MODELLING THE DEGRADATION PROCESSES IN HIGH-IMPACT POLYSTYRENE DURING THE FIRST USE AND SUBSEQUENT RECYCLING

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MODELLING THE DEGRADATION PROCESSES IN HIGH-IMPACT POLYSTYRENE DURING THE FIRST USE AND SUBSEQUENT RECYCLING

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ABSTRACT

Polymers are subjected to physical and chemical changes during their processing, service life, and further recovery, and they may also interact with impurities that can alter their composition. These changes substantially modify the stabilisation mechanisms and mechanical properties of recycled polymers. Detailed knowledge about how the different stages of their life cycle affect the degree of degradation of polymeric materials is important when discussing their further waste recovery possibilities and the performance of recycled plastics.

A dual-pronged experimental approach employing multiple processing and thermo-oxidation has been proposed to model the life cycle of recycled high-impact polystyrene (HIPS). Both reprocessing and thermo-oxidative degradation are responsible for coexistent physical and chemical effects (chain scission, crosslinking, apparition of oxidative moieties, polymeric chain rearrangements, and physical ageing) on the microstructure and morphology of polybutadiene (PB) and polystyrene (PS) phases; these effects ultimately influence the long-term stability, and the rheological and mechanical behaviour of HIPS. The PB phase has proved to be the initiation point of HIPS degradation throughout the life cycle. Thermo-oxidation seems to have more severe effects on HIPS properties; therefore, it can be concluded that previous service life may be the part of the life cycle with the greatest influence on the recycling possibilities and performance of HIPS recyclates in second-market applications.

The results from the life cycle degradation simulation were compared with those obtained from real samples from a large-scale mechanical recycling plant. A combination of different analytical strategies (thermal analysis, vibrational spectroscopy, and chromatographic analysis) is necessary to obtain a detailed understanding of the quality of recycled HIPS as defined by three key properties: degree of mixing, degree of degradation, and presence of low molecular weight compounds.

Keywords: Recycling; high-impact polystyrene; degradation; quality analysis; thermal analysis; vibrational spectroscopy; chromatography techniques; thermo-oxidation; reprocessing; dynamic mechanical properties; polybutadiene microstructure.
SAMMANFATTNING

Under bearbetning, användning och återvinning sker gradvis fysikaliska och kemiska förändringar i polymera material. Lågmolekylära föreningar kommer att diffundera in i polymermatrisen, samtidigt som tillsatser kan diffundera ut från matrisen. Dessa förändringar påverkar återvunna plasters mekaniska egenskaper och kvarvarande livslängd. Möjliheterna att återvinna plast och att använda dessa i nya produkter kräver att de återvunna plasternas egenskaperna är noggrant bestämda. För detta ändamål krävs kunskap om hur det polymera materialet påverkas under användning och återvinning. Genom att designa en tänkbar livcykel där nedbrytning i såväl den första användningen som i själva återvinningsprocessen finns med kan varje nedbrytningsdel och dess inflytande på materialegenskaperna analyseras.

En nedbrytningsmodell designades som innefattade återbearbetning (nio gånger) och termo-oxidation, i denna modell analyserades egenskapsförändringar i återvunnen slagfast polystyren (HIPS). Såval bearbetning som termo-oxidation innebär att parallella fysikalisk och kemisk nedbrytning kan ske (kedeklyvning, tvärbinding, bildning av funktionella grupper, ordning av polymerkedjor) i polybutadien (PB)- och polystyren (PS)-fasernas. Detta resulterar i försämrade långtidegenskaper (dvs. kvarvarande livslängd), reologiska och mekaniska egenskaper. I HIPS sker initieringen av nedbrytningen i PB-fasen. Termo-oxidation påverkar egenskaperna mest, vilket innebär att det är under användningen av HIPS som det största egenskaperförsämringen sker. Själva återvinningsprocessen (upprepad bearbetningen) har i sig ett mindre inflytande på materialegenskaperna.

Resultaten från modelleringen av HIPS under hela livscyklarna jämfördes också med prov tagna direkt från en storskalig mekanisk återvinningsanläggning. En kombination av olika analytiska strategier (termoanalys, vibrationalspektroskopi, och kromatografi) visade sig vara nödvändiga för att i detalj förklara och förstå vilka parametrar som är av betydelse för att ge återvunnen HIPS en kvalitetstämpel.

Keywords: Återvinning; slagfast polystyren (HIPS); nedbrytning; kvalitet; termoanalys; vibrationalspektroskopi; kromatografi; termooxidation; bearbetning; dynamiska mekaniska egenskaper; polybutadien mikrostruktur.
1. INTRODUCTION

1.1 SCOPE OF THE STUDY

Polymeric materials allow the manufacture of low-cost products with excellent performance, contributing to energy saving and a sustainable development. The resistance against biodegradation shown by synthetic polymers has caused, however, an important environmental problem concerning their waste management. Landfill disposal constitutes the main route for plastic waste, but this procedure does not guarantee suitable residue management in terms of resource exploitation and environmental protection. Governmental and regulatory institutions are encouraging alternative strategies, such as the use of biodegradable polymers, and material and energy recovery from plastic waste.

Mechanical recycling has been identified as the preferred route for the recovery of relatively clean and homogeneous plastic waste streams. The study of recycled polymers must consider, however, the degradative processes to which these materials are subjected during processing, service life, and further recovery, which ultimately alter their chemical structure, long-term stability, and mechanical properties. The aim of the study is therefore to give detailed knowledge about the effects of degradation on the properties of recycled polymers during their life cycle.

1.2 PLASTICS RECOVERY IN EUROPE

1.2.1 Analysis of plastic consumption and recovery in Europe

Polymer demand in Western Europe has grown continuously during the past decade, reaching a total volume of 43.5 million tonnes in 2004 [1]. This progressive increment in plastic consumption is consequently responsible for an increase in post-consumer plastic waste, which constitutes a valuable resource in terms of both material and energy. The diversification of plastic waste management procedures is fundamental to minimise the total volume sent for landfill. It has been demonstrated, however, that material recycling and energy recovery alone are unable to meet governmental targets for plastic waste recovery, so a combination of the available recovery options (mechanical recycling, feedstock recycling, and energy recovery) is needed for optimal environmental and economic efficiency [1, 2].
The available options for plastic waste recovery, as alternatives to landfill disposal, include material recycling and energy recovery. Mechanical recycling entails the remelting of plastic waste into new plastic products. In feedstock recycling, plastic wastes are cracked and depolymerised by chemical means into a series of petrochemical products or monomers, which can be later transformed by synthesis into new polymeric products. Finally, energy recovery employs polymeric waste streams as fuel for energy production. Current environmental policies consider the material efficiency of polymers during their service life and the reduction of their environmental impact throughout their entire life cycle. Suitable waste management recovery options contribute therefore to the sustainable development of our societies taking into account a life cycle perspective, by closing the material and energy loop and enhancing the conversion of waste materials into valuable resources (Figure 1.1).

![Figure 1.1. Plastic waste management options in terms of the life cycle of polymeric products.](image)

The rate of plastic waste recovery has increased continuously since the mid 1990’s, due to the establishment of mechanical recycling and energy recovery facilities throughout Europe; feedstock recycling remains, however, as a minor alternative. As a result of these developments, decoupling between the volume of plastic consumption and the volume sent to landfills is currently being achieved in countries with a developed waste management infrastructure (Figure 1.2) [1].
1.2.2 Mechanical recycling. Bottlenecks associated with industrial activity.

