

# Degradation of High-Impact Polystyrene with Processing and Its Recovery via the Addition of Styrene–Butadiene Rubber and Styrene–Ethylene–Butylene–Styrene Block Copolymer

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**ABSTRACT:** This work was divided into three parts. First, high-impact polystyrene (HIPS) was submitted to a series of extrusion cycles with the objective of evaluating the consequent variations in its thermal and mechanical properties. The results showed slight variations in both the thermal and mechanical properties of HIPS. Second, degraded HIPS/styrene–ethylene–butylene–styrene (SEBS) blends and degraded HIPS/styrene–butadiene rubber (SBR) blends were prepared to evaluate the influence of the elastomeric concentration on the polymer's properties. The incorporation of SEBS or SBR allowed the recovery of the initial properties shown by virgin HIPS. Finally, blends of degraded

HIPS with 2 wt % SEBS or SBR were extruded through four cycles. The mechanical properties remained constant with 2% SEBS added, whereas the mixtures of HIPS with 2% SBR showed an increase in the tensile strength as the number of extrusion cycles increased. The Vicat softening temperature decreased in both cases. The use of differential scanning calorimetry permitted the observation of differences in the crosslinking reactions of different samples as a function of the number of extrusion cycles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 574–581, 2011

**Key words:** additives; polystyrene; recycling

## INTRODUCTION

There has been an enormous amount of research into polymer waste materials in recent decades. These studies have been mainly focused on variations in the mechanical properties within the materials with each extrusion cycle.<sup>1–3</sup> There are also many reports on variations in the mechanical, thermal, and even structural properties that may be taking place.<sup>4</sup> The techniques used to carry out these studies have been many and varied and range from simple mechanical tests to extremely sensitive techniques such as pyrolysis gas chromatography/mass spectrometry.<sup>5–7</sup> All these studies have helped us to understand that the degradation and modification of properties result from the thermal cycles undergone by recycled polymers.

On the other hand, the diverse research into the recovery of polymer waste material has revealed the existence of impurities after the recovery process. These impurities cause significant variations in the final properties of recycled polymers.<sup>8</sup>

Finally, there have been many studies in which the incorporation of certain compounds has allowed the initial properties of the virgin materials to be recovered to some degree. In some cases, these compounds have acted directly on the polymer, and in other cases, they have acted as compatibilizing agent between two polymers (the recycled polymer and the impurity).<sup>9,10</sup>

However, no studies have analyzed the long-term effects of the incorporation of these compounds on recycled materials.

High-impact polystyrene (HIPS) has two phases: polystyrene (PS) and polybutadiene. During the recovery process, the various thermal cycles undergone by the material cause crosslinking in the butadiene chains, which results in increased rigidity in HIPS. At an industrial level, with the objective of recovering the ductile properties of the material, some styrene–butadiene rubber (SBR) is added (ca. 2%), and good results are obtained.

Theoretically, if the loss of ductility of recycled HIPS results from the crosslinking of chains in the butadiene phase, the incorporation of more butadiene (SBR) should cause the same effect in the long term; therefore, the problem will reappear.

On the basis of this information, the objective of this work was to analyze the long-term effects of the

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introduction of SBR into recycled HIPS and the possibility of substituting SBR for styrene-ethylene-butylene-styrene (SEBS).

## EXPERIMENTAL

### Preparation of the samples

PS Impact 6541 (Total Petrochemical, El Prat de Llobregat, Spain), SEBS (Applicazioni Plastiche Industriali, Mussolente, Italy), and SBR (Granzas García Quesada S.L., Agost, Spain) were used for this study. The degradation process was conducted with a conventional extrusion machine at extrusion temperatures of 183.5, 185, 190, and 200°C. The injection-molding experiment was conducted with a conventional injection-molding machine at an injection-molding temperature of 220°C.

Figure 1 shows the different stages of the experimental method.

### Characterization

The mechanical properties of the samples were evaluated with an ELIB 30 electromechanical universal testing machine (S.A.E. Ibertest, Madrid, Spain) with a load cell of 5 kN. All tests were carried out according to the UNE-EN ISO 527 standard at a speed of 50 mm/min.

