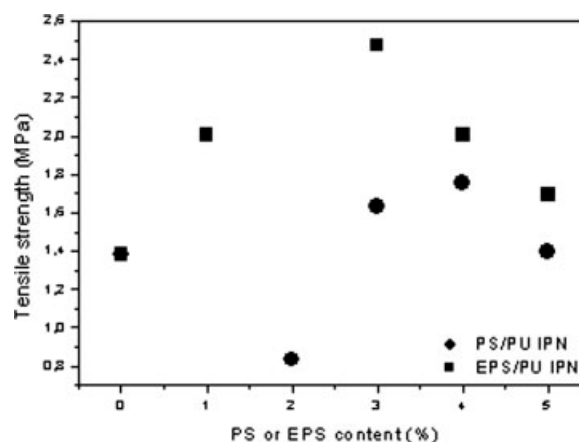
**Figure 4** Dependence of Modulus at 50% elongation with the PS or EPS content.

distribution in the polyurethane matrix. Small fragments of the composition samples were obtained after cryogenic fracture. They were placed in the specific support and recovered using gold as the conducting material. This procedure was performed using a BAL-TEC SCD 005-Sputter Coater system. The metallic samples were visualized and photographed using a Philips XL 30 electronic microscope.

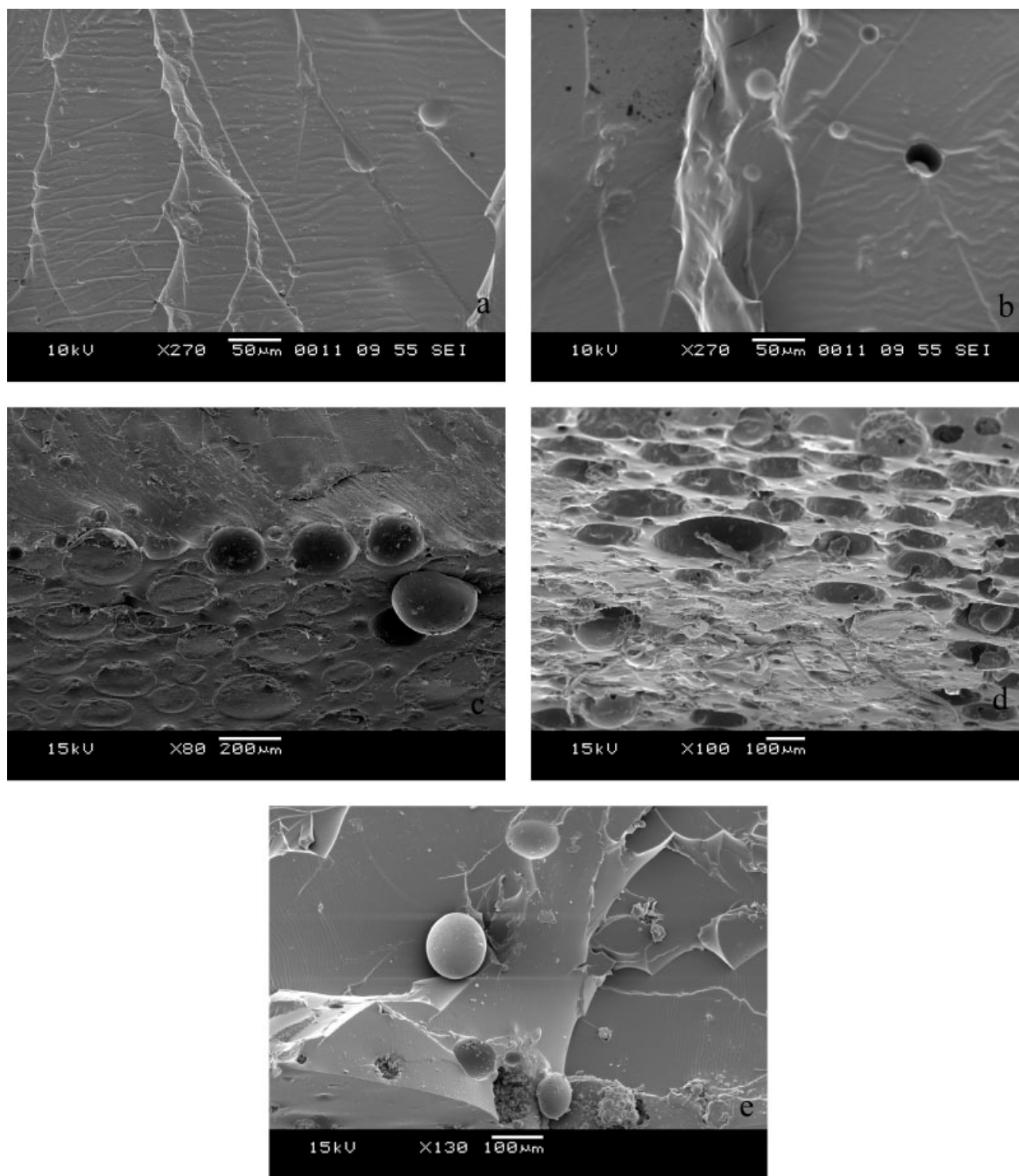
## RESULTS AND DISCUSSION

The visual observation of the IPNs samples showed a homogeneous material at low PS or EPS concentration. When the PS or EPS content reached a certain value (3% for PS and 4% for EPS samples), the samples became opaque indicating phase segregation. This fact shows that there is a limiting value for the PS or EPS content in the PU matrix.