Of the different plastic waste management alternatives, mechanical recycling is the most suitable recovery route for relatively clean and homogeneous waste streams. Recent life-cycle assessment studies have pointed out, moreover, that mechanical recycling is preferable to other management procedures in terms of overall energy use and emissions of gases that contribute to global warming [4]. Nevertheless, there remain technological and commercial difficulties that the plastic recycling industry must overcome.

- **Difficulties in the dismantling, identification and separation of mixed plastic waste streams.**

The integrated nature of consumer products (plastics, metals, and ceramics in close combination) causes difficulties in dismantling and separation of their residues [3, 5]. Moreover, mixed polymer composition and the presence of impurities in plastic waste streams require the development of automatic and effective separation methods prior to reprocessing. Some studies have been done to determine the degree to which prior separation brings value to waste plastics as raw materials for new products [6]. The possibility of reducing separation requirements and broadening the
range of applications for recycled plastics through the addition of elastomers, compatibilisers, fillers, and other additives has also been reported [7, 8].

- **Scientific knowledge about the influence of recycling processes on the composition, structure, and properties of polymeric materials.**

  In recent years, polymer recycling investigation has focused on the effects of multiple processing and artificial ageing on the macroscopic properties of polymers. It is worth mentioning the studies on the upgrading of recycled plastics [7, 9-11], the effects of simulated recycling on the properties of polyolefins [12, 13], and the analysis of the degradative effects of reprocessing [11]. Further investigation is needed, however, about the degradative effects of previous life and recycling on a molecular scale.

- **Presence of hazardous compounds in plastic wastes.**

  Plastic wastes may contain a large number of hazardous compounds that complicate the recycling processes, such as degradation products of additives, brominated flame retardants, and phthalates. The development of procedures to identify, quantify, and extract these products from plastic waste is therefore essential prior to recycling, according to European Union legislation.

- **Development of fast and reliable characterization techniques for quality assessment of recycled plastics.**

  Quality assessment is of significant importance because the properties of the recyclates must be specified and guaranteed within narrow tolerances by the manufacturers, according to the needs of their customers [14].

- **Requirement of standardised methods for the characterisation of recycled materials.**

  Standards are currently under development by the European Committee for Standardisation (CEN/TC 249) that will consider the terminology, characterisation, test methods, and specifications of some plastic families.

- **Design for recycling.**

  There is a need to design products for recycling, to simplify recycling operations such as the dismantling of equipment, separation of homogeneous streams, and identification of individual polymers. This is more important for products in which plastics are usually combined with other materials (automotive components, electrical and electronic equipment).
1.3 QUALITY ASSESSMENT OF RECYCLED PLASTICS

Polymers are subjected to physical and chemical changes during their processing, service life, and further recovery, and they may also interact with impurities that can alter their composition. These changes substantially modify the stabilization mechanisms and the mechanical properties of recycled polymers. The introduction of a quality concept in mechanical recycling industries is therefore necessary to guarantee the performance of recycled products [14, 15]. Three key properties have been proposed for the quality assessment of recycled plastics: degree of mixing (composition), degree of degradation, and presence of low molecular weight compounds (Figure 1.3) [16]. Different fast characterisation methods have been previously developed by our group for the quality assessment of polyolefins, employing vibrational spectroscopy, thermal analysis, chromatography, and chemiluminescence [16-22].

![Figure 1.3. Key properties for quality assessment of recycled plastics (from Analytica Chimica Acta (2007) doi:10.1016/j.aca.2007.04.046 with permission).](image)

The presence of mixed fractions in recycled plastics is a critical parameter influencing the mechanical properties and performance of recycled products in second market applications. The degree of mixing determines therefore the most suitable waste management procedure for waste material streams. In this vein, polypropylene content in polymer blends may be predicted employing spectroscopic techniques [18, 19].

Different strategies can be considered to investigate the degree of degradation in polymers, according to the changes at a macroscopic or microscopic scale (Figure 1.4) [23]. The analysis of the alterations in chemical functional groups, crystallinity, morphology, mechanical properties, molecular weight distribution and composition induced by degradation is a common approach. On the other hand, chromatographic tools have proved to be useful for monitoring ongoing degradation processes in polymers [23-25].
The combination of advanced extraction procedures with chromatographic detection allows the identification and quantification of low molecular weight compounds in recycled plastics; these compounds are usually degradation products from the matrix and the additives, contaminants, and residues of polymerisation. Microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), accelerated solvent extraction (ASE), head-space extraction (HS) and head-space solid-phase microextraction (HS-SPME) have shown to be highly effective in the recovery of low-molecular weight compounds in recycled polyolefins and engineering plastics, with relatively short extraction times and low or no solvent consumption [16, 17, 26, 27].

1.4 DEGRADATION OF HIGH-IMPACT POLYSTYRENE AND OTHER RUBBER-MODIFIED STYRENIC POLYMERS

Styrenic polymers are low-cost and versatile materials that are commonly employed in a wide range of applications including packaging, automotive components, and electrical and electronic equipment. Mechanical recycling has been identified as the preferred route for the recovery of styrenic plastic waste in packaging applications. For end-of-life vehicles (ELV) and electrical and electronic waste (WEEE), additional problems are found, based on the integrated nature of these products, the difficulties of dismantling, and the presence of hazardous substances. It is therefore important to understand the degradation mechanisms to which recycled styrenic polymers are subjected during their life cycle, to better assess their potential for further employment in second-market applications.
The improvement of the impact properties of styrenic polymers such as high-impact polystyrene (HIPS) or acrylonitrile-styrene-butadiene copolymer (ABS) is usually achieved by incorporating a rubber disperse phase (usually polybutadiene or styrene/butadiene rubber) into the styrenic rigid matrix (polystyrene or styrenic copolymers such as styrene/acrylonitrile) \[28\]. In particular, high-impact polystyrene (HIPS) is generally synthesised by the introduction of polybutadiene (PB) before the free radical polymerisation of styrene with a variable content (3-10 mol % PB); the polybutadiene nodules are then compatibilised by the grafting of styrene units \[29\]. The resulting material can be structurally defined as a multiphase system in which PB rubber granules are dispersed in a continuous rigid polystyrene (PS) matrix. The rubber phase contains the three typical microstructural isomeric units of PB: vinyl-1,2, cis-1,4, and trans-1,4 (Figure 1.5). This multiphase structure confers upon HIPS its improved fracture resistance properties (impact strength, elongation at break, and fracture toughness) together with reduced transparency, modulus and tensile strength if compared with unmodified PS \[28\]. The introduction of a rubbery phase alters, however, the stability of the blends in regards to degradation, enhancing the sensitivity of the material to the degradative agents. A brief review of the degradation aspects related to HIPS and other rubber-modified styrenic polymers will be given, with a special focus on photo-oxidative, thermo-oxidative, and thermo-mechanical degradation.

![Figure 1.5. The microstructural isomeric units of polybutadiene.](image)

Previous research has been devoted to the study of the oxidative degradation of ABS \[30-36\] and HIPS \[28, 29, 37-44\]. Early works on the thermal- and photo-oxidation of ABS and HIPS revealed that the PB phase is selectively attacked during the initial stages of degradation, with hydroperoxide formation being the initiation mechanism \[31, 35, 36, 38-41\]. Further studies employing infrared spectroscopy identified the different steps of the oxidation process. An initial induction period is displayed, followed by a fast oxidation related to the PB phase; finally, a slow oxidation rate is observed corresponding to the degradation of PS, which may be initiated by some of the radicals formed in the degradation of PB \[29, 33\].
The initial degradation of the PB phase leads to the progressive consumption of unsaturated groups and the formation of oxidated moieties. The reaction mechanisms are related to the chemistry of the three PB microstructures: vinyl-1,2, cis-1,4, and trans-1,4 [30]. The initiation involves the creation of free radicals and the formation of hydroperoxides; the second stage consists of the decomposition of the hydroperoxides and the formation of different products containing oxidised groups. Further reactions include the formation of stable crosslinked structures, extensive damage in the polymeric chains by scission, and disunification of the polymer graft between the butadiene and styrene units. Different reaction mechanisms have been proposed for the oxidation of PB-modified styrenic polymers (Figure 1.6) [29, 30, 33, 38, 45].

