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**CHEMICAL, PHYSICAL, STRUCTURAL AND MORPHOLOGICAL
CHARACTERIZATION OF RECYCLED MATERIALS TO PROMOTE THE
CIRCULAR ECONOMY IN ITALIAN MANUFACTURING (CPSMR)**

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Abstract

The increasing incorporation of recycled plastics into industrial value chains represents a central pillar of circular economy strategies, yet their quality and reliability remain limited by intrinsic material heterogeneity and insufficient characterisation methodologies. Unlike virgin polymers, inorganic fillers, degradation products, and trace contaminants accumulated over successive life cycles. Conventional quality indicators based on mechanical or physical properties are therefore inadequate to fully describe their structural and chemical state, particularly in the context of End-of-Waste classification and regulatory compliance. This work develops and validates multi-technique analytical framework for the comprehensive characterisation of recycled polymer materials. Fourier Transform Infrared (FTIR) spectroscopy was applied for polymer identification and detection of polymer mixtures; X-ray Powder Diffraction (XRPD) was used to identify mineral filler phases; Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectrometry (SEM-EDX) provided microstructural and compositional mapping of fillers and contaminants; and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) enabled quantitative determination of bulk and trace elements, including regulated heavy metals. These methods were selected through experimental screening and inter-laboratory validation to ensure robustness when applied to heterogeneous, additive-rich recyclates. These results reveal that industrial recycled plastics frequently contain mixed polymer systems, heterogeneous filler distributions, and cumulative trace-metal contamination. Calcite, talc, rutile, and glass fibres were identified as dominant fillers, while Fe, Cu, Zn, Cr, Ni, Pb, and Sb were detected as recurring contaminants. These features strongly influence microstructural integrity, ageing behaviour, and material performance. The integrated analytical framework developed here provides a scientifically grounded basis for assessing recycled plastic quality and supports the development of reliable End-of-Waste and circular economy strategies.

Keyword: Recycled plastics, polymer mixture, Mineral fillers, trace metals, FTIR, XRPD, SEM-EDX, ICP-MS, Circular economy, End-of-Waste, Material characterisation

Sommario

La crescente integrazione delle plastiche riciclate nelle filiere industriali rappresenta un pilastro fondamentale delle strategie di economia circolare; tuttavia, la loro qualità e affidabilità sono fortemente limitate dall'eterogeneità intrinseca dei materiali e dalla carenza di metodologie di caratterizzazione adeguate. A differenza dei polimeri vergini, le plastiche riciclate sono sistemi multi-componente complessi costituiti da miscele polimeriche, cariche inorganiche, prodotti di degradazione e contaminanti in tracce accumulati nel corso di molteplici cicli di vita. I tradizionali indicatori di qualità basati su proprietà fisiche o meccaniche risultano quindi insufficienti per descriverne lo stato chimico e strutturale, in particolare in relazione alla classificazione End-of-Waste e alla conformità normativa. Questo lavoro sviluppa e valida un approccio analitico multi-tecnica per la caratterizzazione completa dei materiali polimerici riciclati. La spettroscopia FTIR è stata utilizzata per l'identificazione dei polimeri e delle miscele polimeriche; la diffrazione a raggi X su polveri (XRPD) per l'analisi della struttura cristallina e l'identificazione delle cariche minerali; la microscopia elettronica a scansione con microanalisi EDX (SEM-EDX) per lo studio della morfologia, della distribuzione delle inclusioni e della loro composizione; mentre la spettrometria ICP-MS ha consentito la quantificazione di elementi maggiori e in tracce, inclusi metalli regolamentati. Le tecniche sono state selezionate attraverso uno screening sperimentale e una validazione inter-laboratorio per garantirne l'affidabilità in matrici eterogenee. I risultati mostrano che le plastiche riciclate industriali contengono frequentemente miscele polimeriche, sistemi di cariche eterogenei e contaminazioni metalliche cumulative. Calcite, talco, rutilo e fibre di vetro risultano essere i principali riempitivi, mentre Fe, Cu, Zn, Cr, Ni, Pb e Sb rappresentano contaminanti ricorrenti. L'approccio integrato proposto fornisce una base scientifica solida per la valutazione della qualità dei riciclati e per lo sviluppo di strategie End-of-Waste e di economia circolare.

Parole Chiave: Plastiche riciclate, Miscele polimeriche, Cariche minerali, Metalli in tracce, FTIR, XRPD, SEM-EDX, ICP-MS, Economia circolare, End-of-Waste, Caratterizzazione dei materiali.

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List Of Abbreviations

AFM:	Atomic Force Microscopy
DSC:	Differential Scanning Calorimetry
FTIR:	Fourier Transform Infrared Spectroscopy
GC:	Gas Chromatography
ICP-MS:	Inductively Coupled Plasma- Mass Spectrometry
ICP-OES:	Inductively Coupled Plasma- Optical Emission Spectrometry
MICS:	Made in Italy Circular and Sustainable
SEM-EDX:	Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy
TGA:	Thermogravimetric Analysis
XRF:	X-ray Fluorescence Spectroscopy
XRPD:	X-ray Powder Diffraction

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Chapter 1: INTRODUCTION

1.1. Project Context

The transition toward a circular economy requires an integrated science-based criteria to assess whether recycled materials can reliably exit the waste stream and be reintroduced into industrial value chains. Within this context, the Waste-End project (Spoke 4 of the MICS initiative), a strategic programme dedicated to advancing sustainable waste management and circular economy solution, aims to develop fundamental knowledge on the chemical, physical, structural and morphological characteristics of recycled materials, providing the analytical foundations necessary to support End-of-Waste (EoW) determinations and second-life performance assessment. This initiative seeks to transform waste streams into certified secondary raw materials through the development of innovative technologies, analytical tools, and regulatory frameworks. A core objective of the Waste-End programme is the establishment of scientifically robust End-o-Waste criteria that allow recycled materials to be formally reclassified as non-waste products suitable for commercial use.

To achieve this objective, the Waste-End project adopts a strongly interdisciplinary and experimentally driven approach. Recycled materials are investigated through advanced chemical, physical, structural and morphological characterisation, both before and after recycling as shown in figure 1. These analyses are complemented by studies of environmental behaviour, durability and second-life performance, allowing the project to evaluate not only the technical suitability of recycled materials but also their long-term stability and environmental compatibility.

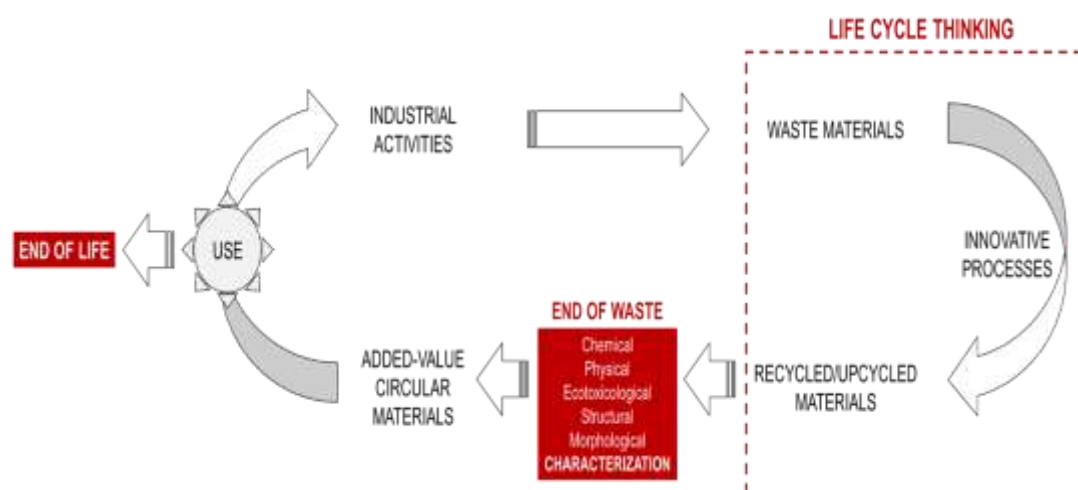


Figure 1: Spoke 4 Waste-End Project illustration (WE project)

This PhD research is fully integrated in this framework and focusses specifically on recycled plastics, whose heterogeneity, additive content, and contamination history pose significant challenges to quality assessment and regulatory compliance. By applying and critically validating complementary analytical techniques: spectroscopy, diffraction, microscopy and trace-element analysis. This work contributes to the broader objectives of the Waste-End project by generating experimentally grounded evidence on material integrity, contamination risks, and structural variability, thereby supporting the development of reliable characterisation protocols for recycled polymers and their safe reintegration into circular industrial systems.

1.2. Plastic Waste and Circular Economy Context

Plastic waste can be either originated at a post-consumer stage, i.e., plastic materials discarded by consumers after use, or at a post-industrial stage, i.e., from plastic scrap generated during the manufacturing phase. In recent years, extensive research has been devoted to improve recycling techniques for managing this plastic waste more effectively. In this context, two recycling approaches can be considered: a “closed-loop”, aimed at processing plastic waste into the same type of product (upcycling), and an “open loop”, where the plastic waste is converted to a different product, usually of lower quality (i.e., downcycling) (Uekert et al., 2023). However, according to the 2024 report from Plastics Europe, only 10-11% of new plastic articles/items currently come from recycled plastics, likely due to its perceived lower quality, often observed as a consequence to the mechanical recycling processes (Plastics Europe, 2024).

1.3. Mechanical recycling and material degradation

In mechanical recycling, the main steps are usually collection, sorting, pre-treatment (e.g., size reduction and melting) and post-processing, towards the production of either, flakes, fragments or pellets. First, the plastic waste is separate collected and further transported to the recycling plants for sorting and processing. Sorting is an essential step in recycling because it permits to remove all unwanted plastics based on their polymer type, colour and additives. This aims to ensure material purity by minimizing unwanted materials before processing. A combination of different sorting techniques is used to obtain a controlled homogeneous stream of material: magnets or magnetic drums, eddy current separators, sink-float separation, induction sorting, X-ray technique, and near infrared (NIR) sensors (Shen & Worrell, 2023). The sorted material is then usually subjected to a size-reduction and washing step for increase

in surface area and dirt removal. For the production of pellets, after sorting, the material is melted at a temperature ranging from 200°C-275°C. The final processing step is determined by the desired final product: injection moulding, blow moulding, film blowing or fibre extrusion.

Mechanical recycling can lead to a decline in the properties of recycled plastics compared to their virgin counterparts, primarily due to polymer degradation. During processing, the scission of long polymer chains reduces the molecular weight of the material, negatively impacting its mechanical performance. For example, studies have shown that the viscosity of recycled polyamide (PA6) decreases due to degradation, as determined through rheological analysis, indicating a reduction in molecular weight and an increased flow rate, which in turn affects the mechanical behavior of the plastic (Yap et al., 2024a). Similarly, properties such as tensile strength, elongation, notched impact strength, and bending strength tend to deteriorate after the recycling of polyethylene and polypropylene. In the case of polypropylene (PP), its shorter polymer chains and higher number of chain ends lead to reduced molecular entanglement and weakened C-C bonding during stretching, ultimately affecting its elongation properties (Carniel et al., 2024; CuPolystyrene (PS)o et al., 2023).

Alternatively, pyrolysis can be used to treat plastic waste for material recovery. First, plastic waste molecules are broken down the different monomers, which are then used as fuels or feedstocks for new plastics. However, the use of this treatment as a proper “recycling” technique is still debated as it alters deliberately the molecular structure of polymers (Pierri et al., 2024).

1.4. Regulatory framework and quality requirements

In Europe, recycled plastics can be remarketed as secondary raw materials whether compliant with the so called "End-of-Waste" criteria (Johansson, 2023). These require that i) the waste-derived material has undergone treatment (e.g., recycling), ii) the outcome from recycling answers to a market need while iii) meeting the performance standards of their virgin counterpart, and iv) avoiding adverse risk on environments or human health from its intended use. For recycled plastics, these general criteria were ultimately translated into specific requirements on input materials, allowed recycling treatments and quality of output plastics (Pierri et al., 2024). While lacking a definitive operational definition, the quality of recycled plastics is evaluated based on the content of hazardous and restricted substances, as well as their potential to substitute raw counterparts. This substitutability is assessed by measuring a set of polymer-specific characteristics outlined in industry-standard technical references, such

as EN 15347, 15342, 15344-46, and 15348. These characteristics include physical parameters (e.g., color, density, shape), chemical (e.g., ash content, volatile content, extraneous polymers), and mechanical properties (e.g., Melt Flow Rate, Impact Strength, Tensile stress at yield). Although this set of parameters is part of the routine characterization of recycled plastics, it could not provide a comprehensive understanding on the degraded quality of recycled plastics when compared with the non-recycled ones. Consequently, there may be a need to expand this operational definition by incorporating less conventional materials' features to gain a more thorough insight into the impact of the mechanical recycling process.

In this context, recycled plastic polymers can be better investigated from a chemical, structural, morphological and physical point of view (Table 1).

Table 1. Summary of properties, and related analytical methods, for an in-depth assessment of recycled plastics quality.

