ANALYTICAL STRATEGIES FOR THE QUALITY ASSESSMENT OF RECYCLED HIGH-IMPACT POLYSTYRENE (HIPS)

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This thesis is a summary of the following papers:

I. **"Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation"**. Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson. Polymer Degradation and Stability, 91, 9 (2006) 2163-2170.

II. **"Changes in the microstructure and morphology of high-impact polystyrene subjected to multiple processing and thermo-oxidation"**. Francisco Vilaplana, Sigbritt Karlsson, Amparo Ribes-Greus. European Polymer Journal, 43, 10 (2007) 4371-4381.

III. **"Chromatographic pattern for mimicking the occurrence of volatiles and low molecular weight compounds in high-impact polystyrene during multiple processing and thermo-oxidation".** Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson. Manuscript.

IV. **"Analytical strategies for the quality assessment of recycled high-impact polystyrene: a combination of thermal analysis, vibrational spectroscopy and thermo-oxidation".** Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson. Analytica Chimica Acta, 604, 1 (2007) 18-28.

V. **"Extraction of brominated flame retardants from styrenic plastic fractions in waste electrical and electronic equipment (WEEE) using microwave-assisted extraction".** Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson. Submitted to The Analyst.

VI. **"Determination of brominated flame retardants in styrenic polymers: A comparison of extraction efficiency among ultrasonication, microwave-assisted extraction, and pressurised liquid extraction".** Francisco Vilaplana, Patrik Karlsson, Amparo Ribes-Greus, Per Ivarsson, Sigbritt Karlsson. Submitted to Journal of Chromatography A.

VII. **"Quality concepts for the improved use of recycled polymeric materials: a review".** Francisco Vilaplana and Sigbritt Karlsson. Accepted by Macromolecular Materials and Engineering. DOI 10.1002/mame.200700393.

ANALYTICAL STRATEGIES FOR THE QUALITY ASSESSMENT OF RECYCLED HIGH-IMPACT POLYSTYRENE

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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. The assessment of the quality properties of recycled polymers is therefore crucial to guarantee the performance of recyclates in further applications. Three key quality properties have been defined for this quality analysis: degree of mixing (composition), degree of degradation, and presence of low molecular weight compounds (degradation products, contaminants, additives). Furthermore, 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 used in packaging applications, and electrical and electronic equipment (E&E). 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 probably 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 the three key quality properties. Special attention has been devoted to the determination of brominated flame retardants in recycled HIPS from electrical and electronic equipment using chromatographic techniques, due to the legislative and environmental implications of these additives, both in terms of waste management and emissions to the environment.

Keywords: Recycling; high-impact polystyrene; degradation; quality analysis; thermal analysis; vibrational spectroscopy; chromatography; thermo-oxidation; reprocessing; polybutadiene microstructure; advanced solvent extraction; brominated flame retardants; waste electrical and electronic equipment (WEEE).

ESTRATÈGIES ANALÍTIQUES PER DETERMINAR LES PROPIETATS DE QUALITAT DE POLIESTIRÉ D' ALT IMPACTE RECICLAT

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RESUM

Els materials polimèrics es veuen sotmesos a canvis químics durant el seu processat, vida en servei i posterior recuperació, i poden simultaneament entrar en contacte amb impureses que poden alterar la seua composició. Aquests canvis modifiquen substancialment els mecanismes d'estabilització i les propietats mecàniques dels polímers reciclats. L'anàlisi de les propietats de qualitat de polímers reciclats és, per tant, crucial per tal de garantir les prestacions dels productes reciclats en futures aplicacions. S'han definit tres propietats clau de qualitat per aquest estudi: el grau de mesclat (composició), l'estat de degradació i la presència de compostos de baix pes mol·lecular (productes de degradació, contaminants, additius). A més, el coneixement de com les diferents etapes del cicle de vida afecten l'estat de degradació dels polímers és fonamental per tal de discutir les possibilitats de gestió dels residus plàstics i l'aplicabilitat dels materials reciclats.

S'ha proposat un doble precediment experimental mitjançant processat múltiple i termo-oxidació, per modelitzar el cicle de vida de poliestiré d'alt impacte (HIPS) procedent d'aplicacions d'envassat i equipament elèctric i electrònic. Tant el processat múltiple com la degradació termo-oxidativa són responsables de diferents efectes físics i químics coexistents (escissió de cadenes, *crosslinking*, aparició de grups funcionals oxidats, reagrupació de cadenes, i probablement envelliment físic) sobre la microstructura i la morfologia de les fases polibutadié (PB) i poliestiré (PS). Aquests efectes afecten l'estabilitat a llarg plaç i les propietats reològiques i mecàniques del HIPS. S'ha demostrat que la fase PB constitueix el punt d'iniciació de la degradació del HIPS en el transcurs del seu cicle de vida. La termo-oxidació sembla exercir efectes més pronunciats sobre les propietats del HIPS; és per això que es pot deduir que la vida en servei pot afectar en major mesura les possibilitats de reciclatge i la futura aplicació de productes de HIPS reciclats.

Els resultats de la simulació degradativa durant el cicle de vida s'han comparat amb els obtinguts a partir de l'anàlisi de mostres reals procedents d'una planta de reciclatge mecànic. La combinació de diferents estratègies analítiques (anàlisi tèrmica, espectroscopia vibracional, i cromatografia) és necessària per entendre en detall les propietats de qualitat del HIPS reciclat, d'acord amb les tres propietats clau propostes. S'ha dedicat especial atenció a la determinació de retardants de flama brominats en HIPS reciclat procedent d'equipament elèctric i electrònic utilitzant tècniques cromatogràfiques, amb motiu de les implicacions mediambientals i legislatives que envolten aquests additius.

Paraules clau: Reciclatge; poliestiré d'alt impacte; degradació; anàlisi de qualitat; termo-oxidació; reprocessat; retardants de flama brominats.

ESTRATEGIAS ANALÍTICAS PARA DETERMINAR LAS PROPIEDADES DE CALIDAD DE POLIESTIRENO DE ALTO IMPACTO RECICLADO

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RESUMEN

Los materiales poliméricos se ven sometidos a cambios químicos durante su procesado, vida en servicio y posterior recuperación, y pueden a su vez entrar en contacto con impurezas que pueden alteran su composición. Estos cambios modifican sustancialmente los mecanismos de estabilización y las propiedades mecánicas de los polímeros reciclados. El análisis de las propiedades de calidad de polímeros reciclados es, por ello, crucial para garantizar las prestaciones de los productos reciclados en futuras aplicaciones. Se han definido tres propiedades de calidad claves para este estudio: el grado de mezclado (composición), el estado de degradación, y la presencia de compuestos de bajo peso molecular (productos de degradación, contaminantes, aditivos). Además, el conocimiento de cómo las diferentes etapas del ciclo de vida afectan el estado de degradación de los polímeros es fundamental para discutir las posibilidades de gestión de los residuos plásticos y la aplicabilidad de los materiales reciclados.

Se ha propuesto un doble procedimiento experimental mediante procesado múltiple y termo-oxidación para modelizar el ciclo de vida de poliestireno de alto impacto (HIPS) reciclado procedente de aplicaciones de envasado y equipamiento eléctrico y electrónico. Tanto el procesado múltiple como la degradación termo-oxidativa son responsables de diferentes efectos físicos y químicos coexistentes (escisión de cadenas, *crosslinking*, aparición de grupos funcionales oxidados, reagrupación de cadenas, y probablemente envejecimiento físico) sobre la microestructura y la morfología de las fases polibutadieno (PB) y poliestireno (PS). Estos efectos afectan la estabilidad a largo plazo y las propiedades reológicas y mecánicas del HIPS. Se ha demostrado que la fase PB constitutye el punto de inicio de la degradación del HIPS a lo largo de su ciclo de vida. La termo-oxidación parece ejercer efectos más severos sobre las propiedades del HIPS; por ello se puede concluir que la vida en servicio previa puede afectar en mayor medida las posibilidades de reciclaje y la futura aplicación de productos reciclados.

Los resultados de la simulación degradativa durante el ciclo de vida se han comparado con los obtenidos a partir del análisis de muestras reales procedentes de una planta de reciclaje mecánico. La combinación de diferentes estrategias analíticas (análisis térmico, espectroscopía vibracional, y análisis cromatográfico) es necesaria para entender en detalle las propiedades de calidad de HIPS reciclado, de acuerdo con las tres propiedades de calidad clave. Se ha dedicado especial atención a la determinación de retardantes de llama brominados en HIPS reciclado procedente de equipamiento eléctrico y electrónico, utilizando técnicas cromatográficas, debido a las implicaciones medioambientales y legislativas de estos aditivos.

Palabras clave: Reciclaje; poliestireno de alto impacto; degradación; análisis de calidad; termo-oxidación; reprocesado; retardantes de llama brominados.

1. INTRODUCTION

1.1 BACKGROUND. SCOPE OF THE STUDY

Polymeric materials allow the manufacture of a wide variety of products with low cost and excellent performance, contributing to a continuous energy saving and to a sustainable development. The inert nature and the resistance towards biodegradation showed by synthetic polymers have caused an important environmental problem concerning their waste management. Disposal in landfills constitutes nowadays the main route for plastic waste, but this procedure does not guarantee a suitable residue management in terms of resources exploitation and environmental protection.

Alternative plastic recovery programs are being encouraged from the different institutions, in order to promote the employment of plastic waste as raw materials to manufacture new products, and the recovery of their calorific content for energy production. In this way, different procedures are being considered for optimising plastic waste management, such as biodegradable polymers, material recovery of plastic waste to manufacture new plastic products (mechanical recycling), and the employment of plastic waste as raw material to obtain new chemical substances with industrial interest (feedstock recycling) or energy (energy recovery). A combination of different plastic recovery options will in conclusion achieve the best economic and environmental efficiency for plastic waste management.

Mechanical recycling has been pointed out as the preferred route for the recovery of relatively clean and homogeneous plastic waste streams. Plastic wastes should receive renewed consideration as valuable resources for product manufacturing through recycling, with a similar status as virgin oil-based plastics and polymers of biological origin. The investigation on recycled polymers must consider, however, the degradative processes to which these materials are subjected during their life cycle, this is, processing, service life and further mechanical recycling, 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 been continuously growing during the past decade, reaching a total demand volume of 43,50 million tonnes in 2004. In terms of end-use applications, packaging is by far the sector with highest polymer demand (37%), followed by building and construction applications (20%), automotive industry (7,5%) and electric and electronic equipment (7,5%); these results prove the versatility and applicability of polymeric materials in wide markets [1].

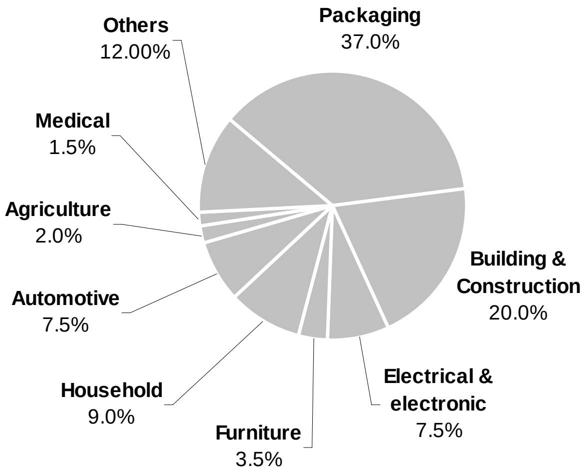


Figure 1.1. Plastic demand by end-use application sector in Western Europe, 2004 (drawn after data in [1])

This progressive increment in plastic consumption is consequently responsible for an increase in post-consumer plastic waste generation. Although plastic waste accounts for only 1% by weight of all solid waste volume, this plastic volume constitutes a valuable resource in terms of both material and energy. The diversification of plastic waste management procedures is therefore extremely important in order to minimise the total volume sent to landfilling disposal. It has been demonstrated, however, that material recycling and energy recovery by themselves are unable to meet the targets demanded in terms of plastic waste recovery, so a combination of the available recovery options (mechanical recycling, feedstock recycling, and energy recovery) is fundamental to achieve best environmental and economic efficiency [1, 2].

The different available options for plastic waste recovery, in contraposition to landfill disposal, include material recycling and energy recovery procedures. As a whole, recycling processes (mechanical and feedstock recycling) involve material recovery from plastic waste streams, whereas combustion procedures for heat production with controlled emissions are included into energy recovery options. Mechanical recycling consists basically on the re-melting of plastic waste into new plastic products; this process can be performed on homogeneous waste streams or on waste streams consisting on a mixture of different plastic materials (mixed waste streams). By feedstock recycling, plastic wastes are cracked and depolymerised by chemical means into a series of petrochemical products or monomers, which can be later transformed again into new polymeric products by synthesis. Finally, energy recovery employs polymeric waste streams as fuel for energy production, since 1 tonne of plastic offers approximately the same amount of energy as 1 tonne of crude oil in the combustion process.

The current environmental policy considers the material efficiency during service life and the reduction of the environmental impact throughout their entire life cycle. Suitable waste management recovery options for plastic waste streams therefore contribute to the sustainable development of our societies taking into account a life cycle perspective, by closing the material and energetic life cycle loop and enhancing the conversion of waste materials into valuable resources (Fig. 1.2).

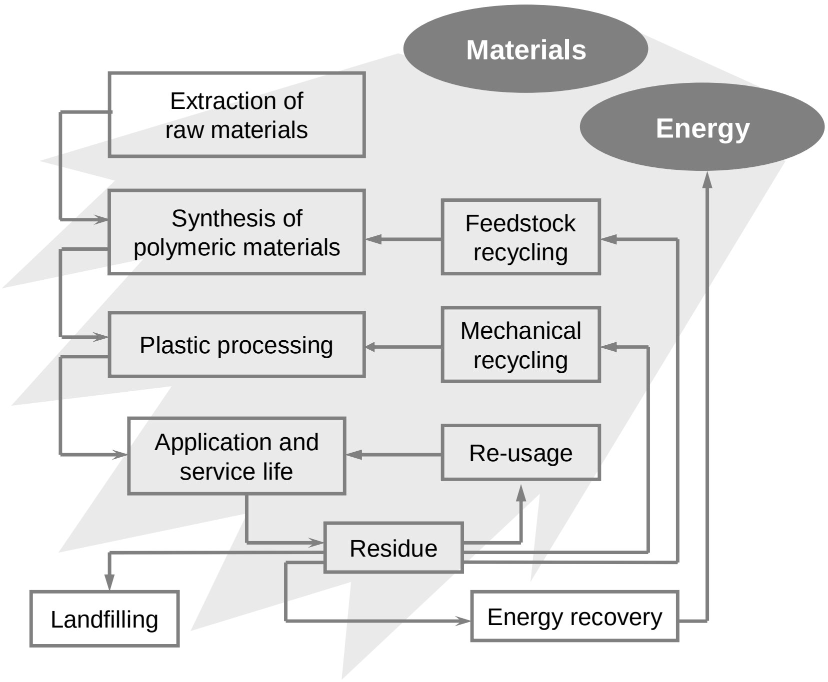


Figure 1.2. Plastic waste management options in terms of the life cycle of polymeric products

The rate of plastic waste recovery has been continuously increasing since the mid-90's, due to the implantation of mechanical recycling and energy recovery facilities all over Europe; feedstock recycling remains still as a minor alternative. As a result of these developments and despite the increasing post-use plastic waste volumes, the amount of residual waste sent to landfill disposal seems to have stabilised. Decoupling between the volume of plastic consumption and the associated amount of residue generation is currently being achieved in the countries with a developed waste management infrastructure [1]. Figure 1.3 proves this progressive decoupling between the plastic waste growth and the volume sent to disposal, due to enhanced plastic waste recovery options.

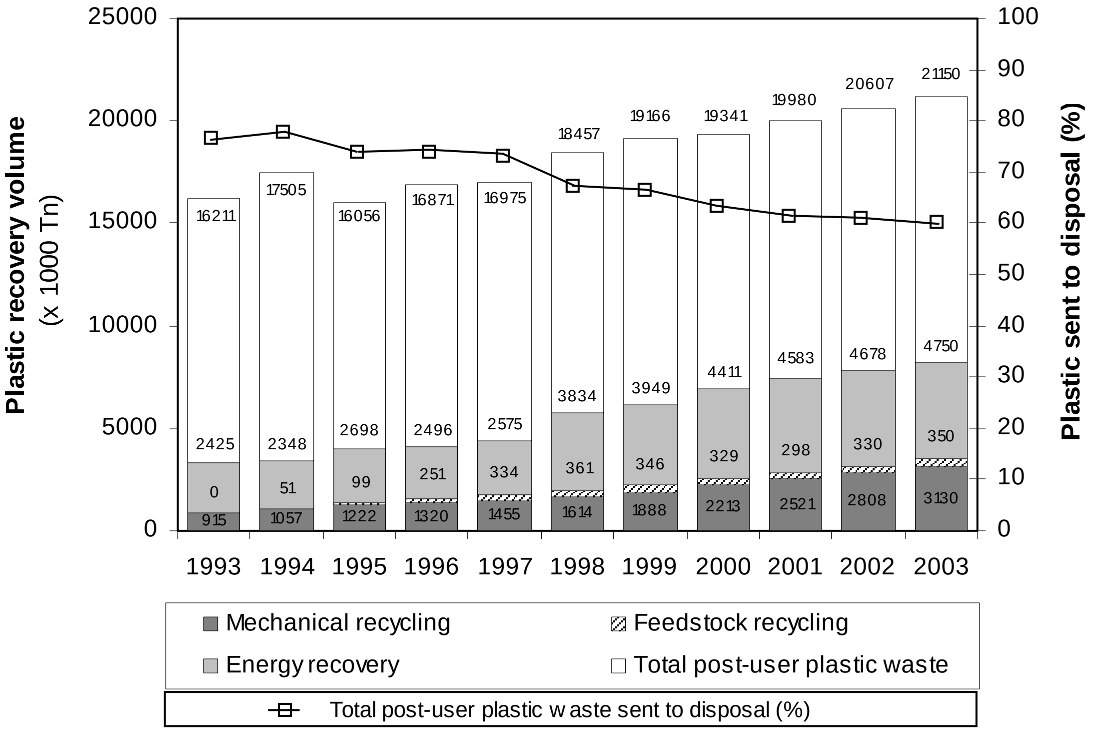


Figure 1.3. Evolution of plastic recovery options and total post-consumer plastic waste volume during 1993-2003 (drawn after [3])

Analysing plastic recovery by end-use applications [3], the largest volume of recovered plastic waste corresponds to municipal solid waste, with a total volume of 5.45 MTonnes in 2002. Sectors like agricultural applications exhibit the highest recovery rates (over 50%), though with lower waste volumes. However, the automotive sector and electrical and electronic equipment showed lower plastic recovery rates in 2002; this situation is expected to be continuously improving due to the implementation of the corresponding *European Directive 2000/53/EC* on end-of-life vehicles (ELV) and *European Directive 2002/96/EC* on waste of electrical and electronic equipment (WEEE).

1.2.2 Mechanical recycling. Bottlenecks associated to the industrial activity.

Among the different procedures for plastic waste management, mechanical recycling is the most suitable recovery route for relatively clean and homogeneous plastic waste streams. It is also the second largest recovery technique after energy recovery, with a constant growth during the last years stimulated mainly by the implementation of the European Directives, which has allowed the adoption of better waste collection and treatment practices [1]. In addition to this, recent life cycle assessment studies have pointed out that mechanical recycling of plastic materials is in general favourable to other management procedures in terms of overall energy use and emissions of gases contributing to global warming [4].

Nevertheless, despite these encouraging results, there are still some difficulties that the plastic recycling industry must overcome, both technological and commercial. The potential demand for plastic recyclates by the end-market is determined by two key factors, which are the market acceptance and the technical acceptance of recycled products. The market acceptance regards what consumers are willing to accept based on the 'image' of recyclates or on health and safety requirements, while the technical acceptance of the recycled plastic materials is related to the need to assess the desired performance of products and suitability for manufacturing processes [2]. In this direction, several bottlenecks can be currently found related to the large–scale mechanical recycling activities.

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

  The closely integrated nature of products (plastics, metals and ceramics in close combination) makes these residues hard to handle and separate. Moreover, plastics cannot be considered on their own, and there are interrelated costs and environmental impacts [3, 5]. The complex nature of the plastic waste streams in terms of polymer composition and presence of impurities requires the development of automatic and effective separation methods for the mixed plastic waste streams prior to reprocessing. Some studies have been done in order to evaluate to what degree separation brings value to waste plastics as raw materials for new products [6]. Moreover, the possibility of reducing separation requirements and broadening the range of application of recycled plastics by the addition of elastomers, compatibilizers, fillers or other additives has also been reported [7, 8].

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

  In the recent years, the investigation on polymer recycling has focused on the effects of multiple processing and artificial ageing on the macroscopic properties of polymers. It is worth mentioning the studies on upgrading of recycled plastics [7, 9-11], the effects of simulated recycling on the properties of polyolefins [12, 13], or the analysis of the degradative effects of reprocessing [11]. Most of the studies have however focused on rheological and mechanical properties of recycled materials, so further investigation about the degradative effects at a molecular scale would be needed.

- **Presence of hazardous compounds in the plastic waste.**

  The plastic waste may contain a large number of hazardous compounds that difficult the recycling processes, such as degradation products of additives, brominated flame retardants, hazardous phtalates, among others. The development of procedures to identify, quantify, and extract these products from plastic waste is therefore necessary prior to recycle them according to the European Legislation.

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

  Quality assessment is a matter of significant importance in order to guarantee a suitable employment of recycled plastic materials in further applications, since 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 standardized methods for the properties of recycled materials.**

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

- **Design for recycling.**

  There is a need of design for recycle in order to enhance the recycling operations such as dismantling of equipments, separation of the homogeneous streams, and identification of individual polymers. This is more important in products where plastics are usually combined with other materials (automotive industry, electrical and electronic equipment).

1.3 QUALITY ASSESSMENT OF RECYCLED PLASTICS

Polymeric materials are subjected to physical and chemical changes during their processing, service life and further mechanical recycling. They suffer chemical degradative reactions in each step of their life cycle that induce alterations in the polymeric chains by chain scission, crosslinking, and formation of new functional groups; the new impurities introduced in the polymeric structure may enhance the sensitivity of recycled materials to thermo- and photo-oxidative degradation. These degradative processes are also responsible of the consumption of the stabilising system introduced in the processing steps, together with a reduction of the long-term stability and a loss of the mechanical properties. The polymeric materials may furthermore come in contact with impurities from the surrounding environment during their service life and recovery due to the permeable nature of polymers; the absorbed contaminations ultimately alter the performance of recyclates [14, 15].

Industrially, plastic recycling is still far from being widely deployed; technical development has been slow and the logistics are not always well implemented by municipalities and other public authorities. In general, recycling industries are characterised by a low degree of knowledge about plastic products and polymeric inherent properties; it is difficult for this industrial segment to compete with the manufacturers of virgin polymers who can assess reliably the quality properties of their synthesised materials. There is, therefore, a clear need to introduce a quality concept in the plastics recycling activities, to assess the properties of recyclates within narrow tolerances, thus satisfying the requirements of both manufacturers and customers, and guaranteeing the performance of recycled products in their second-market applications[14].

Fast, cost-effective and reliable characterisation procedures for plastic recyclates should be developed and implemented in the recycling facilities to guarantee their quality properties. Traditionally, the evaluation of the melt flow rate (MFR) and the mechanical properties of the recyclates were the only properties that are determined in the specification sheets of the final material; however, using only the specification of such macroscopic properties may be misleading in terms of assessing the performance of recycled products in new applications [14, 16].

Recent research carried out by our group on the characterisation of recycled polymers has lead to the identification of three key properties for the quality assessment of recycled plastics: the degree of mixing (composition), the degree of degradation and the presence of low molecular weight compounds (additives, degradation products, and contaminants) (Fig.1.4) [17]. These key properties are necessary to fully guarantee the applicability of recyclates for the manufacture of new products. The degree of mixing (composition) is related to the presence of polymeric impurities in the recycled polymers resulting from impure plastic waste streams and poor separation in the recycling plant. The degree of degradation of recyclates considers the degradation processes to which polymeric materials are subjected during their processing, service life, and further recovery. Finally, the identification of low molecular weight compounds (contaminants, additives, and degradation products) present in recycled polymers is essential to verify that the products are compliant with legislation on the presence of hazardous substances.

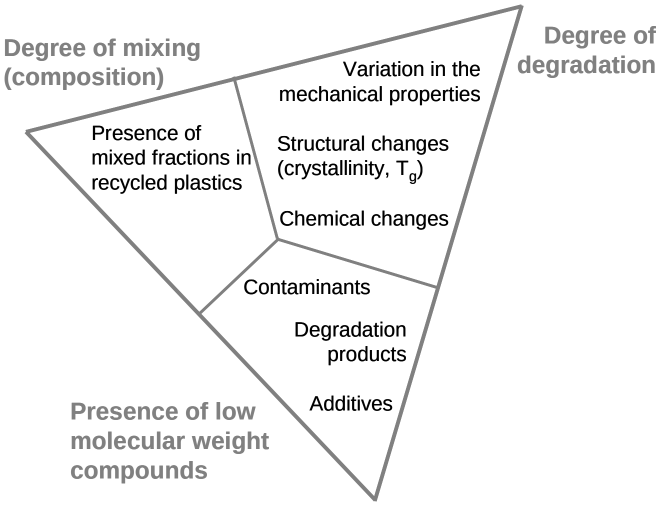


Figure 1.4. Key properties for quality assessment of recycled plastics

1.3.1 Degree of mixing (composition)

The presence of mixed polymeric fractions in recycled plastics is a critical parameter influencing the structure and mechanical properties of the recyclates. Polymers mixed in a recyclate are usually incompatible, and even a low level of polymeric contaminations in a certain waste stream leads to poor adhesion properties in the polymeric mixture interface and thus deterioration of the overall macroscopic properties. The determination of the composition of plastic waste streams is therefore important, because it determines the appropriate management procedure for the end-of-life material and it is also a critical parameter for the future performance of recycled products in second market applications. In this sense, experimental design and statistical approaches such as response surface methodology can be used to predict properties of mixed plastic streams and to discuss whether complete separation is required to obtain recycled materials with acceptable properties [18]. Some strategies to analyse polymer composition and the presence of polymeric impurities in mixed plastic streams are detailed as follows.

Thermal analysis techniques, and in particular differential scanning calorimetry (DSC), are becoming routine analyses for the characterisation of polymer composition. DSC can be employed for compositional analysis above 1% wt, but lower concentrations are not easily detected within reasonable analysis time limits [19]. Another method to detect small polymeric contaminations in recycled PET involves annealing the material at high temperatures (200°C) and analysis of the segregated coloured flakes with DSC and FTIR; contaminations of HDPE, LDPE, PP, PS, and PVC in ranges of 0.01-3%wt. were thus detected in some recycled PET samples [20]. Other non-polymeric contaminations in waste and recycled materials, such as cellulose, soil, metal particles, and adhesives, can be detected by thermogravimetric analysis (TGA).

Vibrational spectroscopy techniques such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy are fast and reliable analytical techniques that are usually employed in polymer production quality control and are potential techniques for online quality analysis in recycling plants. Both the near-infrared (12800-4000 cm^{-1}) and mid-infrared (4000-600 cm^{-1}) range can be used for spectroscopic analysis of physical and chemical polymeric properties. Among the different spectroscopic modes, attenuated total reflectance (ATR) and diffuse reflectance are widely reported for polymer analysis with little or no sample preparation.

The compositional analysis of polymeric blends from recycled mixed-plastic waste can be performed online using either diffuse-reflectance NIR or Raman spectroscopy and chemometrics; fast analytical procedures were developed and validated for recycled PP/HDPE and ABS/PP blends, using FTIR and DSC as reference techniques [19, 21]. PP/HDPE blends are the most abundant components in the plastic waste streams from household packaging; on the other hand, PP and ABS are two of the major plastics materials used in the automotive industry, so blends of these two polymers are common in waste streams from end-of-life vehicles (ELV). Diffuse-reflectance near-infrared (NIR) and Raman spectroscopy allow fast and reliable pellet analysis and require no sample preparation, in contrast to time-consuming FTIR and DSC. The interpretation of the NIR spectra should be performed using multivariate analysis, which allows compositional determination with high precision [19].

1.3.2 Degree of degradation

Polymers suffer chemical and physical changes during processing and service life. They undergo oxidative reactions at every stage of their life cycle, and the new functional groups formed during the oxidation process may enhance the sensitivity of the recyclates to further thermal- and photo-degradation. With the formation of the new oxidative moieties, a substantial part of the stabilizers are consumed, with the consequent decrease of long-term stability and deterioration of mechanical properties. Determining the degree of degradation, that is, the extent to which previous degradation has affected the structure, mechanical properties, and long-term stability of recyclates, is important for the future performance of recycled products. This will be important when a true recycling society is achieved, in which the materials will face several usage-life steps before being discarded as wastes.

Different strategies can be considered to investigate the degree of polymer degradation, depending on the changes at a macroscopic or microscopic scale (Fig. 1.5) [22]. Common approaches to determine degradation effects include analysis of the alterations in chemical functional groups (using vibrational spectroscopy or nuclear magnetic resonance), crystallinity and thermal properties (using thermal analysis), morphology (using electron microscopy), mechanical properties (mechanical testing), and molecular weight distribution and composition (using size exclusion chromatography and mass spectroscopic techniques). Additionally, investigation of degradation products and additives using chromatographic tools have proved to be useful for monitoring ongoing degradation processes in polymers [22-24].

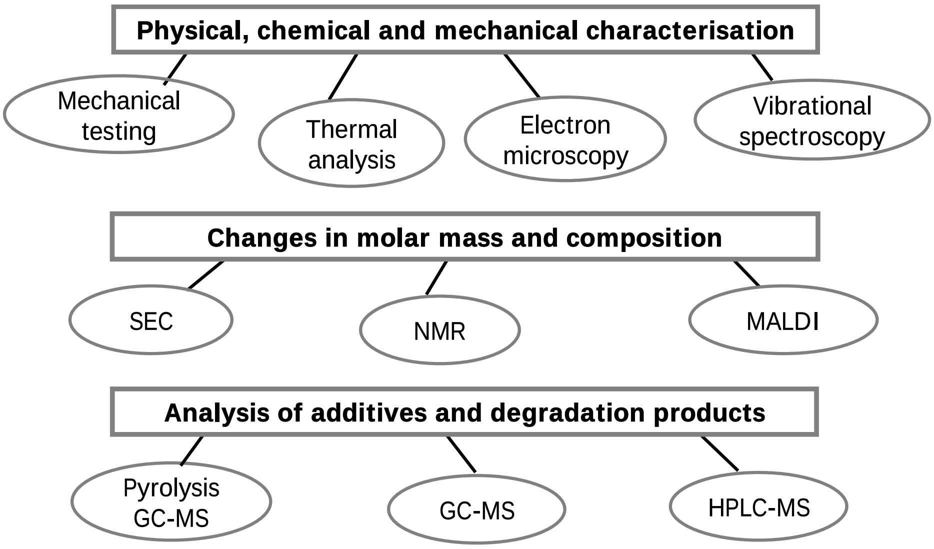


Figure 1.5. Analytical strategies for degradation studies in polymers (drawn after [22])

Rheological properties in general, and melt flow rate (MFR) in particular, are common quality properties for recycled plastics; they can also be an indicator of polymer degradation, since they are related to the melt viscosity and therefore to the molecular weight of the polymer. Thermo-mechanical degradation during processing and mechanical recycling is usually responsible for chain scission phenomena, which result in a decrease in the molecular weight of the recyclates; a progressive increase in the MFR has been extensively reported as a consequence of consecutive processing steps. These variations in MFR differ, on the other hand, among the different families of analysed polymers.

Variations in the mechanical properties are related to the degradation processes undergone by polymers during life cycle; however, the utilisation of mechanical properties as the only parameter to evaluate the degree of degradation for recycled polymers may be misleading, since the degradation at a molecular level may occur before any signs of change at a macroscopic scale are detected [25], and some observed changes in the mechanical properties may be due to physical factors and are hence reversible [16]. Tensile, impact, and flexural properties are often evaluated for recycled plastics; deeper studies of the fracture behaviour and micromechanical properties offer interesting information about the mechanical performance and failure mechanisms in recycled materials [26]. As mentioned earlier, previous degradation causes a deterioration of the molecular structure, resulting in recycled plastics with poorer mechanical properties than the virgin ones. Nevertheless, a more "optimistic" approach can be proposed to explain the changes in mechanical properties. It is true that previous degradation affects the mechanical performance of the materials, but normally these changes are not unidirectional; that is, it could be that the ductility diminishes but stiffness increases, or vice versa, so a suitable application for recyclate materials can be found within the mechanical properties quality range. In conclusion, the mechanical properties should be clearly specified for the recyclates and adjusted for the requirements of the application to which they may be destined.

Changes in physical properties such as crystallinity, melting behaviour, morphology, thermal history, and viscoelastic behaviour can also be used as indicators of the degree of degradation and the quality of recycled plastics. Thermal analysis as DSC and dynamic mechanical analysis (DMA) are widely used for these purposes. By registering different crystallisation and melting behaviour, DSC can detect changes in thermal history in waste PET samples from different origins [20]. Changes in melting and/or crystallisation behaviour are also indicators of polymer degradation; different coexisting phenomena during polymer degradation affect the degree of crystallinity. The formation of smaller polymer chains due to chain scission may lead to an increase of the crystallinity; the presence of impurities (e.g. oxidative moieties) formed during degradation, on the other hand, may hinder recrystallisation processes. Finally, physical processes, such as annealing or even chain reorganisation during processing, also produce crystalline rearrangements. Recycled semi-crystalline polymers are expected to display heterogeneous crystalline structures, and therefore usually show multimodal melting/crystallisation behaviour in the DSC experiments, whereas virgin materials display only one clear peak. The existence of multiple peaks in the melting or crystallisation thermogram can be due to the presence of mixed plastics or the presence of different chain-length populations that lead to heterogeneous crystalline morphologies and lamellar structures [17].

Changes in the glass transition and other viscoelastic relaxations in recycled plastics can be investigated using DMA; the study of the free volume parameter can lead to interesting conclusions about the effects of degradation on the microstructure of recycled polymeric materials. Powerful microscopic techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), can be used to investigate the effects of previous degradation on the morphology and phase distribution in polymer blends and copolymers in recycled plastics. The characterisation of the thermal properties such as thermal diffusivity in recycled plastics that may be used as heat insulators can be performed by laser flash technique [27].

Thermal and thermo-oxidative stability of recycled polymers is usually assessed using thermal analysis techniques as TGA or DSC. TGA measurements under inert atmosphere allow the direct determination of parameters such as the onset temperature or the thermal decomposition maximum temperature, which offer a quantitative measure of the thermal stability of recycled polymers, together with information about the humidity and the content of volatiles, additives, and fillers in recyclates. Deeper kinetic analysis of the thermal decomposition data using dynamic and isothermal methods leads to the determination of the activation energy and the reaction mechanism for the thermal degradation process, providing valuable information about the thermal properties and even the structure of polymeric recyclates, as shown for recycled PP toughened with elastomers [28] and recycled PC/ABS blends from waste electrical and electronic equipment (WEEE) [29].

Thermo-oxidative stability in commercial plastics and recyclates is directly related to the stabilisation system (antioxidants, UV stabilisers) included in the material to prevent thermo-oxidation reactions; analytical methods such as the determination of the oxidation temperature (T_{ox}) and the oxidative induction time (OIT) are standardised and widely used for this purpose. In the field of polymer recycling, OIT and T_{ox} are used for the determination of the residual stabilising system in recycled resins, which is extremely important for evaluating the need for further restabilisation in the mechanical recycling process to guarantee long-term stability [30, 31].

Chemiluminescence (CL) offers a powerful tool to monitor oxidation reactions in polymers and can be therefore employed to assess the thermo-oxidative stability of recycled polymers and investigate the effects of base stabilisation and restabilisation on the recyclability of polyolefins [32-34]. The relationship between polymer oxidation and luminescence is generally associated to the deactivation of an excited carbonyl group formed during the oxidation process. Chemiluminescence provides, according to some authors, higher sensitivity than the determination of OIT using DSC in detecting reduced oxidative stability in recycled and waste polyolefins[32] and allows the analysis of the different oxidative behaviour of PE and PP in their recycled blends [30].

The changes in chemical structure in polymeric materials induced by degradation processes during the entire life cycle can be investigated using vibrational spectroscopic techniques, such as FTIR and Raman spectroscopy. These techniques are complementary and give useful information about different functional groups present in polymeric samples. Different oxidised moieties (hydroxyl, carbonyl, carboxylic, and ether groups) may be formed during the thermo- and photo-oxidation processes to which polymers are subjected throughout their exposure to service environment; other functional groups, on the other hand, may be consumed under these degradative conditions, such as the unsaturated double-bond groups in rubber-based copolymers or the ester linkage in polyesters. The detection and quantification of these specific functional groups using FTIR can be used as a valuable parameter to evaluate the degree of degradation of plastic waste streams and recycled products. Quantification using spectroscopic techniques can be performed by normalising the absorbance peak height or area corresponding to the oxidised functional group to the height/area of a reference peak that is not subjected to degradation; this procedure allows the removal of experimental errors due to differences in sample thickness or instrumental deviations. The carbonyl index is widely employed as a direct indicator of degree of oxidation in polymeric materials; the time dependence of carbonyl group formation during accelerated ageing experiments could be used to predict the formation of new carbonyl groups giving that their initial amount is known [35].

Near and mid-infrared spectroscopy in the diffuse reflectance mode could also be used for the simultaneous determination of molecular weight and crystallinity in recycled HDPE, using size exclusion chromatography (SEC) and DSC, respectively, as reference methods [36]. The use of multivariate analysis allows extracting the information from the spectral data and detecting small differences in them, which could be related to the analysed properties.

Raman spectroscopy is, in many ways, a complementary technique to infrared spectroscopy; analysis of conformation, tacticity, orientation, crystallinity, and functional groups is well established for polymers. Raman spectroscopy measurements can be, however, affected by fluorescence interferences, especially for dark-coloured samples, which restrict the use of this technique. Nevertheless, Raman is a fast and user-friendly technique that allows the recording of the vibrational spectra of polymeric samples in their original form, without sample preparation.

1.3.3 Presence of low molecular weight compounds

Plastic materials include in their formulations a wide range of low molecular weight compounds that contribute to the final properties and performance of the products; these compounds include monomeric and oligomeric residues of polymerisation, solvent residues, traces of initiators and catalysts, and different additives (antioxidants, stabilisers, plasticisers, and flame retardants). Moreover, other low molecular weight compounds may be formed due to the degradation processes affecting both the polymeric matrix and the additives. Finally, polymeric materials may also come in contact with impurities and contaminants from the surrounding environment during service use and further recovery, which can diffuse into the polymeric bulk due to their permeable nature. This wide range of possible low molecular weight compounds, either inherent or externally introduced impurities, can be present in plastic waste streams and recycled plastics, and may affect the performance and applicability in a next generation usage of recycled products. It is, therefore, of great importance to assess the presence of low molecular weight compounds in recyclates, to avoid contaminations and hazardous substances, according to increasingly restrictive legislation.

The development, optimisation and validation of different extractive and analytical methods for the identification and quantification of low-molecular weight compounds in recycled polymers is one of the main challenges for quality analysis. Chromatographic techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) are widely employed for the determination of low molecular weight compounds; different detectors such as mass spectrometry (MS), diode-array detector (DAD), and flame ionisation detector (FID) can be used for the identification and quantification of these analytes. However, different sample extraction procedures must be carried out prior to chromatographic analysis, to extract the low molecular weight compounds from the polymeric matrix. Traditional procedures such as Soxhlet extraction are time consuming (1-2 days per extraction) and require large amounts of solvents. Advanced solvent extraction techniques, including microwave-assisted extraction (MAE), ultrasonication, solid-fluid extraction (SFE), and pressurised liquid extraction (PLE) have been recently introduced for polymer analysis, reducing extraction times and amount of solvents, and allowing automatisation [17, 37-40]. Finally, other non-solvent extraction procedures such as solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are emerging as effective methods for the determination of volatile and semi-volatile compounds in polymers and other substrates, with fast extraction times and no need for solvents. However, some difficulties have been found for developing methods for the analysis of low-molecular weight compounds in recycled materials; the unknown properties and composition of the recycled plastics are perhaps the main hinder in optimizing the characterization methods, together with the fact that it is necessary to develop a specific method for each type of sample (polyolefins, styrenic copolymers, engineering plastics, etc.)[41].

A wide range of volatile organic compounds were detected in both virgin and recycled PP and PE resins, using microwave extraction and GC-MS analysis; the number of volatiles identified in the recycled samples was larger than in the virgin ones. The volatiles detected in recycled and virgin resins could be classified into 8 main categories: aliphatic hydrocarbons, aromatic hydrocarbons, carboxylic acids, esters, ketones, alcohols, aldehydes, and miscellaneous. Aroma and odour compounds, together with other compounds used in cosmetics were identified in recycled HDPE [37].

Volatile and semi-volatile model contaminants (1,1,1-trichloroethane, methylbenzene, chlorobenzene, and phenylcyclohexane) were analysed in recycled high-impact polystyrene from food-contact applications using purge-and-trap, co-evaporation, and total dissolution extraction; the proposed extraction techniques proved suitable for the detection of the model contaminants and could therefore be used for the analysis of hazardous contaminants in recycled HIPS and to assess the possible employment of recycled materials in food-contact applications [42].

Additives are introduced during first manufacturing of polymeric products, to confer specific properties such as long-term light and oxidative stability, fire retardancy, plastification, processability, and toughness upon the final plastic products. These additives may be consumed, suffer chemical transformation or even migrate to the environment during the polymer lifetime. The study of the residual presence of these additives in polymeric waste and recyclates is, therefore, of vital importance in the recycling industry. The methods for the quantitative determination of polymer additives usually combine an extraction step prior to analysis, although some extraction-free methods using spectroscopic and spectrometric techniques have been developed for determining concentrations of additives; a review of the analytical determination of additives in polymers using extractive procedures has been provided by Vandenburg et al [40].

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 pointed out as the preferred route for the recovery of styrenic plastic waste in packaging applications. For end-of-life vehicles (ELV) or electrical and electronic waste (WEEE) additional problems are found, based on the integrated nature of these products, the difficulties for dismantling and separating the plastic waste streams, and the presence of hazardous substances. It is therefore important to understand the degradation mechanisms to which recycled styrenic polymers are subjected under their life cycle in order to better assess their potential for further employment in second-market applications.

The improvement of the impact properties of styrenic polymers as high-impact polystyrene (HIPS) or acrilonitrile-styrene-butadiene copolymer (ABS) is usually achieved by the incorporation of a rubber disperse phase (usually polybutadiene or styrene/butadiene rubber) into the styrenic rigid matrix (polystyrene or styrenic copolymers as styrene/acrilonitrile) [43]. Particularly, 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 grafting of styrene units [44].

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 (Fig. 1.6). This multiphase structure confers HIPS its improved fracture resistance properties (impact strength, elongation at break, and fracture toughness) together with a reduction in transparency, modulus and tensile strength if compared with unmodified PS [43].

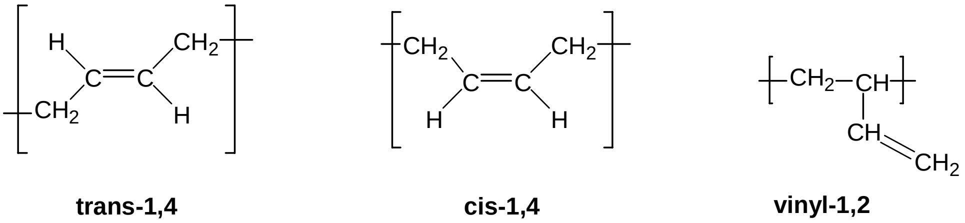


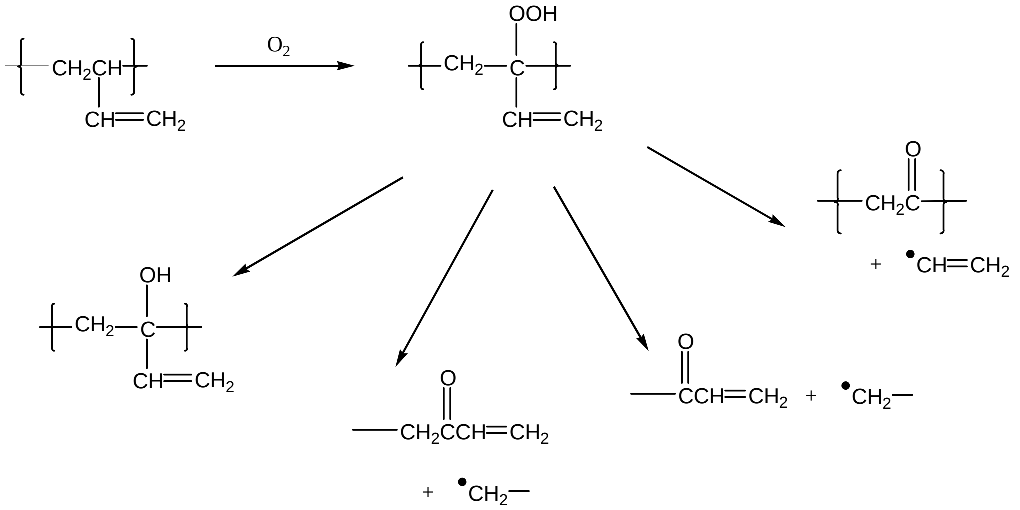
Figure 1.6. Microstructural isomeric units of polybutadiene

The introduction of a rubbery phase alters, however, the stability of the polymer blends towards degradation, enhancing the sensitivity of the material to the degradative agents. Degradation processes are complex phenomena that usually involve different mechanisms and initiating agents, such as temperature, chemical agents, mechanical stress, or radiation. In this chapter a brief review on the degradation aspects related to HIPS and other rubber-modified styrenic polymers will be given, with special focus on photo-oxidative, thermo-oxidative and thermo-mechanical degradation.

Different studies have been devoted to study the oxidative degradation of ABS [16, 45-50] and HIPS [43, 44, 51-58]. Early studies on the thermal- and photo-oxidation of ABS and HIPS pointed out that the PB part is selectively attacked during initial stages of degradation, with hydroperoxide formation as the responsible for the initiation of degradation mechanisms [46, 49, 50, 52-55]. Further studies on photo- and thermo-initiated oxidation by infrared spectroscopy showed the different steps on the oxidation process. An initial induction period is displayed, followed by a fast oxidation related to the PB phase; finally, a slow oxidation rate was observed corresponding to the degradation of PS, which may be initiated by some of the radicals formed in the degradation of PB [44, 47].

The initial degradation of the PB phase in rubber-modified styrenic polymer 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 microstructures of PB: vinyl-1,2, cis-1,4, and trans-1,4 [45]. The initiation, as it has been previously pointed out, involves the creation of free radicals and the formation of hydroperoxides; the second stage includes the decomposition of the hydroperoxides and the formation of different products containing oxidised groups. Further reactions are responsible for the formation of stable crosslinked structures, extensive damage in the polymeric chains by chain scission and the disunification of the polymer graft between butadiene and styrene units. Different reaction mechanisms have been proposed by several authors for the thermo- and photo-oxidation of PB-modified styrenic polymers (Fig. 1.7) [44, 45, 47, 52, 59].

I. Reactions of vinyl-1,2 isomer



II. Reactions of cis-1,4 and trans-1,4 isomers

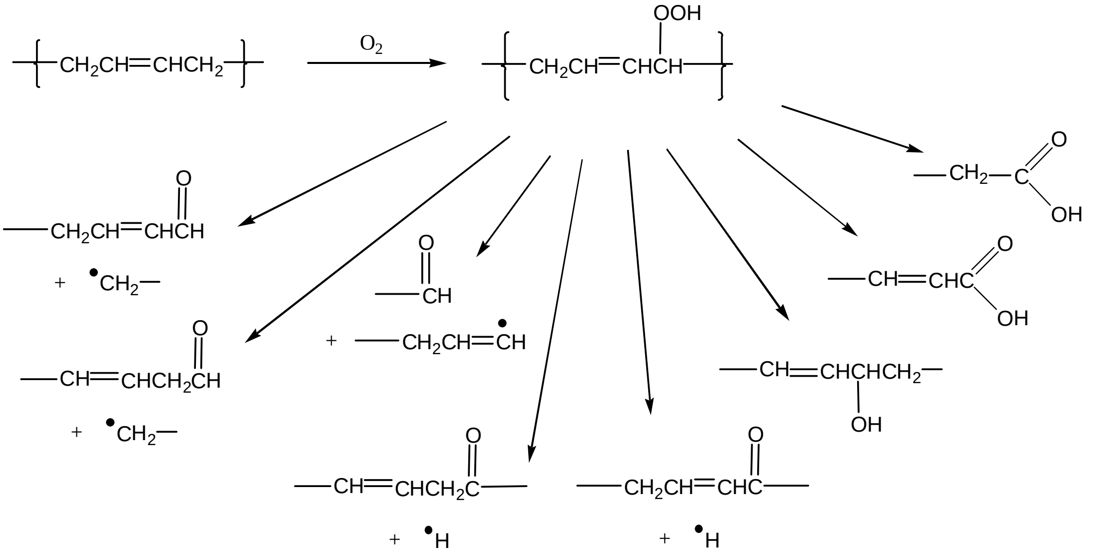


Figure 1.7. Reaction mechanisms proposed for the PB phase during the thermo-and photo-oxidative degradation of rubber-modified styrenic polymers

With prolonged oxidative exposure, a wide range of crosslinking reactions can take place from the oxidised moieties in the presence of alkoxyl ($RO^{\bullet}$) and alkylperoxyl ($ROO^{\bullet}$) radicals; different crosslinked structures can be formed, such as unstable peroxide gel, ether gel, and saturated gel structures [45, 54].

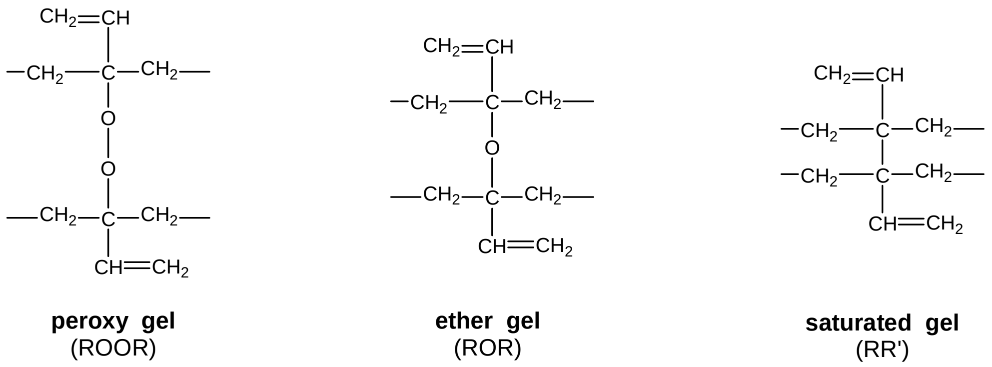


Figure 1.8. Crosslinked gel structures after prolonged exposure of PB-modified styrenic polymer to thermo- and photo-oxidation

Finally, the butadiene grafting sites containing tertiary carbons are oxidised under more severe degradation, leading to the catastrophic disunification of the copolymer matrix by scission of the PB-PS graft [45, 47, 54].

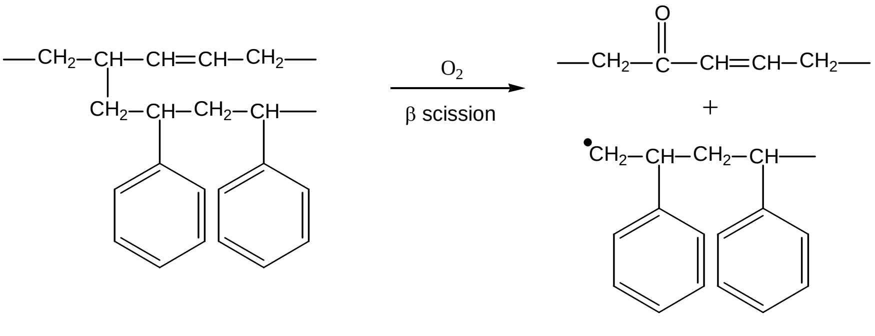


Figure 1.9. Proposed reactions for the oxidation of the PB-PS grafting sites

Further oxidation of the PS phase in PB-modified styrenic polymers is promoted by the free radicals formed during degradation of the rubber phase, compared to the oxidation of pure PS [47]. It is well known that the initiation of PS oxidation takes place by the oxygen attack to the α-hydrogens found on the backbone of the PS chain, leading to the formation of hydroperoxides as the initiation products [60, 61]. Aromatic and aliphatic ketones, peroxyesters, carboxylic acids, and anhydrides are some of the oxidised structures that can be found in PS subjected to thermo- and photo-oxidation; molecular compounds as benzoic acid, benzophenone, acetophenone, benzaldehyde, benzoic anhydride, and dibenzoylmethane are also formed as degradation products [60, 62, 63].

Together with the chemical reactions caused by thermo- and photo-oxidation, further changes at a macroscopic scale are also induced by the degradation processes, which are associated with a deterioration of the mechanical properties and long-term stability. Different authors have studied the changes at the macroscale related to the thermal and UV degradation of rubber-modified styrenic copolymers [16, 48, 51, 52, 64, 65]. Thermo-oxidation involves physical and chemical processes, which affect in different ways the overall properties of the exposed material [51]. Large alterations in the tensile, impact and flow properties have been reported, resulting in an embrittlement of the material [51, 64, 66]. Structural changes as physical ageing in the styrenic phase and a shift in the glass transition temperature of the PB phase have also been shown as consequences of radiation and oxidative degradation [48, 52, 64]. Thermo-oxidative degradation has proved to be a surface effect which promotes mechanical failure to the polymer bulk [48].

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 [16, 67-69]; these changes may be due to chain scission in the PS phase and modifications in the physical structure of the rubber phase [69]. Thermal processing under high mechanical shear in limited oxygen atmosphere may be responsible for the generation of free radicals, which could contribute to the mentioned alterations in the chemical and physical properties of the material [45].

1.5 RECYCLING OF STYRENIC PLASTICS FROM WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE). DETERMINATION OF BROMINATED FLAME RETARDANTS (BFRs)

1.5.1 The problematic of BFRs in recycled plastics from WEEE

As it has been mentioned in the previous section, styrenic polymers are a family of polymeric materials with polystyrene as the main component that are commonly employed in a wide range of applications including packaging, automotive components, and electrical and electronic equipment. Residues from electrical and electronic equipment (WEEE) contain approximately 18% in weight of plastic materials; styrenic polymers constitute an important volume fraction in WEEE plastics, with ABS (33%) and HIPS (19%) ahead of other commodity polymers such as PP (18%) or PU (8%) [70].

The introduction of the *European Directive 2002/96/EC* on waste of electrical and electronic equipment (WEEE) has promoted the development of technological procedures for the recovery of plastic wastes from WEEE. The integrated nature of electrical and electronic equipment (E&E), this is, the close presence of plastic, metals, and ceramic materials in E&E components hinders an effective dismantling and recovery of the different material waste fractions. The presence of hazardous substances in WEEE materials, such as brominated flame retardants, is another factor that restricts the waste management of these residues and that prevents their recycling together with conventional waste fractions. Further research is therefore needed for an efficient identification and separation of BFR-containing waste fractions, together with more knowledge about how the recycling processes affect these plastic fractions.

Halogenated flame retardants have traditionally been employed in plastic materials due to their efficiency and suitability to different types of polymeric matrixes. Brominated and chlorinated flame retardants have prevailed above other families, because less quantities of flame retardant are needed to fulfil certain level of fire protection. In addition to this, the use of brominated flame retardants minimises the impact of this additive on the final properties and applicability of the polymeric material. Brominated flame retardants (BFRs) are commonly employed in a wide range of electrical and electronic components, including casings, insulating components, cables, and printed circuit boards [71].

Brominated flame retardants (BFRs) have gained special attention in recent years both due to their widespread use in fire protection of textiles, building materials and insulation, vehicle equipment, and electrical and electronic equipment, and due to the increasing concern about their effects on human health and the environment. BFRs are a structurally diverse family of halogenated organic compounds, including aromatic, cyclic aliphatic compounds, phenolic derivatives, aliphatic compounds, and phthalic anhydride derivates. Figure 1.10 shows the chemical structure of the different families of brominated flame retardants. Flame retardants can be either reactive, when they are chemically bonded to the polymeric matrix, or additive, when they are added during processing. Four BFR families have traditionally been employed as flame retardant additives in polymeric materials, including tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCD) [72-74].

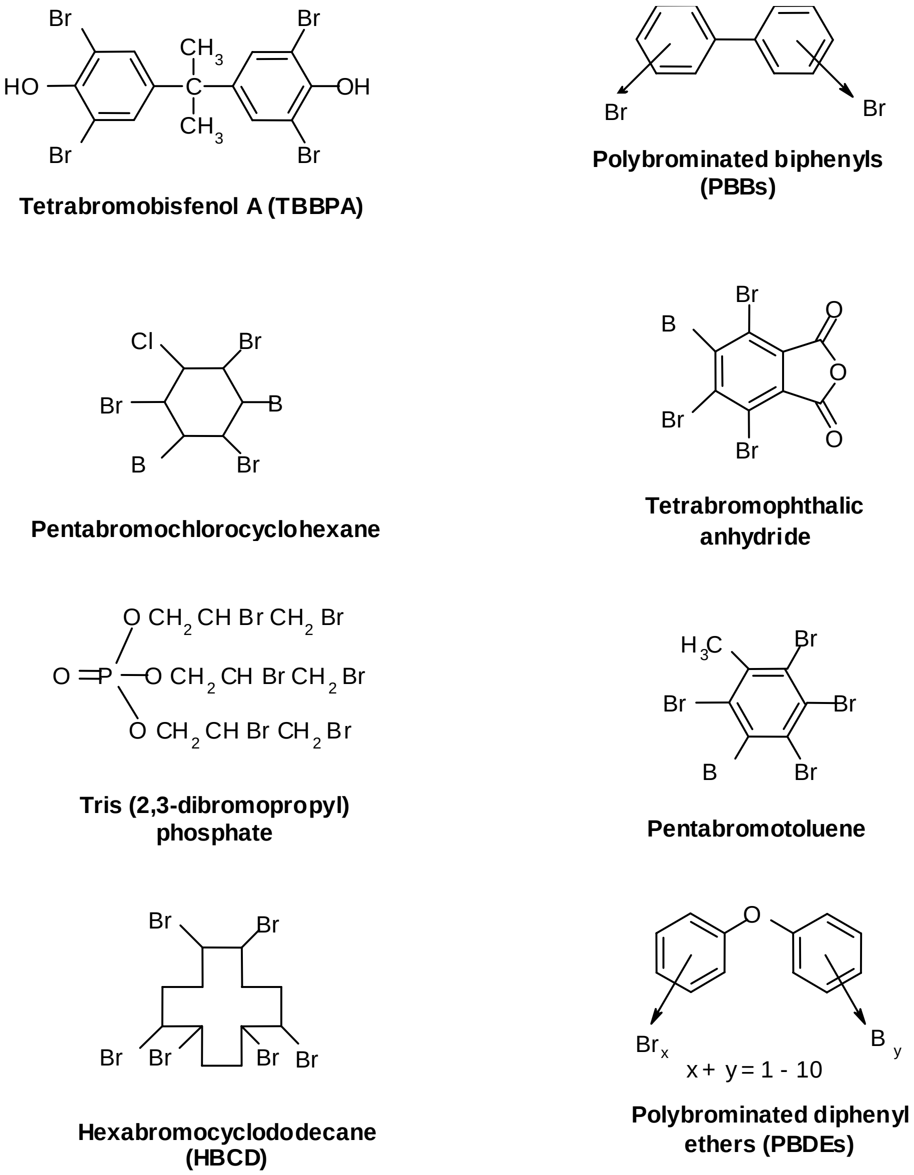


Figure 1.10. Chemical structures of the different families of brominated flame retardants (drawn after [75]).

The increasing environmental concern about BFRs is based on their persistence, bioaccumulation, and possible adverse health effects on humans [76]. It has been demonstrated that TBBPA, HBCD, and PBDEs are present in the environment and they are assimilated by living organisms; however, the long-term impact on health and environment is not well known [74]. Moreover, only limited and rather uncertain data are available regarding the occurrence of BFRs in consumer goods and waste fractions, and little is known regarding their emissions during use and disposal [77].

As a result of this rising concern, the European Union has introduced two Directives (2002/96/EC and 2002/95/EC) that regulate the employment and disposal of BFR-containing plastics in electronic and electrical equipment. Polybrominated biphenyls (PBBs) and some PBDEs (penta- and octa-BDE) have been banned in all applications, but deca-BDE was exempted from this ban in 2004 as a result of risk assessment reports from the European Chemicals Bureau (European Union) that found "no identified risks" to either humans or the environment. Plastics containing BFRs must be, in addition, separated from other WEEE fractions prior to recovery and recycling. Characterisation of the polymeric WEEE fraction may therefore combine different analytical strategies, including polymer identification studies, elemental analysis of metals and halogens, and analysis of brominated flame retardants and their possible degradation products [78].

1.5.2 Analytical procedures for the determination of BFRs

The elemental determination of additives in plastics, including metals and halogens, can be performed using a wide range of analytical procedures. Techniques such as atomic absorption spectrometry or inductively coupled plasma optical emission spectrometry (ICP-OES) require sample solution in aqueous media; analysis using total-reflection X-ray fluorescence spectroscopy (TXRF) and previous dissolution of the polymer in organic solvents allows faster determination of additives containing elements such as Ti, Zn, Br, Cd, Sn, Sb, and Pb in recycled thermoplastics from consumer electronics, with detection limits of around 200 mg/kg [79]. Further studies have led to on-line process analysis of metal-containing additives (Ti, Zn, Sb, Sn, Al, Cd, Cr, and Pb) in recycled thermoplasts from consumer electronics, using laser-induced plasma spectroscopy (LIPS, also called laser-induced breakdown spectroscopy, LIBS) and multivariate methods, for which neither sample preparation nor sample contact is needed, reaching detection limits in the ppm range; this experimental setup was successfully employed for routine on-line process analysis in recycling plants [80]. LIPS can also be employed for the on-line high-speed detection of heavy metals (Pb, Cr, Cd, and Hg) and brominated flame retardants (by analysing elemental Br and eventually synergistic Sb present in Sb_2O_3) in WEEE pieces moving on a conveyor belt; the detection limit for Br (11-15 mg/g) is significantly higher than that of other metal elements (2-50 μg/g), but suffices to detect common concentrations of BFRs in plastics [81].

For a more selective identification and quantification of the different brominated flame retardants present in recycled plastics, other procedures must be performed. The most common approach involves BFR extraction and analysis using gas or liquid chromatography. However, Raman spectroscopy with no sample preparation has been proposed to distinguish PBDEs from TBBPA [82]. Total dissolution of the samples or Soxhlet extraction can be employed, although more sophisticated extraction procedures such as supercritical-fluid extraction (SFE) [83], ultrasonic extraction [84], and pressurised liquid extraction (PLE) [85] have been successfully proposed for the extraction of several commercial flame retardants from WEEE plastic samples. The extraction procedure is usually the time-limiting step during the analytical determination of BFRs in recycled plastics; reduction of the extraction time to approximately 10 min can be achieved using ultrasonication [84].

Both gas and liquid chromatography can be employed for extract analysis and allow high resolution and specific and selective detection of the different BFR families. Gas chromatography with mass-spectrometry detection is widely employed for the determination of PBBs and PBDEs [86, 87]. However, some BFRs have high boiling points and may decompose due to their thermal instability; the use of liquid chromatography has been growingly employed in this case for the determination of TBBPA and HBCD congeners [88], as a result of the advances in instrumentation that allow the coupling of LC and MS through interfaces such as electrospray ionisaiton (ESI) or atmospheric pressure chemical ionisation (APCI). HPLC-UV/MS has been employed to identify and quantify 15 brominated and phosphorous-based flame retardants in polymer fractions from WEEE; however, a combining procedure using size exclusion chromatography (SEC) and HPLC-UV appears to be a more suitable procedure for routine flame retardant screening in actual recycling facilities thanks to easier operating and maintenance of the equipment [85]. No indication of intensive decomposition during repetitive processing of flame retarded styrenic polymers was observed using chromatrographic techniques in different studies [89, 90]; however, evidence of several bromine-containing fragment emissions from polymers with flame retardants were shown using thermo-desorption gas chromatography – mass spectrometry (TDS-GC/MS) [91]. Further attention will be given in the future to the determination of BFR emissions and degradation compounds during use and recycling of polymers with flame retardants.

The analysis of reactive and oligomeric flame retardants, commonly employed in engineering polymers, is difficult to perform using extraction procedures because of the polymers' high molecular weight and immobility; pyrolysis gas chromatography appears to be an effective technique to overcome this dilemma. The analysis of thermal decomposition fragments (monomers, oligomers, and pyrolysis products) from different flame-retarded polymers and resins containing flame retardants allows the identification of the type of flame retardant used [92, 93].

2. AIM OF THE STUDY. METHODOLOGY.

The aim of this Doctoral Thesis was to get a deeper insight on the quality properties of recycled high-impact polystyrene, both from packaging and from electrical and electronic applications. Different analytical strategies involving thermal analysis, vibrational spectroscopy, chromatography, and mass spectrometry have been proposed to study the degree of degradation and the presence of low molecular weight compounds (volatiles, additives, degradation products, contaminants) in recycled HIPS. The degradation processes that may occur in the previous life and subsequent recycling of HIPS wastes and their effects on the structure, long-term stability, and macroscopic properties have been analysed in detail. Finally, further attention has been given to the identification of brominated flame retardants in recycled plastics from WEEE, since it is an actual technological challenge for the recycling of styrenic plastics.

Different methodological steps were considered to achieve a better understanding on the quality properties of recycled HIPS.

- A dual-pronged experimental approach was proposed to model the degradation processes during the previous life and subsequent mechanical recycling of HIPS,. Processing and mechanical recycling was simulated using multiple processing and degradation during service life was modelled by thermo-oxidation. Thermal analysis, mechanical testing, vibrational spectroscopy, and chromatographic techniques were employed to obtain deeper knowledge about the degradation mechanisms and their effects on the chemical structure, properties, and presence of low molecular weight compounds. Articles I to III are devoted to this part of the thesis.

- Real samples from a large-scale mechanical recycling facility that performs recycling of HIPS from packaging waste were analysed to verify the commercial suitability of the proposed analytical strategies for the quality assessment of recycled HIPS. The effects of the different steps of the mechanical recycling process on HIPS properties are also investigated. These results are detailed in Article IV.

- Analytical procedures for the determination of brominated flame retardants in recycled styrenic plastics from WEEE were developed using different advanced extraction procedures (ultrasound-assisted extraction, microwaves-assisted extraction, and pressurised liquid extraction) and chromatographic analysis with UV and mass spectrometric detection (Article V and VI).

- Finally, a review about the different contributions to achieve an improved use of recycled plastics to contribute to sustainable development is presented in Article VII. Three key research fronts for the improvement of mechanical recycling activities are discussed, including the scientific knowledge about degradation processes during previous life, the development of reliable quality analysis procedures for recycled plastics, and the effective upgrading of recyclates using different approaches (restabilisation, rebuilding, compatibilisation, and addition of elastomers and fillers). This review offers an up-to-date state of the art of the technological and scientific research on plastics recycling and offers an excellent background for this Thesis.

3. EXPERIMENTAL

3.1 MATERIALS AND SAMPLE PREPARATION

3.1.1 Simulation of the life cycle of recycled HIPS by multiple processing and thermo-oxidation

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M, was employed for the simulation of the life cycle of recycled HIPS and was provided by BASF Española S.A. (Spain). Figure 3.1 shows the procedure for the simulation of processing, service life and mechanical recycling by multiple processing and thermo-oxidation.

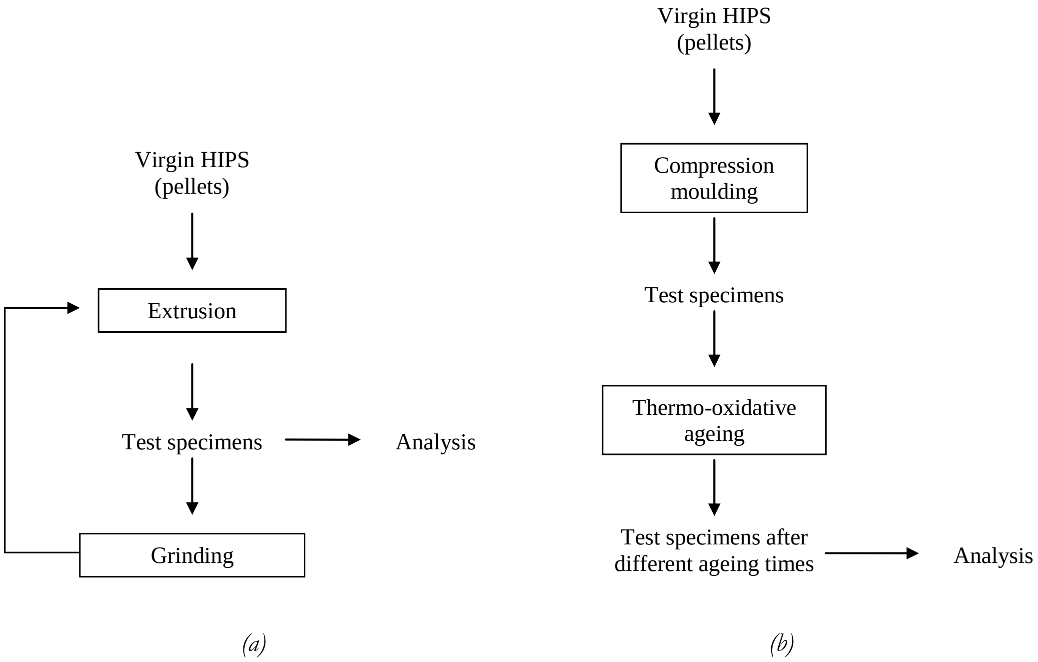


Figure 3.1 Procedure for modelling the life cycle of recycled plastics: a) modelling processing and mechanical recycling by multiple processing; b) modelling service life by thermo-oxidation.

The reprocessing studies were performed on virgin HIPS material 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, grinded and some material was kept for analysis whereas the remaining was reintroduced again for further extrusion. Rectangular sheets of dimensions 85 x 85 x 1 mm for tensile testing were prepared by compression moulding at 200°C and a maximum pressure of 200 bar with a Collin x800 press (Dr. Collin GmbH, Germany).

The virgin HIPS material was subjected to thermo-oxidative ageing in order to simulate its period of service life. The virgin HIPS pellets were compression moulded into sheets with dimensions 85 x 85 x 1 mm employing a Schwabenthan Polystat 400S press (Schawbenthan Maschinenfabrik Berlin, Germany) at a temperature of 200°C and a pressure of 200 bar. The sheets were the introduced 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 different exposure times of 1, 2, 4, 8, 12 and 16 days.

3.1.2 Material sampling in a large-scale mechanical recycling facility

HIPS samples were collected for analysis at different points of the mechanical recycling process (Acteco, Spain). Figure 3.2 shows the mechanical recycling flow diagram and the points at which the different samples were taken: Scrap HIPS employed as raw material in the recycling process, intermediate samples after grinding and washing, and different grades of final recycled HIPS material. Virgin HIPS, commercial grade Polystyrol 486M (BASF Española S.A., Spain), was employed as reference material. Table 3.1 describes the sample materials employed in the analyses.

Materials	Description
Virgin HIPS	Virgin HIPS, commercial grade Polystyrol 486M (BASF, Spain)
HIPS1	Scrap HIPS from yoghurt packaging applications (ACTECO, Spain)
HIPS2	Scrap HIPS from hanger applications (ACTECO, Spain)
HIPS3	Intermediate HIPS material from the mechanical recycling process after washing and grinding, from yoghurt packaging application (ACTECO, Spain)
HIPS4	Intermediate HIPS material from the mechanical recycling process after washing and grinding, material mixture from yoghurt packaging and hanger applications (ACTECO, Spain)
HIPS5	Final recycled grey-coloured material, from yoghurt packaging applications (ACTECO, Spain)
HIPS6	Final recycled white-coloured material, from yoghurt packaging applications (ACTECO, Spain)
HIPS7	Final recycled black-coloured material, from yoghurt packaging and hanger applications (ACTECO, Spain)

Table 3.1 Description of the HIPS materials sampled from the large-scale mechanical recycling facility.

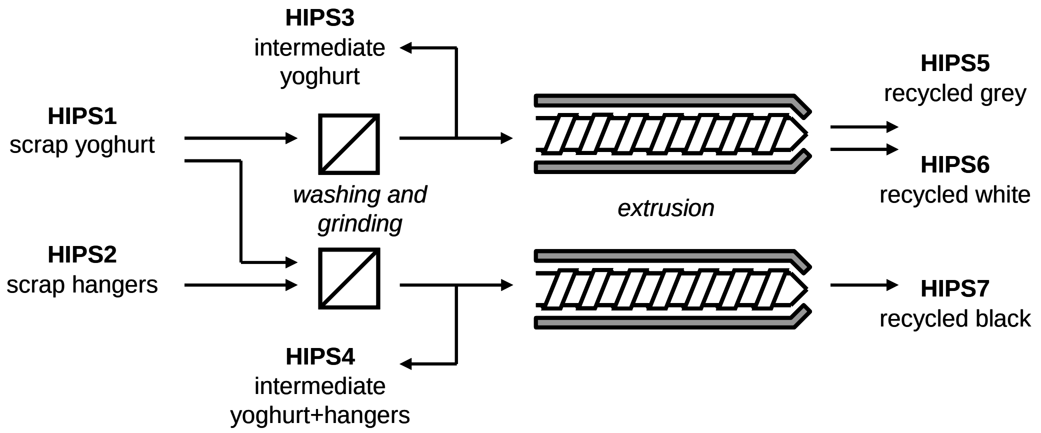


Figure 3.2 Sampling of the HIPS materials through the large-scale mechanical recycling process.

3.1.3 Reference HIPS samples containing brominated flame retardants

Tetrabromobisphenol-A technical grade (TBBPA) (4-4'-isopropylidene bis(2,6-dibromophenol), 97% purity, M_w 543.9 g/mol, CAS number 79-94-7) provided by Aldrich Chemicals (Sweden), hexabromocyclododecane (HBCD) (1,2,5,6,9,10-hexabromocyclododecane, 97% purity, M_w 641.73 g/mol, CAS number 3194-55-6) provided by Aldrich Chemicals (Sweden), and decabromo diphenyl ether, technical grade (Deca-BDE, 95.0% purity, M_w 959.22 g/mol, CAS number 1163-19-5) provided by Sigma Aldrich (Sweden) were employed as flame retardant reference materials.

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M (BASF Española, Spain) was employed as the polymeric matrix for the development and comparison of advanced extractive methods for determination of BFRs in styrenic polymers. Standard samples HIPS containing 50 mg/g TBBPA, 20 mg/g HBCD, and 50 mg/g Deca-BDE were prepared by solution in tetrahydrofurane (THF) in a stirred vessel at 25°C during 12 hours. The fortified polymer solution was dried at ambient temperature for 4 days in a forced ventilation oven. Polymer pellets were obtained through granulation in a Moretto Granulator (Moretto, Italy). Polymer powder was obtained from the polymer pellets by grinding using a rotary mill with liquid nitrogen.

Standard samples from waste electrical and electronic equipment (WEEE) were used as well to verify the applicability of the analytical method for the determination of BFRs in styrenic components from electrical and electronic applications. These standard WEEE samples were provided by Gaiker Centro Tecnológico (España) and their approximate composition is shown in Table 3.2.

WEEE sample	**Matrix**	**Flame retardant**		**Additive**	
		Type	**Conc.** (mg/g)	**Type**	**Conc.** (mg/g)
ABS-GVL2-07	ABS	Deca-BDE	100	Sb_2O_3	50
ABS-GVL2-11	ABS	TBBPA	100	Sb_2O_3	50
SB-GVL2-07	SB	Deca-BDE	100	Sb_2O_3	50

Table 3.2 Composition of the standard polymeric samples from waste electrical and electronic equipment (WEEE) samples containing BFRs.

3.2 CHARACTERISATION TECHNIQUES

3.2.1 Melt-mass flow rate (MFR)

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

3.2.2 Tensile testing

Tensile tests were performed on reprocessed and aged HIPS samples in order to investigate the changes the mechanical properties of the material after reprocessing and ageing. Each test was performed according to the procedure established by the ASTM D882-02 standard on six rectangular specimens of dimensions 85 x 5 x 1 mm cut from the films obtained by compression moulding. The average value of the modulus, stress at break and elongation at break from the six specimens was set as the representative value. The tensile tests were carried out at 23ºC 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}, employing a load of 0.1 kN and a gauge length of 30 mm.