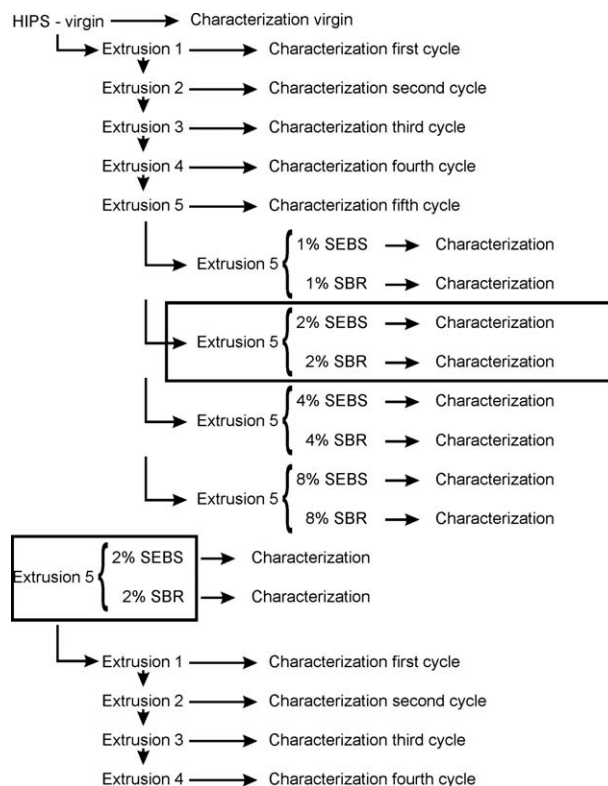
The impact strength was determined with a Charpy impact machine (S.A.E. Ibertest) according to ISO-179.

The values of all mechanical parameters were calculated as averages of five to seven samples for each composition.

To determine the Vicat softening temperature (VST), Vicat/heat deflection temperature equipment (Deflex 687-A2, Metrotec S.A., San Sebastian, Spain) was used. The oil used for the softening was Dow Corning 200 silicon fluid (100 CS) (Midland, Michigan, United States). The development of the test was carried out according to ISO 306 (method A50). For each test, two replica test specimens were taken, and from the obtained experimental data, the average value and the corresponding standard deviation were calculated.

### Color measurements

The color measurements were performed with a Hunter-Lab ColorFlex (Reston, Virginia, United States) reflection spectrophotometer using standard D65 light and a 10° standard observation angle. To measure the color of the specimen, the detector was simply put into contact with the surface. The tristimulus values X, Y, and Z (based on the Commission Internationale de l'Eclairage standard colorimetric system) were measured. The yellowness index (YI), based on ASTM E 313, was calculated according to eq. (1) with X, Y, and Z.  $\Delta YI$  was derived from YI according to eq. (2). The reported values are the averages of five measurements from different samples:



**Figure 1** Scheme of the investigation of the degraded HIPS/SEBS and degraded HIPS/SBR blends.

$$YI = \frac{100(1.3031X - 1.1498Z)}{Y} \quad (1)$$

$$\Delta YI = YI - YI_0 \quad (2)$$

### Thermal analyses [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)]

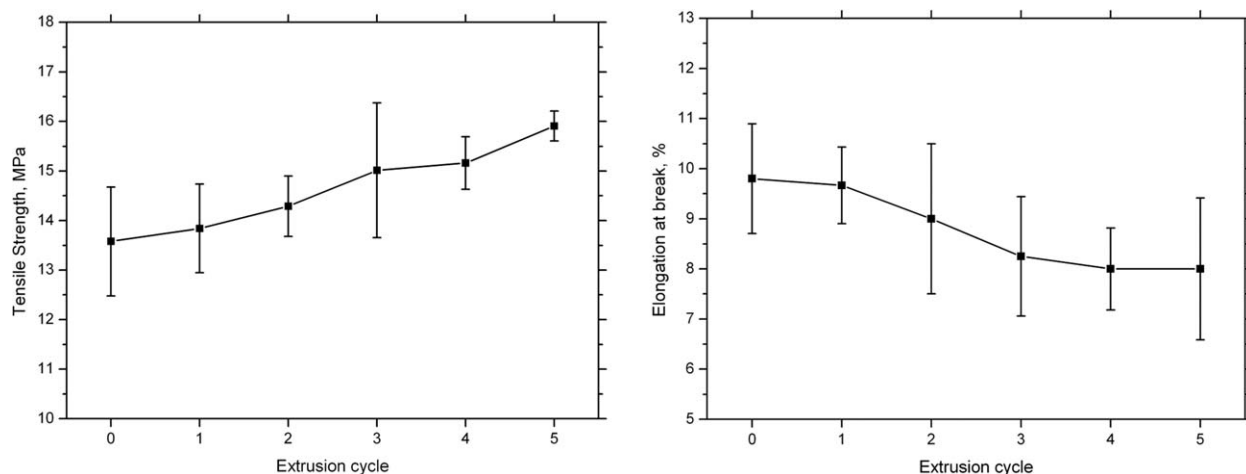
Calorimetric analysis was carried out with an 821 differential scanning calorimeter (Mettler-Toledo, Schwerzenbach, Switzerland). Samples of 9–10 mg were used. The transition temperatures were determined from a heating process (30–250°C at 10°C/min). The tests were performed in a nitrogen environment (flow rate = 50 mL/min).