A) Reactions of the vinyl-1,2 isomer

B) Reactions of cis-1,4 and trans-1,4 isomers

Figure 1.6. Reaction mechanisms proposed for the PB phase during the thermo- and photo-oxidative degradation of rubber-modified styrenic polymers.
With prolonged oxidative exposure, a wide range of crosslinking reactions can take place in the oxidised moieties in the presence of alkoxy (RO•) and alkylperoxy (ROO•) radicals; different crosslinked structures can be formed, such as unstable peroxide gel, ether gel, and saturated gel structures [30, 40].

![Figure 1.7](image1.png)

**Figure 1.7.** Crosslinked gel structures after prolonged exposure of PB-modified styrenic polymers to thermo- and photo-oxidation.

Finally, the butadiene grafting sites containing tertiary carbons are oxidised during more severe degradation, leading to the catastrophic disunification of the copolymer matrix by scission of the PB-PS graft [30, 33, 40].

![Figure 1.9](image2.png)

**Figure 1.9.** Proposed reactions for the oxidation of the PB-PS grafting sites.

Further oxidation of the PS phase in PB-modified styrenic polymers is promoted by the free radicals formed during degradation of the rubber phase, in contrast to the oxidation process of pure PS [33]. The PS oxidation initiation commences with the oxygen attack on the α-hydrogens of the backbone of the PS chain, leading to the formation of hydroperoxides as initiation products [46, 47]. Aromatic and aliphatic ketones, peroxoesters, carboxylic acids, and anhydrides are some of the oxidised structures that can be found in PS subjected to thermo- and photo-oxidation; molecular compounds such as benzoic acid, benzophenone, acetophenone, benzaldehyde, benzoic anhydride, and dibenzoylmethane are also formed as degradation products [46, 48, 49].
In addition to the chemical reactions caused by thermo- and photo-oxidation, further changes at a macroscopic scale in rubber-modified styrenic copolymers are also induced by the degradation processes, which are associated with a deterioration of the mechanical properties and long-term stability [32, 34, 37, 38, 50, 51]. Thermo-oxidation involves physical and chemical processes, which affect the overall properties of the exposed material in different ways [37]. Large alterations in the tensile, impact, and flow properties have been reported, resulting in an embrittlement of the material [37, 50, 52]. Structural changes such as physical ageing in the styrenic phase and a shift in the glass transition temperature of the PB phase have also shown to be consequences of radiation and oxidative degradation [34, 38, 50]. Thermo-oxidative degradation has proved to be a surface effect that promotes mechanical failure of the polymer bulk [34].

Thermo-mechanical degradation induced by multiple processing has been proved to cause alterations in the rheological behaviour and the mechanical properties of ABS and HIPS [32, 53-55]; these changes may be due to chain scission in the PS phase and modifications in the physical structure of the rubber phase [55]. Thermal processing under high mechanical shear in limited oxygen atmosphere may be responsible for the generation of free radicals, which may contribute to the aforementioned alterations in the chemical and physical properties of the material [30].
2. EXPERIMENTAL

2.1 MATERIALS AND SAMPLE PREPARATION

2.1.1 Simulation of the life cycle of recycled HIPS through multiple processing and thermo-oxidation

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M (BASF Española S.A., Spain), was employed to simulate the life cycle of recycled HIPS. A dual-pronged experimental approach was proposed: HIPS processing and recycling was modelled through multiple processing, and the degradation processes during service life were simulated by thermo-oxidation at 90°C in a forced-ventilation oven (Figure 2.1).

Figure 2.1 Modelling the life cycle of recycled plastics: a) modelling processing and mechanical recycling through multiple processing; b) modelling service life with thermo-oxidation (from Polymer Degradation and Stability 91 (2006) 2163-2170, with permission).

Reprocessing was performed by multiple extrusion up to nine cycles, employing a double-screw extruder (Collin Kneader 25x30D, Dr. Collin GmbH, Germany). The temperature profile in the extruder was 130-180-190-200-180-170°C. After each extrusion cycle the material was cooled by air and grinded; some material was kept for analysis and the remaining was reintroduced for further extrusion. Rectangular sheets of 85 x 85 x 1 mm dimensions for tensile testing were prepared by compression moulding at 200°C and 200 bar, with a Collin x800 press (Dr. Collin GmbH, Germany).
Samples for thermo-oxidation were obtained employing compression moulding at 200°C and 200 bar in a Schwabenthan Polystat 400S press (Schawbenthan Maschinenfabrik Berlin, Germany). The resulting sheets with 85 x 85 x 1 mm dimensions were then placed in a forced-ventilation oven (Memmert 600, Memmert GmbH, Germany) under air atmosphere at 90°C, following the guidelines of the ASTM D 5510-94 standard. The samples were removed for analysis after exposure times of 1, 2, 4, 8, 12, and 16 days.

### 2.1.2 Material sampling in a large-scale mechanical recycling facility

Recycled HIPS samples were provided by Acteco (Spain) and were collected for analysis at the following points of the mechanical recycling process (Article III, Scheme 2): scrap HIPS employed as raw material in the recycling process, intermediate samples after grinding and washing, and different grades of end-product recycled HIPS material. Virgin HIPS, commercial grade Polystyrol 486M (BASF Española S.A., Spain), was used as reference material. Table 2.1 describes the sample materials employed in the analyses.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin HIPS</td>
<td>Virgin HIPS, commercial grade Polystyrol 486M</td>
</tr>
<tr>
<td>HIPS1</td>
<td>Scrap HIPS from yoghurt packaging applications</td>
</tr>
<tr>
<td>HIPS2</td>
<td>Scrap HIPS from clothes hanger applications</td>
</tr>
<tr>
<td>HIPS3</td>
<td>Intermediate HIPS material from the mechanical recycling process after washing and grinding, from yoghurt packaging application</td>
</tr>
<tr>
<td>HIPS4</td>
<td>Intermediate HIPS material from the mechanical recycling process after washing and grinding, material mixture from yoghurt packaging and clothes hanger applications</td>
</tr>
<tr>
<td>HIPS5</td>
<td>Final recycled grey material, from yoghurt packaging applications</td>
</tr>
<tr>
<td>HIPS6</td>
<td>Final recycled white material, from yoghurt packaging applications</td>
</tr>
<tr>
<td>HIPS7</td>
<td>Final recycled black material, from yoghurt packaging and clothes hanger applications</td>
</tr>
</tbody>
</table>

*Table 2.1 Description of the HIPS materials sampled from the large-scale mechanical recycling facility.*
2.2 CHARACTERISATION TECHNIQUES

2.2.1 Melt mass-flow rate (MFR)

The melt mass-flow ratio (MFR) of reprocessed HIPS was measured employing a Melt Indexer CFR-91 (Campana Srl., Italy) according to the ISO 1133:1997 standard. The test temperature was set at 200°C and the nominal load was 5 kg. The measurements of each sample were repeated 6 times and the average was taken as the representative value.

