

# Effects of the Injection-Molding Temperatures and Pyrolysis Cycles on the Butadiene Phase of High-Impact Polystyrene

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Received 26 September 2006; accepted 23 March 2007

DOI 10.1002/app.26588

Published online 20 July 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Recycling is a thermal process in which polymers are melted to produce new products. It is possible that these thermal processes could modify their mechanical and thermal properties. Polymer degradation can be characterized with thermogravimetric analysis and differential scanning calorimetry. Recycled materials tested with these methods have shown variations in some thermal properties, such as the glass-transition temperature and thermal degradation onset, but the sensitivity of these methods is not sufficient to investigate the changes in the characteristics of polymers when materials are exposed to moderate temperature conditions or several thermal cycles. To study these structural changes, a much more sensitive technique, such as pyrolysis–gas chromatography/mass

spectrometry (Py–GC/MS), is needed. Small variations in the structure can be determined by Py–GC/MS. Each pyrolysis product can be identified by its retention time and mass spectrum with the use of reference literature. In this work, we have studied structural changes in high-impact polystyrene as a function of the injection-molding temperature and pyrolysis cycles. The results do not show significant changes in samples processed at different temperatures with Py–GC/MS, but the values of the pyrolysis products differ as a function of the pyrolysis cycles. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1903–1908, 2007

**Key words:** degradation; differential scanning calorimetry (DSC); polystyrene; pyrolysis

## INTRODUCTION

Polymers are becoming increasingly important in our society. They have numerous and varied properties that make them useful in many different industrial sectors, and polymers are now in fact replacing many metal and ceramic materials. The consumption of polymer materials has increased greatly since 1950, and this consumption has led to the formation of great amounts of residues that need to be recycled.

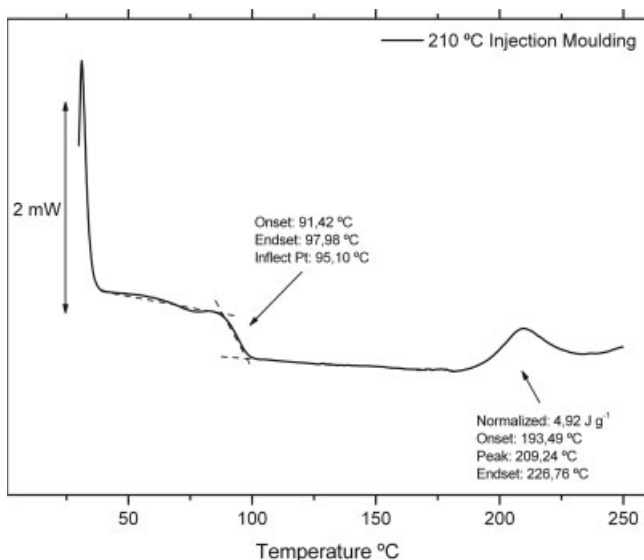
There are two important factors in the recovery process of polymers: environmental and economic. First, the governments of the world have imposed new laws to reduce the environmental impact of waste products and to try to tackle the problem of world climate change. Second, the recovery of polymer materials has become even more important with the increases in petrol prices.<sup>1,2</sup>

These factors, among others, mean that material recycling policies are now more important than ever. However, it is important not to neglect the quality of the materials obtained. Recycling is a thermal pro-

cess in which the polymers are melted to produce new products, and it is possible that these thermal processes could modify the polymer's mechanical and thermal properties. Polymer recycling is very important for the packaging and packing sector as it produces great amounts of residues. Current packaging laws require that in food processing only virgin (not recycled) materials can be used, and this means that residues from this sector are generally of high quality. There are many different polymers that are widely used in the packaging industry, such as high-density polyethylene, low-density polyethylene, and polypropylene, as well as other products that, although less used, are no less important, as is the case for high-impact polystyrene (HIPS), which is widely used in the dairy sector. The quality of the material recovered depends on different factors, such as thermal degradation as a result of different recovery cycles,<sup>3</sup> UV degradation as a result of exposure to solar radiation,<sup>4</sup> and the presence of impurities from an incorrect separation of materials,<sup>1</sup> although occasionally mixtures of polymers have been used to improve thermal and mechanical properties.<sup>5</sup>