TGA was carried out with a TGA/SDTA 851 (Mettler-Toledo) with an initial temperature of 30°C and a final temperature of 600°C at a 10°C/min heating rate in a nitrogen atmosphere (50 mL/min). The samples weighed approximately 7 mg.

## RESULTS AND DISCUSSION

### Effects of the reprocessing cycles on the properties of HIPS

The mechanical properties of any material are fundamental for its use in any particular application.



**Figure 2** Variation of the tensile strength and elongation at break with the number of extrusion cycles.

Traction and impact tests are extremely important because they allow us to understand properties such as the tensile strength, elongation at break, and impact strength.

Thermal degradation due to recycling processes causes changes in the internal structure of a polymer, and these changes in turn cause variations in its mechanical properties.

In this study of HIPS, a graphical representation of the values of the tensile strength with the number of extrusion cycles revealed an increasing linear evolution of the values. Furthermore, the evolution of the elongation values with the number of extrusion cycles was different from that obtained with the ultimate strength; in this case, the loss of elongation was very significant between the first and third cycles, whereas after these extrusion cycles, the values remained constant (Fig. 2).

Initially, the variations in HIPS were not significantly noteworthy, and this behavior was logical because the temperatures used in the extrusion process were not particularly high. Kalfoglou and Chaffey<sup>11</sup> showed that large variations in the mechanical properties of HIPS take place only when extremely high temperatures are used (290°C).

Just like the tensile strength and elongation at break, the impact strength did not show large variations with the number of extrusion cycles (Fig. 3).

Despite relatively low extrusion and injection temperatures, the presence of a polybutadiene phase caused a degree of crosslinking of the chains and, as a result, an increase in the rigidity of HIPS.

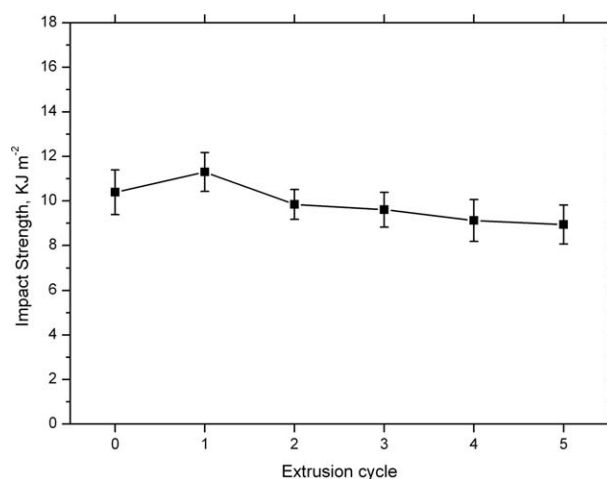
Other authors have carried out studies in this field and observed that significant variations in the mechanical properties do not occur as a result of the slight crosslinking of butadiene chains at processing temperatures around 190°C.<sup>12</sup>

DSC provides information on the transitions that take place in a material because of temperature

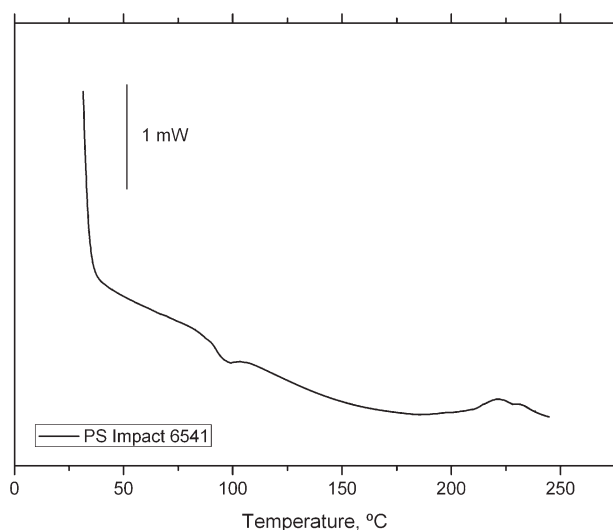
action. The variations in these transitions allow us to identify the structural changes that have occurred in the material. A DSC analysis of HIPS showed two thermal processes: one corresponding to the glass-transition temperature of the styrene phase (ca. 95°C) and the other being the result of the crosslinking reaction of the polybutadiene phase, which is characterized by an exothermic process (ca. 209°C; Fig. 4).