Properties	Characteristic	Analytical method
Chemical	Elemental composition	X-ray Fluorescence (XRF)
	Trace metals concentrations	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
	Organic compounds concentrations	Gas Chromatography-Mass Spectrometry (GC-MS)
	Functional groups	Fourier Transform Infrared Spectroscopy (FTIR)
	Nonpolar molecular structures and conjugation	Raman Spectroscopy
Structural	Crystalline and amorphous phase quantification	X-ray Powdered Diffraction (XRPD)
	Molecular weight distribution	Gel Permeation Chromatography (GPC)
Morphological	Surface morphology and micro void formation	Scanning Electron Microscopy (SEM)
	Nanoscale mechanical property mapping	Atomic Force Microscopy (AFM)
Physical	Melting/Crystallisation behaviour	Differential Scanning Calorimetry (DSC)

Thermal stability and decomposition temperature	Thermogravimetric Analysis (TGA)
Detailed Viscosity profile	Rotational Rheometry

1.5. Limitations of Current Quality Assessment Approaches

Current industrial quality assessment of recycled plastics is largely based on a limited set of bulk physical and processing parameters, such as melt flow index (MFI/MFR), density, tensile strength, impact resistance, colour, and ash content (Dewi et al., 2023). While these parameters are useful for basic process control and batch-to-batch consistency, they provide only indirect and often incomplete information on the chemical, structural, and compositional state of recycled polymers (Gao et al., 2024). In particular, they do not explicitly capture polymer chain degradation, oxidation state, polymer mixture complexity, filler composition, or trace contamination, all of which critically influence long-term performance and application suitability (Esmaeili et al., 2023). Mechanical recycling subjects polymers to repeated thermal, mechanical, and oxidative stresses, leading to chain scission, crosslinking, and additive depletion (Lamtai et al., 2023). These molecular level changes are not directly reflected in standard mechanical or rheological tests, which may remain within acceptable ranges even when significant chemical degradation has occurred (Lamtai et al., 2023). As a result, materials may pass conventional quality control criteria while exhibiting reduced durability, increased brittleness, or altered ageing behaviour in service (Titone et al., 2025).

Furthermore, current quality assessment practices often assume a relatively homogenous polymer composition, whereas post-consumer recycled streams are intrinsically heterogenous. Incomplete sorting, contamination by incompatible polymers, and carry-over of fillers and additives result in materials that are compositionally complex both at the micro and macro scale (Dawoud & Taha, 2024). Conventional quality metrics are poorly suited to detecting such heterogeneity and may therefore mask critical incompatibilities that affect processing stability and product performance (Golkaram et al., 2022).

From a regulatory point of view, recycled plastics must comply with threshold concentration limits for restricted substances as defined by frameworks such as REACH and RoHS, which specify maximum allowable levels for hazardous elements including Pb, Cd, Cr(VI), Hg, and certain flame retardants (M. Bruno & Fiore, 2025). While this is essential for safety, it does not provide insight into the cumulative effects of low-level contaminants, the interaction between fillers and polymer matrices, or the progressive accumulation of impurities

over multiple recycling cycles. Consequently, there is a growing recognition that traditional quality indicators are insufficient to fully characterise the performance potential and risks associated with recycled plastics, particularly in high value or sensitive applications.

1.6. Review of analytical methods

The presence of unknown substances in recycled plastics should be investigated, such as plasticizers, heat and UV stabilizers, flame retardants, pigments for colour, biocides, compatibilizers, fillers (glass and carbon fibres) and anti-sticking agents, which interact with the polymer matrix altering the chemical behaviour of the recycled plastic (Ghosh, 2021). For elemental composition analysis in recycled plastics, the different polymer types, trace metal concentrations, organic compound concentrations, functional groups and nonpolar molecular structures are all studied using specific analytical techniques grouped to provide insights on the chemical properties of the recycled plastics (Mihelčič et al., 2022). To identify the presence of most of the elements in plastics (i.e., occurring in compounds of Ba, Cd, Pb, Sn, Hg, Cu, Sn, Bi) the use of X-Ray Fluorescence (XRF) is suitable (Szeredai et al., 2024). XRF is a destructive rapid analytical technique which provides both quantitative and qualitative analysis for the elemental composition of the recycled plastic (Acquafredda, 2019). To analyse trace metals, such as Pb, Cd, Cr, Hg, Ni, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) are usually used (Klingenberg et al., 2024a). The need to detect and quantify the concentrations of Volatile Organic Compounds (VOCs) is usually addressed by Gas Chromatography coupled with Mass spectrometry (GC-MS). This technique detects and identifies most of organic compounds which could be found in the plastic (Castro et al., 2024). The presence of these VOCs could lead to the formation of peroxides or free radicals in the recycled plastic, thus accelerating degradation. Furthermore, these VOCs with reactive groups may induce oxidation, hydrolysis, or cross-linking in plastics (Janget al., 2022). Fourier-Transform Infra-red Spectroscopy (FTIR) is an appropriate technique in the identification of these reactive groups and other functional groups present in the recycled plastic (Enders et al., 2021). FTIR plays also a crucial role in identifying and classifying polymers (Nel et al., 2021 da Silva & Wiebeck, 2022). One major challenge in plastic recycling is the presence of nonpolar molecules, which could reduce the adhesion of the recycled plastic, reducing its strength thus, affecting its mechanical properties. In this context, Raman spectroscopy, which is also a good tool in identifying polymers (Qin et al., 2024), can help to identify nonpolar molecules due to its ability in detecting vibrational changes in polarizability (Peller et al., 2025).

To have information on polymer chain arrangement, material features at microscopic and molecular level, such as crystallinity and molecular weight distribution of polymers, analytical methods which are grouped in the structural properties sphere have to be used. X-ray Powder Diffraction (XRPD) is a suitable analytical method in quantifying the crystallinity of recycled plastics. This method helps to understand (detect and quantify) the phase transitions (change in crystallinity) during processing and it verifies the crystalline morphology of the recycled plastics (Zeng et al., 2024). Plastics such as polyolefins are highly crystalline with a crystallinity percentage that can be higher than 60%. During recycling of plastics, a reduction in molecular weight can be observed leading to the increase in its crystallinity due to shorter macromolecules in the arrangement of the polymer chain. On the other hand, the degree of crystallinity could decrease due to the presence of contaminants and organics after recycling which can form significant amorphous regions (Zeng et al., 2024). Gel Permeation Chromatography (GPC) allows to obtain the number-average molecular weight (M_n), weight-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) which characterises the recycled plastic (Yap et al., 2024b).

The loss in molecular weight causes the polymer chain to be rearranged influencing also morphological properties, i.e., the surface characteristics of the recycled plastic, with for instance the development of filaments, the deposition of some contaminants and the formation of micro voids due to discontinuity of polymers (Seier et al., 2024). Here, the use of Scanning Electron Microscopy (SEM) permits to have detailed images of the morphology of the plastic to scales that can reach microns (Rodríguez Chialanza et al., 2018). Mostly, it is used as a verification analysis to complement the results of other analyses techniques such as FTIR, XRPD, ICP-OES/ICP-MS. Knowing that molecular rearrangement and change in morphology at small scale is of great importance. This is done using Atomic Force Microscopy (AFM), which allows to map the nanoscale mechanical properties, bringing information on the elasticity, hardness, deformations of the plastic at the nanoscale level (House et al., 2024). This visualisation of the change in mechanical properties at this scale helps have a more detailed comprehensive understanding of the mechanisms happening during degradation (Yavuzyeğit et al., 2023).

Differential Scanning Calorimetry (DSC) is used in analysing the melting/crystallization behaviour of recycled plastic. Also, this method provides info on temperatures at the glass transition, onset of melting, peak of melting and enthalpy of fusion, which are of great importance to measure the crystallinity of the recycled plastic (Lynch et al., 2024). Physical properties are also essential in the description of the material degradation and stiffness. This

thermal analysis technique is appropriate in finger printing the composition of most of recycled polymer blends (Bashirgonbadi et al., 2024a). Thermal stability and decomposition temperature which are major analyses to be performed on recycled plastics are achieved using Thermogravimetric Analysis (TGA) (Periasamy et al., 2024).

1.7. Need for Multi-Dimensional Material Characterisation

The intrinsic complexity of recycled plastics necessitates a multi-dimensional approach to material characterisation that extends beyond conventional bulk properties. Recycled polymers are not merely reprocessed versions of virgin materials; they are the result of multiple life cycles, each contributing to chemical modification, additive consumption, filler redistribution, and contamination (Yaroslavov et al., 2022). As such, their performance is governed by a combination of molecular structure, phase composition, filler systems, microstructural organisation, and trace elemental content (Golkaram et al., 2022). A comprehensive assessment of recycled plastic quality therefore requires analytical techniques capable of probing multiple length scales and compositional domains. Molecular-level information is needed to identify polymer type, detect polymer mixtures, and assess chemical degradation. Crystallographic and structural information is required to identify inorganic fillers and evaluate the degree of crystallinity. Microscopic analysis is necessary to visualise phase distribution, filler dispersion, and morphological integrity. Elemental analysis is essential to quantify both intentional additives and non-intentional contaminants, including heavy metals and residues from previous use or processing (Chibwe et al., 2023a).

No single analytical technique can provide all of this information. Spectroscopic methods, while powerful for polymer identification, cannot alone, resolve filler mineralogy or trace metal content (Stavinski et al., 2023). Microscopic techniques reveal morphology but provide limited bulk chemical information (Albatayneh & Akhtar, 2024). Elemental techniques quantify composition but do not identify polymer structure or phase distribution (Pancholi et al., 2022). This inherent limitation underscores the necessity of combining complementary analytical approaches in order to obtain a coherent and reliable picture of recycled plastic composition and integrity. The adoption of a multi-analytical framework is therefore not a matter of methodological preference but a fundamental requirement imposed by the nature of recycled materials. Such an integrated approach enables cross-validation of results, reduces the risk of misinterpretation and allow the complex interactions between polymer matrices, fillers, and contaminants to be properly understood.

1.8. Research Gaps in the field and problem statement

Despite the extensive body of literature on polymer degradation, recycling technologies, and analytical methods, there remains a significant gap in the integrated characterisation of real post-consumer recycled plastics. Many existing studies focus on virgin polymers, laboratory-prepared blends or model degradation systems, which do not adequately represent the heterogeneity, contamination, and processing history of industrial recyclates. As a result, the analytical strategies reported in literature are often developed under controlled conditions and may not perform robustly when applied to complex, pigment-rich, filler loaded recycled materials.

In the context of a circular economy, the quality of recycled plastic is paramount. Therefore, the analytical methods used to assess recycled plastics must be precise and efficient. The techniques discussed in this chapter (FTIR, Micro-Raman, XRF, ICP, XRPD, SEM, and DSC) are essential for characterizing the physical, chemical, and structural properties of plastics. While each method has proven its value, none alone can provide a complete picture of plastic quality or degradation behaviour; thus, the combination of two or more of these techniques will give more accurate information on a recycled plastic. The majority of studies employ this single-technique approaches or limited combinations of methods, providing fragmented views of material composition. For instance, while FTIR can reveal chemical degradation, it provides little insight into morphological or elemental changes. Similarly, SEM is powerful for visualizing surface damage or filler dispersion but lacks chemical specificity. ICP-MS offers excellent sensitivity for elemental quantification, yet it does not inform on the structural or morphological state of the material. XRPD, while ideal for identifying crystalline phases and fillers, cannot detect amorphous or molecular-level degradation. This siloed application of methods often results in fragmented understanding, with little correlation drawn between the chemical, structural, and morphological transformations occurring in recycled plastics. There is therefore a clear need for an experimentally validated, multi-analytical framework specifically tailored to the characterisation of heterogeneous recycled plastics. Such a framework must be capable of identifying polymer matrices and mixtures, resolving inorganic filler systems, quantifying trace contaminants, and visualising morphological features, while remaining robust in the presence of pigments, additives, and degradation products.

The central problem addressed in this thesis is the absence of an integrated, performance-validated analytical pathway for the comprehensive characterisation of end-of-waste recycled plastics, capable of capturing their chemical, structural, morphological, and

contaminant-related complexity. This work seeks to address this gap by systematically screening, testing, and integrating complementary analytical techniques to develop a robust methodology applicable to real recycled materials, rather than idealised laboratory systems. By correlating results across these complementary methods, this study also provides a more holistic understanding of recycled plastic performance, supporting quality assessment frameworks in the context of circular economy goal.

1.9. Research questions, objectives and Hypothesis

To better perform this research, based on the literature review and the gaps found in the field the following research questions were developed:

- 1- What combination of analytical techniques can provide a comprehensive evaluation of chemical, structural, and physical characteristics of end-of-waste plastic materials?
- 2- How do these properties comply with current European regulations for secondary raw materials?
- 3- Can cross-analysis of data from different techniques provide reliable indicators of recycled material quality and suitability for reintegration into the circular economy?

To address these questions, it is necessary to establish clear assumptions that guide the experimental and analytical phases of the study. Also based on the gaps in the field and regulatory demands the following hypotheses have been formulated:

- 1- A multi-technique analytical pathway integrating FTIR, XRPD, SEM, and ICP methods enables accurate characterization of recycled plastics.
- 2- Some end-of-waste plastic samples do not fully comply with European regulatory thresholds for contaminants and performance criteria.
- 3- Exposure to environmental stressors such as UV and ultrasonic waves accelerates degradation processes and alters the physiochemical properties of recycled plastics.

In order to verify these hypotheses, a set of target research objectives was defined to provide both methodological and analytical direction. These objectives permit to transit from the conceptual framework of the hypotheses into practical steps. Each objective is shaped to generate evidence that supports or refutes the proposed hypotheses, permitting this study to contribute both on the scientific understanding and to advancement of circular economy practices for recycled plastics. The research objectives are:

- 1- To design and implement a comprehensive analytical pathway combining chemical, structural, morphological, and elemental techniques (FTIR, XRPD, SEM, ICP) as seen in figure 2 for the characterisation of end-of-waste plastic materials
- 2- To cross analyse results from difference techniques in order to assess material quality and determine compliance with European regulatory standards (e.g REACh, RoHS)
- 3- To contribute to the development of reliable quality indicators for recycled plastics that support their reintegration into the circular economy.