The evaluation of the numeric medium molecular weight ( $M_n$ ) using a SEC technique showed these values for



**Figure 5** Tensile strength at 50% elongation: profile for PU/PS and PU/EPS IPN with the variation of PS or EPS content.



**Figure 6** a–Micrographs of sample surfaces: pure PU (a), PU/PS 2 wt % (b), PU/PS 3 wt % (c), PU/EPS 1 wt % (d) and PU/EPS 3 wt % (e).

the molecular weight: for pure PS samples  $M_n$  was equal to 135,500; and the polydispersity value ( $M_n/M_w$ ) was 5.6; and for pure EPS samples  $M_n$  was equal to 156,700; and the polydispersity value ( $M_n/M_w$ ) was equal to 4.3.

Figure 2(a,b) shows the mechanical behavior of the PU/PS and PU/EPS IPNs. The strain decreased and the stress at break increased when the PS (or EPS)

concentration was higher. This behavior is due to the addition of a harder polymer in a softer polymer (PU).

Figure 3 shows the profile for elongation at break versus PS/PES content. A small increase of the property values was observed when the PS or EPS concentration reached 3 or 4% respectively. Above these val-



**TABLE I**  
**TGA Data for Pure PU, Pure PS, Pure EPS, and IPNs Compositions**

Sample	Range 1		Range 2		Range 3	
	Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)
PURE PU	316	8	371	10	462	82
PURE PS	–	–	–	–	415	100
PURE EPS	–	–	–	–	416	100
PU/PS 2%	332	7	–	–	446	93
PU/PS 3%	310	9	–	–	460	91
PU/PS 4%	319	16	–	–	446	84
PU/PS 5%	329	18	–	–	456	82
PU/EPS 1%	302	8	375	10	460	82
PU/EPS 2%	301	7	373	11	461	82
PU/EPS 3%	310	9	375	10	462	81
PU/EPS 4%	312	9	374	10	459	81
PU/EPS 5%	311	9	378	11	462	80

ues the elongation decreased. This behavior was stronger for the IPNs based on crystal PS. These results suggest that a phase separation phenomenon occurred.

Figure 4 shows the modulus at 50% elongation while Figure 5 shows the tensile strength at 50% of elongation with the PS or EPS content variation. For both of these properties, the results for the PU/EPS IPN were higher than the PU/PS compositions indicating that the EPS has a better compatibility with the elastomeric matrix. Both IPN series showed a decrease of the values when the concentration was up to the 3–4% range. This behavior can be justified by a different and characteristic morphology of the samples.

Therefore the evaluation of the mechanical properties indicated that the morphology may be changing the performance of the compositions. When the samples were analyzed by scanning electronic microscopy (SEM) the micrographs revealed a different morphology for the materials [Fig. 6(a–e)]. It was observed that the compositions consist of two phases. The INP is formed by PS dispersed domains in the PU continuous matrix. It was also observed that for larger PS (Crystal or EPS) contents the domains became larger. However, for all samples analyzed it was observed that the mechanical properties changed indicating that a semicompatible system was obtained.

TGA data for the pure PU, pure PS, pure EPS and the INP samples are shown in the Table I. It was possible to observe that the pure PU had three clear decomposition ranges while both polystyrene (PS and EPS) presented only one decomposition range near 415°C. The addition of PS 2% for the formation of IPN induced the disappearance of the second temperature range at 371°C. This behavior was not observed for IPN based on EPS. These results suggest that the PU/EPS compositions have a higher degree of mixing.

The PS used has a smaller molecular weight than the EPS. Despite of this, the EPS styrene monomer so-

lution was easier to prepare at the moment of IPN preparation. This behavior can be justified by the previous PS or EPS polymerization method. The PS pellets are obtained by the bulk method resulting in more linked chains whereas the pure EPS is obtained by the action of a solvent inside of the EPS during the polymerization. Consequently the EPS segment presents a better diffusion inside of the PU matrix changing the relationship between the matrix (PU) and the domains (PS or EPS).

## CONCLUSIONS

It was observed that the mechanical properties changed because of the existence of PS or EPS and a reinforced elastomer was obtained.

The saturation of the PU occurred when the PS concentrations was up to 5% (w/w). Above this PS concentration the compositions obtained presented macroscopic phase segregation. This fact was not observed for the compositions with EPS.

It was verified that some properties showed an unexpected behavior. This fact can be justified by the phase segregation: the continuous phase is formed by the PU component with PS or EPS domains.

This investigation showed that it is feasible to obtain compositions between PU and PS or EPS in an attempt to reduce the PS or EPS disposal in the environmental by the reuse of industrial discards. Moreover a new material was obtained with different characteristics and final properties.

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