The crosslinking reaction is an irreversible exothermic reaction that is activated by temperature, so the crosslinking enthalpy decreases as a function of the extrusion cycles; the crosslinking reaction resulting from the break in the carbon-carbon double link has been analyzed in detail by others<sup>13,14</sup> (Fig. 5). This process produces changes in the mechanical properties of degraded HIPS.

Another of the properties that characterize a polymer is VST, which combines the actions of the temperature (°C) and the load (N). Figure 6 shows the effect of extrusion cycles on the VST values of reprocessed



**Figure 3** Variation of the impact strength with the number of extrusion cycles.



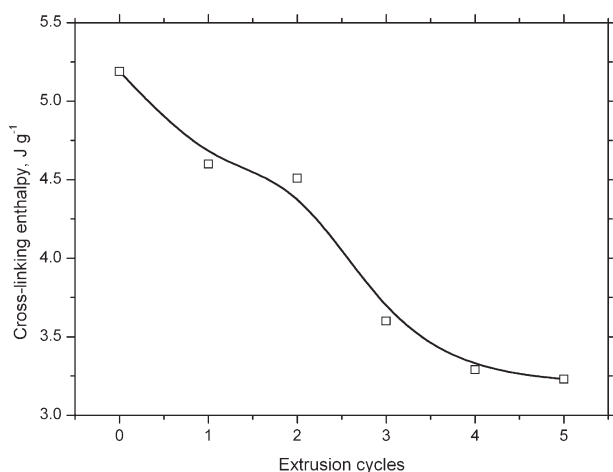
**Figure 4** DSC curve of virgin HIPS.

HIPS. The results show that the VST value of reprocessed HIPS decreased only slightly after the first extrusion cycle. Moreover, VST was almost completely unaffected by further extrusion cycles.

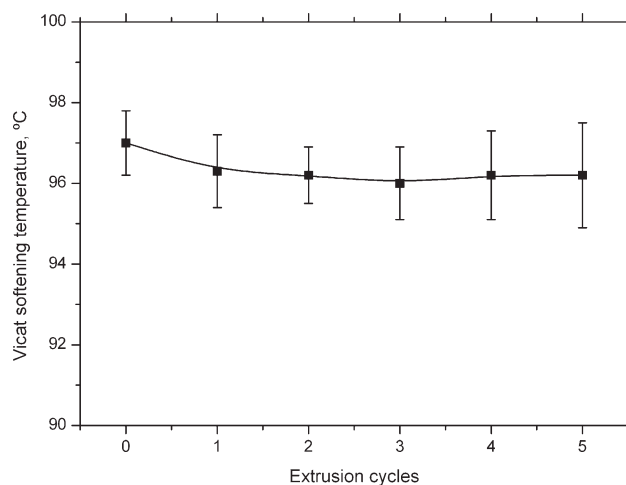
For the results of color measurement, Figure 7 shows  $\Delta YI$  versus the number of extrusion cycles. According to these results,  $\Delta YI$  increased with an increased number of extrusion cycles.

One of the results of the thermal degradation of HIPS is discoloration of the material, and this yellowing has been attributed to variations in the molecular weight, the formation of hydroperoxides, and increases in the number of carbonyl groups by different authors.<sup>15,16</sup>

To acquire further information on the degradation of polymeric materials, TGA was used. In this case, the TGA curves for samples of HIPS with different numbers of extrusion cycles did not show any significant changes in the material's degradation.