2.2.2 Tensile testing

Tensile testing was performed on reprocessed and thermo-oxidated samples according to ASTM D882-02 standard, on six rectangular specimens of 85 x 5 x 1 mm dimensions, cut from the films obtained by compression moulding. The average value of the modulus, stress at break and elongation at break, was set as the representative value. The tensile tests were carried out at 23°C and 40% relative humidity by means of an Instron 5566 universal electromechanical testing machine (Instron Corporation, MA, USA) at a crosshead speed of 15 mm min⁻¹, with a load of 0.1 kN and a gauge length of 30 mm.

2.2.3 Differential scanning calorimetry (DSC)

The thermal properties and the oxidative stability of the HIPS samples were assessed using differential scanning calorimetry (DSC). The analyses were performed on a Mettler Toledo DSC 820 (Columbus, OH) calibrated with indium standard. Approximately 10 mg of sample were weighed and placed in a 40 mL aluminium pan, which was sealed and pierced to allow the entrance of the flow gas. The different measurements were performed on the different HIPS samples in triplicate, and the average of the calculated parameters was taken as the representative value.

The glass transition temperatures ($T_g$) of the polybutadiene (PB) and polystyrene phase (PS) of reprocessed and thermo-oxidated HIPS were obtained from calorimetric measurements under a nitrogen gas flow of 50 mL min⁻¹, with the following temperature programme: The samples were heated from -100°C to 150°C at a heating rate of 10°C min⁻¹, cooled from 150°C to -100°C at -10°C min⁻¹, and again heated from 25°C to 200°C at 10°C min⁻¹. The glass transition temperatures were calculated from the calorimetric data at the second heating ramp.
The presence of polymeric impurities in recycled HIPS samples from the large-scale mechanical recycling facility was assessed employing calorimetric scans under nitrogen atmosphere (50 mL min⁻¹), with the following temperature programme: The samples were heated from 25°C to 200°C at a heating rate of 10°C min⁻¹; cooled from 200°C to 25°C at -10°C min⁻¹; and heated from 25°C to 200°C at 10°C min⁻¹.

To determine the oxidation temperature ($T_{ox}$), the samples were heated from 25°C to 400°C under an oxygen atmosphere of 50 mL min⁻¹. The oxidation temperature was obtained from the onset point of the oxidation process in the calorimetric curves.

The oxidation induction time (OIT) measurements were performed following the ISO 11357-6:2002 Standard. The samples were quickly heated from 25°C to 160°C at a heating rate of 20°C min⁻¹ and kept at that temperature for 5 minutes under a nitrogen gas flow of 50 mL min⁻¹. At this point, the atmosphere was immediately switched to oxygen at a flow rate of 50 mL min⁻¹ and the samples were held at 160°C for 30 minutes. The oxidation induction time was calculated from the instant at which the atmosphere was switched to oxygen to the onset of the oxidation signal in the DSC thermograms.

### 2.2.4 Thermogravimetric analysis (TGA)

The thermal decomposition of the HIPS samples from the mechanical recycling process was evaluated by thermogravimetric analysis (TGA). The measurements were carried out in a Mettler-Toledo SDTA/TGA851 (Columbus, OH). Approximately 10 mg of sample were heated from 40°C to 700°C at a heating rate of 10°C min⁻¹, under a nitrogen gas flow of 50 mL min⁻¹.

### 2.2.5 Fourier transform infrared spectroscopy (FTIR)

The surface of the HIPS samples was analysed by infrared spectroscopy using a FTIR spectrometer Spectrum 2000 (Perkin Elmer, Wellesley, MA) equipped with a Golden Gate single-reflection accessory for attenuated total reflection (ATR). 24 scans between 4000 cm⁻¹ and 600 cm⁻¹ were averaged for each spectrum at intervals of 1 cm⁻¹ with a resolution of 4 cm⁻¹. The samples were analysed in triplicate.
2.2.6 Raman spectroscopy

The Raman spectra of reprocessed and aged HIPS samples were collected using a FT-Raman spectrometer Spectrum 2000 (Perkin Elmer, Wellesley, MA) equipped with an Nd-YAG laser illumination. The different spectra were obtained with a laser power of 900 mW, performing 32 scans between 4000 cm\(^{-1}\) and 600 cm\(^{-1}\) at intervals of 1 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The samples were analysed in triplicate.

2.2.7 Dynamic mechanical thermal analysis (DMTA)

Viscoelastic measurements of thermo-oxidated and reprocessed HIPS samples were carried out in a Rheometric Scientific dynamic-mechanical-thermal analyser MARK IV DMTA (United Kingdom). The sinusoidal deformation was applied to rectangular samples with 50 x 10 x 1 mm dimensions in the double-clamped cantilever mode. The region above ambient temperature was studied for all the samples, performing multifrequency scans from 25°C to 150°C at a rate of 4°C per scan for a range of 5 frequencies per decade between 0.1 Hz and 50 Hz. Selected samples were subjected to subambient multifrequency scans between –110 ºC and 150°C at a scan rate of 5°C per scan over a frequency range of 0.1-50 Hz using 4 frequencies per decade. The values of loss tangent (\(\tan \delta\)), storage modulus (\(E'\)) and loss modulus (\(E''\)) versus temperature and frequency were thus obtained.

2.2.8 Scanning electron microscopy (SEM)

SEM micrographs of selected reprocessed and thermo-oxidated samples were obtained on sectioned HIPS samples after sputtering with gold/palladium, using a JEOL JSM-5400 scanning electron microscope (JEOL Ltd., Japan).

2.2.9 Analysis of low molecular weight compounds

The low molecular weight compounds present in the HIPS samples from different steps of the recycling process were determined by a procedure combining microwave-assisted extraction and further analysis of the extracts by gas chromatography-mass spectrometry.
HIPS samples were extracted using a MES 100 microwave extraction system (CEM Corp., North Carolina, USA), with a nominal power of 1000 W. The extractions were performed at 110°C for 30 minutes with a maximum effective power of 95% of the nominal power. Approximately 1 g of the samples was placed in the microwave closed vessels together with 10 mL of the extractive solution (n-hexane/isopropanol (50% v/v) containing 0.1 μL mL⁻¹ of 4-methylstyrene and 5 μg mL⁻¹ of o-terphenyl as internal standards). The extracts were filtered with a 0.45 mm pore size Teflon filter (Sorbent AB, Sweden) and placed in special vials that were kept at 4°C until further analysis.

The chromatographic analyses of the extracts were performed on an Agilent 6890 Gas Chromatograph (Palo Alto, CA) equipped with a 0.18 mm x 20 m x 0.18 μm Agilent J&W DB-5 capillary column (Palo Alto, CA). A 2 μL sample was injected employing a programmed temperature vaporisation injector (PVT) in the pulsed splitless mode. During injection, the inlet was held at 75 psi with a purge flow of 60 mL min⁻¹ for 1 minute. The PTV temperature program was: 70°C, hold 0.02 min; increase to 290°C at a rate of 720°C min⁻¹; hold 5 min. The chromatographic separation through the column was achieved through a constant column flow of 0.8 mL min⁻¹, with helium as the carrier gas. The temperature program at the column was as follows: hold at 40°C for 1 min; increase to 300°C at a rate of 10°C min⁻¹; hold at 300°C for 5 min. The detection was carried out by a Leco Pegasus 3 (St. Joseph, MI) Time-of-Flight (TOF) mass spectrometry (MS) detector. Electron ionisation was employed with an ion source temperature of 230°C. Mass spectra were collected in the full scan mode (33-500 m/z at a scan rate of 4 spectra s⁻¹) or in the selected ion monitoring (SIM) mode. Compound identification was performed either by comparison of the obtained spectra with the NIST MS search 2.0 database or by comparison with bibliographic references.
3. RESULTS AND DISCUSSION

3.1 DEGRADATION OF RECYCLED HIPS DURING LIFE CYCLE. SIMULATION BY MULTIPLE PROCESSING AND THERMO-OXIDATION.

The properties of recycled materials worsen, in general, due to the degradation processes that may occur during their processing, service life and further mechanical recycling. The aim of the first part of the study, as detailed in Articles I and II, was to investigate the degree of degradation of high-impact polystyrene throughout its reprocessing and thermo-oxidation, to develop detailed knowledge about how and to what extent processing, service life, and mechanical recycling affect the performance of HIPS.