3.2.3 Differential scanning calorimetry (DSC)

The thermal properties and the oxidative stability of the HIPS samples were assessed using DSC. The analyses were performed on a Mettler Toledo DSC 820 (Columbus, OH) calibrated with indium standard. Approximately 10 mg of sample was 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 -100ºC to 150ºC at a heating rate of 10ºC min^{-1}, cooled from 150ºC to -100ºC at -10ºC min^{-1}, and again heated from 25ºC to 200ºC at 10ºC 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 a temperature programme as follows: The samples were heated from 25ºC to 200ºC at a heating rate of 10ºC min^{-1}; cooled from 200ºC to 25ºC at -10ºC min^{-1}; and heated from 25ºC to 200ºC at 10ºC min^{-1}.

To determine the oxidation temperature (T_{ox}), the samples were heated from 25ºC to 400ºC 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 25ºC to 160ºC at a heating rate of 20ºC 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 160ºC 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.

3.2.4 Thermogravimetric analysis (TGA)

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

3.2.5 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.

3.2.6 Raman spectroscopy

Raman spectra of reprocessed and aged HIPS samples were collected by a FT-Raman spectrometer Spectrum 2000 (Perkin Elmer, Wellesley, MA) equipped with an Nd-YAG laser illumination. The different spectra were obtained employing 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.

3.2.7 Dynamic mechanical thermal analysis (DMTA)

Viscoelastic measurements 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 dimensions 50 x 10 x 1 mm in the double clamped cantilever mode. The region above ambient temperature was studied for all the samples performing multifrequency scans from 25ºC to 150ºC at a rate of 4ºC 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 –110ºC and 150ºC at a scan rate of 5ºC per scan for a range of frequencies between 0.1 Hz and 50 Hz using 4 frequencies per decade. The values of damping (tan δ), the storage modulus (E’) and loss modulus (E”) versus temperature and frequency were thus obtained.

3.2.8 Scanning electron microscopy (SEM)

SEM micrographs were obtained on sectioned HIPS samples after sputtering with gold/palladium, using a JEOL JSM-5400 microscope (JEOL Ltd., Japan).

3.2.9 Analysis of low molecular weight compounds in reprocessed, aged, and recycled HIPS samples

The low molecular weight compounds present in the different HIPS samples (virgin, reprocessed, thermo-oxidated, and recycled HIPS) were determined by an analytical 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 110ºC 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 obtained extracts were filtered with a 0.45 mm pore size Teflon filter (Sorbent AB, Sweden) and placed in vials, which were kept at 4ºC until further analysis.

The GC-MS analyses of the extracts from reprocessed and aged HIPS samples were performed on an FinniganMAT GCQ (Thermo, San Jose, CA) equipped with a wall-coated fused silica, low bleed CP-sil 5CB column (dimensions 0.25 mm x 30 m x 0.25μm) from Varian (Lake Forest, CA). A 10 μL volume was injected in the splitless mode at a temperature of 200°C. The chromatographic separation in the column was achieved through a constant flow of 0.8 mL min^{-1} with helium (scientific grade purity) from AGA Gas AB (Sweden) as carrier gas. The temperature program at the column was as follows: hold at 40°C for 1 min; increase to 250°C at a rate of 10°C min^{-1}; hold at 250°C for 20 min. The detection was carried out by ion-trap mass spectrometry. Electron ionisation was employed with an ion source temperature of 280°C. Mass spectra were collected in the full scan mode (35-500 m/z at a scan rate of 2 spectra s^{-1}). Compound identification was performed either by injection of analytical standards, by comparison of the obtained spectra with the NIST MS search 2.0 database, or by comparison with bibliographic references. Each sample was extracted and analysed by triplicate, and the average value was assumed as the representative.

The chromatographic analyses of the extracts from recycled HIPS samples from the mechanical recycling facility were performed on an Agilent 6890 Gas Chromatograph (Palo Alto, CA) equipped with a 0.18 mm x 20 m x 0.18μm Agilent J&W DB-5 capillary column (Palo Alto, CA). A 2 μL volume was injected employing a programmed temperature vaporisation injector (PVT) in the pulsed splitless mode. During the injection process, 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 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.

3.2.10 Extraction of brominated flame retardants from HIPS

3.2.10.1 Ultrasound-assisted extraction (UAE)

Ultrasound extraction was performed using a Branson 2510 ultrasonic bath (Bransonic Ultrasonics, Holland). Approximately 0.5 g of standard HIPS with BFRs (either granule or powder) was placed together in closed vials with 10 ml of either isopropanol/methanol (1:1, v/v) or isopropanol/n-hexane (1:1, v/v) as extractive solutions. The vials were kept in the ultrasonic bath for 60 min at 65ºC and the extracts were then forwarded to the post-treatment procedure.

3.2.10.2 Microwave-assisted extraction (MAE)

The extraction assisted by microwaves was carried out in a MES 100 microwave extraction equipment (CEM Corp., North Carolina, USA), with a nominal power of 1000W. Approximately 0.5 g of HIPS samples with BFRs was introduced with 10 ml of the extractive solution inside MAE closed vessels. As extractive solutions, isopropanol/methanol (IP/MeOH, 1:1 v/v) and isopropanol/n-hexane (IP/hexane, 1:1 v/v) were employed. Different extraction times (20, 30, 45, and 60 minutes) and extraction temperatures (90ºC, 110ºC, and 130ºC) were tested for the optimisation of the method. The extracts were then collected and forwarded to post-treatment.

3.2.10.3 Pressurised liquid extraction (PLE)

Pressurised liquid extraction was performed using a Dionex ASE200 Extractor (Dionex Co., CA, USA). About 0.5 g of standard HIPS with BFRs (powder form) was mixed with laboratory sand and loaded into Dionex standard 22ml stainless steel extraction cells containing Dionex standard 22ml cellulose extraction thimbles. Extractions were performed employing two solvent systems, methanol/isopropanol (MeOH/IP, 1:1, v/v) and isopropanol/n-hexane (IP/n-hexane, 1:1, v/v); four extraction temperatures were tested (90ºC, 110ºC, 130ºC, and 150ºC) at a pressure of 1500psi. Four different extraction steps were performed consecutively on the same sample cell. Each step consisted of an initial cell heat-up time of 6 min, and 2 static 3 min cycles. After each cycle, the cell was flushed with solvent (100% of cell volume) and purged with nitrogen for 60s. The extracts for the different extraction steps were collected in suitable vials with Teflon septa and went through the post-treatment procedure.

3.2.10.4 Extract post-treatment before chromatographic analysis

The extracts collected from the different extraction procedures were evaporated to near dryness in a rotary evaporator. The residue was re-dissolved with tetrahydrofurane to a concentration adjusted to the linearity range of the detection, filtered with a 0.45 mm pore size HPLC Teflon filter (Sorbent AB, Sweden), and placed in HPLC vials, which were kept at 4ºC until further analysis.

3.2.11 Analysis of brominated flame retardants

3.2.11.1 High-performance liquid chromatography – ultraviolet detection (HPLC-UV)

The analyses of the extracts from the reference HIPS samples containing BFRs used for the development of the MAE extraction method and the reference HIPS samples from WEEE were performed employing Hewlett Packard HPLC 1090 equipment (Palo Alto, CA, USA). The chromatograph was equipped with a diode-array detector (DAD) Waters 990 (Milford, MA, USA) and an auto-sampler Waters 712 WISP (Milford, MA, USA). Chromatographic separation was achieved using a reverse phase system consisting on a 5μm frit filter, a Supelguard Discovery 18 guard column (20 x 4mm, 5μm), and a C18 Hypersyl ODS column (250 x 4.6mm, 5μm), all supplied by Supelco (Sweden). The measurements were carried out at 35ºC, employing an isocratic methanol/water (95/5% v/v) mobile phase at a flow of 1ml/min. After some previous experiments, the DAD detector was fixed at a wavelength of 220 nm.

Quantification of TBBPA and Deca-BDE was performed by external calibration, using 7 seven point calibration curves obtained by injection of standard solutions containing 1 – 1000 μg/ml of the technical flame retardants.

3.2.11.2 High-performance liquid chromatography –tandem mass spectrometry (HPLC-MS/MS)

The extracts from reference HIPS samples containing BFRs used for the comparison of extractive techniques were analysed using high-performance liquid chromatography with online tandem mass spectrometry (HPLC-MS/MS). An Agilent 1100 HPLC system (Agilent Technologies, CA, USA), equipped with a G1329A autosampler, a G1312A pump, and a G1316A column oven connected to a Triple Quadrupole Mass Spectrometer API 4000 (Applied Biosystems, CA, USA) were employed for the analyses.

The chromatographic separation was accomplished using a reverse-phase system consisting of a 5μm filter (Supelco, Sweden), a Supelguard Discovery 18 guard column (dimensions 20 x 4 mm, particle size 5μm; Supelco, Sweden), and a C18 Hypersyl ODS column (dimensions 250 x 4.6 mm, particle size 5 μm; Supelco, Sweden). The mobile phase consisted of a gradient system of acetonitrile (solvent A) and 10mM ammonium acetate buffer, pH 4.5 (solvent B) at a flow of 1ml/min with the following elution programme: 0-12 min, gradient from 90% A to 95% A; 12-13 min, gradient from 95% A to 98% A; 13-27 min, isocratic 98% A; 27-28 min, gradient from 98% A to 90% A; 28-35 min, isocratic 90% A. The column was kept at 35°C and the injection volume was 5 μl.

Ionisation was achieved using atmospheric pressure chemical ionisation (APCI) in the negative mode at 600°C with N2 as nebuliser gas and an entrance potential of -10V. Detection was performed by multiple reaction monitoring (MRM) mode of selected ions at the first (Q1) and the third quadrupole (Q3). To choose the fragmentation patterns of m/z (Q1) → m/z (Q3) for each analyte in the MRM mode, direct infusion of standard solutions in acetonitrile into the MS was performed and the product-ion scan mass spectra were recorded.

Quantification of TBBPA, HBCD congeners (α-, β-, and γ-), and Deca-BDE was performed by external calibration, using seven-point calibration curves obtained by the injection of standard solutions containing 0.1 – 50 μg/ml of the technical flame retardants. In the case of HBCD, although the content of each congener in the technical reference material was not known, quantification was performed individually for each congener related to the original concentration of the reference material, to investigate the effect of each extraction procedure on the individual recovery of each congener.

4. RESULTS AND DISCUSSION

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

Recycled materials exhibit in general changes in their structure and properties due to the degradation processes that may occur during its processing, service life and further mechanical recycling. The aim of the first part of the study was the investigation of the degree of degradation of high-impact polystyrene throughout its reprocessing and thermo-oxidation to develop detailed knowledge about how and at which extent processing, service life and mechanical recycling affect the performance of HIPS. A double experimental approach has been proposed to model the life cycle of recycled HIPS, including the processing, the service life and the mechanical recycling. Processing and mechanical recycling was modelled by multiple processing, while degradation processes occurring during the service life were simulated by thermo-oxidation in a forced ventilation oven at 90°C. The samples were characterized by thermal analysis, tensile testing, melt-mass flow ratio (MFR), electron microscopy, and vibrational spectroscopy, to determine the changes in oxidative stability, mechanical properties, structure, morphology, and chemical composition induced by the recycling-related processes. The occurrence of low molecular weight compounds during reprocessing and thermo-oxidation was monitored using microwave-assisted extraction and gas chromatography-mass spectrometry.

4.1.1 Rheological and tensile properties

The influence of multiple processing on the rheological properties of HIPS was assessed by the measurement of the melt mass-flow rate (MFR), which is a commonly employed quality property in recycling industries to guarantee the processing capability for the manufacture of secondary products from recyclates. The MFR slightly increases with reprocessing for HIPS subjected up to nine extrusion cycles, mainly for the first three extrusion cycles (Fig.4.1). 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 [67, 69].

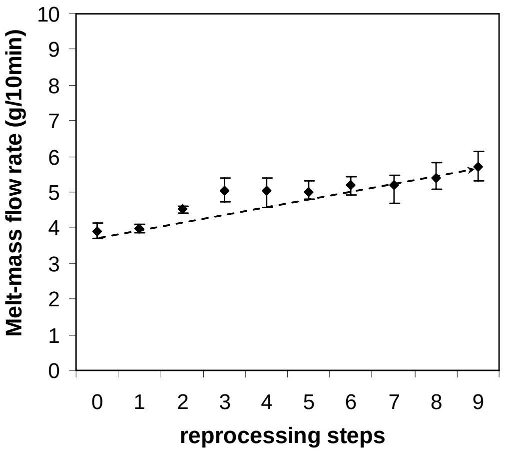
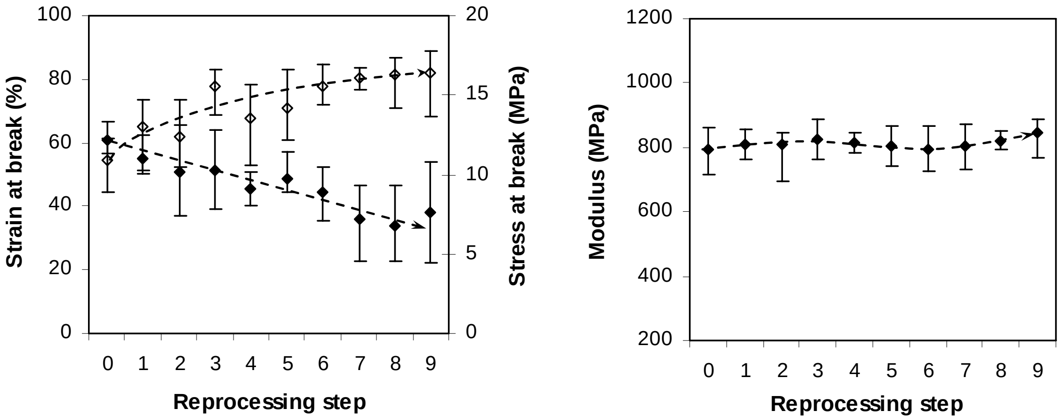


Figure 4.1. Influence of reprocessing on the melt mass-flow rate (MFR) of HIPS.

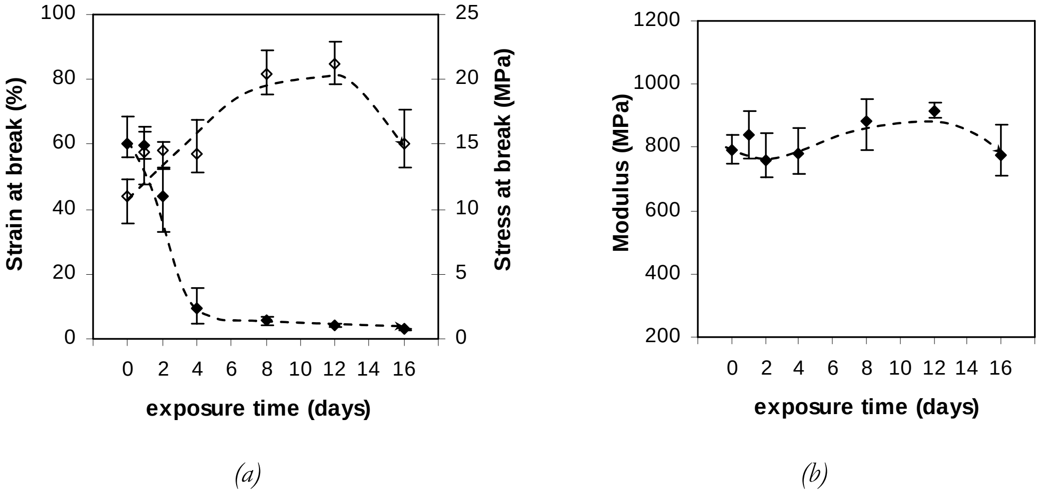
The influence of reprocessing and thermo-oxidation on the mechanical properties (elastic modulus, elongation at break and stress at break) was analysed by tensile testing. Figure 4.2 shows the evolution of tensile properties during consecutive extrusion cycles. The elastic modulus remains practically unaffected; the stress and elongation at break are on the other hand clearly influenced by the successive processing steps, with a progressive diminution of the elongation at break and an increase of the stress at break. Each processing step induces the thermo-mechanical degradation of the HIPS materials, which may introduce alterations in the chemical structure of the polymeric chains, resulting in a slightly more brittle material with lower ductility.



(a) *(b)*

Figure 4.2. Tensile properties of the virgin HIPS subjected to multiple processing: a) tensile properties at break: (●) elongation at break; (○) stress at break; b) Young's modulus.

The effect of thermo-oxidation on the mechanical properties of HIPS is more severe than the one reported for reprocessing (Fig. 4.3). The elongation at break drastically decreases with the ageing time, showing a collapse of this property after 4 days of exposure to thermo-oxidative degradation. On the other hand, the modulus and the stress at break show a slight increase on their values during the initial ageing times but after 12 days of exposure their values drop. This complex behaviour suggests the combination of different physical and chemical effects in thermo-oxidative degradation of HIPS. It is known that ageing of glassy polymers under air atmosphere at temperatures below the glass transition temperature (T_g) is a complex phenomenon that involves both a rearrangement of the polymeric chains towards the equilibrium state (physical ageing) and the degradation of the polymer due to the chemical interaction with oxygen (chemical ageing) [51]. Physical ageing process seems to predominate for shorter exposure times, resulting in a slight increase of the tensile stress and in a collapse of the elongation at break. For longer exposures, however, the chemical attack appears to control the degradation, producing a decrease of the stress at break and modulus. The combined chemical and physical effects in thermo-oxidation of HIPS will be discussed in detail from the results of vibrational spectroscopy and dynamic-mechanical analysis.



(a) *(b)*

Figure 4.3. Tensile properties of the virgin HIPS subjected to thermo-oxidation at 90°C: a) tensile properties at break: (●) elongation at break; (○) stress at break; b) Young's modulus.

As a conclusion, HIPS seems to be a promising material for mechanical recycling, since the processability of the recyclates is guaranteed by the small variation of the MFR after a large number of recycling steps. On the other hand, elongation at break appears as the mechanical property that should determine the second market application for HIPS recyclates. Reprocessing up to nine cycles does not affect to high extent the mechanical properties of HIPS, while thermo-oxidation at 90˚C may be considered to be quite severe for the mechanical properties of HIPS.

4.1.2 Oxidative stability

Oxidative stability of reprocessed and thermo-oxidated HIPS samples was assessed by the determination of the oxidation induction time (OIT) and the oxidation temperature (T_{ox}). Table 4.1 presents the OIT and the T_{ox} average data obtained by the DSC measurements for the HIPS samples. As it can be observed, the stabilising system employed in the material is clearly affected by the reprocessing cycles and by thermo-oxidative degradation, while the largest changes are observed in the aged samples. Each reprocessing step caused a progressive consumption of the stabilisers in the material, mainly during the first three extrusion cycles. In the case of the thermo-oxidated samples, the decrease in the stabilising activity is even more fast and dramatic, with a decrease of the 57% in the value of the OIT after 1 day of exposure at 90°C and a total decrease of 85% of the OIT value after 16 days of ageing.

Reprocessing			**Thermo-oxidation**		
Reprocessing steps	**T_{ox}** (ºC)	**OIT** (min)	**Exposure time** (days)	**T_{ox}** (ºC)	**OIT** (min)
Virgin HIPS	198	28	Virgin HIPS	198	28
1	194	19	1	188	12
2	193	17	2	186	11
3	190	14	4	185	10
4	189	13	8	181	6
5	189	13	12	179	5
6	188	12	16	180	4
7	188	12			
8	187	11			
9	186	10			

Table 4.1. Oxidation temperature (T_{ox}) and oxidation induction time (OIT) for high-impact polystyrene subjected to multiple processing and thermo-oxidation at 90°C.

Similar conclusions can be drawn from the measurement of the OIT and the T_{ox} when comparing the results obtained from both procedures. The OIT method may be more sensitive than the oxidation temperature procedure, but it requires a preliminary optimisation of the analysis temperature. The T_{ox} procedure is, on the other hand, very easy to perform and gives reproducible data similar to the OIT method. Both methods can therefore be successfully employed to assess the oxidative stability of HIPS in the recycling industries.

4.1.3 Study of the chemical changes

The chemical changes induced by multiple processing and thermo-oxidation at 90°C 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) allowed the characterisation of the hydroxyl region (between 3100 and 3600cm^{-1}), carbonyl region (between 1620 and 1780cm^{-1}), and the trans-1,4 (966cm^{-1}) and vinyl-1,2 (911cm^{-1}) unsaturated groups from the PB phase of HIPS. The peak corresponding to the cis-1,4 microstructure from the PB phase (around 730cm^{-1}) could not be studied by FTIR because of the overlapping peak from the C-H out-of-plane vibration of the styrene units in polystyrene at 754 cm^{-1} [94]. To obtain a quantitative insight, the absorbance areas of the peaks corresponding to the hydroxyl region, the carbonyl region, trans-1,4 group, and vinyl-1,2 group were determined, related to the area of a reference peak at 1601 cm^{-1} that is not susceptible to degradation; the normalised areas were named as FTIR functional group indexes.

On the other hand, Raman spectroscopy was employed to assess completely the PB-phase microstructure in HIPS, since the three PB microstructures show clear peaks at 1640 cm^{-1} (vinyl-1,2), 1652 cm^{-1} (cis-1,4), and 1666 cm^{-1} (trans-1,4) [95]. Curve analysis systems have lately allowed the resolution of the three overlapping peaks corresponding to the three structural units and have been used to analyse the reactivity of PB, and identify the PB microstructure in styrene-butadiene copolymers and high-impact polystyrene [96-99]. A curve fitting procedure was here proposed to resolve the individual PB microstructures; the Raman region between 1550 cm^{-1} and 1700 cm^{-1} was thus analysed in detail following the guidelines reported by Meier [100]. 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).

$$L(x) = y_0 + \frac{2 \cdot A}{\pi} \cdot \frac{\omega}{4 \cdot (x - x_c)^2 + \omega^2} \qquad (1)$$

As an example, Figure 4.4 shows the result of curve fitting for virgin HIPS, with the raw spectra and the five resolved components. To get a quantitative insight, the areas of the 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.

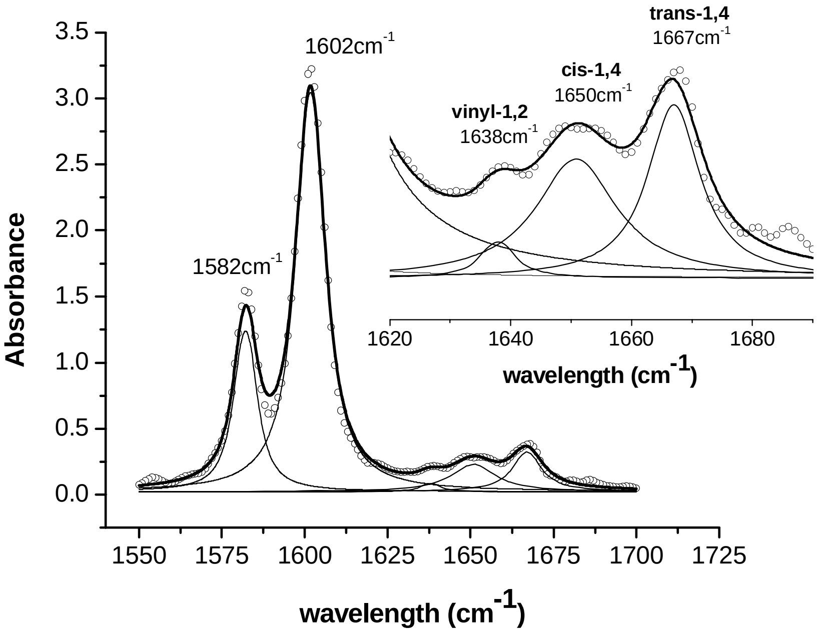
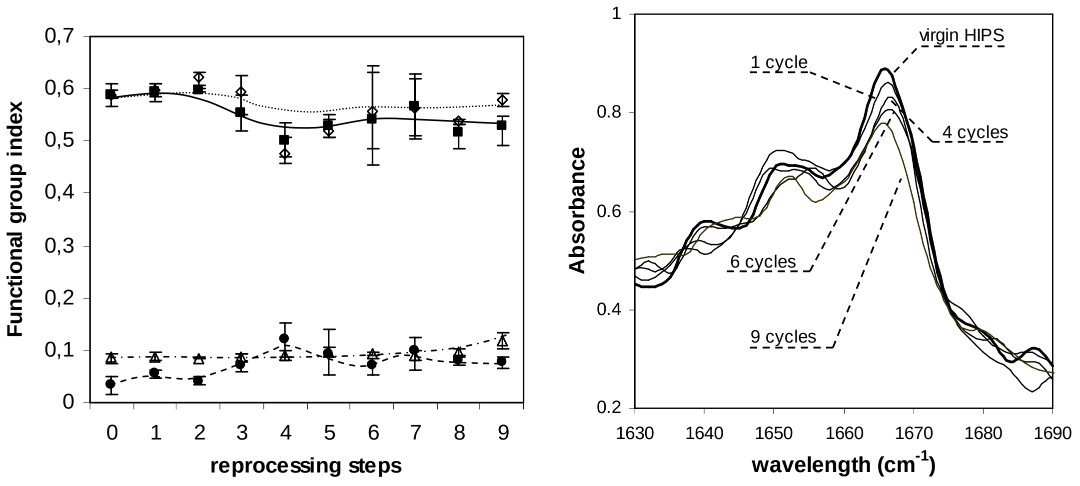


Figure 4.4. Curve fitting of the virgin HIPS Raman spectra to 5 individual bands for the determination of the three individual PB conformers: 1550-1700cm-1 region.

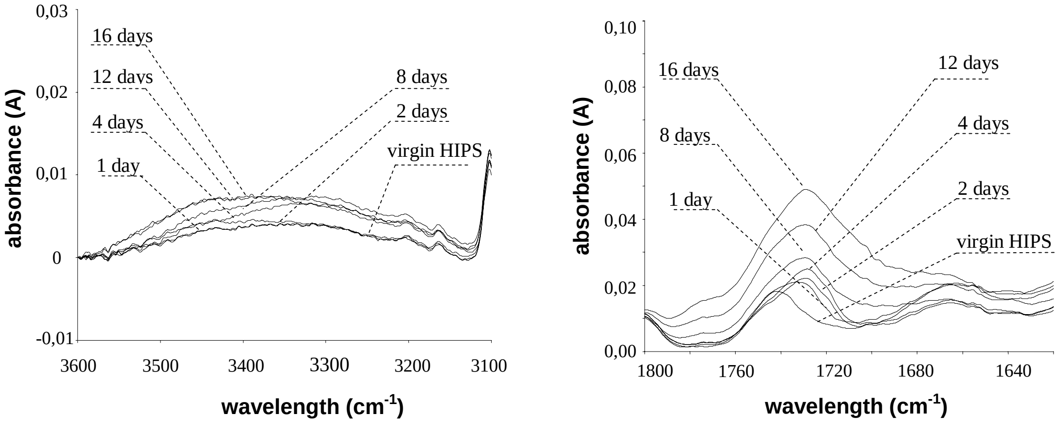
Vibrational spectroscopy (both FTIR and Raman) prove to be useful for the analysis of the chemical changes in HIPS induced by multiple processing. Figure 4.5a shows evolution of the FTIR functional group indexes with consecutive extrusion cycles; a decrease of the trans-1,4 and vinyl-1,2 indexes corresponding to the polybutadiene phase can be noticed, together with a slight increase on the carbonyl and hydroxyl indexes. From Raman results, it can be deduced that PB microstructure is to some extent affected by the repeating extrusion cycles, since the intensities of the three bands corresponding with the PB conformers slightly decrease with the successive reprocessing steps (Fig. 4.5b). The combined results from FTIR and Raman spectroscopy suggest that thermo-mechanical degradation 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 due to the interaction of the polymer with some residual oxygen which could have been present in the extruder. The behaviour of each PB microstructure towards degradation caused by processing is however different. The vinyl-1,2 index is barely affected after nine processing steps, whereas the cis-1,4 and trans-1,4 groups show a progressive decrease after each extrusion.



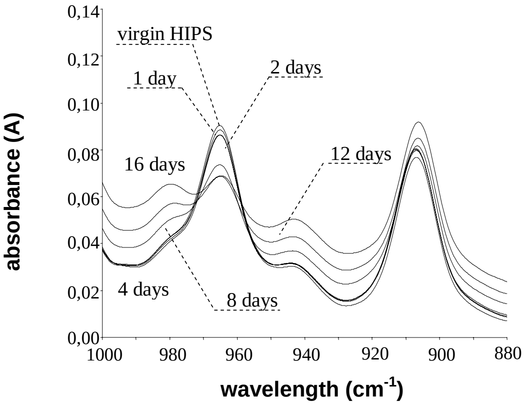
(a) *(b)*

Figure 4.5. Chemical changes induced by reprocessing on the structure of HIPS by vibrational spectroscopy: a) Evolution of the (◊) vinyl-1,2 ratio, (■) trans-1,4 ratio, (Δ) carbonyl ratio and (●) hydroxyl ratio with processing steps by FTIR; b) Raman spectra of the PB microstructure region for selected HIPS samples subjected to multiple processing.

Figure 4.6 shows the FTIR spectra for the HIPS samples subjected to thermo-oxidative ageing at 90°C through the hydroxyl region (between 3600 and 3100cm^{-1}), carbonyl region (between 1800 and 1620cm^{-1}), and the double bond region (between 1000 and 880cm^{-1}). Thermo-oxidation induces, in contrast with the heterogeneous effects reported by reprocessing, quite progressive changes in the analyzed functional group indexes; a marked decrease in the unsaturated groups (trans-1,4 and vinyl-1,2 groups) can be observed employing FTIR, while broad bands appear both in the hydroxyl and the carbonyl regions.



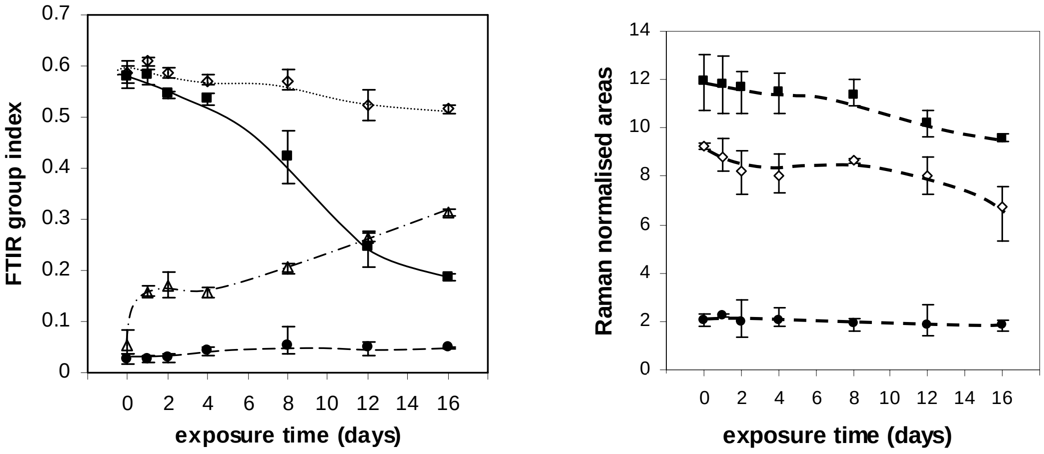
(a) *(b)*



(c)

Figure 4.6. FTIR spectra of the HIPS samples subjected to thermo-oxidative ageing at 90˚C: a) hydroxyl region (3600cm^{-1} – 3100cm^{-1}); b) carbonyl region (1800cm^{-1} – 1620cm^{-1}); c) double bond region (1000cm-1 – 880cm-1).

The effects of thermo-oxidation on the chemical structure of HIPS as exposure goes by can be more clearly observed by the representation of the FTIR and Raman functional groups with degradation time (Figure 4.7). 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 with the marked increase in the hydroxyl and carbonyl oxidated groups. The evolution of the functional groups is therefore assigned to the complex series of thermo-oxidative reactions in the rubber phase that lead to the disappearance of the unsaturated groups and the formation of oxidative moieties, crosslinked structures and chain scission, as it has been described in the introduction. This phenomenon is in accordance with the results of Israeli et al. [44], 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. Therefore, the first step in the thermo-oxidative degradation of HIPS is the degradation of PB, and some of the radicals formed in that degradation can act as initiators for the oxidation of polystyrene. The stability of the different PB microstructures against thermo-oxidation is again different; trans-1,4 and cis-1,4 groups appear to be as preferential sites for the degradative attack of oxygen, while 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 [45, 101].



(a) *(b)*

Figure 4.7. Chemical changes induced by thermo-oxidation at 90°C 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.

4.1.4 Viscoelastic behaviour and morphology

The dynamic mechanical spectrum of high-impact polystyrene presents different characteristic relaxations, which are shown in the isocronal plot for the storage and loss modulus at a range of frequencies between 0.1 Hz and 50 Hz (Fig. 4.8). The glass transition associated to the PB phase appears clearly centred at around 195K, whose intensity is proportional to the concentration of the PB phase in HIPS. The position of the glass transition of the PB phase is related to the microstructure (vinyl content); both pure cis-1,4 and trans-1,4 PB exhibit their T_g at 167 K, whereas pure vinyl-1,2 PB has its glass transition temperature around 258 K. Polybutadienes with higher vinyl content will therefore show higher glass transition temperatures [102, 103]. The glass transition of the PS matrix can be found at around 380 K; a small shoulder appears in the loss modulus and in the storage modulus for higher frequencies just before the PS glass transition starts, which could be attributed to the previous structural relaxation and stress release of the material [104, 105].

The glass transition relaxations related to the PB and PS phase of HIPS can be characterised by their loss modulus maximum values (E''_{max} and T_{max}); these values were obtained for all the HIPS samples and frequencies analysed by the fitting of the loss modulus data to the Fuoss-Kirkwood empirical model. Although the Fuoss-Kirkwood model was originally defined for dielectric secondary relaxations of polymers [106], it could be here successfully applied for the characterisation of dynamical-mechanical primary relaxations due to its simplicity and to the narrow range of frequency decades that can be analysed by DMTA. The modified Fuoss-Kirkwood equation in terms of temperature applied for the fitting of the dynamic-mechanical data is:

$$E''=\frac{E''_{\max}}{\cosh\left[m\cdot\frac{E_a}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_{\max}}\right)\right]} \qquad (2)$$

where E''_{max} is the maximum of the loss modulus; m is the Fuoss-Kirkwood parameter; E_a is the activation energy for the relaxation process; and T_{max} is the temperature of the maximum of the loss modulus, which is usually assumed as the glass transition temperature.

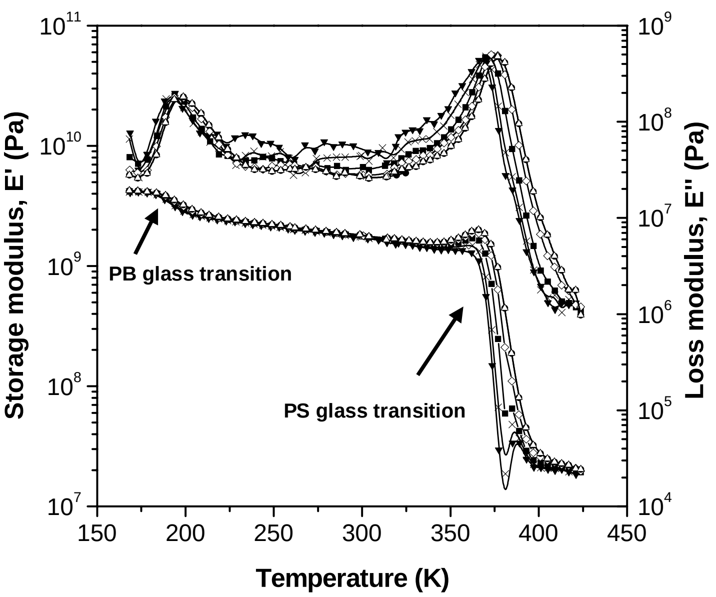


Figure 4.8. Isocronal representation of the storage modulus E' (lower plot) and loss modulus E"(upper plot) for virgin HIPS: (▼) 0.1Hz; (×) 0.25Hz; (■) 1Hz; (◊) 3.98Hz; (●) 10Hz; (8) 39.81Hz.

The analysis of the dynamic mechanical data according to the free volume theory allowed obtaining deeper information about the influence of reprocessing and thermo-oxidative ageing on the viscoelastic behaviour of the PB and PS glass transition. Figure 4.9a and Figure 4.9b represent the Arrhenius maps for the 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_{max} values from the Fuoss-Kirkwood fitting versus the different analysed frequencies.

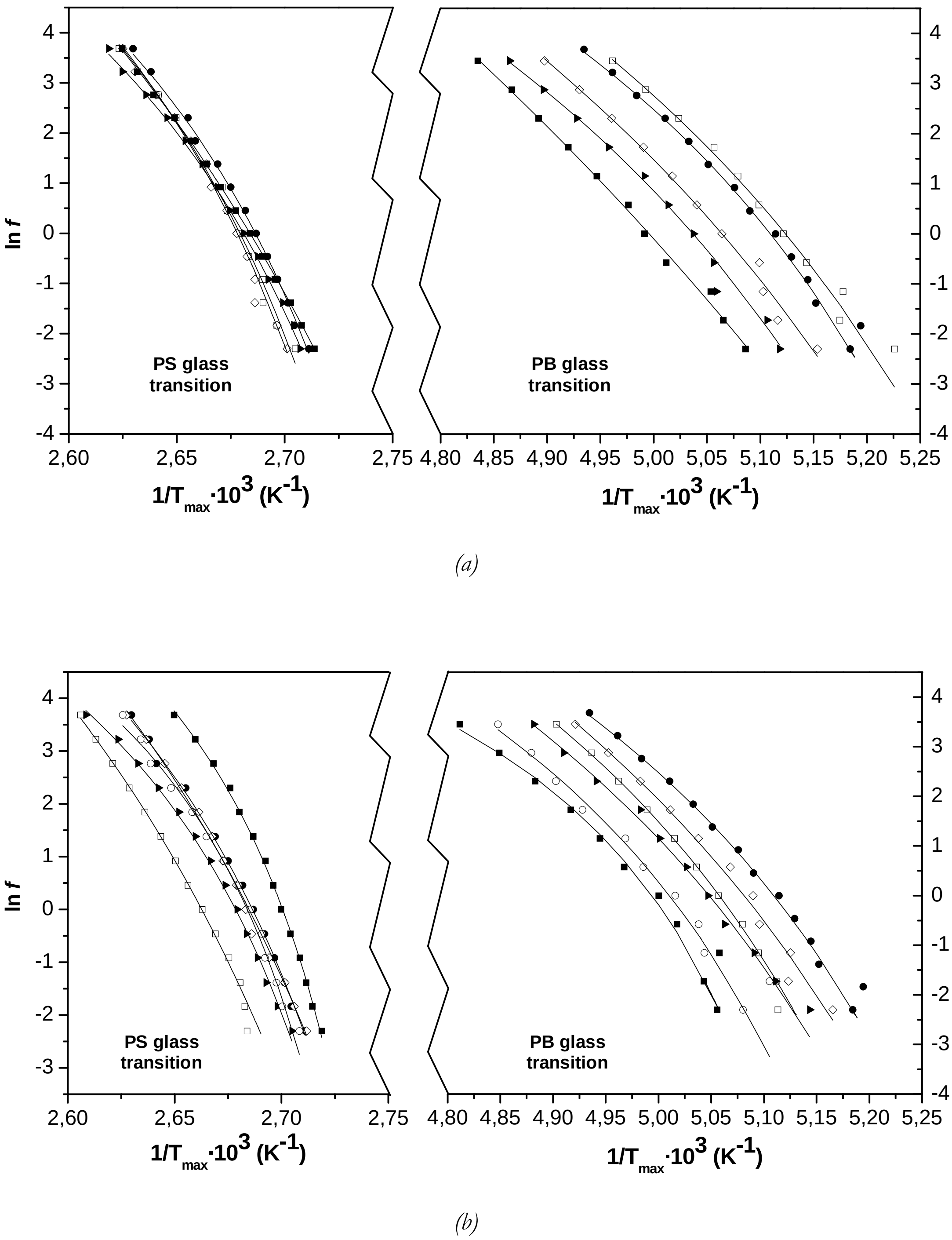


Figure 4.9. Arrhenius maps for the PB and PS glass transition relaxations. a) Influence of multiple processing: (●) virgin HIPS, (□) HIPSr1, (◊) HIPSr4, (▶) HIPSr6, (■) HIPSr9; b) Influence of thermo-oxidation at 90°C: (●) virgin HIPS, (□) aged 2 days, (◊) aged 4 days, (▶) aged 8 days, (○) aged 12 days, (■) aged 16 days.

The Arrhenius curves were fitted to Vogel-Fulcher-Tammann-Hesse equation (VFTH) in order to correlate the temperature dependence of the glass transition relaxation for PB and PS. VFTH equation was first empirically formulated for the viscosity of inorganic glasses at temperatures above the glass transition temperature (T_g) [107-109], and can be deduced as well from the free volume theory.

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

where τ_i is the relaxation time; A´ is an empirical parameter; and T_∞ 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 from the VFTH equation is related with the relative free volume at the glass transition temperature, according to the following expression:

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

where α_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 parameters from the fitting of the Arrhenius plots to VFTH equation are shown in Table 4.2 and Table 4.3 for the HIPS samples subjected to reprocessing and thermo-oxidation, respectively.

Reprocessing steps	**PB glass transition**				**PS glass transition**			
	A'	**m$_v$** (K)	**T$_\infty$** (K)	$\frac{f_g}{B\cdot(T_g - T_\infty)}\cdot 10^4$ (K^{-1})	**A'**	**m$_v$** (K)	**T$_\infty$** (K)	$\frac{f_g}{B\cdot(T_g - T_\infty)}\cdot 10^4$ (K^{-1})
Virgin HIPS	14.1	284.4	175.6	35.2	13.9	321.6	349.1	31.1
1	17.2	434.5	169.9	23.0	15.2	365.5	349.1	27.4
2	-	-	-	-	13.2	312.8	349.2	32.0
3	-	-	-	-	13.7	320.1	349.3	31.3
4	19.4	591.3	166.9	16.9	15.5	372.5	349.4	26.9
5	-	-	-	-	15.2	389.9	347.4	25.7
6	16.0	411.8	172.8	24.3	14.0	365.0	347.0	27.4
7	-	-	-	-	15.7	415.3	346.1	24.1
8	-	-	-	-	16.8	501.6	343.0	19.9
9	32.3	1773.6	145.2	5.6	23.6	1089.7	326.5	9.2

Table 4.2. Influence of multiple processing on the viscoelastic parameters related to the glass transition relaxations of PB and PS phases in HIPS according to the free volume theory.

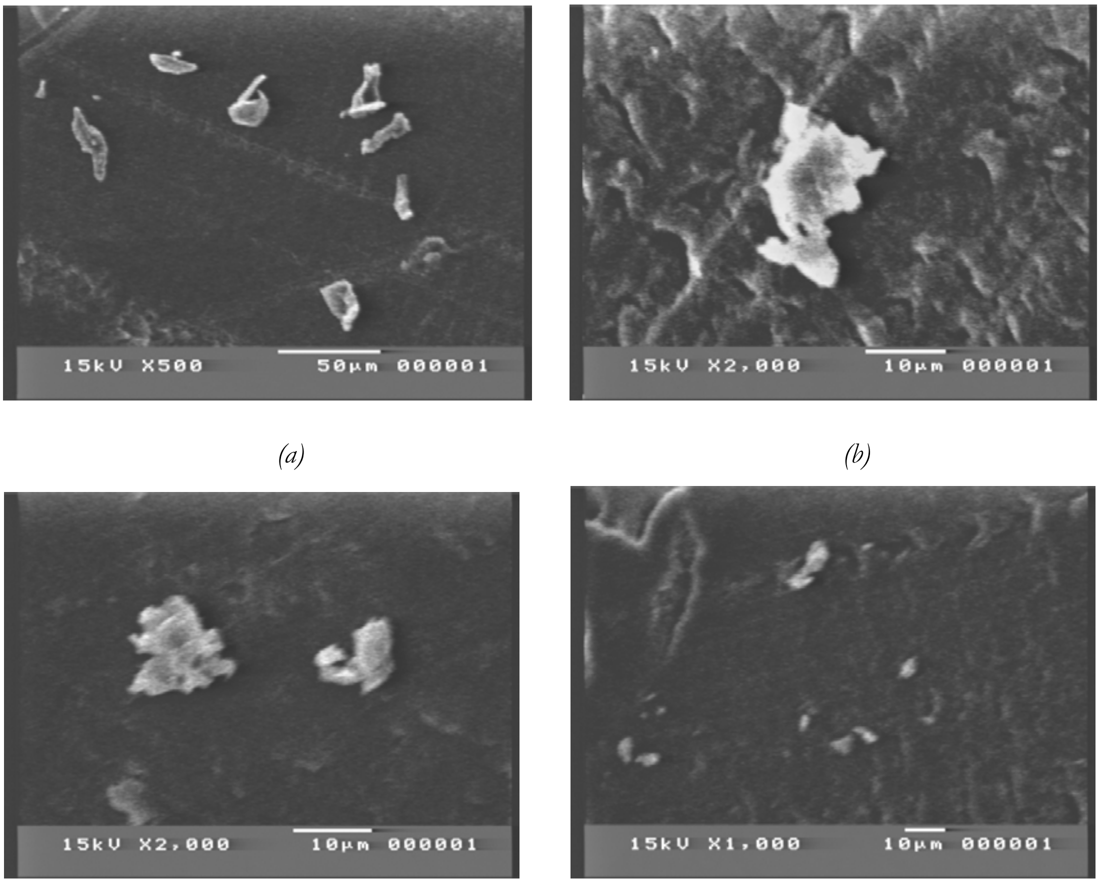
Multiple processing causes a progressive shift in the T_g loss plots for the PB phase to higher temperatures (Fig. 4.9a). This result may prove the occurrence of crosslinking reactions in the PB microstructure as it was suggested by the results of Raman spectroscopy, which generate rigid segments within the PB phase that contribute to the restriction in mobility of the PB chains. The parameter associated to the free volume of the PB phase decreases also through the repeated processing cycles (Table 4.2), which could also be caused by the entanglements in the PB chains due to crosslinking reactions. The Arrhenius curves for the PS phase show a slight shift to higher temperatures for repeated processing cycles (Figure 4.9a). The free volume parameter for PS glass transition is however greatly modified with a progressive diminution during reprocessing (Table 4.2). As it was reported before, repeated processing causes an increase in the melt flow rate and a modification in the rheological properties, which may be induced by chain scission reactions in the PS chain. Multiple processing may also be responsible for a rearrangement of the PS chains, which may progressively occupy the free volume originally present in the matrix. The combined effect of the presence of shorter PS polymeric chains induced by thermo-mechanical degradation and the physical rearrangement of the macromolecular chains within the repeated extrusion process may be responsible for the marked decrease in free volume. This effect here reported on the free volume of both PB and PS phases in HIPS may be responsible of the changes in the macroscopic behaviour, such a decrease in the elongation and break and impact properties reported in other works [67, 69, 110].

Exposure time (days)	**PB glass transition**				**PS glass transition**			
	A'	**m$_v$** (K)	**T$_\infty$** (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\cdot 10^4$ (K^{-1})	**A'**	**m$_v$** (K)	**T$_\infty$** (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\cdot 10^4$ (K^{-1})
Virgin HIPS	14.1	284.4	175.6	35.2	13.9	321.6	349.1	31.1
1	-	-	-	-	17.2	492.5	346.5	20.3
2	14.3	279.8	178.2	35.7	19.3	680.6	340.2	14.7
4	17.2	431.4	171.7	23.2	19.5	665.4	338.4	15.0
8	15.3	356.2	174.8	28.1	11.3	225.7	353.3	44.3
12	12.0	208.8	182.2	47.9	10.0	155.7	357.0	64.2
16	8.6	103.4	188.3	96.7	11.1	153.9	356.4	65.0

Table 4.3. Influence of thermo-oxidation at 90°C on the viscoelastic parameters related to the glass transition relaxations of PB and PS phases in HIPS according to the free volume theory.

The effect of thermo-oxidative ageing on the Arrhenius plot and the free volume parameter is complex for both phases in HIPS. The Arrhenius plots for the PB glass transition shift to higher temperatures with the exposure time to thermo-oxidation, being this effect more noticeable for higher exposure times (Fig. 4.9b). The chemical reactions induced by oxidation are associated with an increase of the glass transition temperature for polybutadiene [52, 64], which can be related to the changes in the PB microstructure. On one hand, oxidation causes extensive crosslinking in the PB phase, which restricts the mobility of the polymeric chains. On the other hand, as it has been confirmed by Raman spectroscopy, oxidation affects more severely the cis-1,4 and trans-1,4 microstructure rather than the vinyl-1,2; this leads to oxidised HIPS samples with higher vinyl content than the original ones, which exhibit higher glass transition temperatures. The free volume parameter, however, shows a slight decrease for shorter exposure times (until 4 days) and a dramatic increase for higher exposure times (Table 4.3). The decrease in the PB free volume at lower exposure times may be related to the initial crosslinking reactions caused by oxidation, which occur at lower incidence due to the protective effect of the stabilising system contained in the material. With longer exposure the oxidation effects become irreversible for polybutadiene, which may lead to a structural collapse of the PB phase in HIPS. This dual behaviour for short and long exposure times to thermo-oxidation becomes more evident for the PS phase. The Arrhenius plots for the PS glass transition shift to higher temperatures for shorter exposure times, but drastically shift to lower temperatures for longer times; similarly, the free volume parameter decreases for the initially thermo-oxidated HIPS samples, but increases markedly from 8 days of exposure on. Diverse phenomena may influence simultaneously the viscoelastic behaviour of the PS phase of HIPS during the exposure to thermo-oxidative ageing. On one hand, physical ageing induces molecular chain rearrangement resulting in significant changes in mechanical properties. On the other hand, chemical ageing is related to the chemical reactions with oxygen, which leads to the formation of oxidative groups and embrittlement [51]. Physical ageing of the PS phase seems to cause structural recovery of the polymeric chains towards lower energy states at short exposure times; this results in a decrease of the free volume, which is responsible of the cohesion of polymeric chains and lower molecular mobility [111]. However, the chemical effects on HIPS for 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, which is related to the lower glass transition temperature and the increase in the free volume.

The complex effects of multiple processing and thermo-oxidation on the microstructure and morphology of HIPS can be verified in the micrograms obtained by scanning electron microscopy (SEM). The typical double phase distribution in HIPS can be observed in virgin HIPS microgram (Fig. 4.10a) where the PB granules are dispersed in the PS matrix. The PB granules exhibit heterogeneous shapes with a particle size in the order of 5-10 μm. After multiple processing (Fig. 4.10b), shrinkage in the shape of the PB granules can be observed together with a clear modification in the surface of the granules; cracks, channels and wrinkles are also appreciated in the PS matrix. The progressive effect of thermo-oxidation on the morphology of HIPS can be followed with the exposure time. For shorter exposure times (Fig. 4.10c), the PB granules seem to crease and contract, showing a rough outer surface; for longer exposure times, however, PB phase appears to have partially lost the granular microstructure, though smaller particle can still be detected (Figure 4.10d). Cracks can be also observed in the PS matrix, which show the evident deterioration of the morphology under thermo-oxidation.



(a) *(b)*

(c) *(d)*

Figure 4.10. SEM micrographs of HIPS samples: a) virgin HIPS: b) reprocessed HIPS (9 cycles); c) thermo-oxidated HIPS at 90°C (4 days); d) thermo-oxidated HIPS at 90°C (16 days).

4.1.5 Occurrence of low molecular weight compounds

The identification and relative quantification of low molecular weight compounds (LMWC) present in high-impact polystyrene (HIPS) was performed using solvent extraction assisted by microwaves and further analysis of the extracts using gas chromatography-mass spectrometry (GC-MS). Monitoring the formation and/or migration of these compounds during the successive reprocessing cycles and during thermo-oxidation could be thus carried out. Figure 4.11 presents a full scan chromatograph from the extract of virgin HIPS, HIPS subjected to 9 reprocessing cycles, and HIPS thermo-oxidated 16 days. As a whole, the chromatographic pattern of the full scan obtained from virgin, reprocessed, and thermo-oxidated HIPS present common features: a first zone at short retention times from 5 – 9 minutes, where different benzene derivate volatile and semi-volatile organic compounds (VOCs and SVOCs) appear; a second zone around 17 minutes where styrene dimers elute; and finally a third zone at longer elution times where different peaks corresponding to styrene trimers and chain fragments from HIPS appear. Table 4.4 presents the retention times, proposed identified compounds, and relative abundance calculated to the intensity of the employed internal standards, of the different peaks obtained from the chromatograms of the virgin and reprocessed HIPS samples. Similarly, Table 4.5 presents the chromatographic results from the extracted HIPS samples subjected to thermo-oxidation at different exposure times. The identification of the corresponding mass spectra associated to the chromatographic peaks was performed either by comparison with injected external standards, by comparison with the available NIST MS search 2.0 database, or by comparison of the spectra with bibliographic references. Relative quantification of the associated peaks with one benzene ring was performed in relation with the signal of the 4-methylstyrene (peak 9) internal standard; on the other hand, the relative abundance of bigger molecules with two or more benzene rings was calculated towards the area of o-terphenyl (peak 30) internal standard.

Peaks 1-15 correspond to a wide variety of volatile organic compounds (VOCs) that are present in the virgin HIPS, reprocessed and thermo-oxidated HIPS samples. These compounds correspond mainly with benzene derivates (styrene, 1-methylethyl benzene, propylbenzene, 1- and 2-propenylbenzene) and oxidated benzene derivates (benzaldehyde, phenol, benzene acetaldehyde, α-methyl-benzenemethanol, acetophenone, benzoic acid), which have also been reported by several authors in studies about VOCs and SVOCs in different styrenic materials and products [112-115]

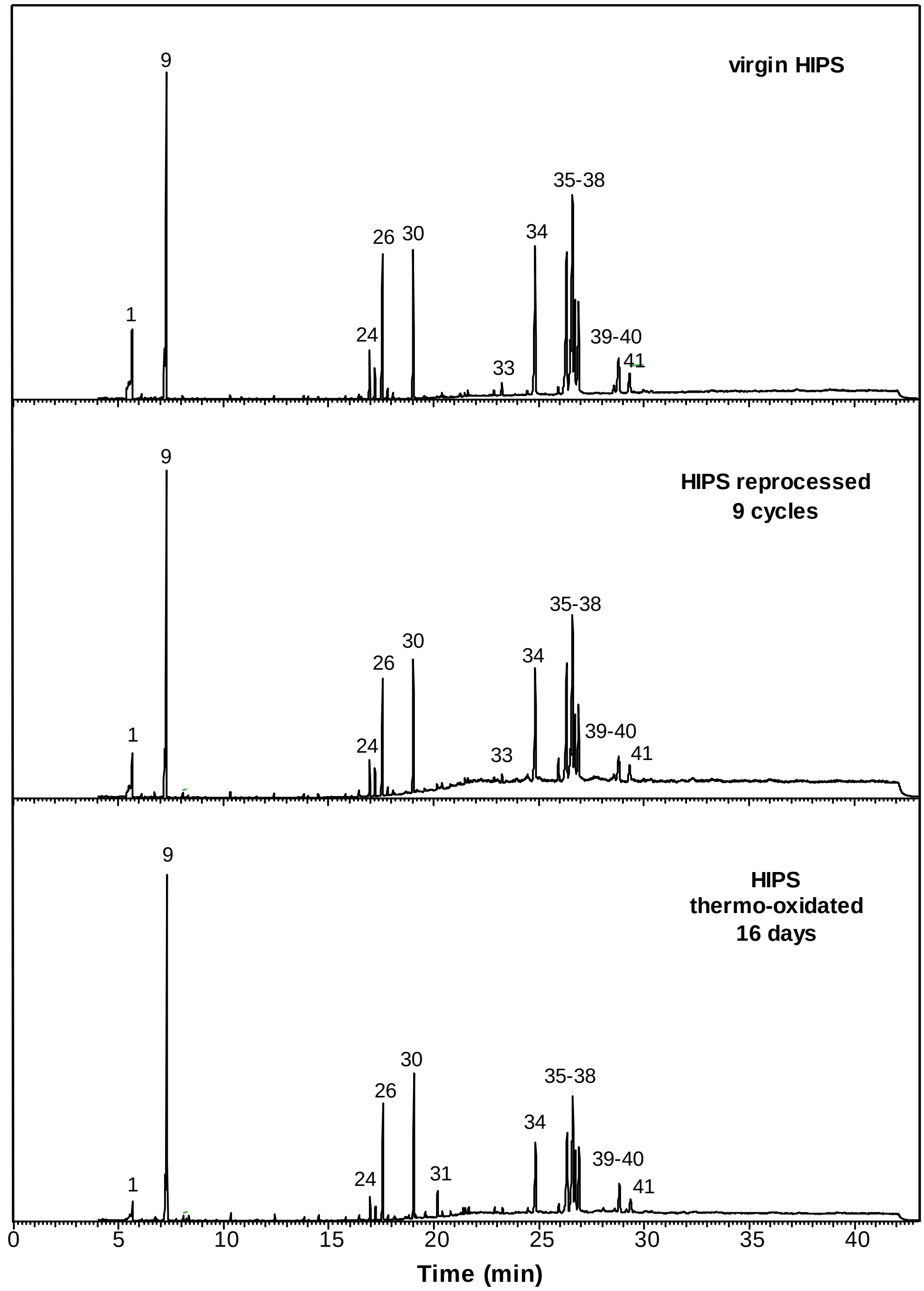


Figure 4.11. Total ion chromatogram (TIC) from the MAE extracts of virgin HIPS, HIPS reprocessed nine cycles, and HIPS thermo-oxidated 16 days at 90°C. NOTE: numbered peaks correspond with the compounds in Table 4.4 and Table 4.5.

Peak 18 can be attributed to 2,6-di-tert-butyl-p-benzoquinone, which is a transformation product from different phenolic antioxidants commonly used in polyolefins and styrenic polymers [116-118]. Peak 21 corresponds to a long aliphatic ester structure that may originate from an additive (lubricant, antioxidant) found in the original material. Peaks 19-30 correspond to styrene dimers that may be formed through side reactions during the polymerisation of styrene or during thermal processing. Benzene, 1,1'-(1,3-propanediyl)bis- (peak 23) has been reported to be produced during hot processing of polystyrene [119]. Some authors have pointed out that other styrene dimers, such as cis- and trans-1,2-diphenylcyclobutane (peaks 24 and 26, respectively), 2,4-diphenyl-1-butene (peak 25), 1-phenyltetralin (peak 27), and 1,2-dihydro-4-phenylnaphtalene (peak 28), can be formed through side reaction during the thermal polymerisation of styrene [120-123]; these compounds are therefore retained in the polymeric matrix as polymerisation residues. Peak 22 could not be fully identified, but it may be classified as a styrene dimer using its mass spectrometry spectra, which shows similar fragmentation pattern as other polystyrenic fragments with main ions m/z 77, 91, 103, 117, and 130.

Peaks 33-41 can be structurally classified as different styrene trimers using their similar mass spectra, with molecular fragments m/z 91, 117, 129, 206-208 corresponding to different styrenic fragments. Some of these trimers, such as 1,3,5-triphenylhexene-5 (peak 34) and the four different diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline (peaks 35-38), could be identified through bibliographic comparison of their mass spectra [121, 124]. These compounds have been also reported to be formed during the polymerisation of styrene [120, 121, 123, 125, 126] and therefore retained as polymerization residues.

New peaks appear in the chromatograms for different aged HIPS samples. These peaks could not be completely identified using the NIST database, but their mass spectra indicate that they may belong to different oxidated and non-oxidated fragments that arise from the grafting points between the polystyrene (PS) and polybutadiene (PB) in HIPS under the thermo-oxidative degradation conditions. Peak 29 may correspond with a polycyclic benzoic compound with both aromatic and cyclic structures; peaks 31-32, on the other hand, may be assigned to oxidated polycyclic and benzoic structures formed by the oxidation of PS and PB grafting points.

Peak nr.	Proposed compound	R.T. (min)	Relative abundance, x10^4 (RSD, in %)									
			Virgin	r1	r2	r3	r4	r5	r6	r7	r8	r9
1	Styrene [a,e]	5.66	4153.6 (9.4)	3605.2 (3.7)	3671.2 (8.2)	3490.9 (4.2)	3284.4 (5.0)	3055.3 (6.9)	2992.7 (1.6)	2694.1 (1.4)	2580.9 (6.2)	2474.9 (6.6)
3	Benzene, (1-methylethyl)- [b,e]	6.11	98.9 (5.2)	91.1 (4.5)	98.0 (5.5)	87.1 (10.3)	86.7 (8.1)	88.2 (5.3)	84.1 (1.8)	83.5 (4.0)	73.5 (4.4)	78.2 (6.7)
4	Benzene, propyl- [b,e]	6.55	27.0 (4.5)	28.0 (24.7)	27.0 (4.6)	26.0 (19.8)	24.4 (12.4)	24.4 (16.7)	23.9 (11.1)	24.4 (7.4)	21.3 (13.0)	24.4 (14.7)
5	Benzaldehyde [a,e]	6.73	7.2 (19.2)	17.8 (44.1)	37.8 (14.1)	48.9 (8.3)	60.3 (2.4)	64.9 (5.5)	64.9 (7.5)	84.9 (25.1)	81.8 (4.2)	90.6 (5.3)
6	Phenol [b,e]	6.85	-	1.3 (20.9)	2.9 (30.0)	3.8 (15.8)	4.6 (16.5)	5.5 (20.3)	5.2 (15.0)	5.5 (17.8)	6.2 (15.7)	7.0 (8.4)
7	Benzene, 1-propenyl [b,e]	6.98	5.6 (1.2)	6.4 (27.0)	7.8 (14.6)	9.7 (27.4)	10.0 (26.8)	11.8 (22.3)	12.1 (13.7)	11.8 (16.2)	13.3 (20.4)	14.4 (7.7)
8	Heptane, 2,2,4,6,6-pentamethyl- [b,e]	7.05	31.8 (8.5)	28.9 (5.1)	32.0 (6.3)	32.9 (15.7)	28.5 (9.9)	28.5 (12.2)	26.3 (11.9)	30.9 (26.9)	25.3 (10.6)	24.3 (5.3)
9	4-methylstyrene	7.29	Internal standard (I.S.)									
10	Benzene, (1-methylpropyl)- [b,e]	7.42	12.1 (5.9)	11.2 (17.3)	13.1 (20.4)	12.5 (16.2)	12.7 (27.7)	13.0 (29.6)	12.2 (20.6)	10.1 (12.4)	11.6 (38.7)	11.2 (19.0)
11	Benzene, 2-propenyl [b,e]	7.72	8.2 (7.9)	8.8 (3.8)	10.8 (6.7)	12.1 (8.8)	13.1 (6.6)	14.4 (7.3)	14.2 (7.4)	16.7 (4.7)	15.3 (3.5)	16.9 (7.0)
13	Benzene acetaldehyde [b,e]	7.98	6.7 (10.4)	5.6 (12.0)	6.8 (4.5)	7.3 (14.9)	5.6 (20.8)	6.1 (4.8)	5.7 (12.4)	5.8 (7.7)	4.3 (29.3)	5.6 (20.8)
14	Benzenemethanol, α-methyl- [b,e]	8.2	0.7 (59.7)	2.0 (4.7)	3.5 (20.4)	4.2 (15.0)	3.8 (8.7)	5.4 (9.6)	5.3 (8.1)	4.8 (13.6)	5.0 (26.7)	6.3 (17.1)
15	Acetophenone [a,e]	8.34	4.9 (6.9)	12.9 (6.8)	19.2 (10.9)	25.3 (13.8)	29.2 (12.9)	34.2 (6.1)	36.1 (6.8)	42.2 (10.7)	43.1 (5.9)	49.2 (6.3)
16	saturated hydrocarbon [e]	8.85	1.5 (29,2)	5.6 (12.7)	3.8 (20.2)	3.6 (19.0)	2.1 (6.5)	3.9 (77.7)	3.5 (48.5)	3.9 (25.0)	4.4 (23.9)	4.3 (80.8)
18	2,6- Di-tert-butyl-p-benzoquinone [f]	14.03	122.8 (19.8)	161.2 (46.5)	162.9 (18.5)	149.3 (37.9)	145.8 (60.8)	185.4 (26.6)	136.6 (36.5)	181.4 (25.5)	156.8 (25.9)	180.0 (24.6)
19	Ethylene, 1,1-diphenyl [b,f]	14.77	13.3 (8.4)	13.2 (16.3)	13.8 (7.7)	14.8 (16.7)	12.9 (13.3)	12.5 (16.3)	13.1 (6.4)	12.7 (4.4)	14.5 (30.0)	13.3 (6.5)
20	1,2-diphenylethylene [b,f]	14.9	41.1 (12.6)	41.9 (28.3)	29.0 (67.7)	34.7 (72.3)	36.5 (40.8)	35.9 (43.9)	34.4 (40.4)	29.1 (59.6)	27.4 (57.2)	32.8 (47.8)
21	Dodecanoic acid, ethyl ester [b,f]	15.93	1.3 (34.7)	13.4 (18.8)	54.9 (21.2	39.9 (29.2)	33.3 (32.3)	23.6 (34.7)	21.5 (13.9)	14.5 (20.8)	17.4 (20.1)	8.9 (48.4)

22	styrene dimer ^{f}	16.1	56.3 (10.1)	56.2 (10.7)	67.2 (13.8)	67.0 (14.0)	63.3 (11.7)	64.5 (10.3)	64.4 (7.2)	65.3 (9.4)	63.5 (19.7)	68. (18.6)6
23	Benzene, 1,1'-(1,3-propanediyl)bis- ^{b,f}	16.46	299.9 (12.6)	364.5 (14.1)	408.8 (12.1)	456.0 (11.4)	483.5 (17.3)	448.2 (9.5)	480.4 (11.9)	458.9 (4.6)	539.5 (15.9)	570.2 (11.8)
24	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis- ^{b,c,f}	16.96	2697.9 (3.8)	2603.7 (8.0)	2812.2 (12.6)	2799.4 (10.5)	2587.3 (13.9)	2450.9 (9.3)	2476.1 (5.0)	2306.2 (6.4)	2440.7 (15.1)	2443.4 (10.7)
25	2,4-diphenyl-1-butene ^{d,f}	17.21	1841.0 (7.2)	1868.7 (7.7)	2019.6 (13.4)	2046.8 (9.6)	1961.0 (12.9)	1861.3 (6.5)	1889.2 (6.8)	1799.8 (5.1)	1939.1 (15.2)	1955.2 (10.7)
26	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans- ^{b,c,f}	17.54	10051.5 (7.3)	10132.3 (9.5)	10959.4 (14.6)	10919.1 (10.5)	10367.3 (14.9)	9806.7 (10.2)	10056.2 (8.6)	9335.5 (5.9)	9866.4 (15.8)	10065.1 (9.8)
27	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- ^{b,f}	17.82	574.6 (4.9)	570.0 (8.4)	655.1 (11.1)	641.4 (14.4)	608.9 (13.3)	549.3 (11.8)	552.6 (10.2)	527.9 (2.2)	588.2 (8.7)	563.6 (9.1)
28	Naphthalene, 1,2-dihydro-4-phenyl- ^{b,f}	18.08	366.5 (3.5)	334.3 (5.0)	401.8 (11.5)	412.4 (19.7)	355.2 (14.2)	330.9 (8.2)	329.0 (7.6)	310.4 (3.1)	323.7 (6.5)	327.4 (4.4)
30	o-Terphenyl	19.04	Internal standard (I.S.)									
33	styrene trimer ^{f}	23.26	1343.4 (12.8)	1103.3 (10.0)	1228.7 (13.6)	1228.4 (7.8)	1113.5 (16.8)	1148.2 (10.5)	1131.6 (9.0)	1029.9 (5.0)	1129.7 (33.9)	1022.6 (18.5)
34	1,3,5-triphenylhexene-5 ^{d,f}	24.83	18003.5 (12.6)	16622.0 (7.0)	18304.6 (11.6)	18073.2 (8.7)	15745.8 (12.6)	15931.8 (6.9)	16077.2 (12.6)	16653.5 (8.3)	15473.9 (3.5)	17169.5 (20.0)
35	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer ^{c,f}	26.33	21223.8 (11.6)	19017.2 (7.7)	21588.3 (11.1)	21512.7 (8.5)	19104.9 (12.9)	19123.2 (4.6)	19469.6 (9.5)	20057.3 (10.7)	19629.9 (6.2)	19772.5 (15.0)
36	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer ^{c,f}	26.61	33491.5 (12.5)	30300.3 (9.7)	34039.9 (12.4)	34231.7 (9.5)	30272.5 (14.8)	30263.7 (7.0)	30712.8 (8.3)	31193.4 (8.9)	30959.6 (6.5)	32096.4 (16.8)
37	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer ^{c,f}	26.72	10350.7 (11.1)	9150.2 (10.9)	9618.9 (11.0)	9626.7 (5.6)	8299.5 (15.9)	8604.4 (12.8)	8792.4 (5.3)	9061.2 (16.3)	8136.2 (6.4)	8743.4 (17.8)
38	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer ^{c,f}	26.9	12433.0 (9.7)	11223.7 (10.0)	11898.8 (10.6)	12060.6 (7.0)	10424.2 (16.9)	10821.9 (11.1)	10884.9 (4.3)	10570.4 (10.6)	10635.0 (5.2)	10846.1 (14.7)
39	styrene trimer ^{f}	28.57	1250.8 (16.3)	1359.9 (15.5)	1508.6 (17.2)	1481.1 (18,2)	1319.9 (10.2)	1145.9 (17.3)	1281.1 (17.0)	1323.1 (3.2)	1391.2 (21.0)	1328.6 (21.1)
40	styrene trimer ^{f}	28.81	7033.5 (10.6)	6449.1 (11.2)	6495.5 (13.1)	6441.3 (3.8)	5631.0 (12.2)	6063.4 (11.8)	6312.8 (7.2)	5424.2 (2.7)	5894.4 (15.4)	5961.5 (15.6)
41	styrene trimer ^{f}	29.31	3743.3 (12.4)	3574.6 (9.7)	3548.5 (14.9)	3765.0 (5.9)	3203.9 (13.3)	3379.2 (12.0)	3793.5 (13.2)	3461.3 (15.0)	3688.5 (4.9)	3483.9 (13.4)

Table 4.4. Relative abundance and chromatographic properties of identified low molecular weight compounds in reprocessed HIPS samples.

^{a} Identification by injection of standard substances; ^{b} Proposed identification by comparison to the NIST database; ^{c} Proposed identification through bibliographic reference [127]; ^{d} Proposed identification through bibliographic reference [124]; ^{e} Relative quantification respect 4-methylstyrene (I.S.); ^{f} Relative quantification respect o-terphenyl (I.S.)

Thermo-mechanical degradation during successive reprocessing cycles induces interconnected tendencies in the relative abundance of the different identified compounds (Table 4.4). In general, the relative abundance of some peaks originally found in virgin HIPS tend to decrease with reprocessing steps; this result is in agreement with previous studies that suggested that reprocessing and recycling may contribute to minimise the presence of some volatile compounds [17]. However, other compounds may be formed during consecutive processing, which proves the importance of monitoring the formation of low molecular weight compounds during recycling.

Different volatile organic compounds, including styrene monomer, exhibit a clear and progressive reduction in their relative abundance with the consecutive reprocessing cycles compared to virgin HIPS. The high processing temperatures may be responsible for the emission of these organic compounds during the extrusion process. Other styrenic derivates, such as 1-propenylbenzene and 2-propenylbenzene, may be on the other hand formed from the degradation of HIPS under the thermo-mechanical stress caused by hot processing, since they show an increasing content with reprocessing cycles. In general, the relative content of styrene dimers and trimers diminishes progressively during successive reprocessing steps. Other styrene dimers, such as 1,1'-(1,3-propanediyl)bis-benzene (peak 23) and 2,4-diphenyl-1-butene (peak 25) show higher relative abundance with consecutive extrusion cycles; this indicates their formation during melt processing of HIPS as it has been previously reported by other authors [119].

The progressive formation of oxidated derivates of styrene during the consecutive reprocessing cycles is one of the main features of the chromatographic study. The temperature conditions and the mechanical stress to which the melt polymeric chains are subjected during processing, and the presence of residual oxygen in the extruder may be responsible of thermo-mechanical and oxidative degradation of HIPS during consecutive reprocessing, which may lead to the formation of oxidation products from polystyrene, such as aldehydes (benzaldehyde), ketones (acetophenone), and alcohols (phenol).

The evolution of the relative abundance with thermo-oxidation exposure time for the different low molecular weight compounds identified in high-impact polystyrene is displayed in Table 4.5. The complex behaviour of high-impact polystyrene subjected to thermo-oxidation throughout exposure time has been previously pointed out; at shorter exposure times physical processes seems to predominate, whereas chemical degradation of the polymeric chains has irreversible effects after longer exposure times. A similar time-dependent pattern can be observed for the different families of low molecular weight compounds during thermo-oxidation exposure.