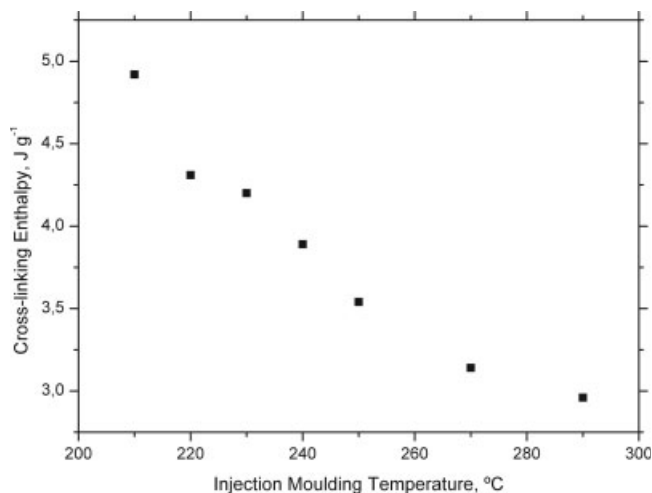
When the recovery of HIPS is studied, complications may arise because there are two material phases, a styrene phase and a butadiene phase, each

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**Figure 1** DSC curve of HIPS injection-molded at 210°C.

of which may react in a different way. The residue's quality depends on different factors. There are thermal analytical techniques that have been used by different authors to analyze the characteristics of polymers, such as dynamic mechanical analysis, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Recycled materials show variations in some thermal properties, such as the glass-transition temperature and thermal degradation onset. However, the sensitivity of TGA and DSC is limited to detecting only significant variations in the characteristics of polymers when they are exposed to low or moderate temperatures or different thermal cycles.<sup>5,6</sup> In this work, polymers have been analyzed with DSC, and significant changes have been observed only in the crosslinking reaction



**Figure 2** Crosslinking enthalpy of the butadiene phase versus the injection-molding temperature.

of the butadiene phase. For these cases, a much more sensitive technique, such as pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS), can be applied to investigate the smaller variations in the structures of the polymers.<sup>7</sup>

The aim of this work is to analyze the results of studies of HIPS with Py–GC/MS, first through the variation of the process temperature and second through the application of successive pyrolysis cycles, with the aim of simulating a high degree of degradation. In this way, we aim to establish the validity of this technique as a control tool for recovered materials as a function of the compounds present.

## EXPERIMENTAL

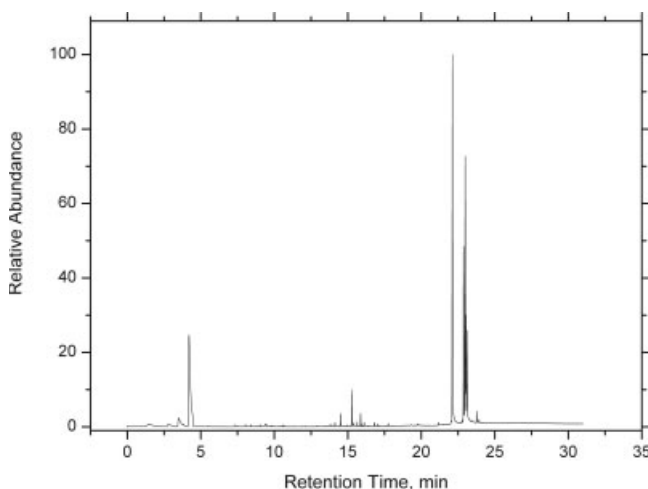
### Sample preparation

The HIPS used in the experiment was a commercial grade (Empera 514, BP Spain S.A.U., Madrid, Spain). The injection molding was carried out in a conventional injection-molding machine (Meteor 270/75, Mateu & Solé, Barcelona, Spain) at different molding temperatures (210, 220, 230, 240, 250, 270, and 290°C).

### Sample characterization

The calorimetric analysis was carried out with a DSC 821 (Mettler–Toledo, Inc., Schwerzenbach, Switzerland). Samples weights between 8 and 9 mg were used. The glass-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).

All samples were pyrolyzed with the use of a pyrolysator (Pyroprobe 1000, CDS Analytical, Inc.), which was interconnected to a gas chromatography/mass spectrometry apparatus (6890N, Agilent Tech-