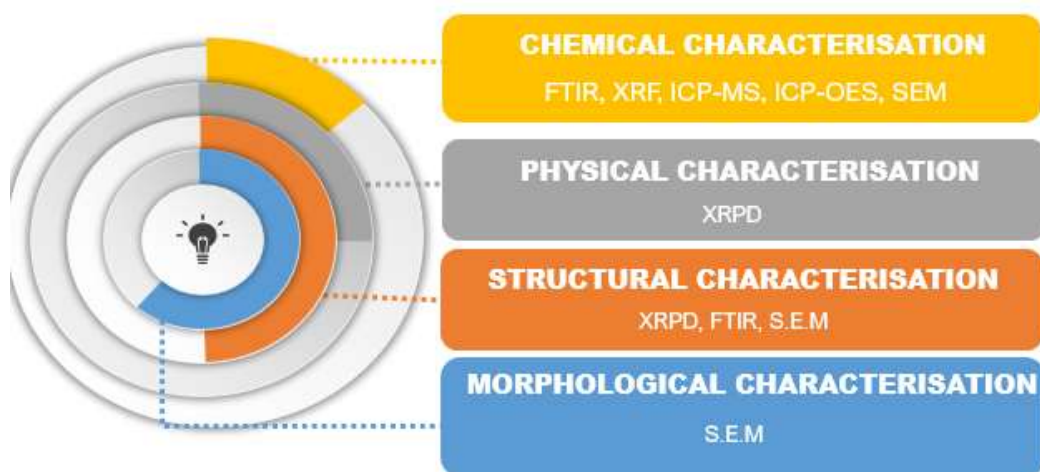


Figure 2: Grouped analytical methods used for the chemical, physical, structural and morphological characterisation of recycled plastics

1.10. Scientific approach and summary of chapters

This thesis adopts a systematic, multi-analytical, and experimentally validated approach to the characterisation of recycled plastics, designed to address the intrinsic heterogeneity and compositional complexity of end-of-waste polymer materials. Rather than relying on a single analytical technique or on idealised laboratory systems, the work is structured around the critical evaluation, selection, and integration of complementary analytical methods capable of analysing recycled plastics across multiple compositional and structural dimensions.

The scientific approach is grounded in three core principles:

- 1- Literature-informed method selection,
- 2- Experimental validation under realistic sample conditions,
- 3- Cross-technique integration.

A comprehensive critical review of analytical techniques for recycled plastic characterisation (chapter 2) was first conducted to identify methods theoretically suitable for

polymer identification, filler analysis, morphological investigation, and trace element quantification. Based on this review, a set of candidate techniques was shortlisted. These techniques were then subjected to systematic experimental screening and performance evaluation (chapter 3), including variations in sample preparation, instrumental conditions, and inter-laboratory comparison where applicable. This screening phase enabled the identification of methodological limitations, robustness issues, and matrix effects specific to heterogeneous recycled plastics, leading to the selection of a final analytical workflow.

The selected workflow integrates Fourier Transform Infrared Spectroscopy (FTIR) for polymer identification and mixture detection, Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDX) for morphological and microchemical analysis, X-ray Powder Diffraction (XRPD) for crystalline filler identification, and Inductively Coupled Plasma Spectrometry (ICP-MS) for bulk elemental and trace metal quantification. These techniques were chosen not only for their individual capabilities but for their complementarity, allowing cross-validation of results and reduction of interpretative ambiguity.

To further assess methodological robustness and sensitivity, targeted experimental tests were incorporated into the approach. These included cryomilling experiments to evaluate the influence of particle size and crystallinity of XRPD performance, accelerated UV ageing experiments to understand stability of polymer identification and morphology under photo-oxidative stress and inter-laboratory comparisons of elemental analysis protocols to determine the most reliable digestion and measurement strategy. The inclusion of these validation steps ensures that the analytical pathway developed in this thesis is not merely theoretically appropriate but demonstrably effective under realistic and challenging conditions.

The experimental results obtained using the final analytical workflow are presented in Chapter 4, where polymer identity, mixture complexity, filler systems, and trace metal content are characterised in detail with an integrated discussion of these findings on material integrity, recyclate quality and circular economy applications. The thesis concludes by synthesising the methodological and scientific contributions of the work and outlining perspectives for future research and industrial implementation.

Through this structured and evidence-based approach, the thesis aims to establish a robust analytical framework for the comprehensive characterisation of recycled plastics, bridging the gap between laboratory-scale analysis and the practical requirements of industrial recycling and regulatory compliance.

1.11. Conclusion

The transition towards a circular economy for plastics represents both an environmental necessity and a scientific challenge. While mechanical recycling remains the most widely implemented strategy, the intrinsic heterogeneity, degradation, and contamination of recycled plastics impose significant limitations on material performance, application potential, and long-term sustainability. Current industrial quality assessment practices, largely based on bulk physical and mechanical parameters, are insufficient to capture the chemical, structural, morphological, and compositional complexity of end-of-waste polymer materials. As a result, critical information related to polymer mixture content, filler systems, additive legacy and trace contamination often remains unresolved.

This thesis is positioned within this context, addressing the need for a comprehensive, multi-dimensional characterisation of recycled plastics. By recognising that recycled polymers are not simply reprocessed virgin materials but complex products of multiple life cycles, the work adopts an integrated analytical strategy designed to interrogate material composition across multiple length scales and chemical domains. The limitations of single-technique approaches and idealised laboratory studies highlight the importance of developing methodologies that are robust under realistic conditions, including pigment-rich, filler-loaded, and contaminated matrices.

The scientific approach of this thesis is therefore based on the critical review, experimental screening, and integration of complementary analytical techniques, with the objective of establishing a validated workflow capable of capturing polymer identity, mixture complexity, filler composition, morphological integrity, and trace elemental content. By bridging the gap between theoretical method suitability and practical performance on real recyclates, this work seeks to contribute both to the scientific understanding of recycled polymer materials and to the development of more reliable quality assessment strategies for circular economy applications. The following chapter presents a critical review of analytical techniques for recycled plastic characterisation, providing the theoretical and methodological foundation upon which the experimental strategy of this thesis is built.

Chapter 2: CRITICAL REVIEW OF ANALYTICAL TECHNIQUES FOR THE CHARACTERISATION OF RECYCLED PLASTICS

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ABSTRACT

Assessing the detailed characteristics of recycled plastics is essential for evaluating their quality and suitability for high-value applications compared to virgin polymers. This review provides a comprehensive overview of advanced analytical techniques used for characterizing the chemical, structural, morphological, and physical properties of recycled polymeric materials. The techniques examined include Fourier Transform Infrared Spectroscopy (FTIR), Micro-Raman spectroscopy, X-ray Fluorescence (XRF), Inductively Coupled Plasma (ICP) techniques, X-ray Powder Diffraction (XRPD), Differential Scanning Calorimetry (DSC), and Scanning Electron Microscopy (SEM). These methods are critically assessed for their effectiveness in detecting polymer degradation, surface and structural alterations, and the presence of contaminants—factors frequently introduced during mechanical recycling processes. For each technique, this review outlines the working principles, sample preparation protocols, and illustrative case studies while discussing their advantages, limitations, and operational challenges. By synthesizing current knowledge and methodological advancements, this review aims to support the development of robust and standardized quality assessment protocols. Enhancing the reliability and precision of recycled plastic characterization will improve their acceptance as high-quality secondary raw materials, thereby facilitating their upcycling and contributing to the broader goals of the circular economy.

Keywords: *spectroscopic analysis; thermal properties; mechanical recycling; degradation; post-consumer; post-industrial; trace elements; functional groups; molecular weight distribution; quality*

2.1 Introduction

The increasing reliance on recycled plastics within circular economy strategies has intensified the need for robust, reliable, and scientifically grounded methods to assess recycled material quality. Unlike virgin polymers, recycled plastics are inherently heterogeneous systems, often composed of mixed polymer phases, residual additives, inorganic filler, degradation products, and trace contaminants originating from multiple use and recycling cycles. This complexity challenges conventional quality assessment approaches, which frequently rely on simplified physical mechanical, or compositional indicators that are insufficient to capture the true chemical and structural state of recycled materials.

In the world, plastic is commonly used, thus generating waste which can be either originated at a post-consumer stage, i.e., plastic materials discarded by consumers after use, or at a post-industrial stage, i.e., from plastic scrap generated during the manufacturing phase. In recent years, extensive research has been devoted to improve recycling techniques for managing this plastic waste more effectively. The plastic can be either downcycled or upcycled depending on the recycling process used. (Uekert et al., 2023). However, according to the 2024 report from Plastics Europe, only about 10-11% of new plastic articles/items currently come from recycled plastics, likely due to its perceived lower quality, often observed as a consequence to the mechanical recycling processes.

Plastic waste can either be recycled by chemical or mechanical processes. In mechanical recycling, the main steps are usually collection, sorting, pre-treatment (e.g., size reduction and melting) and post-processing, towards the production of either, flakes, fragments or pellets. First, the plastic waste is separate collected and further transported to the recycling plants for sorting and processing. Mechanical recycling can lead to a decline in the properties of recycled plastics compared to their virgin counterparts, primarily due to polymer degradation. Alternatively, for chemical recycling pyrolysis can be used to treat plastic waste for material recovery. First, plastic waste molecules are broken down to the different monomers, which are then used as fuels or feedstocks for new plastics. However, the use of this treatment as a proper “recycling” technique is still debated as it alters deliberately the molecular structure of polymers (Pierri et al., 2024).

The primary objective of this chapter is to provide a detailed review of the properties (chemical, structural, physical and morphological) governing recycled plastic quality. After

identifying the properties, discuss the commonly used analytical techniques in the context of the plastic industry as presented in Table 1.

Chemical properties refer to elemental composition of plastics in terms of different polymer types, trace metals concentrations, organic compound concentrations, functional groups and nonpolar molecular structures (Mihelčič et al., 2022). In particular, the presence of unknown substances should be investigated, such as plasticizers, heat and UV stabilizers, flame retardants, pigments for colour, biocides, compatibilizers, fillers (glass and carbon fibres) and anti-sticking agents, which interact with the polymer matrix altering the chemical behaviour of the recycled plastic (Ghosh, 2021). While some of these additives are classified as hazardous, they may still be present in recycled plastic. However, since they no longer serve a functional purpose in the material's second life, they are now regarded as contaminants (Prajapati et al., 2021, Di Duca et al., 2024). To analyse these characteristics, specific analytical techniques are used.

To identify the presence of most of the elements in plastics (i.e., occurring in compounds of Ba, Cd, Pb, Sn, Hg, Cu, Sn, Bi) the use of X-Ray Fluorescence (XRF) is suitable (Szeredai et al., 2024). XRF is a destructive rapid analytical technique which provides both quantitative and qualitative analysis for the elemental composition of the recycled plastic (Acquafredda, 2019). To analyze trace metals, such as Pb, Cd, Cr, Hg, Ni, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) are usually used (Klingenberg et al., 2024a). The need to detect and quantify the concentrations of Volatile Organic Compounds (VOCs) is usually addressed by Gas Chromatography coupled with Mass spectrometry (GC-MS). This technique detects and identifies most of organic compounds which could be found in the plastic (Castro et al., 2024). The presence of these VOCs could lead to the formation of peroxides or free radicals in the recycled plastic, thus accelerating degradation. Furthermore, these VOCs with reactive groups may induce oxidation, hydrolysis, or cross-linking in plastics (Jang et al., 2022). Fourier-Transform Infra-red Spectroscopy (FTIR) is an appropriate technique in the identification of these reactive groups and other functional groups present in the recycled plastic (Enders et al., 2021). FTIR plays also a crucial role in identifying and classifying polymers (Nel et al., 2021 da Silva & Wiebeck, 2022). One major challenge in plastic recycling is the presence of nonpolar molecules, which could reduce the adhesion of the recycled plastic, reducing its strength thus, affecting its mechanical properties. In this context, Raman spectroscopy, which is also a good tool in identifying polymers (Qin et al., 2024), can help to identify nonpolar

molecules due to its ability in detecting vibrational changes in polarizability (Peller et al., 2025).

The **structural properties** include those characteristics providing info on the polymer chain arrangement and features of the material at a microscopic/molecular level, such as crystallinity and molecular weight distribution). A polymer usually shows a dominant crystal type due to the thermodynamic stability of a molecular conformation, but this could be modified through additives such as nucleating agents or flow-induced crystallization (Bowen et al., 2024). Plastics such as polyolefins are highly crystalline with a crystallinity percentage that can be higher than 60%. During recycling of plastics, a reduction in molecular weight can be observed leading to the increase in its crystallinity due to shorter macromolecules in the arrangement of the polymer chain. On the other hand, the degree of crystallinity could decrease due to the presence of contaminants and organics after recycling which can form significant amorphous regions (Zeng et al., 2024). Crystallinity can also affect the morphology and the mechanical properties (e.g., viscosity). X-ray Powder Diffraction (XRPD) is a suitable analytical method in quantifying the crystallinity of recycled plastics. This method helps to understand (detect and quantify) the phase transitions (change in crystallinity) during processing and it verifies the crystalline morphology of the recycled plastics (Zeng et al., 2024). The extent to which the molecular weight is decreased during mechanical recycling can be assessed by the Gel Permeation Chromatography (GPC). GPC allows to obtain the number-average molecular weight (M_n), weight-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) which characterises the recycled plastic (Yap et al., 2024b).