**Figure 5** Crosslinking enthalpy of the polybutadiene phase versus the number of extrusion cycles of HIPS.

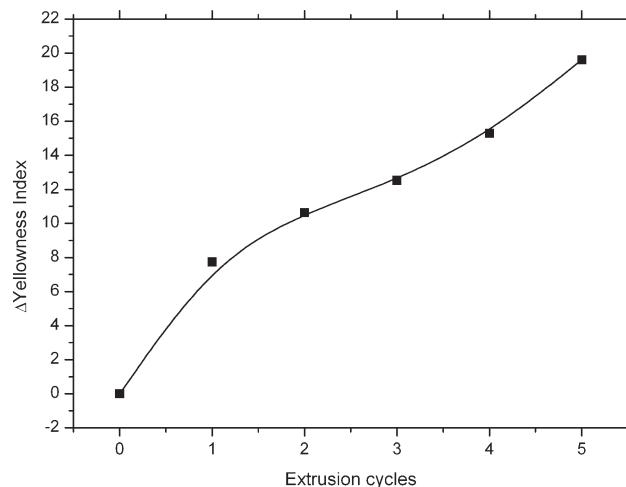


**Figure 6** Influence of the number of extrusion cycles on VST of HIPS.

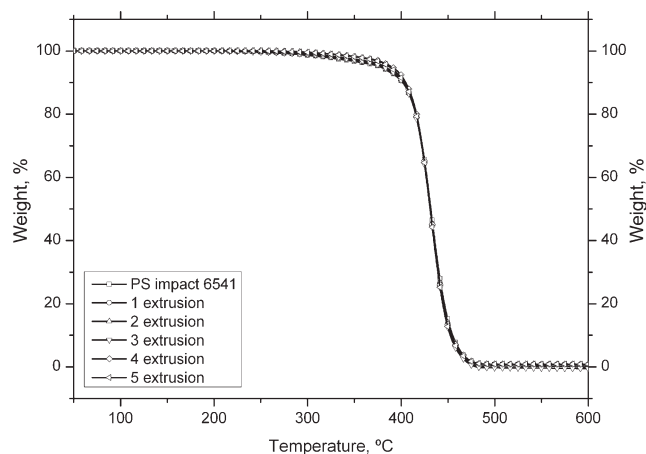
The values obtained for the diverse thermal curves did not indicate a trend in the samples analyzed over various numbers of extrusion cycles. The initial degradation temperature was approximately 410–420°C. Similarly, the analysis of the values of the final degradation temperature did not indicate a trend with respect to the extrusion cycles; values of 460–470°C were reflected (Fig. 8).

#### Analysis of the properties of reprocessed HIPS with low SEBS and SBR contents

The loss of ductility in recycled HIPS limits its use in some applications. Because the change in properties is basically due to the crosslinking of butadiene chains, the addition of SBR is common at an industrial level to increase the flexibility of recycled HIPS. The concentration that is generally used is approximately 2 wt % with respect to HIPS.



**Figure 7** Relationship between YI and the number of extrusion cycles for HIPS.



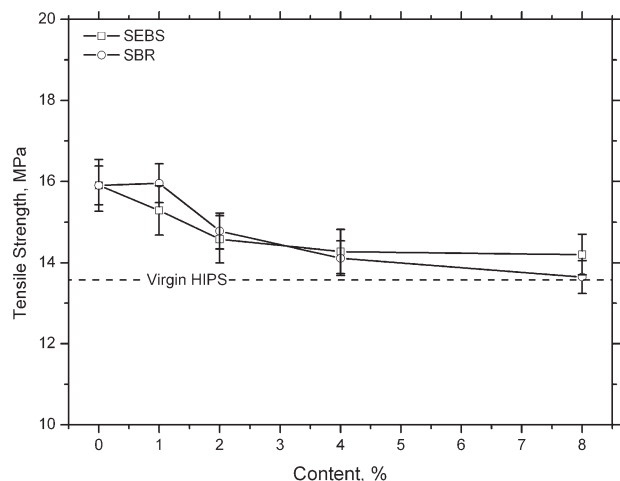
**Figure 8** TGA for the thermal degradation of virgin HIPS and degraded HIPS.

Our study took this a step further and compared SBR and SEBS with different weight percentages (1, 2, 4, and 8%).