3.1.1 Oxidative stability

The oxidative stability of reprocessed and thermo-oxidated HIPS samples was assessed by determining the oxidation induction time (OIT) and the oxidation temperature ($T_{\text{ox}}$) through DSC (Article I, Table 1). The stabilising system of the material is clearly affected by the reprocessing cycles and by thermo-oxidative exposure; the largest changes are observed in the thermo-oxidated samples. Each reprocessing step causes a progressive consumption of the stabilisers in the material, mainly during the first three extrusion cycles. In the case of thermo-oxidation, the decrease in the stabilising activity is even faster and more dramatic, with a decrease of 57% in the OIT value after 1 day of exposure at 90°C.

3.1.2 Rheological and tensile properties

The influence of multiple processing on the rheological properties of HIPS was assessed by measuring the melt mass-flow rate (MFR). The MFR slightly increases with reprocessing for HIPS subjected to nine extrusion cycles, mainly during the first three extrusion cycles (Article I, Figure 1). These results may be attributed to thermo-mechanical degradation caused by successive processing, which may have induced chain scission phenomena and a resulting decrease in the molecular weight of the polymer, in accordance with the work of other authors [53, 55].
The influence of reprocessing and thermo-oxidation on the mechanical properties (elastic modulus, elongation at break, and stress at break) was analysed by tensile testing (Figure 3.1). The stress and elongation at break are clearly influenced by the successive processing steps, with a progressive diminution of elongation at break and an increase of stress at break. Thermo-mechanical degradation by consecutive extrusion may introduce alterations in the chemical structure of HIPS, resulting in a slightly more brittle material with lower ductility. On the other hand, elongation at break drastically decreases with thermo-oxidation, showing a collapse after 4 days of exposure. The stress at break shows, on the contrary, a slight increase during initial exposure times, but after 12 days their values drop. This complex behaviour suggests the combination of different physical and chemical effects in the thermo-oxidative degradation of HIPS. Physical ageing seems to predominate for shorter exposure times, whereas the chemical attack appears to govern the degradation for longer exposures. The combined chemical and physical effects in the thermo-oxidation of HIPS are discussed in detail from the results from vibrational spectroscopy and dynamic-mechanical analysis (Section 3.1.3 and 3.1.4, respectively).

![Figure 3.1](image-url)

*Figure 3.1. Tensile properties of virgin HIPS (●) elongation at break; (○) stress at break. a) influence of multiple processing; b) influence of thermo-oxidation. (from *Polymer Degradation and Stability* 91 (2006) 2163-2170, with permission).*

3.1.3 Changes in chemical functional groups

The chemical changes induced by multiple processing and thermo-oxidation on HIPS structure were studied by infrared and Raman spectroscopy. Both techniques are complementary and give useful information about different functional groups present in the polymeric samples.
Infrared spectroscopy (FTIR) allows the characterisation of the hydroxyl region (3100-3600 cm\(^{-1}\)), the carbonyl region (1620-1780 cm\(^{-1}\)), and the trans-1,4 (966 cm\(^{-1}\)) and vinyl-1,2 (911 cm\(^{-1}\)) unsaturated groups from the PB phase of HIPS. The absorbance areas of the peaks corresponding to the hydroxyl region, the carbonyl region, the trans-1,4 group, and the vinyl-1,2 group were normalised to the area of a reference peak at 1601 cm\(^{-1}\) that is not susceptible to degradation; the FTIR functional group indexes were thus obtained.

![Figure 3.2](image)

**Figure 3.2.** Curve fitting of the virgin HIPS Raman spectra to 5 individual bands for the determination of the 3 individual PB conformers: 1550-1700 cm\(^{-1}\) region.

Raman spectroscopy was employed to assess the complete PB microstructure in HIPS, since the three microstructures show clear peaks at 1640 cm\(^{-1}\) (vinyl-1,2), 1652 cm\(^{-1}\) (cis-1,4), and 1666 cm\(^{-1}\) (trans-1,4) [56]. A curve-fitting procedure was proposed here to resolve the individual PB microstructures (Figure 3.2); the Raman region between 1550 cm\(^{-1}\) and 1700 cm\(^{-1}\) was thus analysed in detail, following the guidelines reported by Meier [57]. Five peaks were considered at approximate wavelengths of 1582 cm\(^{-1}\), 1601 cm\(^{-1}\), 1640 cm\(^{-1}\), 1652 cm\(^{-1}\), and 1666 cm\(^{-1}\), and were fitted to a Lorentzian profile (equation 1). The areas of the resolved vinyl-1,2, cis-1,4, and trans-1,4 bands were calculated and normalised to the area of the band at 1601 cm\(^{-1}\), which is not affected by degradation.

\[ L(x) = y_0 + \frac{2 \cdot A}{\pi} \cdot \frac{\omega}{4 \cdot (x - x_c)^2 + \omega^2} \quad (1) \]
Repeated extrusion of HIPS results in the modification of the carbonyl region in FTIR and the appearance of a peak at around 1560 cm\(^{-1}\) (Article I, Figure 4), which may be attributed to the asymmetric stretching of the carboxylate ion group [23, 58]. PB microstructure is, to some extent, affected by reprocessing, since the intensities of the three Raman bands corresponding to the PB conformers decrease slightly with the successive extrusion steps (Article II, Figure 2). The combined results from FTIR and Raman spectroscopy suggest that thermo-mechanical degradation caused by multiple processing of HIPS in an oxygen-deficient atmosphere may induce a series of heterogeneous and complex chemical reactions that could cause crosslinking and the alteration of the physical structure of the rubber phase, together with the appearance of a wide range of oxidative moieties in the polymeric chains caused by the interaction of the polymer with some residual oxygen that could have been present in the extruder.

Thermo-oxidation induces, in contrast to the heterogeneous effects reported by reprocessing, progressive changes in the analyzed functional group indexes; a marked decrease in the unsaturated groups can be observed employing FTIR, whereas broad bands appear in both the hydroxyl and the carbonyl regions (Article I, Figure 6). The effects of thermo-oxidation on the chemical structure of HIPS can be more clearly observed by the representation of the FTIR and Raman functional groups with degradation time in Figure 3.3. The indexes related to the PB unsaturated groups show a slight decrease for shorter times, due to the protective effect of the stabilising system incorporated in the virgin polymer. A fast reduction rate is, however, appreciated in the unsaturated groups after the fourth day of exposure, which corresponds to a marked increase in the hydroxyl and carbonyl oxidated groups.

![Figure 3.3](image-url)

**Figure 3.3.** Chemical changes induced by thermo-oxidation on the structure of HIPS: a) Evolution of the FTIR functional group indexes: (◊) vinyl-1,2, (■) trans-1,4, (Δ) carbonyl and (●) hydroxyl; b) Evolution of the Raman indexes: (■) trans-1,4; (◇) cis-1,4; (●) vinyl-1,2.
The evolution of the functional groups is therefore assigned to the complex series of thermo-oxidative reactions initiated in the rubber phase that lead to the disappearance of the unsaturated groups and the formation of oxidative moieties, crosslinked structures, and chain scission. This phenomenon is in accordance with the results of Israeli et al. [29], which reported that the thermal oxidation of HIPS shows an induction period, followed by a fast oxidation of PB and then by a slow oxidation rate corresponding to the degradation of PS. The stability of the different PB microstructures against thermo-oxidation is different; trans-1,4 and cis-1,4 groups appear to be preferential sites for the degradative attack of oxygen, whereas the vinyl-1,2 structure is more stable and shows a minor decrease during exposure, in agreement with the results reported for other rubber-modified styrenic polymers such as SBS and ABS [30, 59].