Peak nr.	Proposed compound	R.T. (min)	Relative abundance x10^4 (RSD, in %)						
			Virgin	**a1d**	**a2d**	**a4d**	**a8d**	**a12d**	**a16d**
1	Styrene ^{a,e}	5.66	4153.6 (9.4)	2220.2 (25.4)	2364.3 (7.5)	2713.9 (0.6)	2633.2 (4.4)	2287.1 (4.1)	1799.7 (2.7)
2	Hexanedial ^{b,e}	6.04	-	-	2.5 (64.6)	2.7 (44.7)	9.6 (61.4)	22.4 (22.6)	46.8 (4.5)
3	Benzene, (1-methylethyl)- ^{b,e}	6.11	98.9 (5.2)	47.9 (30.6)	56.4 (4.6)	68.5 (3.0)	73.4 (4.9)	69.4 (9.0)	68.5 (5.8)
4	Benzene, propyl- ^{b,e}	6.55	27.0 (4.5)	13.4 (26.4)	15.6 (20.0)	20.7 (19.6)	21.3 (8.9)	21.7 (7.8)	22.1 (15.2)
5	Benzaldehyde ^{a,e}	6.73	7.2 (19.2)	12.9 (8.0)	19.9 (22.5)	19.9 (13.1)	34.9 (3.1)	58.4 (3.0)	99.5 (5.4)
6	Phenol ^{b,e}	6.85	-	2.0 (13.5)	2.1 (35.6)	4.1 (33.3)	8.0 (11.6)	14.0 (19.0)	43.4 (19.7)
7	Benzene, 1-propenyl ^{b,e}	6.98	5.6 (1.2)	4.6 (25.3)	5.5 (21.0)	6.3 (8.4)	6.3 (7.1)	7.3 (17.7)	6.7 (11.2)
8	Heptane, 2,2,4,6,6-pentamethyl- ^{b,e}	7.05	31.8 (8.5)	22.0 (12.5)	21.0 (7.8)	23.7 (2.2)	25.0 (6.5)	26.7 (8.9)	24.3 (14.5)
9	4-methylstyrene	7.29	Internal standard (I.S.)						
10	Benzene, (1-methylpropyl)- ^{b,e}	7.42	12.1 (5.9)	12.2 (34.2)	14.2 (25.3)	14.4 (13.0)	12.5 (8.3)	14.2 (14.2)	13.5 (19.5)
11	Benzene, 2-propenyl ^{b,e}	7.69	8.2 (7.9)	10.5 (10.1)	9.6 (19.6)	8.9 (21.0)	10.0 (24.4)	9.6 (18.4)	8.6 (37.0)
12	branched hexaketone ^{e}	7.72	-	-	1.0 (31.9)	2.9 (13.2)	7.4 (17.0)	17.5 (17.0)	50.7 (11.7)
13	Benzene acetaldehyde ^{b,e}	7.98	6.7 (10.4)	2.8 (6.9)	3.2 (36.3)	3.2 (15.1)	4.2 (9.3)	6.1 (7.3)	7.4 (10.4)
14	Benzenemethanol, α-methyl- ^{b,e}	8.22	0.7 (59.7)	1.9 (26.7)	2.7 (34.9)	4.1 (18.3)	16.8 (10.7)	35.7 (11.3)	82.1 (10.1)
15	Acetophenone ^{a,e}	8.34	4.9 (6.9)	11.6 (13.0)	16.5 (22.4)	27.0 (9.9)	55.6 (7.2)	87.9 (10.0)	184.1 (8.8)
16	saturated hydrocarbon ^{e}	8.85	1.5 (29.2)	41.1 (58.8)	32.3 (31.6)	12.3 (20.4)	11.1 (7.7)	9.6 (7.7)	13.6 (6.9)
17	Benzoic acid ^{b,e}	9.66	-	-	-	-	1.5 (32.2)	22.6 (35.3)	98.4 (14.6)
18	2,6- Di-tert-butyl-p-benzoquinone ^{b,f}	14.03	122.8 (19.8)	88.0 (10.5)	67.2 (47.1)	89.9 (82.4)	105.4 (54.2)	90.4 (37.3)	90.9 (25.9)
19	Ethylene, 1,1-diphenyl ^{b,f}	14.77	13.3 (8.4)	16.5 (4.0)	13.5 (4.4)	12.2 (30.7)	11.6 (5.3)	8.5 (27.5)	6.9 (21.9)
20	1,2-diphenylethylene ^{b,f}	14.9	41.1 (12.6)	66.0 (7.1)	60.7 (8.2)	57.0 (14.3)	50.2 (3.7)	55.5 (12.6)	59.3 (22.3)
21	Dodecanoic acid, ethyl ester ^{b,f}	15.93	1.3 (34.7)	167.4 (47.2)	108.5 (30.0)	36.9 (22.6)	28.2 (2.7)	22.5 (6.3)	27.9 (14.5)
22	styrene dimer ^{f}	16.1	56.3 (10.1)	45.6 (10.3)	45.1 (8.2)	49.7 (7.1)	48.8 (8.3)	46.7 (13.4)	43.1 (16.0)
23	Benzene, 1,1'-(1,3-propanediyl)bis- ^{b,f}	16.46	299.9 (12.6)	409.6 (12.0)	412.6 (6.0)	440.2 (5.8)	439.3 (13.2)	476.6 (9.8)	491.6 (11.4)
24	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis- ^{b,c,f}	16.96	2697.9 (3.8)	2551.8 (8.3)	2562.6 (5.5)	2494.0 (8.9)	2576.9 (6.4)	2641.4 (13.7)	2209.0 (10.3)
25	2,4-diphenyl-1-butene ^{d,f}	17.21	1841.0 (7.2)	1921.7 (3.7)	1847.8 (4.7)	1857.3 (8.5)	1759.1 (6.9)	1655.8 (8.3)	1339.3 (9.6)
26	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans- ^{b,c,f}	17.54	10051.5 (7.3)	11705.1 (9.6)	11580.0 (5.0)	11925.8 (6.2)	11783.9 (11.0)	11844.1 (8.3)	10776.4 (6.2)
27	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- ^{b,f}	17.82	574.6 (4.9)	654.7 (9.6)	708.3 (9.4)	586.8 (13.1)	566.3 (10.5)	503.6 (44.6)	509.4 (16.1)
28	Naphthalene, 1,2-dihydro-4-phenyl- ^{b,f}	18.08	366.5 (3.5)	359.3 (2.6)	324.5 (4.8)	325.4 (10.0)	291.8 (6.0)	278.1 (8.2)	219.8 (11.8)
29	Polycyclic benzoic structure ^{f}	18.84	-	-	-	-	116.3 (32.6)	235.2 (11.9)	470.0 (12.6)
30	o-Terphenyl	19.04	Internal standard (I.S.)						
31	oxidated styrene trimer ^{f}	20.16	-	210.3 (11.4)	323.6 (26.2)	430.5 (34.9)	999.7 (12.1)	1659.9 (14.2)	2932.8 (7.2)
32	oxidated styrene cyclic structure ^{f}	21.38	-	-	-	51.9 (86.8)	153.6 (31.1)	319.7 (9.7)	702.2 (12.4)

33	styrene trimer [f]	23.26	1343.4 (12.8)	1419.4 (9.8)	1250.4 (4.1)	1223.8 (9.9)	1247.5 (10.4)	1165.9 (20.9)	863.9 (7.0)
34	1,3,5-triphenylhexene-5 [d,f]	24.83	18003.5 (12.6)	19507.7 (3.3)	18923.6 (1.7)	18011.7 (9.4)	17445.9 (6.4)	16254.8 (13.4)	13476.1 (4.5)
35	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.33	21223.8 (11.6)	24266.3 (4.4)	23150.7 (3.9)	21864.5 (11.7)	21523.2 (7.7)	21358.2 (12.9)	18562.5 (3.0)
36	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.61	33491.5 (12.5)	37317.2 (5.0)	34504.1 (2.0)	33233.8 (13.2)	32364.3 (6.4)	31147.0 (12.5)	27399.4 (3.7)
37	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.72	10350.7 (11.1)	13461.9 (6.0)	12838.5 (12.6)	12456.3 (16.0)	11827.0 (6.7)	11489.4 (13.9)	10323.9 (1.5)
38	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.9	12433.0 (9.7)	16393.5 (8.5)	16027.3 (10.9)	14706.5 (10.1)	14216.1 (5.5)	13697.8 (11.4)	12565.9 (3.3)
39	styrene trimer [f]	28.57	1250.8 (16.3)	1216.8 (3.1)	1541.9 (9.1)	1643.3 (5.9)	1371.3 (15.1)	1281.3 (27.0)	1023.8 (3.6)
40	styrene trimer [f]	28.81	7033.5 (10.6)	9734.5 (5.0)	9382.0 (5.8)	9157.1 (9.5)	8655.3 (7.8)	8432.4 (14.8)	7264.9 (6.5)
41	styrene trimer [f]	29.31	3743.3 (12.4)	4088.3 (1.8)	3977.0 (6.9)	3891.4 (14.8)	3906.1 (9.8)	4030.5 (19.6)	3953.3 (7.7)

Table 4.5. Relative abundance and chromatographic properties of identified low molecular weight compounds in thermo-oxidated HIPS samples at 90°C.

[a] Identification by injection of standard substances; [b] Proposed identification by comparison to the NIST database; [c] Proposed identification through bibliographic reference [127]; [d] Proposed identification through bibliographic reference [124]; [e] Relative quantification respect 4-methylstyrene (I.S.); [f] Relative quantification respect o-terphenyl (I.S.)

Styrene (peak 1) shows a dramatic reduction in its relative abundance during short time exposure, together with some other volatile organic compounds as 1-methylethyl-benzene (peak 3), propylbenzene (peak 4), and 1-propenylbenzene (peak 7). This behaviour shows the release of these VOCs from the polymer matrix to the environment during thermo-oxidative exposure. For longer exposure times, the abundance of these compounds tends to stabilise or even increase. Other benzene derivatives, including several semi-volatile organic compounds, styrene dimers, and styrene trimers, exhibit a totally different behaviour; for shorter exposure times, their relative abundance tends to slightly increase, whereas for longer exposure times their abundance decreases. Different phenomena seem to be taking place simultaneously under thermo-oxidation at short and long exposures. For short exposure times, physical ageing in the polymeric structure occurs, which may enhance the migration and release of different low molecular weight compounds (residues of polymerisation, including styrene monomer, dimers, and trimers); on the other hand, thermal initiated reactions of styrene monomer may occur at the temperature conditions of the forced-ventilation oven, with the formation of a wide range of styrenic dimers and trimers [122, 123, 126], and therefore increasing slightly the relative abundance of these styrenic derivates. For longer exposure times, these competing release and formation processes for styrenic dimers and trimers seems to stabilise, due to chemical deterioration of the polymeric structure.

A wide range of oxidated structures can be found in HIPS at different exposure times to the thermo-oxidative environment, including oxidated fragments of the polybutadiene chain, as hexanedial (peak 2) and a branched hexaketone (peak 12), several oxidated benzene derivates such as benzaldehyde (peak 5), phenol (peak 6), benzeneacetaldehyde (peak 13), α-methyl-benzenemethanol (peak 14), acetophenone (peak 15), benzoic acid (peak 17), and several oxidated structures from the grafting points of PS and PB (peaks 29, 31, and 32). At short exposure times until 8 days of ageing, the formation of oxidated derivates occurs at a moderate rate, due to the protective action of the stabilising system in HIPS. At longer exposure times, however, the chemical ageing effects are remarkable, with an exponential raise of the abundance of these oxidated derivates and the formation of new degradation products.

4.2 QUALITY ANALYSIS OF RECYCLED HIPS DURING THE LARGE-SCALE MECHANICAL RECYCLING PROCESS

Different analytical strategies for the quality assessment of recycled HIPS were presented, related to the key aspects showed in Figure 1.4; the presence of other polymeric materials as impurities, the oxidative stability, the chemical changes and the presence of low molecular weight compounds in recycled HIPS are some of the quality parameters that have been selected and studied. Samples extracted from different points of a large-scale mechanical recycling plant have been studied in order to verify the suitability of the proposed analytical strategies (Table 3.1 and Figure 3.2). The effects of the different steps of the recycling process on the properties of the HIPS materials were also investigated.

4.2.1 Presence of polymeric impurities

The presence of mixed polymeric fractions as impurities in recycled polymeric materials clearly affects the macroscopic performance of recyclates. The employment of thermal analysis is suitable for the characterisation of the properties of the material in the bulk. Polymeric contaminations in the recycled materials were detected by DSC. Figure 4.12 shows the thermograms corresponding to the second heating segment for the different HIPS samples, where it can be observed that all the samples exhibit the slope change corresponding to the glass transition of the polystyrene phase at around 90°C. Small melting peaks at temperatures of 120°C and/or 160°C can be observed, however, for samples HIPS2 and HIPS7, which indicate the presence of polyethylene and polypropylene contaminations, respectively, in these materials.

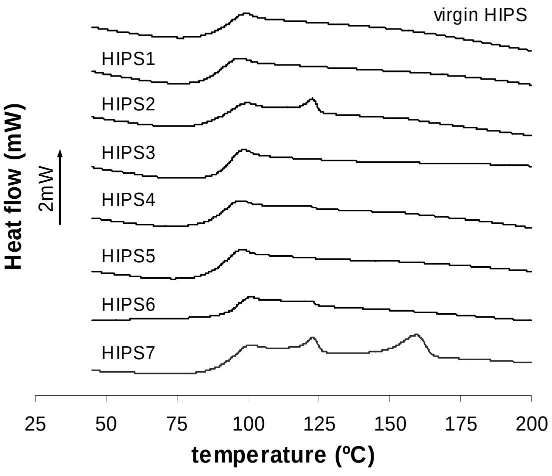


Figure 4.12. Determination of polymeric impurities in the HIPS samples by DSC: Thermograms of the second melting ramp.

4.2.2 Thermal properties and oxidative stability

DSC was employed to calculate the glass transition temperature of the PS matrix and to assess the oxidative stability of the different HIPS samples (Table 4.6). In polymeric materials, the glass transition temperature (T_g) is particularly related to the mobility of the polymeric chains and determines the transition between the glassy and the rubbery polymeric state. Variances in the glass transition temperature may be due to several structural effects of the polymers, such as molar mass, degree of crosslinking, chain branching, or physical ageing phenomena [128]. The different samples present comparable T_g values between 90 and 95ºC for the polystyrene (PS) phase of HIPS, which indicates that the morphology of the samples seems to be similar.

Sample	**T_g** (ºC)		**OIT** (min)		**T_{ox}** (ºC)	
	Mean	*STD*	*Mean*	*STD*	*Mean*	*STD*
Virgin HIPS	94,1	1,5	28,0	3,2	198,1	3,2
HIPS1	90,9	1,1	-	-	187,6	2,4
HIPS2	90,6	0,8	8,1	1,0	183,0	0,6
HIPS3	91,0	1,3	-	-	192,5	3,9
HIPS4	90,2	0,6	14,4	1,2	183,7	5,4
HIPS5	90,9	0,2	4,0	1,0	182,6	1,8
HIPS6	95,4	0,2	10,5	0,2	187,3	1,7
HIPS7	93,4	0,8	13,0	0,5	185,1	0,6

Table 4.6. Thermal parameters of differential scanning calorimetry (DSC): Glass transition temperature of the polystyrene phase (T_g), oxidation induction time (OIT), and oxidation temperature (T_{ox}).

The oxidative stability of the HIPS samples was assessed using DSC, evaluating both the oxidation induction time (OIT) and the oxidation temperature (T_{ox}). The OIT of the samples HIPS1 and HIPS3 could not be calculated due to 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. The mechanical recycling processes show, however, minor effects on the oxidative stability of the recycled samples, because the values of the T_{ox} and OIT of the recycled materials (HIPS5, HIPS6 and HIPS7) are similar or even higher than those of their precedent materials in the recycling flow diagram (HIPS1 to HIPS4); this may be due to the addition of stabilisers in the reprocessing step. These results prove consequently the importance of adjusting the restabilisation level in order to guarantee the oxidative stability of the recyclates in their new service life. From an analytical point of view, the results obtained from the OIT and the T_{ox} parameters can both be employed as quality indicators for the oxidative stability in the recycling activities.

TGA can be employed to study the thermal decomposition of polymers and to analyse the content of humidity, volatiles, additives, and fillers in polymeric materials. The analysed HIPS materials exhibit similar thermal decomposition behaviour in one single stage between 350-500ºC, when the polymeric chains break down and evolve to the gaseous phase. The onset temperature of the thermal decomposition (T_{onset}), the temperature range of decomposition, the temperature of the maximum decomposition rate (T_{max}), and the percentage of non-degraded residue have been calculated from the thermograms of the analysed HIPS samples (Table 4.7). The onset temperature of thermal decomposition has similar values for all the HIPS materials at around 365ºC; only the sample HIPS5 may be more sensitive to thermal degradation, with a lower T_{onset}. The temperature of maximum decomposition rate appears at around 430ºC for all the samples. The residue percentage indicates the content of inorganic material in the different samples. All the samples from the recycling plant possess higher residue content than the virgin material, with HIPS2 and HIPS7 showing the highest residue levels.

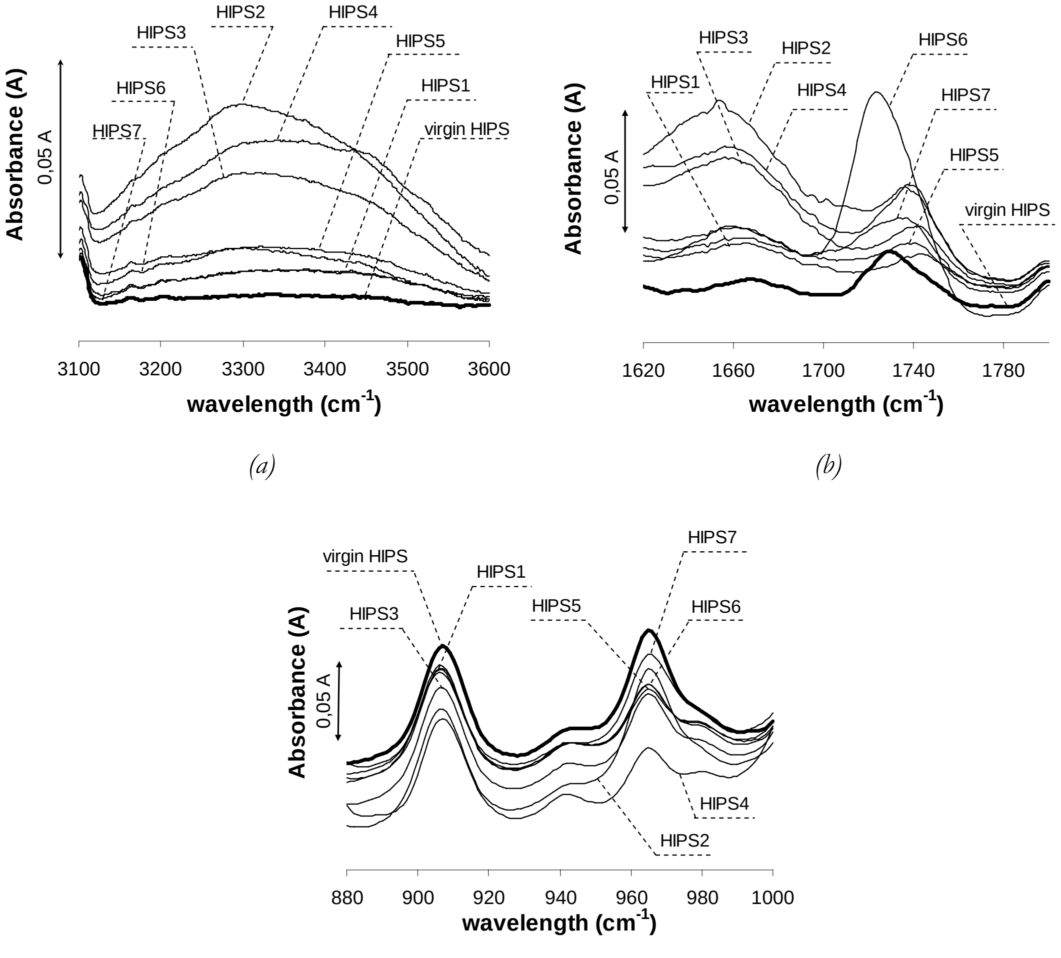
Sample	**T_{onset}** (ºC)	**Decomposition temperature range** (ºC)	**T_{max}** (ºC)	**Residue** (%)
Virgin HIPS	369,1	369-490	433,4	1,2
HIPS1	367,2	367-486	425,6	2,0
HIPS2	366,7	367-500	435,8	3,5
HIPS3	365,2	365-490	422,0	1,5
HIPS4	363,2	363-485	426,8	1,7
HIPS5	353,2	353-480	423,5	1,6
HIPS6	370,5	370-485	428,1	2,9
HIPS7	365,6	366-495	431,1	3,4

Table 4.7. Results from thermogravimetric analysis: Onset temperature of thermal degradation (T_{onset}), decomposition temperature range, temperature of maximum decomposition rate (T_{max}), and residue percentage.

4.2.3 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 in the changes in their chemical structure.

The regions corresponding to the hydroxyl group, the carbonyl groups, and the double bond groups from the PB phase corresponding to the peak of trans-1,4 and vinyl-1,2 groups were analyzed in detail employing FTIR. Figure 4.13 represents the absorbance spectra of the HIPS samples in the hydroxyl, carbonyl, and unsaturated regions. The recycled samples show, in general, higher absorbance in the hydroxyl and carbonyl regions than 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 peaks in the recycled materials can be qualitatively observed.



(a) *(b)*

(c)

Figure 4.13. FTIR spectra of the HIPS samples: a) hydroxyl region (3100-3600cm^{-1}); b) carbonyl region (1620-1800cm^{-1}); c) unsaturated region (880-1000cm^{-1}).

Figure 4.14 represents the FTIR hydroxyl, carbonyl, trans-1,4, and vinyl-1,2, functional group indexes for the analysed HIPS samples. The diminution of the unsaturated functional groups (vinyl-1,2 and trans-1,4) and the increase of the hydroxyl and carbonyl groups in the real recycling samples, compared to the virgin material, may prove the occurrence of PB oxidation during previous life and recycling of HIPS, resulting in a wide variety of oxidised structures in the polymeric chains [44, 45, 53]. The calculation of the hydroxyl, carbonyl, vinyl-1,2 and trans-1,4 indexes could therefore be employed to verify the degree of degradation in recycled plastics and to assess the content of unsaturated groups in recycled HIPS.

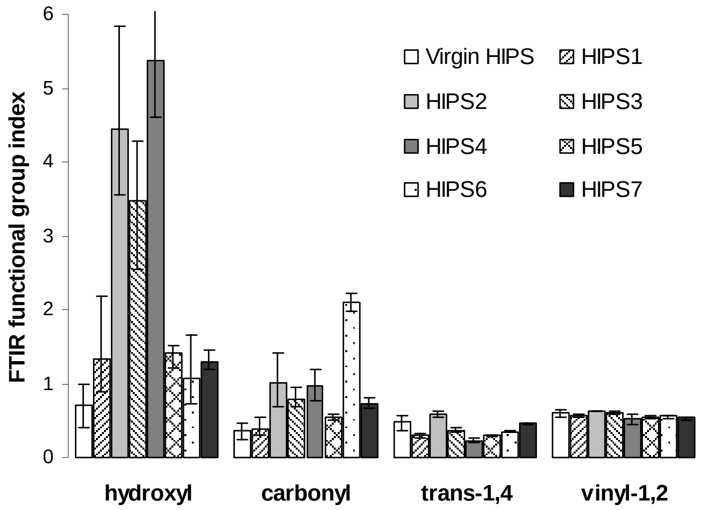


Figure 4.14. FTIR functional group indexes (hydroxyl; carbonyl; trans-1,4; vinyl-1,2) for the HIPS samples.

Raman spectroscopy was used for the analysis of PB-phase microstructure in HIPS samples from the large-scale mechanical recycling process. Conventional Raman spectroscopy has, however, the limitation that it cannot be employed for the analysis coloured samples because of the fluorescence emission that covers the polymer spectrum; 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 in order to resolve the three bands corresponding to the PB microstructure as shown in Figure 4.4; the Raman functional groups for the unsaturated groups were accordingly calculated. As the results in Figure 4.15 indicate, the PB microstructure content is generally lower in the recycled HIPS samples than in the 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.

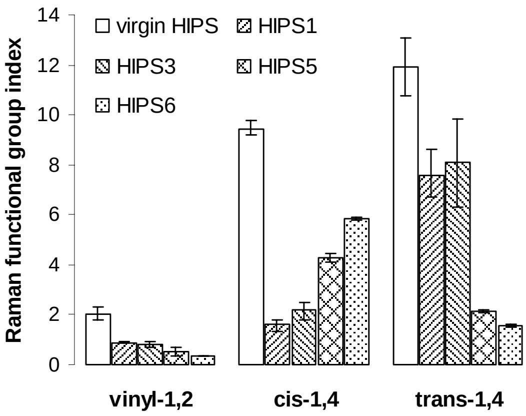


Figure 4.15. Raman functional group indexes (vinyl-1,2; cis-1,4; trans-1,4) for the HIPS samples.

4.2.4 Presence of low molecular weight compounds

The presence of low molecular weight compounds in recycled HIPS was assessed by microwave-assisted extraction followed by analysis of the extracts using GC-MS. Figure 4.16 presents a total ion chromatogram (TIC) from the extract of recycled HIPS as an example of the resulting chromatograms for the analysed materials. At a glance, different zones can be observed: A first zone until approximately 800s where the volatile organic compounds (VOCs) appear; a second zone around 900s where styrene dimers (residues from polymerisation) elute; a third zone around 1400s where different peaks from the styrene trimers (residues of polymerisation) appear; and, finally, a fourth zone at longer elution times where different aliphatic compounds can be found.

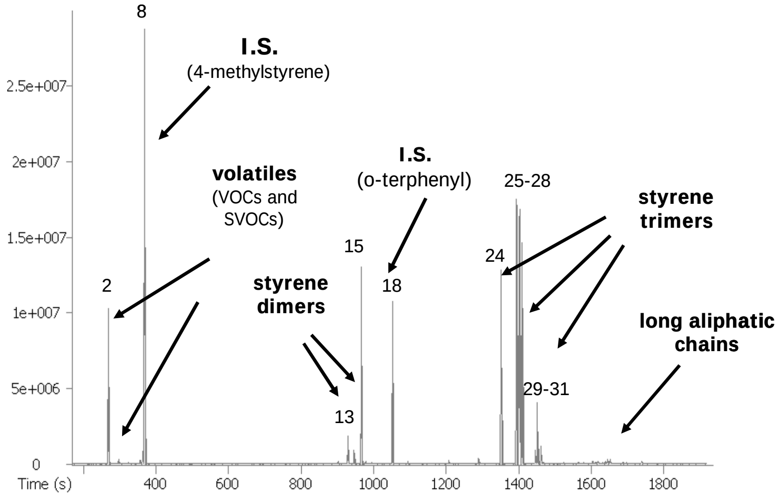


Figure 4.16. Total Ion Chromatogram (TIC) of the low molecular weight compounds extracted from recycled HIPS.

Table 4.8 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 [112, 114, 115]. 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 indicated 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 [17]. Styrene as the monomer residue is the most important compound of this group, in terms of relative abundance, and its content appears to be an important quality property in recycled HIPS. The presence of oxygenated derivates of styrene, such as benzaldehyde (peak 6), α-methylbenzenealdehyde (peak 9), and acetophenone (peak 9), has been attributed to the oxidation of polystyrene [62]; thus, the presence of these compounds in recycled samples with higher relative abundance than in the virgin material may be a result of the degradative processes to which HIPS has been subjected during its previous 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 processing of polystyrene [119],which could explain the higher relative abundance in the recycled samples than in the scrap. Other styrene dimers, such as cis- and trans-1,2-diphenylcyclobutane (peaks 13 and 15, respectively), 2,4-diphenyl-1-butene (peak 14), 1-phenyltetralin (peak 16), and 1,2-dihydro-4-phenylnaphtalene (peak 17), have been reported to be produced during polymerisation of styrene [120-123] and are retained in the polymeric matrix as polymerisation residues. The abundance of peaks 13-17 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 contaminations that may have penetrated the polymeric matrix in recycled materials. Traces of phtalates (dibutylphtalate, diethylphtalate) were also found in the HIPS extracts and in the blank analyses, so these compounds were assumed to be present in the laboratory environment. Different styrene timers have been found in both the virgin and the recycled HIPS samples, which have been also reported to be formed during the polymerisation of styrene [120, 121, 123, 125, 126]. Some of these trimers, such as 1,3,5-triphenylhexene-5 and the four different diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline, could be identified through bibliographic comparison of their mass spectra.

Peak nr.	Proposed compound	R.T. (s)	Quant. ion	Relative abundance (x10^3)							
				Virgin HIPS	HIPS1	HIPS2	HIPS3	HIPS4	HIPS5	HIPS6	HIPS7
1	Ethylbenzene [a]	238	91	-	101	102	66	2	-	2	8
2	Styrene [a]	269	104	2254	714	606	783	892	845	1579	1083
3	Benzene, (1-methylethyl)- [a]	297	105	49	29	40	82	64	31	29	49
4	Benzene, propyl- [a]	325	91	21	46	35	96	50	22	19	40
5	Benzene, 1-ethyl-4-methyl- [a]	333	120	13	2	5	-	-	-	-	-
6	Benzaldehyde [a]	335	106	10	11	35	8	50	25	29	22
7	Heptane, 2,2,4,6,6-pentamethyl- [a]	357	57	66	31	30	-	26	18	14	18
8	4-methylstyrene	368	65	Internal standard (I.S.)							
9	Benzeneacetaldehyde, α-methyl- [a]	376	105	-	4	9	-	10	-	3	9
10	Acetophenone [a]	429	105	6	-	30	5	97	17	42	54
11	Butylated Hydroxytoluene [a]	794	205	-	-	16	-	20	-	-	25
12	Benzene, 1,1'-(1,3-propanediyl)bis- [a]	902	92	17	13	35	11	31	24	29	35
13	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis- [b]	929	104	405	192	231	327	183	123	180	136
14	2,4-diphenyl-1-butene [c]	946	91	137	81	138	73	134	105	142	190
15	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans- [b]	966	104	2757	865	2065	1078	2423	1498	1655	1895
16	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- [a]	979	130	8	17	10	4	9	5	-	-
17	Naphthalene, 1,2-dihydro-4-phenyl- [a]	994	91	7	6	-	5	8	5	8	-
18	o-Terphenyl	1052	114	Internal standard (I.S.)							
19	n-Hexadecanoic acid [a]	1095	60	10	17	98	9	40	42	28	43
20	Octadecanoic acid [a]	1208	60	11	11	54	6	29	48	25	67
21	Hexadecanoic acid, butyl ester [a]	1220	56	-	-	-	-	32	2	69	19
22	octadecanoic acid, butyl ester [a]	1324	129		6	13		8	12	17	8

[a] Proposed identification by comparison to the NIST database; [b] Proposed identification through bibliography [121]; [c] Proposed identification through bibliography [124]

Table 4.8. Relative abundance and chromatographic properties of the identified low molecular weight compounds in HIPS samples

4.3 ANALYSIS OF BROMINATED FLAME RETARDANTS IN STYRENIC POLYMER SAMPLES

The presence of brominated flame retardants (BFRs) in plastic wastes and recyclates from electrical and electronic equipment is one of the main quality aspects for the improved recycling of these polymeric waste streams. Legislation has been recently introduced to restrict the use of different flame retardants in new polymers for electrical and electronic applications, and to regulate the waste disposal of their residues. The development of fast and reliable analytical techniques for the detection and quantification of BFRs in polymeric samples is therefore of great interest, both from a technological and a scientific point of view. Different solvent extraction techniques (microwave-assisted extraction, ultrasonic-assisted extraction, and pressurised liquid extraction) have been compared for the screening and determination of BFRs in HIPS. Liquid chromatography has been employed for detection purposes.

4.3.1 Development of the chromatographic methods for analysis of BFRs

4.3.1.1 HPLC-UV

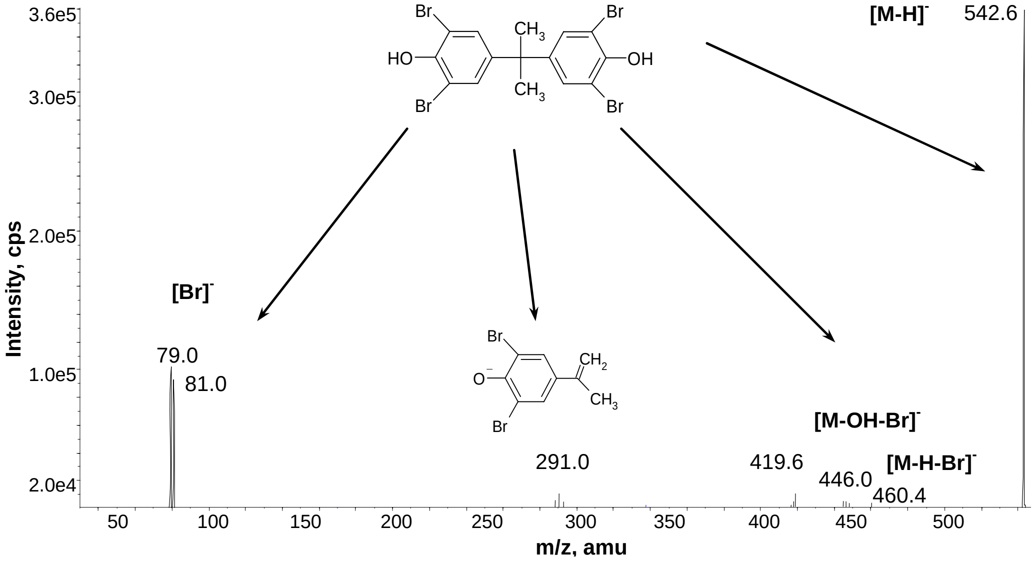
The optimisation of the spectrometric detection was achieved by injection of standard solutions of the analytes in tetrahydrofurane in the range 1 – 1000 μg/ml into the HPLC-UV. The initial chromatographic parameters (column, mobile phase, mobile flow, temperature) were first directly chosen from previous bibliographic results [85], and further adjustments were performed to satisfy the requirements for successful separation and detection. Different wavelengths for the DAD detection were tested and finally a wavelength of 220 nm was selected. The retention times, limit of detection (LOD), limit of quantification (LOQ), and the linearity range for TBBPA and Deca-BDE have been calculated for the developed HPLC-UV method and are presented in Table 4.9.

Analyte	**Retention time, t_R** (min)	**LOD (S/N=3)** (μg/ml)	**LOQ (S/N=10)** (μg/ml)	**Linearity range** (μg/ml) **(regression coefficient)**
TBBPA	11.1	0.49	1.63	5-1000 (0.9962)
Deca-BDE	20.6	0.21	0.68	1-1000 (0.9971)

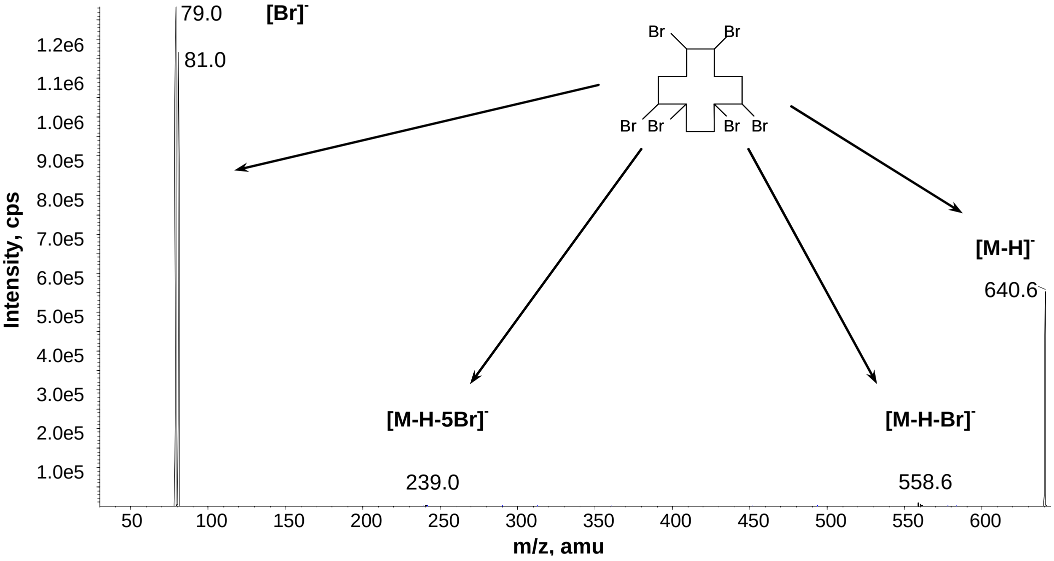
Table 4.9. Limit of detection (LOD), limit of quantification (LOQ) and linearity of the analytical detection for the different BFRs using HPLC-UV.

4.3.1.2 HPLC-MS/MS

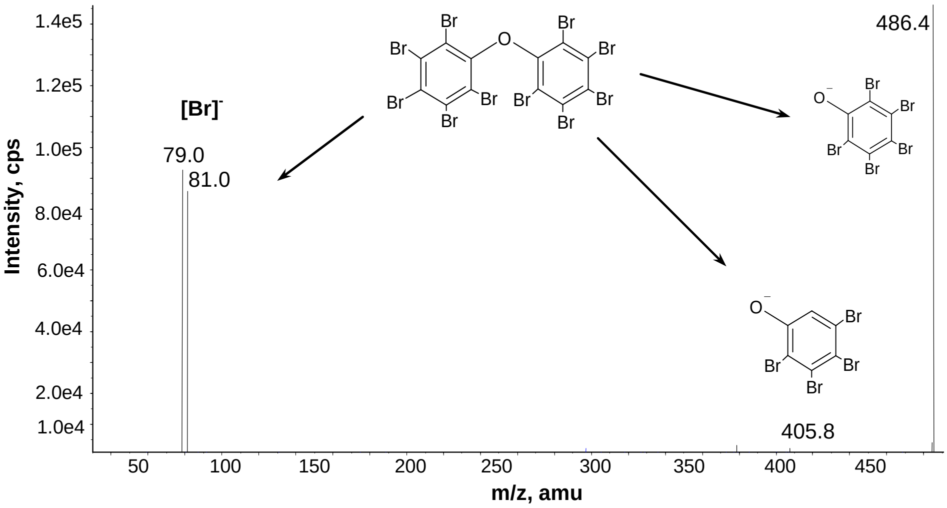
The optimisation of the MS sensitivity was performed by direct infusion of the standard analytes in acetonitrile into the APCI mass spectrometer. Figure 4.17 shows the full scan mass spectra of TBBPA, HBCD, and Deca-BDE. According to these fragmentation results, the MRM signals corresponding to *m/z* 543→79 and *m/z* 543→81 for TBBPA, *m/z* 641→79 and *m/z* 641→81 for the three HBCD congeners, and *m/z* 487→79 and m/z 487→81 for Deca-BDE, were selected and compared in terms of LOD, LOQ and linearity, to detect and quantify the flame retardant content in the extracts.



(a)



(b)



(c)

Figure 4.17. Full scan mass spectra of the BFRs acquired in the APCI negative mode by direct infusion of standard solutions in acetonitrile: a) TBBPA; b) HBCD; c) Deca-BDE.

Chromatographic parameters were adjusted until complete separation of the different analytes, specifically the three different HBCD isomers, was achieved with a reasonable analysis time. Figure 4.18 shows a combined chromatogram of the superposed MRM signals for TBBPA (543→79); α–, β–, and γ-congeners of HBCD (641→79); and Deca-BDE (487→79).

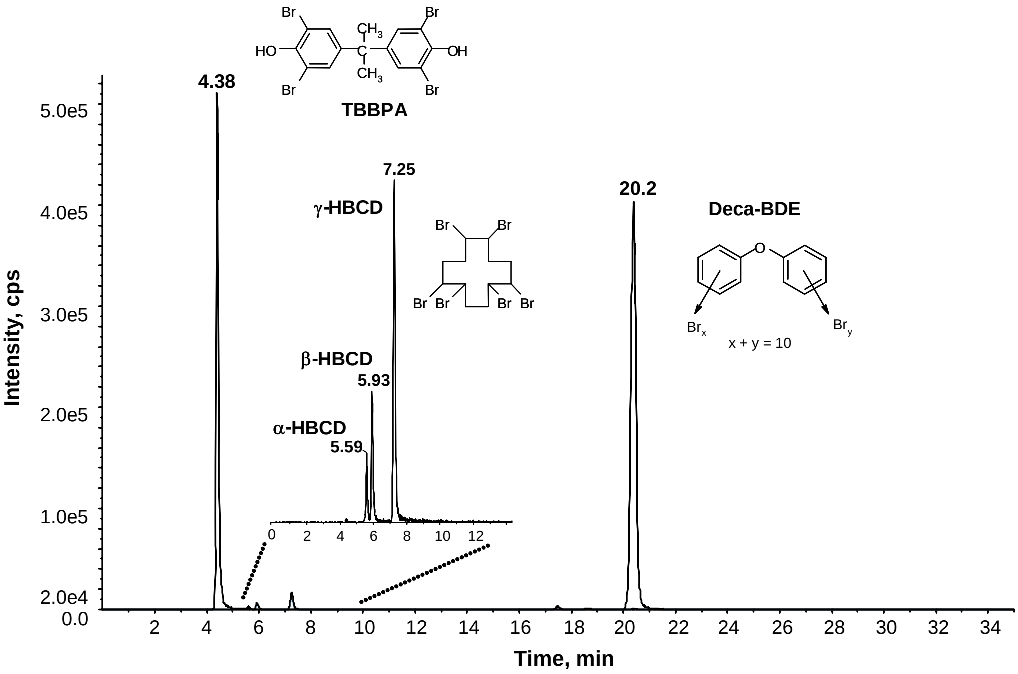


Figure 4.18. Chromatogram for the superposed MRM signals corresponding to TBBPA (543→79), α–, β-, and γ- HBCD congeners (641→79), and Deca-BDE (487→79).

It is worth mentioning that Deca-BDE is especially sensitive to debromination decomposition into lower order PBDEs when exposed to UV and sunlight radiation and/or during solution in alcohols. The extracts and the technical standard solutions were therefore analysed shortly after preparation, and no further sign of Deca-BDE debromination could be observed in the chromatograms.

The limit of detection (LOD) and limit of quantification (LOQ) for the studied flame retardants were calculated from the reference solutions for each compound and quantification MRM ion pairs (Table 4.10). HBCD has a relatively higher LOD and LOQ compared to TBBPA and Deca-BDE due to the relatively low ionisation efficiency in APCI. Other studies have pointed out the idoneity of electrospray ionisation (ESI) for the analysis of more polar flame retardants such as TBBPA and HBCD [129-132], but polybrominated diphenyl ethers generally cannot be analysed using ESI, which is why APCI was selected. The linearity range of each analyte is also shown in Table 3.8; the dynamic range of Deca-BDE was lower compared to the other compounds. Regardless of these differences, the quantification of the extracts was performed adjusting the concentration to the linearity range of the flame retardants in the HPLC-MS/MS method. In general, the MRM signals obtained from both Br_{79} and Br_{81} isotopes at the third quadrupole (Q3), can be used for the determination of the selected BFRs, with similar LOD, LOQ, and linearity conditions.

Analyte	**t_R** (min)	**MRM quant. ions**	**LOD (S/N=3)** (µg/ml)	**LOQ (S/N=10)** (µg/ml)	**Linearity range** (µg/ml) **(regression coefficient)**
TBBPA	4.38	543→79	0.025	0.083	0.1-50 (0.9990)
		543→81	0.014	0.047	0.1-50 (0.9946)
α-HBCD	5.59	641→79	0.8	2.7	0.1-50 (0.9996)
		641→81	1.0	3.4	0.1-50 (0.9994)
β-HBCD	5.93	641→79	0.3	1.2	0.1-50 (0.9954)
		641→81	0.4	1.5	0.1-50 (0.9993)
γ-HBCD	7.25	641→79	0.2	0.5	0.1-50 (0.9993)
		641→81	0.1	0.4	0.1-50 (0.9981)
Deca-BDE	20.2	487→79	0.011	0.036	0.1-25 (0.9938)
		487→81	0.012	0.040	0.1-25 (0.9937)

Table 4.10. Limit of detection (LOD), limit of quantification (LOQ) and linearity of the analytical detection for the different BFRs using HPLC-MS/MS.

4.3.2 Comparison of extraction methods of BFRs from reference HIPS

4.3.2.1 *Choice of operational parameters for the extraction of BFRs*

Several extraction parameters (type of extractive solvent, extraction time, particle size) have been considered to optimise the extraction recovery of BFRs from standard HIPS with known content of BFRs, using different solvent extraction techniques.

The selection of the extractive solution plays a critical role in the extraction of additives from polymeric matrixes. In microwave-assisted extraction, from an operational point of view, the solvent system must possess certain dielectric permittivity to absorb microwave energy in order to be heated. Careful selection of the extraction solution is fundamental when performing pressurised liquid extraction on polymeric samples; solvents that show high extraction efficiency in traditional solvent procedures may not work at the elevated pressure and temperature conditions of PLE. In general, the selected solvents must on one hand exhibit high swelling capability without solving the polymeric matrix at the temperature and pressure ranges of extraction; on the other hand, the analytes of interest should have good affinity for the extraction solution [133]. Mixed solvents with combined polar and non/polar nature normally offer a good approach to extract analytes with different polarities and molecular weight [134]. Finally, the employment of hazardous solvents should try to be avoided, taking into account an occupational health point of view. The selection of the extraction solvents was therefore difficult, due to the nature of the matrix (in the case of HIPS, a blend of polystyrene and polybutadiene), and the low quantity of solvent systems that satisfy *a priori* the aforementioned requirements; solvent mixtures with different polar nature such as isopropanol/methanol (1.1, v/v) and isopropanol/n-hexane (1:1, v/v) were thus considered.

Temperature has a dramatic effect on the extraction of analytes from polymers, due to its synergistic effect on both polymeric structure and extraction kinetics. The extraction temperature should be above the glass transition temperature (T_g) of the polymeric matrix, to increase polymer mobility during extraction conditions. For the case of styrenic copolymers, PS has its T_g at around 90°C, so temperatures above this range should result in enhanced extraction yields. On the other hand, temperature acts upon each stage of the solvent extraction process. Higher temperatures result in higher analyte diffusion rates (both in the polymer core and in the boundary layer around the polymer surface), increase analyte solubility in the extractive solvent, and enhance mass transfer from the boundary layer to the solvent bulk. The swelling ratio between the polymeric matrix and the solvent is also influenced by the extraction temperature.

Finally, particle size also influences the extraction recoveries from polymers. Smaller particle size should result in faster and enhanced extraction rates, due to enhanced diffusion of the analytes from the polymer core to the polymer surface.

4.3.2.2 Pressurised liquid extraction (PLE)

A method for the extraction of selected brominated flame retardants from HIPS using pressurised liquid extraction was developed and optimised, by considering different extraction solvent systems, extraction temperatures, and number of consecutive extraction steps (directly related to the extraction time). Table 4.11 presents the results of the calculated accumulative concentration of TBBPA, HBCD congeners, and Deca-BDE in the standard HIPS samples, using PLE under different operational conditions; the effect of the temperature, extraction steps, and solvent type is discussed from these results.

Considering the type of extraction solvent, an isopropanol/n-hexane extraction agent with combined polar/non-polar behaviour offered significantly higher calculated concentrations of the BFRs than a mixture of polar solvents (isopropanol/methanol) under moderate temperature conditions of 90°C and 110°C in the pressurised PLE cell. For higher temperatures, however, both solvent systems give similar concentrations under the pressurised conditions of PLE; solvents that may not perform as good extractant solutions at moderate pressure and temperature conditions, such as methanol/isopropanol, can therefore be employed at the operation ranges of PLE. On the other hand, extraction of TBBPA at 150°C with isopropanol/n-hexane gives low extraction yield; this may be caused by the excessive swelling and collapse of the polymeric structure caused by the solvent under the extreme temperature and pressure extraction conditions.

Increasing extraction temperatures result generally in faster extraction of the additives from the polymeric matrixes and enhanced recovery rates. However, some precautions have to be taken in the choice of extraction temperature conditions, considering the stability of the analytes. In this direction, anomalous concentrations for the γ-HBCD conformer at 130°C and 150°C can be observed compared to the α- and β-conformers. HBCD is thermally unstable and undergoes conformational changes at temperatures around 160°C [135], which explains the remarkably low γ-HBCD content at these temperatures.

Solvent	T (°C)	Steps	**Calculated BFR accumulative concentration (mg/g)**									
			TBBPA		**α-HBCD**		**β-HBCD**		**γ-HBCD**		**Deca-BDE**	
			543/79	**543/81**	**641/79**	**641/81**	**641/79**	**649/81**	**649/79**	**649/81**	**487/79**	**487/81**
IP MeOH (1:1 v/v)	90	1	45.56	50.43	15.91	14.90	15.53	15.53	15.79	15.04	8.28	8.24
		2	46.23	51.10	16.60	15.59	16.15	16.11	16.39	15.73	12.64	12.87
		3	46.28	51.14	16.66	15.66	16.19	16.11	16.45	15.79	14.24	14.54
		4	46.30	51.15	16.66	15.66	16.19	16.11	16.47	15.80	14.98	15.31
	110	1	49.91	51.09	16.72	16.72	16.62	17.69	16.07	16.07	16.96	17.69
		2	50.00	51.19	16.83	16.81	16.73	17.76	16.17	16.17	18.61	19.46
		3	50.08	51.27	16.88	16.86	16.79	17.80	16.23	16.23	19.18	20.05
		4	50.08	51.32	16.88	16.86	16.79	17.80	16.23	16.23	21.37	22.21
	130	1	50.37	49.86	19.31	21.69	19.48	21.44	19.26	19.09	23.48	24.05
		2	51.31	50.81	20.64	23.00	20.64	22.55	20.49	20.41	24.28	24.87
		3	51.38	50.87	20.64	23.03	20.64	22.55	20.50	20.41	24.39	24.98
		4	51.40	50.88	20.64	23.03	20.64	22.55	20.50	20.41	24.39	24.99
	150	1	23.81	23.81	14.23	13.80	10.91	11.07	7.57	8.49	17.36	17.63
		2	32.32	32.79	21.58	20.37	15.67	15.98	11.40	12.70	25.46	26.03
		3	36.62	37.23	26.83	25.34	18.36	18.60	13.45	14.80	32.42	33.32
		4	38.88	39.51	30.35	28.58	19.82	20.07	14.39	15.75	37.17	38.06
IP hexane (1:1 v/v)	90	1	19.15	19.48	5.88	5.45	5.65	5.45	5.28	5.53	2.41	2.52
		2	25.07	25.00	8.58	8.00	8.48	8.46	7.90	8.15	4.97	5.20
		3	27.48	27.38	9.87	9.21	9.70	9.71	8.94	9.24	6.56	6.90
		4	28.87	28.78	10.57	9.97	10.43	10.52	9.66	9.96	7.84	8.20
	110	1	21.24	22.22	9.48	8.69	8.77	9.62	8.12	8.44	7.02	7.53
		2	23.70	24.66	11.26	10.41	10.45	11.34	9.71	10.09	9.38	10.09
		3	24.35	25.32	11.93	11.00	11.01	11.92	10.27	10.67	10.40	11.18
		4	24.57	25.54	12.18	11.25	11.21	12.07	10.48	10.88	10.96	11.76
	130	1	43.27	45.03	19.91	20.93	16.88	17.37	11.04	10.99	8.46	8.62
		2	48.51	50.51	23.28	24.52	19.55	20.35	13.04	13.01	17.09	17.43
		3	48.64	50.64	23.46	24.70	19.69	20.50	13.18	13.15	18.73	19.09
		4	48.67	50.68	23.53	24.76	19.74	20.55	13.23	13.20	19.51	19.91
	150	1	51.47	52.73	21.30	23.83	18.20	18.35	19.41	18.54	21.73	21.09
		2	53.98	55.26	22.38	24.96	19.12	19.16	20.29	19.39	23.62	23.03
		3	54.02	55.30	22.44	25.02	19.18	19.22	20.34	19.44	23.73	23.14
		4	54.05	55.32	22.44	25.02	19.18	19.22	20.34	19.44	23.79	23.20

Table 4.11. Calculated accumulative concentration of BFRs in the standard HIPS samples using pressurised liquid extraction under different conditions

Finally, the properties of the analytes (molecular weight, polarity, affinity towards polymeric matrix and solvent, stability) play an important role in the mobility and the extraction rate during PLE. Full extraction of medium molecular weight flame retardants such as TBBPA and HBCD can be achieved using only 1-2 extraction steps at temperatures of 110°C - 130°C with a mixture of polar/non-polar solvent. For a higher molecular weight compound such as Deca-BDE, an extraction yield of only approximately 50% could be attained under the same extraction conditions (130°C, isopropanol/n-hexane); further extraction steps do not show an appreciable increase in the extraction yield under the same conditions. However, the extraction yield for Deca-BDE could be increased to nearly 75% using more severe temperature conditions such as 150°C.

4.3.2.3 Ultrasound-assisted extraction (UAE)

Ultrasonication was performed at the maximum operational conditions of the equipment (65°C and 60 minutes) on the standard HIPS samples with BFRs. Low or medium concentrations of BFRs in standard HIPS samples could be calculated using UAE at the extraction conditions (Table 4.12); this low recovery may be due to the limiting temperature extractive conditions far below the T_g of polystyrene, which may hinder polymeric chain mobility and analyte diffusion.

In general, positive effects on the extraction yields are obtained using mixed solvent systems and lower particle size. Extraction recoveries of approximately 50 - 60% compared to the initial concentration could be easily obtained for TBBPA and HBCD from polymer powder using isopropanol/n-hexane as extractant solution; for Deca-BDE, on the other hand, other extraction procedures should be considered with the possibility of applying higher temperatures to increase the poor extraction yield obtained using UAE.

UAE offers a fast extraction procedure for scanning for the presence of BFRs in styrenic plastics, but lower extraction recovery yields are obtained in comparison with other extraction procedures. A similar method for the detection of BFRs from polymeric samples has been proposed earlier, which offers detection limits compliant with European legislation [84], but no results from extraction yields are provided for comparison.

Solvent	Sample size	Calculated BFR concentration, in mg/g (RSD, in %)									
		TBBPA		**α-HBCD**		**β-HBCD**		**γ-HBCD**		**Deca-BDE**	
		543/79	**543/81**	**641/79**	**641/81**	**641/79**	**649/81**	**649/79**	**649/81**	**487/79**	**487/81**
IP/ MeOH (1:1 v/v)	granule	3.16 (28.4)	3.22 (26.2)	0.87 (26.4)	0.88 (35.3)	1.05 (31.0)	0.98 (16.2)	0.74 (21.4)	0.79 (14.8)	1.06 (18.5)	1.07 (32.2)
	powder	4.85 (27.3)	5.04 (9.2)	1.84 (12.9)	1.88 (23.2)	1.51 (25.1)	1.91 (41.2)	1.32 (59.7)	1.43 (20.4)	1.15 (10.1)	1.12 (20.0)
IP/ hexane (1:1 v/v)	granule	21.17 (2.6)	21.76 (1.9)	7.07 (9.0)	7.57 (9.0)	7.07 (6.1)	7.83 (2.8)	6.52 (9.8)	6.64 (5.6)	1.78 (18.2)	1.86 (19.3)
	powder	26.91 (0.8)	27.53 (6.4)	10.29 (11.0)	9.21 (2.7)	9.85 (1.4)	10.42 (7.4)	9.54 (9.1)	9.81 (7.7)	1.60 (15.5)	1.66 (12.6)

Table 4.12. Calculated accumulative concentration of BFRs in the standard HIPS samples using ultrasound-assisted extraction under different conditions.

4.3.2.4 Microwave-assisted extraction (MAE)

MAE offers almost complete recovery of TBBPA and HBCD using isopropanol/n-hexane as solvents at 130°C for 60 minutes, with calculated concentrations similar to the initial BFR composition of the standard HIPS samples, whereas lower calculated concentrations are obtained for Deca-BDE (Table 4.13). The effect of microwaves and high temperatures may cause isomerisation of the β- and γ-HBCD congeners into the more thermally stable α-HBCD, as shown by the anomalous concentration results for the three HBCD congeners.

Solvent	Sample size	Calculated BFR concentration, in mg/g (RSD, in %)									
		TBBPA		**α-HBCD**		**β-HBCD**		**γ-HBCD**		**Deca-BDE**	
		543/79	**543/81**	**641/79**	**641/81**	**641/79**	**649/81**	**649/79**	**649/81**	**487/79**	**487/81**
IP/ MeOH (1:1 v/v)	granule	28.02 (1.1)	26.94 (6.3)	12.16 (9.1)	10.23 (23.1)	9.84 (1.4)	8.61 (12.3)	8.61 (8.1)	8.93 (7.0)	7.04 (13.6)	7.21 (11.5)
	powder	43.83 (1.7)	42.22 (7.1)	21.18 (6.4)	16.34 (5.2)	15.79 (7.5)	14.04 (5.3)	14.04 (5.5)	15.17 (3.2)	8.89 (13.4)	9.01 (14.1)
IP/ hexane (1:1 v/v)	granule	41.21 (7.0)	41.69 (3.2)	19.94 (9.6)	17.23 (11.8)	18.25 (9.2)	15.91 (8.0)	15.91 (7.1)	17.61 (3.2)	11.56 (3.8)	10.31 (24.2)
	powder	42.19 (2.7)	43.15 (3.4)	21.91 (5.8)	19.14 (4.9)	19.20 (1.6)	17.61 (3.3)	17.61 (8.1)	20.61 (5.1)	13.51 (10.8)	13.42 (12.7)

Table 4.13. Calculated accumulative concentration of BFRs in the standard HIPS samples using microwave-assisted extraction under different conditions.

As noted for ultrasonic-assisted extraction, using a mixed polar/non-polar extraction solvent system and reduced particle size enhances the extraction yield, attributable to a higher swelling effect of the solvent, higher affinity of the analytes, and favourable diffusion of the analytes from the polymeric matrix to the extractant media. The ability of MAE to reach extraction temperatures above the solvents boiling point and above the structural T_g of the polymeric material enhances the extraction recoveries and indicates the suitability of this technique for the determination of BFRs in plastic matrixes.

4.3.2.5 Comparison of PLE, UAE, and MAE for the extraction of BFRs from HIPS

Figure 4.19 compares the extraction efficiency of UAE, MAE, and PLE from standard powder-form HIPS samples for the different brominated flame retardants using isopropanol/n-hexane and methanol/isopropanol as solvents for the most suitable extraction conditions (65°C, 60 minutes for ASE; 130°C, 60 minutes for MAE; 130°C, 2 extraction steps for PLE). Complete extraction of TBBPA and HBCD can be achieved using MAE and PLE at the abovementioned conditions; for high molecular weight compounds such as Deca-BDE, the pressurised conditions of PLE offer by far the highest extraction yields. The extraction results obtained using PLE and MAE are similar or even higher that those reported by other authors using supercritical fluid extraction, especially for HBCD [83]. Mixed polar/non-polar solvent systems such as isopropanol/n-hexane allow, in general, higher extraction rates than polar mixtures such as methanol/isopropanol alone.

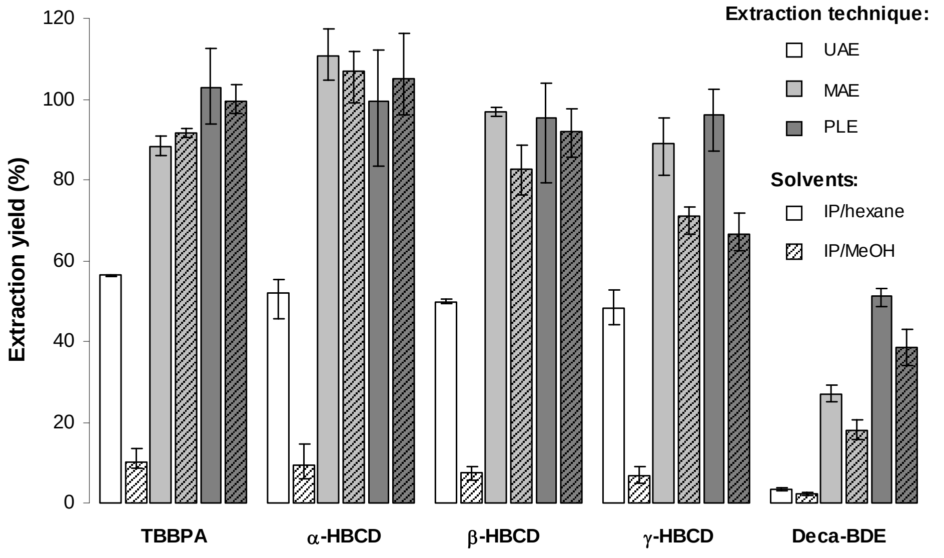
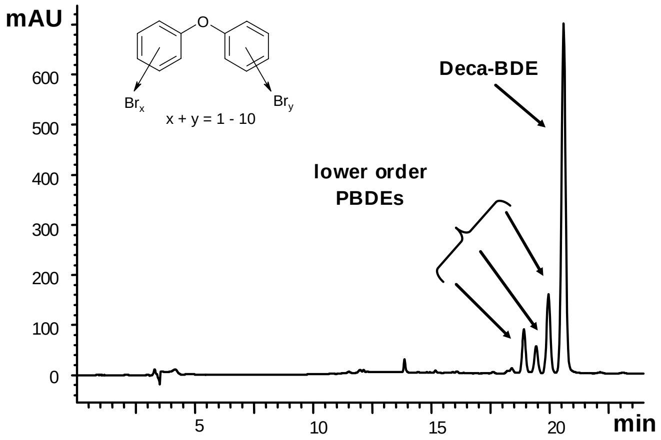


Figure 4.19. Comparison of the extraction yield of PLE, MAE, and PLE for the different BFRs from standard HIPS samples.

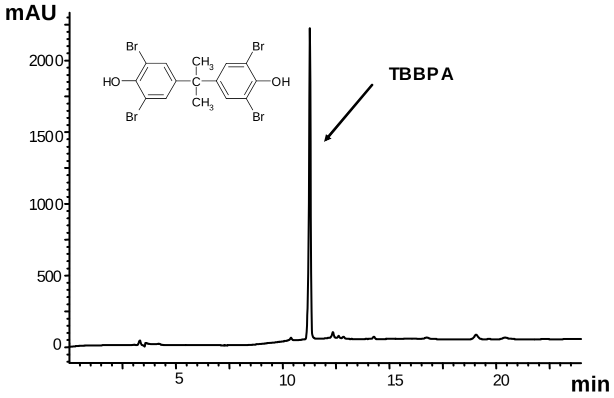
4.3.3 Determination of BFRs from standard samples from WEEE

The analytical method developed for the determination of BFRs in standard styrenic polymeric samples has been further applied for the identification and quantification of BFRs in different recycled polymeric samples from waste electrical and electronic equipment (WEEE). The samples described in Table 3.2 have been therefore extracted using MAE and their extracts have been analysed using HPLC-UV.

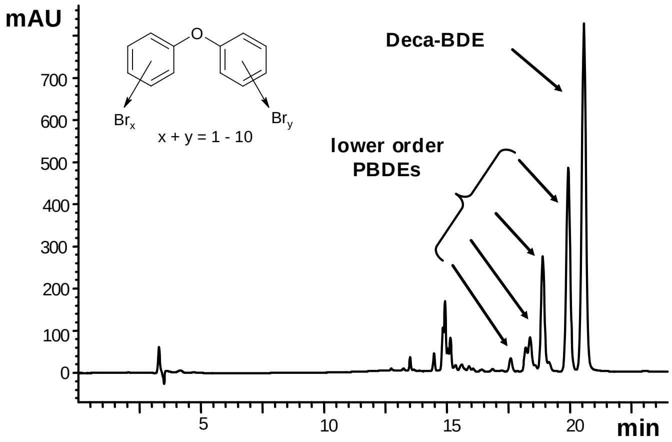
Figure 4.20 shows the chromatograms of the extracts for the standard WEEE samples. The sample ABS-GVL2-07 shows, in addition to the main peak corresponding to Deca-BDE (t_R=20.6 min), other minor peaks that may correspond with other PBDE congeners with lower bromination degree at t_R=20.0 min, t_R=19.4 min, and t_R=18.9 min, either originally contained in the technical Deca-BDE grade used in the manufacture of the plastic component, or due to the debromination of the BFR during service life and further recycling (Figure 4.20a). Sample ABS-GVL2-11 shows a single clear peak corresponding with TBBPA at t_R=11.1 min, proving that the flame retardant has been successfully extracted from the polymeric matrix (Figure 4.20b). Finally, different peaks can be observed in the chromatogram corresponding to sample SB-GVL2-07; the main peak assigned to Deca-BDE at t_R=20.6 min and other peaks that may be attributed to other PBDE congeners at t_R=19.9 min, t_R=18.9 min, and t_R=18.4 min (Figure 4.20c).



(a)



(b)



(c)

Figure 4.20. HPLC-UV chromatograms for the extracted standard WEEE samples using MAE (solvent: isopropanol/n-hexane, 60 minutes, 130ºC): (a) ABS-GVL2-11; (b) SB-GVL2-07; (c) ABS-GVL2-07.

5. CONCLUSIONS

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

  A wide range of analytical techniques such as thermal analysis, mechanical testing, vibrational spectroscopy, chromatography, and electron microscopy were employed to monitor the degree of degradation of HIPS throughout repeated extrusion cycles and thermo-oxidative exposure. The selected procedure proved to be useful to analyse the degradative effects undergone by recycled HIPS during the life cycle.

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

  The oxidative stability of HIPS is clearly affected by both the reprocessing cycles and by thermo-oxidative ageing; this effect was however more noticeable in the aged samples. MFR increased slightly with the reprocessing steps, which may be related to a decrease in the molecular weight of the polymer. The elastic modulus is not severely changed by multiple processing and thermo-oxidative ageing. Contrarily, the elongation at break progressively decreased with the consecutive reprocessing steps and collapsed after long exposure to thermo-oxidation at 90°C. Reprocessing induces heterogeneous changes in the chemical structure of HIPS, with the formation of oxidative moieties and consumption of part of the unsaturations. On the other hand, thermo-oxidative ageing mainly affected the PB phase in HIPS, with a clear reduction of the unsaturated groups and formation of hydroxyl and carboxyl groups. PB microstructures are differently affected by reprocessing and thermo-oxidation, being cis-1,4 and trans-1,4 more susceptible to these degradation mechanisms than vinyl-1,2. The dynamic-mechanical relaxations associated to the glass transition of PB and PS phases are also influenced by multiple processing and thermo-oxidation, as it has been demonstrated by their study according to free volume theory.

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

  Thermo-mechanical degradation caused by multiple processing may be responsible for the alteration of the physical structure and the occurrence of crosslinking in the rubber phase, together with chain scission and rearrangement of the polymeric chains in the PS matrix. Thermo-oxidation shows a complex behaviour during the exposure times on the PB and PS phases. At shorter exposure times, physical ageing seems to predominate over the chemical effects; at a certain point chemical degradation of the PB phase has irreversible effects for longer exposure times, which leads to morphological changes in the PB granules.

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

  HIPS is a promising material for mechanical recycling, since its properties are not extremely affected after multiple processing up to nine cycles. In comparison with reprocessing, however, thermo-oxidative ageing affects more severely the oxidative stability and the mechanical properties of HIPS. Considering the whole life cycle and the mechanical recycling potential of a HIPS material, the previous service life of the material seems therefore to determine the degree of degradation of the HIPS recyclates and its further possibilities of employment in second market applications.

- **A wide range of low molecular weight compounds can be found in virgin, reprocessed, and thermo-oxidated HIPS.**

  Different low molecular weight compounds, such as residues of polymerisation (benzene derivates, styrene monomer, styrene dimers, and styrene trimers), degradation products, and additives have been identified and relatively quantified in HIPS. The release of residues of polymerisation has been proven to occur during reprocessing and thermo-oxidation, which may evidence the risk of emissions of volatile (VOCs) and semi-volatile organic compounds (SVOCs) during the life cycle of HIPS. A wide range of oxidated degradation products have been also identified to be formed during reprocessing and thermo-oxidation; these products can be identified as oxidative derivates of polystyrene, oxidated fragments from polybutadiene phase, and even oxidated fragments from the grafting points between the PS and PB phase.

- **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 contaminations, oxidative and thermal stability, changes in chemical structure, and morphological properties of recycled materials. The oxidative stability was assessed by thermal analysis and shows the importance of adjusting the stabilisation in the recycling activities. Vibrational spectroscopy is particularly useful to assess the unsaturated groups and the presence of oxidative moieties in recycled HIPS formed due to oxidative degradation during previous life of the material. Different low molecular weight species were found among the HIPS samples, including volatile organic compounds, styrene dimers and trimers residues from polymerisations, additives, and contaminations. The different relative abundance of these compounds in the different samples may be evidence of emission of volatiles during processing and service life in some cases, and the formation of degradation products in other cases.

- **Different analytical procedures for the determination of brominated flame retardants in recycled styrenic polymers from waste electrical and electronic equipment (WEEE) have been proposed using advanced extraction techniques and liquid chromatographic detection (HPLC).**

  HPLC-UV and HPLC-MS/MS methods have been proposed for the simultaneous separation and quantification of tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) stereoisomers, and decabromodiphenyl ether (Deca-BDE) extracted from plastic fractions from WEEE. The extraction efficiency of pressurised liquid extraction, microwave-assisted extraction, and ultrasonic-assisted extraction under different extractive conditions has been compared. Careful selection of extraction parameters, such as extraction solvent, extraction temperature and time, and particle size, is necessary to obtain enhanced recovery yields.

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7. REFERENCES

[1] Plastics Europe, An analysis of plastics production, demand, and recovery in Europe (2006).

[2] APME (Association of Plastic Manufacturers), Assessing the potential for post-use plastics waste recycling - predicting recovery in 2001 and 2006 (1999).

[3] Plastics Europe, Plastics in Europe: An analysis of plastics consumption and recovery in Europe 2002-2003 (2004).

[4] G. Finnveden, J. Johansson, P. Lind, and A. Moberg, *Journal of Cleaner Production* 13, (3), 213-229 (2005).

[5] L. B. Brennan, D. H. Isaac, and J. C. Arnold, *Journal of Applied Polymer Science* 86, (3), 572-578 (2002).

[6] S. Tall, Recycling of mixed plastic waste – Is separation worthwile?, Doctoral Thesis, Department of Polymer Technology, Royal Institute of Technology, Stockholm (Sweden) (2000).

[7] J. Pospisil, F. A. Sitek, and R. Pfaendner, *Polymer Degradation and Stability* 48, (3), 351-358 (1995).

[8] A. Espert, W. Camacho, and S. Karlsson, *Journal of Applied Polymer Science* 89, (9), 2353-2360 (2003).

[9] C. N. Kartalis, C. D. Papaspyrides, and R. Pfaendner, *Polymer Degradation and Stability* 70, (2), 189-197 (2000).

[10] F. P. La Mantia, *Macromolecular Symposia* 152, 201-210 (2000).

[11] F. P. La Mantia, *Handbook of plastics recycling*. Rapra Technology Ltd.: 2002.

[12] A. Jansson, K. Moller, and T. Gevert, *Polymer Degradation and Stability* 82, (1), 37-46 (2003).

[13] A. Jansson, K. Moller, and T. Hjertberg, *Polymer Degradation and Stability* 84, (2), 227-232 (2004).

[14] S. Karlsson, *Advances in Polymer Science* 169, 201-229 (2004).

[15] E. Strömberg, F. Vilaplana, S. Ågren, A. Ribes-Greus, and S. Karlsson, in *Identiplast 2005 - Identifying the Opportunities for Plastics Recovery*, ed. Europe, P., Brussels, 2005.

[16] A. Boldizar, and K. Moller, *Polymer Degradation and Stability* 81, (2), 359-366 (2003).

[17] F. Stangenberg, S. Ågren, and S. Karlsson, *Chromatographia* 59, (January), 101-106 (2004).

[18] S. Tall, A.-C. Albertsson, and S. Karlsson, *Journal of Applied Polymer Science* 70, (12), 2381-2390 (1998).

[19] W. Camacho, and S. Karlsson, *Polymer Engineering and Science* 41, (9), 1626-1635 (2001).

[20] A. Pawlak, M. Pluta, J. Morawiec, A. Galeski, and M. Pracella, *European Polymer Journal* 36, (9), 1875-1884 (2000).

[21] W. Camacho, and S. Karlsson, *Polymer Recycling* 6, (2/3), 89-98 (2001).

[22] S. Karlsson, and A.-C. Albertsson, in *Degradable Polymers (2nd Edition)*, ed. Scott, G., Kluwer Academic Publishers: Dordrecht, Netherlands, 2002; pp 51-69.

[23] A.-C. Albertsson, and S. Karlsson, *Journal of Polymers and the Environment* 4, (1), 51-53 (1996).

[24] S. Karlsson, *Polymer News* 27, (9), 305-309 (2002).

[25] M. Hakkarainen, M. Gröning, and A.-C. Albertsson, *Journal of Applied Polymer Science* 89, (3), 867-873 (2003).
[26] J. Aurrekoetxea, M. A. Sarrionandia, I. Urrutibeascoa, and M. L. Maspoch, *Polymer* 44, (22), 6959-6964 (2003).
[27] W. Nunes dos Santos, J. Augusto Marcondes Agnelli, P. Mummery, and A. Wallwork, *Polymer Testing* 26, (2), 216-221 (2007).
[28] R. Navarro, L. Torre, J. M. Kenny, and A. Jimenez, *Polymer Degradation and Stability* 82, (2), 279-290 (2003).
[29] R. Balart, L. Sanchez, J. Lopez, and A. Jimenez, *Polymer Degradation and Stability* 91, (3), 527-534 (2006).
[30] W. Camacho, and S. Karlsson, *Polymer Degradation and Stability* 78, (2), 385-391 (2002).
[31] S. A. Kyriakou, M. Statherpoulos, G. K. Parissakis, C. D. Papaspyrides, and C. N. Kartalis, *Polymer Degradation and Stability* 66, (1), 49-53 (1999).
[32] G. Ahlblad, P. Gijsman, B. Terselius, A. Jansson, and K. Moller, *Polymer Degradation and Stability* 73, (1), 15-22 (2001).
[33] M. Hamskog, M. Klugel, D. Forsstrom, B. Terselius, and P. Gijsman, *Polymer Degradation and Stability* 86, (3), 557-566 (2004).
[34] M. Hamskog, M. Klugel, D. Forsstrom, B. Terselius, and P. Gijsman, *Polymer Degradation and Stability* 91, (3), 429-436 (2006).
[35] F. P. La Mantia, and N. T. Dintcheva, *Plastics, Rubber and Composites* 33, (4), 184-186 (2004).
[36] W. Camacho, and S. Karlsson, *Journal of Applied Polymer Science* 85, (2), 321-324 (2002).
[37] W. Camacho, and S. Karlsson, *Polymer Degradation and Stability* 71, (1), 123-134 (2000).
[38] N. Haider, and S. Karlsson, *The Analyst* 124, 797-800 (1999).
[39] M. Gröning, and M. Hakkarainen, *Journal of Chromatography A* 932, (1-2), 1-11 (2001).
[40] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, J. Carroll, I. Newton, L. M. Garden, J. R. Dean, and C. T. Costley, *Analyst* 122, 101R-115R (1997).
[41] J. Möller, E. Strömberg, and S. Karlsson, *Manuscript in preparation*,
[42] J. Salafranca, J. Cacho, and C. Nerín, *Chromatographia* 51, (9-10), 615-622 (2000).
[43] A. Vishwa-Prasad, and R. P. Singh, *Journal of Macromolecular Science, Part C - Reviews in Macromolecular Chemistry and Physics* C37, (4), 581-598 (1997).
[44] Y. Israeli, J. Lacoste, J. Lemaire, R. P. Singh, and S. Sivaram, *Journal of Polymer Science: Part A: Polymer Chemistry* 32, 485-493 (1994).
[45] J. B. Adeniyi, *European Polymer Journal* 20, (3), 291-299 (1984).
[46] J. B. Adeniyi, and E. G. Kolawole, *European Polymer Journal* 20, (1), 43-47 (1984).
[47] M. Piton, and A. Rivaton, *Polymer Degradation and Stability* 55, (2), 147-157 (1997).
[48] B. E. Tiganis, L. S. Burn, P. Davis, and A. J. Hill, *Polymer Degradation and Stability* 76, (3), 425-434 (2002).
[49] J. Shimada, and K. Kabuki, *Journal of Applied Polymer Science* 12, (4), 655-669 (1968).
[50] J. Shimada, and K. Kabuki, *Journal of Applied Polymer Science* 12, (4), 671-682 (1968).

[51] C. C. Chen, M. Habibullah, and J. A. Sauer, *Journal of Applied Polymer Science* 28, 391-406 (1983).

[52] A. Ghaffar, A. Scott, and G. Scott, *European Polymer Journal* 11, (3), 271-275 (1975).

[53] A. Ghaffar, A. Scott, and G. Scott, *European Polymer Journal* 12, (9), 615-620 (1976).

[54] A. Ghaffar, A. Scott, and G. Scott, *European Polymer Journal* 13, (2), 89-93 (1977).

[55] A. Ghaffar, A. Scott, and G. Scott, *European Polymer Journal* 13, (2), 83-88 (1977).

[56] T. H. Grguric, V. Rek, Z. Jelcic, D. Hace, and Z. Gomzi, *Polymer Engineering and Science* 39, (8), 1394-1397 (1999).

[57] G. I. Kostov, P. G. Komitov, and Z. G. Nikolova, *European Polymer Journal* 21, (6), 561-564 (1985).

[58] C. Saron, and M. I. Felisberti, *Materials Science and Engineering A* 370, (1-2), 293-301 (2004).

[59] M. Piton, and A. Rivaton, *Polymer Degradation and Stability* 53, (3), 343-359 (1996).

[60] H. C. Beachell, and L. H. Smiley, *Journal of Polymer Science Part A-1: Polymer Chemistry* 5, (7), 1635-1643 (1967).

[61] H. H. G. Jellinek, *Journal of Polymer Science* 4, (1), 1-12 (1949).

[62] B. Mailhot, and J. L. Gardette, *Macromolecules* 25, (16), 4119-4126 (1992).

[63] B. Mailhot, and J. L. Gardette, *Macromolecules* 25, (16), 4127-4133 (1992).

[64] C. B. Bucknall, and V. L. P. Soares, *Journal of Polymer Science Part B: Polymer Physics* 42, (11), 2168-2180 (2004).

[65] M. Mlinac-Misak, J. Jelencic, M. Bravar, and R. Dejanovic, *Angewandte Makromolekulare Chemie* 176, (1), 105-112 (1990).

[66] A. Boldizar, A. Jansson, T. Gevert, and K. Moller, *Polymer Degradation and Stability* 68, (3), 317-319 (2000).

[67] R. C. Santana, and S. Manrich, *Progress in Rubber, Plastics and Recycling Technology* 18, (2), 99-110 (2002).

[68] R. C. Santana, and S. Manrich, *Journal of Applied Polymer Science* 87, (5), 747-751 (2003).

[69] F. Soriano, G. Morales, and R. Díaz de León, *Polymer Engineering & Science* 46, (12), 1698-1705 (2006).

[70] Plastics Europe, Plastics in Europe: An analysis of plastics consumption and recovery in Europe 2002-2003 (Summer 2004).

[71] M. Alaee, P. Arias, A. Sjodin, and A. Bergman, *Environment International* 29, (6), 683-689 (2003).

[72] T. Hyotylainen, and K. Hartonen, *TrAC Trends in Analytical Chemistry* 21, (1), 13-30 (2002).