**Figure 3** Pyrogram of HIPS injection-molded at 210°C.

TABLE I  
Structures for the Peaks in the Gas Chromatography Traces

| Compound                | Time (min) | Structure | Compound                                       | Time (min) | Structure |
|-------------------------|------------|-----------|--|------------|-----------|
| 1,3-Butadiene           | 1.46       |           | 1,3-Diphenylpropane                            | 14.52      |           |
| Benzene                 | 2.14       |           | Styrene dimer                                  | 15.28      |           |
| Toluene                 | 2.81       |           | 2,4-Diphenyl-1-pentene                         | 15.40      |           |
| Cyclohexene-4-ethenyl   | 3.49       |           | Benzene, 1,1'(1,2-cyclobutanediyl)bis-, trans- | 15.64      |           |
| Ethyl benzene           | 3.84       |           | Naphthalene-1,2,3,4-tetrahydro-1-phenyl        | 15.87      |           |
| Styrene monomer         | 4.20       |           | 1-Phenyl-1,2-dihydronaphthalene                | 16.03      |           |
| $\alpha$ -Methylstyrene | 5.49       |           | Styrene trimer                                 | 22.12      |           |

nologies, España S.L., Madrid, Spain) equipped with a 5973N mass selective detector (Agilent Technologies). A 30-m-long capillary column (HP-5ms), 0.25 mm thick, with a 0.25- $\mu$ m stationary phase was programmed from 40 to 300°C at 10°C/min and was subsequently maintained at the highest temperature for 5 min. The gas used was helium with a 50:1 split ratio. The mass selective detector was programmed to detect masses between 50 and 650 amu. Samples of HIPS processed at different temperatures (ca. 1.2–1.1 mg) were pyrolyzed at 450°C for 10 s. The samples were subjected to different pyrolysis cycles under the same conditions time after time until the four cycles were completed.

## RESULTS AND DISCUSSION

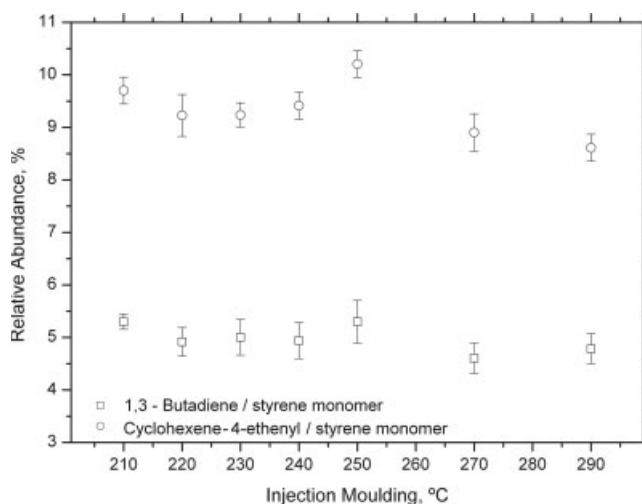
### Thermal analysis

DSC provides information on the transitions that take place in a material due to 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 shows two thermal processes: one corresponding to the glass-transition temperature of the styrene phase around 95°C and the other being the result of the crosslinking reaction of butadiene characterized by an exothermic process around 209°C (Fig. 1).

The glass-transition temperature is highly related to the mobility of the polymer chain. The use of high temperatures can provoke breaks in the chain, thus reducing their length. In these cases, the glass-transition temperature shows a decrease in its value because of the increase in mobility,<sup>8</sup> but in this work, the values of the glass-transition temperature are very similar (glass-transition temperature = 95.2  $\pm$  0.4°C). It is highly probable that the structural variations of the HIPS samples processed at different temperatures will be too small to be observed with this technique. Thus, much more sensitive techniques that allow the detection of structural changes as a function of the injection-molding temperature are needed.

The DSC method also shows the temperature of the onset of polymer degradation, but because of the thermal crosslinking reaction, which is related to the presence of the double bonds in the butadiene structure, the detection of the onset temperature is quite difficult, in that both processes are overlapped. Butadiene is very sensitive to thermal oxidation reactions, which also take place in other materials containing butadiene, such as acrylonitrile–butadiene–styrene.<sup>9</sup>

The crosslinking reaction is an irreversible exothermic reaction that is activated by temperature, so the crosslinking enthalpy decreases as a function of the injection-molding temperature; the crosslinking



**Figure 4** Plot of the evolution of the butadiene compound/styrene monomer ratio versus the injection-molding temperature.

reaction coming as a result of the break in the carbon–carbon double link has been analyzed in detail by others<sup>10,11</sup> (Fig. 2).

In this work, the DSC method shows only differences in the crosslinking enthalpy and does not show differences in the glass-transition temperature, which indicates differences in the styrene phase. Therefore, a much more sensitive technique is needed that allows the observation of structural differences as a function of the injection-molding temperature.