3.1.4 Viscoelastic behaviour and morphology

The dynamic mechanical spectrum of high-impact polystyrene presents different characteristic relaxations (Article II, Figure 6). The glass transition associated with the PB phase appears clearly centred at around 195K in virgin HIPS. The position of the PB glass transition is related to the microstructure (vinyl content); polybutadienes with higher vinyl content show higher glass transition temperatures, since pure vinyl-1,2 PB has its glass transition temperature around 258K and both pure cis-1,4 and trans-1,4 PB exhibit their $T_g$ at 167K [60, 61]. The glass transition of the PS matrix can be found at around 380K for virgin HIPS.

The glass transition relaxations related to the PB and PS phases of HIPS can be characterised by their loss modulus maximum values ($E''_{\text{max}}$ and $T_{\text{max}}$); these values have been obtained for all samples and frequencies by fitting the loss modulus data to the Fuoss-Kirkwood empirical model [62]. The modified Fuoss-Kirkwood equation, in terms of temperature applied for the fitting of the dynamic-mechanical data is:

$$E'' = \frac{E''_{\text{max}}}{\cosh \left[ m \cdot \frac{E_a}{R} \cdot \frac{1}{T} \cdot \frac{T_{\text{max}}}{T_{\text{max}}} \right]}$$

(2)

where $E''_{\text{max}}$ is the maximum of the loss modulus; $m$ is the Fuoss-Kirkwood parameter; $E_a$ is the activation energy of the relaxation process; and $T_{\text{max}}$ is the temperature of the maximum of the loss modulus, usually assumed as the glass transition temperature.
The analysis of the dynamic-mechanical data according to the free-volume theory gives detailed information about the influence of reprocessing and thermo-oxidation on both PB and PS glass transitions. Figures 3.4a and 3.4b represent the Arrhenius maps of PB and PS glass transition relaxations for the reprocessed and thermo-oxidated samples, respectively; these Arrhenius maps are obtained by the representation of the $T_{\text{max}}$ values from the Fuoss-Kirkwood fitting against the different analysed frequencies.

![Arrhenius maps for PB and PS glass transition relaxations.](attachment:image.png)

**Figure 3.4.** Arrhenius maps for the PB and PS glass transition relaxations. a) Influence of multiple processing: (●) virgin HIPS, (□) HIPSr1, (◊) HIPSr4, (►) HIPSr6, (■) HIPSr9; b) Influence of thermo-oxidation: (●) virgin HIPS, (□) 2 days, (◊) 4 days, (►) 8 days, (○) 12 days, (■) 16 days.
The Arrhenius curves were fitted to the Vogel-Fulcher-Tammann-Hesse equation (VFTH) to correlate the temperature dependence of the glass transition relaxation for PB and PS. The VFTH equation was first empirically formulated for the viscosity of inorganic glasses at temperatures above the glass transition temperature ($T_g$) [63-65], and can be deduced from the free-volume theory.

$$\ln \tau = A' + \frac{m_v}{T - T_\infty} \quad (3)$$

Here, $\tau$ is the relaxation time; $A'$ is an empirical parameter; and $T_\infty$ is the temperature at which the free volume would be zero were it not for the formation of the glassy state. The parameter $m_v$ is related to the relative free volume at the glass transition temperature, according to the following expression:

$$m_v = \frac{B}{\alpha_f} = \frac{B}{f_g} \cdot (T_g - T_\infty) \quad (4)$$

where $\alpha_f$ is the expansion coefficient of the free volume; $T_g$ is the glass transition temperature; $B$ is an empirical parameter, and $f_g$ is the relative free volume associated to the glass transition. The free-volume parameters associated with the PB and PS glass transitions, obtained by the fitting of the Arrhenius plots to the VFTH equation, are shown in Table 3.1 for HIPS samples subjected to reprocessing and thermo-oxidation.

Multiple processing causes a progressive shift in the Arrhenius plots for the PB phase to higher temperatures (Figure 3.4a) and a decrease of the parameter associated with the free volume of the PB phase (Table 3.1). This result may prove the occurrence of crosslinking reactions in the PB microstructure suggested by the results of Raman spectroscopy, which generate rigid segments that contribute to a mobility restriction of the PB chains. The Arrhenius curves for the PS phase show a slight shift towards higher temperatures for repeated processing cycles (Figure 3.4a), whereas the free volume parameter for PS glass transition is greatly modified with a progressive diminution during reprocessing (Table 3.1). The combined effect of the presence of shorter PS polymeric chains caused by chain scission during thermo-mechanical degradation, as revealed by MFR analysis, and the physical rearrangement of the macromolecular chains within repeated extrusion may be responsible for this behaviour. These effects on the free volume of both PB and PS phases in HIPS caused by multiple processing may be responsible for the changes in the macroscopic behaviour, such a decrease in the elongation at break and poorer impact properties reported in other works [53, 55].
Modelling the degradation processes in high-impact polystyrene during the first use and subsequent recycling

Multiple processing  

<table>
<thead>
<tr>
<th>Reprocessing steps</th>
<th>Free volume parameter for the glass transition $\frac{f_v}{B \cdot (T_g - T_v)} \times 10^4$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PB phase</td>
</tr>
<tr>
<td>Virgin HIPS</td>
<td>35.2</td>
</tr>
<tr>
<td>1</td>
<td>23.0</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>16.9</td>
</tr>
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<tr>
<td>6</td>
<td>24.3</td>
</tr>
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<td>7</td>
<td>-</td>
</tr>
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<td>8</td>
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<tr>
<td>9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Thermo-oxidation  

<table>
<thead>
<tr>
<th>Exposure time (days)</th>
<th>Free volume parameter for the glass transition $\frac{f_v}{B \cdot (T_g - T_v)} \times 10^4$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB phase</td>
<td>PS phase</td>
</tr>
<tr>
<td>Virgin HIPS</td>
<td>35.2</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>35.7</td>
</tr>
<tr>
<td>4</td>
<td>23.2</td>
</tr>
<tr>
<td>8</td>
<td>28.1</td>
</tr>
<tr>
<td>12</td>
<td>47.9</td>
</tr>
<tr>
<td>16</td>
<td>96.7</td>
</tr>
</tbody>
</table>

Table 3.1. The influence of multiple processing and thermo-oxidation on the free-volume parameter associated with the PB and PS glass transitions in HIPS.

The effect of thermo-oxidation on the Arrhenius plots and the free volume parameter is complex for both phases in HIPS. The Arrhenius plot for the PB glass transition shifts towards higher temperatures with increasing exposure time (Figure 3.4b). The free volume parameter, however, shows a slight decrease for shorter exposure times (0-4 days) and a dramatic increase for higher exposure times (Table 3.1). The decrease in the PB free volume at shorter exposure times may be related to the initial crosslinking reactions caused by oxidation, which occur at a lower incidence due to the protective effect of the stabilising system. With longer exposure, the oxidation effects become irreversible for PB, and may lead to a structural collapse of the PB phase in HIPS.