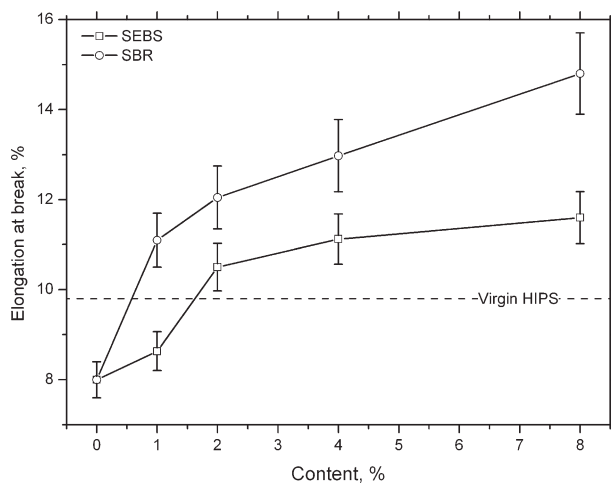
For both SBR and SEBS, the evaluations of the values of different mechanical properties (the tensile strength, elongation at break, and impact strength) were very similar, with the ductility of the mixtures increasing as a function of the SBR or SEBS content. First, the tensile strength fell gradually until it reached values closest to those of virgin HIPS with a concentration of 8% (Fig. 9).

In contrast, the addition of SEBS and SBR caused the opposite effect on the elongation at break. In this case, the values increased significantly even with relatively low percentages and surpassed the initial properties of virgin HIPS with 1% SBR or 2% SEBS (Fig. 10).

Similarly to the previous case, the impact strength increased with an increase in the percentage of SBR or SEBS, although in this case, the impact strength



**Figure 9** Evolution of the tensile strength as a function of the SBR and SEBS contents.



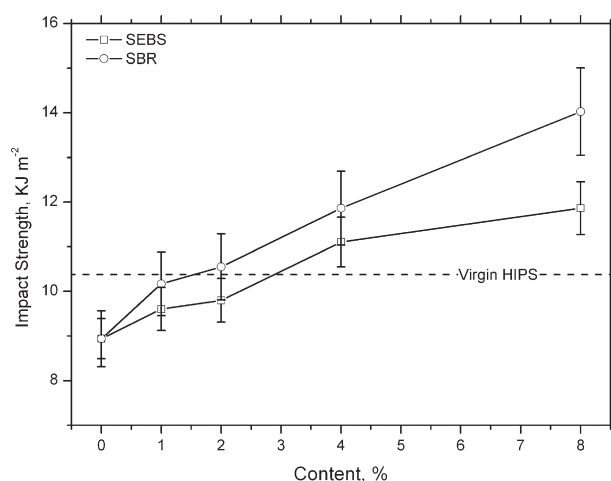
**Figure 10** Evolution of the elongation at break as a function of the SBR and SEBS contents.

did not surpass that of virgin HIPS until a concentration of approximately 4% was reached (Fig. 11).

The incorporation of SBR or SEBS into HIPS after the fifth extrusion allowed the recovery of the initial properties of virgin HIPS to a degree, and in some cases, the initial properties were even surpassed. Initially, the addition of 2% SBR or SEBS allowed the recovery of the original properties of HIPS (mechanical and thermal properties).

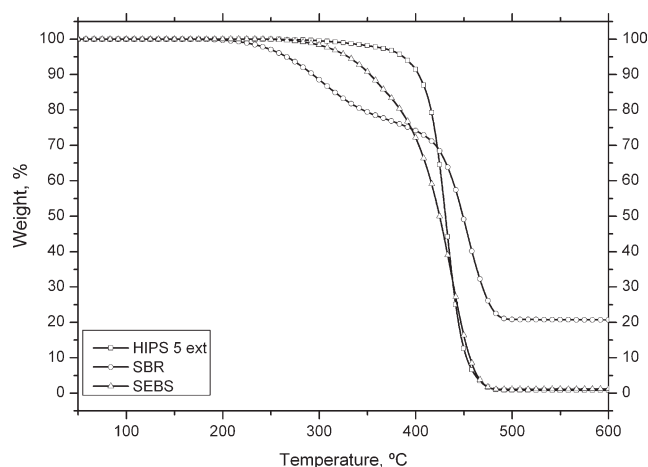
On the other hand, the thermal stability, which is an important property, can be affected if a mixture of polymers is used. TGA is one of the techniques most widely used to evaluate the thermal stability, composition, and thermal degradation kinetics of polymer materials, blends, and composites.