### Py-GC/MS analysis

Py-GC/MS has been used in the degradation of HIPS, and these studies show variations in the ratios of the different components in terms of the molecular weight and pyrolysis temperature. Other authors have used this technique to find differences in block and random copolymers and in the calculation of the crosslinking density of natural rubber.<sup>12–15</sup>

The evolved products can be classified into three groups (Fig. 3): compounds having one benzene ring and butadiene compounds (retention time = 1–7 min) having two benzene rings (retention time = 13–17 min) or three benzene rings (retention time = 22–24 min). There are no compounds that have four or five benzene rings (Table I). Other authors have observed the same behavior in the thermal degradation of polystyrene nanocomposites.<sup>16</sup> There are also diverse compounds, with a retention time understood to be between 7 and 12 min, that lose intensity, depending on the process temperature or increases in the number of pyrolysis cycles. Among these, we can find benzene-3-pentenyl (8.15 min), cyclohexene-1,5-diethenyl-3-methyl-2-methylene (8.38

**TABLE II**  
**Relative Intensities of Compounds with Two Benzene Rings (wt %) in Terms of the Injection-Molding Temperature**

| Product with two benzene rings                 | Injection-molding temperature (°C) |     |     |     |     |     |     |
|--|------------------------------------|-----|-----|-----|-----|-----|-----|
|  | 210                                | 220 | 230 | 240 | 250 | 270 | 290 |
| Styrene monomer                                | 100                                | 100 | 100 | 100 | 100 | 100 | 100 |
| 1,2-Diphenylpropane                            | 2.4                                | 2.4 | 2.0 | 2.1 | 2.1 | 2.4 | 2.3 |
| Styrene dimer                                  | 6.7                                | 6.5 | 5.8 | 5.8 | 6.6 | 7.3 | 7.1 |
| 2,4-Diphenyl-1-pentene                         | 0.7                                | 1.1 | 0.7 | 0.9 | 1.0 | 1.0 | 1.0 |
| Benzene, 1,1'(1,2 cyclobutanediyl)bis-, trans- | 1.0                                | 0.5 | 0.5 | 0.3 | 0.5 | 0.6 | 0.4 |
| Naphthalene-1,2,3,4-tetrahydro-1-phenyl        | 2.4                                | 3.0 | 2.2 | 2.7 | 3.0 | 3.3 | 2.9 |
| 1-Phenyl-1,2-dihydronaphthalene                | 0.5                                | 1.0 | 0.5 | 0.5 | 0.5 | 0.6 | 0.5 |

min), and benzene-3-cyclohexen-1-yl (10.55 min). Other compounds present have not been identified. Taking as a reference the peak that corresponds to the styrene monomer and relating it to the products that are due to the presence of butadiene, we did not observe significant differences when the processing temperatures used were those recommended by the manufacturer, whereas for the samples processed at 270 and 290°C, we saw slight decreases in the butadiene monomer/styrene monomer ratio and the butadiene dimer/styrene monomer ratio<sup>13</sup> (Fig. 4).

Given the small variation that HIPS undergoes when processed just once, and with the aim of determining the use of Py-GC/MS as a control tool, we have analyzed the results of a sample pyrolyzed up to four times with the objective of causing in the material a high degree of thermal degradation and thus simulating successive cycles of thermal degradation in the material. In this case, the results are very informative and show significant differences in the products of pyrolysis. In contrast, the rest of the compounds do not show significant changes (Table II).

The results show that pyrolysis products do not change when HIPS is processed only once; it only

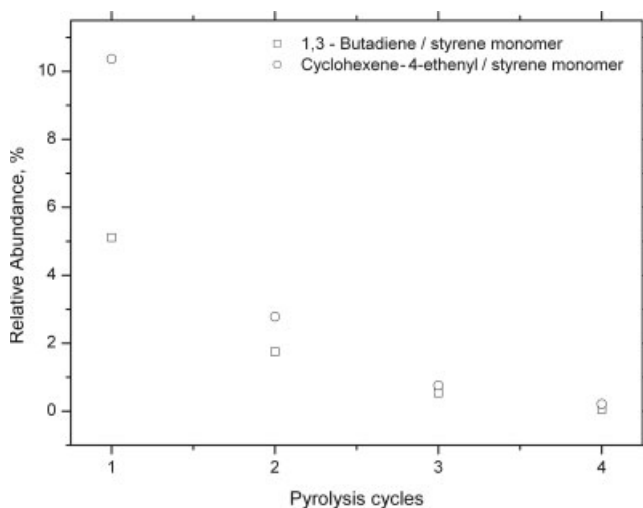
slows the reduction of the butadiene compounds. Obviously, the butadiene phase is more sensitive to temperature than the styrene phase.<sup>11,17</sup>

On the other hand, pyrolysis products show significant differences when pyrolysis cycles are used. First, butadiene compounds (1,3-butadiene and cyclohexene-4-ethenyl) decrease quickly in terms of pyrolysis cycles because butadiene is very sensitive to the temperature (Fig. 5).