Considering the PS phase, the Arrhenius plots shift to higher temperatures for shorter exposure times, but shift drastically to lower temperatures for longer times (Fig.3.4b); similarly, the free volume parameter decreases for the initially thermo-oxidated HIPS samples, but increases markedly from 8 days of exposure onwards (Table 3.1). Diverse phenomena may influence simultaneously the viscoelastic behaviour of the PS phase of HIPS during exposure to thermo-oxidative ageing. Physical ageing of the PS phase seems to predominate during shorter exposure times, which results in a decrease in the free volume and lower molecular mobility [66]. However, the chemical effects on HIPS at longer exposure times clearly affect the structure of the PS phase at a molecular level; the
deterioration of the PB phase microstructure and the apparition of structural defects may lead to a heterogeneous distribution of the PS chains with higher molecular mobility at the nanoscale, with a lower glass transition temperature and an increase in free volume.

The complex effects of multiple processing and thermo-oxidation on HIPS microstructure and morphology can be verified with the micrograms obtained using scanning electron microscopy (SEM). The typical double-phase distribution in HIPS can be observed in the virgin HIPS microgram (Fig. 3.5a), with the PB granules dispersed in the PS matrix. The PB granules exhibit heterogeneous shapes with a particle size of 5-10 µm. After multiple processing (Fig. 3.5b), shrinkage in PB granules can be observed together with a clear modification in their surface. The progressive effect of thermo-oxidation on HIPS morphology can be followed with exposure time. For shorter exposure times (Fig. 3.5c), the PB granules seem to crease and contract, showing a rough outer surface; for longer exposure times, however, the PB phase appears to have partially lost the granular microstructure, though smaller particles can still be detected (Figure 3.5d). Cracks can also be observed in the PS matrix, which shows the evident deterioration of the morphology under thermo-oxidation.

![Figure 3.5](image-url)

**Figure 3.5.** SEM micrographs of HIPS samples: a) virgin HIPS; b) reprocessed HIPS (9 cycles); c) thermo-oxidated HIPS (4 days); d) thermo-oxidated HIPS (16 days).
3.2 QUALITY ANALYSIS OF RECYCLED HIPS DURING THE LARGE-SCALE MECHANICAL RECYCLING PROCESS

Different analytical strategies for the quality assessment of recycled HIPS are presented, including the study of the presence of other polymeric materials as impurities, the oxidative stability, the chemical changes, and the presence of low molecular weight compounds. Samples extracted from different points of a large-scale mechanical recycling plant have been studied to verify the commercial suitability of the proposed analytical strategies. The effects of the different steps of the mechanical recycling process on HIPS properties are also investigated. These results are detailed in Article III.

3.2.1 Presence of polymeric impurities

Polymeric contaminants in the recycled materials were detected by differential scanning calorimetry (DSC); small melting peaks at temperatures of 120°C and/or 160°C were observed for HIPS2 and HIPS7 samples, which indicate the presence of polyethylene and polypropylene contaminants, respectively, in these materials (Article III, Figure 1).

3.2.2 Thermal properties and oxidative stability

Differential scanning calorimetry (DSC) was used to calculate the glass transition temperature of the PS matrix and to assess the oxidative stability of the different HIPS samples, by evaluating both the oxidation induction time (OIT) and the oxidation temperature ($T_{\omega}$) (Article III, Table 3.3). The OIT of the HIPS1 and HIPS3 samples could not be calculated because of the low intensity of the oxidation signal in the thermograms. The materials from the recycling plant show, in general, lower oxidative stability than the virgin material, due to the degradation effects that may have occurred in their previous life. These results prove, consequently, the importance of adjusting the restabilisation level to guarantee the oxidative stability of the recyclates in their new service life. From an analytical point of view, both OIT and $T_{\omega}$ parameters prove to be useful as quality indicators for the oxidative stability in the recycling activities.

Thermogravimetric analysis has been employed to study the thermal decomposition of recycled HIPS samples. The analysed HIPS materials exhibit similar thermal stability and decomposition behaviour, with one single stage at 350-500°C (Article III, Table 3). On the other hand, all samples from the recycling plant possess higher residue content than does the virgin material.
3.2.3 Chemical changes in HIPS structure

The absorbance spectra of the different HIPS samples were recorded by Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy to obtain a deeper insight into the changes in their chemical structure.

The recycled samples display, in general, higher indexes in the hydroxyl and carbonyl regions than does the virgin material, because of the presence of humidity and other oxidative moieties. Considering the unsaturated region from the PB phase, a general decrease of the vinyl-1,2 and trans-1,4 groups in the recycled materials can be observed (Figure 3.6); these results may prove the occurrence of PB oxidation during previous life and HIPS recycling, resulting in a wide variety of oxidised structures in the polymeric chains [29, 30, 39]. The calculation of the hydroxyl, carbonyl, vinyl-1,2, and trans-1,4 indexes could therefore be employed to verify the presence of oxidative moieties and to assess the content of unsaturated groups in recycled HIPS.

![Image](image.png)

**Figure 3.6.** FTIR functional group indexes (hydroxyl; carbonyl; trans-1,4; vinyl-1,2) for the HIPS samples (from *Analytica Chimica Acta* (2007) doi:10.1016/j.aca.2007.04.046 with permission).

Raman spectroscopy has been used to analyse PB-phase microstructure in HIPS samples from the large-scale mechanical recycling process. Conventional Raman spectroscopy cannot be employed, however, for the analysis of coloured samples because of fluorescence emission; consequently, only the Raman spectra of virgin HIPS, HIPS1, HIPS3, HIPS5 and HIPS6 could be recorded. Curve fitting to the Laurentz equation was applied to the recorded Raman spectra to resolve the three bands corresponding to the PB microstructure (Figure 3.1); the Raman functional groups for the unsaturated groups were calculated accordingly (Figure 3.7). PB microstructure content is generally lower in the recycled HIPS samples than in virgin HIPS, which is related to the degradation
effects on the rubber phase during previous life. The cis-1,4 microstructure seems to predominate in HIPS5 and HIPS6, whereas the trans-1,4 microstructure is prevalent in HIPS1 and HIPS3. This effect could be due to the possible addition of PB rubber during the extrusion process.

![Graph](image)

**Figure 3.7.** Raman functional group indexes (vinyl-1,2; cis-1,4; trans-1,4) for the HIPS samples (from *Analytica Chimica Acta* (2007) doi:10.1016/j.aca.2007.04.046 with permission).

### 3.2.4 Presence of low molecular weight compounds

The presence of low molecular weight compounds in recycled HIPS was investigated using microwave-assisted extraction followed by analysis of the extracts using GC-MS. Figure 3.8 presents a total ion chromatogram (TIC) from the virgin HIPS extract, as an example of the resulting chromatograms for the analysed materials. At a glance, different compound groups can be observed: volatile organic compounds (VOCs), styrene dimers and trimers (residues from polymerisation), and different aliphatic compounds.

![Graph](image)

**Figure 3.8.** Total ion chromatogram of the low molecular weight compounds extracted from virgin HIPS (from *Analytica Chimica Acta* (2007) doi:10.1016/j.aca.2007.04.046 with permission).
Table 3.2 presents the retention times, quantification ions, and abundance of the compounds found in the different HIPS samples, relative to the intensity of the 4-methylstyrene internal standard. Peaks 1-11 correspond to a wide range of VOCs that are present in different HIPS samples and products, in agreement with several publications [67-69]. Some of these compounds are found in the virgin material, whereas their relative abundance is lower in the scrap and the recycled samples. This fact indicates that migration of these volatiles to the environment might occur during the processing and service life of the products; additionally, the recycling process itself may contribute to minimising the presence of some volatile compounds [16]. The presence of oxygenated derivates of styrene (peaks 6, 9, 10) has been attributed to the oxidation of polystyrene [48]; thus, the presence of these compounds in recycled samples may be a result of the degradative processes to which HIPS has been subjected during its previous service life.