The loss in molecular weight causes the polymer chain to be rearranged influencing also **morphological properties**, i.e., the surface characteristics of the recycled plastic, with for instance the development of filaments, the deposition of some contaminants and the formation of micro voids due to discontinuity of polymers (Seier et al., 2024). Here, the use of Scanning Electron Microscopy (SEM) permits to have detailed images of the morphology of the plastic to scales that can reach microns (Rodríguez Chialanza et al., 2018). Mostly, it is used as a verification analysis to complement the results of other analyses techniques such as FTIR, XRPD, ICP-OES/ICP-MS. Knowing that molecular rearrangement and change in morphology at small scale is of great importance. This is done using Atomic Force Microscopy (AFM), which allows to map the nanoscale mechanical properties, bringing information on the elasticity, hardness, deformations of the plastic at the nanoscale level (House et al., 2024). This visualisation of the change in mechanical properties at this scale helps have a more detailed

comprehensive understanding of the mechanisms happening during degradation (Yavuzyeğit et al., 2023).

Finally, the **physical properties** refer to the response of recycled plastics to temperature and applied stresses, i.e., melting/crystallization behaviour, thermal stability, decomposition temperatures and viscosity profiles. Differential Scanning Calorimetry (DSC) is used in analysing the melting/crystallization behaviour of recycled plastic. This thermal analysis technique is appropriate in finger printing the composition of most of recycled polymer blends. Based on the known melting and crystallization degrees, it permits to identify the polymers present (Bashirgonbadi et al., 2024b). Also, this method provides info on temperatures at the glass transition, onset of melting, peak of melting and enthalpy of fusion, which are of great importance to measure the crystallinity of the recycled plastic (Lynch et al., 2024). Physical properties are also essential in the description of the material degradation and stiffness. One of the major analyses on the physical properties of these recycled plastics is the thermal stability and decomposition temperature which is mostly performed using Thermogravimetric Analysis (TGA) (Periasamy et al., 2024). With the addition of some compatibilizers, the thermal stability of some plastics can either increase or decrease during recycling, TGA evaluates the changes and with a good interpretation, we could determine how it affects degradation of the recycled plastic (Nizamuddin et al., 2024). As temperature affects the recycled plastic, so does processing conditions and shear rate. The combination of these changes results in a resistance to flow of the polymer known as viscosity of the polymer. This property of the plastic gives insights into the molecular weight, degradation level and processability (J. Zhang et al., 2024). To follow these changes during recycling, a detailed viscosity profile is needed, it is obtained using Rotational Rheometric Analysis (Kneidinger et al., 2024).

In this context, this review aims to provide a comprehensive overview of the analytical techniques used for the in-depth assessment of the quality of recycled plastics, focusing on the chemical, physical, structural and morphological characteristics. It will introduce the principles of each analytical technique, sample preparation and discuss case studies emphasizing on their applications in recycled plastics. Also, their advantages, limitations and ongoing challenges will be discussed in this review. By synthesizing current knowledge and identifying research gaps, this review seeks to contribute to the development of improved quality assessment methods ultimately supporting upcycling of recycled plastics as good quality secondary raw materials.

2.2 Analytical Techniques For The Characterization Of Recycled Plastics.

I. Chemical Characterization Techniques.

Chemical characterization plays an important role in evaluating the composition and potential contaminants in recycled plastics. These methods provide essential insights into the presence of additives, residual monomers, degradation products, and trace metals that may affect the performance and reusability of recycled materials. In this section, major chemical techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Micro-Raman Spectroscopy, X-ray Fluorescence (XRF), and Inductively Coupled Plasma (ICP) are discussed, highlighting their principles, applications and relevance in the quality assessment of recycled plastics.

A. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique for the characterization of recycled plastics, providing essential chemical and structural information. It enables the identification of polymer types, additives, and degradation products by analysing the vibrational modes of molecular bonds (Alqaheem & Alomair, 2020). This technique is very important in recycling applications, as it helps in the determination of the purity and composition of recovered plastics, ensuring their suitability for reuse. FTIR spectroscopy works by measuring the absorption of infrared light at specific wavelengths corresponding to the vibrational frequencies of chemical bonds within a polymer. This produces a characteristic spectrum, often referred to as a molecular fingerprint, which can be compared against reference databases for material identification (Xiao et al., 2019). In recycled plastics, FTIR is particularly useful for detecting oxidation, hydrolysis, and other chemical modifications resulting from processing and environmental exposure which are related to the material degradation and guiding the development of more sustainable recycling methods.

Proper sample preparation is critical for obtaining high-quality FTIR spectra. Recycled plastic samples can be analysed in various forms, including thin films, pressed pellets, and powders. ATR-FTIR (Attenuated Total Reflectance) is commonly used for plastics (figure 3), as it allows direct analysis without extensive sample preparation. Cryomilling may be employed to produce fine powders from bulk recycled plastics, improving spectral homogeneity and ensuring consistent measurements. During FTIR measurements, the choice between transmission and reflection modes depends on sample thickness and transparency.

Transmission mode is ideal for thin films, while ATR mode is preferred for bulk samples as it enhances surface sensitivity. Reflection techniques, such as specular and diffuse reflection, can also be applied to detect surface modifications in recycled plastics. Ensuring proper contact between the sample and ATR crystal improves data quality and reproducibility. FTIR spectrometers typically consist of a broadband infrared light source, an interferometer, and a detector. The interferometer modulates the infrared light, and the resulting signal is processed using Fourier transformation to generate the absorption spectrum (C. Bruno et al., 2022). Modern FTIR instruments are equipped with highly sensitive detectors, such as mercury cadmium telluride (MCT) or deuterated triglycine sulphate (DTGS), which enable precise spectral acquisition.

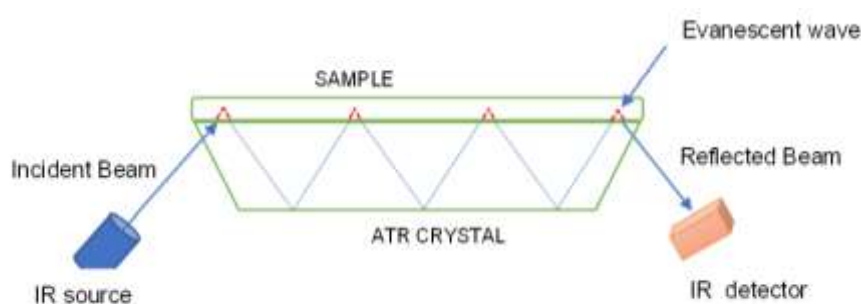


Figure 3: general principle of ATR-FTIR spectroscopy

The selection of spectral resolution and scanning parameters depends on the level of detail required. A resolution of 4 cm^{-1} is commonly used for general polymer identification, while higher resolutions (e.g., 1 cm^{-1}) are preferred for detecting subtle chemical changes (Rosalina et al., 2024). Data acquisition software facilitates spectrum processing, peak assignment, and quantitative analysis, helping researchers determine polymer composition and detect contaminants in recycled plastics.

Several literature studies discuss the results of FTIR analysis on recycled plastic samples. (Dodi et al., 2022) in their recent study on substrate-contamination identification on recycled polyethylene terephthalate (PET) using ATR-FTIR, used rat DNA samples to contaminate blends of recycled PET. In the bare (100%) recycled PET substrate, the ATR spectrum showed absorption bands of the main functional groups present in PET. 2960cm^{-1} for the aliphatic C-H symmetrical bond stretching, 1712cm^{-1} for the ester carbonyl stretching, 1407cm^{-1} for stretching of the C-O group deformation of the O-H group, 1236cm^{-1} for the terephthalate group, 1088cm^{-1} to the methylene group and 722cm^{-1} to the polar ester groups interactions with benzene rings. FTIR results after this experiment permitted to see the

differences in peaks (corresponding to specific chemical groups at specific vibrational modes) present between the 100% recycled PET with those present in the recycle PET blends. This helped identify the presence of PP, HDPE and AL nano powder in every sample where they were blended. In the determination of differences present between virgin Polyethylene (vPE) and recycled Polyethylene (rPE), some peaks due to the combined action of oxygen, heat and ultraviolet light are altered (W. Zhang et al., 2024). The peaks involved were; the 1240cm^{-1} corresponding to the in-plane bending vibration peak of alcohol hydroxyl group in rPE which was significantly enhanced compared to vPE. A new peak was generated at 1720cm^{-1} in the rPE which corresponded to the stretching vibration peak of the carbonyl group. At about $3300\text{--}3500\text{cm}^{-1}$, rPE had a weak broad peak, corresponding to the stretching vibration peak of the hydroxyl group in the carboxyl group. The increase in peak strength in rPE compared to vPE indicates the molecular chain breakage in rPE which caused an increase in the number of molecular chains relative to vPE. As for vPP and rPP, differences could be seen in the broadness of the peak at 1744cm^{-1} which was broader for rPP, this peak is associated to the carbonyl peak. They attributed this observation to the short service life and limited degree of degradation in rPP, indicating it was in a relatively early stage of degradation. Mwanzia et al., 2023 were able to correlate the qualitative results from FTIR for 2 different samples to the mechanical properties in order to choose which sample is more appropriate for upcycling into the manufacturing of composite panels. Their FTIR results showed that one sample of recycled PP had weaker intensities and these intensities were not too similar to those of the reference PP, whereas the second sample had similar intensities as those of the reference PP thus better for upcycling than its counterpart. To continue, FTIR has been successfully applied in plastic waste recycling to identify polymer types within mixed streams and to detect the presence of common fillers, including rutile, talc, clay, silica, and calcite (Audy et al., 2022). These results highlight the versatile utility of FTIR in chemical characterization of recycled plastics.

FTIR faces some challenges in plastic analysis. Firstly, the plastic samples have to be dry to avoid interference with moisture and give false results. This is because FTIR is sensitive to moisture because water strongly absorbs infrared (IR) radiation- especially in the O-H stretching region ($3200\text{--}3600\text{cm}^{-1}$) and bending region (approximately 1600cm^{-1}). Secondly it faces some challenges with irregular shaped microplastics as reflectance measurements can cause refractive (Maria, 2012). It is also less effective for plastic samples smaller than 500microns and can take time to analyse large samples with high spatial resolution (Nguyen et al., 2023).

B. Micro-Raman Spectroscopy.

Micro-Raman spectroscopy is a sensitive and non-destructive analytical technique widely used for the characterization of recycled plastics as FTIR. It provides molecular-level information on polymer structure, chemical composition, and material degradation. By analysing the vibrational modes of polymer chains, Micro-Raman spectroscopy enables the identification of different plastic types, distinguishing between polymers with similar elemental compositions but different molecular arrangements. One of the primary advantages of Micro-Raman spectroscopy is its ability to detect chemical modifications induced by recycling processes (Pantoja Munoz et al., 2018). Variations in peak intensities and shifts in Raman spectra can indicate oxidative degradation, cross-linking, or chain scission, which are crucial for understanding material aging and performance (Cialla-May et al., 2019). Also, the technique permits the analysis of polymer blends, fillers, and additives, making it a valuable tool for assessing the quality and consistency of recycled plastics.

Micro-Raman spectroscopy requires minimal sample preparation, making it an efficient technique for recycled plastic analysis. Solid plastic fragments, thin films, or even microplastics can be directly analysed without extensive pre-processing. However, for enhanced spectral quality, surface cleaning may be performed to remove contaminants that could interfere with Raman signals. Measurements are typically carried out using a Raman spectrometer equipped with a microscope, allowing for high spatial resolution and targeted analysis of microscopic regions. Different laser wavelengths (e.g., 532 nm, 785 nm, or 1064 nm) can be used depending on the polymer type and fluorescence interference. The choice of excitation wavelength is critical, as certain polymers exhibit fluorescence that may overshadow Raman signals, necessitating the use of longer-wavelength lasers (Cialla-May et al., 2019). Micro-Raman analysis is performed in either confocal or non-confocal mode, with confocal setups offering improved spatial resolution and depth profiling capabilities. The laser is focused on the sample using high-magnification objectives (figure 4), ensuring precise Raman signal acquisition. The collected spectra are then processed using software such as WiRE, LabSpec, or Origin for baseline correction, peak fitting, and spectral deconvolution.

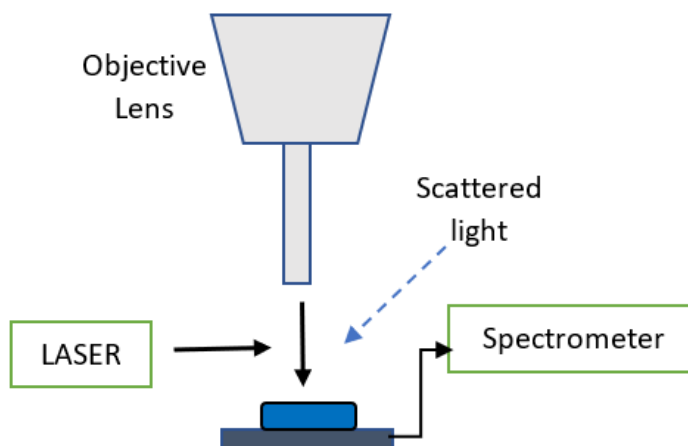


Figure 4: Micro-Raman functioning principle

Raman spectral databases, including those provided by commercial libraries or open-source platforms, are used for polymer identification and comparison. Advanced analysis techniques such as principal component analysis (PCA) can be applied to differentiate between similar plastic types and detect subtle structural changes caused by recycling processes.