[73] J. B. Manchester-Neesvig, K. Valters, and W. C. Sonzogni, *Environ. Sci. Technol.* 35, (6), 1072-1077 (2001).

[74] C. A. de Wit, *Chemosphere* 46, (5), 583-624 (2002).

[75] T. Hyotylainen, and K. Hartonen, *TrAC, Trends in Analytical Chemistry* 21, (1), 13-30 (2002).

[76] L. Birnbaum, and D. F. Statskal, *Environmental Health Perspective* 112, 9-17 (2004).

[77] L. S. Morf, J. Tremp, R. Gloor, Y. Huber, M. Stengele, and M. Zennegg, *Environ. Sci. Technol.* 39, (22), 8691-8699 (2005).

[78] M. Schlummer, L. Gruber, A. Maurer, G. Wolz, and R. van Eldik, *Chemosphere* 67, (9), 1866-1876 (2007).
[79] H. Fink, U. Panne, M. Theisen, R. Niessner, T. Probst, and X. Lin, *Fresenius' Journal of Analytical Chemistry,* 368, (2), 235-239 (2000).
[80] H. Fink, U. Panne, and R. Niessner, *Anal. Chem.* 74, (17), 4334-4342 (2002).
[81] M. Stepputat, and R. Noll, *Applied Optics* 42, (30), 6210-6220 (2003).
[82] S. Kikuchi, K. Kawauchi, S. Ooki, M. Kurosawa, H. Honjho, and T. Yagishita, *Analytical Sciences* 20, (8), 1111-1112 (2004).
[83] A. m. Altwaiq, M. Wolf, and R. van Eldik, *Analytica Chimica Acta* 491, (1), 111-123 (2003).
[84] M. Pohlein, A. S. Llopis, M. Wolf, and R. v. Eldik, *Journal of Chromatography A* 1066, (1-2), 111-117 (2005).
[85] M. Schlummer, F. Brandl, A. Maurer, and R. van Eldik, *Journal of Chromatography A* 1064, (1), 39-51 (2005).
[86] J. de Boer, and R. J. Law, *Journal of Chromatography A* 1000, (1-2), 223-251 (2003).
[87] P. Korytar, A. Covaci, J. de Boer, A. Gelbin, and U. A. T. Brinkman, *Journal of Chromatography A* 1065, (2), 239-249 (2005).
[88] A. Covaci, S. Voorspoels, L. Ramos, H. Neels, and R. Blust, *Journal of Chromatography A* 1153, 145-171 (2007).
[89] S. Hamm, M. Strikkeling, P. F. Ranken, and K. P. Rothenbacher, *Chemosphere* 44, (6), 1353-1360 (2001).
[90] M. Riess, T. Ernst, R. Popp, B. Muller, H. Thoma, O. Vierle, M. Wolf, and R. van Eldik, *Chemosphere* 40, (9-11), 937-941 (2000).
[91] M. Wolf, M. Riess, D. Heitmann, M. Schreiner, H. Thoma, O. Vierle, and R. van Eldik, *Chemosphere* 41, (5), 693-699 (2000).
[92] F. Cheng-Yu Wang, *Analytical Chemistry* 71, 2037-2045 (1999).
[93] M. Riess, H. Thoma, O. Vierle, and R. van Eldik, *Journal of Analytical and Applied Pyrolysis* 53, (2), 135-148 (2000).
[94] G. Socrates, *Infrared and Raman Characteristic Group Frequencies. Tables and charts.* Wiley: Chichester, 2001.
[95] S. W. Cornell, and J. L. Koenig, *Macromolecules* 2, (5), 540-545 (1969).
[96] J. A. Frankland, H. G. M. Edwards, A. F. Johnson, I. R. Lewis, and S. Poshyachinda, *Spectrochimica Acta Part A: Molecular Spectroscopy* 47, (11), 1511-1524 (1991).
[97] J. Guilment, and L. Bokobza, *Vibrational Spectroscopy* 26, (1), 133-149 (2001).
[98] J. Lacoste, J. Delor, J. F. Pilichowski, R. P. Singh, A. Vishwa-Prasad, and S. Sivaram, *Journal of Applied Polymer Science* 59, 953-959 (1996).
[99] S. Poshyachinda, H. G. M. Edwards, and A. F. Johnson, *Polymer* 32, (2), 338-342 (1991).
[100] R. J. Meier, *Vibrational Spectroscopy* 39, (2), 266-269 (2005).
[101] S. M. Wang, J. R. Chang, and R. C. C. Tsiang, *Polymer Degradation and Stability* 52, (1), 51-57 (1996).
[102] S. Poshyachinda, H. G. M. Edwards, and A. F. Johnson, *Polymer* 37, (23), 5171-5177 (1996).
[103] A. K. Sircar, *Journal of Thermal Analysis and Calorimetry* 49, (1), 293-301 (1997).
[104] S. N. Goyanes, *Journal of Applied Polymer Science* 75, (7), 865-873 (2000).
[105] J. F. Mano, *Thermochimica Acta* 332, (2), 171-177 (1999).

[106] R. M. Fuoss, and J. G. Kirkwood, *J. Am. Chem. Soc.* 63, (2), 385-394 (1941).

[107] G. S. Fulcher, *Journal of the American Ceramic Society* 8, (6), 339-355 (1925).

[108] G. Tammann, and W. Hesse, *Zeitschrift für anorganische und allgemeine Chemie* 156, (1), 245-257 (1926).

[109] H. Vogel, *Phys Z* 22, 645-646 (1921).

[110] F. Vilaplana, A. Ribes-Greus, and S. Karlsson, *Polymer Degradation and Stability* 91, (9), 2163-2170 (2006).

[111] A. Wypych, E. Duval, G. Boiteux, J. Ulanski, L. David, G. Seytre, A. Mermet, I. Stevenson, M. Kozanecki, and L. Okrasa, *Journal of Non-Crystalline Solids* 351, (33-36), 2593-2598 (2005).

[112] G. A. Eiceman, and M. Carpen, *Analytical Letters* 15, (A14), 1169-1177 (1982).

[113] P. Kusch, and G. Knupp, *Journal of Separation Science* 25, (8), 539-542 (2002).

[114] P. Kusch, and G. Knupp, *Journal of Polymers and the Environment* 12, (2), 83-87 (2004).

[115] W. V. Ligon Jr., and M. C. George, *Journal of Polymer Science: Polymer Chemistry Edition* 16, (10), 2703-2709 (1978).

[116] L. Coulier, H. G. M. Orbons, and R. Rijk, *Polymer Degradation and Stability* 92, (11), 2016-2025 (2007).

[117] R. G. Lichtenthaler, and F. Ranfelt, *Journal of Chromatography A* 149, 553-560 (1978).

[118] J. Virt, L. Rosík, J. Kováová, and J. Pospisil, *European Polymer Journal* 16, (3), 247-253 (1980).

[119] S. L. Hathcock, and W. Bertsch, *Journal of High Resolution Chromatography* 16, (11), 651-659 (1993).

[120] W. G. Brown, *Die Makromolekulare Chemie* 128, (1), 130-136 (1969).

[121] H. F. Kauffmann, *Die Makromolekulare Chemie* 180, (11), 2649-2663 (1979).

[122] K. S. Khuong, W. H. Jones, W. A. Pryor, and K. N. Houk, *J. Am. Chem. Soc.* 127, (4), 1265-1277 (2005).

[123] K. Kirchner, and K. Riederle, *Angewandte Makromolekulare Chemie* 111, (1), 1-16 (1983).

[124] T. Yamada, M. Tanaka, S. Hirano, Y. Nagao, K. Kobayashi, T. Sakurai, Y. Furukawa, and Y. Nobuhara, *Bunseki Kagaku* 49, (11), 857-867 (2000).

[125] J. Schellenberg, S. Knoll, G. Nord, and W. Leukefeld, *European Polymer Journal* 39, (12), 2351-2357 (2003).

[126] J. Wiesner, and P. Mehnert, *Die Makromolekulare Chemie* 165, (1), 1-9 (1973).

[127] Harald Friedrich Kauffmann, *Die Makromolekulare Chemie* 180, (11), 2649-2663 (1979).

[128] U. W. Gedde, *Polymer physics*. Kluwer Academic Publishers: Dordrechts, The Netherlands, 1999.

[129] W. Budakowski, and G. Tomy, *Rapid Communications in Mass Spectrometry* 17, (13), 1399-1404 (2003).

[130] N. G. Dodder, A. M. Peck, J. R. Kucklick, and L. C. Sander, *Journal of Chromatography A* 1135, (1), 36-42 (2006).

[131] R. Saint-Louis, and E. Pelletier, *The Analyst* 129, (8), 724-730 (2004).

[132] J. Tollback, C. Crescenzi, and E. Dyremark, *Journal of Chromatography A* 1104, (1-2), 106-112 (2006).

[133] X. Lou, H. G. Janssen, and C. A. Cramers, *Anal. Chem.* 69, (8), 1598-1603 (1997).

[134] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, S. A. Zhu, J. Carroll, I. D. Newton, and L. M. Garden, *Anal. Chem.* 70, (9), 1943-1948 (1998).

[135] U. Sellström, A. Kierkegaard, C. de Wit, and B. Jansson, *Environmental Toxicology and Chemistry* 17, (6), 1065–1072 (1998).

Article I

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Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation

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Abstract

A simulation of the degradation of high-impact polystyrene (HIPS), occurring during service life and mechanical recycling, was performed by multiple processing and thermo-oxidative ageing. All samples were characterized by differential scanning calorimetry (DSC), melt mass-flow rate (MFR) measurements, tensile testing and infrared spectroscopy (FTIR). Multiple processing and thermo-oxidative ageing clearly alter the oxidative stability and the elongation at break of the materials. These changes observed at a macroscopic scale have been related to chemical alterations in the structure of HIPS. The polybutadiene phase was demonstrated to be the initiation point of the degradative processes induced by processing, service life and mechanical recycling. Thermo-oxidative degradation affects more severely the degree of degradation of the material, so it may be deduced that the changes occurring during service life of HIPS are the part of the life cycle that mostly affects its further recycling possibilities and performance in second-market applications.

Keywords: Recycling; Degree of degradation; High-impact polystyrene; Reprocessing; Thermo-oxidation

1. Introduction

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. Therefore, there is a special need to introduce the concept of quality assessment in the recycling activities, in order to guarantee and specify the properties of the recyclates within narrow tolerances by the manufacturers according to the needs of their customers [1,2]. According to this, three key properties have been proposed in order to guarantee the quality of the recycled plastic materials: they are degree of mixing (composition), degree of degradation, and the presence of low-molecular weight compounds (degradation products, contaminants, etc.) [3]. In order to investigate the degree of degradation of polymeric materials, several approaches can be considered, taking into account the changes in their macroscopic or microscopic properties. The functional group changes by Fourier Transform Infrared (FTIR) spectroscopy, the alterations in the mechanical properties by tensile tests, the thermal properties such as the glass transition temperature (T_g) or the degree of crystallinity by differential scanning calorimetry (DSC) are some of the physical, chemical and mechanical analyses which are commonly employed to monitor polymer degradation [4].

In the recent years, little attention has, however, been given to styrenic polymers such as high-impact polystyrene, although this family of polymers constituted approximately 12% of the total consumption of thermoplastics in Europe during the year 2003 [5]. Some studies on the morphological and thermo-mechanical properties of post-consumer high-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene

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(ABS) under different reprocessing conditions have pointed out the potential of styrenic polymers for mechanical recycling [6–9]. High-impact polystyrene (HIPS) consists of a blend of polystyrene and polybutadiene where the latter is in low content (2–8 mol%), which possesses enhanced impact properties. The improvement of the impact resistance of polystyrene is generally ensured by the polybutadiene introduced before the free radical polymerization of styrene. The polybutadiene nodules are then compatibilised by grafting of styrene units [10].

In general, recycled materials show a loss in their properties due to the degradation processes that have occurred during their processing, service life and further mechanical recycling. The aim of the study was to investigate the degree of degradation of high-impact polystyrene during its reprocessing and thermo-oxidation to develop detailed knowledge about how and at which extent processing, service life and mechanical recycling affect the performance of HIPS. A double experimental approach has been undertaken in order to model the second life for the HIPS material, including the processing, the service life and the mechanical recycling. The processing and recycling of the plastic material were modelled by multiple processing, while the degradation processes occurring during the service life was simulated by thermo-oxidative ageing in a forced-ventilation oven at 90 °C. Scheme 1 shows the procedure followed for modelling the second life for plastics. The samples were characterized by differential scanning calorimetry (DSC), tensile testing and Fourier Transform Infrared spectroscopy (FTIR), to determine the changes in oxidative stability, mechanical properties and chemical composition induced by the recycling-related processes.

2. Experimental

2.1. Materials and preparation of samples: reprocessing and thermo-oxidative ageing

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M, was employed as control material and was provided by BASF Española S.A. (Spain).

The reprocessing studies were performed on virgin HIPS material by multiple extrusion up to nine cycles, employing a double-screw extruder Collin Kneader 25 × 30*D* (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, ground and some material was kept for analysis whereas the remaining was reintroduced again for further extrusion. Rectangular sheets of dimensions 85 × 85 × 1 mm for tensile testing were prepared by compression moulding at 200 °C and by a maximum pressure of 200 bar with a Collin x800 press (Dr. Collin GmbH, Germany).

The virgin HIPS material was subjected to thermo-oxidative ageing in order to simulate its period of service life. The virgin HIPS pellets were compression moulded into sheets of dimensions 85 × 85 × 1 mm employing a Schwabenthan Polystat 400S press (Schwabenthan Maschinenfabrik Berlin, Germany) at a temperature of 200 °C and a pressure of 200 bar. The sheets were the introduced into 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 different exposure times of 1, 2, 4, 8, 12 and 16 days.

2.2. Differential scanning calorimetry

Differential scanning calorimetry was employed in order to assess the oxidative stability of the different samples and the glass transition temperature (T_g) of both the polybutadiene (PB) and polystyrene (PS) phases of thermo-oxidised HIPS. The analyses were performed on a Mettler Toledo DSC 820 instrument (Columbus, OH) calibrated with indium standard. About 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.

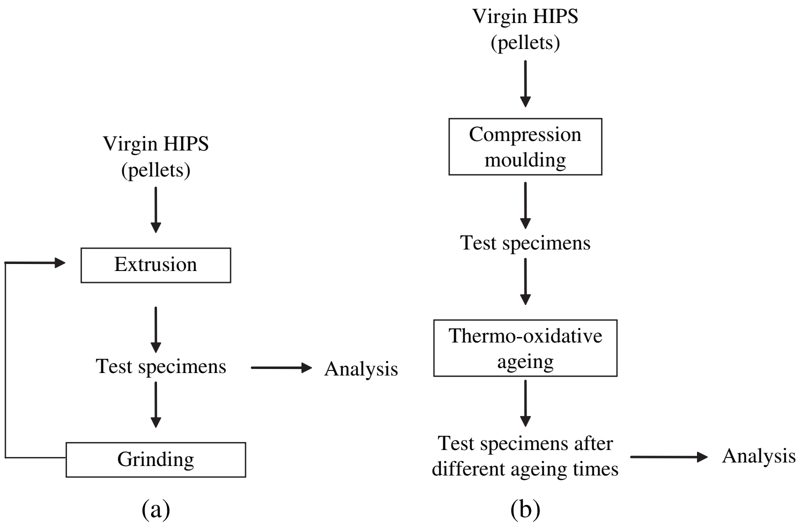
To determine the oxidation temperature (T_{ox}) the samples were heated from 25 °C up to 400 °C at 10 °C/min under an oxygen atmosphere of 50 ml/min. The oxidation temperature was obtained from the onset point of the oxidation curve showed by the calorimetric analysis. Each measurement of the oxidation temperature was performed in triplicate and the average of the three experiments was considered as the representative value.

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 and kept at that temperature for 5 min under a nitrogen gas flow of 50 ml/min. After reaching this point, the atmosphere was instantaneously switched to oxygen at a flow rate of 50 ml/min and the DSC oven was held at a temperature of 160 °C for 30 min. The oxidation induction time was calculated as the difference between the instant when the atmosphere was switched to oxygen and the onset of the oxidation signal at the DSC thermograms. Each sample was analyzed three times and the average was assumed as the representative value.

To calculate the glass transition temperatures, the calorimetric measurements were carried out under a nitrogen gas flow of 50 ml/min and the temperature programme was as follows. First, the samples were heated from −100 °C to 150 °C at a heating rate of 10 °C/min; then, cooled from 150 °C to −100 °C at −10 °C/min, and finally a new heating ramp was performed from −100 °C to 150 °C at 10 °C/min. The glass transition temperatures were calculated from the calorimetric data obtained at the second heating ramp.

2.3. Melt mass-flow rate (MFR)

The melt mass-flow rate (MFR) measurements of the reprocessed HIPS virgin material were performed on a Melt Indexer CFR-91 (Campana Srl., Italy). The procedure was followed according to the ISO 1133:1997 standard. The test temperature was set at 200 °C and the nominal load was



Scheme 1. Procedure employed for the modelling of the second life for plastics, (a) modelling of processing and mechanical recycling; (b) modelling of service life.

5 kg. The measurements on each sample were repeated six times and the average was taken as the representative value.

2.4. Tensile properties

Tensile tests were performed on reprocessed and aged HIPS samples in order to investigate the changes in the mechanical properties of the material after reprocessing and ageing. Each test was performed according to the procedure established by the ASTM D882-02 standard on six rectangular specimens of dimensions 85 mm long × 5 mm width × 1 mm thickness cut from the films obtained by compression moulding. The average value of the modulus, stress at break and elongation at break from the six specimens 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, employing a load of 0.1 kN and a gauge length of 30 mm.

2.5. Fourier Transform Infrared (FTIR) spectroscopy

The spectrograms of the surface of the polymeric films were recorded by means of an FTIR spectrometer Spectrum 2000 from Perkin Elmer (Wellesley, MA) equipped with a Golden Gate single-reflection accessory for attenuated total reflection (ATR) measurements. Each spectra was obtained by the performance of 24 scans between 4000 and 600 cm^{-1} at intervals of 1 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Oxidative stability

The oxidation induction time (OIT) and the oxidation temperature (T_{ox}) were calculated by differential scanning calorimetry (DSC) in order to assess the oxidative stability of reprocessed and aged samples of high-impact polystyrene. The oxidation induction time procedure is regulated by international standards and is more commonly employed than the oxidation temperature measurements for quality control purposes as a quick screening method to check the activity of the stabilization system used [11]. The use of OIT and T_{ox} methods for the analysis of the oxidative stability of polymeric materials is also evaluated.

Table 1 presents the OIT and the T_{ox} average data obtained by the DSC measurements for the HIPS samples. As it can be observed, the stabilising system employed in the material is clearly affected by the reprocessing cycles and by thermo-oxidative ageing, while the largest changes are observed in the aged samples. Each reprocessing step caused a progressive consumption of the stabilisers in the material, mainly during the first three extrusion cycles, with a total decrease in the OIT value of approximately 65% after nine cycles. In the case of the thermo-oxidised samples, the decrease in the stabilising

Table 1
Oxidation temperature (T_{ox}) and oxidation induction time (OIT) for high-impact polystyrene subjected to multiple processing and thermo-oxidative ageing at 90 °C

Reprocessing			Thermo-oxidative ageing		
Reprocessing steps	T_{ox} (°C)	OIT (min)	Ageing time (days)	T_{ox} (°C)	OIT (min)
Virgin HIPS	198	28	Virgin HIPS	198	28
1	194	19	1	188	12
2	193	17	2	186	11
3	190	14	4	185	10
4	189	13	8	181	6
5	189	13	12	179	5
6	188	12	16	180	4
7	188	12			
8	187	11			
9	186	10			

activity is even more fast and dramatic, with a decrease of 57% in the value of the OIT after 1 day of ageing at 90 °C and a total decrease of 85% of the OIT value after 16 days of ageing.

Similar conclusions can be drawn from the measurement of the OIT and the T_{ox} when comparing the results obtained from both the procedures. The OIT method may be more sensitive than the oxidation temperature procedure, but it requires a preliminary optimisation of the temperature of the analyses. The T_{ox} procedure is, on the other hand, very easy to perform and gives reproducible data similar to the OIT method, but is not standardised at the moment. Therefore, both methods can be successfully employed for assessing the oxidative stability of high-impact polystyrene in the recycling industries.

3.2. Melt mass-flow rate (MFR)

The melt mass-flow rate (MFR) is a common property employed in the recycling industries for quality control of the final recycled material, in order to guarantee its further processing capability for the manufacture of secondary products from these recyclates. Fig. 1 shows the slight increase in the MFR of the high-impact polystyrene subjected up to nine extrusion cycles, where the increase is more pronounced for the first three extrusion cycles. These results may be attributed to the 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 [9].

From a recycling point of view, HIPS seems to be a promising material for mechanical recycling, since the MFR values only increase approximately 2% in the first reprocessing step and a total of 45% after nine extrusion cycles. This small variation of the MFR with a large number of recycling steps would guarantee the processability of the recyclates during the mechanical recycling processes.

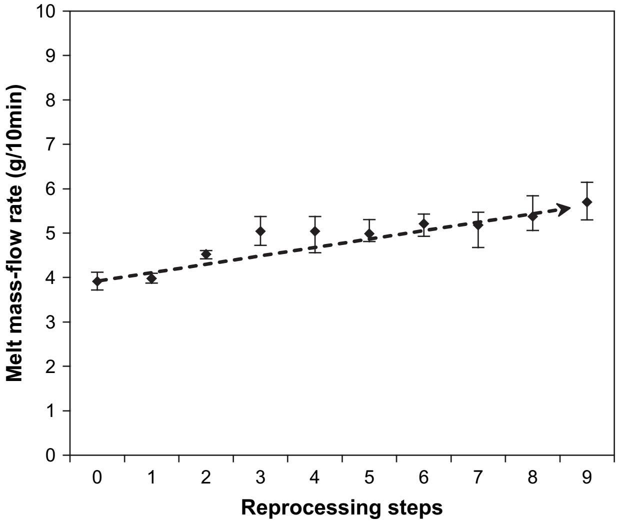


Fig. 1. Influence of reprocessing on the melt mass-flow rate (MFR) of HIPS.

3.3. Tensile tests

The influence of reprocessing and thermo-oxidative ageing on the elastic modulus, elongation at break and stress at break was analyzed by tensile testing. Some studies about the effects of reprocessing on the mechanical properties of high-impact polystyrene have been previously reported, showing some disagreements in their results [7,9]. An increase in the impact strength and a decrease in the tensile properties such as the tensile stress, the elastic modulus, and the elongation at break, with the reprocessing were observed by Santana and Manrich [9]. On the other hand, Brennan et al. [7] have stated that recycling has no substantial effect on the tensile strength and elastic modulus of ABS and HIPS, while the ductility is reduced significantly, particularly in HIPS. The changes in the tensile properties of HIPS during the consecutive extrusion cycles are represented in Fig. 2, showing a behaviour more in accordance to the latest [7]. As it can be observed, the elastic modulus remains practically unaltered during the nine reprocessing cycles with slight deviations from the original value for virgin HIPS. However, the stress and elongation at break are clearly influenced by the successive processing steps, with a progressive diminution of the elongation at break and an increase of the stress at break. Each processing step induces the thermo-mechanical degradation of the HIPS materials, which may introduce alterations in the chemical structure of the polymeric chains, resulting in a slightly more brittle material with lower ductility. These structural changes in the components of the HIPS material will be studied in more detail in the discussion of the infrared spectroscopy results.

Fig. 3 shows the influence of thermo-oxidative ageing at 90 °C on the tensile properties of high-impact polystyrene. It can be observed that the effect of ageing on the mechanical properties of HIPS is more severe than the one reported for reprocessing. The elongation at break drastically decreases with the ageing time, showing a collapse of this property after 4 days of exposure to thermo-oxidative degradation. On the other hand, the modulus and the stress at break show a slight increase in their values during the initial ageing times but after 12 days of exposure their values drop. The explanation to this complex behaviour could be obtained from the different processes that are involved in thermo-oxidative ageing. It is known that ageing of glassy polymers under air atmosphere at temperatures below the glass transition temperature (T_g) is a complex phenomenon that involves both a rearrangement of the polymeric chains towards the equilibrium state (physical ageing) and the degradation of the polymer due to the chemical interaction with oxygen (chemical ageing) [12]. It has been reported that for short times of ageing, the physical ageing process seems to predominate upon the chemical ageing, resulting in a slight increase of the tensile stress and in a strong decrease in ductility. However, during longer periods of exposure the chemical ageing begins to dominate, which results in a decrease of the stress at break and modulus [12]. These phenomena may explain the collapse of the elongation at break after a short exposure to thermo-oxidative environment and the behaviour of the tensile stress and modulus with ageing time,

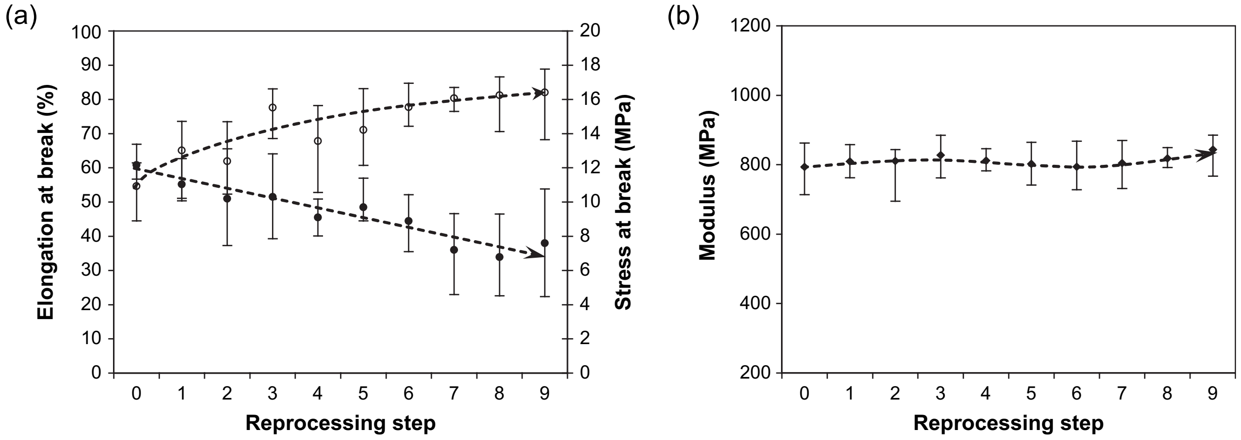


Fig. 2. Tensile properties of the virgin HIPS subjected to multiple processing, (a) tensile properties at break: (●) elongation at break; (○) stress at break; (b) Young's modulus.

demonstrating the first increase and the posterior drop in their values during ageing. Moreover, this behaviour is in agreement with the evolution of the glass transition temperatures of both the polybutadiene and the polystyrene phases with the ageing time, which are shown in Table 2. As it can be observed, the T_g of both phases remains practically unaltered during the initial ageing times, but after longer exposure they show a slight decrease.

As a conclusion, the elongation at break appears to be the mechanical property that should determine the recycling possibilities and the second-market application for high-impact polystyrene recyclates. It was observed that reprocessing up to nine cycles does not affect to any high extent the mechanical properties of HIPS, with a decrease of 15% in elongation at break after three extrusion steps, and a total decrease of around 38% in the elongation at break after nine cycles. On the other hand, the thermo-oxidative ageing at 90 °C may be considered to be quite severe for the mechanical properties of HIPS, since it remarkably affects the elongation at break values of HIPS, with a decrease of 85% after only 4 days of exposure.

3.4. Infrared spectroscopy

The absorbance spectra of the surface of the HIPS samples subjected to multiple processing and thermo-oxidative ageing at 90 °C were recorded and studied. In particular, the regions corresponding to the hydroxyl groups (between 3100 and 3600 cm^{-1}), carbonyl groups (between 1620 and 1780 cm^{-1}), and the unsaturated groups from the polybutadiene phase of HIPS corresponding to the peak of *trans*-1,4 (966 cm^{-1}) and vinyl-1,2 (911 cm^{-1}) were analyzed in detail. The peak corresponding to the *cis*-1,4 double bond group from the polybutadiene phase (around 730 cm^{-1}) could not be studied because of the overlapping peak from the C–H out-of-plane vibration of the styrene units in polystyrene at 754 cm^{-1} [13]. Moreover, in order to obtain a quantitative picture of the structural changes caused by reprocessing and ageing, the relative absorbance ratios of the peaks corresponding to the maximum of the hydroxyl region (3287 cm^{-1}), the maximum of the carbonyl region (1729 cm^{-1}), *trans*-1,4 group (965 cm^{-1}), and vinyl-1,2 group (907 cm^{-1}) were determined,

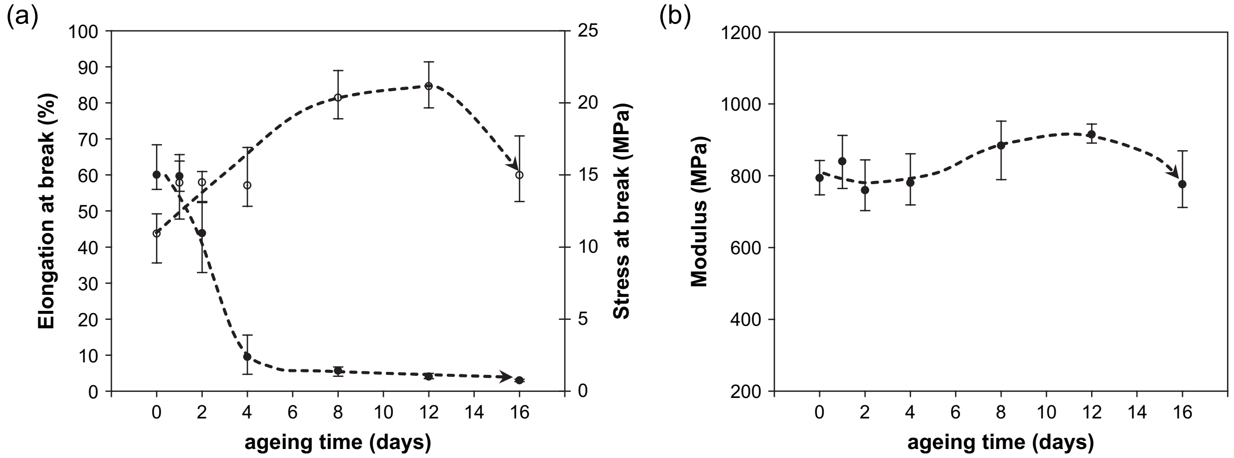


Fig. 3. Tensile properties of the virgin HIPS subjected to thermo-oxidative ageing at 90 °C, (a) tensile properties at break: (●) elongation at break; (○) stress at break; (b) Young's modulus.

Table 2
Glass transition temperatures (T_g) of the polybutadiene (PB) and the polystyrene (PS) phases of the high-impact polystyrene thermo-oxidised samples

Ageing time (days)	T_g PB (°C)	T_g PS (°C)
Virgin HIPS	−59	95
1	−58	95
2	−59	95
4	−59	95
8	−57	95
12	−58	93
16	−56	90

related to the height of a reference peak at 1601 cm^{-1}, in order to make their results comparable and to eliminate the effect of the thickness of the films [6].

Fig. 4 shows the absorbance infrared spectra for some selected reprocessed HIPS samples at the region between 1400 and 1800 cm^{-1}. Apart from the characteristic peaks related to the aromatic ring stretching vibrations at 1492 and 1451 cm^{-1}, and the peaks at 1600 and 1580 cm^{-1} caused by the aromatic C═C stretching vibration, all of them originated by the polystyrene units in HIPS [13], some peculiarities in the analyzed spectra could be found. It is believed that the thermo-mechanical degradation processes caused by the multiple processing of the high-impact polystyrene in an oxygen deficient atmosphere induce a series of heterogeneous and complex chemical reactions that may be responsible for the appearance of a wide range of oxidative moieties in the polymeric chains. As it can be observed in Fig. 4, the repeated extrusion of HIPS results in the appearance of a peak at around 1560 cm^{-1}, which may be attributed to the asymmetric stretching of the carboxylate ion group [4,13]. The intensity of this peak increases progressively until the seventh extrusion cycle, but it decreases afterwards, without an apparent reason for this strange behaviour.

Fig. 5 represents the spectroscopic results of the analyzed functional group indexes as a function of the reprocessing steps. It can be observed that repeated processing steps induce complex changes in the absorbance of the selected functional group. As a whole, a decrease in the *trans*-1,4 and vinyl-1,2 indexes corresponding to the polybutadiene phase can be noticed, together with a slight increase in the carbonyl and hydroxyl indexes. This decrease in the double bond groups from polybutadiene could be caused by some crosslinking reactions occurring during the extrusion or also by some minor oxidation processes due to the interaction of the polymer with some residual oxygen which could have been present in the extruder. The diminution in the unsaturated groups, together with the possible decrease in the molecular weight of the HIPS suggested by the MFR measurements, may explain the decrease in the elongation at break with successive extrusion steps reported by the tensile testing.

Fig. 6 shows the infrared spectra for the HIPS samples subjected to thermo-oxidative ageing at 90 °C through the hydroxyl region (between 3600 and 3100 cm^{-1}), carbonyl region (between 1800 and 1620 cm^{-1}), and the double bond region (between 1000 and 880 cm^{-1}). In addition, a quantitative study of the selected functional groups was performed and the evolution of their indexes with the ageing time was then plotted in Fig. 7. Figs. 6 and 7 demonstrate that thermo-oxidative ageing induces, in contrast with the heterogeneous effects reported by reprocessing, quite progressive changes in the analyzed functional group indexes. As a whole, thermo-oxidative ageing caused a marked decrease in the unsaturated groups (*trans*-1,4 and vinyl-1,2 groups), while broad bands appear both in the hydroxyl and the carbonyl regions. These results are in agreement with previous studies performed on the photo- and thermo-oxidation of HIPS and other styrene/butadiene copolymers by FTIR spectroscopy [14–16]. The *trans*-1,4 group index showed a slight decrease at the initial ageing time due to the protective effect of the antioxidants, but after the fourth day of thermo-oxidative ageing, the reduction was considerable. This phenomenon is in accordance with the results of Israeli et al. [14], which reported that the thermal oxidation of HIPS shows an induction period, followed by a fast oxidation of polybutadiene and then by a slow oxidation

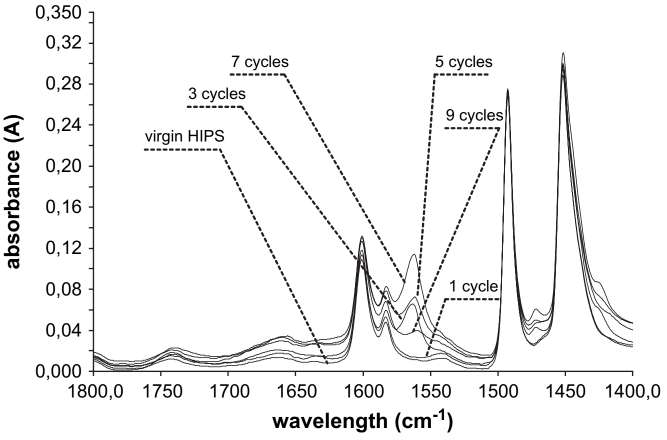


Fig. 4. FTIR absorbance spectra at the region between 1800 and 1400 cm^{-1} for HIPS samples subjected to different steps of multiple processing.

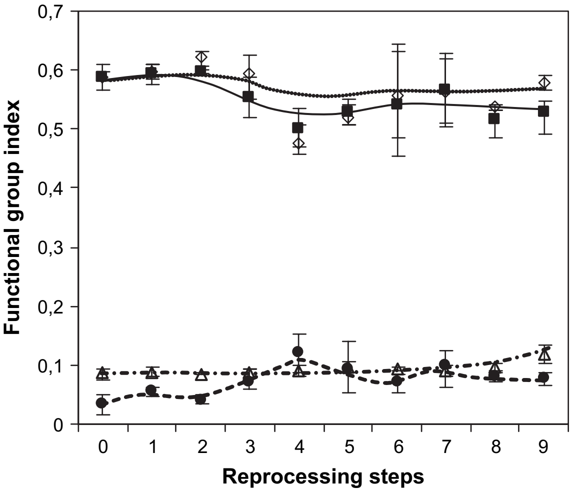


Fig. 5. Evolution of the (◇) vinyl-1,2 ratio, (■) *trans*-1,4 ratio, (△) carbonyl ratio and (●) hydroxyl ratio, with the reprocessing steps for HIPS.

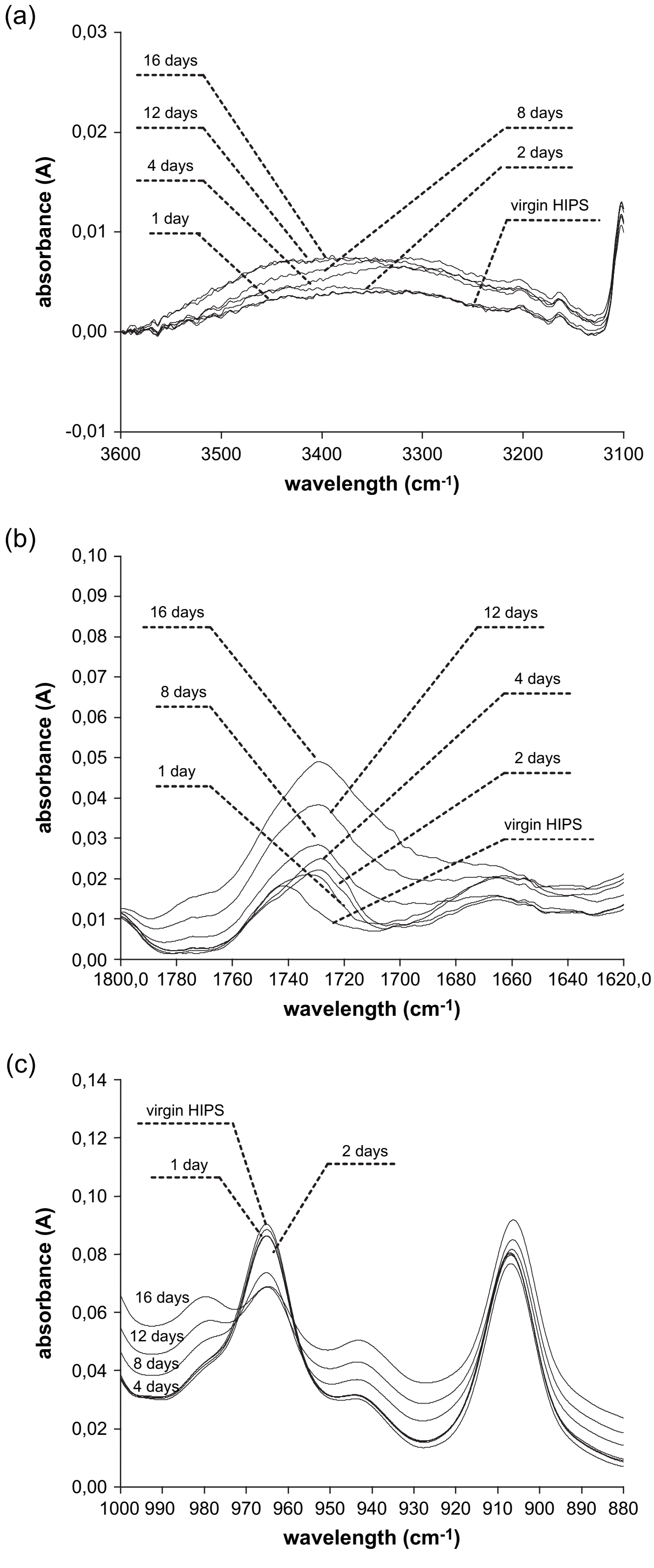


Fig. 6. FTIR spectra of the HIPS samples subjected to thermo-oxidative ageing at 90 °C, (a) hydroxyl region (3600–3100 cm^{-1}); (b) carbonyl region (1800–1620 cm^{-1}); (c) double bond region (1000–880 cm^{-1}).

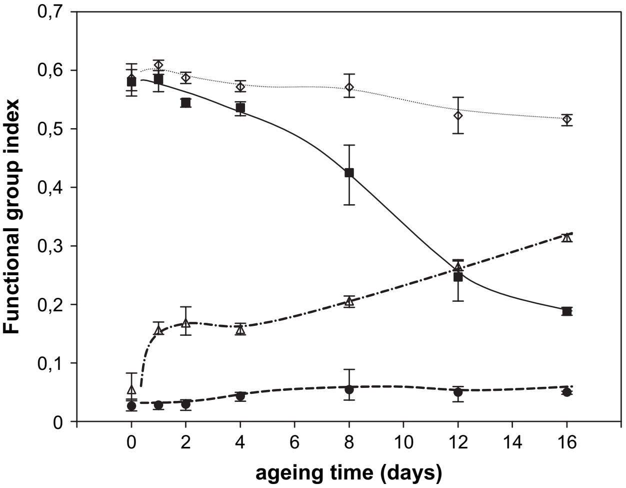


Fig. 7. Evolution of the (◇) vinyl-1,2 ratio, (■) *trans*-1,4 ratio, (△) carbonyl ratio and (●) hydroxyl ratio, with the time for HIPS subjected to thermo-oxidative ageing at 90 °C.

rate corresponding to the degradation of polystyrene. Therefore, the first step in the thermo-oxidative ageing of HIPS is the degradation of polybutadiene, and some of the radicals formed in that degradation can act as initiators for the oxidation of polystyrene [14,16]. Moreover, comparing the different unsaturated groups of the polybutadiene phase (*trans*-1,4 and vinyl-1,2), it can be observed that they present different stability to degradation. The *trans*-1,4 group is more susceptible towards thermo-oxidative ageing than the vinyl-1,2 group as it is shown by the different magnitude of the decrease of their respective indexes in Fig. 7, in agreement with previous results about the thermo-oxidative degradation of styrene–butadiene–styrene (SBS) rubber [17].

4. Conclusions

Multiple processing and accelerated ageing were employed in order to model the processing, recycling and service life of high-impact polystyrene (HIPS). The oxidative stability, melt mass-flow rate (MFR), tensile properties and the functional group chemical changes were selected as the properties to analyze the modelling of recycling of HIPS. The selected procedure showed to be useful to model the effect of degradation of HIPS recyclates occurring during its life cycle.

It was demonstrated that the oxidative stability of HIPS is clearly affected by both the reprocessing cycles and by thermo-oxidative ageing; this effect was, however, more noticeable in the aged samples. In addition, the melt mass-flow rate increased slightly with the reprocessing steps, which may be related to a decrease in the molecular weight of the polymer caused by chain scission mechanisms induced by multiple processing. The elastic modulus is not severely changed by multiple processing and thermo-oxidative ageing. Contrarily, the elongation at break progressively decreased with the consecutive reprocessing steps and collapsed after long exposure to thermo-oxidative ageing at 90 °C due to the combined effect of physical and chemical ageing. The

FTIR spectroscopic studies showed that reprocessing induces heterogeneous changes in the chemical structure of HIPS, with the formation of oxidative moieties and consumption of part of the unsaturations. On the other hand, the thermo-oxidative ageing mainly affected the polybutadiene phase in HIPS, with a clear reduction of the *trans*-1,4 functional group and formation of hydroxyl and carboxyl groups.

HIPS is a promising material for mechanical recycling, since its properties are not extremely affected after multiple processing up to nine cycles. In comparison with reprocessing, however, thermo-oxidative ageing affects more severely the oxidative stability and the mechanical properties of HIPS. Therefore, considering the whole life cycle and the mechanical recycling potential of a HIPS material, the previous service life of the material seems to determine in a very important way the degree of degradation of the HIPS recyclates and its further possibilities of employment in second-market applications.

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References

[1] Karlsson S. Recycled polyolefins. Material properties and means for quality determination. Advances in Polymer Science 2004;169:201–29.

[2] Strömberg E, Vilaplana F, Ågren S, Ribes-Greus A, Karlsson S. Quality assessment of recycled plastics. In: Conference proceedings; Identiplast 2005 – identifying the opportunities for plastics recovery, Brussels; 2005.

[3] Stangenberg F, Ågren S, Karlsson S. Quality assessment of recycled plastics by spectroscopy and chromatography. Chromatographia 2004; 59:101–6.

[4] Karlsson S, Albertsson A-C. In: Scott G, editor. Degradable polymers. 2nd ed. Dordrecht, Netherlands: Kluwer Academic Publishers; 2002. p. 51–69.

[5] Plastics Europe. Plastics in Europe: an analysis of plastics consumption and recovery in Europe 2002–2003 [on line]; Summer 2004.

[6] Boldizar A, Moller K. Degradation of ABS during repeated processing and accelerated ageing. Polymer Degradation and Stability 2003;81:359–66.

[7] Brennan LB, Isaac DH, Arnold JC. Recycling of acrylonitrile–butadiene–styrene and high-impact polystyrene from waste computer equipment. Journal of Applied Polymer Science 2002;86:572–8.

[8] Santana RC, Manrich S. Studies on morphology and mechanical properties of PP/HIPS blends from postconsumer plastic waste. Journal of Applied Polymer Science 2003;87:747–51.

[9] Santana RC, Manrich S. Studies on thermo-mechanical properties of post-consumer high impact polystyrene in five reprocessing steps. Progress in Rubber, Plastics and Recycling Technology 2002;18: 99–110.

[10] Lacoste J, Delor J, Pilichowski JF, Singh RP, Vishwa-Prasad A, Sivaram S. Polybutadiene content and microstructure in high-impact polystyrene. Journal of Applied Polymer Science 1996;59:953–9.

[11] Schmid M, Affolter S. Interlaboratory tests on polymers by differential scanning calorimetry (DSC): determination and comparison of oxidation induction time (OIT) and oxidation induction temperature (OIT*). Polymer Testing 2003;22:419–28.

[12] Chen CC, Habibullah M, Sauer JA. Elevated temperature ageing of HIPS. Journal of Applied Polymer Science 1983;28:391–406.

[13] Socrates G. Infrared and Raman characteristic group frequencies. Tables and charts. Chichester: Wiley; 2001.

[14] Israeli Y, Lacoste J, Lemaire J, Singh RP, Sivaram S. Photo- and thermoinitiated oxidation of high-impact polystyrene: characterization by FT-IR spectroscopy. Journal of Polymer Science: Part A Polymer Chemistry 1994;32:485–93.

[15] Kostov GI, Komitov PG, Nikolova ZG. Application of IR-compensation technique for study of the oxidation degree of high impact polystyrene. European Polymer Journal 1985;21:561–4.

[16] Grguric TH, Rek V, Jelcic Z, Hace D, Gomzi Z. Determination of the kinetic parameters of the thermal oxidative degradation of styrene/butadiene copolymers. Polymer Engineering and Science 1999;39:1394–7.

[17] Wang S-M, Chang J-R, Tsiang RC-C. Infrared studies of thermal oxidative degradation of polystyrene-block polybutadiene-block-polystyrene thermoplastic elastomers. Polymer Degradation and Stability 1996; 52:51–7.

Article II

Changes in the microstructure and morphology of high-impact polystyrene subjected to multiple processing and thermo-oxidation.

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Changes in the microstructure and morphology of high-impact polystyrene subjected to multiple processing and thermo-oxidative degradation

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Abstract

Multiple processing and thermo-oxidation have been employed to simulate the degradative processes to which high-impact polystyrene (HIPS) is subjected during processing, service life, and mechanical recycling. A curve-fitting procedure has been proposed for the analysis of the individual bands corresponding to polybutadiene microstructure resulting from Raman spectroscopy. The analysis of the glass transition relaxations associated with the polybutadiene (PB) and polystyrene (PS) phases has been performed according to the free-volume theory. Both reprocessing and thermo-oxidative degradation are responsible for complex physical and chemical effects on the microstructure and morphology of PB and polystyrene PS phases, which ultimately affect the macroscopic performance of HIPS. Multiple processing affects PB microstructure and the free-volume parameter associated with the PS phase. Physical ageing of the PS phase predominates for shorter exposure to thermo-oxidation; after prolonged exposure, however, the chemical effects on the PB phase become significant and strongly influence the overall structure.

Keywords: High-impact polystyrene; Degradation; Raman spectroscopy; Dynamic-mechanical properties; Polybutadiene microstructure

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1. Introduction

The optimisation of waste plastic management procedures is one of the most important issues that our society faces in terms of sustainable development. Mechanical recycling has been identified as the preferred route for plastic waste management, in terms of minimising overall energy use and emission of gases that contribute to global warming [1]. Knowledge about the effects of degradation processes that occur during previous service life and subsequent mechanical recycling is needed, however, to predict life span of new products made from recycled material [2].

Styrenic polymers are employed in a wide range of applications, such as packaging, automotive

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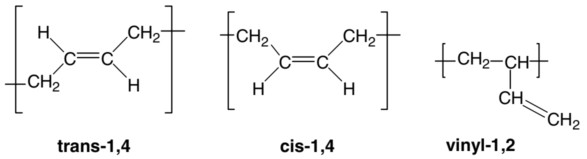
components, and electrical and electronic equipment. High-impact polystyrene (HIPS) is a multiphase copolymer system in which polybutadiene (PB) rubber particles are dispersed in the polystyrene (PS) rigid matrix. A combined experimental approach, consisting of multiple processing and thermo-oxidation, was proposed in a previous work to simulate the degradation processes to which HIPS is subjected during processing, service life, and further mechanical recycling. Thermo-oxidation was demonstrated to have the greatest effect on the long-term stability and mechanical properties of HIPS, suggesting that the service life of the material is the part of the life cycle with the greatest consequences for HIPS degradation [3]. Repeated extrusion may induce chain scission in the PS matrix and physical changes in the rubber phase, which ultimately affect the mechanical properties of HIPS [3–5]. Thermo-oxidative degradation of HIPS appears to be a complex phenomenon with both physical and chemical features [6]. The PB phase has been reported to be the initiation point of photo-oxidative, thermo-oxidative, and thermo-mechanical degradation in styrenic copolymers, which induce alterations in the chemical structure of the material [3,7–10]. The oxidation of rubber-modified polymers shows an initial induction time, followed by a fast oxidation of PB and then by a slow oxidation rate corresponding to PS degradation [7].

This paper aims to give a deeper insight into the effects of the degradation processes induced by multiple processing and thermo-oxidation on the morphology and microstructure of HIPS. Raman spectroscopy was employed for PB microstructure characterisation in HIPS, by analysing the vinyl-1,2, *cis*-1,4, and *trans*-1,4 functional groups. The morphology changes induced by reprocessing and thermo-oxidation were observed by scanning electron microscopy (SEM). These morphological alterations at a microscopic level can be correlated to the mechanical and viscoelastic behaviour of the material, which has been characterised employing dynamic-mechanical-thermal analysis (DMTA).

2. Theoretical background

2.1. Determination of PB microstructure in HIPS using Raman spectroscopy

Polybutadiene contains three different structural units: vinyl-1,2, *cis*-1,4, and *trans*-1,4 (Scheme 1).



Scheme 1. Polybutadiene microstructures: *trans*-1,4; *cis*-1,4; vinyl-1,2 groups.

Raman spectroscopy can be employed to identify the microstructure of polybutadienes since the stretching vibration of the v(C=C) bond of these units are Raman active. Early studies by Cornell and Koenig calculated the microstructure in polybutadiene by analysing the Raman peaks at 1639, 1650, and 1664 cm^{-1}, which correspond to the vinyl-1,2, *cis*-1,4, and *trans*-1,4 units, respectively [11]. Recent developments in curve analysis systems have enabled the resolution of the three overlapping peaks corresponding to these three units, and have been used to analyse the reactivity of polybutadienes and identify the PB microstructure in styrene-butadiene copolymers and high-impact polystyrene [12–15].

The overlapping of individual bands in vibrational spectroscopy is a common phenomenon that is usually solved by curve-fitting. Some guidelines should be followed, however, to perform a suitable curve-fitting of the vibrational spectra [16]. The line-profile in Raman spectra is Lorentzian in nature, but there may be Gaussian line broadening due to instrumental effects or sample characteristics. The Lorentzian profile for Raman bands is represented by Eq. (1). In addition, the envelope and the background should preferably be fitted simultaneously, to avoid serious errors. Lastly, the proper selection of the width, position, and number of bands is extremely important for a suitable curve-fitting

$$L(x) = y_0 + \frac{2 \cdot A}{\pi} \cdot \frac{\omega}{4 \cdot (x - x_c)^2 + \omega^2}. \tag{1}$$

2.2. Free-volume theory for glass transition

The Vogel–Fulcher–Tammann–Hesse equation (VFTH) was employed to study the viscoelastic relaxation associated with the glass transition of PB and PS in HIPS. VFTH equation was first empirically formulated for the viscosity of inorganic glasses at temperatures above the glass transition temperature (T_g) [17–19]. This equation is suitable for correlating the temperature dependence of the glass transition relaxation for viscoelastic materials, and can be deduced as well from the free-volume theory

$$\ln \tau_i = A' + \frac{m_v}{T - T_\infty}. \tag{2}$$

Here, τ_i is the relaxation time; A' is an empirical parameter; and T_∞ 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:

$$m_v = \frac{B}{\alpha_f} = \frac{B}{f_g} \cdot (T_g - T_\infty), \tag{3}$$

where α_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 with the glass transition.

3. Experimental

3.1. Materials and preparation of samples: multiple processing and thermo-oxidation

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M, was provided by BASF Española S.A. (Spain). The material was subjected to multiple processing and thermo-oxidation, to model the life cycle of recycled HIPS as described in previous work [3]. Multiple processing was performed up to nine extrusion cycles with a maximum extrusion temperature of 200 °C. Thermo-oxidation was performed using a forced-ventilation oven under air atmosphere at 90 °C; the samples were removed for analysis after different exposure times of 1, 2, 4, 8, 12 and 16 days.

3.2. Raman spectroscopy

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

3.3. Dynamic-mechanical-thermal analysis (DMTA)

The viscoelastic measurements were carried out in a dynamic-mechanical-thermal analyser MARK IV DMTA (Rheometric Scientific, United Kingdom). The sinusoidal deformation was applied to rectangular samples with dimensions of $50 \times 10 \times 1$ mm, in the double clamped cantilever mode. The region above ambient temperature was studied for all samples by performing multifrequency scans from 25 °C to 150 °C at a step rate of 4 °C/scan for a range of 5 frequencies per decade between 0.1 Hz and 50 Hz. Additional scans were performed on selected samples to further characterise PB glass transition relaxation; the multifrequency measurements were made between −110 °C and 150 °C at a step rate of 5 °C/scan, over a frequency range of 0.1–50 Hz, using four frequencies per decade. The values of loss tangent ($\tan\delta$), storage modulus (E'), and loss modulus (E'') versus temperature and frequency were thus obtained.

3.4. Scanning electron microscopy (SEM)

SEM micrographs were obtained from sectioned HIPS samples after sputtering with gold/palladium, using a JEOL JSM-5400 scanning electron microscope (JEOL Ltd., Japan).

4. Results and discussion

4.1. Raman spectroscopy

Raman microscopy was employed to characterise PB microstructure in HIPS, taking into account the bands corresponding to the vinyl-1,2 (1639 cm^{-1}), *cis*-1,4 (1650 cm^{-1}), and *trans*-1,4 (1664 cm^{-1}) groups. A curve-fitting procedure was proposed to resolve the individual microstructures; the Raman region between 1550 cm^{-1} and 1700 cm^{-1} was thus analysed in detail, following the guidelines reported by Meier [16]. Five peaks were considered at wavelengths of 1582 cm^{-1}, 1601 cm^{-1}, 1639 cm^{-1}, 1650 cm^{-1}, and 1664 cm^{-1}, and were fitted to a Lorentzian profile (Eq. (1)). Fig. 1 is an example of curve-fitting for virgin HIPS, with the raw spectra and the five resolved components. The PB phase in this specific commercial-grade HIPS contains mainly the *trans*-1,4 structure, followed by *cis*-1,4 and vinyl-1,2. To obtain a quantitative insight, the areas of the vinyl-1,2, *cis*-1,4, and *trans*-1,4 bands were calculated and normalised to the area of the

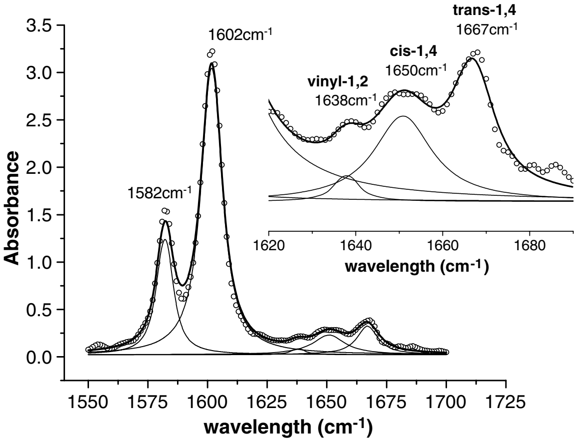


Fig. 1. Curve-fitting of the virgin HIPS Raman spectra to five individual bands for the determination of the three individual PB conformers: 1550–1700 cm^{-1} region.

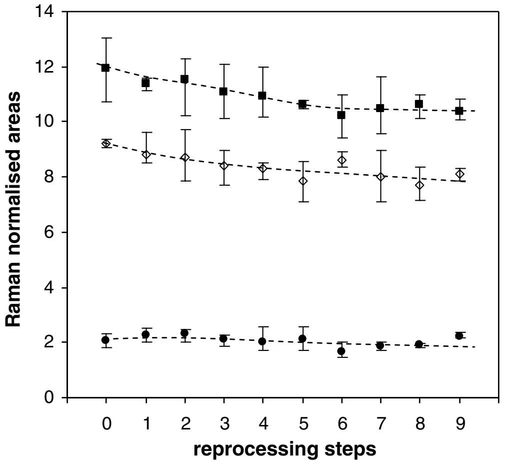


Fig. 3. Raman functional group indexes for the PB microstructure of HIPS subjected to multiple processing: (■) *trans*-1,4; (○) *cis*-1,4; (●) vinyl-1,2.

band at 1601 cm^{-1}, which is not affected by degradation.

Fig. 2 shows the effect of multiple processing on polybutadiene microstructure in selected HIPS samples; PB microstructure is, to some extent, affected by the repeated extrusion cycles, since the intensities of the bands slightly decrease with the successive reprocessing steps. The influence of multiple processing on the Raman indexes can be observed in Fig. 3; in general, the normalised areas for the three microstructures decrease slightly under the consecutive extrusion cycles. The thermo-mechanical degradation produced by the processing steps may induce chemical reactions in polybutadiene that could cause crosslinking of the rubber phase and alter the physical structure of the rubber phase. The behaviour of each PB microstructure in regards to degradation caused by processing is, however, different. The vinyl-1,2 index is barely affected after nine processing steps, whereas the *cis*-1,4 and *trans*-1,4 groups show a progressive decrease after each extrusion.

The effect of thermo-oxidation on the polybutadiene microstructure in HIPS during different exposure times has also been analysed using Raman spectroscopy (Fig. 4). As a whole, thermo-oxidation clearly affects the PB microstructure in HIPS, since the peaks of the different unsaturated groups decrease markedly with exposure time. The same

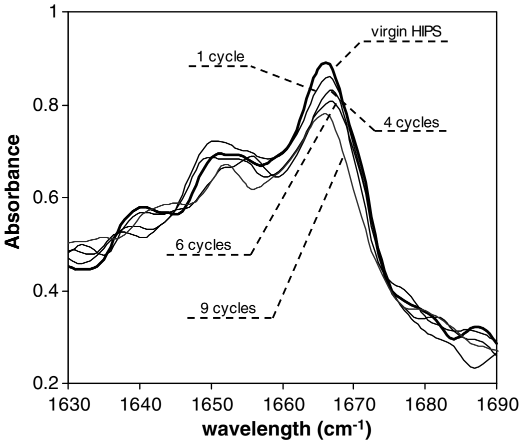


Fig. 2. Raman spectra of the PB microstructure region of selected HIPS samples subjected to multiple processing.

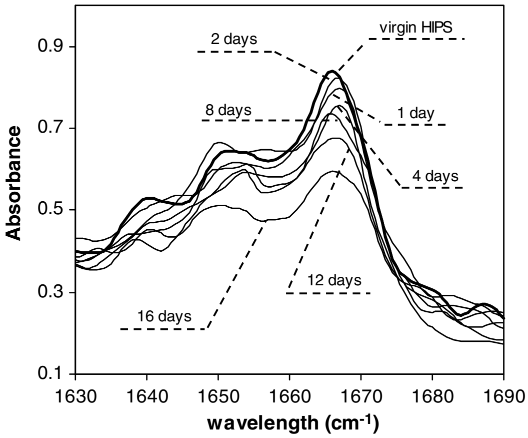


Fig. 4. Raman spectra of the PB microstructure region of selected HIPS samples subjected to thermo-oxidation.

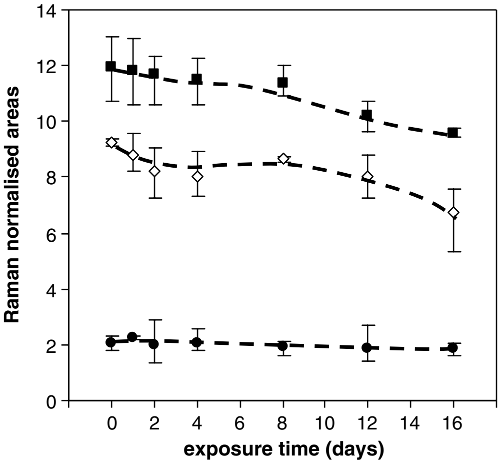


Fig. 5. Evolution of the Raman functional group indexes with exposure time for the PB microstructure of HIPS subjected to thermo-oxidation at 90 °C: (■) *trans*-1,4; (○) *cis*-1,4; (●) vinyl-1,2.

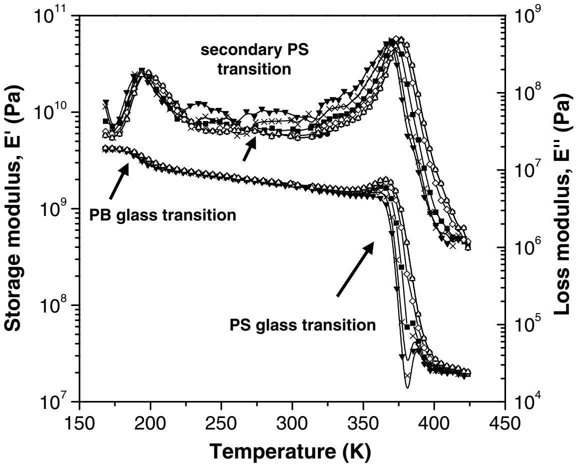


Fig. 6. Isocronal representation of the storage modulus E' (lower plot) and loss modulus E'' (upper plot) for virgin HIPS: (▼) 0.1 Hz; (×) 0.25 Hz; (■) 1 Hz; (◇) 3.98 Hz; (●) 10 Hz; (8) 39.81 Hz.

curve-fitting procedure has been applied to resolve the different PB microstructures and to calculate their normalised areas for HIPS samples exposed to thermo-oxidation. As it can be observed in Fig. 5, the Raman indexes show an initial induction period with 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, noted after the eighth day of exposure, which is assigned to the complex series of thermo-oxidative reactions leading to the disappearance of the unsaturated groups and the formation of oxidative moieties, crosslinked structures, and chain scission [20]. The different microstructures also resist thermo-oxidation differently; the *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 [10,21].

4.2. Dynamic-mechanical-thermal analysis (DMTA)

The dynamic-mechanical spectrum of high-impact polystyrene presents different characteristic relaxations, which are shown in the isocronal plot for the storage and loss modulus at a frequency range of 0.1–50 Hz (Fig. 6). The glass transition associated with the PB phase appears clearly centred at around 195 K; its intensity is proportional to the concentration of the PB phase in HIPS. The position of the PB phase glass transition is related to the microstructure (vinyl content); both pure *cis*-1,4 and *trans*-1,4 PB exhibit their T_g at 167 K, whereas pure vinyl-1,2 PB has its glass transition temperature at around 258 K. Polybutadienes with higher vinyl content will therefore show higher glass transition temperatures [22,23]. A small but wide transition at 250 K can be detected at higher frequencies, which can be explained by the rotation of the polystyrene phenyl groups [24]. This relaxation has not been considered in this study due to its complex nature. The glass transition of the PS matrix can be found at around 380 K; a small shoulder appears in both the loss and storage moduli at higher frequencies just before the PS glass transition starts, which could be attributed to the previous structural relaxation and stress release of the material [25,26].

The viscoelastic properties as a function of temperature for different HIPS samples subjected to multiple processing are represented in Fig. 7. The reprocessed samples show, in general, a slight decrease in both the storage and loss moduli compared to the virgin HIPS material. This decrease in both mechanical modules may be explained by the thermo-mechanical degradation induced by repeated extrusion cycles, which may have caused embrittlement of the material, with a loss of stiffness (associated to the storage modulus) and a change of impact properties (associated to the loss modulus).

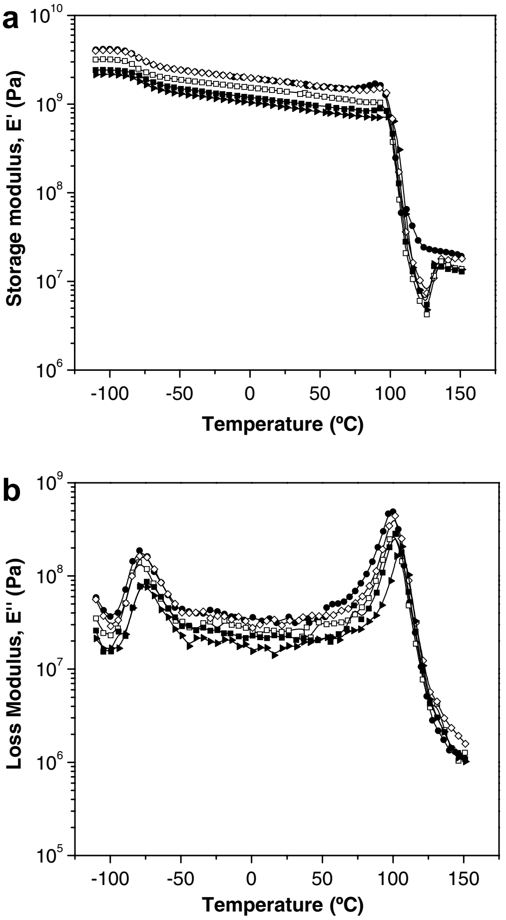


Fig. 7. Viscoelastic properties as a function of temperature for selected HIPS samples subjected to multiple processing; (a) storage modulus (E') and (b) loss modulus (E''): (●) virgin HIPS; (□) HIPSr1; (◇) HIPSr4; (▶) HIPSr6; (■) HIPSr9.

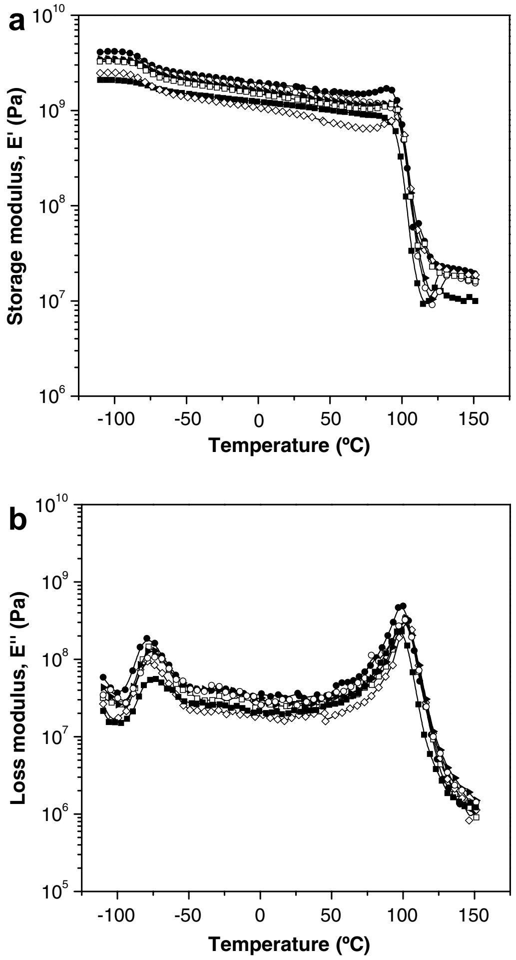


Fig. 8. Viscoelastic properties as a function of temperature for selected HIPS samples subjected to thermo-oxidation at 90 °C; (a) storage modulus (E') and (b) loss modulus (E''): (●) virgin HIPS, (□) aged 2 days, (◇) aged 4 days, (▶) aged 8 days, (○) aged 12 days, (■) aged 16 days.

A similar behaviour for the storage modulus can be observed for the thermo-oxidated samples, with a decrease in values for the whole temperature range for the exposed samples, as compared to the virgin HIPS material (Fig. 8). The loss modulus, however, does not show a clear behaviour with thermo-oxidative exposure due to the complex combination of effects involved in thermo-oxidation; only the intensity of the PB glass transition decreases markedly for the samples exposed for longer times, in agreement with the Raman results pointing to the decrease in the PB microstructure caused by thermo-oxidation at longer exposure times.

The glass transition relaxations related to the PB and PS phases of HIPS can be characterised by their loss modulus maximum values ($E''_{\max}$ and $T_{\max}$); these values were obtained for all the HIPS samples and frequencies and were analysed by fitting the loss modulus data to the Fuoss–Kirkwood empirical model. Although the Fuoss–Kirkwood model was originally defined for dielectric secondary relaxations of polymers [27], it could be successfully applied here to characterise dynamical-mechanical primary relaxations, due to its simplicity and to the narrow range of frequency decades that can be analysed by DMTA. The modified Fuoss–Kirkwood equation in terms of temperature applied for the fitting of the dynamic-mechanical data is

$$E'' = \frac{E''_{\max}}{\cosh\left[m \cdot \frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{\max}}\right)\right]}, \tag{4}$$

where $E''_{\max}$ is the maximum of the loss modulus; m is the Fuoss–Kirkwood parameter; E_a is the activation energy of the relaxation process; and $T_{\max}$ is the temperature of the maximum of the loss modulus, which is usually assumed as the glass transition temperature. The $E''_{\max}$ and $T_{\max}$ values obtained from the Fuoss–Kirkwood fit at 1 Hz for the PB and PS glass transition relaxations for samples subjected to multiple processing and thermo-oxidation are shown in Tables 1 and 2, respectively.

The analysis of the dynamic-mechanical data according to the free-volume theory gave detailed information about the influence of reprocessing and thermo-oxidative degradation on the viscoelastic behaviour of the PB and PS glass transition. Figs. 9 and 10 represent the Arrhenius maps for the PB and PS glass transition relaxations for the reprocessed and thermo-oxidated samples, respectively; these Arrhenius maps are obtained by plotting the $T_{\max}$ values from the Fuoss–Kirkwood fitting against the different analysed frequencies. The Arrhenius curves were fitted to the VFTH equation and parameters A', m_v, and T_∞ were thus obtained; the parameter related to the free-volume, $\frac{f_g}{B\cdot(T_g-T_\infty)}$, was also calculated for the reprocessed and thermo-oxidated samples (Tables 1 and 2, respectively).

Multiple processing causes a progressive shift in the T_g loss plots for the PB phase to higher temperatures (Fig. 9). This result may prove the occurrence of crosslinking reactions in the PB microstructure, as suggested by the results of Raman spectroscopy, which generate rigid segments within the PB phase that contribute to the mobility restrictions of the PB chains. The parameter associated with the free-volume of the PB phase also decreases with repeated

Table 1
Influence of multiple processing on the viscoelastic parameters related to the glass transition relaxations of PB and PS phases in HIPS according to the free-volume theory

Reprocessing steps	PB glass transition						PS glass transition					
	$E''_{\max}$[a] (×10^6) (Pa)	$T_{\max}$[a] (K)	A'	m_v (K)	T_∞ (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\times 10^4$ (K^{-1})	$E''_{\max}$[a] (×10^6) (Pa)	$T_{\max}$[a] (K)	A'	m_v (K)	T_∞ (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\times 10^4$ (K^{-1})
Virgin HIPS	181.9	196	14.1	284.4	175.6	35.2	505.3	371	13.9	321.6	349.1	31.1
1	136.1	195	17.2	434.5	169.9	23.0	291.7	373	15.2	365.5	349.1	27.4
2	–	–	–	–	–	–	362.8	373	13.2	312.8	349.2	32.0
3	–	–	–	–	–	–	353.4	373	13.7	320.1	349.3	31.3
4	164.8	198	19.4	591.3	166.9	16.9	440.6	374	15.5	372.5	349.4	26.9
5	–	–	–	–	–	–	187.4	373	15.2	389.9	347.4	25.7
6	76.8	199	16.0	411.8	172.8	24.3	208.7	376	14.0	365.0	347.0	27.4
7	–	–	–	–	–	–	314.3	373	15.7	415.3	346.1	24.1
8	–	–	–	–	–	–	298.9	373	16.8	501.6	343.0	19.9
9	85.2	200	32.3	1773.6	145.2	5.6	277.4	374	23.6	1089.7	326.5	9.2

[a] Parameters calculated from the Fuoss–Kirkwood plot at a frequency of 1 Hz.

Table 2
Influence of thermo-oxidation on the viscoelastic parameters related to the glass transition relaxations of PB and PS phases in HIPS according to the free-volume theory

Exposure time (days)	PB glass transition						PS glass transition					
	$E''_{\max}$[a] (×10^6) (Pa)	$T_{\max}$[a] (K)	A'	m_v (K)	T_∞ (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\times 10^4$ (K^{-1})	$E''_{\max}$[a] (×10^6) (Pa)	$T_{\max}$[a] (K)	A'	m_v (K)	T_∞ (K)	$\frac{f_g}{B\cdot(T_g-T_\infty)}\times 10^4$ (K^{-1})
Virgin HIPS	181.9	196	14.1	284.4	175.6	35.2	505.3	371	13.9	321.6	349.1	31.1
1	–	–	–	–	–	–	339.8	375	17.2	492.5	346.5	20.3
2	138.8	198	14.3	279.8	178.2	35.7	332.6	374	19.3	680.6	340.2	14.7
4	93.1	197	17.2	431.4	171.7	23.2	326.2	375	19.5	665.4	338.4	15.0
8	128.4	198	15.3	356.2	174.8	28.1	332.3	374	11.3	225.7	353.3	44.3
12	111.4	199	12.0	208.8	182.2	47.9	316.0	373	10.0	155.7	357.0	64.2
16	55.1	200	8.6	103.4	188.3	96.7	243.4	370	11.1	153.9	356.4	65.0

[a] Parameters calculated from the Fuoss–Kirkwood plot at a frequency of 1 Hz.

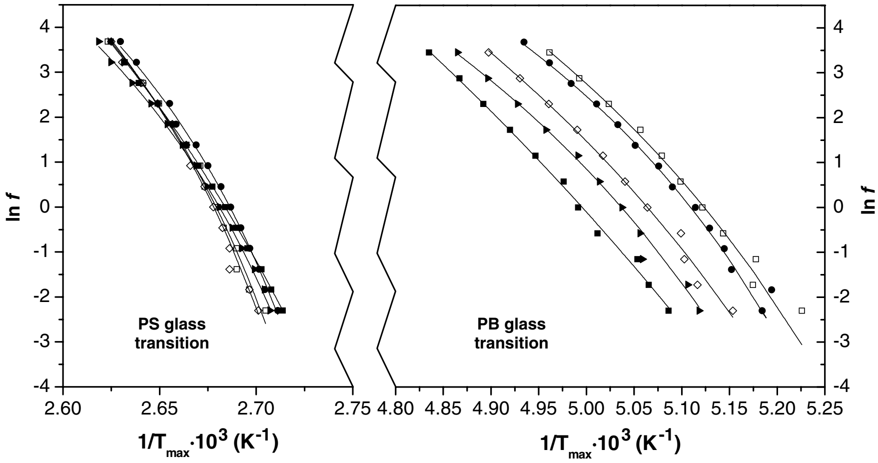


Fig. 9. Arrhenius maps for the PB and PS glass transition relaxations for selected HIPS samples subjected to multiple processing: (●) virgin HIPS; (□) HIPSr1; (◇) HIPSr4; (▶) HIPSr6; (■) HIPSr9.