Figure 12 shows the degradation processes of the polymers used in this study (HIPS with five extrusion cycles, SBR, and SEBS). Here we can see the following phenomena. First, the thermal stability of



**Figure 11** Influence of the SEBS and SBR contents on the Charpy impact strength of degraded HIPS.



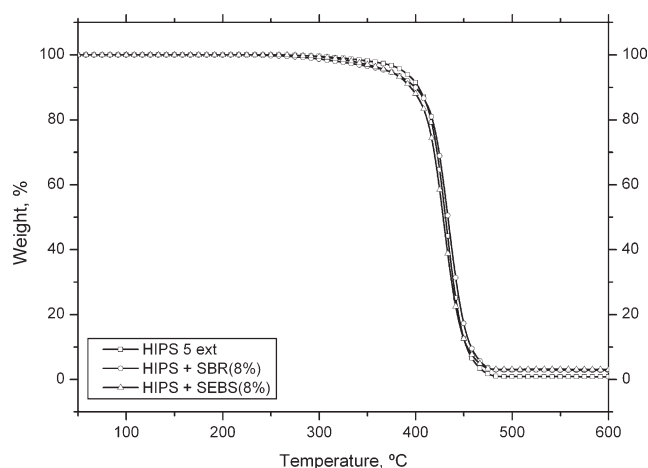


**Figure 12** Thermogravimetric curves of degraded HIPS (five cycles), SBR, and SEBS.

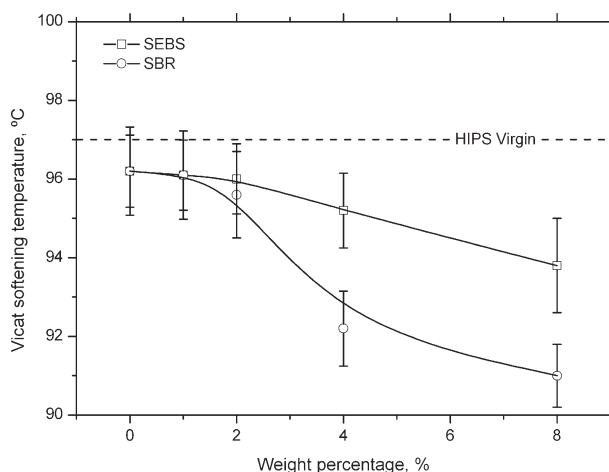
HIPS was greater than that of SBR or SEBS; second, the first and second steps of the thermal degradation of SBR occurred in the temperature ranges of 200–375 and 375–475°C, respectively, whereas the thermal degradation of HIPS with five cycle and SEBS took place after only one step.

Despite these differences, the concentration of SBR and SEBS was so low (8% maximum) that any change in the thermal stability of HIPS was also relatively low (Fig. 13).

Finally, Figure 14 shows the effects of the SEBS and SBR contents on the VST values of degraded HIPS/SEBS and HIPS/SBR blends. The VST values remained constant with concentrations of 1 and 2 wt % in both cases, but the VST values were different when the SEBS and SBR concentrations were higher than 2 wt %. First, in degraded HIPS/SBR blends, the VST values show a marked decrease; second, the VST values of degraded HIPS/SEBS blends showed a slight decrease with increased SEBS content.<sup>17,18</sup> In this case, the addi-



**Figure 13** Thermogravimetric curves of degraded HIPS (five cycles), HIPS and 8% SBR, and HIPS and 8% SEBS.



**Figure 14** Influence of the number of extrusion cycles on the VST values of degraded HIPS with 2 wt % SEBS and HIPS with 2 wt % SBR.

tion of SBR or SEBS did not allow the recovery of the initial properties of virgin HIPS.

The results have led us to the conclusion that the most viable percentage for the recovery of properties of degraded HIPS is 2 wt % because the various mechanical properties (tensile strength, elongation at break, and impact strength) are all close to those of virgin HIPS, and the VST value does not fall excessively.

#### Properties of degraded HIPS/SEBS blends and degraded HIPS/SBR blends after several reprocessing cycles

The addition of compounds to recycled polymers has, in most cases, beneficial effects on the recycled materials. However, a fact that is often neglected in the study of the recycling of such materials is the effect that these compounds may have when the materials are subjected to a number of reprocessing cycles.

Table I summarizes the mechanical test results and VST results for degraded HIPS/SBR (2 wt %) blends and degraded HIPS/SEBS (2 wt %) blends according to the number of extrusion cycles.

With a 2% addition of SEBS or SBR to HIPS extruded 5 times, the evolution of the tensile strength values differed. The values corresponding to the addition of SEBS remained practically constant, whereas with the addition of SBR, we saw a slight increase in the tensile strength with each new extrusion cycle.

On the other hand, the elongation at break of the samples remained practically constant during the first few cycles, but after the third cycle, the values decreased slightly.