Micro-Raman was used in the identification of nano particles (NPs) on the surface of recycled PVC powder (RPP) from commercially available recycled plastics. They performed Raman single-spot analysis on the NPs obtained from the shedding of the powder and had as result Raman spectral features with characteristic adsorption peaks at 639 and 697cm^{-1} which are assigned to the C-CL stretching vibration in the PVC polymer, also adsorption peaks at 1178 , 1432 and 2917cm^{-1} corresponding to the C-H rocking vibration, C-H bending vibration, and C-H stretching vibration respectively (W. Zhang et al., 2020). These peaks matched with the spectrum of the RPP matrix indicating that these NPs originates from the grinding of RPP. (Marica et al., 2022) studied the vibrational changes after 5 years of degradation of LDPE plastic using Micro-Raman spectroscopy and compared it to a reference LDPE polymer before it could be recycled. As results, they observed a higher background on the waste's spectra compared to that of the reference spectra indicating a possible presence of micro-impurities, persistent even after regular washing of the plastic waste. Also, they observed a change in functional groups orientation or interaction between adjacent polymer chains due to continuous photo-oxidation. Micro-Raman spectroscopy is widely used in the identification of microplastics and it was used to assess the quality of recycled plastic bottles. The PET bottles made of PP caps and PE seals were found to have about 242 ± 64 MPP/L after 11 openings of

the bottle (Giese et al., 2021). 80% of the MPP were identified in the smallest size class investigated (10-50 μm) These above results show the importance of Micro-Raman in the specific chemical characterization of recycled plastics.

Micro-Raman is a technique which is easily affected with fluorescence interference especially with samples containing dyes or additives which mask the Raman signal, a common example is the presence of carbon black in the recycled plastic analysed which causes total fluorescence during analysis with micro-Raman. As compared to FTIR it may require higher acquisition times and sample preparation needs to be keenly done to avoid any surface contamination (Xu et al., 2018)

C. X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) is a widely used analytical technique for the elemental analysis of recycled plastics. This method provides qualitative and quantitative information on the elemental composition of materials, making it particularly useful in assessing the presence of additives, contaminants, and hazardous elements in recycled plastic waste (Acquafredda, 2019). By detecting elements ranging from sodium (Na) to uranium (U), XRF plays a critical role in ensuring compliance with regulatory standards, such as the Restriction of Hazardous Substances (RoHS) directive, which limits toxic elements like lead (Pb), cadmium (Cd), and mercury (Hg) in consumer products. XRF analysis essential insights into the composition of recycled plastics, including: identification of additives and fillers, detection of heavy metals, verification of polymer, homogeneity and contamination assessment (Chibwe et al., 2023a).

XRF analysis requires minimal sample preparation, making it highly efficient for routine screening of recycled plastics. Solid samples, including plastic pellets, flakes, or films, can be directly analysed using handheld or benchtop XRF instruments. For better precision in quantitative analysis, samples are ground into fine powders and pressed into pellets to ensure uniform measurement conditions. Calibration with certified reference materials (CRMs) is crucial to obtaining accurate elemental concentrations. XRF instruments operate in two main configurations: energy Dispersive X-ray Fluorescence (EDXRF) and Wavelength Dispersive X-ray Fluorescence (WDXRF). EDXRF uses a solid-state detector to simultaneously detect multiple elements. It is widely used for rapid screening and portable applications whereas WDXRF utilizes a crystal-based wavelength dispersion system to achieve higher resolution and sensitivity, making it ideal for detailed quantitative analysis (Acquafredda, 2019). A primary X-ray source, typically an X-ray tube, excites the sample, causing characteristic

secondary X-rays to be emitted (figure 5). These emissions are detected and analysed to determine the elemental composition. The choice of detection system and operating parameters depends on the required sensitivity and the specific elements of interest. Data processing is performed using specialized software such as Bruker's SPECTRA.ELEMENTS or PANalytical's SuperQ, which facilitate elemental quantification, peak deconvolution, and background subtraction. These software solutions enable precise interpretation of XRF spectra, ensuring reliable identification of elements even at trace levels.

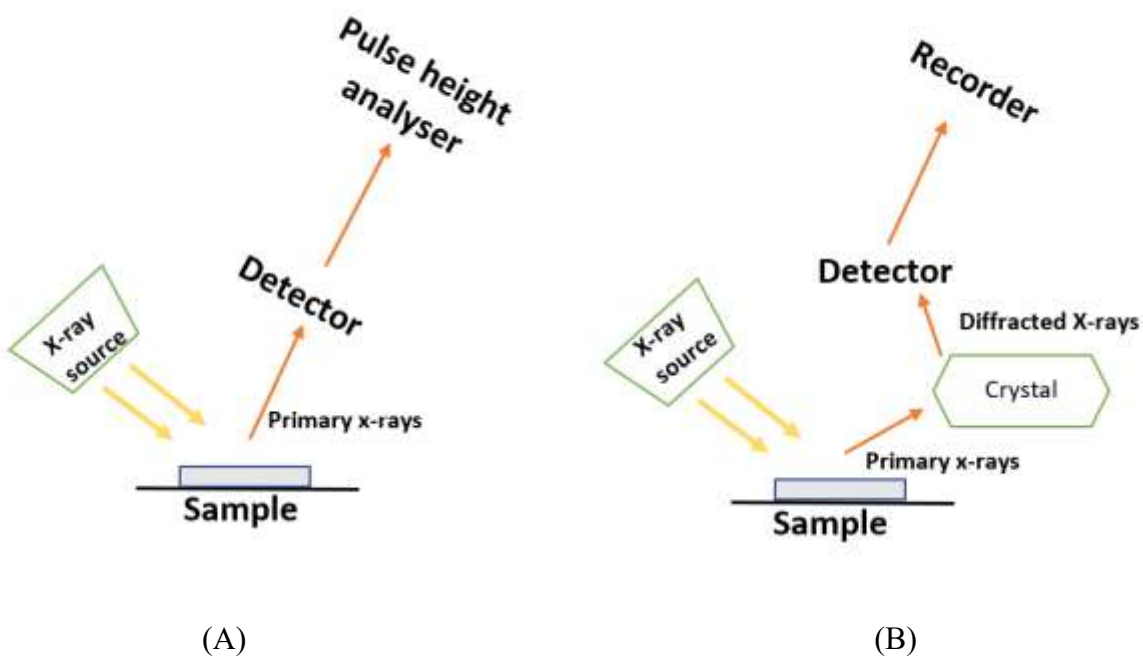


Figure 5: XRF functioning principle, A represents EDXRF, and B is the WDXRF.

Several studies have shown the use and importance of XRF in recycled plastic analysis. Kajiwarra et al., 2022 used XRF to identify and quantify bromine in 540 recycled plastic consumer products including children's toys, and found that 19% of these samples contained bromine at a concentration of $\geq 30\text{mg/kg}^{-1}$. This XRF step was a first step to identify the bromine positive samples. These samples were further chemically analysed using combustion-ion chromatography to reveal the presence of polybrominated diphenyl ether (PBDEs). In the aim of removing bromine from recycled plastic from waste electric and electronic equipment, Charitopoulou et al.,(2023) used XRF as in the previous study to identify the bromine positive samples with aim to reduce the bromine quantity in these samples , because they hypothesized that the bromine present represented Brominated flame retardants (BFR's). With the use of Soxhlet extraction they were able to reduce the bromine incorporated into the samples and studied their degradation behaviour using Evolved Gas Analysis (EGA). The results showed

that the thermal degradation in most cases followed a one-step mechanism, verifying their hypothesis on BFR's. In these two cases, we see the use of XRF as a primary tool to screen samples for a deeper analysis in detecting contaminants in recycled plastics. Also XRF was used to detect rare earth oxides markers in recycled polyoxymethylene (POM). The use of these rare earth oxides markers is used to mark the POM before it enters the recycling process for improvement in tracer-based sorting (Jandric et al., 2024). XRF showed the accumulation of these rare earth oxides into the mechanically recycled POM.

With all the above applications in recycled plastic analysis, XRF have some challenges in quantifying light elements like carbon, nitrogen and oxygen which are fundamental components of plastic polymers due to their low fluorescence and absorption effects. These elements emit low-energy fluorescence signals that are easily absorbed by the air or the sample. Additionally, there is the problem due to matrix effects, especially in heterogenous recycled plastic samples where different densities, compositions and surface characteristics can impact on the fluorescence intensities. If the instrument is not properly calibrated, it might lead to inaccurate readings.

D. Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) techniques, including ICP-Optical Emission Spectroscopy (ICP-OES) and ICP-Mass Spectrometry (ICP-MS), are good analytical tools for detecting and quantifying trace elements in recycled plastics. These techniques provide high sensitivity and precision on materials in general, making them essential for assessing the presence of heavy metals and additives in plastic waste streams. ICP is particularly useful for ensuring compliance with environmental and safety regulations, such as the Restriction of Hazardous Substances (RoHS) directive and the European Union's REACH regulation (Holub et al., 2023). ICP analysis enables the detection and quantification of a wide range of toxic metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) to assess the safety of recycled plastics (Chibwe et al., 2023b). It also helps in obtaining additive composition through the identification of elements like antimony (Sb) used as a catalyst in polyethylene terephthalate (PET) production, or zinc (Zn) and calcium (Ca) in stabilizers for polyvinyl chloride (PVC). Finally, with ICP techniques we can perform material purity verification which consist of determining contamination levels and the presence of foreign elements that may have been introduced during the recycling process.

like XRF, which is destructive, ICP requires extensive sample preparation. Plastic samples must first undergo digestion to convert solid material into a liquid form suitable for analysis. This process typically involves: acid Digestion: the use of strong acids, such as nitric acid (HNO_3) or hydrochloric acid (HCl), often combined with hydrogen peroxide (H_2O_2), to break down the polymer matrix and release elements into solution. Microwave-Assisted Digestion: a more controlled and efficient method that speeds up the dissolution process and ensures complete digestion of the plastic sample (Holub et al., 2023). Filtration and Dilution: ensuring that the final solution is free from particulates and at a suitable concentration for analysis.

Once prepared, the liquid sample is introduced into the ICP instrument, where it is nebulized and transported into the high-temperature plasma (6000–10,000 K). The elements in the sample are ionized, and their emission spectra (ICP-OES) or mass-to-charge ratios (ICP-MS) are measured for quantitative analysis. ICP instruments operate in two primary modes: ICP-Optical Emission Spectroscopy (ICP-OES): uses the emitted light from excited atoms and ions to determine elemental concentrations. It is well-suited for multi-element analysis at moderate concentrations. ICP-Mass Spectrometry (figure 6), detects ions based on their mass-to-charge ratio, offering ultra-trace sensitivity, making it ideal for detecting elements at parts-per-billion (ppb) or even parts-per-trillion (ppt) levels. The choice between ICP-OES and ICP-MS depends on the required sensitivity and the specific elements of interest. A well-optimized setup includes appropriate calibration with certified reference materials (CRMs) and internal standards to correct for matrix effects and instrument drift. Data analysis is performed using specialized software, such as Agilent's ICP Expert or Thermo Fisher's Qtegra, which allows for peak identification, quantitative calibration, and interference correction. These tools ensure accurate element quantification and data validation, critical for quality control in recycled plastic applications.

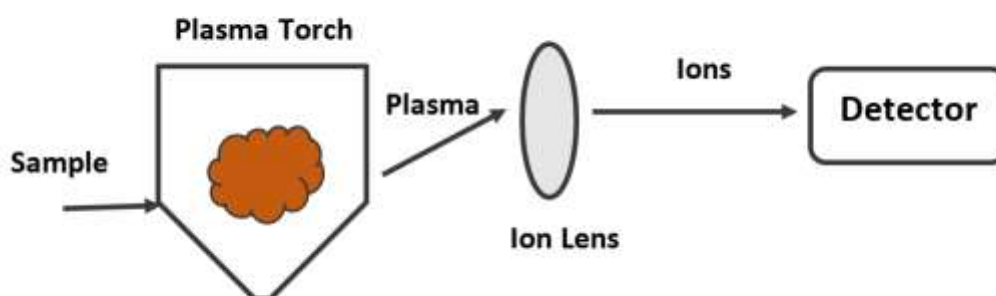


Figure 6: ICP-MS functioning principle

To determine the exact heavy metal load in recycled plastics, Klingenberg et al. (2024) used ICP-MS for this quantification. They were able to determine the quantities of ten regulated metals (automotive regulatory basis; Global automotive declarable substance list); Hg, As, Cd, Cr, Co, Cu, Se, Pb, Sn and Ni in post-consumer (PCR), post-industrial (PIR) and virgin polypropylene. Cu and As showed the highest and lowest concentration respectively in both PCR and the virgin material. Also, regarding health and regulatory concerns, the measured heavy metal content of PCR material did not meet the threshold. The virgin PP is less contaminated than the recycling samples as expected with .. On the other hand, Chibwe et al., (2023) analysed 60 elements (metals and metalloids) from 21 recycled plastic samples (HDPE, LDPE, PP, PE) using ICP-MS. They detected at least 36 of the 60 elements in every sample and their concentrations varied by almost 7 orders of magnitude (<0.005 -2980 mg/kg). Ca, Na and Fe had the highest concentrations whereas Hg, Zn, Pb, Cr, Ca, Sb, Na, Sr, Fe, Co were the most frequently detected. In the aim to determine different contaminants such as metals, polycyclic aromatic hydrocarbons (PAHs), dioxin-like biphenyl polychlorides (PCBs) and polychlorinated-dibenzo-p-dioxins and furans (PCDD/Fs) in recycled polyethylene (R-LDPE) samples of agricultural, post-commercial, post-industrial and post-consumer origin, Núñez et al.(2022) used ICP-MS as preferred technique for the determination of metals in these samples. They were analysed for the following metals: Li, B, Na, Mg, Al, Ca, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Ag, Cd, In, Ba, Tl, Pb and Bi. Amongst these metals, those present in most samples and in higher concentration were: Fe, Al, Cu, Pb, Zn, and Ti. The samples with the higher concentrations of these metals, were found to be those who were recycled through traditional washing and were also the dirtiest, as they contained inks and were coloured samples.