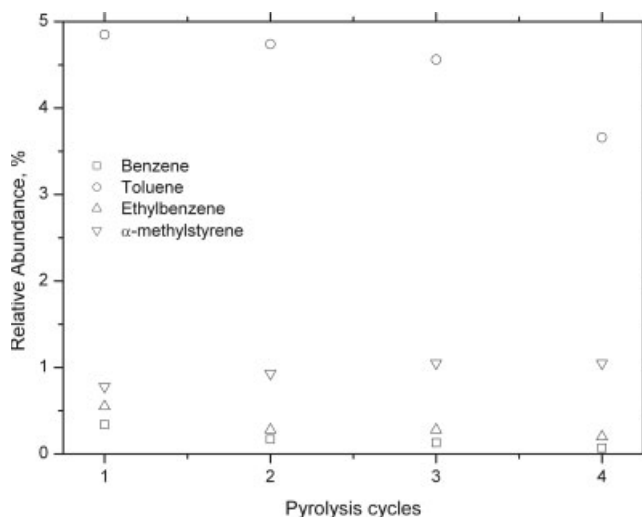
Second, compounds having one benzene ring evolve in a different way.  $\alpha$ -Methylstyrene increases in terms of the pyrolysis cycles; however, benzene decreases when pyrolysis cycles are used<sup>18</sup> (Fig. 6).

Third, the evolution of compounds having two benzene rings is similar to that of compounds with one benzene ring, but a styrene dimer increases much more than other pyrolysis products. On the other hand, naphthalene-1,2,3,4-tetrahydro-1-phenyl decreases with the pyrolysis time. However, the 1,2-diphenylpropane, 2,4-diphenyl-1-pentene, 2-phenylcyclobutyl benzene, and 1-phenyl-1,2-dihydronaphthalene contents remain constant (Fig. 7).

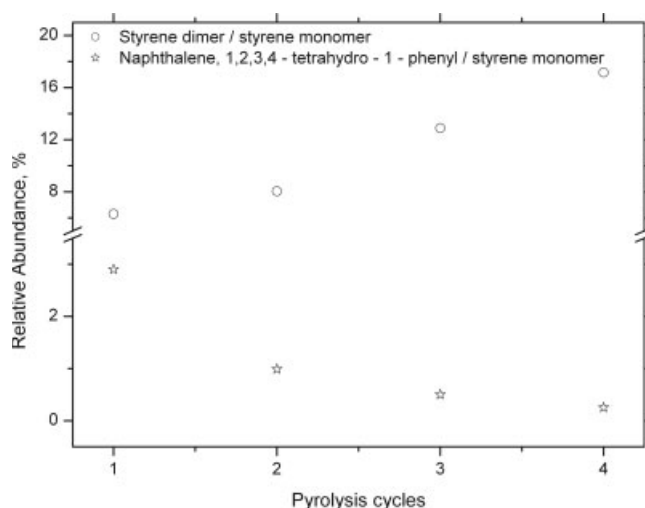
Finally, compounds having three benzene rings do not show any differences with pyrolysis cycles.



**Figure 5** Effect of the pyrolysis cycles on the butadiene compound/styrene monomer ratio.



**Figure 6** Effect of the pyrolysis cycles on the one-benzene-ring compound/styrene monomer ratio.



**Figure 7** Effect of the pyrolysis cycles on the two-benzene-ring compound/styrene monomer ratio.

### CONCLUSIONS

The high consumption of polymers creates a lot of residues. The need to recycle these residues has led to detailed studies into the different variations occurring in the materials after various recycling processes. Thermal analytical methods study only polymer thermal degradation.

In this work, DSC methods did not show significant changes at different injection-molding temperatures. The crosslinking reaction of butadiene did not allow the quantification of the onset degradation temperature, but the crosslinking enthalpy decreased, depending on the injection-molding temperature.

Thermal analytical methods do not show great changes in the thermal properties of HIPS. We need a much more sensitive technique for the detection of small structural changes. Py-GC/MS allows the analysis of pyrolysis compounds of HIPS, but the results do not show significant changes in terms of the injection-molding temperature. They show differ-

ences only in butadiene compounds; however, styrene compounds do not change with the injection-molding temperature.

Finally, the results show important changes for pyrolysis cycles in virgin HIPS. Butadiene compounds are very sensitive to temperature, and the results show that small compounds increase as a function of the pyrolysis cycles; thus, Py-GC/MS can be used as a control tool for recovered material and as such be used to improve its properties, possibly with the use of additives or in a mixture with virgin material.

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