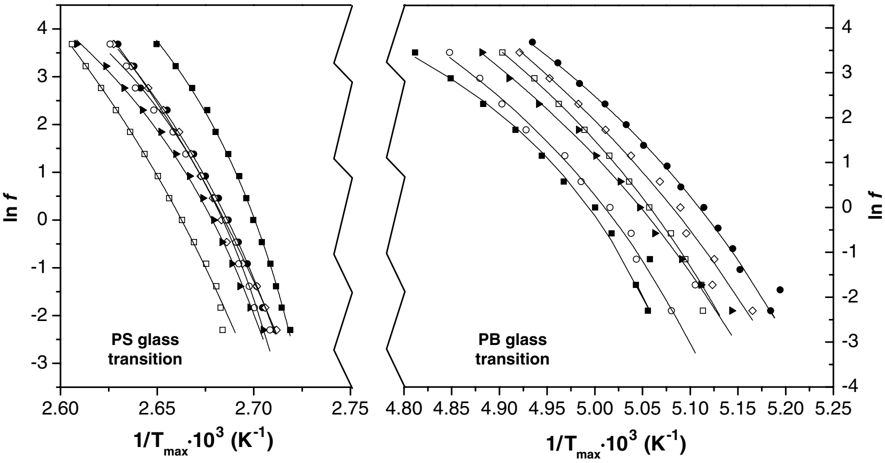


Fig. 10. Arrhenius maps for the PB and PS glass transition relaxations for selected HIPS samples subjected to thermo-oxidation: (●) virgin HIPS, (□) aged 2 days, (◇) aged 4 days, (▶) aged 8 days, (○) aged 12 days, (■) aged 16 days.

processing cycles (Table 1), which could also be caused by entanglements in the PB chains due to crosslinking reactions. The Arrhenius curves for the PS phase show a slight shift to higher temperatures for repeated processing cycles (Fig. 9). The free-volume parameter for PS glass transition is, however, greatly affected, showing progressive diminution during reprocessing (Table 1). Previous studies have reported that repeated processing causes an increase in the melt flow rate and a modification in the rheological properties, which may be induced by chain scission reactions in the PS chain [3]. Multiple processing may also be responsible for a rearrangement of the PS chains, which may progressively occupy the free-volume originally present in the matrix. The combined effect of the presence of shorter PS polymeric chains induced by thermo-mechanical degradation and the physical rearrangement of the macromolecular chains within the repeated extrusion process may be responsible for the marked decrease in free-volume. This effect on the free-volume of both PB and PS phases in HIPS reported here may be responsible for the changes in the macroscopic behaviour, such a decrease in the elongation at break and impact properties reported in other works [3–5].

The effect of thermo-oxidative ageing on the Arrhenius plot and the free-volume parameter is complex for both phases in HIPS. The Arrhenius plots for the PB glass transition shift to higher temperatures with increasing exposure time to thermo-oxidation, and is especially noticeable for longer exposure times (Fig. 10). The chemical reactions induced by oxidation are associated with an increase in the glass transition temperature of polybutadiene [8,28], which can be related to the changes in the PB microstructure. On one hand, oxidation causes extensive crosslinking in the PB phase, which restricts the mobility of the polymeric chains. On the other hand, as confirmed by Raman spectroscopy, oxidation affects the *cis*-1,4 and *trans*-1,4 conformers more severely than it does that of vinyl-1,2; this leads to oxidised HIPS samples with higher vinyl content than the original ones, which exhibit higher glass transition temperatures. The free-volume parameter, however, shows a slight decrease for shorter exposure times (0–4 days) and a dramatic increase for longer exposure times (Table 2). The decrease in PB free-volume at lower exposure times may be related to initial crosslinking reactions caused by oxidation, which occur at a lower incidence due to the protective effect of the stabilising system contained in the material [3]. With longer exposure, the oxidation effects become irreversible for polybutadiene, which may lead to a structural collapse of the PB phase in HIPS.

This contrasting behaviour for short and long exposure times to thermo-oxidation becomes more evident for the PS phase. The Arrhenius plots for the PS glass transition shift to higher temperatures for shorter exposure times, but drastically shift to lower temperatures for longer times; similarly, the

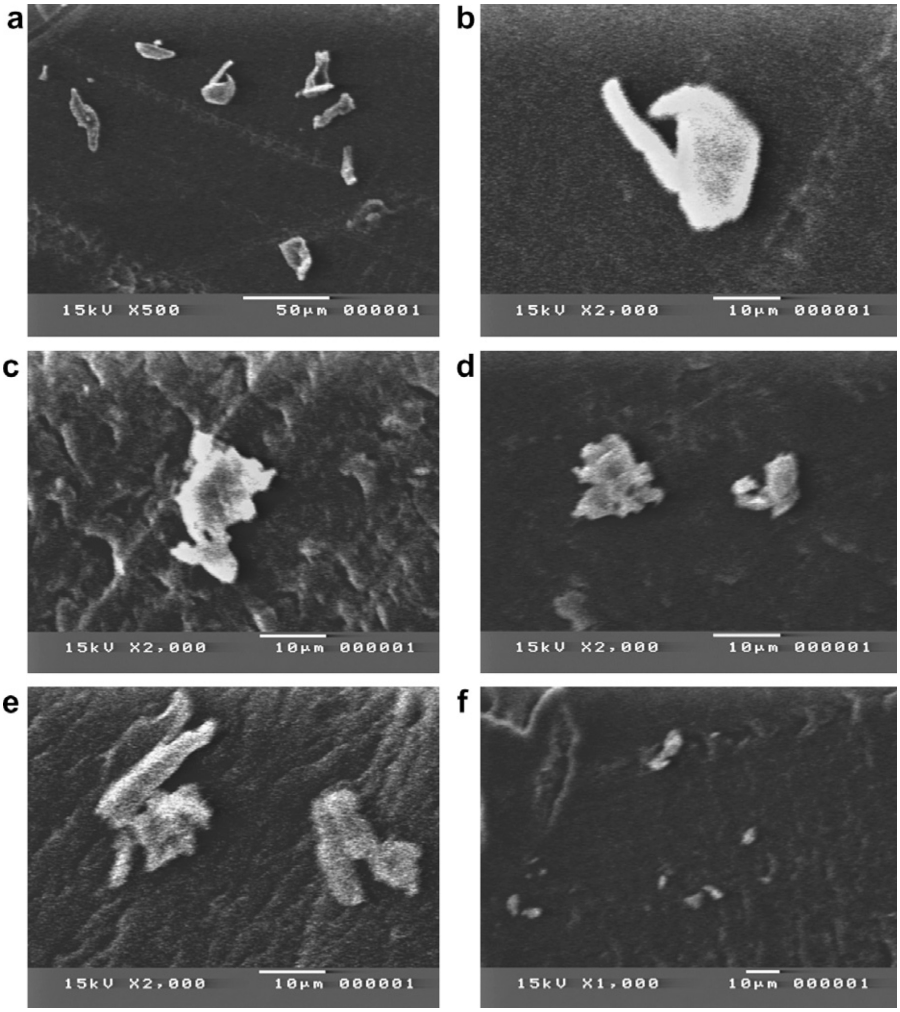


Fig. 11. SEM micrographs of HIPS samples: (a) virgin HIPS (low magnification); (b) virgin HIPS (high magnification); (c) reprocessed HIPS (9 cycles); (d) thermo-oxidated HIPS (4 days); (e) thermo-oxidated HIPS (8 days) and (f) thermo-oxidated HIPS (16 days).

free-volume parameter decreases initially for the thermo-oxidated HIPS samples, but increases markedly from 8 days of exposure onward. Diverse phenomena may influence simultaneously the viscoelastic behaviour of the PS phase of HIPS during exposure to thermo-oxidative ageing. Physical ageing induces molecular chain rearrangement resulting in significant changes in mechanical properties. In contrast, chemical ageing is related to chemical reactions with oxygen, which leads to the formation of oxidative groups and embrittlement [6]. Physical ageing of the PS phase seems to predominate during shorter exposure times, which causes structural recovery of the polymeric chains towards lower energy states [29]; this results in a decrease in the free-volume, which is responsible for the cohesion of polymeric chains and lower molecular mobility [24]. 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, which is related to the lower glass transition temperature and the increase in the free-volume.

4.3. Scanning electron microscopy (SEM)

Fig. 11 shows selected micrographs of sectioned HIPS samples subjected to multiple processing and thermo-oxidation. Virgin HIPS (Fig. 11a and b) shows the typical double-phase distribution with PB granules dispersed in the PS matrix. The PB granules exhibit heterogeneous shapes with particle sizes of 5–10 μm. After multiple processing (Fig. 11c), shrinkage of the PB granules can be observed together with a clear modification of their surfaces; cracks, channels and wrinkles are also visible in the PS matrix, which may be caused by the rearrangement of the PS chains during repetitive extrusion steps.

The progressive effect of thermo-oxidation on HIPS morphology can be followed with the exposure time. For shorter exposure times (Fig. 11d) the PB granules seem to crease and contract, showing a rough outer surface. After 8 days of thermo-oxidation (Fig. 11e), the PB granules develop irregular shapes, on the verge of losing their granular structure, while wrinkles can be observed in the PS matrix. For the sample subjected to the longest thermo-oxidative exposure time (Fig. 11f), the PB phase appears to have partially lost the granular microstructure, though small granules can still be detected. Cracks can be also observed in the PS matrix, which show the evident deterioration of HIPS morphology under thermo-oxidation.

5. Conclusions

Multiple processing and thermo-oxidation affect severely HIPS microstructure and morphology; both processes exhibit complex chemical and physical components that result in a modification of the PB and PS phases. Raman spectroscopy allows the study of PB microstructure in HIPS and a method for the deconvolution of the vinyl-1,2, *trans*-1,4, and *cis*-1,4 contributions has been proposed for the evaluation of the degradative effects of reprocessing and thermo-oxidation. PB microstructure is clearly modified, with *cis*-1,4 and *trans*-1,4 being more susceptible to these degradation mechanisms than vinyl-1,2.

The dynamic-mechanical relaxations associated with the PB and PS phase glass transitions are also influenced by multiple processing and thermo-oxidation, as demonstrated by the analysis of their loss plots and free-volume parameters. Reprocessing causes both a displacement of the PB and PS loss curves towards higher temperatures and a reduction in the free-volume, which suggest the occurrence of crosslinking in the PB phase and the rearrangement of PS chains. Thermo-oxidation results in a complex behaviour of the PB and PS phases throughout the exposure time. At shorter exposure times, physical ageing seems to predominate over the chemical effects, resulting in a decrease in the free-volume of the PS phase and a shift of the Arrhenius plot towards higher temperatures. The dramatic increase of the free-volume parameter for both the PB and PS phases at specific exposure points suggests, however, that chemical degradation of the PB phase at longer exposure times results in irreversible morphological changes in the PB granules, as confirmed by electron microscopy.

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References

[1] Finnveden G, Johansson J, Lind P, Moberg A. Life cycle assessment of energy from solid waste-part 1: general methodology and results. J Cleaner Production 2005;13(3): 213–29.

[2] Karlsson S. Recycled Polyolefins. Material properties and means for quality determination. Adv Polym Sci 2004;169:201–29.

[3] Vilaplana F, Ribes-Greus A, Karlsson S. Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation. Polym Degrad Stabil 2006;91(9): 2163–70.

[4] Santana RC, Manrich S. Studies on thermo-mechanical properties of post-consumer high impact polystyrene in five reprocessing steps. Prog Rubber, Plast Recyc Technol 2002;18(2):99–110.

[5] Soriano F, Morales G, Díaz de León R. Recycling of high impact polystyrene in coextruded sheet: Influence of the number of processing cycles on the microstructure and macroscopic properties. Polym Eng Sci 2006;46(12): 1698–705.

[6] Chen CC, Habibullah M, Sauer JA. Elevated temperature ageing of HIPS. J Appl Polym Sci 1983;28:391–406.

[7] Israeli Y, Lacoste J, Lemaire J, Singh RP, Sivaram S. Photo- and thermoinitiated oxidation of high-impact polystyrene: characterization by FT-IR spectroscopy. J Polym Sci: Part A: Polym Chem 1994;32:485–93.

[8] Ghaffar A, Scott A, Scott G. The chemical and physical changes occurring during U.V. degradation of high impact polystyrene. Eur Polym J 1975;11(3):271–5.

[9] Ghaffar A, Scott A, Scott G. Initiation processes in the photodegradation of high impact polystyrene–I Effects of prior thermal oxidation. Eur Polym J 1976;12(9):615–20.

[10] Adeniyi JB, Kolawole EG. Thermal and photo-degradation of unstabilized ABS. Eur Polym J 1984;20(1):43–7.

[11] Cornell SW, Koenig JL. The Raman Spectra of Polybutadiene Rubbers. Macromolecules 1969;2(5):540–5.

[12] Frankland JA, Edwards HGM, Johnson AF, Lewis IR, Poshyachinda S. Critical assessment of vibrational and NMR spectroscopic techniques for the microstructure determination of polybutadienes. Spectrochim Acta Part A: Molecular Spectrosc 1991;47(11):1511–24.

[13] Guilment J, Bokobza L. Determination of polybutadiene microstructures and styrene-butadiene copolymers composition by vibrational techniques combined with chemometric treatment. Vibrat Spectrosc 2001;26(1):133–49.

[14] Lacoste J, Delor J, Pilichowski JF, Singh RP, Vishwa-Prasad A, Sivaram S. Polybutadiene content and microstructure in high-impact polystyrene. J Appl Polym Sci 1996;59:953–9.

[15] Poshyachinda S, Edwards HGM, Johnson AF. Raman spectroscopic characterization of high-vinyl polybutadienes produced from anionic polymerization. Polymer 1991;32(2):338–42.

[16] Meier RJ. On art and science in curve-fitting vibrational spectra. Vibrat Spectrosc 2005;39(2):266–9.

[17] Fulcher GS. Analysis of recent measurements of the viscosity of glasses. J Am Ceram Soc 1925;8(6):339–55.

[18] Tammann G, Hesse W. Die Abhängigkeit der Viscosität von der Temperatur bie unterkühlten Flüssigkeiten. Z Anorg Allg Chem 1926;156(1):245–57.

[19] Vogel H. Temperature Dependence of Viscosity of Melts. Phys Z 1921;22:645–6.

[20] Piton M, Rivaton A. Photooxidation of polybutadiene at long wavelengths ([lambda] > 300 nm). Polym Degrad Stabil 1996;53(3):343–59.

[21] Wang SM, Chang JR, Tsiang RCC. Infrared studies of thermal oxidative degradation of polystyrene-block polybutadiene-block-polystyrene thermoplastic elastomers. Polym Degrad Stabil 1996;52(1):51–7.

[22] Poshyachinda S, Edwards HGM, Johnson AF. Dynamic mechanical thermal analysis of homopolymeric and diblock polybutadienes and polybutadiene blends. Polymer 1996;37(23):5171–7.

[23] Sircar AK. Characterization of isomeric elastomers using thermal analysis. J Therm Anal Calorim 1997;49(1):293–301.

[24] Wypych A, Duval E, Boiteux G, Ulanski J, David L, Seytre G, et al. Physical aging of atactic polystyrene as seen by dielectric relaxational and low-frequency vibrational Raman spectroscopies. J Non-Cryst Solids 2005;351(33–36):2593–8.

[25] Mano JF. Stress release in oriented HIPS as observed by dynamic mechanical analysis. Thermochim Acta 1999; 332(2):171–7.

[26] Goyanes SN. Dynamic mechanical behavior of atactic and high-impact polystyrene. J Appl Polym Sci 2000;75(7): 865–73.

[27] Fuoss RM, Kirkwood JG. Electrical Properties of Solids. VIII. Dipole Moments in Polyvinyl Chloride-Diphenyl Systems. J Am Chem Soc 1941;63(2):385–94.

[28] Bucknall CB, Soares VLP. Cavitation of rubber particles in high-impact polystyrene: Effects of crosslinking by Gamma-irradiation. J Polym Sci Part B: Polym Phys 2004;42(11): 2168–80.

[29] Struik LCE. Physical ageing in amorphous polymers and other materials. Amsterdam: Elsevier; 1978.

Article III

Chromatographic pattern for mimicking the occurrence of volatiles and low molecular weight compounds in high-impact polystyrene during multiple processing and thermo-oxidation.

Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson. Manuscript.

Title:

CHROMATOGRAPHIC PATTERN FOR MIMICKING THE OCCURRENCE OF LOW MOLECULAR WEIGHT COMPOUNDS IN HIGH-IMPACT POLYSTYRENE DURING MULTIPLE PROCESSING AND THERMO-OXIDATION

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CHROMATOGRAPHIC PATTERN FOR MIMICKING THE OCCURRENCE OF LOW MOLECULAR WEIGHT COMPOUNDS IN HIGH-IMPACT POLYSTYRENE DURING MULTIPLE PROCESSING AND THERMO-OXIDATION

Abstract

The analysis of the chromatographic pattern of virgin, reprocessed, and thermo-oxidated high-impact polystyrene (HIPS) proves to be a suitable and sensitive method to assess the degree of degradation of HIPS during its first life and subsequent recycling. Different low molecular weight compounds, such as residues of polymerisation (benzene derivates, styrene monomer, styrene dimers, and styrene trimers), degradation products, and additives have been identified and relatively quantified in HIPS. The release of residues of polymerisation has been proven to occur during reprocessing and thermo-oxidation, which may evidence the risk of emissions of volatile (VOCs) and semi-volatile organic compounds (SVOCs) during the life cycle of HIPS. A wide range of oxidated degradation products have been also identified to be formed during reprocessing and thermo-oxidation; these products can be identified as oxidative derivates of polystyrene, oxidated fragments from polybutadiene phase, and even oxidated fragments from the grafting points between the PS and PB phase.

Keywords

Chromatographic pattern, high-impact polystyrene; degradation; thermo-oxidation; processing.

Introduction

Plastic materials include in their formulations a wide range of low molecular weight compounds that may contribute to the final properties and performance of the final products; these compounds comprise monomeric and oligomeric residues of polymerisation, solvent residues, traces of initiators and catalysts, and different additives (antioxidants, stabilisers, plasticisers, and flame retardants). Other low molecular weight compounds may, on the other hand, be formed from the polymeric matrix and the additives due to the degradation processes during every step of the life cycle. Finally, polymeric materials may also come in contact with impurities and contaminants from the surrounding environment during service use and further recovery, which can diffuse into the polymeric bulk due to their permeable nature [1, 2]. This wide range of possible low molecular weight compounds, either inherent or externally introduced impurities, may affect the future performance and applicability of plastic products, and may even migrate and be released to the environment.

The emission of organic low molecular weight compounds during the life cycle of polymeric materials has become an important environmental concern. These volatile (VOCs) and semi-volatile organic compounds (SVOCs) can be released at every step of the life cycle, including manufacture, service life, and posterior waste management. Many studies have been made on the volatile emissions during processing and thermal degradation of polymers and particularly styrenic plastics [3-7]; a wide range of compounds, from degradative polymeric segments to additives, have been identified and associated to their release during the thermal treatment of polymeric materials. Patel and Xanthos have provided a wide review on the analysis on air emissions close to processing equipment, in which they indicate the types of volatiles emanating during processing of commodity thermoplastics and reinforced thermosets, together with the analytical procedures for their measurement [8]. These studies are interesting related to the migration of low molecular weight compounds to surrounding environments during use, and also related to the emissions during processing and mechanical recycling processes in terms of health at work. In this study, however, a different approach will be considered by studying the low molecular weight compounds present in the material bulk and analyse their relative abundance in terms of formation of new degradation products and/or migration to the environment.

The analysis of the chromatographic pattern of degradation products from natural and synthetic polymers is a valuable tool to investigate the degree of degradation and the degradation mechanisms in different environments [9-13]. The chromatographic analysis of certain degradation products, designed as indicator products, could be useful to predict the remaining life time and correlate the changes with macroscopic properties such as molecular weight distribution and mechanical properties [14-16]. The aim of the study is to investigate the occurrence of low molecular weight compounds during the life cycle of recycled high-impact polystyrene products. In recent studies, an integrated approach using multiple processing and thermo-oxidation has been proposed to model the degradation processes during the first use and subsequent mechanical recycling in synthetic polymers [17]. The thermo-mechanical degradation conditions to which styrenic polymers are subjected to during processing and mechanical recycling of the plastic material is modelled by multiple processing, whereas the degradation processes occurring during the service life is simulated by thermo-oxidative ageing in a forced ventilation oven. Important information about the degradation mechanisms and their effects on chemical structure, morphology, and macroscopic properties induced during life cycle can be provided these modelling procedures. This procedure to model the life cycle of polymeric materials is used here to track the occurrence of low molecular weight compounds in high-impact polystyrene under different degradative conditions.

Experimental

Materials and preparation of samples: multiple processing and thermo-oxidation

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M, was provided by BASF Española S.A. (Spain). The material was subjected to multiple processing and thermo-oxidation, to model the life cycle of recycled HIPS as described in a previous work [17]. Multiple processing was performed up to nine extrusion cycles with a maximum extrusion temperature of 200ºC. Thermo-oxidation was performed using a forced-ventilation oven under air atmosphere at 90ºC; the samples were removed for analysis after different exposure times of 1, 2, 4, 8, 12 and 16 days.

Microwave-assisted extraction (MAE)

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 110ºC 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 obtained extracts were filtered with a 0.45 mm pore size Teflon filter (Sorbent AB, Sweden) and placed in special vials, which were kept at 4ºC until further analysis.

Gas chromatography – mass spectrometry (GC-MS)

The GC-MS analyses of the extracts were performed on an FinniganMAT GCQ (Thermo, San Jose, CA) equipped with a wall-coated fused silica, low bleed CP-sil 5CB column (dimensions 0.25 mm x 30 m x 0.25μm) from Varian (Lake Forest, CA). A 10 μL volume was injected in the splitless mode at a temperature of 200°C. The chromatographic separation in the column was achieved through a constant flow of 0.8

mL min^{-1} with helium (scientific grade purity) from AGA Gas AB (Sweden) as carrier gas. The temperature program at the column was as follows: hold at 40°C for 1 min; increase to 250°C at a rate of 10°C min^{-1}; hold at 250°C for 20 min. The detection was carried out by ion-trap mass spectrometry. Electron ionisation was employed with an ion source temperature of 280°C. Mass spectra were collected in the full scan mode (35-500 m/z at a scan rate of 2 spectra s^{-1}). The mass spectra were collected after 5 minutes, after the main peak from the extraction solvents had reached the detector, to avoid ion saturation of the ion trap. Compound identification was performed either by injection of analytical standards, by comparison of the obtained spectra with the NIST MS search 2.0 database, or by comparison with bibliographic references.

Each sample was extracted and analysed by triplicate, and the average value was assumed as the representative.

Results and discussion

Identification of low molecular weight compounds (LMWC) in high-impact polystyrene (HIPS)

The identification and relative quantification of low molecular weight compounds (LMWC) present in high-impact polystyrene (HIPS) was performed using solvent extraction assisted by microwaves and further analysis of the extracts using gas chromatography-mass spectrometry (GC-MS). Monitoring the formation and/or migration of these compounds during the successive reprocessing cycles and during thermo-oxidation could be thus carried out. Figure 1 presents a full scan chromatograph from the extract of virgin HIPS, HIPS subjected to 9 reprocessing cycles, and HIPS thermo-oxidated 16 days. As a whole, the chromatographic pattern of the full scan obtained from virgin, reprocessed, and thermo-oxidated HIPS present common features: a first zone at short retention times from 5 – 9 minutes, where different benzene derivate volatile and semi-volatile organic compounds (VOCs and SVOCs) appear; a second zone around 17 minutes where styrene dimers elute; and finally a third zone at longer elution times where different peaks corresponding to styrene trimers and chain fragments from HIPS appear.

Table 1 presents the retention times, proposed identified compounds, and relative abundance calculated to the intensity of the employed internal standards, of the different peaks obtained from the chromatograms of the virgin and reprocessed HIPS samples. Similarly, Table 2 presents the chromatographic results from the extracted HIPS samples subjected to thermo-oxidation at different exposure times. The identification of the corresponding mass spectra associated to the chromatographic peaks was performed either by comparison with injected external standards, by comparison with the available NIST MS search 2.0 database, or by comparison of the spectra with bibliographic references. Relative quantification of the associated peaks with one benzene ring was performed in relation with the signal of the 4-methylstyrene (peak 9) internal standard; on the other hand, the relative abundance of bigger molecules with two or more benzene rings was calculated towards the area of o-terphenyl (peak 30) internal standard.

Peaks 1-15 correspond to a wide variety of volatile organic compounds (VOCs) that are present in the virgin HIPS and in the reprocessed and thermo-oxidated HIPS samples. These compounds are mainly benzene derivates and oxidated benzene derivates. Some of these compounds have also been reported by several authors in studies about VOCs and SVOCs in different styrenic materials and products [7, 18, 19]. Hexanedial (peak 2) appears at the thermo-oxidated samples with longer exposure time, and it may appear as an oxidation product of the polybutadiene segments present in HIPS. A closer look at the differences of the chromatographic pattern for the virgin HIPS, HIPS reprocessed 9 cycles, and HIPS thermo-oxidated 16 days at the VOC and SVOC region (between 6 and 10 minutes of retention time) is offered in Figure 2. Some peaks corresponding to benzene derivates (styrene, 1-methylethyl benzene, propylbenzene, 1- and 2-propenylbenzene) are already found in virgin HIPS. The apparition of new peaks for HIPS reprocessed 9 cycles but especially for HIPS aged 16 days can be clearly observed in the chromatograms, which can be assigned to oxidated benzene derivates (benzaldehyde, phenol, benzene acetaldehyde, α-methyl-benzenemethanol, acetophenone, benzoic acid) that may be formed during the degradative processes to which HIPS is subjected under the processing and thermo-oxidative conditions.

Peak 18 can be attributed to 2,6-di-tert-butyl-p-benzoquinone, which is a transformation product from different phenolic antioxidants commonly used in polyolefins and styrenic polymers [20-22]. Peak 21 corresponds to a long aliphatic ester structure that may originate from an additive (lubricant, antioxidant) found in the original material. Peaks 19-30 correspond to styrene dimers that may be formed through side reactions during the polymerisation of styrene or during thermal processing. Benzene, 1,1’-(1,3-propanediyl)bis- (peak 23) has been reported to be produced during hot processing of polystyrene [5]. Some authors have pointed out that other styrene dimers, such as cis- and trans-1,2-diphenylcyclobutane (peaks 24 and 26, respectively), 2,4-diphenyl-1-butene (peak 25), 1-phenyltetralin (peak 27), and 1,2-dihydro-4-phenylnaphtalene (peak 28), can be formed through side reaction during the thermal polymerisation of styrene [23-26]; these compounds are therefore retained in the polymeric matrix as polymerisation residues. Peak 22 could not be fully identified, but it may be classified as a styrene dimer using its mass spectrometry spectra, which shows similar fragmentation pattern as other polystyrenic fragments with main ions *m/z* 77, 91, 103, 117, and 130.

Peaks 33-41 can be structurally classified as different styrene trimers using their similar mass spectra, with molecular fragments *m/z* 91, 117, 129, 206-208 corresponding to different styrenic fragments. Some of these trimers, such as 1,3,5-triphenylhexene-5 (peak 34) and the four different diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline (peaks 35-38), could be identified through bibliographic comparison of their mass spectra [24, 27]. These compounds have been also reported to be formed during the polymerisation of styrene [24-26, 28, 29] and therefore retained as polymerization residues.

New peaks appear in the chromatograms for different aged HIPS samples. These peaks could not be completely identified using the NIST database, but their mass spectra indicate that they may belong to different oxidated and non-oxidated fragments that arise from the grafting points between the polystyrene (PS) and polybutadiene (PB) in HIPS under the thermo-oxidative degradation conditions. Peak 29 may correspond with a polycyclic benzoic compound with both aromatic and cyclic structures; peaks 31-32, on the other hand, may be assigned to oxidated polycyclic and benzoic structures formed by the oxidation of PS and PB grafting points.

Evolution of the relative abundance of LMWC in HIPS during consecutive reprocessing

Table 1 presents the data about the relative abundance, calculated towards the two injected internal standards, of the identified low molecular weight compounds in the HIPS samples subjected to nine reprocessing cycles. Interconnected tendencies in the relative abundance of the different identified compounds can be observed related to the thermo-mechanical degradation induced by the consecutive reprocessing steps. In general, the relative abundance of some peaks originally found in virgin HIPS tend to decrease with reprocessing steps; this result is in agreement with previous studies that suggested that reprocessing and recycling may contribute to minimise the presence of some volatile compounds [30]. However, other compounds may be formed during consecutive processing, which proves the importance of monitoring the formation of low molecular weight compounds during mechanical recycling.

Different volatile organic compounds, including styrene monomer, exhibit a clear and progressive reduction in their relative abundance with the consecutive reprocessing cycles compared to virgin HIPS. The high processing temperatures may be responsible for the emission of these organic compounds during the extrusion process. Other styrenic derivates, such as 1-propenylbenzene and 2-propenylbenzene, may be on the other hand formed from the degradation of HIPS under the thermo-mechanical stress caused by hot processing, since they show an increasing content with reprocessing cycles.

In general, the relative content of styrene dimers and trimers diminishes progressively during successive reprocessing steps. The evolution of the relative content of selected interesting compounds originally retained in the HIPS matrix as polymerisation residues can be followed in Figure 3a, for the case of styrene (peak 1, polystyrene monomer), trans-1,1'-(1,2-cyclobutanediyl)bis-benzene, (peak 26, styrene dimer), and one of the diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline (peak 35, styrene trimer). Other styrene dimers, such as 1,1'-(1,3-propanediyl)bis-benzene (peak 24) and 2,4-diphenyl-1-butene (peak 25) show higher relative abundance with consecutive extrusion cycles; this indicates their formation during melt processing of HIPS as it has been previously reported by other authors [5].

The progressive formation of oxidated derivates of styrene during the consecutive reprocessing cycles is one of the main features of the chromatographic study. The relative presence of oxidated derivatives of styrene can be traced in Figure 3b for benzaldehyde (peak 5), phenol (peak 6), and acetophenone (peak 15). The temperature conditions and the mechanical stress to which the melt polymeric chains are subjected during processing, and the presence of residual oxygen in the extruder may be responsible of thermo-mechanical and oxidative degradation of HIPS during consecutive reprocessing, which may lead to the formation of oxidation products from polystyrene, such as aldehydes (benzaldehyde), ketones (acetophenone), and alcohols (phenol).

Evolution of the relative abundance of LMWC in HIPS during thermo-oxidation

The evolution of the relative abundance with thermo-oxidation exposure time for the different low molecular weight compounds identified in high-impact polystyrene is displayed in Table 2. In previous studies, the complex behaviour of high-impact polystyrene subjected to thermo-oxidation throughout exposure time was pointed out; at shorter exposure times physical ageing seems to predominate, whereas chemical degradation of the polymeric chains has irreversible effects after longer exposure times [17, 31]. A similar time-dependent pattern can be observed for the different families of low molecular weight compounds during thermo-oxidation exposure.

Styrene (peak 1) shows a dramatic reduction in its relative abundance during short time exposure, together with some other volatile organic compounds as 1-methylethyl-benzene (peak 3), propylbenzene (peak 4), and 1-propenylbenzene (peak 7). This behaviour shows the release of these VOCs from the polymer matrix to the environment during thermo-oxidative exposure. For longer exposure times, the abundance of these compounds tends to stabilise or even increase. Other benzene derivatives, including several semi-volatile organic compounds, styrene dimers, and styrene trimers, exhibit a totally different behaviour; for shorter exposure times, their relative abundance tends to slightly increase, whereas for longer exposure times their abundance decreases. Different phenomena seem to be taking place simultaneously under thermo-oxidation at short and long exposures. For short exposure times, physical ageing in the polymeric structure occurs, which may enhance the migration and release of different low molecular weight compounds (residues of polymerisation, including styrene monomer, dimers, and trimers); on the other hand, thermal initiated reactions of styrene monomer may occur at the temperature conditions of the forced-ventilation oven, with the formation of a wide range of styrenic dimers and trimers [23, 32, 33], and therefore increasing slightly the relative abundance of these styrenic derivates. For longer exposure times, these competing release and formation processes for styrenic dimers and trimers seems to stabilise, due to chemical deterioration of the polymeric structure. Figure 4a represents graphically the evolution of different residues of polymerisation (styrene monomer, trans-1,1'-(1,2-cyclobutanediyl)bis-benzene, and one of the diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline), exhibiting their complex behaviour with exposure time.

Thermo-oxidation has been pointed out to more severe effects than reprocessing on the structure and properties of HIPS [17]. This fact can be again verified by the formation of different oxidative degradation products of polystyrene during thermo-oxidation. A wide range of oxidated structures can be found in HIPS at different exposure times to the thermo-oxidative environment, including oxidated fragments of the polybutadiene chain, as hexane dial (peak 2), and a branched hexaketone (peak 12), several oxidated benzene derivates such as benzaldehyde (peak 5), phenol (peak 6), benzeneacetaldehyde (peak 13), α-methyl-benzenemethanol (peak 14), acetophenone (peak 15), benzoic acid (peak 17), and several oxidated structures from the grafting points of PS and PB (peaks 29, 31, and 32). The evolution of the relative abundance of selected oxidated structures, including benzaldehyde, phenol, acetophenone, and benzoic acid, with exposure time can be clearly observed at Figure 4b, proving again the different phenomena involved in thermo-oxidation of HIPS. At short exposure times until 8 days of ageing, the formation of oxidated derivates occurs at a moderate rate, due to the protective action of the stabilising system in HIPS. At longer exposure times, however, the chemical ageing effects are remarkable, with an exponential raise of the abundance of these oxidated derivates and the formation of new degradation products.

Conclusions

The occurrence of low molecular weight compounds during multiple processing and thermo-oxidation of high-impact polystyrene (HIPS) has been analysed using microwave-assisted extraction (MAE) prior to detection by gas chromatography-mass spectrometry (GC-MS). A wide range of low molecular weight compounds have been identified in virgin HIPS, including different residues of polymerisation (styrene monomer, styrene dimers, and styrene trimers), benzene derivates, and additives. The migration of different volatile organic compounds (VOCs) during multiple processing and thermo-oxidation has been evidenced. On the other hand, the formation of several degradation products, including oxidative derivates of polystyrene (benzaldehyde, acetophenone, phenol, benzoic acid), oxidated fragments from polybutadiene phase, and even oxidated fragments from the grafting points between the PS and PB phase has been reported under reprocessing and thermo-oxidation. Thermo-oxidation leads to a more intense release of oxidated degradation products than multiple processing. The analysis of the chromatographic pattern of HIPS subjected to thermo-oxidation and multiple processing gives useful information for monitoring the degradative changes of HIPS during its life cycle, including processing, service life, and further mechanical recycling.

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References

[1] S. Karlsson, *Advances in Polymer Science* 169, 201-229 (2004).

[2] F. Vilaplana, and S. Karlsson, *Macromolecular Materials and Engineering* DOI: 10.1002/mame.200700393, (2008).

[3] I. Ciucanu, M. Kaykhaii, L. Montero, J. Szubra, and J. Pawliszyn, *Journal of Chromatographic Science* 40, (July 2002), 350-354 (2002).

[4] M. Watanabe, C. Nakata, W. Wu, K. Kawamoto, and Y. Noma, *Chemosphere* 68, (11), 2063-2072 (2007).

[5] S. L. Hathcock, and W. Bertsch, *Journal of High Resolution Chromatography* 16, (11), 651-659 (1993).

[6] P. Kusch, and G. Knupp, *Journal of Separation Science* 25, (8), 539-542 (2002).

[7] P. Kusch, and G. Knupp, *Journal of Polymers and the Environment* 12, (2), 83-87 (2004).

[8] S. H. Patel, and M. Xanthos, *Advances in Polymer Technology* 20, (1), 22-41 (2001).

[9] A.-C. Albertsson, and S. Karlsson, *Journal of Polymers and the Environment* 4, (1), 51-53 (1996).

[10] A.-C. Albertsson, C. Barenstedt, and S. Karlsson, *Journal of Chromatography A* 690, (2), 207-217 (1995).

[11] M. Hakkarainen, A.-C. Albertsson, and S. Karlsson, *Journal of Chromatography A* 741, (2), 251-263 (1996).

[12] S. Karlsson, M. Hakkarainen, and A.-C. Albertsson, *Journal of Chromatography A* 688, (1-2), 251-259 (1994).

[13] S. Karlsson, M. Hakkarainen, and A.-C. Albertsson, *Macromolecules* 30, (25), 7721-7728 (1997).

[14] M. Gröning, and M. Hakkarainen, *Journal of Applied Polymer Science* 86, (13), 3396-3407 (2002).

[15] M. Hakkarainen, and A. C. Albertsson, *Biomacromolecules* 6, (2), 775-779 (2005).

[16] G. Gallet, S. Carroccio, P. Rizzarelli, and S. Karlsson, *Polymer* 43, (4), 1081-1094 (2002).

[17] F. Vilaplana, A. Ribes-Greus, and S. Karlsson, *Polymer Degradation and Stability* 91, (9), 2163-2170 (2006).

[18] Woodfin V. Ligon Jr., and Marcia C. George, *Journal of Polymer Science: Polymer Chemistry Edition* 16, (10), 2703-2709 (1978).

[19] G. A. Eiceman, and M. Carpen, *Analytical Letters* 15, (A14), 1169-1177 (1982).

[20] J. Virt, L. Rosík, J. Kováová, and J. Pospisil, *European Polymer Journal* 16, (3), 247-253 (1980).

[21] L. Coulier, H. G. M. Orbons, and R. Rijk, *Polymer Degradation and Stability* 92, (11), 2016-2025 (2007).

[22] R. G. Lichtenthaler, and F. Ranfelt, *Journal of Chromatography A* 149, 553-560 (1978).

[23] K. S. Khuong, W. H. Jones, W. A. Pryor, and K. N. Houk, *J. Am. Chem. Soc.* 127, (4), 1265-1277 (2005).

[24] Harald Friedrich Kauffmann, *Die Makromolekulare Chemie* 180, (11), 2649-2663 (1979).

[25] Weldon G. Brown, *Die Makromolekulare Chemie* 128, (1), 130-136 (1969).

[26] K. Kirchner, and K. Riederle, *Angewandte Makromolekulare Chemie* 111, (1), 1-16 (1983).

[27] T. Yamada, M. Tanaka, S. Hirano, Y. Nagao, K. Kobayashi, T. Sakurai, Y. Furukawa, and Y. Nobuhara, *Bunseki Kagaku* 49, (11), 857-867 (2000).
[28] Jürgen Wiesner, and Peter Mehnert, *Die Makromolekulare Chemie* 165, (1), 1-9 (1973).
[29] J. Schellenberg, S. Knoll, G. Nord, and W. Leukefeld, *European Polymer Journal* 39, (12), 2351-2357 (2003).
[30] F. Stangenberg, S. Ågren, and S. Karlsson, *Chromatographia* 59, (January), 101-106 (2004).
[31] F. Vilaplana, S. Karlsson, and A. Ribes-Greus, *European Polymer Journal* 43, (10), 4371-4381 (2007).
[32] K. Kirchner, and K. Riederle, *Angewandte Makromolekulare Chemie* 111, (1), 1-16 (1983).
[33] J. Wiesner, and P. Mehnert, *Die Makromolekulare Chemie* 165, (1), 1-9 (1973).

Table 4. Relative abundance and chromatographic properties of identified low molecular weight compounds in HIPS samples

Peak nr.	Proposed compound	R.T. (min)	Relative abundance, x10^4 (RSD, in %)									
			Virgin	r1	r2	r3	r4	r5	r6	r7	r8	r9
1	Styrene [a,e]	5.66	4153.6 (9.4)	3605.2 (3.7)	3671.2 (8.2)	3490.9 (4.2)	3284.4 (5.0)	3055.3 (6.9)	2992.7 (1.6)	2694.1 (1.4)	2580.9 (6.2)	2474.9 (6.6)
3	Benzene, (1-methylethyl)- [b,e]	6.11	98.9 (5.2)	91.1 (4.5)	98.0 (5.5)	87.1 (10.3)	86.7 (8.1)	88.2 (5.3)	84.1 (1.8)	83.5 (4.0)	73.5 (4.4)	78.2 (6.7)
4	Benzene, propyl- [b,e]	6.55	27.0 (4.5)	28.0 (24.7)	27.0 (4.6)	26.0 (19.8)	24.4 (12.4)	24.4 (16.7)	23.9 (11.1)	24.4 (7.4)	21.3 (13.0)	24.4 (14.7)
5	Benzaldehyde [a,e]	6.73	7.2 (19.2)	17.8 (44.1)	37.8 (14.1)	48.9 (8.3)	60.3 (2.4)	64.9 (5.5)	64.9 (7.5)	84.9 (25.1)	81.8 (4.2)	90.6 (5.3)
6	Phenol [b,e]	6.85	-	1.3 (20.9)	2.9 (30.0)	3.8 (15.8)	4.6 (16.5)	5.5 (20.3)	5.2 (15.0)	5.5 (17.8)	6.2 (15.7)	7.0 (8.4)
7	Benzene, 1-propenyl [b,e]	6.98	5.6 (1.2)	6.4 (27.0)	7.8 (14.6)	9.7 (27.4)	10.0 (26.8)	11.8 (22.3)	12.1 (13.7)	11.8 (16.2)	13.3 (20.4)	14.4 (7.7)
8	Heptane, 2,2,4,6,6-pentamethyl- [b,e]	7.05	31.8 (8.5)	28.9 (5.1)	32.0 (6.3)	32.9 (15.7)	28.5 (9.9)	28.5 (12.2)	26.3 (11.9)	30.9 (26.9)	25.3 (10.6)	24.3 (5.3)
9	4-methylstyrene	7.29	Internal standard (I.S.)									
10	Benzene, (1-methylpropyl)- [b,e]	7.42	12.1 (5.9)	11.2 (17.3)	13.1 (20.4)	12.5 (16.2)	12.7 (27.7)	13.0 (29.6)	12.2 (20.6)	10.1 (12.4)	11.6 (38.7)	11.2 (19.0)
11	Benzene, 2-propenyl [b,e]	7.72	8.2 (7.9)	8.8 (3.8)	10.8 (6.7)	12.1 (8.8)	13.1 (6.6)	14.4 (7.3)	14.2 (7.4)	16.7 (4.7)	15.3 (3.5)	16.9 (7.0)
13	Benzene acetaldehyde [b,e]	7.98	6.7 (10.4)	5.6 (12.0)	6.8 (4.5)	7.3 (14.9)	5.6 (20.8)	6.1 (4.8)	5.7 (12.4)	5.8 (7.7)	4.3 (29.3)	5.6 (20.8)
14	Benzenemethanol, α-methyl- [b,e]	8.2	0.7 (59.7)	2.0 (4.7)	3.5 (20.4)	4.2 (15.0)	3.8 (8.7)	5.4 (9.6)	5.3 (8.1)	4.8 (13.6)	5.0 (26.7)	6.3 (17.1)
15	Acetophenone [a,e]	8.34	4.9 (6.9)	12.9 (6.8)	19.2 (10.9)	25.3 (13.8)	29.2 (12.9)	34.2 (6.1)	36.1 (6.8)	42.2 (10.7)	43.1 (5.9)	49.2 (6.3)
16	saturated hydrocarbon [e]	8.85	1.5 (29,2)	5.6 (12.7)	3.8 (20.2)	3.6 (19.0)	2.1 (6.5)	3.9 (77.7)	3.5 (48.5)	3.9 (25.0)	4.4 (23.9)	4.3 (80.8)
18	2,6- Di-tert-butyl-p-benzoquinone [f]	14.03	122.8 (19.8)	161.2 (46.5)	162.9 (18.5)	149.3 (37.9)	145.8 (60.8)	185.4 (26.6)	136.6 (36.5)	181.4 (25.5)	156.8 (25.9)	180.0 (24.6)
19	Ethylene, 1,1-diphenyl [b,f]	14.77	13.3 (8.4)	13.2 (16.3)	13.8 (7.7)	14.8 (16.7)	12.9 (13.3)	12.5 (16.3)	13.1 (6.4)	12.7 (4.4)	14.5 (30.0)	13.3 (6.5)
20	1,2-diphenylethylene [b,f]	14.9	41.1 (12.6)	41.9 (28.3)	29.0 (67.7)	34.7 (72.3)	36.5 (40.8)	35.9 (43.9)	34.4 (40.4)	29.1 (59.6)	27.4 (57.2)	32.8 (47.8)

21	Dodecanoic acid, ethyl ester [b,f]	15.93	1.3 (34.7)	13.4 (18.8)	54.9 (21.2	39.9 (29.2)	33.3 (32.3)	23.6 (34.7)	21.5 (13.9)	14.5 (20.8)	17.4 (20.1)	8.9 (48.4)
22	styrene dimer [f]	16.1	56.3 (10.1)	56.2 (10.7)	67.2 (13.8)	67.0 (14.0)	63.3 (11.7)	64.5 (10.3)	64.4 (7.2)	65.3 (9.4)	63.5 (19.7)	68. (18.6)6
23	Benzene, 1,1'-(1,3-propanediyl)bis- [b,f]	16.46	299.9 (12.6)	364.5 (14.1)	408.8 (12.1)	456.0 (11.4)	483.5 (17.3)	448.2 (9.5)	480.4 (11.9)	458.9 (4.6)	539.5 (15.9)	570.2 (11.8)
24	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis- [b,c,f]	16.96	2697.9 (3.8)	2603.7 (8.0)	2812.2 (12.6)	2799.4 (10.5)	2587.3 (13.9)	2450.9 (9.3)	2476.1 (5.0)	2306.2 (6.4)	2440.7 (15.1)	2443.4 (10.7)
25	2,4-diphenyl-1-butene [d,f]	17.21	1841.0 (7.2)	1868.7 (7.7)	2019.6 (13.4)	2046.8 (9.6)	1961.0 (12.9)	1861.3 (6.5)	1889.2 (6.8)	1799.8 (5.1)	1939.1 (15.2)	1955.2 (10.7)
26	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans- [b,c,f]	17.54	10051.5 (7.3)	10132.3 (9.5)	10959.4 (14.6)	10919.1 (10.5)	10367.3 (14.9)	9806.7 (10.2)	10056.2 (8.6)	9335.5 (5.9)	9866.4 (15.8)	10065.1 (9.8)
27	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- [b,f]	17.82	574.6 (4.9)	570.0 (8.4)	655.1 (11.1)	641.4 (14.4)	608.9 (13.3)	549.3 (11.8)	552.6 (10.2)	527.9 (2.2)	588.2 (8.7)	563.6 (9.1)
28	Naphthalene, 1,2-dihydro-4-phenyl- [b,f]	18.08	366.5 (3.5)	334.3 (5.0)	401.8 (11.5)	412.4 (19.7)	355.2 (14.2)	330.9 (8.2)	329.0 (7.6)	310.4 (3.1)	323.7 (6.5)	327.4 (4.4)
30	o-Terphenyl	19.04	Internal standard (I.S.)									
33	styrene trimer [f]	23.26	1343.4 (12.8)	1103.3 (10.0)	1228.7 (13.6)	1228.4 (7.8)	1113.5 (16.8)	1148.2 (10.5)	1131.6 (9.0)	1029.9 (5.0)	1129.7 (33.9)	1022.6 (18.5)
34	1,3,5-triphenylhexene-5 [d,f]	24.83	18003.5 (12.6)	16622.0 (7.0)	18304.6 (11.6)	18073.2 (8.7)	15745.8 (12.6)	15931.8 (6.9)	16077.2 (12.6)	16653.5 (8.3)	15473.9 (3.5)	17169.5 (20.0)
35	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.33	21223.8 (11.6)	19017.2 (7.7)	21588.3 (11.1)	21512.7 (8.5)	19104.9 (12.9)	19123.2 (4.6)	19469.6 (9.5)	20057.3 (10.7)	19629.9 (6.2)	19772.5 (15.0)
36	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.61	33491.5 (12.5)	30300.3 (9.7)	34039.9 (12.4)	34231.7 (9.5)	30272.5 (14.8)	30263.7 (7.0)	30712.8 (8.3)	31193.4 (8.9)	30959.6 (6.5)	32096.4 (16.8)
37	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.72	10350.7 (11.1)	9150.2 (10.9)	9618.9 (11.0)	9626.7 (5.6)	8299.5 (15.9)	8604.4 (12.8)	8792.4 (5.3)	9061.2 (16.3)	8136.2 (6.4)	8743.4 (17.8)
38	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.9	12433.0 (9.7)	11223.7 (10.0)	11898.8 (10.6)	12060.6 (7.0)	10424.2 (16.9)	10821.9 (11.1)	10884.9 (4.3)	10570.4 (10.6)	10635.0 (5.2)	10846.1 (14.7)
39	styrene trimer [f]	28.57	1250.8 (16.3)	1359.9 (15.5)	1508.6 (17.2)	1481.1 (18,2)	1319.9 (10.2)	1145.9 (17.3)	1281.1 (17.0)	1323.1 (3.2)	1391.2 (21.0)	1328.6 (21.1)
40	styrene trimer [f]	28.81	7033.5 (10.6)	6449.1 (11.2)	6495.5 (13.1)	6441.3 (3.8)	5631.0 (12.2)	6063.4 (11.8)	6312.8 (7.2)	5424.2 (2.7)	5894.4 (15.4)	5961.5 (15.6)
41	styrene trimer [f]	29.31	3743.3 (12.4)	3574.6 (9.7)	3548.5 (14.9)	3765.0 (5.9)	3203.9 (13.3)	3379.2 (12.0)	3793.5 (13.2)	3461.3 (15.0)	3688.5 (4.9)	3483.9 (13.4)

[a] Identification by injection of standard substances; [b] Proposed identification by comparison to the NIST database; [c] Proposed identification through bibliographic reference [24]; [d] Proposed identification through bibliographic reference [27]; [e] Relative quantification respect 4-methylstyrene (I.S.); [f] Relative quantification respect o-terphenyl (I.S.)

Table 2. Relative abundance and chromatographic properties of identified low molecular weight compounds in HIPS samples

Peak nr.	Proposed compound	R.T. (min)	Relative abundance x10^4 (RSD, in %)						
			Virgin	a1d	a2d	a4d	a8d	a12d	a16d
1	Styrene [a,e]	5.66	4153.6 (9.4)	2220.2 (25.4)	2364.3 (7.5)	2713.9 (0.6)	2633.2 (4.4)	2287.1 (4.1)	1799.7 (2.7)
2	Hexanedial [b,e]	6.04	-	-	2.5 (64.6)	2.7 (44.7)	9.6 (61.4)	22.4 (22.6)	46.8 (4.5)
3	Benzene, (1-methylethyl)- [b,e]	6.11	98.9 (5.2)	47.9 (30.6)	56.4 (4.6)	68.5 (3.0)	73.4 (4.9)	69.4 (9.0)	68.5 (5.8)
4	Benzene, propyl- [b,e]	6.55	27.0 (4.5)	13.4 (26.4)	15.6 (20.0)	20.7 (19.6)	21.3 (8.9)	21.7 (7.8)	22.1 (15.2)
5	Benzaldehyde [a,e]	6.73	7.2 (19.2)	12.9 (8.0)	19.9 (22.5)	19.9 (13.1)	34.9 (3.1)	58.4 (3.0)	99.5 (5.4)
6	Phenol [b,e]	6.85	-	2.0 (13.5)	2.1 (35.6)	4.1 (33.3)	8.0 (11.6)	14.0 (19.0)	43.4 (19.7)
7	Benzene, 1-propenyl [b,e]	6.98	5.6 (1.2)	4.6 (25.3)	5.5 (21.0)	6.3 (8.4)	6.3 (7.1)	7.3 (17.7)	6.7 (11.2)
8	Heptane, 2,2,4,6,6-pentamethyl- [b,e]	7.05	31.8 (8.5)	22.0 (12.5)	21.0 (7.8)	23.7 (2.2)	25.0 (6.5)	26.7 (8.9)	24.3 (14.5)
9	4-methylstyrene	7.29	Internal standard (I.S.)						
10	Benzene, (1-methylpropyl)- [b,e]	7.42	12.1 (5.9)	12.2 (34.2)	14.2 (25.3)	14.4 (13.0)	12.5 (8.3)	14.2 (14.2)	13.5 (19.5)
11	Benzene, 2-propenyl [b,e]	7.69	8.2 (7.9)	10.5 (10.1)	9.6 (19.6)	8.9 (21.0)	10.0 (24.4)	9.6 (18.4)	8.6 (37.0)
12	branched hexaketone [e]	7.72	-	-	1.0 (31.9)	2.9 (13.2)	7.4 (17.0)	17.5 (17.0)	50.7 (11.7)
13	Benzene acetaldehyde [b,e]	7.98	6.7 (10.4)	2.8 (6.9)	3.2 (36.3)	3.2 (15.1)	4.2 (9.3)	6.1 (7.3)	7.4 (10.4)
14	Benzenemethanol, α-methyl- [b,e]	8.22	0.7 (59.7)	1.9 (26.7)	2.7 (34.9)	4.1 (18.3)	16.8 (10.7)	35.7 (11.3)	82.1 (10.1)
15	Acetophenone [a,e]	8.34	4.9 (6.9)	11.6 (13.0)	16.5 (22.4)	27.0 (9.9)	55.6 (7.2)	87.9 (10.0)	184.1 (8.8)
16	saturated hydrocarbon [e]	8.85	1.5 (29.2)	41.1 (58.8)	32.3 (31.6)	12.3 (20.4)	11.1 (7.7)	9.6 (7.7)	13.6 (6.9)
17	Benzoic acid [b,e]	9.66	-	-	-	-	1.5 (32.2)	22.6 (35.3)	98.4 (14.6)
18	2,6- Di-tert-butyl-p-benzoquinone [b,f]	14.03	122.8 (19.8)	88.0 (10.5)	67.2 (47.1)	89.9 (82.4)	105.4 (54.2)	90.4 (37.3)	90.9 (25.9)
19	Ethylene, 1,1-diphenyl [b,f]	14.77	13.3 (8.4)	16.5 (4.0)	13.5 (4.4)	12.2 (30.7)	11.6 (5.3)	8.5 (27.5)	6.9 (21.9)
20	1,2-diphenylethylene [b,f]	14.9	41.1 (12.6)	66.0 (7.1)	60.7 (8.2)	57.0 (14.3)	50.2 (3.7)	55.5 (12.6)	59.3 (22.3)
21	Dodecanoic acid, ethyl ester [b,f]	15.93	1.3 (34.7)	167.4 (47.2)	108.5 (30.0)	36.9 (22.6)	28.2 (2.7)	22.5 (6.3)	27.9 (14.5)
22	styrene dimer [f]	16.1	56.3 (10.1)	45.6 (10.3)	45.1 (8.2)	49.7 (7.1)	48.8 (8.3)	46.7 (13.4)	43.1 (16.0)
23	Benzene, 1,1'-(1,3-propanediyl)bis- [b,f]	16.46	299.9 (12.6)	409.6 (12.0)	412.6 (6.0)	440.2 (5.8)	439.3 (13.2)	476.6 (9.8)	491.6 (11.4)
24	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis- [b,c,f]	16.96	2697.9 (3.8)	2551.8 (8.3)	2562.6 (5.5)	2494.0 (8.9)	2576.9 (6.4)	2641.4 (13.7)	2209.0 (10.3)
25	2,4-diphenyl-1-butene [d,f]	17.21	1841.0 (7.2)	1921.7 (3.7)	1847.8 (4.7)	1857.3 (8.5)	1759.1 (6.9)	1655.8 (8.3)	1339.3 (9.6)
26	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans- [b,c,f]	17.54	10051.5 (7.3)	11705.1 (9.6)	11580.0 (5.0)	11925.8 (6.2)	11783.9 (11.0)	11844.1 (8.3)	10776.4 (6.2)
27	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- [b,f]	17.82	574.6 (4.9)	654.7 (9.6)	708.3 (9.4)	586.8 (13.1)	566.3 (10.5)	503.6 (44.6)	509.4 (16.1)
28	Naphthalene, 1,2-dihydro-4-phenyl- [b,f]	18.08	366.5 (3.5)	359.3 (2.6)	324.5 (4.8)	325.4 (10.0)	291.8 (6.0)	278.1 (8.2)	219.8 (11.8)
29	Polycyclic benzoic structure [f]	18.84	-	-	-	-	116.3 (32.6)	235.2 (11.9)	470.0 (12.6)

30	o-Terphenyl	19.04	Internal standard (I.S.)						
31	oxidated styrene trimer [f]	20.16	-	210.3 (11.4)	323.6 (26.2)	430.5 (34.9)	999.7 (12.1)	1659.9 (14.2)	2932.8 (7.2)
32	oxidated styrene cyclic structure [f]	21.38	-	-	-	51.9 (86.8)	153.6 (31.1)	319.7 (9.7)	702.2 (12.4)
33	styrene trimer [f]	23.26	1343.4 (12.8)	1419.4 (9.8)	1250.4 (4.1)	1223.8 (9.9)	1247.5 (10.4)	1165.9 (20.9)	863.9 (7.0)
34	1,3,5-triphenylhexene-5 [d,f]	24.83	18003.5 (12.6)	19507.7 (3.3)	18923.6 (1.7)	18011.7 (9.4)	17445.9 (6.4)	16254.8 (13.4)	13476.1 (4.5)
35	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.33	21223.8 (11.6)	24266.3 (4.4)	23150.7 (3.9)	21864.5 (11.7)	21523.2 (7.7)	21358.2 (12.9)	18562.5 (3.0)
36	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.61	33491.5 (12.5)	37317.2 (5.0)	34504.1 (2.0)	33233.8 (13.2)	32364.3 (6.4)	31147.0 (12.5)	27399.4 (3.7)
37	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.72	10350.7 (11.1)	13461.9 (6.0)	12838.5 (12.6)	12456.3 (16.0)	11827.0 (6.7)	11489.4 (13.9)	10323.9 (1.5)
38	1-phenyl-4-(1-phenylethyl)-tetraline diastereomer [c,f]	26.9	12433.0 (9.7)	16393.5 (8.5)	16027.3 (10.9)	14706.5 (10.1)	14216.1 (5.5)	13697.8 (11.4)	12565.9 (3.3)
39	styrene trimer [f]	28.57	1250.8 (16.3)	1216.8 (3.1)	1541.9 (9.1)	1643.3 (5.9)	1371.3 (15.1)	1281.3 (27.0)	1023.8 (3.6)
40	styrene trimer [f]	28.81	7033.5 (10.6)	9734.5 (5.0)	9382.0 (5.8)	9157.1 (9.5)	8655.3 (7.8)	8432.4 (14.8)	7264.9 (6.5)
41	styrene trimer [f]	29.31	3743.3 (12.4)	4088.3 (1.8)	3977.0 (6.9)	3891.4 (14.8)	3906.1 (9.8)	4030.5 (19.6)	3953.3 (7.7)

[a] Identification by injection of standard substances; [b] Proposed identification by comparison to the NIST database; [c] Proposed identification through bibliographic reference [24]; [d] Proposed identification through bibliographic reference [27]; [e] Relative quantification respect 4-methylstyrene (I.S.); [f] Relative quantification respect o-terphenyl (I.S.)

Figure Captions

Figure 1. Complete total ion chromatogram (TIC) from the MAE extracts of virgin HIPS, HIPS reprocessed nine cycles, and HIPS thermo-oxidated 16 days. NOTE: numbered peaks correspond with the compounds in Table 1 and Table 2.

Figure 2. Chromatographic pattern of the VOC and SVOC region for virgin HIPS, HIPS reprocessed 9 times, and HIPS thermo-oxidated 16 days. NOTE: numbered peaks correspond with the compounds in Table 1 and Table 2. Peaks marked with (*) correspond with different background compounds (septa peaks, peaks from the extraction blank).

Figure 3. Evolution of the relative abundance of selected interesting low molecular weight compounds with reprocessing steps: a) residues from polymerisation (styrene monomer, dimers, and trimers); b) oxidated derivates of benzene.

Figure 4. Evolution of the relative abundance of selected interesting low molecular weight compounds with thermo-oxidation time: a) residues from polymerisation (styrene monomer, dimers, and trimers); b) oxidated derivates of benzene.

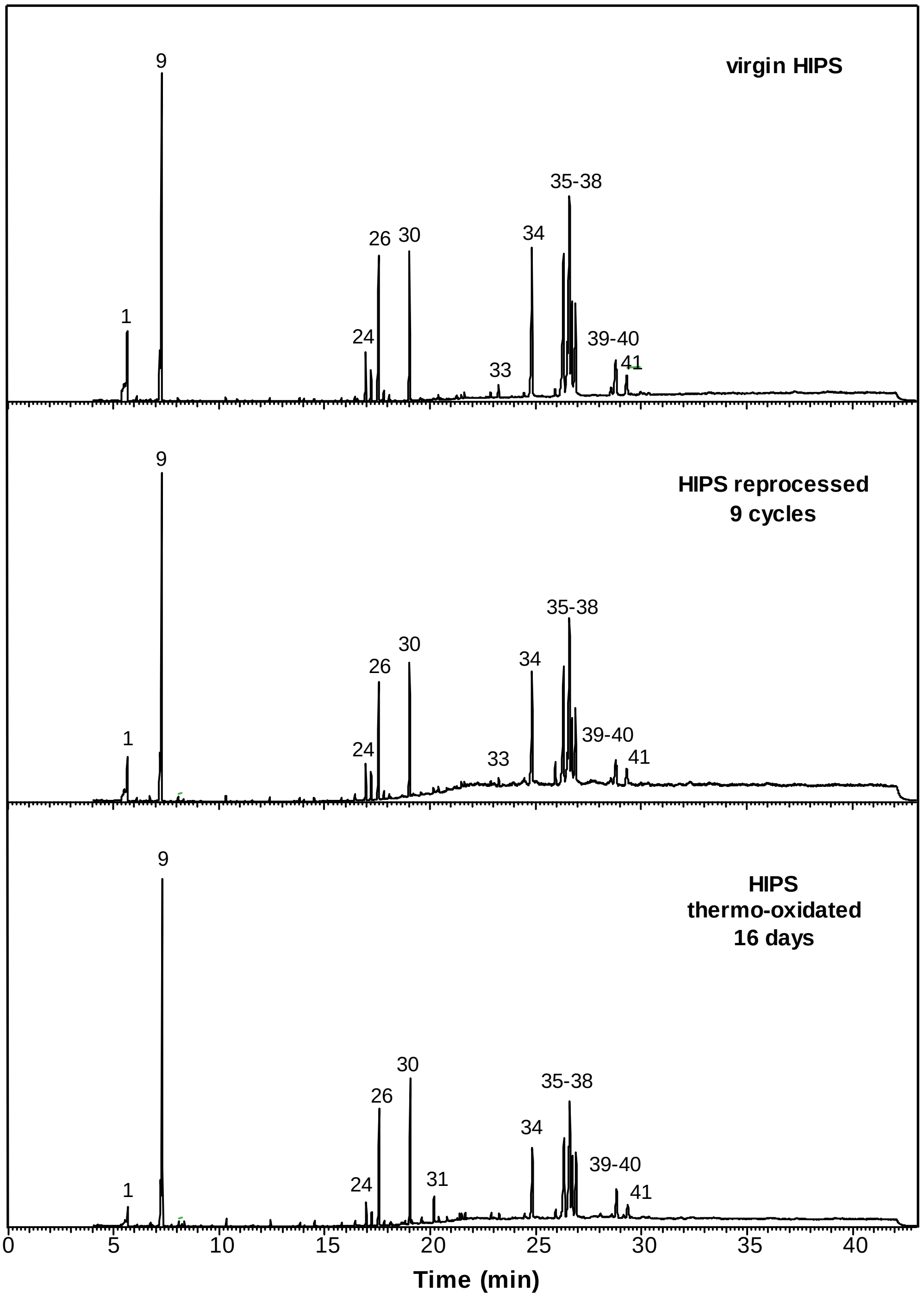

virgin HIPS
9
1
24
26
30
33
34
35-38
39-40
41
HIPS reprocessed
9 cycles
9
1
24
26
30
33
34
35-38
39-40
41
HIPS
thermo-oxidated
16 days
9
1
24
26
30
31
34
35-38
39-40
41
0
5
10
15
20
25
30
35
40
Time (min)

Figure 1

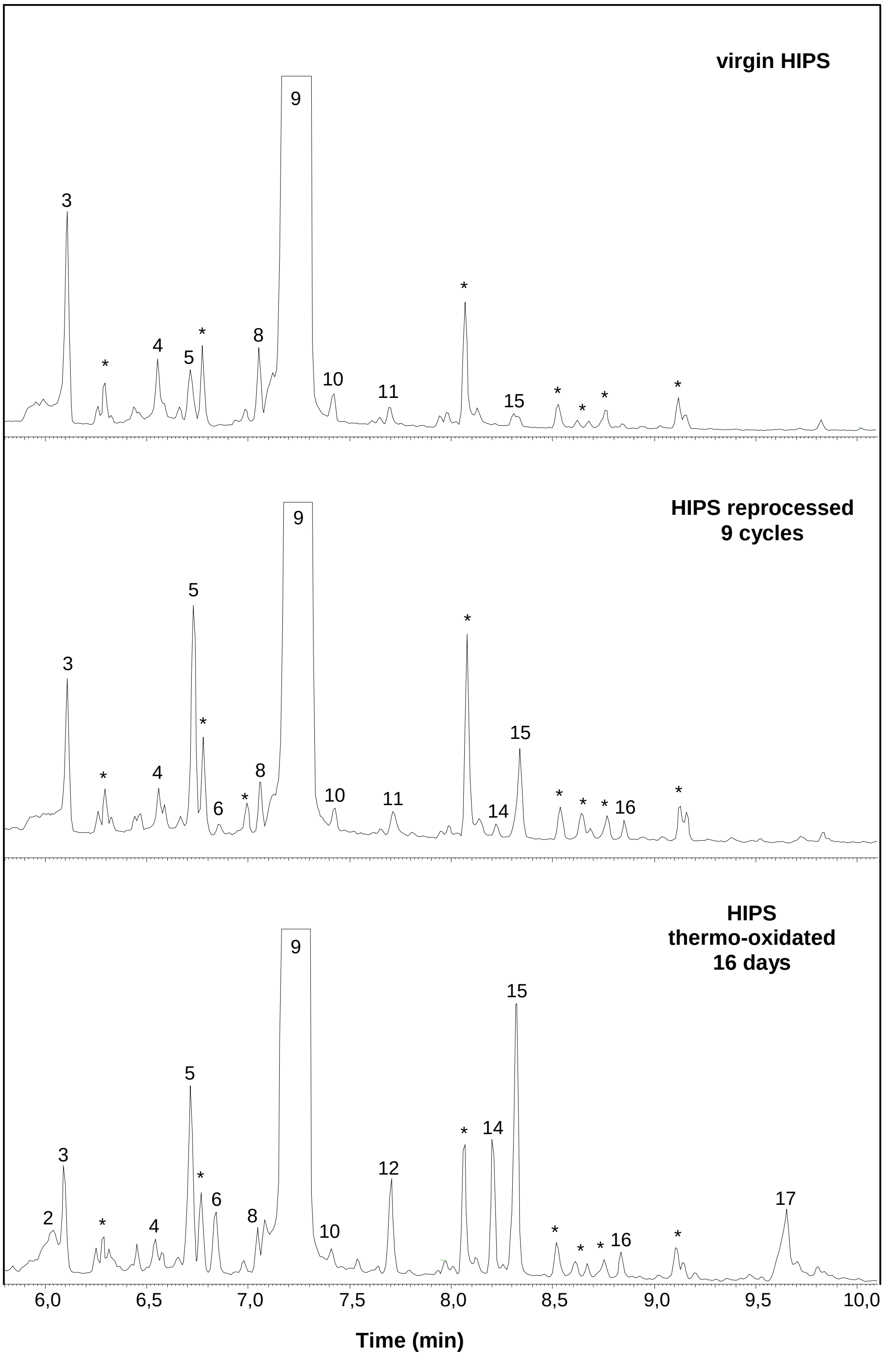
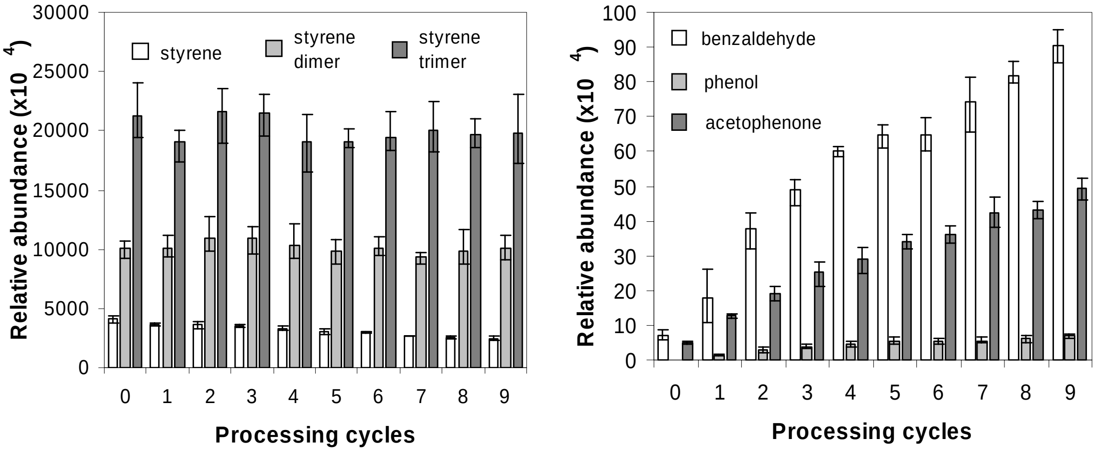

virgin HIPS
9
3
*
4
5
*
8
10
11
*
15
*
*
*
*
HIPS reprocessed
9 cycles
9
5
3
*
*
4
6
*
8
10
11
*
15
14
*
*
*
16
*
HIPS
thermo-oxidated
16 days
9
15
5
3
2
*
4
*
6
8
10
12
*
14
*
*
*
16
*
17
6,0
6,5
7,0
7,5
8,0
8,5
9,0
9,5
10,0
Time (min)

Figure 2


30000
25000
20000
15000
10000
5000
0
Relative abundance (x10 4)
☐ styrene
▨ styrene dimer
■ styrene trimer
0 1 2 3 4 5 6 7 8 9
Processing cycles
100
90
80
70
60
50
40
30
20
10
0
Relative abundance (x10 4)
☐ benzaldehyde
▨ phenol
■ acetophenone
0 1 2 3 4 5 6 7 8 9
Processing cycles

(a) *(b)*

Figure 3

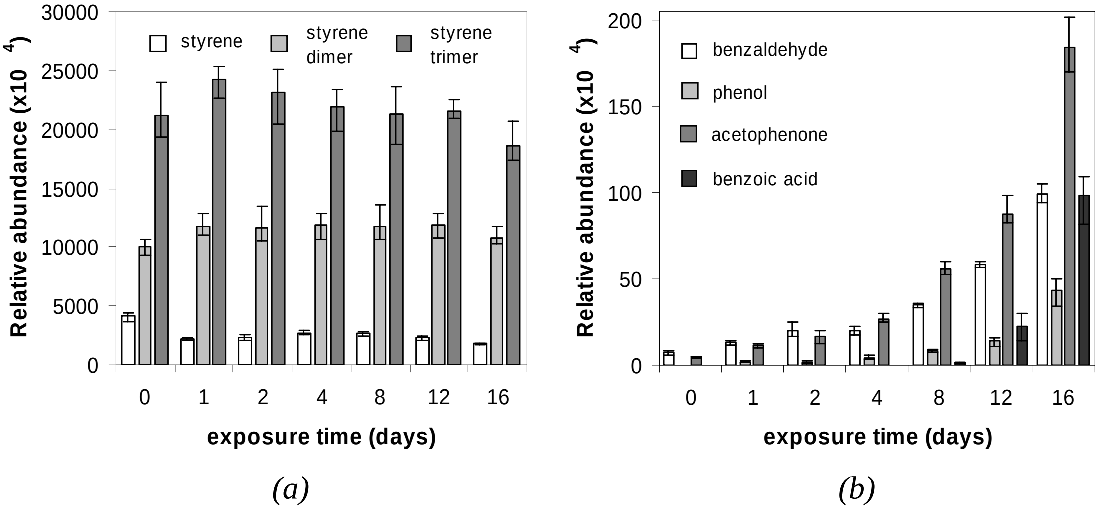

30000
25000
20000
15000
10000
5000
0
Relative abundance (x10 4)
styrene
styrene dimer
styrene trimer
0
1
2
4
8
12
16
exposure time (days)
(a)
200
150
100
50
0
Relative abundance (x10 4)
benzaldehyde
phenol
acetophenone
benzoic acid
0
1
2
4
8
12
16
exposure time (days)
(b)

Figure 4

Article IV

Analytical strategies for the quality assessment of recycled high-impact polystyrene: a combination of thermal analysis, vibrational spectroscopy and thermo-oxidation.

Francisco Vilaplana, Amparo Ribes-Greus, Sigbritt Karlsson.

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Analytical strategies for the quality assessment of recycled high-impact polystyrene: A combination of thermal analysis, vibrational spectroscopy, and chromatography

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ABSTRACT

Various analytical techniques (thermal analysis, vibrational spectroscopy, and chromatographic analysis) were used in order to monitor the changes in polymeric properties of recycled high-impact polystyrene (HIPS) throughout mechanical recycling processes. Three key quality properties were defined and analysed; these were the degree of mixing (composition), the degree of degradation, and the presence of low molecular weight compounds. Polymeric contaminations of polyethylene (PE) and polypropylene (PP) were detected in some samples using differential scanning calorimetry (DSC). Vibrational spectroscopy showed the presence of oxidised parts of the polymeric chain and gave also an assessment of the microstructure of the polybutadiene phase in HIPS. The presence of low molecular weight compounds in the HIPS samples was demonstrated using microwave-assisted extraction followed by gas chromatography–mass spectrometry (GC–MS). Several volatile organic compounds (VOCs), residues from the polymerisation, additives, and contaminations were detected in the polymeric materials. Styrene was identified already in virgin HIPS; in addition, benzaldehyde, α-methylbenzenaldehyde, and acetophenone were detected in recycled HIPS. The presence of oxygenated derivates of styrene may be attributed to the oxidation of polystyrene (PS). Several styrene dimers were found in virgin and recycled HIPS; these are produced during polymerisation of styrene and retained in the polymeric matrix as polymerisation residues. The amount of these dimers was highest in virgin HIPS, which indicated that emission of these compounds may have occurred during the first lifetime of the products. This paper demonstrates that a combination of different analytical strategies is necessary to obtain a detailed understanding of the quality of recycled HIPS.

1. Introduction

As the availability of raw materials for the production of polymer products becomes limited and as special attention is focussed on environmental issues, it is necessary to close the material life cycle loop and focus on the recovery of plastic waste materials and their conversion into new products. Recent life cycle assessment studies have, on the other hand, pointed out that mechanical recycling of plastic materials is favourable to other management procedures in terms of

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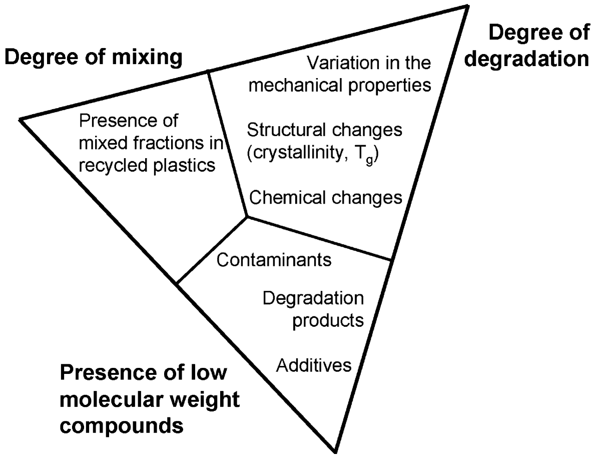


Scheme 1 – Key parameters for the quality assessment of recycled plastics.

overall energy use and emission of gases contributing to global warming [1]. It is therefore important to develop fast and reliable analytical methods for the determination of the properties of recycled plastics, in order to fulfil the requirements of manufacturers and consumers, and to guarantee the performance of recycled products in second-market applications. Three key aspects have been proposed for the quality assessment of recyclates: The degree of degradation, the degree of mixing (presence of polymeric materials as impurities), and the presence of low molecular weight compounds (degradation products, additives, and contaminants) [2–4]. Scheme 1 shows the significance of the key parameters for the quality analysis in recycled plastics.