ICP being a good elemental analytical technique, but it is a destructive technique and require complex, and time-consuming sample preparation. Cryomilling and acid digestion are necessary for the plastic matrix breakdown and this step is at risk of contamination and/or incomplete digestion (Di Duca et al., 2024). To continue, ICP-MS is very sensitive to matrix effects and spectral interferences (e.g. polyatomic ions), which must be corrected through careful method development. Finally certified reference materials are essential to ensure reliable results.

II. Structural Characterization Techniques

In structural characterization, the techniques used are essential in the understanding how recycling processes affect internal arrangement of polymer chains, particularly in terms

of crystallinity and phase composition. These structural properties have a direct impact on the mechanical strength, thermal stability, and performance of recycled plastics. X-ray Powder Diffraction (XRPD) is a widely used technique in this context, giving information into crystalline phases, crystallite size, and the degree of crystallinity. In this section, the application of XRPD in analysing recycled plastics is explored, with attention to its role in evaluating structural changes and identifying phase transitions caused by degradation or reprocessing.

X-ray Powder Diffraction (XRPD)

X-ray Powder Diffraction (XRPD) is a powerful analytical technique widely used in the characterization of recycled plastics, providing crucial insights into their structural properties. It enables the identification of crystalline phases, determination of the degree of crystallinity, and estimation of crystalline domain sizes (Bunaciu et al., 2015). These aspects are essential in assessing the impact of recycling processes on polymer structure, as changes in crystallinity can influence the mechanical performance and thermal stability of the material. Beyond phase identification, XRPD also allows for the quantitative determination of crystalline and amorphous phases, offering a deeper understanding of the molecular organization within recycled plastics (Rajeswari et al., 2019). Structural refinement techniques further aid in determining atomic coordinates and crystallographic occupancies (Epp, 2016), providing detailed structural information that helps evaluate material consistency and degradation effects caused by recycling. This level of analysis is fundamental in optimizing recycling processes and improving the quality of secondary raw materials.

The accuracy of XRPD analysis depends on proper sample selection, preparation, and loading. Recycled plastic samples are typically processed into fine powders using cryomilling, a technique where materials are milled at extremely low temperatures to prevent thermal degradation and minimize structural alterations. This ensures a more homogeneous sample and enhances the quality of diffraction data. Proper sample loading into the XRPD instrument, such as ensuring even distribution and minimizing preferred orientation effects, is crucial for obtaining reliable diffraction patterns and precise structural information. XRPD measurements can be performed using diffractometers operating in either reflection or transmission geometry, depending on the sample characteristics and analytical requirements (Khan et al., 2020). Reflection mode is more commonly used for bulk materials, while transmission geometry is advantageous for thin or low-density samples, as it enhances sensitivity to weakly scattering

phases. The choice of geometry affects data quality and should be carefully considered based on the nature of the recycled plastic sample.

A monochromatic X-ray source is typically used (figure 7) to improve the resolution and accuracy of diffraction patterns, reducing background noise and improving phase identification. Data collection involves scanning over a range of diffraction angles (2θ) to capture the characteristic diffraction peaks of the crystalline phases present (Bunaciu et al., 2015). For phase identification, XRPD data is compared against reference databases such as the ICDD Powder Diffraction File (PDF), using software like Profex and HighScore Plus. These programs facilitate peak fitting, phase quantification, and structural refinement, ensuring a thorough interpretation of the data.

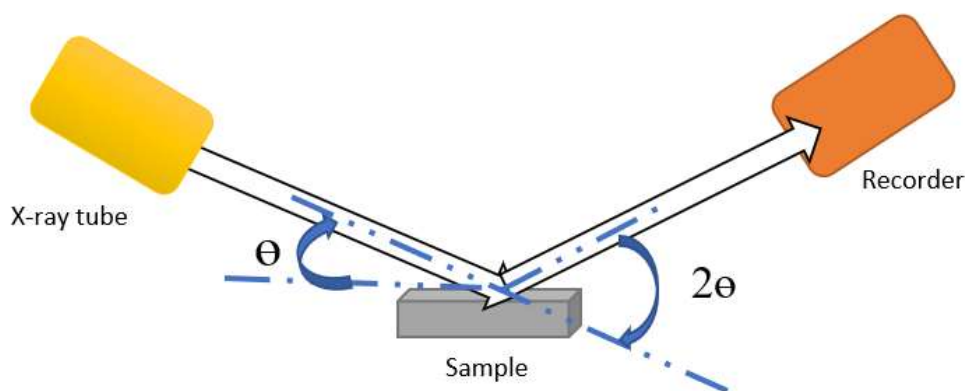


Figure 7: XRPD Instrument major components

XRPD has been widely used to evaluate the effects of fillers on crystallization and to identify the phases of filler materials (Świetlicki et al., 2020) detected brucite, periclase and quartz in talc filled recycled PP and observed an increase in elasticity modulus with increasing talc content. To study the interaction between calcite and plastics in plastic-reinforced mortar (Kane et al., 2021) used XRPD to determine which treatment technique between microbially induced calcium carbonate precipitation (MICP) and enzymatically induced calcium carbonate precipitation (EICP) deposited more calcite on recycled PET, PVC, LDPE, PP, PS or ABS flakes and their results showed that MICP deposited more calcite with 5% MICP-treated rPET having 88% of the compressive strength of the plastic-free mortar. For crystallite size evaluation (Mekprasart et al., 2018) saw a decrease in the crystallite size of recycled PET nanocomposites when increasing rutile content from 2% to 10%. This reduction might be attributed to the photocatalytic activity of rutile, which could induce some changes in PET crystal structure through light-induced reactions or stress relaxation.

XRPD is usually limited when analysing highly degraded plastics, because it requires finely powdered samples and may not detect low levels of crystallinity or subtle structural changes without advanced data analysis. This technique is not also suitable for identifying chemical composition or non-crystalline additives. Finally, phase identification relies on comprehensive reference databases, and overlapping peaks in complex mixtures can complicate interpretation.

III. Physical Characterization Technique

Here, the understanding of how materials respond to temperature, mechanical stress, and processing conditions will be discussed. Amongst the techniques used, Differential Scanning Calorimetry (DSC) is particularly important for assessing thermal transitions such as melting, crystallization, and glass transition temperatures. These properties provide understanding into the thermal history, degree of crystallinity, and potential degradation of the plastic. This section highlights the use of DSC in recycled plastic analysis, with emphasis on its ability to track thermal behaviour and support the assessment of material consistency.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to characterize the thermal properties of recycled plastics. It measures the heat flow associated with phase transitions, providing critical information on the thermal behaviour of polymers. DSC plays a crucial role in assessing the quality and consistency of recycled plastics, ensuring they meet performance standards for reuse in various applications. DSC analysis provides information into several important properties of recycled plastics, including: glass Transition Temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity. T_g indicates the temperature at which the polymer transitions from a rigid to a rubbery state, crucial for determining processing and application conditions. T_m helps in identifying the crystalline phase melting point, helping differentiate polymer types and assess thermal stability whereas crystallization Temperature (T_c) shows the temperature at which polymer chains arrange into a crystalline structure upon cooling, useful in evaluating recrystallization behaviour (Müller & Michell, 2016). Degree of Crystallinity quantifies the proportion of crystalline material in a polymer, influencing mechanical properties like strength and rigidity. By conducting DSC under oxidative conditions, it is possible to study the degradation and stability of recycled plastics, essential for quality assurance (Gliński et al., 2024).

DSC requires careful sample preparation to ensure accurate thermal analysis, the recycled plastic samples can be in the form of pellets, films, or powders. Samples are typically cryomilled to obtain fine powders, ensuring homogeneity and reproducibility in measurements. A small, precisely weighed amount of the sample (typically 5-10 mg) is placed in an Aluminium pan, which is then sealed and loaded into the DSC instrument (figure 8). A reference pan, usually empty, is placed alongside for comparison. DSC operates by heating or cooling the sample at a controlled rate while measuring the heat flow differences between the sample and reference (Šudomová et al., 2023). The key parameters include the heating rate: commonly set between 5-20 °C/min to optimize resolution and sensitivity. It can be performed under nitrogen to prevent oxidation or air to study degradation processes and finally the last parameter is the temperature range: typically, between -50 °C to 300 °C, depending on the polymer type . Specialized software such as TA Instruments' Universal Analysis or Netzsch Proteus is used to analyse DSC thermograms. These tools allow for: baseline corrections, Peak integration for enthalpy calculations and Curve fitting to determine precise transition temperatures.

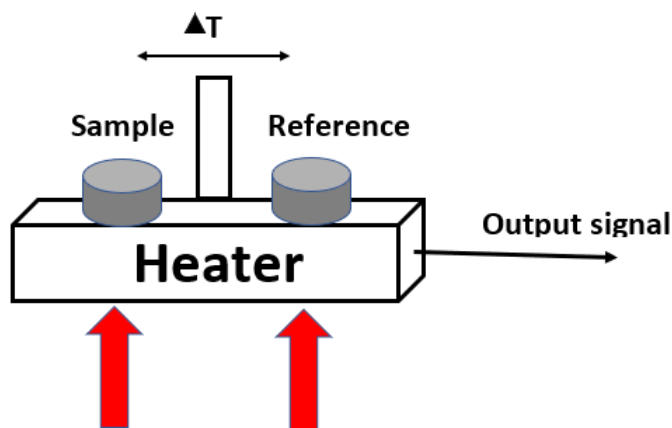


Figure 8: DSC Instrument main components and basic principle.

Petrovič et al. (2022) performed a comparative analysis of virgin and recycled plastics based on thermochemical characteristics to study the impact of recycling on the material properties. The plastic chosen in this study was High Dense Polyethylene (HDPE) and from the results obtained, it is shown that the ash content was much higher in the recycled HDPE (5.18wt%) than in virgin HDPE (0.03wt%), differences between the samples were seen in their different crystallinity degrees: 79.8% for virgin HDPE and 19% for recycled HDPE. R-HDPE

exhibited lower degradation temperatures as compared to virgin HDPE, most likely due to presence of impurities. Knowing that varying amounts of polypropylene are usually found in recycled high-density polyethylene (rHDPE), Juan et al. (2021) used DSC to determine the presence of PP in these blends. The different melting temperatures (T_m) of both polymers allows to differentiate PP from HDPE. The T_m corresponding to the rHDPE appears around 131°C, while a small peak is observed at 163°C for PP impurities in these recyclates, thus confirming contamination of the rHDPE. In the same line with Juan et al. (2021), Scoppio et al. (2022) used DSC, to evaluate PE and low-density PE (LDPE) content in recycled polyolefin blends. Firstly, they performed DSC analysis on 29 virgin PE materials; HDPE, LDPE, linear low-density polyethylene (LLDPE), metallocene linear low-density polyethylene (m-LLDPE), secondly, some HDPE, LLDPE and LDPE grades were blended with PP homopolymer and block copolymer in different concentrations and finally recycled grades from post-consumer feedstocks streams were analysed with the virgin and blended materials. Results showed that, heating up samples at 10°C/min after a first heating and subsequent cooling cycle, the different types of PE grades melt in separate temperature ranges, depending on their microstructures. The different PE melting points found for the PE types analysed with the DSC, were essential in determining the content of the corresponding grades in the polymer blends. Furthermore, the change in thermal behaviour of the recycled grades indicates a change in microstructure and possibly the presence of impurities other than PE and PP.

The presence of additives, plasticizers and fillers can make it difficult for data interpretation of thermal transitions because they could be affected by sample mass, heating rate, and preparation inconsistencies. With blends, analysing the polymer will be challenging due to the overlapping or interfering thermal transitions. DSC being a bulk technique, localized degradation or surface-level differences in recycled plastics may go undetected.

IV. Morphological Characterization Techniques

Morphological characterization provides valuable information about the surface and microstructural features of recycled plastics, revealing the physical effects of degradation, contamination, or filler distribution. Scanning Electron Microscopy (SEM) is a key technique in this domain, offering high resolution imaging of surface texture and internal structural features. In this section, the role of SEM in evaluating the morphology of recycled plastics is discussed.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique used for analysing the surface morphology and microstructural properties of recycled plastics. By providing high-resolution imaging, SEM allows for detailed examination of polymer degradation, contamination, and structural modifications that occur during recycling processes (Saleh et al., 2024). It is particularly useful in assessing the impact of mechanical, thermal, and chemical treatments on plastic materials, helping to ensure quality control and optimize recycling techniques. SEM helps in observing the Surface Morphology, filler and additive distribution, micro-structural defects. Detailed imaging of surface textures, defects, and irregularities, can be obtained and they can indicate the effects of mechanical recycling, degradation, or contamination. Also, the identification of inorganic fillers, reinforcements, and additives such as calcium carbonate, glass fibres, and titanium dioxide dispersed within the polymer matrix can be seen. Microstructural Defects such as detection of voids, cracks, and delamination within recycled plastics (Seier et al., 2024), which may affect mechanical properties and processing performance are also visible with the help of SEM.