Finally, the trend for the impact strength depended on whether SBR or SEBS was used. For samples with 2 wt % SBR, the impact strength increased linearly with the number of extrusion cycles, whereas the impact strength of the mixtures

**TABLE I**  
**Mean Mechanical and Thermal Properties of Degraded HIPS/SBR (2 wt %)**  
**Blends and Degraded HIPS/SEBS (2 wt %) Blends with Respect to the Number**  
**of Extrusion Cycles**

Extrusion cycles	0	1	2	3	4
HIPS/SBR (2 wt %)					
Tensile strength (MPa)	14.78	16.05	16.14	16.47	16.82
Elongation at break (%)	12.05	11.62	11.63	11.12	10.04
Impact strength (kJ/m <sup>2</sup> )	10.55	10.73	11.29	12.02	12.53
VST (°C)	95.6	96.4	95.8	94.6	94.2
HIPS/SEBS (2 wt %)					
Tensile strength (MPa)	14.57	14.27	14.14	14.04	13.9
Elongation at break (%)	10.50	10.42	10.32	9.82	9.51
Impact strength (kJ/m <sup>2</sup> )	9.81	9.93	10.16	10.19	10.20
VST (°C)	96.0	96.2	95.2	94.6	94.6

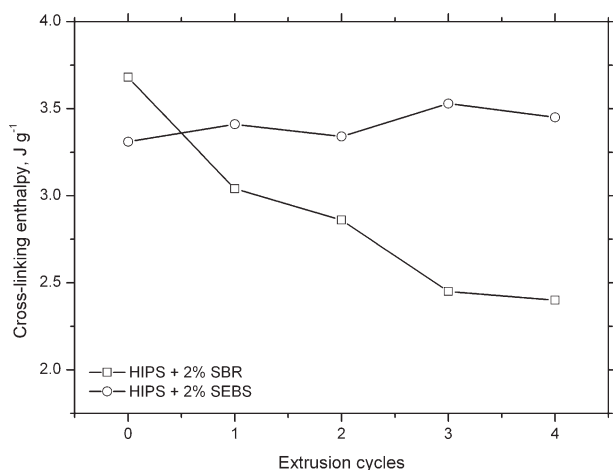
of HIPS and SEBS remained constant and independent of the number of extrusion cycles.

The VST results for the degraded HIPS/SEBS blends and degraded HIPS/SBR blends showed that VST suffered a slight decrease after the first extrusion cycle, and it was almost completely unaffected by the SEBS and SBR contents.

Once again, DSC allowed us to observe changes in the crosslinking reaction, which was the cause of the variations in the mechanical behavior of the mixtures with 2 wt % SBR. However, the crosslinking reaction occurring in the mixtures of HIPS and SEBS (2 wt %) remained more or less unaffected, regardless of the number of extrusion cycles (Fig. 15).

## CONCLUSIONS

The application of successive extrusion cycles to HIPS caused slight variations in the mechanical, thermal, and physical properties of the material, even when low extrusion temperatures were used.



**Figure 15** Crosslinking enthalpy of the polybutadiene phase of degraded HIPS/SBR (2 wt %) and degraded HIPS/SEBS (2 wt %) blends versus the number of extrusion cycles.

These variations could be attributed mainly to a crosslinking process in the polybutadiene phase, which was observed with the DSC technique.

The loss of properties resulting from extrusion cycles could be counteracted by the addition of other polymers. The addition of SBR and SEBS allowed us to recover the initial properties of the virgin material to some degree. In contrast, the VST value remained constant with 2 wt % SBR or SEBS but decreased sharply when more than 2 wt % SBR or SEBS was added. This behavior was due mainly to the incorporation of a new elastic phase (SBR and SEBS) into the degraded HIPS. Examining the results, we can conclude that both polymers are technically viable for the recovery of the initial properties of virgin HIPS.

Finally, the reprocessed mixtures of degraded HIPS and SBR (2 wt %) and degraded HIPS and SEBS (2 wt %) caused new variations in the mechanical properties, although the values for the mixtures with SEBS were closer to those of virgin HIPS than the values of the mixtures with SBR. These differences were due to the chain crosslinking that took place with the incorporation of SBR into degraded HIPS.

On the basis of these results, although the addition of SEBS or SBR allowed us to recover the properties of degraded HIPS, the recycled materials with SEBS performed better and generally had better values than the mixtures with SBR.

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