Polymeric materials suffer degradation processes in each step of their life cycle, mostly in processing and service life, which modify their mechanical properties and long-term stability [2]. An experimental approach entailing multiple processing and thermo-oxidation has been proposed, to model the degradation processes undergone by recycled polymers during their life cycle [5]. Different strategies can be employed for the characterisation of polymer degradation: analysing the changes in the chemical, physical and mechanical properties; studying the variations in molar mass and composition; or determining the degradation products [6]. An integrated analytical approach considering the macroscopic properties, chemical structure, morphology, long-term stability and presence of contaminants should therefore be considered in the property determination of recycled plastics. In the field of recycled polyolefins, work has been done using several analytical techniques including Fourier-transform infrared spectroscopy (mid-infrared and near-infrared), chromatographic techniques, thermal analysis, Raman spectroscopy, or chemiluminescence [3,7–12].

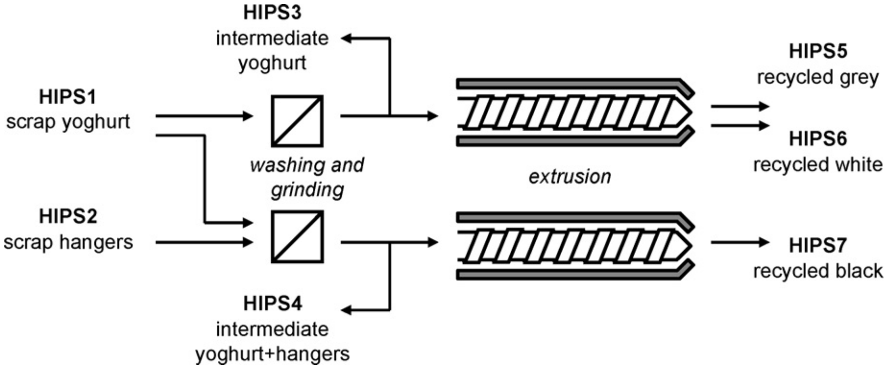
Mechanical recycling of styrenic polymers such as high-impact polystyrene (HIPS) has garnered attention due to the promulgation of the recent European Directives on Waste of Electric and Electronic Equipment (WEEE) and End-of-Life Vehicles (ELV), because styrenic plastics are often present in such equipment. HIPS is a multiphase system with a polystyrene (PS) rigid matrix with dispersed polybutadiene (PB) rubber particles that enhance the impact properties of the blend. The development of knowledge about how the degradation processes occurring on the previous life of recycled HIPS affects the properties of both phases of the material is consequently basic to predict the performance of new products made from HIPS recyclates.

The aim of the work is to present different analytical strategies for the quality assessment of recycled HIPS. The presence of other polymeric materials that may be considered as impurities, the structural properties, the oxidative stability, the chemical changes and the presence of low molecular weight compounds in recycled HIPS are some of the quality parameters that have been selected, related to the key aspects showed in Scheme 1. Samples extracted from different points of a large-scale mechanical recycling plant have been studied in order to verify the suitability of the proposed analytical strategies. The effects of the different steps of the mechanical recycling process on the properties of the HIPS materials were also investigated.

2. Experimental

2.1. *Sampling and description of materials*

HIPS samples were collected for analysis at different points of the mechanical recycling process (Acteco, Spain). Scheme 2 shows the mechanical recycling flow diagram and the points at which the different samples were taken: Scrap HIPS employed as raw material in the recycling process, intermediate samples



Scheme 2 – Sampling of the different HIPS materials through the mechanical recycling process.

Table 1 – Description of the materials characterised in this study

Materials	Description
Virgin HIPS	Virgin HIPS, commercial grade Polystyrol 486M (BASF, Spain)
HIPS1	Scrap HIPS from yoghurt packaging applications (ACTECO, Spain)
HIPS2	Scrap HIPS from hanger applications (ACTECO, Spain)
HIPS3	Intermediate HIPS material from the mechanical recycling process after washing and grinding, from yoghurt packaging application (ACTECO, Spain)
HIPS4	Intermediate HIPS material from the mechanical recycling process after washing and grinding, material mixture from yoghurt packaging and hanger applications (ACTECO, Spain)
HIPS5	Final recycled grey-coloured material, from yoghurt packaging applications (ACTECO, Spain)
HIPS6	Final recycled white-coloured material, from yoghurt packaging applications (ACTECO, Spain)
HIPS7	Final recycled black-coloured material, from yoghurt packaging and hanger applications (ACTECO, Spain)

after grinding and washing, and different grades of final recycled HIPS material. Virgin HIPS, commercial grade Polystyrol 486M (BASF Española S.A., Spain), was employed as reference material. Table 1 describes the sample materials employed in the analyses.

2.2. *Differential scanning calorimetry (DSC)*

The thermal properties and the oxidative stability of the HIPS samples were assessed using differential scanning calorimetry. The analyses were performed on a Mettler Toledo DSC 820 (Columbus, OH) calibrated with indium standard. Approximately 10 mg of sample was 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 temperature of the polystyrene phase was obtained from calorimetric measurements under a nitrogen gas flow of 50 mL min^{-1}, with a temperature programme as follows: 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 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.

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 min 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 min. 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.

2.3. *Thermogravimetric analysis (TGA)*

The thermal decomposition of the HIPS samples was evaluated by thermogravimetric analysis (TGA). The measurements were carried out in a Mettler-Toledo SDTA/TGA851 (Columbus, OH). Approximately 10 mg of sample was 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}.

2.4. *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). Twenty-four 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.

2.5. *Raman spectroscopy*

Raman spectra of reprocessed and aged HIPS samples were collected by a FT-Raman spectrometer Spectrum 2000 (Perkin Elmer, Wellesley, MA) equipped with an Nd-YAG laser illumination. The different spectra were obtained employing 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.

2.6. *Analysis of low molecular weight compounds*

The low molecular weight compounds present in the different HIPS samples were determined by an analytical 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 min 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 obtained extracts were filtered with a 0.45 mm pore size Teflon filter (Sorbent AB, Sweden) and placed in special vials, which 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 × 20 m × 0.18 μm Agilent J&W DB-5 capillary column (Palo Alto, CA). A 2 μL volume was

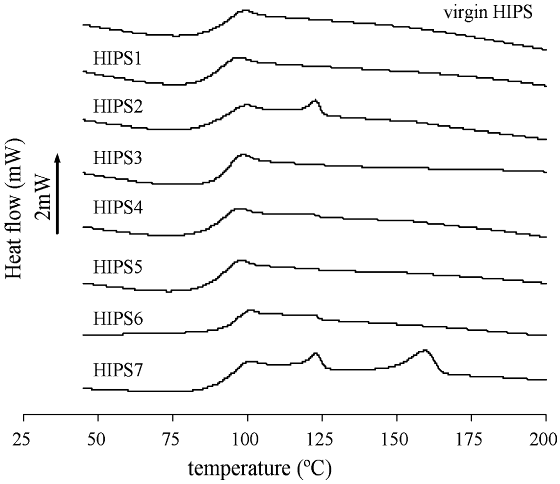


Fig. 1 – Determination of polymeric impurities in the HIPS samples by DSC: thermograms of the second melting ramp.

injected employing a programmed temperature vaporisation injector (PVT) in the pulsed splitless mode. During the injection process, the inlet was held at 75 psi with a purge flow of 60 mL min^{-1} for 1 min. 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 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. *Differential scanning calorimetry (DSC)*

The presence of mixed polymeric fractions as impurities in recycled polymeric materials clearly affects the macroscopic performance of recyclates. The employment of thermal analysis is suitable for the characterisation of the properties of the material in the bulk. Polymeric contaminations in the recycled materials were detected by differential scanning calorimetry (DSC). Fig. 1 shows the thermograms corresponding to the second heating segment for the different HIPS samples, where it can be observed that all the samples exhibit the slope change corresponding to the glass transition of the polystyrene phase at around 90 °C. Small melting peaks at temperatures of 120 °C and/or 160 °C can be observed, however, for samples HIPS2 and HIPS7, which indicate the presence of polyethylene and polypropylene contaminations, respectively, in these materials.

Table 2 – Thermal parameters of differential scanning calorimetry: glass transition temperature of the polystyrene phase (T_g), oxidation induction time (OIT), and oxidation temperature (T_{ox})

Sample	T_g (°C)		OIT (min)		T_{ox} (°C)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Virgin HIPS	94	1.5	28.0	3.2	198	3.2
HIPS1	91	1.1	–	–	188	2.4
HIPS2	91	0.8	8.1	1.0	183	0.6
HIPS3	91	1.3	–	–	193	3.9
HIPS4	90	0.6	14.4	1.2	184	5.4
HIPS5	91	0.2	4.0	1.0	183	1.8
HIPS6	95	0.2	10.5	0.2	187	1.7
HIPS7	93	0.8	13.0	0.5	185	0.6

In polymeric materials, the glass transition temperature (T_g) is particularly related to the mobility of the polymeric chains and determines the transition between the glassy and the rubbery polymeric state. Variances in the glass transition temperature may be due to several structural effects of the polymers, such as molar mass, degree of crosslinking, chain branching, or physical ageing phenomena [13]. The different samples present comparable T_g values between 90 °C and 95 °C for the polystyrene (PS) phase of HIPS (Table 2), which indicates that the morphology of the samples seems to be similar.

The oxidative stability of the HIPS samples was assessed using DSC, evaluating both the oxidation induction time (OIT) and the oxidation temperature (T_{ox}) (Table 2). The OIT of the samples HIPS1 and HIPS3 could not be calculated due to 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. The mechanical recycling processes show, however, minor effects on the oxidative stability of the recycled samples, because the values of the T_{ox} and OIT of the recycled materials (HIPS5, HIPS6 and HIPS7) are similar or even higher than those of their precedent materials in the recycling flow diagram (HIPS1 to HIPS4); this may be due to the addition of stabilisers in the reprocessing step. These results prove consequently the importance of adjusting the restabilisation level in order to guarantee the oxidative stability of the recyclates in their new service life. From an analytical point of view, the results obtained from the OIT and the T_{ox} parameters can both be employed as quality indicators for the oxidative stability in the recycling activities [5].

3.2. *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis can be employed to study the thermal decomposition of polymers and to analyse the content of humidity, volatiles, additives, and fillers in polymeric materials. The analysed HIPS materials exhibit similar thermal decomposition thermogravimetric curves (Fig. 2). The thermal decomposition of HIPS takes place in one single stage between 350 °C and 500 °C, when the polymeric chains break down and evolve to the gaseous phase. The onset temperature

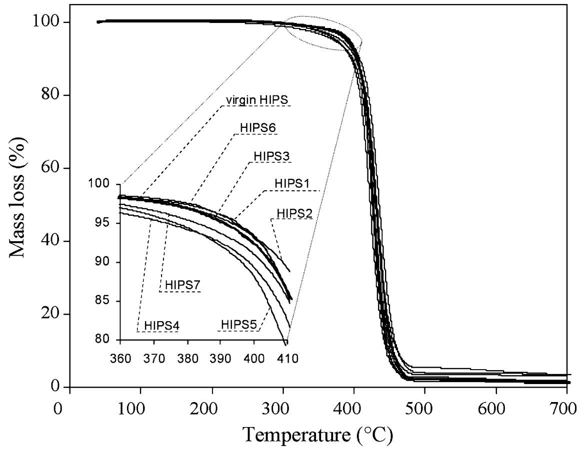


Fig. 2 – TGA mass-loss thermograms resulting from the thermal decomposition of the HIPS samples.

of the thermal decomposition (T_{onset}), the temperature range of decomposition, the temperature of the maximum decomposition rate (T_{max}), and the percentage of non-degraded residue have been calculated from the thermograms of the analysed HIPS samples (Table 3). The onset temperature of thermal decomposition has similar values for all the HIPS materials at around 365 °C; only the sample HIPS5 may be more sensitive to thermal degradation, with a lower T_{onset}. The temperature of maximum decomposition rate appears at around 430 °C for all the samples. The residue percentage indicates the content of inorganic material in the different samples. All the samples from the recycling plant possess higher residue content than the virgin material, with HIPS2 and HIPS7 showing the highest residue levels.

3.3. *Vibrational spectroscopy (FTIR and Raman)*

The absorbance spectra of the different HIPS samples were recorded by Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy to obtain a deeper insight in the changes in their chemical structure. Both techniques are complementary and give useful information about different functional groups present in the polymeric samples.

The regions corresponding to the hydroxyl group (3100–3600 cm^{-1}), the carbonyl groups (1620–1780 cm^{-1}), and the double bond groups from the PB phase corresponding to the peak of *trans*-1,4 (966 cm^{-1}) and vinyl-1,2 (911 cm^{-1}) groups were analyzed in detail employing FTIR. The *cis*-1,4 microstructure of PB in HIPS cannot be studied with FTIR because of the overlapping styrene unit peak in polystyrene at 754 cm^{-1}. Fig. 3 represents the absorbance spectra of the HIPS samples in the hydroxyl, carbonyl, and unsaturated regions. The recycled samples show, in general, higher absorbance in the hydroxyl and carbonyl regions than 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 peaks in the recycled materials can be qualitatively observed.

To obtain a quantitative insight into the changes in chemical structure of the HIPS materials through the mechanical recycling process, the relative absorbance areas of the peaks corresponding to the hydroxyl region, the carbonyl region, *trans*-1,4 group, and vinyl-1,2 group were determined, relative to the area of a reference peak at 1601 cm^{-1} that is not susceptible to degradation [14]. Fig. 4 represents the different FTIR functional group indexes for the analysed HIPS samples. The unsaturated groups in the polybutadiene phase have been identified as the initiation point of the thermo-oxidative and photo-oxidative degradation of styrene-butadiene copolymers, resulting in a wide variety of oxidised structures in the polymeric chains including hydroxyl, ketone, and aldehyde groups [15–17]. The diminution of the unsaturated functional groups (vinyl-1,2 and *trans*-1,4) and the increase of the hydroxyl and carbonyl groups in the real recycling samples, compared to the virgin material, may prove the occurrence of PB oxidation during the previous life and recycling of HIPS. Furthermore, the *trans*-1,4 index shows more variance among the different samples than the vinyl-1,2 index, which may evidence the higher susceptibility of this functional group to degradation, as suggested by several authors [5,18]. The calculation of the hydroxyl, carbonyl, vinyl-1,2 and *trans*-1,4 indexes could therefore be employed to verify the degree of degradation in recycled plastics and to assess the content of unsaturated groups in recycled HIPS.

Raman spectroscopy is useful for a detailed analysis of the PB-phase microstructure in HIPS. This method has an advantage over FTIR, in that the three PB microstructures can be studied without interference from other bands, and showed clear peaks at 1640 cm^{-1}, 1652 cm^{-1}, and 1666 cm^{-1} for the vinyl-1,2, *cis*-1,4, and *trans*-1,4 groups, respectively. Conventional Raman spectroscopy cannot be employed, however, for coloured samples because of the fluorescence emission

Table 3 – Results from thermogravimetric analysis: onset temperature of thermal degradation (T_{onset}), decomposition temperature range, temperature of maximum decomposition rate (T_{max}), and residue percentage

Sample	T_{onset} (°C)	Decomposition temperature range (°C)	T_{max} (°C)	Residue (%)
Virgin HIPS	369	369–490	433	1.2
HIPS1	367	367–486	426	2.0
HIPS2	367	367–500	436	3.5
HIPS3	365	365–490	422	1.5
HIPS4	363	363–485	427	1.7
HIPS5	353	353–480	424	1.6
HIPS6	371	370–485	428	2.9
HIPS7	366	366–495	431	3.4

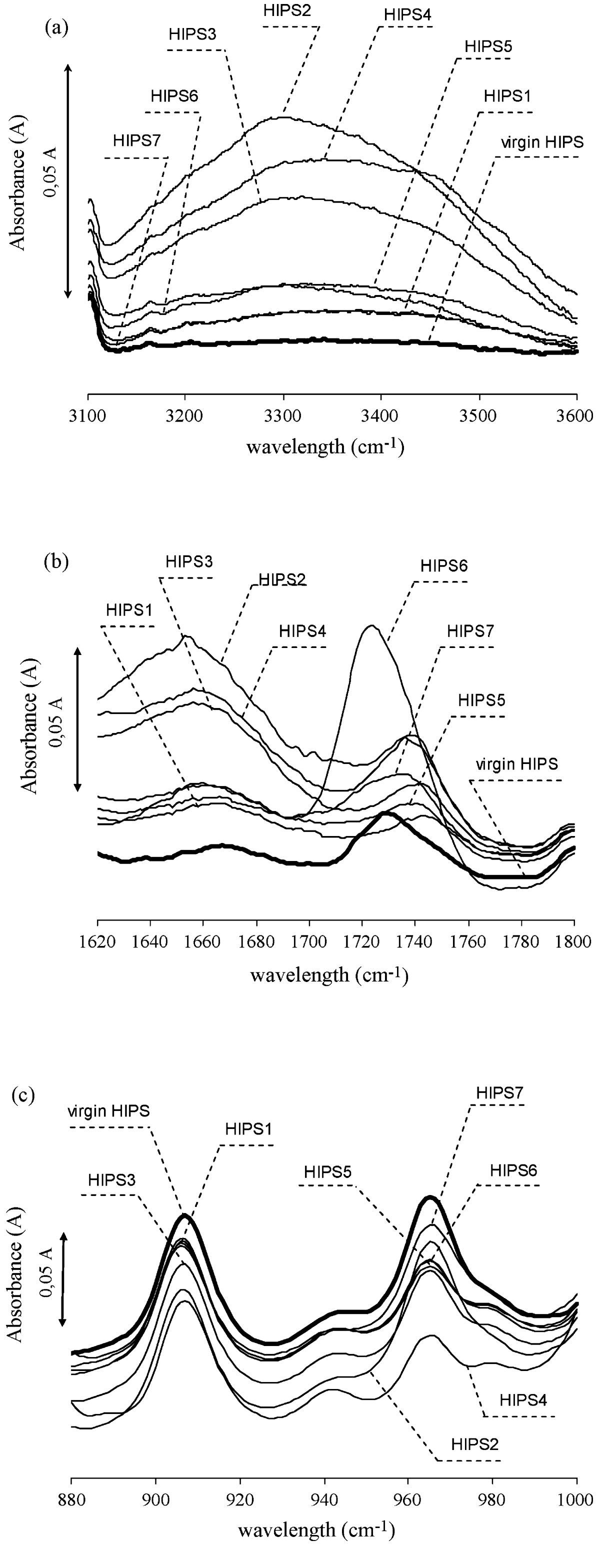


Fig. 3 – FTIR spectra of the HIPS samples: (a) hydroxyl region (3100–3600 cm^{-1}); (b) carbonyl region (1620–1800 cm^{-1}); (c) unsaturated region (880–1000 cm^{-1}).

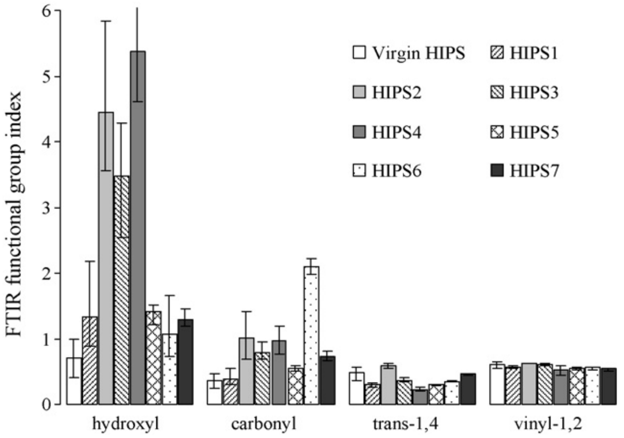


Fig. 4 – FTIR functional group indexes (hydroxyl; carbonyl; *trans*-1,4; vinyl-1,2) for the HIPS samples.

that covers the polymer spectrum; consequently, only the Raman spectra of virgin HIPS, HIPS1, HIPS3, HIPS5 and HIPS6 could be recorded in this study. Curve fitting to the Laurentz equation was applied to the recorded Raman spectra in order to resolve the three bands corresponding to the PB microstructure, following the guidelines proposed by Meier [19] and employed in previous work [20]. Fig. 5 shows the Raman spectra together with the resolved bands from the curve-fitting procedure for the analysed HIPS materials. The PB microstructures can be clearly observed, with varying distributions for the different samples. The Raman functional groups for the unsaturated groups were obtained by relating the absorbance areas for the vinyl-1,2 (1638 cm^{-1}), *cis*-1,4 (1652 cm^{-1}), and *trans*-1,4 (1666 cm^{-1}) resolved bands to the area of a reference resolved band at 1602 cm^{-1}. As the results in Fig. 6 indicate, the PB microstructure content is generally lower in the recycled HIPS samples than in the virgin HIPS. 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.

3.4. *Presence of low molecular weight compounds*

The presence of low molecular weight compounds in recycled HIPS was assessed by microwave-assisted extraction followed by analysis of the extracts using GC–MS. Fig. 7 presents a total ion chromatogram (TIC) from the extract of virgin HIPS as an example of the resulting chromatograms for the analysed materials. At a glance, different zones can be observed in the analysed TICs: A first zone until approximately 800 s where the volatile organic compounds (VOCs) appear; a second zone around 900 s where styrene dimers (residues from polymerisation) elute; a third zone around 1400 s where different peaks from the styrene trimers (residues of polymerisation) appear; and, finally, a fourth zone at longer elution times where different aliphatic compounds can be found. Table 4 presents the retention times, quantification ions, and abundance of the compounds found in the different HIPS sam-

Table 4 – Relative abundance and chromatographic properties of identified low molecular weight compounds in HIPS samples

Peak no.	Proposed compound	RT (s)	Quant. ion	Relative abundance ($\times 10^3$)							
				Virgin HIPS	HIPS1	HIPS2	HIPS3	HIPS4	HIPS5	HIPS6	HIPS7
1	Ethylbenzene[a]	238	91	–	101	102	66	2	–	2	8
2	Styrene[a]	269	104	2254	714	606	783	892	845	1579	1083
3	Benzene, (1-methylethyl)-[a]	297	105	49	29	40	82	64	31	29	49
4	Benzene, propyl-[a]	325	91	21	46	35	96	50	22	19	40
5	Benzene, 1-ethyl-4-methyl-[a]	333	120	13	2	5	–	–	–	–	–
6	Benzaldehyde[a]	335	106	10	11	35	8	50	25	29	22
7	Heptane, 2,2,4,6,6-pentamethyl-[a]	357	57	66	31	30	–	26	18	14	18
8	4-Methylstyrene	368	65	Internal standard (I.S.)							
9	Benzeneacetaldehyde, α-methyl-[a]	376	105	–	4	9	–	10	–	3	9
10	Acetophenone[a]	429	105	6	–	30	5	97	17	42	54
11	Butylated Hydroxytoluene[a]	794	205	–	–	16	–	20	–	–	25
12	Benzene, 1,1′-(1,3-propanediyl)bis-[a]	902	92	17	13	35	11	31	24	29	35
13	Benzene, 1,1′-(1,2-cyclobutanediyl)bis-, *cis*-[b]	929	104	405	192	231	327	183	123	180	136
14	2,4-Diphenyl-1-butene[c]	946	91	137	81	138	73	134	105	142	190
15	Benzene, 1,1′-(1,2-cyclobutanediyl)bis-, *trans*-[b]	966	104	2757	865	2065	1078	2423	1498	1655	1895
16	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-[a]	979	130	8	17	10	4	9	5	–	–
17	Naphthalene, 1,2-dihydro-4-phenyl-[a]	994	91	7	6	–	5	8	5	8	–
18	*o*-Terphenyl	1052	114	Internal standard (I.S.)							
19	*n*-Hexadecanoic acid[a]	1095	60	10	17	98	9	40	42	28	43
20	Octadecanoic acid[a]	1208	60	11	11	54	6	29	48	25	67
21	Hexadecanoic acid, butyl ester[a]	1220	56	–	–	–	–	32	2	69	19
22	Octadecanoic acid, butyl ester[a]	1324	129		6	13		8	12	17	8

[a] Proposed identification by comparison to the NIST database.

[b] Proposed identification through bibliographic Ref. [27].

[c] Proposed identification through bibliographic Ref. [32].

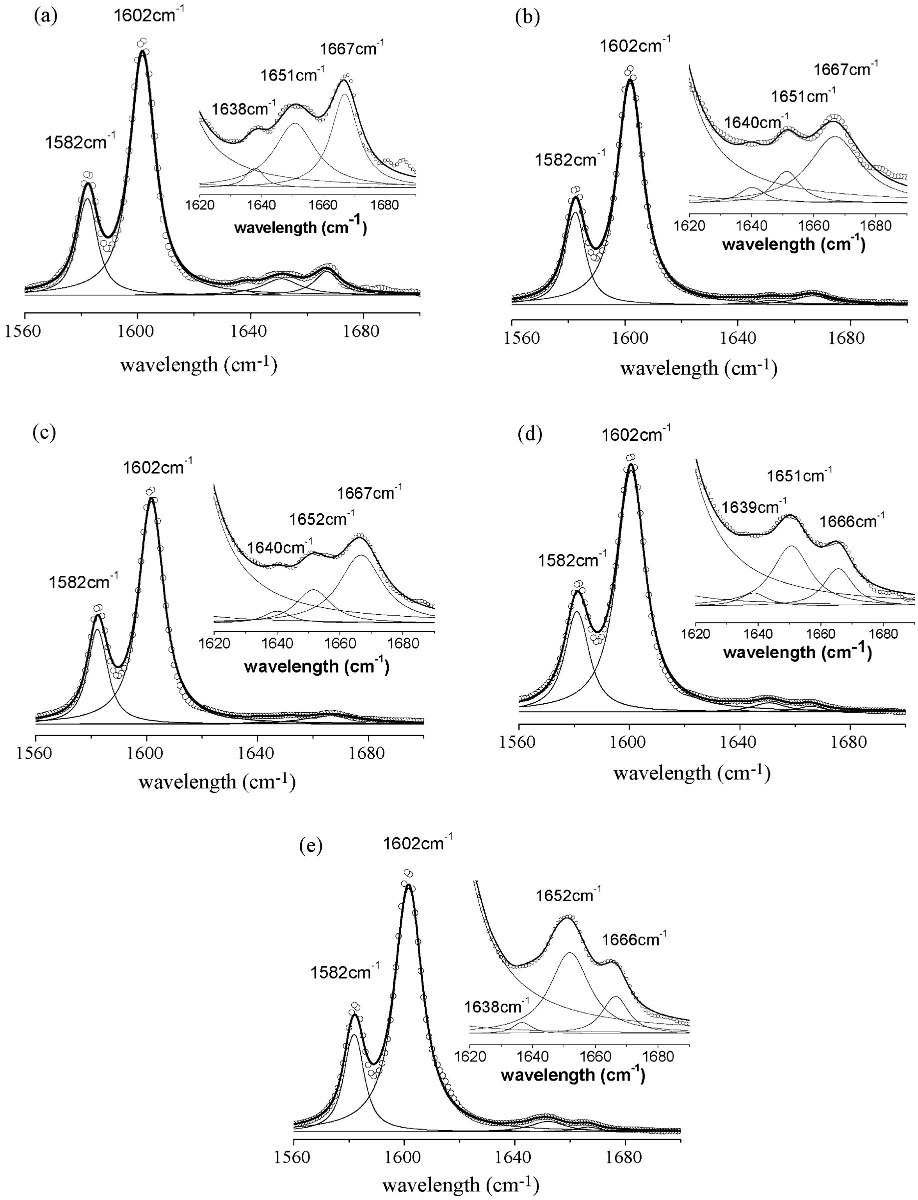


Fig. 5 – Curve fitting of the Raman spectra for the determination of the three individual PB conformers in the 1550–1700 cm^{-1} region: (a) virgin HIPS; (b) HIPS1; (c) HIPS3; (d) HIPS5; (e) HIPS6.

ples, 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 [21–23]. 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 indicated 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, as also suggested in previous works [3]. Styrene as the monomer residue is the most important compound of this group, in terms of relative abundance, and its content appears to be an important quality property in recycled HIPS. Other compounds, such as benzaldehyde (peak 6), α-methylbenzenealdehyde (peak 9), and acetophenone (peak 10), either do not appear in the virgin HIPS and can be found in the recycled samples, or are found in a higher relative abundance in the recycled samples compared to the virgin one. The presence of oxygenated derivates of styrene, such as benzaldehyde and acetophenone, has been attributed to the oxidation of polystyrene [24]; 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 life. Traces of butylated hydroxytoluene (peak 11) can be found in the recycled samples that contain scrap hanger (samples HIPS2, HIPS4, and HIPS7), suggesting the presence of this compound as a traditional antioxidant in the aforementioned material.

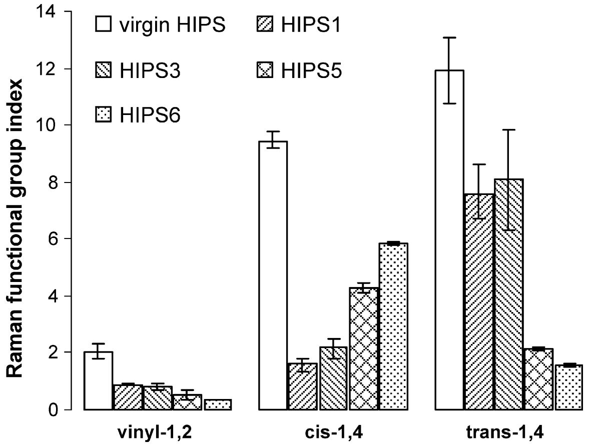


Fig. 6 – Raman functional group indexes (vinyl-1,2; *cis*-1,4; *trans*-1,4) for different HIPS samples.

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 processing of polystyrene [25], which could explain the higher relative abundance in the recycled samples than in the scrap. Other styrene dimers, such as *cis*- and *trans*-1,2-diphenylcyclobutane (peaks 13 and 15, respectively), 2,4-diphenyl-1-butene (peak 14), 1-phenyltetralin (peak 16), and 1,2-dihydro-4-phenylnaphtalene (peak 17), have been reported to be produced during polymerisation of styrene [26–29] and are retained in the polymeric matrix as polymerisation residues. The abundance of peaks 13–17 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 contaminations that may have penetrated the polymeric matrix in recycled materials. Traces of phtalates (dibutylphtalate, diethylphtalate) were also found in the HIPS extracts and in the blank analyses, so these compounds were assumed to be present in the laboratory environment.

Peaks 23-31 have been attributed to different styrene timers that can be found in both the virgin and the recycled HIPS samples. The analysed peaks have similar mass spectra as can be observed in their *m*/*e* fragments and percentages presented in Table 5. These compounds have been also reported to be formed during the polymerisation of styrene [27–31]. Some of these trimers, such as 1,3,5-triphenylhexene-5 and the four different diastereomers of 1-phenyl-4-(1-phenylethyl)-tetraline, could be identified through bibliographic comparison of their mass spectra [27,32].

Finally, traces of aliphatic compounds have been found in the analysed HIPS materials. Although no quantification of the aliphatic compounds have been performed, it is worth mentioning, as a qualitative remark, that the presence of these contaminations is slightly higher in the recycled materials than in the virgin ones.

Table 5 – Retention time and principal ion fragments for the styrene trimers found in the HIPS samples

Peak no.	Proposed compound	RT (s)	Ion mass intensity, *m*/*e* (%)												
23	Styrene trimer	1290		207 (22)	194 (14)	178 (7)	165 (5)	129 (100)	115 (21)	105 (54)	91 (75)	77 (52)	65 (14)	51 (21)	39 (14)
24	1,3,5-Triphenylhexene-5[a]	1352		207 (7)	194 (5)			129 (3.5)	117 (25)	103 (4)	91 (100)	77 (11)	65 (14)	51 (7)	39 (6)
25	T_1-diastereomer[b]	1395		207 (25)		178 (5)	165 (4)	129 (54)	115 (6)	105 (16)	91 (100)	77 (14)	65 (7)	51 (8)	39 (5)
26	T_1-diastereomer[b]	1403		207 (15)		178 (5)	165 (3.5)	129 (44)	115 (5)	105 (21)	91 (100)	77 (19)	65 (11)	51 (9)	39 (5)
27	T_1-diasteremer[b]	1405		207 (25)		178 (5)	165 (4)	129 (55)	115 (5)	105 (14)	91 (100)	77 (19)	65 (7)	51 (9)	39 (5)
28	T_1-diastereomer[b]	1410		207 (25)		178 (5)	165 (3.5)	129 (54)	115 (5)	105 (16)	91 (100)	77 (16)	65 (7)	51 (9)	39 (5)
29	Styrene trimer	1446		208 (9)					115 (3.5)	104 (100)	91 (7)	78 (19)	71 (3.5)	51 (7)	39 (5)
30	Styrene trimer	1452	312 (5)	207 (11)		180 (9)	143 (7)	129 (56)	115 (3.5)	104 (15)	91 (100)	77 (29)	65 (14)	51 (10)	39 (7)
31	Styrene trimer	1461	312 (5)	207 (11)		180 (16)	143 (11)	129 (39)	115 (14)	104 (14)	91 (100)	77 (14)	65 (15)	51 (11)	39 (8)

T_1: 1-phenyl-4-(1-phenylethyl)-tetralin.

[a] Proposed identification through bibliographic Ref. [32].

[b] Proposed identification through bibliographic Ref. [27].

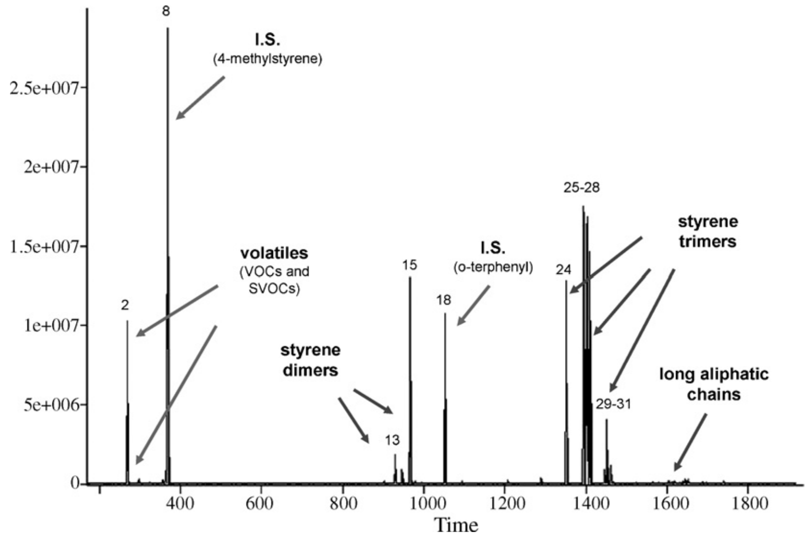


Fig. 7 – Total ion chromatogram (TIC) of the low molecular weight compounds extracted from virgin HIPS.

4. Conclusions

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 contaminations, oxidative and thermal stability, changes in chemical structure, and morphological properties of recycled materials. The oxidative stability was assessed by thermal analysis and shows the importance of adjusting the stabilisation in the recycling activities. Infrared spectroscopy is particularly useful to assess the unsaturated groups (vinyl-1,2 and *trans*-1,4) and the presence of oxidative moieties (carbonyl and hydroxyl groups) in recycled HIPS formed due to oxidative degradation during previous life of the material. Raman spectroscopy was employed to identify the polybutadiene microstructure (vinyl-1,2, *cis*-1,4, and *trans*-1,4) in recycled HIPS. Different low molecular weight species were found among the HIPS samples, including volatile organic compounds, styrene dimers and trimers residues from polymerisations, additives, and contaminations. The different relative abundance of these compounds in the different samples may be evidence of emission of volatiles during processing and service life in some cases, and the formation of degradation products in other cases.

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REFERENCES

[1] G. Finnveden, J. Johansson, P. Lind, A. Moberg, J. Cleaner Prod. 13 (3) (2005) 213–229.
[2] S. Karlsson, Adv. Polym. Sci. 169 (2004) 201–229.
[3] F. Stangenberg, S. Ågren, S. Karlsson, Chromatographia 59 (2004) 101–106.
[4] E. Strömberg, F. Vilaplana, S. Ågren, A. Ribes-Greus, S. Karlsson, Quality Assessment of Recycled Plastics, In Identiplast 2005—Identifying the Opportunities for Plastics Recovery, Brussels, 2005.
[5] F. Vilaplana, A. Ribes-Greus, S. Karlsson, Polym. Degrad. Stab. 91 (9) (2006) 2163–2170.
[6] S. Karlsson, A.-C. Albertsson, Techniques and mechanisms of polymer degradation, in: G. Scott (Ed.), Degradable Polymers, 2nd ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002, pp. 51–69.
[7] W. Camacho, S. Karlsson, Polym. Eng. Sci. 41 (9) (2001) 1626–1635.
[8] W. Camacho, S. Karlsson, Polym. Degrad. Stabil. 71 (1) (2000) 123–134.
[9] W. Camacho, S. Karlsson, Polym. Degrad. Stabil. 78 (2) (2002) 385–391.
[10] W. Camacho, S. Karlsson, Int. J. Polym. Anal. Characterization 7 (2002) 41–51.
[11] W. Camacho, S. Karlsson, J. Appl. Polym. Sci. 85 (2) (2002) 321–324.
[12] W. Camacho, S. Karlsson, Polym. Recycl. 6 (2/3) (2001) 89–98.
[13] U.W. Gedde, Polymer Physics, Kluwer Academic Publishers, Dordrechts, The Netherlands, 1999.
[14] A. Boldizar, K. Moller, Polym. Degrad. Stabil. 81 (2) (2003) 359–366.

[15] A. Ghaffar, A. Scott, G. Scott, Eur. Polym. J. 12 (9) (1976) 615–620.
[16] J.B. Adeniyi, Eur. Polym. J. 20 (3) (1984) 291–299.
[17] Y. Israeli, J. Lacoste, J. Lemaire, R.P. Singh, S. Sivaram, J. Polym. Sci.: Part A: Polym. Chem. 32 (1994) 485–493.
[18] S.M. Wang, J.R. Chang, R.C.C. Tsiang, Polym. Degrad. Stabil. 52 (1) (1996) 51–57.
[19] R.J. Meier, Vibrational Spectrosc. 39 (2) (2005) 266–269.
[20] F. Vilaplana, S. Karlsson, A. Ribes-Greus, manuscript in preparation.
[21] P. Kusch, G. Knupp, J. Polym. Environ. 12 (2) (2004) 83–87.
[22] V. Woodfin, Ligon Jr., C. Marcia, George, J. Polym. Sci.: Polym. Chem. Ed. 16 (10) (1978) 2703–2709.
[23] G.A. Eiceman, M. Carpen, Analyt. Lett. 15 (A14) (1982) 1169–1177.
[24] B. Mailhot, J.L. Gardette, Macromolecules 25 (16) (1992) 4119–4126.
[25] S.L. Hathcock, W. Bertsch, J. High Resolution Chromatogr. 16 (11) (1993) 651–659.
[26] K.S. Khuong, W.H. Jones, W.A. Pryor, K.N. Houk, J. Am. Chem. Soc. 127 (4) (2005) 1265–1277.
[27] H.F. Kauffmann, Die Makromolekulare Chemie 180 (11) (1979) 2649–2663.
[28] W.G. Brown, Die Makromolekulare Chemie 128 (1) (1969) 130–136.
[29] K. Kirchner, K. Riederle, Angewandte Makromolekulare Chemie 111 (1) (1983) 1–16.
[30] J. Wiesner, P. Mehnert, Die Makromolekulare Chemie 165 (1) (1973) 1–9.
[31] J. Schellenberg, S. Knoll, G. Nord, W. Leukefeld, Eur. Polym. J. 39 (12) (2003) 2351–2357.
[32] T. Yamada, M. Tanaka, S. Hirano, Y. Nagao, K. Kobayashi, T. Sakurai, Y. Furukawa, Y. Nobuhara, Bunseki Kagaku 49 (11) (2000) 857–867.

Article V

Extraction of brominated flame retardants from styrenic plastic fractions in waste electrical and electronic equipment (WEEE) using microwave-assisted extraction”.

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EXTRACTION OF BROMINATED FLAME RETARDANTS FROM STYRENIC PLASTIC FRACTIONS IN WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE) USING MICROWAVE-ASSISTED EXTRACTION

Abstract

A fast method for the determination of brominated flame retardants (BFRs) in styrenic polymers has been developed using microwave-assisted extraction (HPLC) and liquid chromatography with UV detection (HPLC-UV). Different extraction parameters (extraction temperature and time, type of solvent, particle size) have been first optimised for standard high-impact polystyrene (HIPS) samples containing known amounts of tetrabromobisphenol A (TBBPA) and decabromodiphenyl ether (Deca-BDE). Complete extraction of TBBPA was achieved by using a combination of polar/non-polar solvent system (isopropanol/n-hexane) and high extraction temperatures (130°C). Lower extraction yields could be, however, reached for Deca-BDE, due to its high molecular weight and its non-polar nature. The developed method was successfully applied for the screening of BFRs in standard plastic samples from waste electrical and electronic equipment (WEEE); TBBPA could be fully recovered, and Deca-BDE could be identified, together with minor order polybrominated diphenyl ether (PBDE) congeners.

Keywords

Microwave-assisted extraction; brominated flame retardants; polymers; HPLC-UV

1. Introduction

Brominated flame retardants (BFRs) are organic compounds containing bromine that are added to polymers and other materials to improve their fire-resistant properties in diverse applications, such as textiles, building materials and insulation, vehicle equipment, and electrical and electronic equipment [1]. In the case of polymeric samples, brominated flame retardants can be either chemically bonded to the polymeric matrix or incorporated as additives with high concentrations (around 10-15% w/w). BFRs constitute a heterogeneous family of halogenated organic compounds, but tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and polybrominated biphenyls (PBBs) have been traditionally employed in the last years. It has been demonstrated that BFRs are present in the environment and are bio-assimilable with increasing concentrations in water, air, soil, and biota; the effects of BFRs on the environment and the human health are still not very well known [2, 3]. The concern about these additives has encouraged restrictive legislation, to regulate the employment of BFRs in polymeric components for electronic and electrical equipment and the management of their residues. Waste from electrical and electronic equipment (WEEE) contains approximately 18% of plastics, mainly styrenic polymers such as ABS, HIPS or PS. The development of analytical procedures for the identification and determination of BFRs in styrenic polymers in WEEE is therefore interesting from both a scientific and technological point of view.

Different reviews have been published in the recent years dealing with the analysis of brominated flame retardants in different matrixes. The analytical procedures usually involve different steps, including sample pre-treatment, extraction, clean-up and fractionation, and extract analysis using chromatographic techniques [4-8]. For the determination of additive BFRs in polymeric matrixes, an efficient extraction step is mandatory prior to chromatographic determination. Liquid extraction from polymers has traditionally been performed by Soxhlet extraction, which requires long extraction times and consumes high solvent volumes. Different advanced solvent extraction techniques including supercritical-fluid extraction (SFE), pressurised liquid extraction (PLE); ultrasonic-assisted extraction (UAE), and microwave-assisted extraction (MAE), have been introduced in the recent years and are available as routine extraction procedures in many laboratories with shorter extraction times, lower solvent consumption and automatisation possibilities [9]. Some studies have been devoted to the determination of BFRs in different polymeric samples, using Soxhlet extraction with methanol/isopropanol as solvents [10], supercritical-fluid extraction (SFE) [11], pressurised liquid extraction (PLE) with iso-octane [12], and ultrasonication with isopropanol [13] as extraction techniques before extract analysis. For detection, liquid chromatography (HPLC) with either ultraviolet (UV) or mass spectrometry (MS) detection have proven to be robust methods for the quantification of the relatively high concentrations of BFRs in plastic fractions from WEEE [5, 12, 13]. However, no studies have been reported for the employment of microwave-assisted extraction for the determination of BFRs in polymeric matrixes.

Microwave-assisted extraction (MAE) is based on the application of microwave energy to heat the solvent employed in the liquid-solid extraction. The instrumental equipment consists basically in several closed extraction vessels where the sample and the solvent system are introduced, with temperature and pressure control allowing the heating of the solvent system under pressure above its normal boiling point [14-16]. The solvent remains in liquid phase in these high temperature conditions, promoting analyte diffusion and swelling between polymer and solvent. The employed solvent system must contain some component with dielectric permittivity, to absorb the microwave energy and therefore be heated; mixtures of polar/non-polar solvents are commonly employed for MAE (acetone/n-hexane, isopropanol/cyclohexane, dichloromethane/xylene) [9]. The kinetic mechanism plays an essential role in the efficiency of solvent extraction from polymeric materials. Three kinetic consecutive steps can be identified in this process: (i) diffusion of the analytes from the core of polymer particles to their surface; (ii) transfer of the analytes from the polymer surface to the solvent boundary layer; (iii) mass transfer of the analytes into the extractive solvent [17]. Different parameters such as the nature of the extractive solvents, the extraction temperature and the polymeric particle size influence the kinetics of the extraction process and hence the extraction yield [14, 15]. Microwave-assisted extraction has been successfully employed for the extraction of a wide range of additives (antioxidants, stabilisers, plasticisers) from polymer matrixes, especially polyolefins as polyethylene (HDPE and LDPE), polypropylene (PP), poly(vinyl chloride) (PVC) [18-20] or silicones as polydimethyl siloxane (PDMS) [21], with high effectivity and low solvent consumption and extraction times. MAE has also been useful for the analysis of the oligomer content in poly(ethylene terephthalate) (PET) [22] and for the identification of contaminants and low molecular weight compounds in recycled polyolefins from packaging wastes [23].

The aim of this study is to develop and optimise an analytical procedure for the determination of BFRs in styrenic samples from WEEE using MAE and HPLC-UV. Two model flame retardants, tetrabromobisphenol A (TBBPA) and decabromodiphenyl ether (Deca-BDE), and high-impact polystyrene (HIPS) as the polymeric matrix, have been chosen for this purpose, since they are widely employed in plastic components for the electrical and electronic industry. Different extraction parameters (solvent system, extraction temperature and time, particle size) have been considered for optimising the recovery rates during extraction. The proposed analytical procedure has been further applied to the identification and quantification of BFRs in standard samples from recycled plastic fraction from WEEE.

2. Experimental

2.1 Chemicals and polymeric samples

Two commercial brominated flame retardants, tetrabromobisphenol A technical grade (TBBPA) (4-4'-isopropylidene bis(2,6-dibromophenol), 97% purity, M_w 543.9 g/mol, CAS number 79-94-7) provided by Aldrich Chemicals (Sweden) and decabromodiphenyl ether, technical grade (Deca-BDE, 95.0% purity, M_w 959.22 g/mol, CAS number 1163-19-5) provided by Sigma Aldrich (Sweden), were employed as model compounds for the development of the extraction method from styrenic plastics. The solvents for the extraction and analysis of the brominated flame retardants (n-hexane, isopropanol, methanol, tetrahydrofurane, and water) were all chromatographic grades and provided by Acros Organics (Sweden).

Virgin high-impact polystyrene (HIPS), Polystyrol 486M (BASF Española, Spain) was employed as the polymeric matrix for the development of the extraction method for determination of BFRs in styrenic plastics. Standard samples of HIPS containing 50 mg/g TBBPA and 50 mg/g Deca-BDE were prepared by solution in tetrahydrofurane (THF) in a stirred vessel at room temperature. After drying at 25°C, the polymer was granulated in a Moretto Granulator (Moretto, Italy). To analyse the influence of particle size on extraction efficiency, the polymeric granules were further grinded into powder using a rotary mill with liquid nitrogen.

Standard samples from waste electrical and electronic equipment (WEEE) were used as well to verify the applicability of the analytical method for the determination of BFRs in styrenic components from electrical and electronic applications. These standard WEEE samples were provided by Gaiker Centro Tecnológico (España) and their approximate composition is shown in Table 1.

2.2 Microwave-assisted extraction (MAE)

The extraction assisted by microwaves was carried out in a MES 100 microwave extraction equipment (CEM Corp., North Carolina, USA), with a nominal power of 1000W. Approximately 0.5 g of the standard HIPS sample with BFRs (either in granule or powder) was introduced with 10 ml of the extractive solution inside MAE closed vessels. As extractive solutions, isopropanol/methanol (IP/MeOH, 1:1 v/v) and isopropanol/n-hexane (IP/hexane, 1:1 v/v) were employed. Different extraction times (20, 30, 45, and 60 minutes) and extraction temperatures (90ºC, 110ºC, and 130ºC) were tested for the optimisation of the method. The extracts were evaporated close to dryness and the residue was re-dissolved with THF. The solutions were filtered with a 0.45 mm pore size HPLC Teflon filter (Sorbent AB, Sweden) and placed in HPLC vials, which were kept at 4ºC until further analysis. Each extraction was carried out three times and the average of the calculated HPLC-UV concentration was assumed as the representative value.

2.3 High-performance liquid chromatography (HPLC/UV)

The analyses of the extracts containing brominated flame retardants was performed by high-performance liquid chromatography, employing a Hewlett Packard HPLC 1090 equipment (Palo Alto, CA, USA). The chromatograph was equipped with a diode-array detector (DAD) Waters 990 (Milford, MA, USA) and an auto-sampler Waters 712 WISP (Milford, MA, USA). Chromatographic separation was achieved using a reverse phase system consisting on a 5µm frit filter, a Supelguard Discovery 18 guard column (20 x 4mm, 5µm), and a C18 Hypersyl ODS column (250 x 4.6mm, 5µm), all supplied by Supelco (Sweden). The measurements were carried out at 35ºC, employing an isocratic methanol/water (95/5% v/v) mobile phase at a flow of 1ml/min. After some previous experiments, the DAD detector was fixed at a wavelength of 220 nm.

Quantification of TBBPA and Deca-BDE was performed by external calibration, using 7 seven point calibration curves obtained by injection of standard solutions containing 1 – 1000 µg/ml of the technical flame retardants.

3. Results and discussion

3.1 Development of the detection method by HPLC-UV

The optimisation of the spectrometric detection was achieved by injection of standard solutions of the analytes in tetrahydrofurane in the range 1 – 1000 μg/ml into the HPLC-UV. The initial chromatographic parameters (column, mobile phase, mobile flow, temperature) were first directly chosen from previous bibliographic results [12], and further adjustments were performed to satisfy the requirements for successful separation and detection. Different wavelengths for the DAD detection were tested and finally a wavelength of 220 nm was selected. The retention times, limit of detection (LOD), limit of quantification (LOQ), and the linearity range for TBBPA and Deca-BDE have been calculated for the developed HPLC-UV method and are presented in Table 2.

3.2 Evaluation of different extraction conditions for the recovery of BFRs from styrenic polymers using MAE

Different extraction parameters (type of extractive solvent, extraction time, particle size) were evaluated in order to optimise the extraction recovery of TBBPA and Deca-BDE from the standard HIPS samples with known content of BFRs using MAE. Quantification of the BFR content was performed by analysis of the MAE extracts using HPLC-UV. Figure 1 shows an example of a chromatogram of the polymeric extract after MAE at 130°C and 60 minutes using isopropanol/n-hexane as solvent. Two clear peaks corresponding to TBBPA (at 11.1 min) and Deca-BDE (at 20.6 min) can be observed, together with different peaks around 14-15 min, which may correspond with styrenic oligomers present in the HIPS matrix, as proved by the extracts analysis from virgin HIPS without flame retardants. It is worth mentioning that Deca-BDE is especially sensitive to undergo debromination decomposition into lower order PBDEs when exposed to UV- and sunlight radiation and/or during long-term solution in alcohols [4]. The extracted samples and the technical standard solutions were therefore analysed shortly after preparation, and no further sign of Deca-BDE debromination induced by microwaves or during storage could be observed in the chromatograms.

The calculated concentration and the relative standard deviation (RSD) for TBBPA and Deca-BDE in the standard HIPS samples using different extractive conditions is presented in Table 2. As it can be observed, TBBPA extraction can be optimised varying the conditions to reach a calculated concentration similar to the theoretical one of the standard HIPS samples. For the case of Deca-BDE, however, the extractive conditions with MAE offer a calculated concentration value far below the theoretical value, with maximum extraction recoveries of approximately 30%. This fact could be due to the different molecular weight and polarity of the two extracted BFRs; the extraction efficiency of additives using MAE is highly conditioned by the molecular weight of the analytes to extract [9], so the high molecular weight and low polarity of Deca-BDE (959.17g/mol) could hinder its complete extraction from the polymeric matrix in comparison with TBBPA (543.87g/mol).

The selection of the extractive solution plays a critical role in the extraction of additives from polymeric matrixes using MAE. From an operational point of view, the solvent system must possess certain dielectric permittivity to absorb microwave energy in order to be heated. The solvent system should have, moreover, high affinity with the analytes to be extracted and with the polymeric matrix, inducing certain swelling effect in the polymer but without causing the dissolution of any matrix component [17]. Finally, the employment of hazardous solvents should try to be avoided, taking into account an occupational health point of view. The selection of the extraction solvents was therefore difficult, due to the nature of the matrix (in the case of HIPS, a blend of polystyrene and polybutadiene), and the low quantity of solvent systems that satisfy *a priori* the aforementioned requirements; solvent mixtures with different polar nature such as isopropanol/methanol (1.1, v/v) and isopropanol/n-hexane (1:1, v/v) were thus considered. As the results of Table 2 show, the type of solvent clearly affects the extraction recovery and therefore the calculated concentration of BFRs in the standard HIPS solvent. A mixed polar/non-polar extractant solution such as isopropanol/n-hexane offers higher calculated concentrations of TBBPA and Deca-BDE than a polar mixture as methanol/isopropanol, due to the higher affinity with both matrix and analytes.

Particle size also influences the calculated concentration of TBBPA and Deca-BDE after MAE extraction (Table 2). Higher extraction rates can be obtained with HIPS powder than with HIPS granules, due to enhanced diffusion of the analytes from the polymer core to the polymer surface. However, this increase in extraction rate with decreasing particle size is lower than expected, especially for the case of Deca-BDE, indicating that the addition of an additional cryogenic reduction size step in the analytical procedure may not be worthwhile in terms of recovery rates. This result suggests that diffusion of BFRs in the polymeric matrix may not the limiting step in the solvent extraction process [17], and other external parameters may be adjusted to favour the extraction kinetics and increase the recovery rates.

Extraction temperature substantially influences the extraction efficiency and the calculated BFR concentration from standard HIPS samples. The extraction yield of Deca-BDE and particularly TBBPA are greatly improved by using higher extraction temperatures, both with methanol/isopropanol and isopropanol/n-hexane as extractive solutions, as it can be observed in the plot of extraction yield versus extraction temperature in Figure 2. Temperature acts upon each stage of the solvent extraction process of low molecular weight compounds from polymeric particles. Higher temperatures result in higher diffusion rates of the analytes, both in the polymer core and in the boundary layer around the polymer surface. Higher temperatures also increase the solubility of the analytes in the extractive solvents and enhance the mass transfer from the boundary layer to the solvent bulk. The swelling ratio between the polymeric matrix and the solvent are as well influenced by the extraction temperature. Finally, temperature plays an essential role in the polymeric structure, in terms of the mobility of polymeric chains directly related to their viscoelastic behaviour and the glass transition temperature (T_g). In our case of study, HIPS is basically constituted by polystyrene (PS) with a low content of polybutadiene (PB) rubber; taking into account that the T_g of PS is around 90°C, temperatures above this range should favour polymer mobility and therefore a marked increase in extraction rates for additives, as observed in Figure 2.

The extraction time was optimised for an extraction temperature of 130°C using both solvent systems (Figure 3). Almost a complete recovery of TBBPA can be achieved at an extraction time of 60 minutes with isopropanol/n-hexane as the extractive solution, whereas only a partial recovery of 30% can be reached for Deca-BDE at the same conditions. In general, the extraction yields for TBBPA and Deca-BDE are similar or even higher than the reported by other authors obtained using supercritical-fluid extraction (SFE) with CO_2 and 1-propanol [11]. Other more aggressive extraction conditions and/or procedures may be therefore employed when a complete recovery of Deca-BDE were needed. In fact, almost complete recovery of Deca-BDE was reported in the aforementioned study [11], but employing toluene as solvent modifier in the SFE method, which dissolves the HIPS matrix. The proposed analytical method combining MAE and HPLC-UV detection offers, finally, excellent reproducibility (n=3) for the calculated BFR concentrations, with low RSD values for the different extractive conditions proposed.

3.3 Extraction of brominated flame retardants from standard samples from WEEE

The analytical method developed for the determination of BFRs in standard styrenic polymeric samples has been further applied for the identification and quantification of BFRs in standard recycled polymeric samples from waste electrical and electronic equipment (WEEE). The samples described in Table 1 have been therefore extracted using MAE and their extracts have been analysed using HPLC-UV. Figure 4 shows the chromatograms of the extracts for the standard WEEE samples. The sample ABS-GVL2-07 shows, in addition to the main peak corresponding to Deca-BDE (t_R=20.6 min), other minor peaks that may correspond with other PBDE congeners with lower bromination degree at t_R=20.0 min, t_R=19.4 min, and t_R=18.9 min, either originally contained in the technical Deca-BDE grade used in the manufacture of the plastic component, or due to the debromination of the BFR during service life and further recycling (Figure 4a). Sample ABS-GVL2-11 shows a single clear peak corresponding with TBBPA at t_R=11.1 min, proving that the flame retardant has been successfully extracted from the polymeric matrix (Figure 4b). Finally, different peaks can be observed in the chromatogram corresponding to sample SB-GVL2-07; the main peak assigned to Deca-BDE at t_R=20.6 min and other peaks that may be attributed to other PBDE congeners at t_R=19.9 min, t_R=18.9 min, and t_R=18.4 min (Figure 4c).

The calculated concentration of TBBPA and Deca-BDE in the standard WEEE samples is provided in Table 3. It is worth mentioning that for the case of samples ABS-GVL2-07 and SB-GVL2-07, the Deca-BDE concentration has been calculated considering only the main peak at t_R=20.6 min and not the other peaks assigned to minor congeners. The calculated concentration for TBBPA is very similar to the approximate theoretical concentration provided by the supplier, proving the complete extraction of this flame retardant, whereas the concentration of Deca-BDE is lower and a complete recovery cannot be achieved.

Conclusions

An analytical method for the determination of brominated flame retardants in styrenic polymers has been developed for standard high-impact polystyrene (HIPS) with TBBPA and Deca-BDE using microwave-assisted extraction and HPLC-UV. The optimisation of the extractive conditions such as solvent system, extraction temperature and time, and particle size has been carried out and discussed. The employment of a mixed polar/non-polar solvent as isopropanol/n-hexane offers higher recovery rates in terms of higher affinity to the analytes and higher swelling effect with the matrix. Temperature has a remarkable effect on the extraction; high temperatures above the glass transition of the polymer should be used to obtain improved diffusion rates and faster recovery of the analytes. However, the diminution of particle size has a minor influence on the extraction recovery, which suggests that the diffusion of the additives in the polymer core may not be the limiting stage in the extraction. Complete recovery of TBBPA from the polymeric matrix can be achieved by adjusting the extraction parameters. The complete extraction of Deca-BDE proves to be a complex analytical process, which may require more extreme extraction conditions (temperature, time) or even other extraction processes with higher pressure conditions and increased affinity with extraction solvents. The method has been successfully applied to identify and determine the presence of BFRs in standard WEEE samples, which proves the idoneity of the proposed analytical procedure for the fast screening the presence of BFRs in recycled samples from WEEE in order to fulfil the current restrictive legislation.

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References

[1] M. Alaee, P. Arias, A. Sjodin, and A. Bergman, *Environment International* 29, (6), 683-689 (2003).

[2] C. A. de Wit, *Chemosphere* 46, (5), 583-624 (2002).

[3] R. C. Hale, M. J. La Guardia, E. Harvey, M. O. Gaylor, and T. M. Mainor, *Chemosphere* 64, (2), 181-186 (2006).

[4] A. Covaci, S. Voorspoels, and J. de Boer, *Environment International* 29, (6), 735-756 (2003).

[5] A. Covaci, S. Voorspoels, L. Ramos, H. Neels, and R. Blust, *Journal of Chromatography A* 1153, (1-2), 145-171 (2007).

[6] J. de Boer, and R. J. Law, *Journal of Chromatography A* 1000, (1-2), 223-251 (2003).

[7] T. Hyotylainen, and K. Hartonen, *TrAC Trends in Analytical Chemistry* 21, (1), 13-30 (2002).

[8] E. Eljarrat, and D. Barceló, *TrAC Trends in Analytical Chemistry* 23, (10-11), 727-736 (2004).

[9] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, J. Carroll, I. Newton, L. M. Garden, J. R. Dean, and C. T. Costley, *Analyst* 122, 101R-116R (1997).

[10] M. Riess, and R. van Eldik, *Journal of Chromatography A* 827, (1), 65-71 (1998).

[11] A. m. Altwaiq, M. Wolf, and R. van Eldik, *Analytica Chimica Acta* 491, (1), 111-123 (2003).

[12] M. Schlummer, F. Brandl, A. Maurer, and R. van Eldik, *Journal of Chromatography A* 1064, (1), 39-51 (2005).

[13] M. Pohlein, A. S. Llopis, M. Wolf, and R. v. Eldik, *Journal of Chromatography A* 1066, (1-2), 111-117 (2005).

[14] M. Letellier, and H. Budzinski, *Analusis* 27, (3), 259-271 (1999).

[15] V. Lopez-Avila, R. Young, and W. F. Beckert, *Anal. Chem.* 66, (7), 1097-1106 (1994).

[16] J. L. Luque-Garcıa, and M. D. Luque de Castro, *Trends in Analytical Chemistry* 22, (2), 90-98 (2003).

[17] X. Lou, H.-G. Janssen, and C. A. Cramers, *Anal. Chem.* 69, (8), 1598-1603 (1997).

[18] J. M. Cano, M. L. Marín, A. Sánchez, and V. Hernandis, *Journal of Chromatography A* 963, (1-2), 401-409 (2002).

[19] W. Freitag, and O. John, *Angewandte Makromolekulare Chemie* 175, (1), 181-185 (1990).

[20] B. Marcato, and M. Vianello, *Journal of Chromatography A* 869, (1-2), 285-300 (2000).

[21] K. Fateh-Alavi, S. Karlsson, and U. W. Gedde, *Journal of Applied Polymer Science* 93, (5), 2185-2192 (2004).

[22] C. T. Costley, J. R. Dean, I. Newton, and J. Carroll, *Analytical Communications* 34, (3), 89-91 (1997).

[23] W. Camacho, and S. Karlsson, *Polymer Degradation and Stability* 71, (1), 123-134 (2000).

Table 1. Composition of the standard WEEE samples containing BFRs

WEEE sample	**Matrix**	**Flame retardant**		**Additive**	
		Type	**Conc.** (mg/g)	**Type**	**Conc.** (mg/g)
ABS-GVL2-07	ABS	Deca-BDE	100	Sb_2O_3	50
ABS-GVL2-11	ABS	TBBPA	100	Sb_2O_3	50
SB-GVL2-07	SB	Deca-BDE	100	Sb_2O_3	50

Table 2. Chromatographic parameters (retention time, limit of detection, limit of quantification, and linearity range) for proposed analytical method

Analyte	**Retention time, t_R** (min)	**LOD (S/N=3)** (μg/ml)	**LOQ (S/N=10)** (μg/ml)	**Linearity range** (μg/ml) **(regression coefficient)**
TBBPA	11.1	0.49	1.63	5-1000 (0.9962)
Deca-BDE	20.6	0.21	0.68	1-500 (0.9971)

Table 3. Calculated concentration of BFRs in the standard HIPS samples using microwave-assisted extraction under different conditions

Solvent	Sample size	T (°C)	Time (min)	Calculated concentration, mg/g (RSD, %)	
				TBBPA	Deca-BDE
IP MeOH (1:1 v/v)	Granule	90	30	10.44 (7.46)	2.82 (11.29)
		110	30	27.16 (1.11)	5.04 (3.10)
		130	20	33.37 (3.32)	7.77 (3.44)
			30	33.97 (4.87)	7.98 (3.70)
			45	39.69 (4.05)	8.99 (0.42)
			60	41.98 (2.16)	9.27 (5.06)
	Powder	130	60	45.91 (7.1)	11.01 (14.1)
IP hexane 1:1 v/v	Granule	90	30	36.62 (2.33)	5.46 (1.49)
		110	30	38.00 (4.59)	6.92 (3.18)
		130	20	37.65 (5.69)	9.36 (0.80)
			30	44.93 (0.91)	10.77 (6.55)
			45	46.06 (1.53)	12.04 (7.82)
			60	48.55 (1.31)	13.69 (8.75)
	Powder	130	60	48.19 (3.4)	16.54 (12.7)

Table 4. Calculated concentration of BFRs in the standard WEEE samples using microwave-assisted extraction.

Sample	Matrix	BFR	Extraction solvent	Calculated concentration, mg/g (RSD, %)
ABS-GVL2-11	ABS	TBBPA	IP/MeOH	124.14 (3.18)
			IP/hexane	109.53 (0.90)
SB-GVL2-07	SB	Deca-BDE	IP/MeOH	10.83 (24.60)
			IP/hexane	26.90 (11.28)
ABS-GVL2-07	ABS	Deca-BDE	IP/MeOH	18.23 (6.12)
			IP/hexane	29.03 (20.04)

Figure captions

Figure 1. Chromatogram of the extraction of the HIPS standard sample with BFRs by MAE (solvent: isopropanol/n-hexane, 30 minutes, 130ºC).

Figure 2. Influence of the extraction temperature on the recovery of brominated flame retardants by microwave-assisted extraction (MAE) at an extraction time of 30 minutes, employing as solvents (full symbol, ––) isopropanol/n-hexane; (hollow symbol, - - -) isopropanol/methanol: (●) TBBPA; (■) Deca-BDE.

Figure 3. Influence of the extraction time on the recovery of brominated flame retardants by microwave assisted extraction (MAE) at a temperature of 130ºC, employing as solvents (full symbol, ––) isopropanol/n-hexane; (hollow symbol, - - -) isopropanol/methanol: (●) TBBPA; (■) Deca-BDE.

Figure 4. Chromatograms for the extracted standard WEEE samples using MAE (solvent: isopropanol/n-hexane, 60 minutes, 130ºC): (a) ABS-GVL2-11; (b) SB-GVL2-07; (c) ABS-GVL2-07.

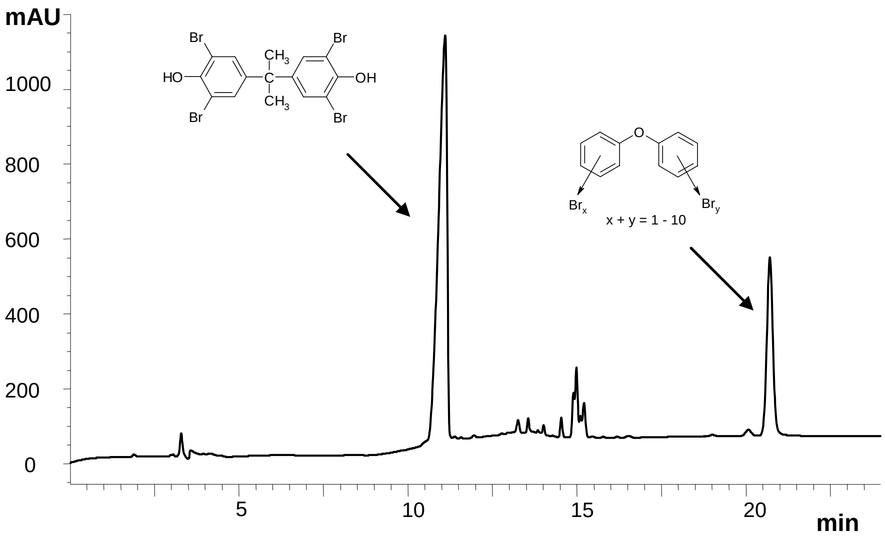

mAU
1000
800
600
400
200
0
5
10
15
20
min
Br
HO
Br
CH3
C
CH3
Br
OH
Br
O
Brx
Bry
x + y = 1 - 10

Figure 1

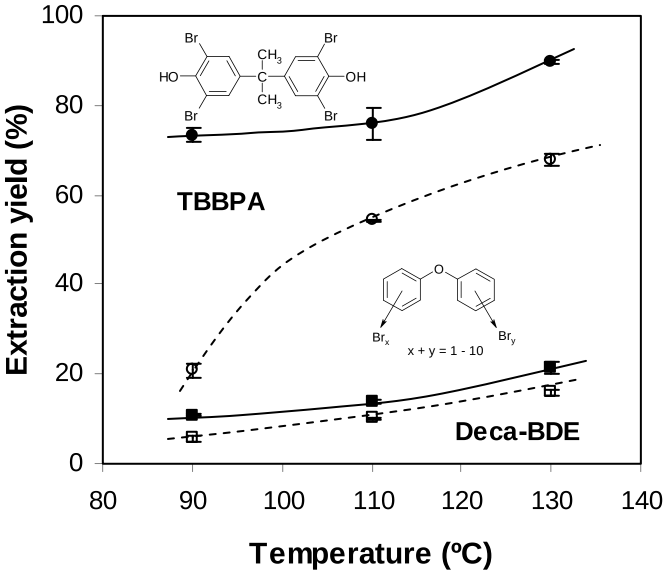
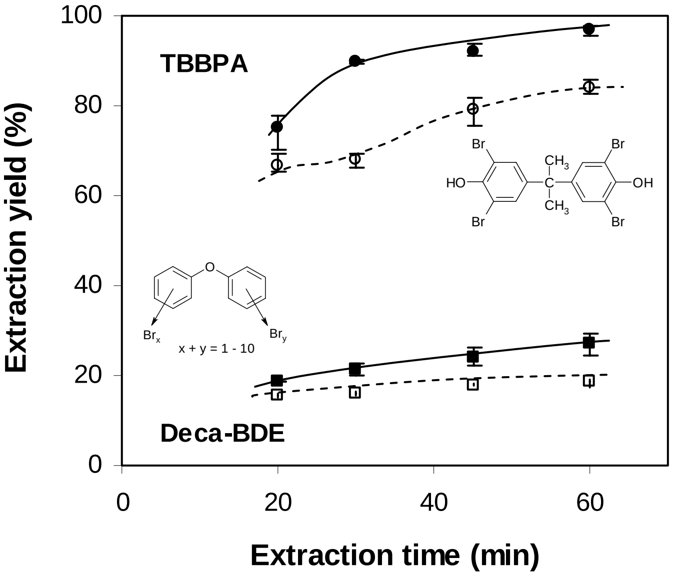

Extraction yield (%)
0
20
40
60
80
100
Temperature (ºC)
80
90
100
110
120
130
140
TBBPA
Br
HO
Br
CH3
C
CH3
Br
OH
Br
Deca-BDE
O
Brx
Bry
x + y = 1 - 10

Figure 2


TBBPA
Deca-BDE
Extraction yield (%)
Extraction time (min)
0
20
40
60
80
100
0
20
40
60
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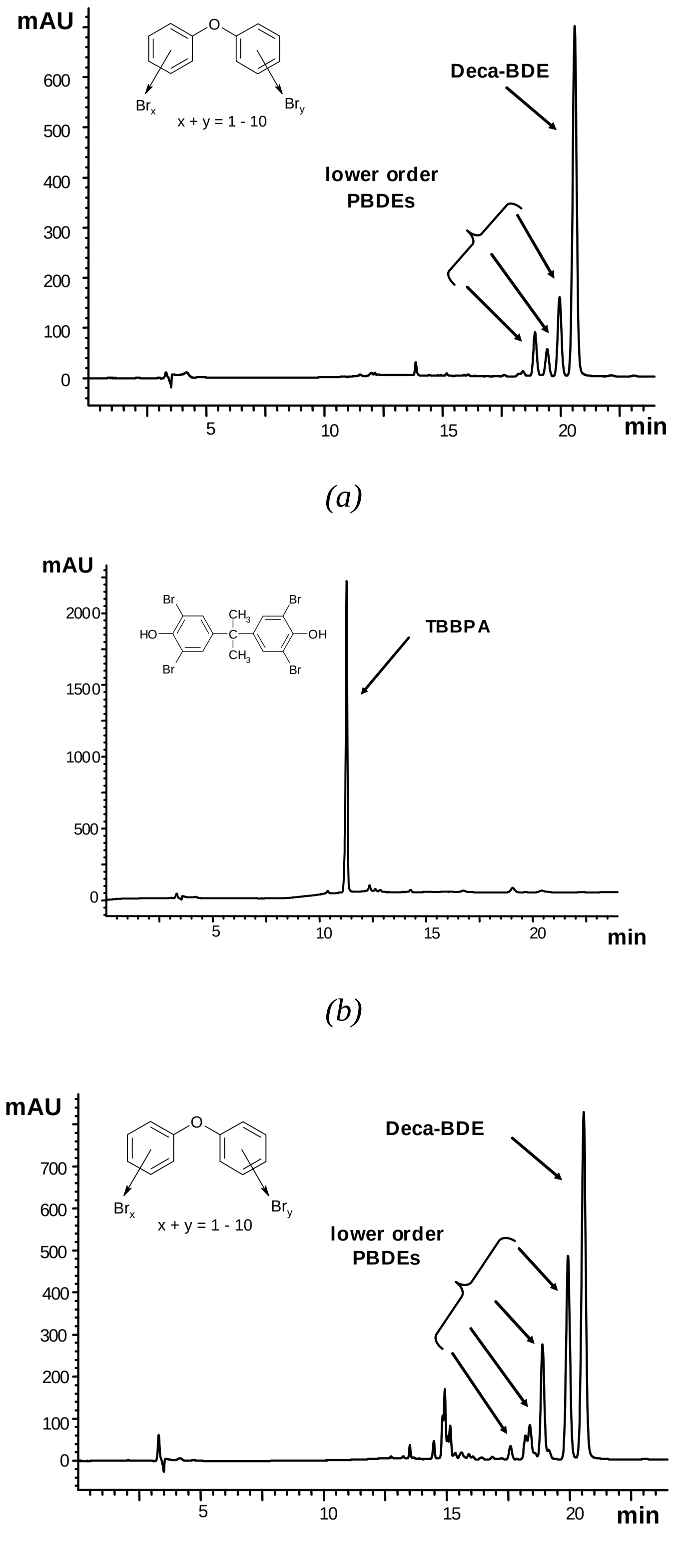
Br
Br
HO
OH
CH3
C
CH3
O
Brx
Bry
x + y = 1 - 10

Figure 3


mAU
600
500
400
300
200
100
0
5
10
15
20
min
O
Br$_x$
Br$_y$
x + y = 1 - 10
Deca-BDE
lower order PBDEs
mAU
2000
1500
1000
500
0
5
10
15
20
min
Br
HO
CH$_3$
C
CH$_3$
OH
TBBPA
mAU
700
600
500
400
300
200
100
0
5
10
15
20
min
O
Br$_x$
Br$_y$
x + y = 1 - 10
Deca-BDE
lower order PBDEs

(a)

(b)

(c)

Figure 4

Article VI

Determination of brominated flame retardants in styrenic polymers: A comparison of extraction efficiency among ultrasonication, microwave-assisted extraction, and pressurised liquid extraction.

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IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN STYRENIC POLYMERS: A COMPARISON OF THE EXTRACTION EFFICIENCY OF ULTRASONICATION, MICROWAVE-ASSISTED EXTRACTION AND PRESSURISED LIQUID EXTRACTION

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IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN STYRENIC POLYMERS: A COMPARISON OF THE EXTRACTION EFFICIENCY OF ULTRASONICATION, MICROWAVE-ASSISTED EXTRACTION AND PRESSURISED LIQUID EXTRACTION

Abstract

The extraction efficiency of pressurised liquid extraction, microwave-assisted extraction, and ultrasonic-assisted extraction under different extractive conditions has been compared for the recovery of the most commonly employed brominated flame retardants (BFRs) from polymeric matrixes. A HPLC-MS/MS method has been proposed for the simultaneous separation and quantification of tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) stereoisomers, and decabromodiphenyl ether (Deca-BDE) in the polymeric extracts. Pressurised liquid extraction (PLE) and microwave-assisted extraction (MAE) result in complete extraction of TBBPA and HBCD, and high recovery rates for Deca-BDE; ultrasonication, on the other hand, offers relatively low extraction recoveries. The proposed analytical procedures could be used for the effective identification and quantification of BFRs in styrenic plastics and for quality purposes in recycling facilities that separate polymer fractions from waste electrical and electronic equipment (WEEE).