Proper sample preparation is critical for obtaining high-quality SEM images of recycled plastics. Since plastics are typically insulating materials, they require specific preparation steps: cryo-fracturing: to examine internal structures, samples may be cryogenically fractured using liquid nitrogen, producing clean, non-deformed surfaces. Coating with Conductive Materials: to prevent charging effects in non-conductive plastics, a thin layer of gold (Au), platinum (Pt), or carbon (C) is often sputter-coated onto the sample surface before SEM imaging. Embedding and Sectioning: in cases where cross-sectional analysis is required, samples can be embedded in epoxy resin and microtome to reveal internal structures (Karaagac et al., 2021). To obtain accurate and detailed microstructural information of recycled plastics, careful selection of imaging and detection parameters should be done during SEM analysis (Fang et al., 2024). The choice of the electron beam source influences image quality, with Field Emission Gun (FEG) Sem offering a better resolution compared to conventional tungsten filament SEMs,. Acceleration voltage is mostly set between 1 and 20kV, depending on the desired depth of penetration and image resolution. For surface imaging, lower voltages are preferred. Whereas for deeper structural analysis higher voltages are preferred. SELS systems have various detectors (figure 9), including Secondary Electron Detector (SED) and Back scattered electrons (BSE) detectors, which highlights compositional differences by detecting contrasts in atomic number. With SEM varying magnification ranges can be obtained going from 10x to over 100

000x making ideal for both low-resolution overview scans and high resolution analysis of surface features and internal microstructures in recycled samples. SEM images are processed and analysed using specialized software such as ImageJ, Thermo Fisher's Avizo, and Oxford Instruments' AZtec. These tools facilitate: image enhancement and contrast adjustment, particle size and shape analysis, elemental mapping when combined with EDX (Energy Dispersive X-ray Spectroscopy).

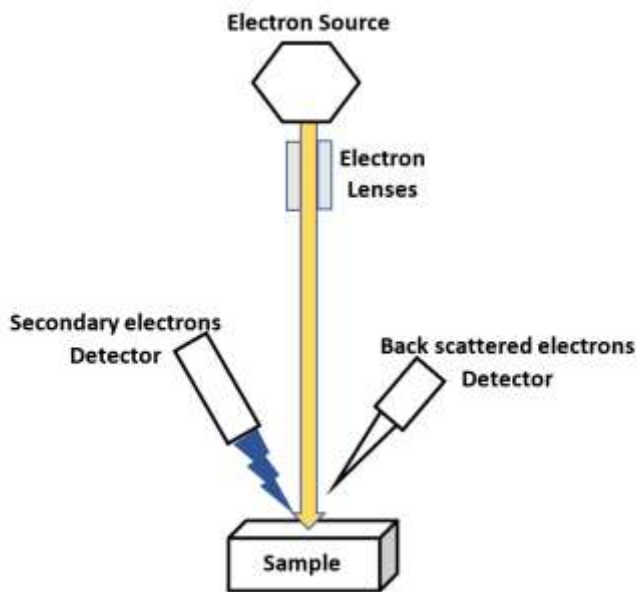


Figure 9: SEM principle with SED and BSE detectors.

In the plastic industry, SEM has been used to detect impurities and assess the effectiveness of various recycling techniques. For example, in the dissolution and filtration of polypropylene composites with glass fibres, SEM images demonstrated that the recycling technique successfully recovered clean glass fibres with minimal organic matter (Gravgaard et al., 2024). Additionally, this technique has been used to monitor the recycling process of polymer composites filled with quartz. SEM analysis revealed that during the molding process, quartz can redistribute and form agglomerates, particularly in areas where the polymer is depleted of filler (Pavlyuchkova et al., 2024). To upcycle buffing leather fibres from industrial waste streams and explore their potential as flame-retardant additives for polypropylene, (Sanchez-Olivares et al., 2024) used SEM to investigate the impact of these fibres on polypropylene morphology and its other properties. Their findings revealed that the addition of buffing leather fibres significantly enhances the flame retardancy of polypropylene without significantly altering its morphology. In the aim of evaluating the effects of mechanical

recycling on microstructure of recycled high-density polyethylene pellets and bottles, (Zeng et al., 2023) evaluated the morphological properties of the rHDPE and virgin HDPE using High Resolution SEM (HR-SEM) at 25 and 1000m magnifications. The surface of region of the rHDPE pellets exhibited relatively rough textures compared to the vHDPE and the with magnifications at 1000x, rHDPE pellets has large pits and cracks in the wake of the formation of rugged textures. This shows how good SEM can present immediate differences between recycled and virgin plastics.

SEM provides limited chemical composition of the sample on its surface or fractured cross-section providing only point information and not bulk information of heterogenous recycled materials. Moreover, non-conductive polymers as plastics, can accumulate charges on the surface thus leading to image distortion after a period time. Interpretation of degradation mechanisms (e.g oxidation) only through SEM imaging is often insufficient without supporting techniques.

2.3 Conclusion

In the context of a circular economy, the quality of recycled plastic is paramount. Therefore, analytical methods used to assess recycled plastic must be precise and efficient. The techniques discussed in this review (FTIR, micro-Raman, XRF, ICP, XRPD, SEM, and DSC) are essential for characterizing the physical, chemical, and structural properties of plastics. While each method has proven its value, none alone can provide a complete picture of plastic quality or degradation behaviour, thus the combination of 2 or more of these techniques will give more accurate information on the recycled plastic.

However, as specified in this review, each technique also faces specific limitations-whether related to sample preparation, sensitivity, matrix effects, or interpretation complexity. These challenges show the need for standardizing protocols, proper calibration, and complementary use of methods to overcome analytical gap. This characterization is invaluable to polymer engineers in designing new products. While other techniques exist, this review focused on the most commonly used methods for determining the chemical composition, structure, and reorganization of polymeric chains in plastics. The underlying principles of each technique were explained to illustrate the type of results they provide.

Chapter 3: METHODOLOGICAL APPROACH FOR ADOPTION OF THE ANALYTICAL PATHWAY.

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ABSTRACT

The characterisation of recycled plastics presents significant analytical challenges due to their intrinsic heterogeneity, complex additive formulations, and potential contamination arising from multiple life cycles. This work describes the methodological approach adopted to identify, test and validate an appropriate analytical pathway for the comprehensive characterisation of heterogeneous recycled polymer materials. Building on a critical review of analytical techniques presented in chapter 2, a set of complementary methods; Micro-Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, X-ray Fluorescence (XRF), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-ray Powder Diffraction (XRPD), and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX) were shortlisted and experimentally evaluated. Each technique was assessed through targeted experimental testing, focusing on sample preparation strategies, analytical sensitivity, reproducibility, and suitability for complex recycled plastic matrices. Micro-Raman Spectroscopy was limited by fluorescence due to pigments and carbonaceous additives commonly present in recyclates. XRF was tested for bulk elemental analysis, but calibration constraints resulted in unreliable quantification. Comparative inter-laboratory testing of ICP-OES and ICP-MS, combined with different digestion protocols, demonstrated that ICP-MS coupled with closed-vessel digestion provided better results for trace and ultra-trace elemental analysis. XRPD was investigated to determine the optimal sample form for crystalline phase identification, revealing that cryo-milling enhanced diffraction

quality and filler detectability compared to bulk pellets or flakes. SEM-EDX analysis, conducted without coating, proved effective for direct observation of surface morphology, filler dispersion, and inorganic inclusions at the microscale. FTIR spectroscopy emerged as an important tool for polymer identification and functional group analysis, remaining effective even in the presence of fillers and following accelerated ageing experiments. The outcome of this methodological screening led to the final selection of FTIR, XRPD, SEM-EDX and ICP-MS as the core analytical techniques employed in this thesis.

Keywords: *Recycled plastics, methodological screening, FTIR, XRPD, SEM-EDX, ICP-MS.*

3.1 Introduction

For the previous years, recycled plastics have drawn interests in the world of science. Many characterisations have been performed on these materials to better understand the composition and performance of these materials before re-inserting into the market (Claeys et al., n.d.). In the recycling industry, those driving the market are the industries and regulations giving the direction to the kind of testing to be performed. Usually, the characterisations performed are to determine the mechanical performance, and response to external stresses like temperature and applied forces (Hassan et al., 2022a). The mechanical performance is one of the most important properties of plastics to determine its final use. Also, thermal properties are of good importance because they help determine the processing and application conditions of the plastic (Wang et al., 2023). For recycling plastics, which are intended to replace the virgin in the cycle, they need to have the same mechanical properties as those of the virgin plastic. In recycling plastics these properties may vary considerably due to contamination, degradation and presence of some fillers within the polymer matrix (Paiva et al., 2022). This complexity of recycled plastics has a resultant of affecting the mechanical properties but before affecting the mechanical and thermal properties, they start by changing the chemical properties, structural and morphological properties of the plastic (Paiva et al., 2022). In this logic, to better understand why and how the mechanical property of a certain recycled plastics, varies it is crucial to first understand the chemical composition (functional groups, presence of fillers and polymer mix), crystallinity, structural alignment of molecules and crystals, finally the morphology of the recycled plastic to see if there is any change compared to the virgin corresponding plastic (Gnoffo et al., 2025).

To better understand these properties of recycled plastics, many analytical techniques have been developed. Some techniques provide specific information on a specific property, where as some are versatile and provide insights on many properties. Concerning chemical properties, techniques like Fourier Transform Infra-Red (FTIR) spectroscopy, X-ray Fluorescence (XRF), Gas Chromatography coupled with Mass Spectroscopy (GC-MS) and Inductively Coupled Plasma coupled with Optical Emission Spectroscopy (ICP-OES) or Mass Spectrometry (ICP-MS) are usually used. For structural properties, X-ray Powdered Diffraction (XRPD) and Scanning Electron Microscopy (SEM). SEM is a versatile technique because it provides insights on the structural, morphological and chemical properties of the recycled plastic. For morphological characterisation, Atomic Force Microscopy is also used to

have information on the morphology of the material. Regarding physical properties techniques like Dynamic Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Rotational Rheometric Analysis are used for thermal and viscosity properties of the recycled plastic.

FTIR is a chemical analytical technique used for identification of polymer types, additives and degradation products by the detection of vibrational transitions characteristic of chemical groups and/or given molecule (Alqaheem & Alomair, 2020). It produces a characteristic spectrum (molecular fingerprint) which can be compared against reference databases for material identification (Xiao et al., 2019). Its application in recycled plastics, permits the detection of oxidation, hydrolysis and other modifications as polymer mixing resulting from processing and environmental exposure. XRF is a quantitative chemical analytical technique which detects elements ranging from Sodium (Na) to Uranium (U), which identifies additives, contaminants and hazardous elements in recycled plastic. XRF provides essential insights into the composition of the material and ensuring compliance with regulatory standards, such as the Restriction of Hazardous Substances (RoHS) directive, which limits toxic elements like lead (Pb), cadmium (Cd) and mercury (Hg) in consumer products (Chibwe et al., 2023a). In XRF calibration with certified reference materials (CRMs) is crucial to obtaining accurate elemental concentrations. As for ICP-OES and ICP-MS, they are good chemical analytical techniques for the detection and quantification of trace elements in recycled plastics. It enables the detection of wide range of metals and toxic metals such as Pb, Cd, Hg and Arsenic (As) to assess the safety of recycled plastics (Chibwe et al., 2023a). GC-MS is also a chemical analytical technique used for the detection of organic compounds which could be found in plastic (Castro et al., 2024). These organic compounds mostly volatile (VOCs), could lead to the formation of peroxides or free radicals in recycled plastics, thus accelerating degradation by inducing oxidation, hydrolysis or cross-linking in plastics (Jang et al., 2022). XRPD on its part is a technique which permits the evaluation of crystallinity and detect the presence of inorganic fillers in polymer matrices (Bunaciu et al., 2015). It helps to understand the phase transitions during processing and it verifies the crystalline morphology of the recycled plastics (Epp, 2016). As for morphological characterisation, SEM is an appropriate technique to have detailed images of the morphology of the plastic to scales that can reach microns (Saleh et al., 2024). With the EDX coupling SEM, permits also to have point elemental composition of the analysed sample. AFM allows to map the nanoscale mechanical properties, giving information on the elasticity, hardness, deformations of the plastic at the nanoscale level (House et al., 2024). For physical properties (thermal analysis) DSC is used for analysing the

melting/crystallization behaviour of the samples. Based on the known melting and crystallisation degrees, it permits to identify the polymers present (Bashirgonbadi et al., 2024a). TGA on the other side evaluates the changes or the thermal stability and decomposition temperature of the sample (Periasamy et al., 2024). All these techniques are unique based on their results and sample preparation methods, but due to processing, industry realities (time consumption) and heterogeneity of recycled plastics it is important to select the best techniques which offers good results in an appropriate time lapse.

With these multitude of analytical techniques, the aim of this work is to establish an approach for the choice of the appropriate analytical pathway (combination of analytical techniques) suitable for a direct comprehension of the complexity of the recycled material. This approach is based on the complementarity of the techniques, the results obtained and the sample preparation methods used per technique.

3.2 Materials And Methods

3.2.1 Samples

For this research, many plastic samples were received and only the ones categorised as End of Waste were chosen to be worked with. End of Waste samples are those secondary raw materials coming from collected plastic waste to be re-used as main intrant instead of virgin plastic in the production of recycled products. They have undergone either mechanical crushing (flakes), some melting (melted and processed) or even further, they were crushed, melted and pelletized (pellets) as shown in figure 10. A total of 34 different end of waste plastic samples from different Italian companies working on the recycling plastics.