Peaks 12-17 correspond to styrene dimers that are usually formed by side reactions during the polymerisation of styrene or during material processing. Benzene, 1,1’-(1,3-propanediyl)bis- (peak 12) can be formed during polystyrene processing [70]. Other styrene dimers (peaks 13-17) have been reported to be produced during styrene polymerisation [71-74] and are retained in the polymeric matrix as polymerisation residues; the abundance of these compounds is highest in the virgin material, which could confirm the emission of these compounds during the processing and usage period. The presence of carboxylic acids and plasticizer residues (peaks 19-22) in the recycled samples shows the importance of controlling the presence of foreign contaminants that may have penetrated the polymeric matrix in recycled materials.

Different styrene trimers have also been found in both virgin and recycled HIPS samples (Article III, Table 5), which have been also reported to be formed during styrene polymerisation [71, 72, 74-76]. Some of these trimers, such as 1,3,5-triphenylhexene-5 and the four different 1-phenyl-4-(1-phenylethyl)-tetraline diastereomers, were identified through bibliographic comparison of their mass spectra [72, 77].
### Table 3.2. Relative abundance and chromatographic properties of the identified low molecular weight compounds in HIPS samples

<table>
<thead>
<tr>
<th>Peak nr.</th>
<th>Proposed compound</th>
<th>R.T. (s)</th>
<th>Quant. ion</th>
<th>Virgin HIPS</th>
<th>HIPS1</th>
<th>HIPS2</th>
<th>HIPS3</th>
<th>HIPS4</th>
<th>HIPS5</th>
<th>HIPS6</th>
<th>HIPS7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylbenzene</td>
<td>238</td>
<td>91</td>
<td>-</td>
<td>101</td>
<td>102</td>
<td>66</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Styrene</td>
<td>269</td>
<td>104</td>
<td>2254</td>
<td>714</td>
<td>606</td>
<td>783</td>
<td>892</td>
<td>845</td>
<td>1579</td>
<td>1083</td>
</tr>
<tr>
<td>3</td>
<td>Benzene, (1-methyl-1-propyl)-</td>
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<td>105</td>
<td>49</td>
<td>29</td>
<td>40</td>
<td>82</td>
<td>64</td>
<td>31</td>
<td>29</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>Benzene, propyl-</td>
<td>325</td>
<td>91</td>
<td>21</td>
<td>46</td>
<td>35</td>
<td>96</td>
<td>50</td>
<td>22</td>
<td>19</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>Benzene, 1-ethyl-4-methyl-</td>
<td>333</td>
<td>120</td>
<td>13</td>
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<td>5</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Benzaldehyde</td>
<td>335</td>
<td>106</td>
<td>10</td>
<td>11</td>
<td>35</td>
<td>8</td>
<td>50</td>
<td>25</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
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<td>Heptane, 2,2,4,6,6-pentamethyl-</td>
<td>357</td>
<td>57</td>
<td>66</td>
<td>31</td>
<td>30</td>
<td>-</td>
<td>26</td>
<td>18</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>4-methylstyrene</td>
<td>368</td>
<td>65</td>
<td>Internal standard (I.S.)</td>
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<td></td>
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<tr>
<td>9</td>
<td>Benzeneacetaldheyde, α-methyl-</td>
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<td>105</td>
<td>-</td>
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<td>10</td>
<td>-</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>Acetophenone</td>
<td>429</td>
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<td>17</td>
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<td>54</td>
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<tr>
<td>11</td>
<td>Butylated Hydroxytoluene</td>
<td>794</td>
<td>205</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>25</td>
<td>-</td>
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<tr>
<td>12</td>
<td>Benzene, 1,1′-(1,3-propanediyl)bis-</td>
<td>902</td>
<td>92</td>
<td>17</td>
<td>13</td>
<td>35</td>
<td>11</td>
<td>31</td>
<td>24</td>
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</tr>
<tr>
<td>13</td>
<td>Benzene, 1,1′-(1,2-cyclobutanediyl)bis-, cis-</td>
<td>929</td>
<td>104</td>
<td>405</td>
<td>192</td>
<td>231</td>
<td>327</td>
<td>183</td>
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<td>2,4-diphenyl-1-butene</td>
<td>946</td>
<td>91</td>
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<td>73</td>
<td>134</td>
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<td>966</td>
<td>104</td>
<td>2757</td>
<td>865</td>
<td>2065</td>
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<td>2423</td>
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<td>1052</td>
<td>114</td>
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<td>40</td>
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<td>Octadecanoic acid</td>
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<td>12</td>
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*Proposed identification by comparison to NIST database; †Proposed identification through bibliography [72]; ‡Proposed identification through bibliography [77]
4. CONCLUSIONS

- A dual-pronged experimental procedure employing multiple processing and thermo-oxidation has been proposed to model the processing, mechanical recycling, and service life of recycled HIPS. The results were compared with those obtained from real samples from a large-scale mechanical recycling plant.

The procedure proved to be useful to analyse the degradative effects undergone by recycled HIPS during its life cycle.

- Multiple processing and thermo-oxidation clearly affect the oxidative stability, rheological and mechanical properties, chemical structure, and morphology of HIPS, resulting in a modification of the PB and PS phases.

Multiple processing and thermo-oxidation induce changes in the chemical structure of HIPS, with the formation of oxidative moieties and consumption of part of the unsaturations. The PB phase is the initiation point for HIPS degradation processes induced during the life cycle. These chemical changes are related to modifications at a macroscopic scale in the mechanical and viscoelastic behaviour.

- Multiple processing and thermo-oxidation exhibit complex chemical and physical implications for the structure and properties of recycled HIPS.

Thermo-mechanical degradation caused by multiple processing may induce alterations of the physical structure and may cause crosslinking in the rubber phase, together with chain scission and chain rearrangement in the PS matrix. Thermo-oxidation shows a complex behaviour throughout exposure times; at shorter exposure times, physical ageing seems to predominate, whereas chemical degradation of the PB phase has irreversible effects after longer exposure times.

- Thermo-oxidative degradation affects more severely than multiple processing the chemical structure, oxidative stability and mechanical properties of HIPS.

HIPS is a promising material for mechanical recycling, since its properties are not drastically affected by multiple processing. Thermo-oxidation, on the other hand, affects more severely the oxidative stability and the mechanical properties of HIPS. Considering the life cycle and the mechanical recycling potential of HIPS, its
previous service life seems, therefore, to determine the degree of degradation of HIPS recyclates and its further possibilities for use in second-market applications.

- The proposed key parameters (degree of mixing, degree of degradation, and presence of low molecular weight compounds) prove to be suitable for the quality assessment of recycled high impact polystyrene.

An integrated approach involving different analytical strategies, such as thermal analysis, vibrational spectroscopy, and chromatography, is necessary to characterise fully the presence of volatiles and contaminants, the oxidative and thermal stability, the changes in chemical structure, and the morphological properties of recycled materials.
5. **FUTURE WORK**

- Employment of chromatographic techniques (GC-MS) to analyse the low molecular weight degradation products formed during multiple processing and the thermo-oxidation of HIPS.

- Development and optimisation of fast analytical strategies based on advanced extraction procedures and chromatographic detection for quality purposes in recycled styrenic polymers (detection of styrene, oxidised derivates, and other volatiles in recycled HIPS; determination of brominated flame retardants in recycled styrenic plastics from waste electrical and electronic equipment).

- Use of mass spectrometric techniques (MALDI TOF/MS) for the analysis of the degradative effects in HIPS.
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