Keywords

Brominated flame retardants; TBBPA, HBCD, PBDEs; Solvent extraction; Polymers; HPLC-MS/MS; WEEE

Introduction

Brominated flame retardants (BFRs) have been widely employed as additives in plastic components of electrical and electronic equipment and in building applications, to improve their fire retardancy properties such as ignition resistance, flame propagation and smoke emission [1]. BFRs are a structurally diverse family of chemical organic halogen compounds, tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls (PBBs) being the most widespread BFR additives in terms of production and consumption [2]. However, there is increasing concern about the adverse effects of these brominated compounds on human health and the environment, due to their lipophilic and bioaccumulative nature. It has been demonstrated that BFRs are present in the environment and they are assimilated by living organisms; however, the long-term health and environmental impacts are still not well known [3]. This environmental concern has raised significant attention to the presence of BFRs in plastics from electrical and electronic equipment (E&E) and their waste streams (WEEE). European legislation (Directives 2002/96/EC and 2002/95/EC) has been introduced to regulate the employment and disposal of BFR-containing plastics in E&E equipment. PBBs and some PBDEs (Penta- and Octa-BDE) have been banned in all new applications, but the use of Deca-BDE is still being discussed at the legislative level due to uncertainties in the results of the risk assessment report commissioned by the European Union [4]. Plastics containing BFRs must also be separated from other WEEE fractions prior to recovery and recycling; limits of 0.1% (w/w) have been set for the presence of PBBs and certain PBDEs in recycled products. These legislative implications strengthen the need for analytical procedures to determine the presence of BFRs and their possible degradation products in WEEE plastics [5].

Several reviews have been published in recent years that deal with the analytical procedures to determine the presence of brominated flame retardants in environmental, biological, and human samples. The determination of BFRs includes several analytical steps depending on the complexity of the matrix, with sample pre-treatment, extraction, clean-up and fractionation, and BFR detection as the common sequence [2, 3, 6-8]. Separation, identification, and quantification of BFRs are usually performed using chromatographic techniques, independent of the type of matrix. GC-MS has been traditionally employed for the analysis of PBBs, PBDEs, TBBPA, and HBCD; several problems, however, arise from this procedure, such as degradation problems in PBDEs, interconversion of HBCD diastereomers at certain temperatures, and the need for derivatisation in TBBPA analysis. To avoid these inconveniences, LC coupled to electrospray ionisation (ESI) and/or atmospheric pressure chemical ionisation (APCI) mass spectrometry have been developed recently for the determination of TBBPA, separation of HBCD congeners, and Deca-BDE analysis [7, 9-14].

For the determination of additive BFRs in polymeric materials, solvent extraction plays an important role in the overall procedure. Soxhlet extraction has been traditionally employed for the extraction of additives from polymers; advanced extraction procedures such as supercritical-fluid extraction (SFE), pressurised solvent extraction (PLE), ultrasonic-assisted extraction (UAE), and microwave-assisted extraction (MAE) have been successfully introduced, offering in contrast shorter extraction times, lower solvent consumption, and the possibility for automatisation [15]. Soxhlet extraction with methanol/isopropanol was first employed for the identification of different BFRs from plastic waste from electronic equipment [16]. Supercritical-fluid extraction with different solvents (SFE) [17], pressurised liquid extraction with iso-octane [18], and ultrasonic-assisted extraction with isopropanol [19], have proved to be useful as fast extraction methods to screen for BFRs in plastic fractions from WEEE. However, no comparative studies about the extraction yields of these procedures for different BFRs have yet been performed.

The purpose of this study is to compare the efficiency of different advanced extraction techniques (pressurised liquid extraction, microwave-assisted extraction, and ultrasonication under different operation conditions) for the recovery of some important brominated flame retardants (TBBPA, HBCD, and Deca-BDE) from WEEE polymeric fractions. Standard samples of high-impact polystyrene (HIPS) with BFRs were used as matrix for this comparison, since HIPS is a polymeric material widely employed for the manufacture of electrical and electronic plastic components. A reverse-phase high-performance liquid chromatography with online tandem mass spectrometry method (HPLC-MS/MS) was also developed for the separation and quantification of TBBPA, HBCD diastereomers, and Deca-BDE in the polymeric solvent extracts. The overall aim of the study was to propose valuable assistance in the quality analysis of waste and recycled polymer materials from electrical and electronic applications.

2. Experimental

2.1 Chemicals and preparation of materials

Tetrabromobisphenol-A technical grade (TBBPA) (4-4'-isopropylidene bis(2,6-dibromophenol), 97% purity, M_w 543.9 g/mol, CAS number 79-94-7) provided by Aldrich Chemicals (Sweden), hexabromocyclododecane (HBCD) (1,2,5,6,9,10-hexabromocyclododecane, 97% purity, M_w 641.73 g/mol, CAS number 3194-55-6) provided by Aldrich Chemicals (Sweden), and decabromo diphenyl ether, technical grade (Deca-BDE, 95.0% purity, M_w 959.22 g/mol, CAS number 1163-19-5) provided by Sigma Aldrich (Sweden) were employed as flame retardant reference materials. The solvents for the extraction and analysis of the brominated flame retardants (n-hexane, isopropanol, methanol, tetrahydrofurane, acetonitrile, and water) were all chromatographic grades and provided by Acros Organics (Sweden).

Virgin high-impact polystyrene (HIPS), commercial grade Polystyrol 486M (BASF Española, Spain) was employed as the polymeric matrix for the development and comparison of advanced extractive methods for determination of BFRs in styrenic polymers. Standard samples HIPS containing 50 mg/g TBBPA, 20 mg/g HBCD, and 50 mg/g Deca-BDE were prepared by solution in tetrahydrofurane (THF) in a stirred vessel at 25ºC during 12 hours. The fortified polymer solution was dried at ambient temperature for 4 days in a forced ventilation oven before granulating in a Moretto Granulator (Moretto, Italy). To analyse the influence of particle size on extraction efficiency, the polymeric granules were further grinded into powder using a rotary mill with liquid nitrogen.

2.2 Extraction

2.2.1 Pressurised liquid extraction (PLE)

Pressurised liquid extraction was performed using a Dionex ASE200 Extractor (Dionex Co., CA, USA). About 0.5 g of standard HIPS with BFRs (powder form) was mixed with laboratory sand and loaded into Dionex standard 22ml stainless steel extraction cells containing Dionex standard 22ml cellulose extraction thimbles. Extractions were performed employing two solvent systems, methanol/isopropanol (MeOH/IP, 1:1, v/v) and isopropanol/n-hexane (IP/n-hexane, 1:1, v/v); four extraction temperatures were tested (90ºC, 110ºC, 130ºC, and 150ºC) at a pressure of 1500psi. Four different extraction steps were performed consecutively on the same sample cell. Each step consisted of an initial cell heat-up time of 6 min, and 2 static 3 min cycles. After each cycle, the cell was flushed with solvent (100% of cell volume) and purged with nitrogen for 60s. The extracts for the different extraction steps were collected in suitable vials with Teflon septa and went through the post-treatment procedure.

2.2.2 Ultrasonic-assisted extraction (UAE)

Ultrasound extraction was performed using a Branson 2510 ultrasonic bath (Bransonic Ultrasonics, Holland). Approximately 0.5 g of standard HIPS with BFRs (either granule or powder) was placed together in closed vials with 10 ml of either isopropanol/methanol (1:1, v/v) or isopropanol/n-hexane (1:1, v/v) as extractive solutions. The vials were kept in the ultrasonic bath for 60 min at 65ºC and the extracts were then forwarded to the post-treatment procedure. The extraction temperature and time were optimised for ultrasound extraction of Deca-BDE and TBBPA from HIPS in a previous work [20].

2.2.3 Microwave-assisted extraction (MAE)

The microwave extraction was carried out in a MES 100 microwave extraction system (CEM Corp., North Carolina, USA), with a nominal power of 1000W. About 0.5g of the standard HIPS with BFRs (in either granule or powder form) was introduced with 10ml of the extractive solution to the closed vessels designed for microwave extraction. As extractive solutions, both methanol/isopropanol (1:1, v/v) and n-hexane/isopropanol (1:1, v/v) were employed. The extractions were carried out at 130°C for 60 min and the extracts were collected and forwarded to post-treatment. The conditions for microwave-assisted extraction of Deca-BDE and TBBPA from HIPS were optimised in a previous work [20].

2.2.4 Extract post-treatment before chromatographic analysis

The extracts collected from the different extraction procedures were evaporated to near dryness in a rotary evaporator. The residue was re-dissolved with tetrahydrofurane to a concentration adjusted to the linearity range of the detection, filtered with a 0.45 mm pore size HPLC Teflon filter (Sorbent AB, Sweden), and placed in HPLC vials, which were kept at 4ºC until further analysis.

2.3 Analysis using HPLC-MS/MS

The extracts were analysed using high-performance liquid chromatography with online tandem mass spectrometry (HPLC-MS/MS). An Agilent 1100 HPLC system (Agilent Technologies, CA, USA), equipped with a G1329A autosampler, a G1312A pump, and a G1316A column oven connected to a Triple Quadrupole Mass Spectrometer API 4000 (Applied Biosystems, CA, USA) were employed for the analyses.

The chromatographic separation was accomplished using a reverse-phase system consisting of a 5μm filter (Supelco, Sweden), a Supelguard Discovery 18 guard column (dimensions 20 x 4 mm, particle size 5μm; Supelco, Sweden), and a C18 Hypersyl ODS column (dimensions 250 x 4.6 mm, particle size 5 μm; Supelco, Sweden). The mobile phase consisted of a gradient system of acetonitrile (solvent A) and 10mM ammonium acetate buffer, pH 4.5 (solvent B) at a flow of 1ml/min with the elution programme shown in Table 1. The column was kept at 35°C and the injection volume was 5 μl.

Ionisation was achieved using atmospheric pressure chemical ionisation (APCI) in the negative mode at 600°C with N_2 as nebuliser gas and an entrance potential of -10V. Detection was performed by multiple reaction monitoring (MRM) mode of selected ions at the first (Q1) and the third quadrupole (Q3). To choose the fragmentation patterns of *m/z* (Q1) → *m/z* (Q3) for each analyte in the MRM mode, direct infusion of standard solutions in acetonitrile into the MS was performed and the product-ion scan mass spectra were recorded. Once the fragment ions were chosen, the MRM conditions were further optimised for each analyte to obtain maximum sensitivity for the compound of interest (Table 1).

2.4 Quantification

Quantification of TBBPA, HBCD congeners (α-, β-, and γ-), and Deca-BDE was performed by external calibration, using seven-point calibration curves obtained by the injection of standard solutions containing 0.1 – 50 μg/ml of the technical flame retardants. In the case of HBCD, although the content of each congener in the technical reference material was not known, quantification was performed individually for each congener related to the original concentration of the reference material, to investigate the effect of each extraction procedure on the individual recovery of each congener.

3. Results and discussion

3.1 Development of the analytical method for TBBPA, HBCD and Deca-BDE using HPLC-MS/MS

The optimisation of the MS sensitivity was performed by direct infusion of the standard analytes in acetonitrile into the APCI mass spectrometer. Figure 1 shows the full scan mass spectra of TBBPA, HBCD, and Deca-BDE. The main MS peak for TBBPA is found at *m/z 542.6*, which corresponds to the deprotonated molecule $[M-H]^-$ (Figure 1a), together with the corresponding peaks for Br^{79} and Br^{81}. Several peaks corresponding to different daughter ions can also be observed in the spectra, and have been identified according to a recent paper [21]. The full scan spectrum of HBCD is characterised by the main peaks corresponding to the Br isotopes (Br^{79} and Br^{81}), which exhibit the highest signal, together with the molecular ion at a *m/z 640.6*; minimal signal clusters can be observed at *m/z 558.6* and *m/z 239.0*, corresponding to different degrees of debromination of the original HBCD molecule (Figure 1b). Deca-BDE exhibits the main MS signal for the fragment ion corresponding to *m/z = 486.4* and for the Br isotopes, together with minor daughter ion clusters associated with other molecular fragments (Figure 1c). According to these fragmentation results, the MRM signals corresponding to *m/z* 543→79 and *m/z* 543→81 for TBBPA, *m/z* 641→79 and *m/z* 641→81 for the three HBCD congeners, and *m/z* 487→79 and *m/z* 487→81 for Deca-BDE, were selected and compared in terms of LOD, LOQ and linearity, to detect and quantify the flame retardant content in the extracts.

Chromatographic parameters were adjusted until complete separation of the different analytes, specifically the three different HBCD isomers, was achieved with a reasonable analysis time; the chromatographic conditions, in terms of mobile phase gradient programme, temperature and injection volume are shown in Table 1. Figure 2 shows a combined chromatogram of the superposed MRM signals for TBBPA (543→79), which elutes at a retention time of 4.38 min; α-, β-, and γ-congeners of HBCD (641→79), at a retention time of 5.59 min, 5.93 min, and 7.25 min, respectively; and Deca-BDE (487→79), which elutes last at 20.20 min. Small peaks at retention times of 16.72 min and 18.21 min appear for the MRM (487→79) signal, which correspond to lower-brominated congeners of the Deca-BDE technical-grade flame retardant, but they were not considered further for quantification in the study. It is worth mentioning that Deca-BDE is especially sensitive to debromination decomposition into lower order PBDEs when exposed to UV and sunlight radiation and/or during solution in alcohols. The extracts and the technical standard solutions were therefore analysed shortly after preparation, and no further sign of Deca-BDE debromination could be observed in the chromatograms.

The limit of detection (LOD) and limit of quantification (LOQ) for the studied flame retardants were calculated from the reference solutions for each compound and quantification MRM ion pairs (Table 2). HBCD has a relatively higher LOD and LOQ compared to TBBPA and Deca-BDE due to the relatively low ionisation efficiency in APCI. Other studies have pointed out the idoneity of electrospray ionisation (ESI) for the analysis of more polar flame retardants such as TBBPA and HBCD [10, 13, 14, 21], but polybrominated diphenyl ethers generally cannot be analysed using ESI, which is why APCI was selected. The linearity range of each analyte is also shown in Table 2;

the dynamic range of Deca-BDE was lower compared to the other compounds. Regardless of these differences, the quantification of the extracts was performed adjusting the concentration to the linearity range of the flame retardants in the HPLC-MS/MS method. In general, the MRM signals obtained from both Br_{79} and Br_{81} isotopes at the third quadrupole (Q3), can be used for the determination of the selected BFRs, with similar LOD, LOQ, and linearity conditions.

3.2 Extraction of BFRs using pressurised liquid extraction (PLE)

A method for the extraction of selected brominated flame retardants from HIPS using pressurised liquid extraction was developed and optimised, by considering different extraction solvent systems, extraction temperatures, and number of consecutive extraction steps (directly related to the extraction time). Table 3 presents the results of the calculated accumulative concentration of TBBPA, HBCD congeners, and Deca-BDE in the standard HIPS samples, using PLE under different operational conditions; the effect of the temperature, extraction steps, and solvent type is discussed from these results.

Careful selection of the extraction solution is fundamental when performing PLE on polymeric samples; solvents that show high extraction efficiency in traditional solvent procedures may not work at the elevated pressure and temperature conditions of PLE. The selected solvents must on one hand exhibit high swelling capability without solving the polymeric matrix at the temperature and pressure ranges of extraction; on the other hand, the analytes of interest should have good affinity for the extraction solution [22].

Mixed solvents with combined polar and non/polar nature normally offer a good approach to extract analytes with different polarities and molecular weight [23]. In our case, an isopropanol/n-hexane extraction agent with combined polar/non-polar behaviour offered significantly higher calculated concentrations of the BFRs than a mixture of polar solvents (isopropanol/methanol) under moderate temperature conditions of 90°C and 110°C in the pressurised PLE cell. For higher temperatures, however, both solvent systems give similar concentrations under the pressurised conditions of PLE; solvents that may not perform as good extractant solutions at moderate pressure and temperature conditions, such as methanol/isopropanol, can therefore be employed at the operation ranges of PLE. On the other hand, extraction of TBBPA at 150°C with isopropanol/n-hexane gives low extraction yield; this may be caused by the excessive swelling and collapse of the polymeric structure caused by the solvent under the extreme temperature and pressure extraction conditions (Figure 3).

Temperature has a dramatic effect on the extraction of analytes from polymers, due to its synergistic effect on both polymeric structure and extraction kinetics. The extraction temperature should be above the glass transition temperature (T_g) of the polymeric matrix, to increase polymer mobility during extraction conditions and favour analyte mobility. For the case of styrenic copolymers, polystyrene has its T_g at around 90°C, so temperatures above this range should result in markedly higher extraction yields. Increasing temperature also favours the swelling rate between polymer and solvent, but this effect may be controlled in order to avoid polymer dissolution in the solvent or collapse of polymer structure under extraction. Finally, the diffusion and mass transfer kinetics of the analyte from the polymeric structure into the solvent bulk are generally favoured by increasing temperatures. Choice of extraction temperature conditions must also take into consideration the stability of the analytes. In this direction, anomalous concentrations for the γ-HBCD conformer at 130°C and 150°C can be observed compared to the α- and β-conformers. HBCD is thermally unstable and undergoes conformational changes at temperatures around 160°C [24], which explains the remarkably low γ-HBCD content at these temperatures. Figure 3 shows the evolution of extraction yield for TBBPA under successive extraction steps using different extraction temperatures and solvents. The enhancing effect of increasing extraction temperature and mixed polar/non-polar solvent system can be clearly observed for TBBPA, taking into consideration the special behaviour pointed out at 150°C for isopropanol/n-hexane.

Figure 4 compares the results of PLE extraction for the different BFRs at 130°C using isopropanol/n-hexane as extractant solution. Full extraction of medium molecular weight flame retardants such as TBBPA and HBCD can be achieved using only 1-2 extraction steps at temperatures of 110°C - 130°C with a mixture of polar/non-polar solvent. For a higher molecular weight compound such as Deca-BDE, an extraction yield of only approximately 50% could be attained under the same extraction conditions (130°C, isopropanol/n-hexane); further extraction steps do not show an appreciable increase in the extraction yield under the same conditions. However, the extraction yield for Deca-BDE could be increased to nearly 75% using more severe temperature conditions such as 150°C; this observation indicates that the molecular weight of the analyte plays an important role in the mobility and the extraction rate during PLE.

3.3 Extraction of BFRs using ultrasound-assisted extraction (UAE)

Ultrasonication was performed at 65°C during 60 minutes on the standard HIPS samples with BFRs; the extraction conditions have been optimised in a previous study [20]. Low or medium concentrations of BFRs in standard HIPS samples could be calculated using UAE at the extraction conditions (Table 4); this low recovery may be due to the limiting temperature extractive conditions far below the T_g of polystyrene, which may hinder polymeric chain mobility and analyte diffusion [20]. In general, positive effects on the extraction yields are obtained using mixed solvent systems and lower particle size. Extraction recoveries of approximately 50 - 60% compared to the initial concentration could be easily obtained for TBBPA and HBCD from polymer powder using isopropanol/n-hexane as extractant solution; for Deca-BDE, on the other hand, other extraction procedures should be considered with the possibility of applying higher temperatures to increase the poor extraction yield obtained using UAE. A similar method for the detection of BFRs from polymeric samples has been proposed earlier, which offers detection limits compliant with European legislation [19], but no results from extraction yields are provided for comparison.

3.4 Extraction of BFRs using microwave-assisted extraction (MAE)

Microwave-assisted extraction (MAE) offers almost complete recovery of TBBPA and HBCD using isopropanol/n-hexane as solvents at 130°C for 60 minutes, with calculated concentrations similar to the initial BFR composition of the standard HIPS samples, whereas lower calculated concentrations are obtained for Deca-BDE (Table 4). The effect of microwaves and high temperatures may cause isomerisation of the β- and γ-HBCD congeners into the more thermally stable α-HBCD, as shown by the anomalous concentration results for the three HBCD congeners. As noted previously for ultrasonic-assisted extraction, using a mixed polar/non-polar extraction solvent system and reduced particle size enhances the extraction yield, attributable to a higher swelling effect of the solvent, higher affinity of the analytes, and favourable diffusion of the analytes from the polymeric matrix to the extractant media. The ability of MAE to reach extraction temperatures above the solvents boiling point and above the structural T_g of the polymeric material enhances considerably the extraction recovery of the additives and indicates the suitability of this technique for the determination of brominated flame retardants in plastic matrixes.

3.5 Comparison of PLE, UAE, and MAE for the extraction of BFRs from styrenic polymers

Figure 5 compares the extraction efficiency of UAE, MAE, and PLE from standard powder-form HIPS samples for the different brominated flame retardants using isopropanol/n-hexane and methanol/isopropanol as solvents for the most suitable extraction conditions (65°C, 60 minutes for ASE; 130°C, 60 minutes for MAE; 130°C, 2 extraction steps for PLE). Complete extraction of TBBPA and HBCD can be achieved using MAE and PLE at the abovementioned conditions; for high molecular weight compounds such as Deca-BDE, the pressurised conditions of PLE offer by far the highest extraction yields. The extraction results obtained using PLE and MAE are similar or even higher that those reported by other authors using supercritical fluid extraction, especially for HBCD [17]. Mixed polar/non-polar solvent systems such as isopropanol/n-hexane allow, in general, higher extraction rates than polar mixtures such as methanol/isopropanol alone. Table 4 presents the results of the average calculated concentration and the relative standard deviation (RSD) for the extraction procedures after reproducibility tests (n=3); overall, the different procedures show similar reproducibility, with MAE exhibiting slightly lower deviation results than the other extraction procedures.

Conclusions

Analytical procedures using different extraction techniques and HPLC-MS/MS for the simultaneous determination of the three most important commercial additive brominated flame retardants (TBBPA, HBCD congeners, and Deca-BDE) from styrenic polymeric matrixes have been proposed. The HPLC-MS/MS method allows the separation and identification of the analytes with low detection limits, which can be applied for the trace analysis of BFRs in recycled plastics from WEEE. The extraction efficiency of three advanced solvent extraction procedures UAE, MAE, and PLE have been compared using different extractive conditions for the proposed flame retardants from a styrenic matrix. MAE and PLE show, in general, similar extraction yields for the determination of brominated flame retardants, with low solvent consumption, short extraction times, easy operation, and high reproducibility. The extraction of high molar mass BFRs such as Deca-BDE could be accomplished by using PLE in the upper limit of its performance temperature and pressure conditions. UAE offers a fast extraction procedure for scanning for the presence of BFRs in styrenic plastics, but lower extraction recovery yields are obtained in comparison with other extraction procedures.

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References

[1] M. Alaee, P. Arias, A. Sjodin, and A. Bergman, *Environment International* 29, (6), 683-689 (2003).

[2] T. Hyotylainen, and K. Hartonen, *TrAC Trends in Analytical Chemistry* 21, (1), 13-30 (2002).

[3] C. A. de Wit, *Chemosphere* 46, (5), 583-624 (2002).

[4] European Union Risk Assessment Report: Bis(pentabromophenyl ether). 1st Priority List, Volume 17. European Commission Joint Research Centre, EUR 20402 EN, 2002. (2002).

[5] M. Schlummer, L. Gruber, A. Maurer, G. Wolz, and R. van Eldik, *Chemosphere* 67, (9), 1866-1876 (2007).

[6] A. Covaci, S. Voorspoels, and J. de Boer, *Environment International* 29, (6), 735-756 (2003).

[7] A. Covaci, S. Voorspoels, L. Ramos, H. Neels, and R. Blust, *Journal of Chromatography A* 1153, (1-2), 145-171 (2007).

[8] E. Eljarrat, and D. Barceló, *TrAC Trends in Analytical Chemistry* 23, (10-11), 727-736 (2004).

[9] L. Debrauwer, A. Riu, M. Jouahri, E. Rathahao, I. Jouanin, J.-P. Antignac, R. Cariou, B. Le Bizec, and D. Zalko, *Journal of Chromatography A* 1082, (1), 98-109 (2005).

[10] N. G. Dodder, A. M. Peck, J. R. Kucklick, and L. C. Sander, *Journal of Chromatography A* 1135, (1), 36-42 (2006).

[11] T. Hayama, H. Yoshida, S. Onimaru, S. Yonekura, H. Kuroki, K. Todoroki, H. Nohta, and M. Yamaguchi, *Journal of Chromatography B* 809, (1), 131-136 (2004).

[12] S. Morris, P. Bersuder, C. R. Allchin, B. Zegers, J. P. Boon, P. E. G. Leonards, and J. de Boer, *TrAC Trends in Analytical Chemistry Organohalogen Analysis* 25, (4), 343-349 (2006).

[13] R. Saint-Louis, and E. Pelletier, *The Analyst* 129, (8), 724-730 (2004).

[14] W. Budakowski, and G. Tomy, *Rapid Communications in Mass Spectrometry* 17, (13), 1399-1404 (2003).

[15] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, J. Carroll, I. Newton, L. M. Garden, J. R. Dean, and C. T. Costley, *Analyst* 122, 101R-116R (1997).

[16] M. Riess, and R. van Eldik, *Journal of Chromatography A* 827, (1), 65-71 (1998).

[17] A. m. Altwaiq, M. Wolf, and R. van Eldik, *Analytica Chimica Acta* 491, (1), 111-123 (2003).

[18] M. Schlummer, F. Brandl, A. Maurer, and R. van Eldik, *Journal of Chromatography A* 1064, (1), 39-51 (2005).

[19] M. Pohlein, A. S. Llopis, M. Wolf, and R. v. Eldik, *Journal of Chromatography A* 1066, (1-2), 111-117 (2005).

[20] F. Vilaplana, A. Ribes-Greus, and S. Karlsson, *Manuscript in preparation*,

[21] J. Tollback, C. Crescenzi, and E. Dyremark, *Journal of Chromatography A* 1104, (1-2), 106-112 (2006).

[22] X. Lou, H. G. Janssen, and C. A. Cramers, *Anal. Chem.* 69, (8), 1598-1603 (1997).

[23] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, S. A. Zhu, J. Carroll, I. D. Newton, and L. M. Garden, *Anal. Chem.* 70, (9), 1943-1948 (1998).

[24] U. Sellström, A. Kierkegaard, C. de Wit, and B. Jansson, *Environmental Toxicology and Chemistry* 17, (6), 1065–1072 (1998).

Table 1. Instrumental conditions for the separation and optimised detection of TBBPA, HBCD congeners, and Deca-BDE using HPLC-MS/MS

Liquid Chromatography

Injection volume:	5 μl		
Column temperature:	35°C		
Flow rate:	1ml/min		
Mobile phase gradient:	time (min)	A (%)	B (%)
	0	90.0	10.0
	12	95.0	5.0
	13	98.0	2.0
	27	98.0	2.0
	28	90.0	10.0
	35	90.0	10.0

Mass spectrometry

Ionisation:	APCI negative mode				
Curtain gas Pressure:	10 psi				
Source gas Pressure:	90 psi				
Nebulising Current:	-4 V				
Ion source Temperature:	600°C				
CAD:	12				
Entrance Potential:	-10 V				
Dwell time:	100msec				
MRM parameters:	Q1 Mass (amu)	Q3 Mass (amu)	DP	CE	CXP
TBBPA	542.8	78.9	-85	-86	-5
	542.8	80.9	-85	-92	-1
HCBD (α, β, γ)	640.6	78.9	-50	-34	-5
	640.6	80.9	-50	-58	-7
Deca-BDE	486.6	78.9	-40	-76	-1
	486.6	80.9	-40	-76	-7

CAD: collision-activated dissociation; DP: declustering potential; CE: collision energy; CXP: collision cell exit potential; MRM: multiple reaction monitoring.

Table 2. Limit of detection (LOD), limit of quantification (LOQ) and linearity of the analytical detection for the different BFRs

Analyte	**t_R** (min)	**MRM quant. ions**	**LOD (S/N=3)** (µg/ml)	**LOQ (S/N=10)** (µg/ml)	**Linearity range** (µg/ml) **(regression coefficient)**
TBBPA	4.38	543→79	0.025	0.083	0.1-50 (0.9990)
		543→81	0.014	0.047	0.1-50 (0.9946)
α-HBCD	5.59	641→79	0.8	2.7	0.1-50 (0.9996)
		641→81	1.0	3.4	0.1-50 (0.9994)
β-HBCD	5.93	641→79	0.3	1.2	0.1-50 (0.9954)
		641→81	0.4	1.5	0.1-50 (0.9993)
γ-HBCD	7.25	641→79	0.2	0.5	0.1-50 (0.9993)
		641→81	0.1	0.4	0.1-50 (0.9981)
Deca-BDE	20.2	487→79	0.011	0.036	0.1-25 (0.9938)
		487→81	0.012	0.040	0.1-25 (0.9937)

Table 3. Calculated accumulative concentration of BFRs in the standard HIPS samples using pressurised liquid extraction under different conditions

Solvent	T (°C)	Steps	Calculated BFR accumulative concentration (mg/g)									
			TBBPA		**α-HBCD**		**β-HBCD**		**γ-HBCD**		**Deca-BDE**	
			543→79	543→81	641→79	641→81	641→79	649→81	649→79	649→81	487→79	487→81
IP MeOH (1:1 v/v)	90	1	45.56	50.43	15.91	14.90	15.53	15.53	15.79	15.04	8.28	8.24
		2	46.23	51.10	16.60	15.59	16.15	16.11	16.39	15.73	12.64	12.87
		3	46.28	51.14	16.66	15.66	16.19	16.11	16.45	15.79	14.24	14.54
		4	46.30	51.15	16.66	15.66	16.19	16.11	16.47	15.80	14.98	15.31
	110	1	49.91	51.09	16.72	16.72	16.62	17.69	16.07	16.07	16.96	17.69
		2	50.00	51.19	16.83	16.81	16.73	17.76	16.17	16.17	18.61	19.46
		3	50.08	51.27	16.88	16.86	16.79	17.80	16.23	16.23	19.18	20.05
		4	50.08	51.32	16.88	16.86	16.79	17.80	16.23	16.23	21.37	22.21
	130	1	50.37	49.86	19.31	21.69	19.48	21.44	19.26	19.09	23.48	24.05
		2	51.31	50.81	20.64	23.00	20.64	22.55	20.49	20.41	24.28	24.87
		3	51.38	50.87	20.64	23.03	20.64	22.55	20.50	20.41	24.39	24.98
		4	51.40	50.88	20.64	23.03	20.64	22.55	20.50	20.41	24.39	24.99
	150	1	23.81	23.81	14.23	13.80	10.91	11.07	7.57	8.49	17.36	17.63
		2	32.32	32.79	21.58	20.37	15.67	15.98	11.40	12.70	25.46	26.03
		3	36.62	37.23	26.83	25.34	18.36	18.60	13.45	14.80	32.42	33.32
		4	38.88	39.51	30.35	28.58	19.82	20.07	14.39	15.75	37.17	38.06
IP hexane (1:1 v/v)	90	1	19.15	19.48	5.88	5.45	5.65	5.45	5.28	5.53	2.41	2.52
		2	25.07	25.00	8.58	8.00	8.48	8.46	7.90	8.15	4.97	5.20
		3	27.48	27.38	9.87	9.21	9.70	9.71	8.94	9.24	6.56	6.90
		4	28.87	28.78	10.57	9.97	10.43	10.52	9.66	9.96	7.84	8.20
	110	1	21.24	22.22	9.48	8.69	8.77	9.62	8.12	8.44	7.02	7.53
		2	23.70	24.66	11.26	10.41	10.45	11.34	9.71	10.09	9.38	10.09
		3	24.35	25.32	11.93	11.00	11.01	11.92	10.27	10.67	10.40	11.18
		4	24.57	25.54	12.18	11.25	11.21	12.07	10.48	10.88	10.96	11.76
	130	1	43.27	45.03	19.91	20.93	16.88	17.37	11.04	10.99	8.46	8.62
		2	48.51	50.51	23.28	24.52	19.55	20.35	13.04	13.01	17.09	17.43
		3	48.64	50.64	23.46	24.70	19.69	20.50	13.18	13.15	18.73	19.09
		4	48.67	50.68	23.53	24.76	19.74	20.55	13.23	13.20	19.51	19.91
	150	1	51.47	52.73	21.30	23.83	18.20	18.35	19.41	18.54	21.73	21.09
		2	53.98	55.26	22.38	24.96	19.12	19.16	20.29	19.39	23.62	23.03
		3	54.02	55.30	22.44	25.02	19.18	19.22	20.34	19.44	23.73	23.14
		4	54.05	55.32	22.44	25.02	19.18	19.22	20.34	19.44	23.79	23.20

Table 4. Calculated BFR concentration and relative standard deviation (RSD, n=3) for the standard HIPS samples using ultrasonic-assisted extraction (UAE), microwave-assisted extraction (MAE), and pressurised liquid extraction (PLE)

T (°C)	time (min)	Solvent	Sample size	Calculated BFR concentration, in mg/g (RSD, in %)									
				TBBPA		α-HBCD		β-HBCD		γ-HBCD		Deca-BDE	
				543→79	543→81	641→79	641→81	641→79	649→81	649→79	649→81	487→79	487→81
Ultrasonic-assisted extraction (UAE)													
65	60	IP/MeOH (1:1 v/v)	granule	3.16(28.4)	3.22(26.2)	0.87(26.4)	0.88(35.3)	1.05(31.0)	0.98(16.2)	0.74(21.4)	0.79(14.8)	1.06(18.5)	1.07(32.2)
			powder	4.85(27.3)	5.04(9.2)	1.84(12.9)	1.88(23.2)	1.51(25.1)	1.91(41.2)	1.32(59.7)	1.43(20.4)	1.15(10.1)	1.12(20.0)
		IP/hexane (1:1 v/v)	granule	21.17(2.6)	21.76(1.9)	7.07(9.0)	7.57(9.0)	7.07(6.1)	7.83(2.8)	6.52(9.8)	6.64(5.6)	1.78(18.2)	1.86(19.3)
			powder	26.91(0.8)	27.53	10.29(11.0)	9.21(2.7)	9.85(1.4)	10.42(7.4)	9.54(9.1)	9.81(7.7)	1.60(15.5)	1.66(12.6)
Microwave-assisted extraction (MAE)													
130	60	IP/MeOH (1:1 v/v)	granule	28.02(1.1)	26.94(6.3)	12.16(9.1)	10.23(23.1)	9.84(1.4)	8.61(12.3)	8.61(8.1)	8.93(7.0)	7.04(13.6)	7.21(11.5)
			powder	43.83(1.7)	42.22(7.1)	21.18(6.4)	16.34(5.2)	15.79(7.5)	14.04(5.3)	14.04(5.5)	15.17(3.2)	8.89(13.4)	9.01(14.1)
		IP/hexane (1:1 v/v)	granule	41.21(7.0)	41.69(3.2)	19.94(9.6)	17.23(11.8)	18.25(9.2)	15.91(8.0)	15.91(7.1)	17.61(3.2)	11.56(3.8)	10.31(24.2)
			powder	42.19(2.7)	43.15(3.4)	21.91(5.8)	19.14(4.9)	19.20(1.6)	17.61(3.3)	17.61(8.1)	20.61(5.1)	13.51(10.8)	13.42(12.7)
Pressurised liquid extraction (PLE)													
130	3 (1 cycle)	IP/MeOH (1:1 v/v)	powder	45.70(4.8)	45.90(4.3)	19.72(1.4)	21.35(13.3)	16.47(9.7)	16.84(18.1)	12.07(13.7)	11.69(10.6)	12.97(34.3)	13.27(33.3)
	6 (2 cycles)			49.73(4.0)	49.73(3.3)	21.04(9.8)	22.62(10.3)	18.39(6.6)	18.86(13.8)	13.33(7.3)	13.27(3.9)	19.32(11.6)	19.67(13.0)
	3 (1 cycle)	IP/hexane (1:1 v/v)		50.23(6.7)	50.39(6.3)	19.27(13.7)	19.89(12.1)	18.56(13.1)	19.19(15.6)	18.62(6.1)	18.30(13.1)	23.51(3.2)	24.12(4.3)
	6 (2 cycles)			51.56(6.7)	51.73(8.7)	19.93(14.7)	20.56(14.3)	19.12(14.7)	19.74(17.6)	19.23(8.3)	18.94(14.7)	25.70(4.9)	26.38(4.9)

Figure Captions

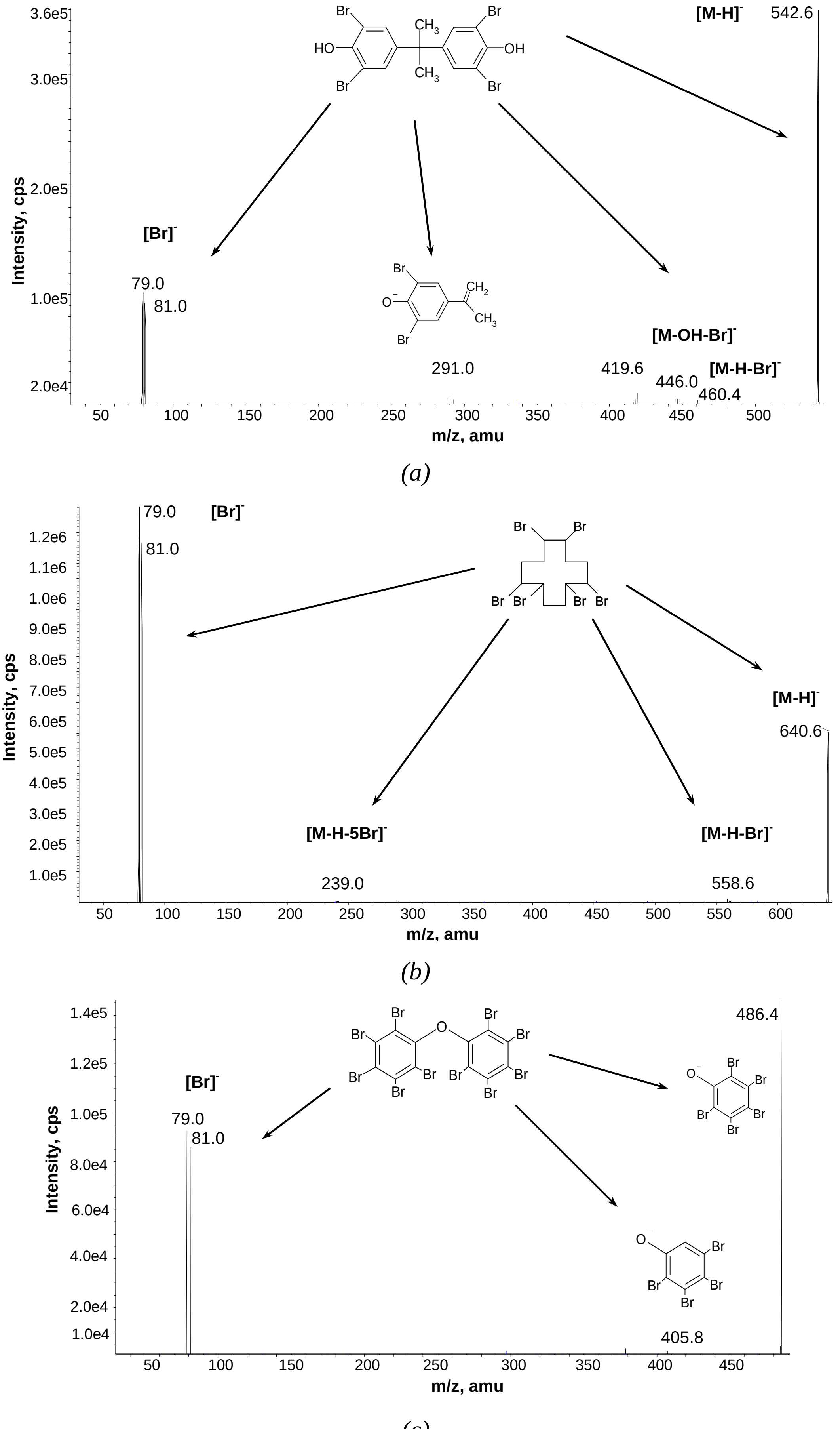
Figure 1. Full scan mass spectra of the BFRs acquired in the APCI negative mode by direct infusion of standard solutions in acetonitrile: a) TBBPA; b) HBCD; c) Deca-BDE

Figure 2. Chromatogram for the superposed MRM signals corresponding to TBBPA (543→79), α-, β-, and γ- HBCD congeners (641→79), and Deca-BDE (487→79).

Figure 3. Evolution of the extraction yield for TBBPA under successive extraction steps using PLE under different temperatures and solvents: (●) isopropanol/n-hexane; (○) isopropanol/methanol

Figure 4. Comparison of the extraction yield for the different BFRs using PLE with IP/n-hexane at a temperature of 130°C: (•) TBBPA; (*) α-HBCD; (■) β-HBCD; (▲) γ-HBCD; (♦) Deca-BDE.

Figure 5. Comparison of the extraction yield of ASE, MAE, and PLE for the different BFRs from standard HIPS samples.


Intensity, cps
m/z, amu
3.6e5
3.0e5
2.0e5
1.0e5
2.0e4
50
100
150
200
250
300
350
400
450
500
Br
HO
OH
CH3
[M-H]⁻
542.6
[Br]⁻
79.0
81.0
O⁻
CH2
291.0
[M-OH-Br]⁻
419.6
446.0
[M-H-Br]⁻
460.4
1.2e6
1.1e6
1.0e6
9.0e5
8.0e5
7.0e5
6.0e5
5.0e5
4.0e5
3.0e5
550
600
[M-H]⁻
640.6
[M-H-5Br]⁻
239.0
[M-H-Br]⁻
558.6
1.4e5
1.2e5
1.0e5
8.0e4
6.0e4
4.0e4
2.0e4
1.0e4
O
486.4
405.8

(a)

(b)

(c)

Figure 1

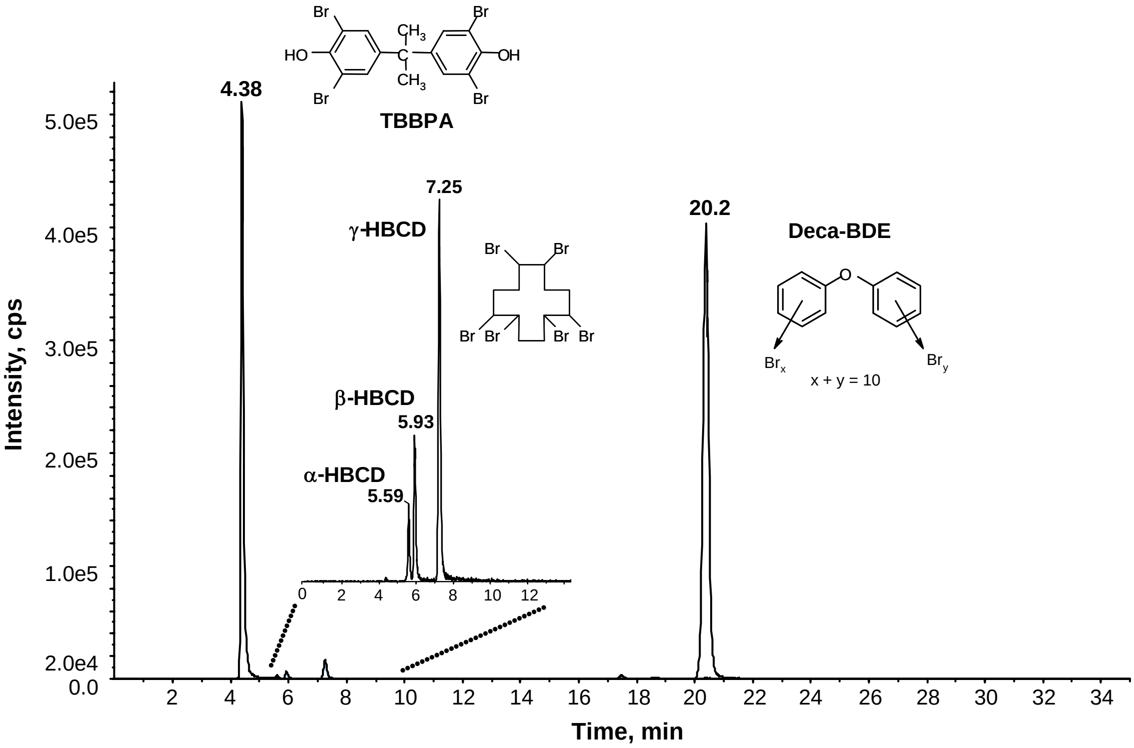

TBBPA
Br
HO
CH_3
C
CH_3
OH
4.38
7.25
γ-HBCD
20.2
Deca-BDE
O
Br_x
Br_y
x + y = 10
β-HBCD
5.93
α-HBCD
5.59
Intensity, cps
5.0e5
4.0e5
3.0e5
2.0e5
1.0e5
2.0e4
0.0
0 2 4 6 8 10 12
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
Time, min

Figure 2

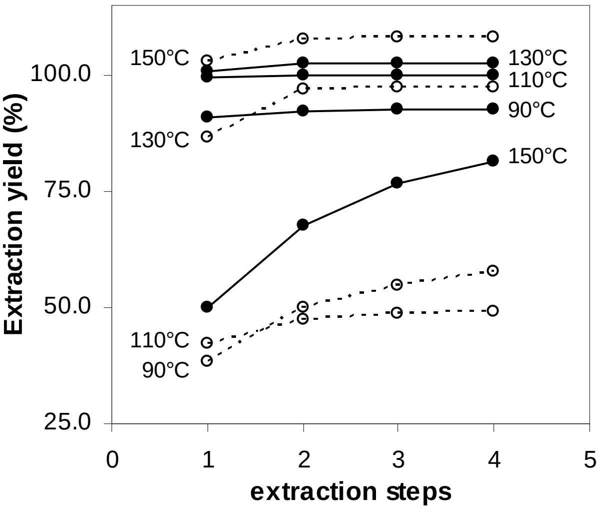

Extraction yield (%)
100.0
75.0
50.0
25.0
0
1
2
3
4
5
extraction steps
150°C
130°C
110°C
90°C
130°C
110°C
90°C
150°C

Figure 3

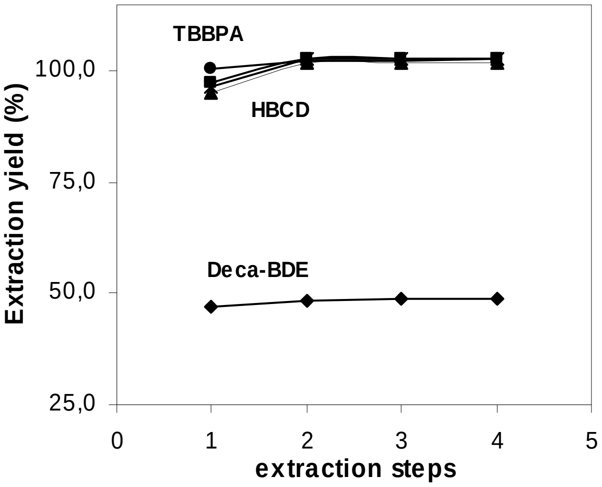

TBBPA
HBCD
Deca-BDE
Extraction yield (%)
100,0
75,0
50,0
25,0
0
1
2
3
4
5
extraction steps

Figure 4

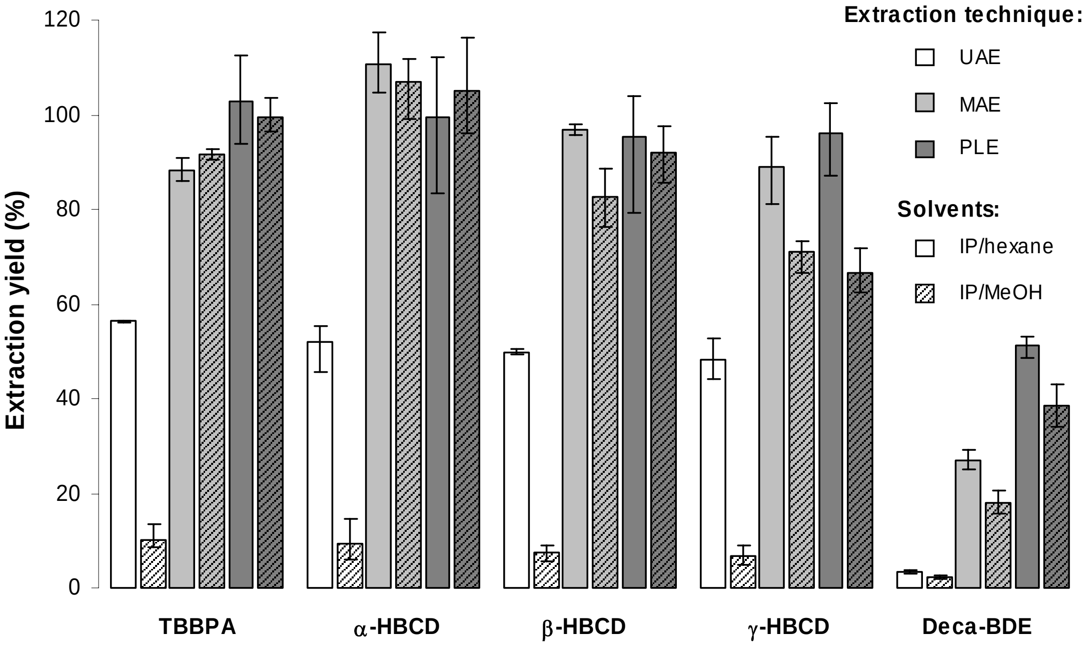

Extraction yield (%)
0
20
40
60
80
100
120
TBBPA
α-HBCD
β-HBCD
γ-HBCD
Deca-BDE
Extraction technique:
UAE
MAE
PLE
Solvents:
IP/hexane
IP/MeOH

Figure 5

Article VII

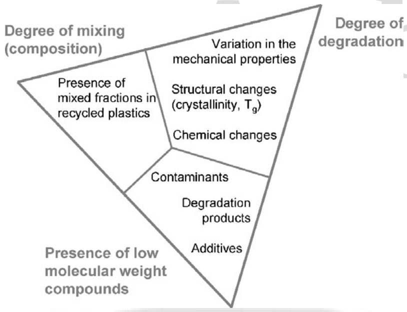
Quality concepts for the improved use of recycled polymeric materials: a review.

Francisco Vilaplana and Sigbritt Karlsson.

Accepted by Macromolecular Materials and Engineering. DOI 10.1002/mame.200700393 mame.200700393C

Review

Plastic wastes should be considered suitable raw materials for the manufacturing of new plastic products and therefore close the material and energy loop through recycling. This review presents three key research fronts for the improvement of mechanical recycling activities: scientific knowledge about degradation processes during previous life, development of reliable quality analysis procedures for recycled plastics, and effective upgrading of recyclates.



Quality Concepts for the Improved Use of Recycled Polymeric Materials: A Review

F. Vilaplana, S. Karlsson*

Macromol. Mater. Eng. **2008**, *293*, 000–000

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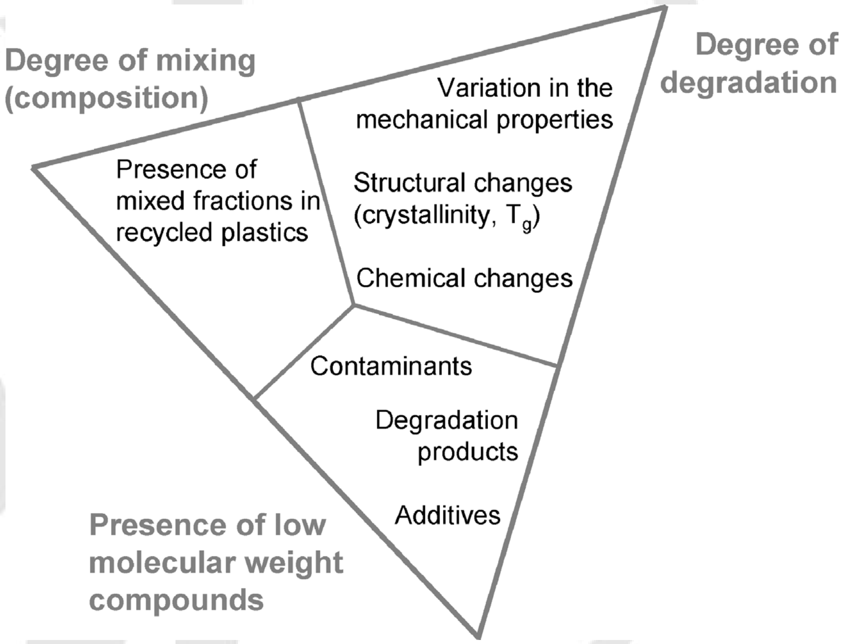
Quality Concepts for the Improved Use of Recycled Polymeric Materials: A Review

Francisco Vilaplana, Sigbritt Karlsson*

Polymeric waste materials should be considered resources for the manufacture of new products through recycling processes, with a similar status to virgin fossil-based plastics and biopolymers from renewable resources. Several efforts can be made to achieve this qualitative quantum leap in plastics recycling, and consequently introduce recycled products, with competitive performance, to the market. Scientific knowledge about the degradation processes during the life cycle and the development of fast and reliable analytical methods for the quality assessment of reccycled plastics are fundamental to guarantee their performance in new applications. Different strategies — restabilisation, rebuilding, compatibilisation, and addition of elastomers and fillers — can be used to upgrade the structure and properties of polymeric waste streams. This review discusses recent developments in the mechanical recycling of plastics, focusing on how to produce quality materials from waste streams and, thus, contribute to a sustainable management of resources and energy.



Introduction

Polymeric materials allow the manufacture of a wide variety of low-cost, high-performance products, and contribute to continuous energy saving and sustainable development. The inert nature and biodegradation resistance of synthetic polymers have created, however, an important environmental dilemma concerning their waste management. The optimisation of waste management procedures should imply a multidisciplinary approach based on a hierarchy, in which prevention, waste minimisation, waste reuse, waste recovery and, lastly, disposal should be prioritised, in that order. Options for plastic waste recovery, in contraposition to landfill

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Sigbritt Karlsson, with an educational background in Biochemistry, has developed her academic and research career in the field of Polymer Technology at the Department of Fibre and Polymer Technology, KTH Royal Institute of Technology (Stockholm, Sweden). She was appointed Professor in Environmental Interaction of Polymeric Materials in 1999. She has been coordinator of several national and international research projects and is author and/or co-author of over 150 scientific papers, proceedings, and abstracts. Her research interests have always been devoted to bio- and environmental chemistry: biopolymers (polysaccharides, proteins); biocomposites; cellulose and cellulose derivatives; chromatography and mass spectrometry of polymers and monomers, additives and degradation products; biochemical and microbial effects on polymers; recycling of polymers and quality aspects; separation and extraction techniques for monitoring small molecules in natural and synthetic polymers; biofilms and adhesion mechanisms on polymers. She has been recently appointed responsible for undergraduate studies on the Board of KTH Royal Institute of Technology.

disposal, include material recycling and energy recovery procedures. As a whole, recycling processes (mechanical and feedstock recycling) involve material recovery from plastic waste streams, whereas combustion procedures for heat production with controlled emissions are included in energy recovery options. Mechanical recycling entails the production through physical means of new plastic products from plastic waste. 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 into new polymeric products by synthesis. Finally, energy recovery employs polymeric waste streams as fuel for energy production, exploiting the high calorific content of plastics.

Plastic wastes should receive renewed consideration as valuable resources for product manufacturing, with a similar status to virgin oil-based plastics and polymers of biological origin.[1] The origin of the plastic waste streams — that is, the end-of-life application sector — determines the management challenges and the technological procedures to be implemented for the successful recycling of their plastic wastes. A valuable classification has been proposed for the plastic waste streams according to their origin, based on the following sources: packaging, agriculture, municipal solid waste (MSW), construction and demolition (C&D), end-of-life vehicles (ELV), and waste electrical and electronic equipment (WEEE). General bottlenecks that restrict the effective implementation of recycling activities include technological, management, and commercial issues. There are inherent difficulties in the management, dismantling, identification, and separation of mixed plastic waste streams, together with limited scientific knowledge about the influence of recycling processes on the composition, structure, and properties of polymeric materials. In addition, plastic wastes may contain contaminants and hazardous substances; consequently, environmental concerns and policy issues hinder their reuse. The introduction of standardised procedures for the quick and reliable characterisation of recycled materials would unquestionably help in the quality assessment of recycled products. Finally, there is a need to design products for recycling, in order to simplify operations such as the dismantling of equipment, separation of homogeneous streams, and identification of individual polymers.

Mechanical recycling is usually performed by physical means and involves separation, washing, grinding, re-melting and processing polymeric wastes. Some studies have proposed alternatives such as dissolution/reprecipitation procedures for the mechanical recycling of some mixed streams, but this review focuses only on thermoplastic polymers and their common re-melting mechanical recycling approach. Mechanical recycling has been identified as the most suitable recovery route for relatively clean and homogeneous plastic waste streams. Additionally, recent life cycle assessment studies indicate that mechanical recycling of plastic materials is, in general, preferable to other management procedures in terms of optimising overall energy use and minimising the emission of gases that contribute to global warming.[2] This review focuses on the recent developments in effective mechanical recycling of polymeric waste streams to produce quality materials and products. The modelling of the life cycle of recycled products is considered to investigate the mechanisms and effects of the degradative processes to which recycled products are exposed. Different analytical strategies are suggested for the quality assessment of recycled plastics, considering three key quality properties: the degree of mixing (composition), the degree of degradation (chemical and morphological alterations, and changes in the mechanical and rheological properties), and the presence of low molecular weight compounds (contaminants, additives, and degradation products).[1,3] The upgrading of polymeric waste streams to obtain recycled

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products with improved properties is extensively discussed, analysing the recent developments in the restabilisation, rebuilding of molecular structure and compatibilisation of mixed waste plastic blends. Finally, the implications of the different waste stream sources on effective mechanical recycling are examined, taking into account their specific management and technological issues.

Modelling the Degradation Processes Undergone by Recycled Plastics during First Use and Subsequent Recycling

Product design should consider not only performance during the main use of the product, but also throughout its entire life cycle, from initial manufacture to final disposal. The life cycle of polymeric materials is becoming increasingly complex; from the cradle, which is the extraction of the raw materials used for synthesis into polymers, through processing activities, service life in intended applications, and further discard and waste management, until the grave and the return of the material and/or energetic value to the environment. The life cycle of synthetic polymers traditionally only included one usage pass until the product was discarded as a waste material and often land filled, with the associated loss of the energetic and material value. In a current scenario, in which the availability of raw materials is becoming complicated and environmental issues are a crucial part of the product-development process, attention will be devoted to enhancing the recovery possibilities of the material once discarded as waste, and providing technologically viable alternatives to return the waste material back to the usage cycle through various recycling alternatives. Therefore, the life of a polymeric material will be extended through consecutive usage cycles in different applications and recovery by mechanical or chemical recycling processes (Figure 1).

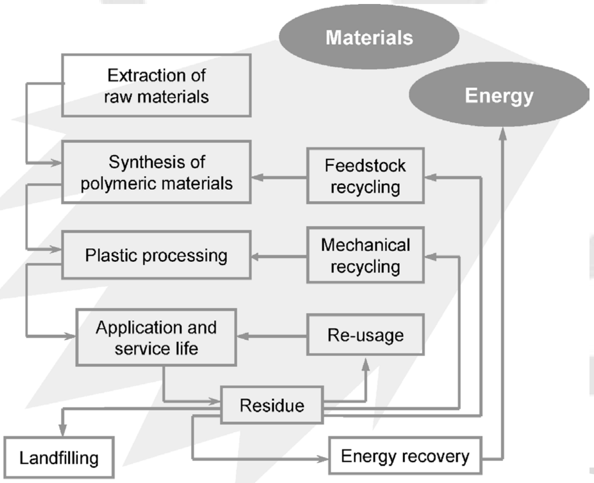

Figure 1. Plastic waste management options in terms of the life cycle of polymeric products.

The degradation processes to which polymeric materials are exposed in each step of their life cycle is a fundamental factor for consideration when discussing their further waste recovery possibilities and the performance of recycled plastics. Polymeric materials are exposed to thermo-mechanical degradation during processing, which may be responsible for chain scission and other chemical reactions caused by high shear forces and high temperatures in an oxygen-deficient atmosphere. Service life may also induce physical and chemical changes in the polymeric structure, due to exposure to specific environmental conditions during normal use of the product. These chemical changes may introduce structural heterogeneities in the material, which affect the mechanical properties and stability of the recycled material; the oxidised moieties introduced through previous oxidation and other significant structural changes may enhance the sensitivity of recyclates to further degradation and reduce the long-term stability of the material.[1] Detailed knowledge, at a molecular level, about the degradative mechanisms undergone by polymers during their life cycle and the effects on macroscopic properties is therefore needed to assess the applicability of recyclates in further applications.

New experimental strategies have been developed recently to mimic the degradation processes undergone by synthetic polymers during their first use and subsequent mechanical recycling. Reprocessing by multiple extrusion or injection moulding is the common approach to assess the recyclability of polymeric materials and to study the thermo-mechanical degradation during processing and mechanical recycling. Degradation processes undergone during the material service life are usually simulated by accelerated ageing experiments in different environments, trying to reproduce as closely as possible the real external effects to which the material is exposed during application. Recent approaches have tried to combine reprocessing and accelerated ageing to obtain an overall picture of the extent of the degradation processes that affect the polymers during the entire life cycle.

Multiple Processing

Multiple processing is the most common approach to assess the recycling possibilities of homogeneous polymeric waste fractions, such as films from agricultural applications, industrial scrap, and polymers from structural applications; reprocessing studies can also be performed by theoretical investigation of thermo-mechanical degradation mechanisms. The analysis of the structural and morphological changes induced by consecutive processing steps offers important information for the optimisation of the processing conditions during mechanical recycling to avoid further degradation; for example, the choice of processing conditions and further addition of stabilisers and other additives. Starting in the 1980s and developing in the 1990s, research elucidated the effects of multiple processing on the structural, rheological and mechanical properties of the most common polymers, including commodity polymers (PE, PP, PVC, PS), engineering plastics (PC, polyesters, polyamides), and composites; a complete overview on the topic is provided by La Mantia and co-workers.[4] These works revealed key factors that affect the final properties of reprocessed polymers: the condition of incoming waste material (degradation state, presence of impurities, degree of branching, residual presence of additives, constituent copolymers), and reprocessing conditions (temperature profiles, screw type, presence of residual oxygen in the extruder). Thermo-mechanical degradation during reprocessing usually induces chain scission of the polymeric chains, but crosslinking and chain branching reactions have also been reported for PE under specific reprocessing conditions, and dehydrochlorination reactions may occur for PVC. The structural and macroscopic properties of polymers are therefore modified during multiple processing; chain scission is responsible for a decrease in the molecular weight of the polymeric chains, which leads to an increase in the degree of crystallinity in semicrystalline polymers, a decrease in viscosity, and a modification of the mechanical properties, thus resulting in a progressive embrittlement of the reprocessed material.

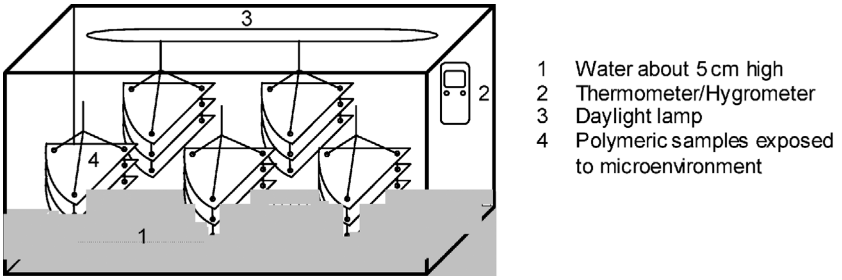

Figure 2. Schematic drawing of microenvironment chamber for accelerated ageing tests. Wallström et al., Microbiological growth testing of polymeric materials: an evaluation of new methods, *Polym. Test.* **24**, *5*, 557, Copyright *Elsevier* (2005); *Printed with permission.*

Modelling of Service Life using Accelerated Ageing Tests

Modelling of service life is usually performed using different accelerated ageing tests, in an attempt to mimic accurately the environmental conditions to which polymeric materials are exposed during their application (temperature, air, humidity or other chemical environment; radiation; biological and microbial attack; mechanical stress). Thermo-oxidation is a traditional method to simulate degradation processes in polymers for indoor applications; it uses high temperatures in order to accelerate the degradation mechanisms undergone by polymeric materials under air exposure. Photo-oxidation and weathering tests may also be employed for simulating degradation of polymers in outdoor applications, by exposing polymeric materials to visible and/or UV radiation under certain temperatures and atmospheric conditions. Prior thermo- and photo-oxidisation has proved to increase the sensitivity of a material to further processing; the pro-degradant nature of previously degraded material being thus confirmed.[5] More complicated environments involving microorganisms may be simulated using specifically defined environmental chambers, where UV exposure, temperature, humidity, chemical conditioning such as pH or salt content, and the presence of microorganisms can be designed and monitored; Figure 2 shows a self-designed environmental chamber for analysing the biodegradation and bio fouling of polymeric films, where control of the humidity, light exposure, chemical environment, and presence of microorganisms is possible.[6] Finally, parameters such as temperature, time, and environment must be selected carefully to meet several requisites when performing accelerated ageing experiments: throughout the ageing temperature range, the main degradation mechanism must be maintained, and significant transitions such as crystallisation, melting and glass transitions must not occur.

Modelling the Life Cycle of Recycled Polymers

An integrated approach using multiple processing and thermo-oxidation to model the degradation processes during the first use and subsequent mechanical recycling in synthetic polymers such as polyolefins and styrenic polymers has also been proposed.[7,8] The processing and recycling of the plastic material is modelled by multiple processing, whereas the degradation processes occurring during the service life is simulated by thermo-oxidative ageing in a forced ventilation oven (Figure 3a and b). This procedure is useful in identifying which part of the life

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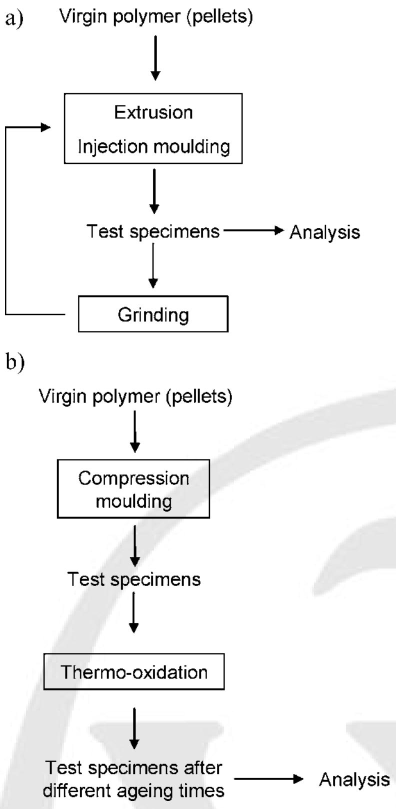

Figure 3. Procedure for modelling the life cycle of recycled plastics: a) multiple processing; b) thermo-oxidation. Vilaplana et al., Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation, *Polym. Degrad. Stab.* **91**, *9*, 2163, Copyright *Elsevier* (2006); *Printed with permission.*

cycle of a polymeric material most affects the degree of degradation of the recyclates, taking into account the whole life cycle and the mechanical recycling potential of the material. In the case of styrenic polymers such as HIPS, thermo-oxidative degradation affects more severely than multiple processing the long-term stability and properties; degradation during service life seems therefore to determine the further possibilities of employing HIPS recyclates in second-market applications.[7] Other synthetic plastics such as polyolefins (HDPE and PP) and PET are more affected by thermo-mechanical degradation by multiple processing than they are by thermo-oxidative ageing, indicating that special attention should be focused on controlling the processing conditions during mechanical recycling.[8,9]

Important information about the degradation mechanisms and their effects on chemical structure, morphology, and macroscopic properties induced during life cycle can also be provided these modelling procedures. The PB phase was demonstrated to be the initiation point of the degradative processes induced by processing, service life and mechanical recycling in HIPS.[7] These chemical changes are related to modifications at a macroscopic scale in the mechanical and viscoelastic behaviour. Both reprocessing and thermo-oxidative degradation are responsible for complex physical and chemical effects (chain scission, crosslinking, apparition of oxidative moieties, polymeric chain rearrangements, and physical ageing) on the microstructure and morphology of PB and PS phases, which ultimately influence the long-term stability, and the rheological and mechanical behaviour of recycled HIPS.[10]

Simulated Recycling

Another approach to simulate the life cycle of recycled polymeric materials involves the alternate combination of processing (to simulate manufacturing of the product) and accelerated ageing (to simulate the usage phase) in a cyclic procedure; this procedure has been employed to investigate the degradation profiles in HDPE, LDPE, ABS, and PP.[11–14] The ageing steps are responsible for a drastic deterioration in the mechanical properties, such as elongation at break, whereas reprocessing steps almost restore the mechanical properties, showing a zigzag-shaped behaviour during simulated recycling; reprocessing may help to homogenise and dilute the degraded polymer chains and the oxidative moieties formed during ageing and therefore improve the mechanical properties of polymeric wastes.[13] The combination of alternate processing and ageing cycles causes more severe degradation than either the reprocessing or the ageing series performed separately.[12] The hydroperoxides formed during the ageing step may decompose into radicals in the subsequent processing step, which could be responsible for the acceleration of polymer degradation during simulated recycling; this emphasizes the importance of adjusting the stabilising content at every reprocessing step.[14] Similar conclusions were drawn by studying the effect of previous thermo- and photo-oxidative accelerated ageing and subsequent reprocessing in different commercial grades of LDPE, HDPE, PP, and HIPS, to model different degradation states of polymeric waste prior to mechanical recycling.[15]

Quality Analysis of Recycled Plastics for Improved Use in New Products

The large-scale use of recycled plastics in the manufacturing of second-market plastic products is still hindered by a wide range of barriers. The image of recycled plastics in comparison to the equivalent virgin polymers is distorted by several factors, which may lead to the manufacturers' mistrust of the recyclate's performance in their products:

recycled plastics usually come from unknown origin, they may be subjected to degradation processes, and they may have been contaminated during previous usage. Industrially, plastic recycling is still far from being widely deployed; technical development has been slow and the logistics are not always well implemented by municipalities and other public authorities. In general, recycling industries are characterised by a low degree of knowledge about plastic products and polymeric inherent properties; it is difficult for this industrial segment to compete with the manufacturers of virgin polymers who can assess reliably the quality properties of their synthesised materials. There is, therefore, a clear need to introduce a quality concept in plastics recycling activities, to assess the properties of recyclates within narrow tolerances, thus satisfying the requirements of both manufacturers and customers, and guaranteeing the performance of recycled products in their second-market applications.[1] Fast, cost-effective and reliable characterisation procedures for plastic recyclates should be developed and implemented in recycling facilities to guarantee their quality properties. Traditionally, the evaluation of the melt flow rate (MFR) and the mechanical properties of the recyclates were the only properties that are determined in the specification sheets of the final material; however, using only the specification of such macroscopic properties may be misleading in terms of assessing the performance of recycled products in new applications.[1,12,16]

Recent research carried out by our group on the characterisation of recycled polymers has lead to the identification of three key properties for the quality assessment of recycled plastics: the degree of mixing (composition), the degree of degradation, and the presence of low-molecular weight compounds (Figure 4).[1,3,16] These key properties are necessary to fully guarantee the applicability of recyclates for the manufacture of new products. The degree of mixing (composition) is related to the presence of polymeric impurities in the recycled polymers resulting from impure plastic waste streams and poor separation in the recycling plant. The degree of degradation of recyclates considers the degradation processes to which polymeric materials are subjected during their processing, service life, and further recovery. Finally, the identification of low molecular weight compounds (contaminants, additives, and degradation products) present in recycled polymers is essential to verify that the products are compliant with legislation on the presence of hazardous substances.

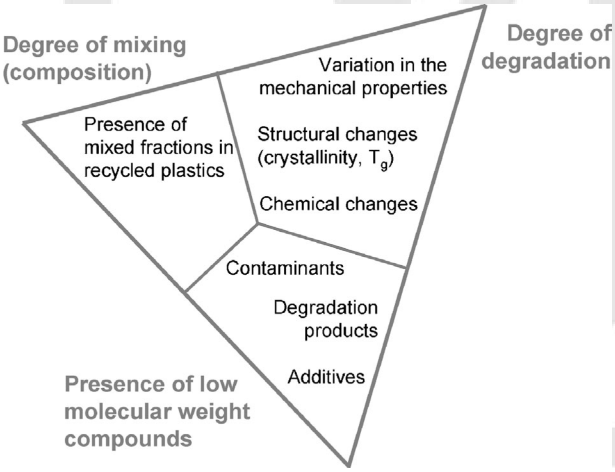

Figure 4. Key properties for quality assessment of recycled plastics. Vilaplana et al., Analytical strategies for the quality assessment of recycled high-impact polystyrene: A combination of thermal analysis, vibrational spectroscopy, and chromatography, *Anal. Chim. Acta* **604**, *1*, 18, Copyright *Elsevier* (2007); *Printed with permission*.

Degree of Mixing (Composition)

The presence of mixed polymeric fractions in recycled plastics is a critical parameter influencing the structure and mechanical properties of the recyclates. Polymers mixed in a recyclate are usually incompatible, and even a low level of polymeric contaminations in a certain waste stream leads to poor adhesion properties in the polymeric mixture interface and, thus, deterioration in overall macroscopic properties. The determination of the composition of plastic waste streams is therefore important, because it determines the appropriate management procedure for the end-of-life material and it is also a critical parameter for the future performance of recycled products in second market applications. In this sense, experimental design and statistical approaches such as response surface methodology can be used to predict properties of mixed plastic streams and to discuss whether complete separation is required to obtain recycled materials with acceptable properties.[17] Some strategies to analyse polymer composition and the presence of polymeric impurities in mixed plastic streams are detailed as follows.

Thermal analysis techniques, and in particular differential scanning calorimetry (DSC), are becoming routine analyses for the characterisation of polymer composition. Polymeric contaminations in recycled HIPS from packaging applications could be detected using DSC; small melting peaks at temperatures of 120 and/or 160 °C were observed in certain recycled HIPS grades, indicating the presence of PE and PP contaminations, respectively, in these materials.[16] DSC can be employed for compositional analysis above 1 wt.-%, but lower concentrations are not easily detected within reasonable analysis time limits.[18] Another method to detect small polymeric contaminations in recycled PET involves annealing the material at high temperatures (200 °C) and analysis of the segregated coloured flakes with

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DSC and FTIR; contaminations of HDPE, LDPE, PP, PS, and PVC in ranges of 0.01–3 wt.-% were thus detected in some recycled PET samples.[19] Other non-polymeric contaminations in waste and recycled materials, such as cellulose, soil, metal particles, and adhesives, can be detected by thermogravimetric analysis (TGA).

Vibrational spectroscopy techniques, such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, are fast and reliable analytical techniques that are usually employed in polymer production quality control and are potential techniques for online quality analysis in recycling plants. Both the near-infrared (12 800–4 000 cm^{-1}) and mid-infrared (4 000–600 cm^{-1}) ranges can be used for spectroscopic analysis of physical and chemical polymeric properties. Among the different spectroscopic modes, attenuated total reflectance (ATR) and diffuse reflectance are widely reported for polymer analysis with little or no sample preparation. ATR-FTIR proved here to be a very useful technique for identification of PE and PP in a blend from a waste stream[20] (Figure 5).

The compositional analysis of polymeric blends from recycled mixed-plastic waste can be performed online using either diffuse-reflectance NIR or Raman spectroscopy and chemometrics; fast analytical procedures were developed and validated for recycled PP/HDPE and ABS/PP blends, using FTIR and DSC as reference techniques.[18,21] PP/HDPE blends are the most abundant components in the plastic waste streams from household packaging; on the other hand, PP and ABS are two of the major plastics materials used in the automotive industry, so blends of these two polymers are common in waste streams from end-of-life vehicles (ELV). Diffuse-reflectance near-infrared (NIR) and Raman spectroscopy allow fast and reliable pellet analysis and require no sample preparation, in contrast to time-consuming FTIR and DSC. The interpretation of the NIR spectra should be performed using multivariate analysis, which allows compositional determination with high precision.[18]

Degree of Degradation

Polymers suffer chemical and physical changes during their processing and service life. They undergo oxidative reactions at every stage of their life cycle, and the new functional groups formed during the oxidation process may enhance the sensitivity of the recyclates to further thermal- and photo-degradation. With the formation of the new oxidative moieties, a substantial part of the stabilizers is consumed, with a consequent decrease of long-term stability and deterioration of mechanical properties. Determining the degree of degradation – that is, the extent to which previous degradation has affected the structure, mechanical properties and long-term stability of recyclates – is important for the future performance of recycled products; this will be important when a true recycling society is achieved, in which the materials will face several usage-life steps before being discarded as wastes.

Different strategies can be considered to investigate the degree of polymer degradation, depending on the changes at a macroscopic or microscopic scale. Common approaches to determine degradation effects include: analysis of the alterations in chemical functional groups (using vibrational spectroscopy or nuclear magnetic resonance), crystallinity and thermal properties (using thermal analysis), morphology (using electron microscopy), mechanical properties (mechanical testing), and molecular weight distribution and composition (using size exclusion chromatography and mass spectroscopic techniques). Additionally, investigation of degradation products and additives using chromatographic tools have proved to be

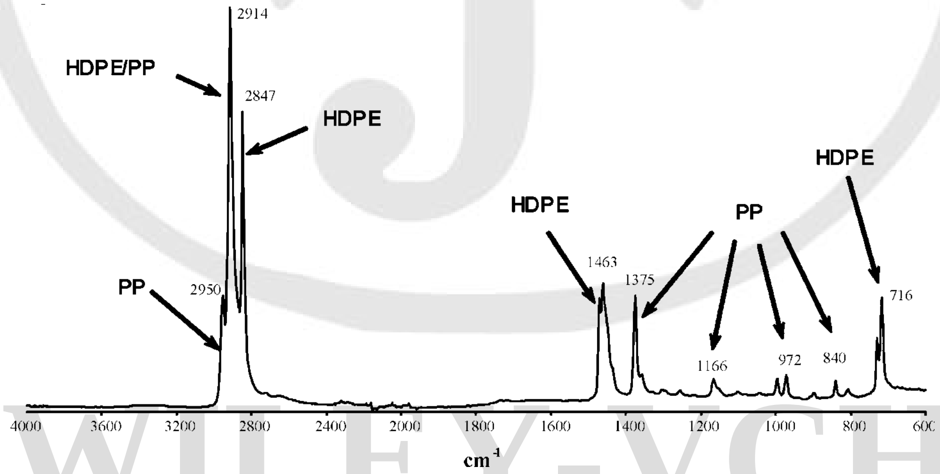

Figure 5. FTIR spectrogram of a post-consumer recycled plastic based on HDPE and PP.

useful for monitoring ongoing degradation processes in polymers.[22–24]

Rheological properties in general, and melt flow rate (MFR) in particular, are common quality properties for recycled plastics; they can also be an indicator of polymer degradation, since they are related to the melt viscosity and therefore to the molecular weight of the polymer. Thermo-mechanical degradation during processing and mechanical recycling is usually responsible for chain scission phenomena, which result in a decrease in the molecular weight of the recyclates; a progressive increase in the MFR has been extensively reported as a consequence of consecutive processing steps. These variations in MFR differ, on the other hand, among the different families of analysed polymers. Figure 6 shows the evolution of the MFR for HIPS, PP and HDPE subjected to six reprocessing cycles; although the MFR increases for all the materials with reprocessing, it can be observed that this process does not provoke changes to the same extent in all materials, PP being the most susceptible to changes in MFR.[7,8,25]

Variations in the mechanical properties are related to the degradation processes undergone by polymers during life cycle; however, the utilisation of mechanical properties as the only parameter to evaluate the degree of degradation for recycled polymers may be misleading, since the degradation at a molecular level may occur before any signs of change at a macroscopic scale are detected,[26] and some observed changes in the mechanical properties may be due to physical factors and are hence reversible.[12] Tensile, impact, and flexural properties are often evaluated for recycled plastics; deeper studies of the fracture behaviour and micromechanical properties offer interesting information about the mechanical performance and failure mechanisms in recycled materials.[27] As mentioned earlier, previous degradation causes a deterioration of the molecular structure, resulting in recycled plastics with poorer mechanical properties than the virgin ones. Nevertheless, we propose a more "optimistic" approach to the changes in mechanical properties. It is true that previous degradation affects the mechanical performance of the materials, but normally these changes are not unidirectional; that is, it could be that the ductility diminishes but stiffness increases, or vice versa, so a suitable application for recyclate materials can be found within the mechanical properties quality range. There are several examples of this wide-ranging behaviour. Elongation at break has been identified as the determining quality mechanical property for HIPS, since it is the property the most affected by reprocessing and thermo-oxidation, while elastic modulus remains unaltered or even increases.[7] A progressive diminution of the elastic modulus has been reported for PP during reprocessing, whereas the mechanical properties of HDPE remain almost unaltered.[8] Some authors have reported that blends of virgin and recycled HIPS present improved mechanical and physical properties compared to virgin material.[28] In conclusion, the mechanical properties should be clearly specified for the recyclates and adjusted for the requirements of the application to which they may be destined.

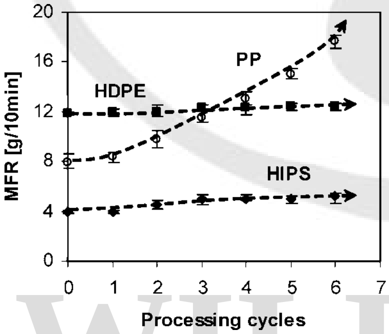

Figure 6. Evolution of the melt flow rate (MFR) during repetitive extrusion processes: (○) PP; (■) HDPE; (◆) HIPS.

Changes in physical properties, such as crystallinity, melting behaviour, morphology, thermal history, and viscoelastic behaviour, can also be used as indicators of the degree of degradation and the quality of recycled plastics. Thermal analysis (by DSC) and dynamic mechanical analysis (DMA) are widely used for these purposes. By registering different crystallisation and melting behaviour, DSC can detect changes in thermal history in waste PET samples from different origins.[19] Changes in melting and/or crystallisation behaviour are also indicators of polymer degradation; different coexisting phenomena during polymer degradation affect the degree of crystallinity. The formation of smaller polymer chains due to chain scission may lead to an increase in the crystallinity; on the other hand, the presence of impurities (e.g., oxidative moieties) formed during degradation may hinder recrystallisation processes. Finally, physical processes, such as annealing or even chain reorganisation during processing, also produce crystalline rearrangements. Recycled semi-crystalline polymers are expected to display heterogeneous crystalline structures, and therefore usually show multimodal melting/crystallisation behaviour in the DSC experiments, whereas virgin materials display only one clear peak. The existence of multiple peaks in the melting or crystallisation thermogram can be due to the presence of mixed plastics or the presence of different chain-length populations that lead to heterogeneous crystalline morphologies and lamellar structures.[3,9] Changes in the glass transition and other viscoelastic relaxations in recycled plastics can be investigated using DMA; the study of the free volume parameter can lead to interesting conclusions about the effects of degradation on the microstructure of recycled polymeric

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materials.[10] Powerful microscopic techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), can be used to investigate the effects of previous degradation on the morphology and phase distribution in polymer blends and copolymers in recycled plastics. Characterisation of the thermal properties, such as thermal diffusivity, in recycled plastics that may be used as heat insulators can be performed by the laser flash technique.[29]

Thermal and thermo-oxidative stability of recycled polymers is usually assessed using thermal analysis techniques as TGA or DSC. TGA measurements under inert atmosphere allow the direct determination of parameters such as the onset temperature or the thermal decomposition maximum temperature, which offer a quantitative measure of the thermal stability of recycled polymers, together with information about the humidity and the content of volatiles, additives, and fillers in recyclates.[16] Deeper kinetic analysis of the thermal decomposition data, using dynamic and isothermal methods, leads to the determination of the activation energy and the reaction mechanism for the thermal degradation process, providing valuable information about the thermal properties and even the structure of polymeric recyclates, as shown for recycled PP toughened with elastomers[30] and recycled PC/ABS blends from waste electrical and electronic equipment (WEEE).[31]

Thermo-oxidative stability in commercial plastics and recyclates is directly related to the stabilisation system (antioxidants, UV stabilisers) included in the material to prevent thermo-oxidation reactions; analytical methods such as the determination of the oxidation temperature (T_{ox}) and the oxidative induction time (OIT) are standardised and widely used for this purpose. In the field of polymer recycling, OIT and T_{ox} are used for the determination of the residual stabilising system in recycled resins, which is extremely important for evaluating the need for further restabilisation in the mechanical recycling process to guarantee long-term stability.[7,32,33] As an example, Figure 7 shows the OIT curves obtained using DSC for reprocessed and recycled high-impact polystyrene; it is clear that the stabiliser system is progressively consumed during the repetitive reprocessing steps. Moreover, the low value of the OIT for the recycled material suggests the special necessity of restabilisation for the HIPS reprocessing and recycling.[7]

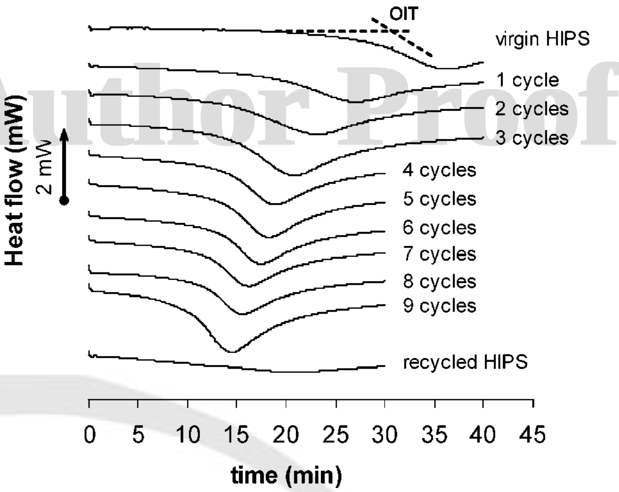

Figure 7. DSC analysis of oxidative stability of reprocessed and recycled HIPS using OIT measurements at 160 °C.

Chemiluminescence (CL) offers a powerful tool to monitor oxidation reactions in polymers and can be therefore employed to assess the thermo-oxidative stability of recycled polymers and investigate the effects of base stabilisation and restabilisation on the recyclability of polyolefins.[34–36] The relationship between polymer oxidation and luminescence is generally associated to the deactivation of an excited carbonyl group formed during the oxidation process. Chemiluminescence provides, according to some authors, higher sensitivity than the determination of OIT using DSC in detecting reduced oxidative stability in recycled and waste polyolefins[34] and allows the analysis of the different oxidative behaviour of PE and PP in their recycled blends.[32]

The changes in the chemical structure of polymeric materials induced by degradation processes during the entire life cycle can be investigated using vibrational spectroscopic techniques, such as FTIR and Raman spectroscopy. These techniques are complementary and give useful information about different functional groups present in polymeric samples. Different oxidised moieties (hydroxyl, carbonyl, carboxylic, and ether groups) may be formed during the thermo- and photo-oxidation processes to which polymers are subjected throughout their exposure to service environment; other functional groups, on the other hand, may be consumed under these degradative conditions, such as the unsaturated double-bond groups in rubber-based copolymers or the ester linkage in polyesters. The detection and quantification of these specific functional groups using FTIR can be used as a valuable parameter to evaluate the degree of degradation of plastic waste streams and recycled products. Quantification using spectroscopic techniques can be performed by normalising the absorbance peak height or area corresponding to the oxidised functional group to the height/area of a reference peak that is not subjected to degradation; this procedure allows the removal of experimental errors due to differences in sample thickness or instrumental deviations. The carbonyl index is widely employed as a direct indicator of degree of oxidation in polymeric materials; the time dependence of carbonyl group formation during accelerated ageing experiments

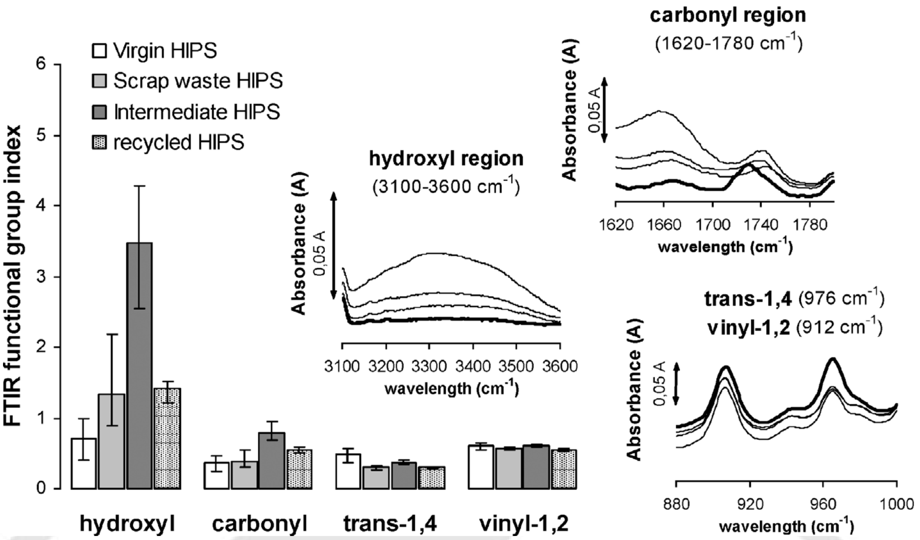

Figure 8. Monitoring the FTIR functional group indexes in waste HIPS samples throughout the mechanical recycling process.

could be used to predict the formation of new carbonyl groups giving that their initial amount is known.[37] In a recent work,[16] monitoring of the carbonyl, hydroxyl, vinyl-1,2, and *trans*-1,4 indexes in waste HIPS samples from packaging applications through the mechanical recycling process was performed using ATR-FTIR (Figure 8). The diminution of the unsaturated functional groups (vinyl-1,2 and *trans*-1,4) and the increase of the hydroxyl and carbonyl groups in the real recycling samples, compared to the virgin material, could verify the degradative effects during the previous life and recycling of HIPS.[16]

Near and mid-infrared spectroscopy in the diffuse reflectance mode could also be used for the simultaneous determination of molecular weight and crystallinity in recycled HDPE, using size exclusion chromatography (SEC) and DSC, respectively, as reference methods.[38] The use of multivariate analysis allows extracting the information from the spectral data and detecting small differences in them, which could be related to the analysed properties.

Raman spectroscopy is, in many ways, a complementary technique to infrared spectroscopy; analysis of conformation, tacticity, orientation, crystallinity, and functional groups is well established for polymers. Raman spectroscopy measurements can be, however, affected by fluorescence interferences, especially for dark-coloured samples, which restrict the use of this technique. Nevertheless, Raman is a fast and user-friendly technique that allows the recording of the vibrational spectra of polymeric samples in their original form, without sample preparation. Raman spectroscopy has proved to be useful for the analysis of the rubber phase in recycled rubber-modified styrenic copolymers such as HIPS, through deconvolution of the peaks corresponding to the three different structural units (vinyl-1,2, *cis*-1,4, and *trans*-1,4) in PB.[10,16]

Presence of Low Molecular Weight Compounds

Plastic materials include in their formulations a wide range of low molecular weight compounds that contribute to the final properties and performance of the products; these compounds include monomeric and oligomeric residues of polymerisation, solvent residues, traces of initiators and catalysts, and different additives (antioxidants, stabilisers, plasticisers, and flame retardants). Moreover, other low molecular weight compounds may be formed due to the degradation processes affecting both the polymeric matrix and the additives. Finally, polymeric materials may also come into contact with impurities and contaminants from the surrounding environment during service use and further recovery, which can diffuse into the polymeric bulk due to their permeable nature. This wide range of possible low molecular weight compounds, either inherent or externally introduced impurities, can be present in plastic waste streams and recycled plastics, and may affect the performance and applicability in a next generation usage of recycled products. It is, therefore, of great importance to assess the presence of low molecular weight compounds in recyclates, to avoid contaminations and hazardous substances, according to increasingly restrictive legislation.

The development, optimisation and validation of different extractive and analytical methods for the

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identification and quantification of low-molecular weight compounds in recycled polymers is one of the main challenges for quality analysis. Chromatographic techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) are widely employed for the determination of low molecular weight compounds; different detectors such as mass spectrometry (MS), diode-array detector (DAD), and flame ionisation detector (FID) can be used for the identification and quantification of these analytes. However, different sample extraction procedures must be carried out prior to chromatographic analysis, to extract the low molecular weight compounds from the polymeric matrix. Traditional procedures such as Soxhlet extraction are time consuming (1–2 d per extraction) and require large amounts of solvents. Advanced solvent extraction techniques, including microwave-assisted extraction (MAE), ultrasonication, solid-fluid extraction (SFE), and pressurised liquid extraction (PLE) have been recently introduced for polymer analysis, reducing extraction times and amount of solvents, and allowing automatisation.[39] Finally, other non-solvent extraction procedures such as solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are emerging as effective methods for the determination of volatile and semi-volatile compounds in polymers and other substrates, with fast extraction times and no need for solvents. However, some difficulties have been found for developing methods for the analysis of low-molecular weight compounds in recycled materials; the unknown properties and composition of the recycled plastics are perhaps the main hindrance in optimizing the characterization methods, together with the fact that it is necessary to develop a specific method for each type of sample (polyolefins, styrenic copolymers, engineering plastics, etc.).[40]

In the following section some examples will be given of the current research in the identification and determination of low molecular weight compounds in recycled plastics. Special attention will be devoted to the emissions of volatiles from recycled plastics, and to the analysis of additives in recycled plastics, especially brominated flame retardants, since both are currently topics of special concern, from an environmental, technological, and regulatory perspective.

Volatile Organic Compounds in Recycled Plastics

Emissions of volatile organic compounds from polymeric materials have become an important environmental issue; they can be emitted at every step of the life cycle, including manufacture, service life, and posterior waste management. Many studies have been made of the volatile emissions in polymer processing, through analysing the air emissions close to processing equipment; a broad review has been provided by Patel and Xanthos,[41] in which they indicate the types of volatiles emanating during processing of commodity thermoplastics and reinforced thermosets, together with the analytical procedures for their measurement.

Volatile and semi-volatile model contaminants (1,1,1-trichloroethane, methylbenzene, chlorobenzene and phenylcyclohexane) were analysed in recycled HIPS from food-contact applications using purge-and-trap, co-evaporation, and total dissolution extraction; the proposed extraction techniques proved suitable for the detection of the model contaminants and could therefore be used for the analysis of hazardous contaminants in recycled HIPS and to assess the possible employment of recycled materials in food-contact applications.[42]

A wide range of volatile organic compounds were detected in both virgin and recycled PP and PE resins, using microwave extraction and GC-MS analysis; the number of volatiles identified in the recycled samples was larger than in the virgin ones. The volatiles detected in recycled and virgin resins could be classified into 8 main categories: aliphatic hydrocarbons, aromatic hydrocarbons, carboxylic acids, esters, ketones, alcohols, aldehydes, and miscellaneous. Aroma and odour compounds, together with other compounds used in cosmetics were identified in recycled HDPE.[43]

Tracking the formation and/or release of low-molecular weight compounds in actual styrenic samples taken from different points of a large-scale mechanical recycling plant (scrap waste material, intermediate samples after washing and grinding, and final recycled HIPS) was performed using microwave extraction and chromatographic analysis.[16] Several volatile and semivolatile compounds, including residues from the polymerisation (styrene monomer, styrene dimers and trimers), additives, and contaminations were found in both virgin and recycled HIPS from packaging applications. The content of styrene and other polymerisation residues was higher in virgin HIPS than in recycled material, which could prove the emission of these compounds during the first lifetime of the products. Oxidated derivates of styrene were also detected in recycled HIPS, which could have been formed by degradation of polystyrene during previous service life.

Headspace SPME combined with chromatographic detection is a promising tool for monitoring the presence of volatiles in recycled samples. This procedure has been employed for the detection of low molecular weight compounds in different grades of recycled PE obtained from a recycling plant, employing headspace SPME extraction and GC-MS analysis;[3] the results showed that the mechanical recycling process could contribute to the removal of some of these compounds, in agreement with other authors reporting that recycled LDPE releases less volatiles compared with virgin LDPE, presumably because the main amount of volatiles were already emitted during the first processing.[44] A similar procedure has been employed for the detection of odorous volatile compounds released from recycled PP/natural fibre composites; alcohols, carboxylic acids, and phenolic compounds were thus identified.[45]

SPME has been used again for the quality control of recycled polyamide-6,6, to prove plasticiser migration from nitrile rubber during long-term ageing, and to detect early signs of degradation in thermo-oxidated virgin and in-plant recycled polyamide-6,6.[26,46] Different groups of degradation products were identified in virgin polyamide-6,6 and during its thermo-oxidation and recycling: cyclic imides, pyridines, chain fragments, and cyclopentanone and its derivatives. Cyclic imides, pyridines, and chain fragments showed higher amounts in thermo-oxidated and recycled samples, 1-pentyl-2,5-pyrrolidinedione being the main degradation product; cyclopentanones, on the other hand, were present in virgin material, and their content decreased during oxidation and recycling.[46]

Spectroscopic techniques can also be used for the online detection of low molecular weight compounds in recycled plastics. The water content in hydrophilic polymers such as polyamides and polyesters is a common concern during their manufacture and recycling, since moisture can enhance hydrolysis reactions at the high processing temperatures and cause a decrease in the molecular weight of the recyclates. A method using NIR and chemometrics for the at/in-line detection of moisture content in polyamide-6,6 has been proposed, which gives accuracy similar to traditional destructive gravimetric, chemical and calorimetric (DSC) methods.[47,48]

Additives. Brominated Flame Retardants in Recycled Plastics from WEEE

Additives are introduced during first manufacturing of polymeric products, to confer specific properties such as long-term light and oxidative stability, fire retardancy, plastification, processability, and toughness upon the final plastic products. These additives may be consumed, suffer chemical transformation or even migrate to the environment during the polymer lifetime. The study of the residual presence of these additives in polymeric waste and recyclates is, therefore, of vital importance in the recycling industry. The methods for the quantitative determination of polymer additives usually combine an extraction step prior to analysis, although some extraction-free methods using spectroscopic and spectrometric techniques have been developed for determining concentrations of additives; a review of the analytical determination of additives in polymers using extractive procedures has been provided by Vandenburg and co-workers.[39] Recent developments in determining polymeric additives in recycled plastics are discussed in the following section, with special focus on the determination of brominated flame retardants in plastic waste from electrical and electronic equipment (WEEE).

Brominated flame retardants (BFRs) have gained special attention in recent years, both due to their widespread use in fire protection of textiles, building materials and insulation, vehicle equipment, and electrical and electronic equipment, and due to the increasing concern about their effects on human health and the environment. Three BFRs families dominate the organic flame retardant market: tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD). Flame retardants can be either reactive, when they are chemically bonded to the polymeric matrix, or additive, when they are added during processing. The increasing environmental concern about BFRs is based on their persistence, bioaccumulation, and possible adverse health effects on humans.[49] It has been demonstrated that TBBPA, HBCD, and PBDEs are present in the environment and they are assimilated by living organisms; however, the long-term impact on health and environment is not well known.[50] Moreover, only limited and rather uncertain data are available regarding the occurrence of BFRs in consumer goods and waste fractions, and little is known regarding their emissions during use and disposal.[51] As a result of this rising concern, the European Union has introduced two Directives (2002/96/EC and 2002/95/EC) that regulate the employment and disposal of BFR-containing plastics in electronic and electrical equipment. Polybrominated biphenyls (PBBs) and some PBDEs (penta- and octa-BDE) have been banned in all applications, but deca-BDE was exempted from this ban in 2004 as a result of risk assessment reports from the European Chemicals Bureau (European Union) that found "no identified risks" to either humans or the environment. Plastics containing BFRs must be, in addition, separated from other WEEE fractions prior to recovery and recycling. Characterisation of the polymeric WEEE fraction may therefore combine different analytical strategies, including polymer identification studies, elemental analysis of metals and halogens, and analysis of brominated flame retardants and their possible degradation products.[52]

The elemental determination of additives in plastics, including metals and halogens, can be performed using a wide range of analytical procedures. Techniques such as atomic absorption spectrometry or inductively coupled plasma optical emission spectrometry (ICP-OES) require sample solution in aqueous media; analysis using total-reflection X-ray fluorescence spectroscopy (TXRF) and previous dissolution of the polymer in organic solvents allows faster determination of additives containing elements such as Ti, Zn, Br, Cd, Sn, Sb and Pb in recycled thermoplastics from consumer electronics, with detection limits of around 200 $\text{mg} \cdot \text{kg}^{-1}$.[53] Further studies have led to on-line process analysis of metal-containing additives

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(Ti, Zn, Sb, Sn, Al, Cd, Cr and Pb) in recycled thermoplasts from consumer electronics, using laser-induced plasma spectroscopy (LIPS, also called laser-induced breakdown spectroscopy, LIBS) and multivariate methods, for which neither sample preparation nor sample contact is needed, reaching detection limits in the ppm range; this experimental setup has been successfully employed for routine on-line process analysis in recycling plants.[54] LIPS can also be employed for the on-line high-speed detection of heavy metals (Pb, Cr, Cd and Hg) and brominated flame retardants (by analysing elemental Br and eventually synergistic Sb present in Sb_2O_3) in WEEE pieces moving on a conveyor belt; the detection limit for Br ($11–15\ mg \cdot g^{-1}$) is significantly higher than that of other metal elements ($2–50\ \mu g \cdot g^{-1}$), but suffices to detect common concentrations of BFRs in plastics.[55]

For a more selective identification and quantification of the different brominated flame retardants present in recycled plastics, other procedures must be performed. The most common approach involves BFR extraction and analysis using gas or liquid chromatography. However, Raman spectroscopy with no sample preparation has been proposed to distinguish PBDEs from TBBPA.[56] Total dissolution of the samples or Soxhlet extraction can be employed, although more sophisticated extraction procedures, such as supercritical-fluid extraction (SFE),[57] ultrasonic extraction,[58] microwave-assisted extraction (MAE)[59] and pressurised liquid extraction (PLE),[60] have been successfully proposed for the extraction of several commercial flame retardants from WEEE plastic samples. The extraction procedure is usually the time-limiting step during the analytical determination of BFRs in recycled plastics; reduction of the extraction time to approximately 10 min can be achieved using ultrasonication.[58] A comparison of the extraction efficiency using different extraction procedures (MAE, ultrasonication, and PLE) for TBBPA, HBCD, and Deca-BDE is presented in Figure 9.

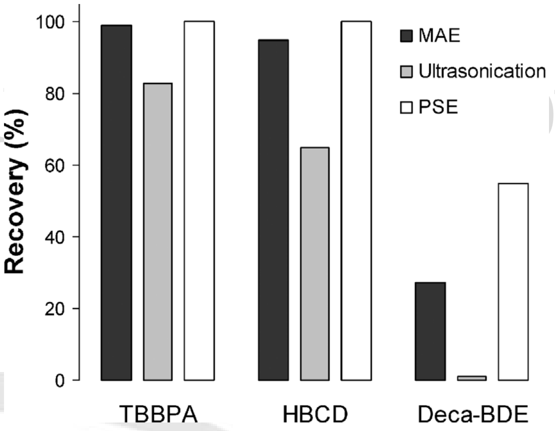

Figure 9. Comparison of the efficiency of brominated flame retardant extraction using different extraction procedures.

Both gas and liquid chromatography can be employed for extract analysis and allow high resolution and specific and selective detection of the different BFR families. Gas chromatography with mass-spectrometry detection is widely employed for the determination of PBBs and PBDEs.[61,62] However, some BFRs have high boiling points and may decompose due to their thermal instability; the use of liquid chromatography has been growingly employed in this case for the determination of TBBPA and HBCD congeners,[63] as a result of the advances in instrumentation that allow the coupling of LC and MS through interfaces such as electrospray ionisation (ESI) or atmospheric pressure chemical ionisation (APCI). HPLC-UV/MS has been employed to identify and quantify 15 brominated and phosphorous-based flame retardants in polymer fractions from WEEE; however, a combining procedure using size exclusion chromatography (SEC) and HPLC-UV appears to be a more suitable procedure for routine flame retardant screening in actual recycling facilities, thanks to easier operating and maintenance of the equipment.[60] No indication of intensive decomposition during repetitive processing of flame retarded styrenic polymers was observed using chromatographic techniques in different studies;[64,65] however, evidence of several bromine-containing fragment emissions from polymers with flame retardants were shown using thermo-desorption gas chromatography-mass spectrometry (TDS-GC/MS).[66] Further attention will be given in the future to the determination of BFR emissions and degradation compounds during use and recycling of polymers with flame retardants.

The analysis of reactive and oligomeric flame retardants, commonly employed in engineering polymers, is difficult to perform using extraction procedures because of the polymers' high molecular weight and immobility; pyrolysis gas chromatography appears to be an effective technique to overcome this dilemma. The analysis of thermal decomposition fragments (monomers, oligomers, and pyrolysis products) from different flame-retarded polymers and resins containing flame retardants allows the identification of the type of flame retardant used.[67,68]

Upgrading Recycled Plastics

Plastic products have traditionally been synthesised from non-renewable resources such as petroleum or natural gas; recently, biopolymers or polymers from natural renewable resources have emerged as an alternative to synthetic plastics. However, plastic waste should also be considered as a resource for the production of new plastic items, with a similar status to fossil- and natural-based polymers. To reach this status as a reliable resource for plastic products, the development of a suitable technology for the recycling and upgrading of the properties of the waste materials is needed, to make them suitable for the new applications. Some approaches for effective waste plastics upgrading are discussed here.

Restabilisation of Recycled Plastics

Previous degradation alters the mechanical properties and long-term stability of recyclates, and enhances their sensitivity to further deterioration; restabilisation — for example, fresh addition of stabilisers in the mechanical recycling process — is therefore mandatory to protect recycled materials from thermo-mechanical degradation acting during the melt, and to assure suitable stability throughout re-use. Restabilisation does not effectively recover the degraded material, but prevents further degradation processes that may be catalysed by the oxidative moieties present in its structure. Different processing and light stabilisers, including combinations of hindered phenols and hindered amine stabilisers, can be employed for successful restabilisation of recycled plastics, which can interfere in the auto-oxidation cycle by neutralising peroxide radicals and decomposing hydroperoxides. Restabilisation was already proposed many years ago to improve the performance of recycled plastics; there is, indeed, a 1995 review article by Pospisil and co-workers that summarises the existing knowledge at that moment.[69] Many articles have been published since, dealing with the restabilisation of different post-consumer plastics, including HDPE,[70–76] LDPE,[77] PP,[78–81] polyolefinic blends[82] and PVC.[83]

Upgrading Recycled Plastics by Blending with Virgin Polymers

Blending recycled polymers with virgin materials is one of the most common and well-established procedures for upgrading the properties of single-stream waste polymeric materials. This practice is widely employed for the recycling of industrial scrap, in which these industrial residues are ground and directly introduced in the processing machinery together with the virgin material. Monopolymeric blends of virgin and recycled polymers may have different molecular weight distribution, molecular structures (branching, crosslinking, and presence of oxidative moieties), degree of degradation and semicrystalline morphology; the adjustment of the composition of recycled material in the blend and the optimisation of the processing procedure are the main technological implications to be considered in order to achieve material properties similar to those of the virgin one. A encompassing review of the properties of several virgin/recycled homopolymer blends is provided by Scaffaro and La Mantia.[84]

Compatibilisation agents and restabilisers can also be used to improve the performance of virgin/post-consumer homopolymer blends. LDPE, LLDPE, and EVA were successfully employed for the compatibilisation of virgin/recycled HDPE, leading to blends with properties similar to those of virgin material and minimising the effect of previous degradation on the rheological and mechanical properties of the material.[85,86] Statistical factorial design proved to be a useful tool to optimise the formulation and compounding of virgin/recycled PP blends, by analysing different blend compositions and additive content.[87,88]

Rebuilding Post-Consumer Single-Plastic Waste Streams

The mechanical recycling of severely degraded plastics leads to materials with generally worse properties than those of the original materials, due to the changes in the chemical structure caused by previous degradation processes. The addition of new stabilisers during recycling (restabilisation) may help to both protect the thermo-mechanical degradation during processing and enhance the long-term stability of the recycled products, but is not enough to improve their mechanical properties and performance. Modification of the chemical structure and molecular architecture of the recyclates is needed to upgrade effectively the properties of recycled products; this approach has been inspiringly designated as "rebuilding" by La Mantia and co-workers.[89–92] The use of certain additives during mechanical recycling, such as radical generators or compounds with reactive functional groups, can be effective in inducing branching or crosslinking reactions in the degraded polymeric chains from waste materials during melt reprocessing (reactive extrusion); this increases the molecular weight of the chains and improves rheological and mechanical properties. This procedure has been successfully applied to upgrade degraded post-consumer PE from greenhouse films[89,90,92] and pipes.[91]

The application of reactive extrusion to rebuild the molecular structure of waste polymeric fractions during mechanical recycling indeed appears to be a promising procedure to upgrade recycled plastics. Reactive extrusion facilitates polymer chemical modifications during melting by using the extruder as a reactor. Another good example of rebuilding recycled materials is chain extension of recycled PET during reactive extrusion.[93–95] Chain extension is a process for increasing the molecular weight and the intrinsic viscosity of degraded low-molecular weight PET, using effective additives (chain extenders) during the extrusion, which may react with the PET hydroxyl and carbonyl end groups by polyaddition and therefore increase chain length. A review of the chain extension

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process for the mechanical recycling of PET has been presented by Awaja and co-workers.[96] Chain extenders can be classified according to the PET functional groups with which they react — either carboxyl- or hydroxyl-end chain extenders; common chain extenders are dianhydrides, bis(oxazolines), bis(hydrooxazine), carbodiimides, diepoxides, and diisocyanates.[97] The chain extension process depends fundamentally on the chain extender concentration and the processing parameters; it is critical to adjust the concentration of chain extender to successfully achieve chain extension and avoid undesired extensive branching and crosslinking reactions.[94]

Compatibilisation and Rebuilding of Mixed Plastic Waste Fractions

Mechanical recycling of mixed plastic waste streams, such as post-consumer municipal solid waste, is a technological challenge, due to the presence of a wide variety of commodity polymers in waste streams. Recycled mixed polymeric blends usually have low compatibility between the different polymeric components, due to limited interfacial adhesion, which leads to polymeric dispersion microstructures with poor mechanical properties. Improvements in the procedures for separating commingled waste streams may lead to more effective mechanical recycling, but this procedure is time consuming and never fully effective. Another possibility for the mechanical recycling of mixed waste streams could be the upgrading of mixed polymeric fractions through the inclusion of suitable additives, which could protect the recyclate blend components from degradation during reprocessing (restabilisation), improve the interfacial adhesion and dispersion of the blend components (compatibilisation), and even enhance the molecular structure of the mixed polymeric system by promoting chemical reactions during melt processing (rebuilding by reactive extrusion).[98] The effective compatibilisation of recycled mixed plastic systems has garnered special attention lately, as shown by the increasing number of paper published recently on the topic. This section describes the most relevant advances for upgrading recycled polymeric waste mixtures.

Many commercial compatibilisers and impact modifiers are available for upgrading mixed waste polymers during mechanical recycling. These compatibilising additives base their function on physical or chemical effects; non-reactive compatibilisers improve the interfacial adhesion due to good miscibility with both polymers of the blend, whereas reactive compatibilisers have chemical activity and create effective links among the components of the blend through reactive extrusion. Non-reactive compatibilisers are usually graft or block copolymers, in which the blocks are chemically similar or even identical to the blend components to be compatibilised; the interfacial adhesion is therefore improved by the physical miscibility of the copolymer segments in the different blend phases. The effect of reducing the interfacial tension and promoting adhesion among the blend components results in a finer phase dispersion morphology and improved mechanical properties. Some non-reactive compatibilisers are: polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-polystyrene (SEBS), styrene-butadiene copolymer rubber (SBR), ethylene-propylene elastomers (EPR) including ethylene-propylene copolymer (EPM) and ethylene-propylene-diene copolymer (EPDM), ethylene-vinyl acetate (EVA), methyl methacrylate-butadiene-styrene copolymer (MBS), and styrene-isoprene-styrene (SIS). Reactive compatibilisers usually include some functional groups that can react with the components of the blend, such as epoxy, anhydrides, (meth)acrylates, or acrylic acids. The most common reactive segments used for the synthesis of reactive compatibilisers are maleic anhydride (MA), glycidyl methacrylate (GMA), and acrylic acid (AA); these functional groups may be grafted to non-reactive compatibilisers or even to the real polymeric components of the blend to create reactive compatibilisers such as PP-*g*-MA, PE-*g*-MA, SEBS-*g*-MA, EPR-*g*-MA, PP-*g*-AA, styrene maleic anhydride (SMA), ethylene-glycidyl methacrylate (EGMA), ethylene-butyl acrylate-glycidyl methacrylate (EBAGMA), and trimethylol propane trimethacrylate (TMPTA). Figure 10 shows the chemical structure of the most common functional groups used for reactive compatibilisation and reactive extrusion of polymeric wastes.

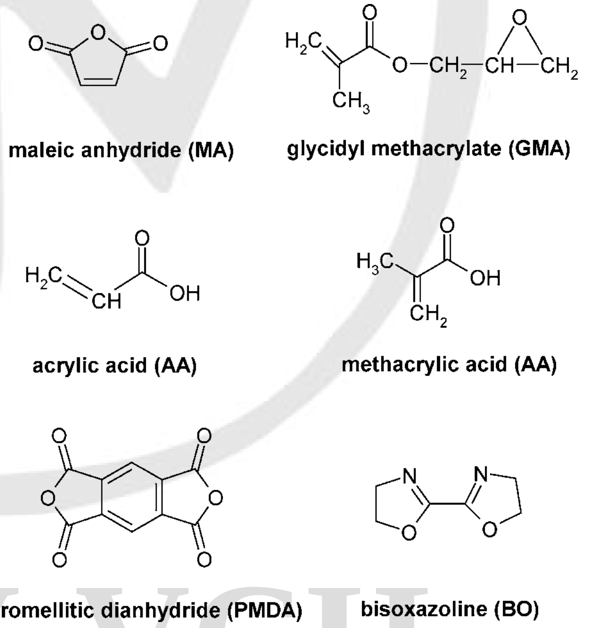

Figure 10. Common functional groups used for reactive compatibilisers and chain extenders.

Reactive compatibilisation is therefore an additive effect to the physical compatibilisation, in which the interfacial effects of the compatibiliser are enhanced by the chemical linkages and grafting among the polymeric components of the blends induced by the reactive groups. Another approach to accomplish effective compatibilisation of the components of mixed waste polymeric blends consists of the addition of suitable monomers [butylmethacrylate (BMA); *t*-butylamino ethyl methacrylate, TBAEMA; and styrene-maleic anhydride (SMA)] and initiators (peroxides), to carry out the compatibility reactions inside the extruder through reactive extrusion.[99] Table 1 summarises the recent literature regarding upgrading mixed plastic wastes by compatibilisation, and indicates the nature and proportion of the recycled blends, the type of compatibiliser employed, and the physical blending process.

Compatibility between polyolefins (PE and PP) and condensation polymers such as polyesters (e.g., PET) or polyamides can be effectively accomplished by introducing reactive compatibilisers that are capable of reacting with polyester and polyamide end groups. Post-consumer PET usually possesses a lower molecular weight than virgin material, which enhances the reactivity and the compatibilisation effect of the additives, due to the presence of a larger number of group ends.[100] This fact can also be employed for the rebuilding of the chemical structure of partially miscible PET/PC blends using chain extenders.[97]

Compatibilisation of complex waste mixed fractions from municipal solid waste containing polyolefins (PE and PP), styrenic polymers (PS and HIPS), and impurities such as PET or PVC may require the combination of different compatibilisers. The combined effect of SBR and EPM or EPDM showed higher efficiency for polyolefin/PS and polyolefin/HIPS blend compatibilisation; this effect is due to the improved location of the compatibilisers in the interfaces. In addition to this, a synergistic effect between compatibilising and restabilising agents was observed in municipal solid waste containing polyolefin and styrenic polymers; the synergism between compatibiliser and stabiliser in this complex system is caused by grafting the degraded polyolefins to the double bonds of the SBR compatibiliser.[98,101] Hence, previous degradation of the recycled materials may have beneficial effects for their further upgrading, using suitable synergistic compatibilisers and stabilisers to react with the existing functional groups and degradative moieties in recyclates and to enhance the grafting and crosslinking capability of the compatibilisers.[98]

Recycling engineering plastics from the automotive industry or electrical and electronic equipment usually involves complex blends with styrenic polymers (ABS, PS, HIPS, SAN), PC, PET, PBT, PVC, PMMA and polyamides. Compatibilisation of ABS with PC and PMMA is easily done, due to the miscibility of these polymers. On the other hand, PA6 presents more difficulties since it is not miscible with ABS; the addition of reactive compatibilising agents may help to achieve better mechanical properties, but the potential presence of glass fibres in the PA phase results in inferior performance.[102,103]

High-energy radiation (γ radiation), a powerful method to generate crosslinking, grafting, and surface functionalisation of some polymers, can be employed for the mechanical recycling of complex mixtures, together with selected compatibilisers.[104,105] Irradiation has proven to be useful to improve the toughness of waste mixed systems, through the generation of crosslinked and grafted structures between the chains of the different mixed polymers; compatibilisers, on the other hand, show great efficiency in improving the dispersion of the components of the system and the flexibility.[104]

Thermoplastic Elastomers from Recycled Polyolefins and Ground Tyre Rubber

Another route for the preparation of new materials from post-consumer products has been developed in the field of thermoplastic elastomers (TPEs), consisting of blends of a thermoplastic matrix and elastomeric materials through dynamic vulcanisation of the rubber in the thermoplastic. Several studies have been carried out to prepare TPEs using recycled polymers as matrixes and different elastomers, including waste ground tyre rubber (GTR).[106–111] These blends are originally incompatible, however, and proper phase morphology and interfacial adhesion is needed to achieve good mechanical properties, especially ultimate elongation; compatibilisation and/or chemical treatment of the rubber are therefore necessary. Ismail and Supri employed dynamic vulcanisation and different compatibilisers such as GMA and AA to obtain recycled PVC/NBR blends.[109,111] Ground tyre rubber could also be used to prepare TPEs with recycled thermoplastics, contributing to reduce environmental problems related to their disposal. Thus, GTR should be surface-activated to enhance reactive compatibilisation using different devulcanisation methods.[107] Preparation of TPEs from recycled HDPE and GTR was successfully performed using reactive compatibilisation with EPDM and GTR devulcanisation through the addition of bitumen, and resulted in improved mechanical properties, thermal stability, and reprocessability.[107]

Upgrading through the Addition of Inorganic and Organic Fillers

Fillers can be added to recycled polymers and mixed recycled blends to improve their mechanical properties;

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Table 1. Compatibilisation of mixed plastic waste fractions.

Mixed Polymeric System	Composition	Compatibilising Agent	Processing Procedure	Reference
	wt.-%			
LDPE/PP	90/10	EPM EPDM Ozonised PE graft copolymer	Single-screw Twin-screw Extruders	[132]
HDPE/PP	90/10	Initiators (peroxides) Monomers (BMA, TBAEMA, SMA)	Single-screw Twin-screw extruders	[99]
PET/HDPE (2–3% PP)	75/25 25/75	SEBS-*g*-MA EGMA	Twin-screw extruder	[133]
PET/LLDPE	80/20	HDPE-*g*-MA SEBS-*g*-MA SEBS	Twin-screw extruder	[134]
PET/polyolefins	90/10 80/20 70/30	MA-functionalised polyolefin	Melt mixing	[100]
PET/HDPE	75/25 25/75	HDPE-*g*-MA EPR-*g*-MA PP-*g*-AA EGMA E-AA SEBS-*g*-MA	Melt mixing	[135]
LDPE/PET	90/10 80/20 70/30	EBAGMA	Single-screw (double extrusion)	[136]
PP/PET	80/20	PP-*g*-MA	Twin-screw extruder	[137]
PA6/PP	80/20	PP-*g*-GMA PP-*g*-MA PP-*g*-AA	Single-screw extruder	[138,139]
PP (PE, PET)/PA (PE, LLDPE)	75/25	SEBS-*g*-MA PP-*g*-MA PP-*g*-AA	Twin-screw extruder	[140,141]
ABS/PC/PMMA/PA6 (glass fibre)	80/20/0/0 65/35/0/0 60/30/10/0 55/25/10/10	MBS SMA	Twin-screw extruder	[102]
ABS/PA6 (glass fibre)	80/20	SMA SMA/ABS blend ABS/PA6 blend	Twin-screw extruder	[103]

Table 1. Continued.

Mixed Polymeric System	Composition wt.-%	Compatibilising Agent	Processing Procedure	Reference
ABS/PA	80/20	Oxazoline-modified SAN	Melt mixing	[127]
SAN/PA	80/20		Twin-screw extruder	
ABS/PET	95/5	SMA	Twin-screw extruder	[142]
	90/10			
PVC/ABS	100/0–0/100	–	Two-roll mill	[143]
PVC/SAN	80/20–10/90	–	Two-roll mill	[144]
PC/ABS	70/30	SIS	Twin-screw extruder	[145]
LDPE/HIPS (PET)	70/30	EPDM/SBR	Melt mixing	[98]
		SEBS		
HDPE/PS	75/25	SEBS-*g*-MA	Twin-screw extruder	[112]
		($CaCO_3$ as filler)		
PP/HIPS	6:1			
	6:2	SEBS	Single-screw extruder	[146,147]
	6:3			
			Melt mixing	[101]
LDPE/HIPS	50/50	SBR		
HDPE/HIPS	50/50	EPM		
LDPE/PP	50/50	EPDM		
HDPE/PS	50/50	EPM/SBR		
LDPE/HDPE/PP/HIPS	54/18/18/10	EPDM/SBR		
LDPE/HDPE/PP/PS	54/18/18/10			
		SEBS-*g*-MA		
LDPE/HDPE/PP/PS/PET	24/23/21/15/17	TMPTA	Single-screw extruder	[105]
		γ-irradiation		
	70/15/15			
	80/10/10	EVA		
HDPE/PVC/PS	90/5/5	SEBS	Single-screw extruder	[104]
	60/20/20	γ-irradiation		
	50/25/25			
PE/PP/PS	70/20/10			
PE/PP/HIPS	70/20/10	SEBS/EPR	Melt mixing	[123]
PE/PP/PS/HIPS	60/20/10/10	SBR/EPR		
PET/PC	80/20	–	Twin-screw extruder	[148]
	70/30			
	50/50			
PET/PC	70/30	MDI	Twin-screw extruder	[97]
PE/PP/PET/PA		E-AA		
Upholstery scrap from ELV	50/3/46/1	EGMA	Melt mixing	[125]
		SEBS-*g*-MA		
		PE-MA		
PP/EPR	78/22		Twin-screw extruder	[126]
PP/EPR/EOC	62/18/20	PP-*g*-MA		

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these fillers can be inorganic (calcium carbonate,[112] calcium silicate) or organic (natural fibres,[113,114] wood and cellulose residues,[115,116] and other organic materials[117]). In the case of inorganic fillers, compatibilisers might also be used to improve the adhesion of the system and the impact properties, but the interaction among the different system components (single polymer or polymeric blend, compatibiliser and filler) at their respective interfaces must be studied to optimise their respective effects. Encapsulation of filler particles by the compatibiliser must be avoided to preserve the effect of the filler on the stiffness of the system.[112] Reutilisation of the fibrous fraction of thermoset composites (glass, carbon, and aramide fibres) after fibre grinding and recovery is feasible for the preparation of thermoplastic composites for sheet moulding applications.[118]

Recycled polymeric materials and organic fillers as reinforcements replacing inorganic materials can be used to produce sustainable composites, due to the fact that the resulting material is environmentally-friendly without an appreciable performance loss. Nevertheless, these composites face some inconveniences, such as poor compatibility between the fibres and matrix, and the elevated rate of moisture absorption; compatibilisation using common reactive groups (maleic anhydride, acrylic acid) is therefore mandatory. Recycled polymers as matrix may even show better interfacial adhesion with the organic fillers and contribute to a diminished water absorption compared to the virgin materials, due to the residual presence of other impurities, such as EVA, that may have a compatibilising effect.[114]

Another valuable contribution to the upgrading of recycled polymers is the preparation of in situ microfibrillar-reinforced composites (iMFCs), through reinforcing polymeric matrixes with recycled polyester fibres using suitable compatibilisers.[119] Extrusion and further fibrillation by drawing successfully generates microfibrillar recycled polyester structures dispersed in the polymeric matrix.

Considerations for the Mechanical Recycling of Plastics from Different Applications

Mechanical recycling of plastics in practice is strongly dependent on the previous application of the products and on other external agents, such as waste management procedures, environmental policy, and legislation. The different implications affecting the mechanical recycling of plastic waste from different applications are discussed in the following chapter, according to the classification of plastic waste streams proposed by the European Union.

Plastics from Packaging

Packaging is the economic sector with the highest volume consumption of polymeric materials; typical polymers employed in packaging applications are LDPE, HDPE, PP, PS, HIPS, PET, PBT, and PVC. The presence of large quantities of mixed plastic waste, impurities and contamination are the main challenge for the effective recycling of plastics from packaging; however, during the last decade, effective management of the different waste streams (selective sorting, automatic separation) has allowed the recovery of large volumes of relatively clean and homogeneous polymeric fractions that are viable for mechanical recycling. Many of the studies reviewed here deal with the effective mechanical recycling of plastic wastes from packaging applications, using some of the different upgrading strategies described in the previous chapter. The limited use of recycled plastics in food packaging applications due to migration of contaminants, food safety concerns, and strict regulations is one of the main economical drawbacks; the development of multilayer packaging systems with recycled material between virgin layers could be an interesting alternative.[120]

Plastics from Agriculture

Although the total volume of plastics employed in agricultural applications is small compared to other economical segments, this sector offers a good potential for mechanical recycling, because agricultural films are extensively collected and constitute a homogeneous waste polymeric stream. The mechanical recycling of waste plastic from agriculture may be limited, however, because of high degree of degradation (in this case, photodegradation due to extensive exposure to UV-radiation), moisture and mud content, and due to the presence of dangerous agrochemical residues such as pesticides and fertilisers. Despite these inconveniences, some researchers have reported successful recycling of greenhouse PE films by employing restabilisation techniques,[77,121,122] rebuilding the molecular structure,[89,92] and adding organic fillers[115,117]

Plastics from Municipal Solid Waste (MSW)

Waste plastics in MSW are mainly composed of lightweight, unsorted and dirty plastic fractions, which make them difficult and inefficient to recycle by mechanical means due to technological and economical difficulties in separation, cleaning and processing. In these cases, other recovery options, such as energy recovery by incineration, may have an important role to play. However, some researchers have presented interesting results on the compatibilisation and rebuilding of complex mixed waste polymeric systems, including polyolefins, styrenic polymers and polyesters, by using suitable additive systems and/or energy radiation,[101,104,105,123] which could open alternative doors for the mechanical recycling of plastics from MSW.

Plastics from Construction and Demolition (C&D)

Plastic materials, mainly PVC, PU, PS, and PP, can be used in construction applications such as pipes and ducts, insulation, floor and wall coverings, windows, and profiles. The C&D sector offers a good scope for the mechanical recycling of massive single polymer fractions, such as pipes, windows frames, and cables made of PVC. However, the weathering effects on long-life applications may lead to the recycling of recovered materials with poorer properties ("downcycling").

Plastics from End-of-Life Vehicles (ELV)

Plastics are being increasingly employed for the manufacturing of different automotive components, because of their properties and low density, which allow a reduction in the total weight of the vehicles and lower energy consumption. Plastics can be found in bumpers (PP, ABS, PC, HIPS), seats (PU, PVC, PA, ABS), dashboards (PP, ABS, PA), interior and exterior trim (PP, ABS, HIPS, PA) and upholstery (PVC, PU, PP). The development of effective dismantling procedures would allow a continuous flow of plastic waste streams that could be effectively recycled. Some studies have analysed the recycling of different post-consumer blends from different car components (dashboards with multilayer structures, upholstery) by blending with virgin material[124] and by reactive compatibilisation.[102,103,125–127]

Plastics from Waste Electrical and Electronic Equipment (WEEE)

Recycling of WEEE plastics involves a technological challenge due to the complex nature of electrical and electronic equipment (E&E). The integrated nature of E&E products, with plastics and metals in close combination, complicates dismantling and separation of their components. Polymers represent approximately 20% of the total weight of E&E equipment and are based on more than 15 different types of engineering plastics, including ABS, HIPS, PP, PS, SAN, polyesters, PU, PA, blends of ABS/PC and blends of HIPS/PPO. Styrenic polymers and ABS/PC blends may exhibit compatibility problems and previous degradation, which limit their mechanical properties and performance.[128,129] Moreover, plastics from WEEE may contain hazardous substances, such as heavy metals and brominated flame retardants (BFRs), which affect waste management procedures due to their potential to form brominated dioxins and furans.[52,130] Recent European directives (WEEE and RoHS Directives) have been introduced to regulate the management of plastic WEEE containing BFRs and to ban the use of certain BFRs in new products and, consequently, in recycled plastics. The first approach to recycle WEEE plastics may consist of the separation of the flame-retarded polymeric fraction from the non-retarded fraction, using spectroscopic techniques or density-based technologies.[131] Another approach to the recycling of WEEE plastics involves the use of extractive recycling processes to separate the different polymer fractions and eliminate hazardous contaminants such as heavy metals, brominated flame retardants, dioxins, and furans;[52] in this direction, the solvent-based CreaSolv® extractive process has been developed for the recycling of flame- retarded plastics.[130] However, material recycling of WEEE plastics may be limited to certain fractions, so energy recovery treatments such as incineration, pyrolysis or gasification should be considered.

Conclusion

The goal of a sustainable society is obtained by a material and energetic symbiosis between the needs for economic growth and the maintenance of environmental and social wealth. Mechanical recycling clearly favours this sustainable development by introducing a clever use of the raw materials and expanding the life cycle of materials and products. Recent developments in giving a quality insight into recycled polymeric products and effectively achieving a valuable status as resources have been discussed. Modelling the environmental conditions to which polymers are exposed during their life cycle is a valuable tool to obtain scientific knowledge about their degradative processes and the effects on structure and performance. The introduction of a quality concept in plastics recycling activities is a critical factor; several analytical procedures can be considered for the study of the degree of mixing (composition), the degree of degradation, and the presence of low molecular weight compounds. The upgrading of the molecular structure, phase morphology, and mechanical properties of plastic waste streams can be accomplished using different strategies, including restabilisation, rebuilding of the macromolecular architecture, compatibilisation of mixed recycled blends and addition of elastomers and fillers. The implications of existing waste management routes, environmental policy and legislation concerning mechanical recycling of plastic waste from different original applications should also be considered.

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The main challenge for the recycling industry is to effectively combine the scientific knowledge about the degradation state and the quality properties of their recyclates, and effectively design the upgrading process for each specific waste stream, in order to tailor the properties of the final recycled material and, thus, meet the requirements of the destined application. The achievement of this goal would improve the public image of recycled products and contribute to the efficient use of recycled materials as valuable resources.

List of Abbreviations

AA:	acrylic acid
ABS:	acrylonitrile-butadiene-styrene
BFRs:	brominated flame retardants
C&D:	construction and demolition
DMA:	dynamic mechanical analysis
DSC:	differential scanning calorimetry
EBAGMA:	ethylene-butyl acrylate-glycidyl methacrylate
EGMA:	ethylene-glycidyl methacrylate
ELV:	end-of-life vehicles
EPDM:	ethylene-propylene-diene copolymer
EPM:	ethylene-propylene copolymer
EPR:	ethylene-propylene rubber
EVA:	ethylene-vinyl acetate
FTIR:	Fourier-transform infrared spectroscopy
GC:	gas chromatography
GMA:	glycidyl methacrylate
GTR:	ground tyre rubber
HDPE:	high-density polyethylene
HIPS:	high-impact polystyrene
HPLC:	high-performance liquid chromatography
LDPE:	low-density polyethylene
LLDPE:	linear low-density polyethylene
MA:	maleic anhydride
MAE:	microwave-assisted extraction
MBS:	methyl methacrylate-butadiene-styrene copolymer
MFR:	melt flow rate
MS:	mass spectrometry
MSW:	municipal solid waste
NBR:	acrylonitrile-butadiene rubber
PA:	polyamide
PB:	polybutadiene
PBT:	poly(butylene terephthalate)
PC:	polycarbonate
PE:	polyethylene
PLE:	pressurised liquid extraction
PP:	poly(propylene)
PS:	polystyrene
PVC:	poly(vinyl chloride)
PU:	polyuretane
SBR:	styrene-butadiene copolymer rubber
SBSE:	stir bar sorptive extraction
SEBS:	polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-polystyrene
SEC:	size exclusion chromatography
SEM:	scanning electron microscopy
SFE:	supercritical-fluid extraction
SIS:	styrene-isoprene-styrene
SMA:	styrene maleic anhydride
SPME:	solid-phase microextraction
TEM:	transmission electron microscopy
TGA:	thermogravimetric analysis
TMPTA:	trimethylol propane trimethacrylate
TPEs:	thermoplastic elastomers
WEEE:	waste electrical and electronic equipment

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[1] S. Karlsson, *Adv. Polym. Sci.* **2004**, *169*, 201.
[2] G. Finnveden, J. Johansson, P. Lind, A. Moberg, *J. Cleaner Production* **2005**, *13*, 213.
[3] F. Stangenberg, S. Ågren, S. Karlsson, *Chromatographia* **2004**, *59*, 101.
[4] F. P. La Mantia, M. Gaztelumendi, J. I. Eguiazábal, J. Nazábal, "*Properties - Reprocessing Behaviour of Recycled Plastics*", Rapra Technology Limited, Shawbury 2002.
[5] I. H. Craig, J. R. White, *J. Mater. Sci.* **2006**, *41*, 993.
[6] S. Wallström, E. Strömberg, S. Karlsson, *Polym. Test.* **2005**, *24*, 557.
[7] F. Vilaplana, A. Ribes-Greus, S. Karlsson, *Polym. Degrad. Stab.* **2006**, *91*, 2163.
[8] E. Stromberg, S. Karlsson, *Eur. Polym. J.* (in preparation).
[9] J. D. Badia, F. Vilaplana, S. Karlsson, A. Ribes-Greus, manuscript in preparation.
[10] F. Vilaplana, S. Karlsson, A. Ribes-Greus, *Eur. Polym. J.* **2007**, *43*, 4371.
[11] A. Boldizar, A. Jansson, T. Gevert, K. Moller, *Polym. Degrad. Stab.* **2000**, *68*, 317.
[12] A. Boldizar, K. Moller, *Polym. Degrad. Stab.* **2003**, *81*, 359.
[13] A. Jansson, K. Moller, T. Gevert, *Polym. Degrad. Stab.* **2003**, *82*, 37.
[14] A. Jansson, K. Moller, T. Hjertberg, *Polym. Degrad. Stab.* **2004**, *84*, 227.
[15] S. Luzuriaga, J. Kovarova, I. Fortelny, *Polym. Degrad. Stab.* **2006**, *91*, 1226.
[16] F. Vilaplana, A. Ribes-Greus, S. Karlsson, *Anal. Chim. Acta* **2007**, *604*, 18.

[17] S. Tall, A.-C. Albertsson, S. Karlsson, *J. Appl. Polym. Sci.* **1998**, *70*, 2381.
[18] W. Camacho, S. Karlsson, *Polym. Eng. Sci.* **2001**, *41*, 1626.
[19] A. Pawlak, M. Pluta, J. Morawiec, A. Galeski, M. Pracella, *Eur. Polym. J.* **2000**, *36*, 1875.
[20] E. Strömberg, F. Vilaplana, S. Ågren, A. Ribes-Greus, S. Karlsson, Identiplast 2005 – Identifying the Opportunities for Plastics Recovery, Brussels 2005, Conference Proceedings.
[21] W. Camacho, S. Karlsson, *Polym. Recycling* **2001**, *6*, 89.
[22] A.-C. Albertsson, S. Karlsson, *J. Polym. Environ.* **1996**, *4*, 51.
[23] S. Karlsson, *Polym. News* **2002**, *27*, 305.
[24] S. Karlsson, A.-C. Albertsson, "*Degradable Polymers*", 2nd Ed., G. Scott, Ed., Kluwer Academic Publishers, Dordrecht, Netherlands 2002, pp. 51–69.
[25] E. Stromberg, F. Vilaplana, S. Karlsson, A. Ribes-Greus, European Polymer Congress - EPF 2005, Moscow 2005.
[26] M. Hakkarainen, M. Gröning, A.-C. Albertsson, *J. Appl. Polym. Sci.* **2003**, *89*, 867.
[27] J. Aurrekoetxea, M. A. Sarrionandia, I. Urrutibeascoa, M. L. Maspoch, *Polymer* **2003**, *44*, 6959.
[28] G. Xu, J. Qiao, C. Kuswanti, K. Koelling, J. A. Stuart, B. Lilly, *J. Appl. Polym. Sci.* **2002**, *84*, 1.
[29] W. Nunes dos Santos, J. Augusto Marcondes Agnelli, P. Mummery, A. Wallwork, *Polym. Test.* **2007**, *26*, 216.
[30] R. Navarro, L. Torre, J. M. Kenny, A. Jimenez, *Polym. Degrad. Stab.* **2003**, *82*, 279.
[31] R. Balart, L. Sanchez, J. Lopez, A. Jimenez, *Polym. Degrad. Stab.* **2006**, *91*, 527.
[32] W. Camacho, S. Karlsson, *Polym. Degrad. Stab.* **2002**, *78*, 385.
[33] S. A. Kyriakou, M. Statherpoulos, G. K. Parissakis, C. D. Papaspyrides, C. N. Kartalis, *Polym. Degrad. Stab.* **1999**, *66*, 49.
[34] G. Ahlblad, P. Gijsman, B. Terselius, A. Jansson, K. Moller, *Polym. Degrad. Stab.* **2001**, *73*, 15.
[35] M. Hamskog, M. Klugel, D. Forsstrom, B. Terselius, P. Gijsman, *Polym. Degrad. Stab.* **2004**, *86*, 557.
[36] M. Hamskog, M. Klugel, D. Forsstrom, B. Terselius, P. Gijsman, *Polym. Degrad. Stab.* **2006**, *91*, 429.
[37] F. P. La Mantia, N. T. Dintcheva, *Plast. Rubber Compos.* **2004**, *33*, 184.
[38] W. Camacho, S. Karlsson, *J. Appl. Polym. Sci.* **2002**, *85*, 321.
[39] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, J. Carroll, I. Newton, L. M. Garden, J. R. Dean, C. T. Costley, *Analyst* **1997**, *122*, 101R.
[40] J. Möller, E. Strömberg, S. Karlsson, manuscript in preparation.
[41] S. H. Patel, M. Xanthos, *Adv. Polym. Technol.* **2001**, *20*, 22.
[42] J. Salafranca, J. Cacho, C. Nerín, *Chromatographia* **2000**, *51*, 615.
[43] W. Camacho, S. Karlsson, *Polym. Degrad. Stab.* **2000**, *71*, 123.
[44] T. Andersson, B. Wesslén, J. Sandström, *J. Appl. Polym. Sci.* **2002**, *86*, 1580.
[45] A. Espert, L. A. de las Heras, S. Karlsson, *Polym. Degrad. Stab.* **2005**, *90*, 555.
[46] M. Gröning, M. Hakkarainen, *J. Appl. Polym. Sci.* **2002**, *86*, 3396.
[47] W. Camacho, M. S. Hedenqvist, S. Karlsson, *Polym. Int.* **2002**, *51*, 1366.
[48] W. Camacho, A. Vallés-Lluch, A. Ribes-Greus, S. Karlsson, *J. Appl. Polym. Sci.* **2003**, *87*, 2165.
[49] L. Birnbaum, D. F. Statskal, *Environ. Health Perspective* **2004**, *112*, 9.
[50] C. A. de Wit, *Chemosphere* **2002**, *46*, 583.
[51] L. S. Morf, J. Tremp, R. Gloor, Y. Huber, M. Stengele, M. Zennegg, *Environ. Sci. Technol.* **2005**, *39*, 8691.
[52] M. Schlummer, L. Gruber, A. Maurer, G. Wolz, R. van Eldik, *Chemosphere* **2007**, *67*, 1866.
[53] H. Fink, U. Panne, M. Theisen, R. Niessner, T. Probst, X. Lin, *Fresenius' J. Anal. Chem.* **2000**, *368*, 235.
[54] H. Fink, U. Panne, R. Niessner, *Anal. Chem.* **2002**, *74*, 4334.
[55] M. Stepputat, R. Noll, *Appl. Optics* **2003**, *42*, 6210.
[56] S. Kikuchi, K. Kawauchi, S. Ooki, M. Kurosawa, H. Honjho, T. Yagishita, *Anal. Sci.* **2004**, *20*, 1111.
[57] A. M. Altwaiq, M. Wolf, R. van Eldik, *Anal. Chim. Acta* **2003**, *491*, 111.
[58] M. Pohlein, A. S. Llopis, M. Wolf, R. v. Eldik, *J. Chromatogr. A* **2005**, *1066*, 111.
[59] F. Vilaplana, P. Karlsson, P. Ivarsson, A. Ribes-Greus, S. Karlsson, manuscript in preparation.
[60] M. Schlummer, F. Brandl, A. Maurer, R. van Eldik, *J. Chromatogr. A* **2005**, *1064*, 39.
[61] J. de Boer, R. J. Law, *J. Chromatogr. A* **2003**, *1000*, 223.
[62] P. Korytar, A. Covaci, J. de Boer, A. Gelbin, U. A. T. Brinkman, *J. Chromatogr. A* **2005**, *1065*, 239.
[63] A. Covaci, S. Voorspoels, L. Ramos, H. Neels, R. Blust, *J. Chromatogr. A* **2007**, *1153*, 145.
[64] S. Hamm, M. Strikkeling, P. F. Ranken, K. P. Rothenbacher, *Chemosphere* **2001**, *44*, 1353.
[65] M. Riess, T. Ernst, R. Popp, B. Muller, H. Thoma, O. Vierle, M. Wolf, R. van Eldik, *Chemosphere* **2000**, *40*, 937.
[66] M. Wolf, M. Riess, D. Heitmann, M. Schreiner, H. Thoma, O. Vierle, R. van Eldik, *Chemosphere* **2000**, *41*, 693.
[67] F. Cheng-Yu Wang, *Anal. Chem.* **1999**, *71*, 2037.
[68] M. Riess, H. Thoma, O. Vierle, R. van Eldik, *J. Anal. Appl. Pyrol.* **2000**, *53*, 135.
[69] J. Pospisil, F. A. Sitek, R. Pfaendner, *Polym. Degrad. Stab.* **1995**, *48*, 351.
[70] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *Polym. Degrad. Stab.* **2000**, *70*, 189.
[71] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *Macromol. Mater. Eng.* **2003**, *288*, 124.
[72] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *J. Appl. Polym. Sci.* **1999**, *73*, 1775.
[73] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *J. Appl. Polym. Sci.* **2000**, *77*, 1118.
[74] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *Polym. Eng. Sci.* **2001**, *41*, 771.
[75] C. Tsenoglou, C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *J. Appl. Polym. Sci.* **2001**, *80*, 2207.
[76] M. K. Loultcheva, M. Proietto, N. Jilov, F. P. La Mantia, *Polym. Degrad. Stab.* **1997**, *57*, 77.
[77] N. Tzankova Dintcheva, F. P. La Mantia, R. Scaffaro, M. Paci, D. Acierno, G. Camino, *Polym. Degrad. Stab.* **2002**, *75*, 459.
[78] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *J. Appl. Polym. Sci.* **2002**, *86*, 2472.
[79] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *J. Appl. Polym. Sci.* **2003**, *89*, 1311.
[80] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *J. Appl. Polym. Sci.* **2003**, *88*, 3033.
[81] C. J. Tsenoglou, C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, *Adv. Polym. Technol.* **2002**, *21*, 260.
[82] A. S. F. Santos, J. A. M. Agnelli, D. W. Trevisan, S. Manrich, *Polym. Degrad. Stab.* **2002**, *77*, 441.
[83] F. P. La Mantia, *Macromol. Symposia* **2000**, *152*, 201.

DOI: 10.1002/mame.200700393

[84] R. Scaffaro, F. P. La Mantia, "*Virgin/Recycled Homopolymer Blends*", Rapra Technology Limitedm, Shawbury 2002.
[85] N. Kukaleva, G. P. Simon, E. Kosior, *Polym. Eng. Sci.* **2003**, *43*, 26.
[86] E. Ramírez-Vargas, Z. Sandoval-Arellano, J. S. Hernández-Valdez, J. G. Martínez-Colunga, S. Sánchez-Valdés, *J. Appl. Polym. Sci.* **2006**, *100*, 3696.
[87] M. H. Martins, M.-A. De Paoli, *Polym. Degrad. Stab.* **2001**, *71*, 293.
[88] M. H. Martins, M.-A. De Paoli, *Polym. Degrad. Stab.* **2002**, *78*, 491.
[89] F. P. La Mantia, N. Tzankova Dintcheva, *Macromol. Mater. Eng.* **2005**, *290*, 970.
[90] F. P. La Mantia, N. Tzankova Dintcheva, *Macromol. Rapid Commun.* **2005**, *26*, 361.
[91] R. Scaffaro, F. P. La Mantia, N. Tzankova Dintcheva, *Eur. Polym. J.* **2007**, *43*, 2947.
[92] R. Scaffaro, N. Tzankova Dintcheva, F. P. La Mantia, *Polym. Degrad. Stab.* **2006**, *91*, 3110.
[93] F. Awaja, F. Daver, E. Kosior, *Polym. Eng. Sci.* **2004**, *44*, 1579.
[94] L. Incarnato, P. Scarfato, L. Di Maio, D. Acierno, *Polymer* **2000**, *41*, 6825.
[95] P. Kiliaris, C. D. Papaspyrides, R. Pfaendner, *J. Appl. Polym. Sci.* **2007**, *104*, 1671.
[96] F. Awaja, D. Pavel, *Eur. Polym. J.* **2005**, *41*, 1453.
[97] X. Tang, W. Guo, G. Yin, B. Li, C. Wu, *J. Appl. Polym. Sci.* **2007**, *104*, 2602.
[98] J. Pospisil, I. Fortelny, D. Michalkova, Z. Krulis, M. Slouf, *Polym. Degrad. Stab.* **2005**, *90*, 244.
[99] R. Hettema, J. Pasman, L. P. B. M. Janssen, *Polym. Eng. Sci.* **2002**, *42*, 665.
[100] M. Aglietto, M.-B. Coltelli, S. Savi, F. Lochiatto, F. Ciardelli, M. Giani, *J. Mater. Cycles Waste Manage.* **2004**, *6*, 13.
[101] I. Fortelny, D. Michalkova, Z. Krulis, *Polym. Degrad. Stab.* **2004**, *85*, 975.
[102] X. Liu, H. Bertilsson, *J. Appl. Polym. Sci.* **1999**, *74*, 510.
[103] X. Liu, A. Boldizar, M. Rigdahl, H. Bertilsson, *J. Appl. Polym. Sci.* **2002**, *86*, 2535.
[104] F. Elmaghor, L. Zhang, H. Li, *J. Appl. Polym. Sci.* **2003**, *88*, 2756.
[105] M. Zenkiewicz, J. Dzwonkowski, *Polym. Test.* **2007**, *26*, 903.
[106] O. Grigoryeva, A. Fainleib, O. Starostenko, A. Tolstov, W. Brostow, *Polym. Int.* **2004**, *53*, 1693.
[107] O. Grigoryeva, A. Fainleib, A. Tolstov, P. Pissis, A. Spanoudaki, A. Vatalis, C. Delides, *J. Therm. Anal. Calorimetry* **2006**, *86*, 229.
[108] O. P. Grigoryeva, A. M. Fainleib, A. L. Tolstov, O. M. Starostenko, E. Lievana, J. Karger-Kocsis, *J. Appl. Polym. Sci.* **2005**, *95*, 659.
[109] H. Ismail, Supri[Q1], A. M. M. Yusof, *J. Appl. Polym. Sci.* **2005**, *96*, 2181.
[110] R. Scaffaro, N. T. Dintcheva, M. A. Nocilla, F. P. La Mantia, *Polym. Degrad. Stab.* **2005**, *90*, 281.
[111] Supri[Q2], H. Ismail, *Polym. Test.* **2006**, *25*, 318.
[112] F. Sahnoune, J. M. Lopez Cuesta, A. Crespy, *Polym. Eng. Sci.* **2003**, *43*, 647.
[113] A. Espert, W. Camacho, S. Karlsson, *J. Appl. Polym. Sci.* **2003**, *89*, 2353.
[114] A. Espert, F. Vilaplana, S. Karlsson, *Composites Part A: Appl. Sci. Manufact.* **2004**, *35*, 1267.
[115] F. P. La Mantia, M. Morreale, *Polym. Eng. Sci.* **2006**, *46*, 1131.
[116] M. Mehrabzadeh, F. Farahmand, *J. Appl. Polym. Sci.* **2001**, *80*, 2573.
[117] F. La Mantia, N. Tzankova Dintcheva, M. Morreale, C. Vaca-Garcia, *Polym. Int.* **2004**, *53*, 1888.
[118] C. E. Kouparitsas, C. N. Kartalis, P. C. Varelidis, C. J. Tsenoglou, C. D. Papaspyrides, *Polym. Compos.* **2002**, *23*, 682.
[119] P. Taepaiboon, J. Junkasem, R. Dangtungee, T. Amornsakchai, P. Supaphol, *J. Appl. Polym. Sci.* **2006**, *102*, 1173.
[120] A. Feigenbaum, S. Laoubi, J. M. Vergnaud, *J. Appl. Polym. Sci.* **1997**, *66*, 597.
[121] N. Tzankova Dintcheva, F. P. La Mantia, *Polym. Degrad. Stab.* **2004**, *85*, 1041.
[122] N. Tzankova Dintcheva, F. P. La Mantia, D. Acierno, L. Di Maio, G. Camino, F. Trotta, M. P. Luda, M. Paci, *Polym. Degrad. Stab.* **2001**, *72*, 141.
[123] N. Equiza, W. Yave, R. Quijada, M. Yazdani-Pedram, *Macromol. Mater. Eng.* **2007**, *292*, 1001.
[124] G. Ragosta, P. Musto, E. Martuscelli, P. Russo, L. Zeloni, *J. Mater. Sci.* **2001**, *36*, 1231.
[125] A. Correnti, M. Bocchino, S. Filippi, P. L. Magagnini, G. Polacco, F. P. La Mantia, *J. Appl. Polym. Sci.* **2005**, *96*, 1716.
[126] M. Jaziri, N. Mnif, V. Massardier-Nageotte, H. Perier-Camby, *Polym. Eng. Sci.* **2007**, *47*, 1009.
[127] X. Liu, F. La Mantia, R. Scaffaro, *J. Appl. Polym. Sci.* **2002**, *86*, 449.
[128] R. Balart, J. Lopez, D. Garcia, M. Dolores Salvador, *Eur. Polym. J.* **2005**, *41*, 2150.
[129] L. B. Brennan, D. H. Isaac, J. C. Arnold, *J. Appl. Polym. Sci.* **2002**, *86*, 572.
[130] M. Schlummer, A. Mäurer, T. Leitner, W. Spruzina, *Waste Manage. Res.* **2006**, *24*, 573.
[131] M. Schlummer, A. Mäurer, *J. Appl. Polym. Sci.* **2006**, *102*, 1262.
[132] S. Bertin, J.-J. Robin, *Eur. Polym. J.* **2002**, *38*, 2255.
[133] A. Pawlak, J. Morawiec, F. Pazzagli, M. Pracella, A. Galeski, *J. Appl. Polym. Sci.* **2002**, *86*, 1473.
[134] H. Zhang, W. Guo, Y. Yu, B. Li, C. Wu, *Eur. Polym. J.* **2007**, *43*, 3662.
[135] M. Pracella, D. Chionna, R. Ishak, A. Galeski, *Polym.-Plast. Technol. Eng.* **2004**, *43*, 1711.
[136] M. Kaci, A. Benhamida, S. Cimmino, C. Silvestre, C. Carfagna, *Macromol. Mater. Eng.* **2005**, *290*, 987.
[137] Y. Tao, K. Mai, *Eur. Polym. J.* **2007**, *43*, 3538.
[138] F. P. La Mantia, L. Capizzi, *Polym. Degrad. Stab.* **2001**, *71*, 285.
[139] F. P. La Mantia, C. Mongiovi, *Polym. Degrad. Stab.* **1999**, *66*, 337.
[140] S. M. Hong, S. S. Hwang, J. S. Choi, H. J. Choi, *J. Appl. Polym. Sci.* **2006**, *101*, 1188.
[141] G. H. Kim, S. S. Hwang, B. G. Cho, S. M. Hong, *Macromol. Symposia* **2007**, *249–250*, 485.
[142] S. Paul, D. D. Kale, *J. Appl. Polym. Sci.* **2001**, *80*, 2593.
[143] D. Garcia, R. Balart, L. Sánchez, J. López, *Polym. Eng. Sci.* **2007**, *47*, 789.
[144] D. Garcia, R. Balart, F. Parres, J. López, *J. Appl. Polym. Sci.* **2007**, *106*, 20.
[145] M. Tascedil, S. Karatop, *J. Appl. Polym. Sci.* **2006**, *101*, 559.
[146] R. M. Campomanes Santana, S. Manrich, *J. Appl. Polym. Sci.* **2003**, *87*, 747.
[147] R. M. Campomanes Santana, S. Manrich, *J. Appl. Polym. Sci.* **2003**, *88*, 2861.
[148] F. Fraisse, V. Verney, S. Commereuc, M. Obadal, *Polym. Degrad. Stab.* **2005**, *90*, 250.