Figure 10: The forms and colours of the sample are varying; could be fragmented, processed or pelletized. Homogenous or heterogenous in colour

The samples were codified, in order to Identify the origin of the sample (company), it's category i.e., end of waste. The polymer of the plastic sample was stated on the technical sheet with which the sample was handed in. the polymers were: Polypropylene, Polyamide,

Polystyrene, Polycarbonate, Polyoxymethylene, Acrylonitrile Butadiene Styrene and Polystyrene (PS). Table 2 below shows the number of samples each polymer represented. The main intended end-use of these samples were for packaging, furniture and housing.

Table 2: Table representing all 34 samples with their form, homogeneity and main polymer

SAMPLE ID	PELLET FORM	Homogeneity	Polymer
MMPS1	Fragments	homogenous	polyamide
MMPS2	Fragments	homogenous	polyamide
MMPS3	Processed	homogenous	polypropylene, polyethylene
MMPS4	Fragments	homogenous	polyamide
MMPS5	Fragments	heterogenous	polypropylene, polyethylene
MMPS6	Processed	heterogenous	polypropylene, polyethylene
MMPS7	processed	heterogenous	polypropylene, polyethylene
MMPS8	Fragments	homogenous	polypropylene
MMPS9	Fragments	heterogenous	polypropylene, polyethylene
MMPS10	pellet	homogenous	polypropylene
MMPS11	Fragments	heterogenous	Non identified
MMPS12	Fragments	heterogenous	polypropylene
MMPS13	pellet	homogenous	polypropylene
MMPS14	Fragments	heterogenous	polypropylene, polyethylene
MMPS15	pellet	homogenous	polypropylene, polyethylene
MMPS16	pellet	homogenous	polypropylene
MV1	pellet	homogenous	polypropylene
MMPS17	Fragments	heterogenous	polyamide 6
MMPS18	Fragments	heterogenous	polypropylene, polyethylene

MMPS19	Processed	heterogenous	polypropylene
MMPS20	Fragments	heterogenous	polypropylene, polyethylene
STMP21	pellet	homogenous	ABS
MMPS22	Fragments	heterogenous	polypropylene
SIMPS23	Fragments	homogenous	polycarbonate, polyamide
SIMPS24	pellet	heterogenous	polypropylene, polyethylene
SIMPS25	Fragments	heterogenous	POM
SIMPS26	Fragments	homogenous	polycarbonate
STMP27	pellet	homogenous	Polystyrene
SIMPS28	Fragments	heterogenous	polyamide
SIMPS29	Fragments	heterogenous	ABS
SIMPS30	pellet	homogenous	polypropylene, polyethylene
STMP31	pellet	homogenous	ABS
SIMPS32	Fragments	homogenous	Polystyrene
SIMPS33	pellet	homogenous	polyethylene

3.2.2 Methodological Screening: shortlisting of Analytical Techniques

In order to establish a robust and reliable analytical pathway, a structured methodological approach was adopted to choose the adequate and appropriate analytical technique for the given samples described in section 3.2.1. Based on the critical review of analytical techniques for recycled plastic characterisation presented in Chapter 2, Micro-Raman spectroscopy, FTIR, SEM-EDX, XRPD, ICP-OES and ICP-MS were shortlisted for this study. These methods were identified in the literature as complementary tools capable of addressing polymer identification, morphological heterogeneity, filler characterisation, and trace elemental analysis respectively (Hassan et al., 2022b). The detailed theoretical background advantages and limitations of each technique are discussed in chapter 2. The following sections focus on the experimental validation and selection of these techniques for the specific case of heterogenous recycled plastics.

Following the literature-based identification of suitable methods, it was necessary to evaluate their practical applicability under real laboratory conditions. This included assessing

the availability of the shortlisted techniques within laboratories involved in the project, as well as investigating their performance through targeted experiments involving variations in sample preparation and operating conditions. The shortlisted techniques were applied to representative samples in order to test their sensitivity, accuracy, and suitability for heterogeneous polymer matrices. The results obtained were critically evaluated and, where appropriate, compared with reference values or expected trends reported in the literature. This comparative assessment provided the basis for the subsequent selection or exclusion of techniques and protocols, leading to the definition of the final analytical workflow adopted in this study.

3.2.2.1 Analytical techniques

I. Instruments and protocols screened during method selection

Micro-Raman Spectroscopy

To test Micro-Raman, the instrument used was Oribi Jobin Yvon Labram HR800 spectrometer combined with an Olympus BX41 microscope. Available laser lines: 1) Melles-Griot HeNe laser at 633 nm, 35 mW power, or 2) Torus solid-state laser at 532 nm, 300 mW power. For measurements, samples are placed as-is under the microscope and observed with a 10X objective to select the analysis point. Spectra are recorded with a 50X objective that focuses the laser beam on a 1-micron diameter spot, taking care to set the laser power on the sample to a few mW to avoid degradation. The reported spectra were obtained by averaging three or four 20-second spectra of the desired spectral regions. This technique was evaluated as a complementary technique for polymer identification; however frequent fluorescence and unstable spectra for pigmented recyclates limited reliability, and the technique was not retained as a core method.

X-ray Fluorescence (XRF)

The XRF analysis samples were subjected to high-temperature to enable accurate bulk chemical quantification of inorganic components. Sample preparation followed a standard fusion-bead protocol to minimise matrix effects and improve analytical reproducibility. Initially, a known mass of each sample was used to determine the loss of ignition (LOI) by heating in a Nabertherm L15/11 furnace at 860°C for approximately 20 minutes, followed by calcination at 980°C for 2 hours. The calcined material was subsequently homogenised and mixed with di-lithium tetraborate flux ($\text{Li}_2\text{B}_4\text{O}_7$) in a 1:10 sample-to-flux ratio. The mixture was fused at approximately 1150°C using a Claisse Eagon 2 fluxer to produce homogeneous glass beads suitable for XRF measurement.

XRF analyses were carried out using a PANalytical Zetium wavelength-dispersive X-ray fluorescence (WDS-XRF) spectrometer operated under vacuum conditions and controlled by SuperQ software. The instrument was equipped with a 2.4 kW rhodium (Rh) X-ray tube, five analysing crystals (LiF220, LiF200, Ge, PE, PX1), three detectors (flow counter, scintillation detector, and sealed Xe detector), two collimators (150 μm and 550 μm), and four primary beam filters (Al 200 μm , Al 750 μm , brass 100 μm , brass 400 μm). An automated sample changer accommodating up to 16 samples holders was used to ensure consistent analytical conditions and efficient throughput.

Chemical analysis targeted a broad suite of major and trace elements, including Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd, Pb, Th and U. Quantification was performed using calibration curves established with certified natural geological reference materials (Geostandards Newsletter, Vol. XVIII, Special Issue, July 1994, K. Govindaraju, ed.). Instrumental precision, defined from repeated measurements of the same sample, was better than 0.6% relative for major elements and 3% relative for trace elements, while analytical accuracy was within 0.5% for Si, below 3% for other major elements, and below 5% for trace elements. Detection limits ranged from 0.005-0.2 wt% for major oxides and from 3-10ppm for trace elements, depending on the element. Iron was quantified as total Fe_2O_3 by XRF, while the FeO content was independently determined by potassium permanganate titration (Pratt method to refine Iron speciation). This protocol while good for geological matrices, is not ideal for polymer samples because high temperatures ashing and fusion fundamentally alter the original matrix and may bias volatile or additive related elements; therefore XRF was treated strictly as a screening attempt and not retained for quantitative interpretation.

II. Instruments and protocols retained in the final workflow

Fourier Transform Infra-Red (FTIR) spectroscopy

For FTIR, a Thermo Nicolet 6700 FT-IR spectrometer, coupled with a ThermoElectron-Nicolet Continuum Infrared microscope (15X Infinity Corrected Cassegrain objective), in ATR configuration, using a silicon tip ATR single bounce slide on accessory (128 scan and 4 cm^{-1}) was used. Spectra were recorded by placing the samples (prepared as small pieces with a flat surface) on the microscope stage and bringing them into contact with the ATR tip. To correct the ATR spectra for the shifting of infrared absorption bands and the effects of variation in depth of penetration the Advanced ATR Correction function available in the software OMNIC 8.2.0.387 was applied. With this instrument, the analyses performed

produced reliable results with appreciable signals with stable baselines with scattering artefacts. This is mostly due to the sample preparation procedure adopted; For absorption experiments, samples were prepared as thin (50 – 80 micrometers thick) films by compression moulding at 180°C and analysed in transmission mode in the main sample compartment of the same spectrometer. The spectral scanning range was set at 4000-600cm⁻¹. The laboratory temperature was maintained at 20-25°C and the relative humidity was controlled at 25%-35%. Most samples were analysed in ATR mode. All spectra were baseline corrected and normalised.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The ICP-OES and ICP-MS test performances, was to determine the proper analytical technique for elemental composition as XRF. Using results of XRF, 10 out of the 34 samples were chosen for testing the best technique amongst the 2 techniques and also which sample preparation was more adequate. For that, the samples were analysed via ICP-OES and ICP-MS, conducted independently in two laboratories: in Lab G (Geochemical laboratory, Geoscience department of the University of Padova) and Lab L (Laboratorio di Ingegneria Sanitaria Ambientale, of the Civil, Architecture and Environmental Engineering department of the University of Padova) to validate inter-laboratory reproducibility and choose the best analysis protocol. The metals chosen to be analysed were: Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Ni, Pb, Sb, Ti, and Zn. Divided into two groups; one representing the filler constituent elements (Al, Ba, Ca, Mg and Ti) commonly used in plastics representing Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), Calcite (CaCO_3), Rutile (TiO_2), Barite (BaSO_4). The second set is a set of contaminants: heavy metals (Co, Cr, Ni, Pb, Sb) and recycling machinery particles which could be found in the recycled plastic (Cu, Fe and Zn). The heavy metals and recycling machinery particles were all grouped together to make the second set of metals analysed. The two labs had two different sample preparation methods and the overall procedure adopted is shown in the schematic representation in figure 14.

- Sample digestion protocol

10ml volume equivalent of each Samples were ground into fine powders through cryomilling using liquid nitrogen jar cooling for 3 minutes, 30 Hz milling frequency for 3 minutes, to produce plastic powders. To all ground samples, 10mL of HNO₃ was added and heated at 95°C for 2hours. Afterwards 5mL H₂O₂ was added to the solution and heated at 95°C for 2hours. Finally, 10mL of HCL was added and heated at 95°C for 15minutes. The heating method differed in the 2 labs: in Lab G (Geochemical laboratory, Geoscience department of

the University of Padova) the solutions were heated on a hotplate in open digestion vessels (appendix C) while in Lab L (Laboratorio di Ingegneria sanitaria Ambientale, Civil, Architecture and Environmental Engineering department of the University of Padova) the solutions were heated in a heating block (castle device) with closed vessels as seen in appendix B. In Lab L, the ICP-OES analysis was performed using the PerkinElmer Optima 4200DV (Dual view). The plasma conditions and gas flow used was the Flow plasma (Ar): 15l/min, the samples were introduced using a peristaltic pump; 1.5ml/min and Nebulizer of 0.55l/min. For the torch, the power (radio-frequency generator) was at 1400watt and a CCD (Charge coupled devices) used as detector. In Lab G, where ICP-MS was performed, the instrument used was an Agilent 8900 triple quadrupole spectrometer. For the introduction of the samples, the instrument is equipped with a MicroMist concentric nebulizer fitted into a Peltier-cooled Scott double-pass spray chamber and a quartz torch with a quartz injector (2 mm i.d.). The operational conditions are reported in Table 3. The Agilent 8900 is equipped with a Ni sampler cone and a Ni skimmer cone and two quadrupole mass filters (Q1 and Q2) and an octopole CRC cell mounted in-between. Use of the MS/MS mode facilitates the study of the reactions occurring within the CRC as a result of the different scanning tools available. In this work, the CRC of the instrument was pressurized with different gases, He (grade of purity 5.0) and O₂ (grade of purity 5.0). Re and Rh were used as internal standards.

Table 3: Operational conditions for the determination of Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Ni, Pb, Sb, Ti, and Zn by ICP-MS.

Parameter	Value
RF power (W)	1550
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	0.90
Nebulizer gas flow rate (L min ⁻¹)	1.01

Each lab used matrix-matched calibration standards. In lab L (ICP-OES) a calibration curve was used, without internal standard. The standard concentrations were: 100, 500, 1000 and 10000 ppb with 3 reading replicates for both standards and samples. In lab G (ICP-MS) Calibration was performed using different standards: ICP-MS Standard 4 components (Labiking) for Ca and Mg, Multi-element solution 33 components (Labiking) for Al, Ba, Co, Cr, Cu, Fe, Ni, Pb, Sb, and Zn, Titanium standard solution traceable to SRM from NIST

(NH₄)₂TiF₆ for Ti. For each element a calibration curve with 7 points was created (1, 2, 5, 10, 20, 50, 100 ppb), with the exception of Ca and Mg, whose calibration curve was created with 7 points at higher concentrations (100, 200, 500, 1000, 3000, 5000, 8000 ppb) as they were considered major elements. Samples were diluted at 1:10 or 1:100 with a 2% solution of suprapure HNO₃. Accuracy ranges from 2 to 8 relative percent and it was determined using several international certified materials (CRPG BE-N basalt and water certified material NIST 1643) as unknown samples.

Results were statistically compared through Z-scores to choose which lab has a better protocol for sample preparation and which analytical method (ICP-OES or ICP-MS) is better for analysis. The Z-score analysis is used to assess analytical accuracy and inter-laboratory consistency across different sample-preparation and instrumental workflows. For each element, Z-scores were calculated by normalizing individual concentration measurements against a consensus reference value derived from the complete dataset. The consensus mean and standard deviation for each element were obtained by pooling all valid measurements across laboratories, preparation methods, and analytical techniques. Z-scores were then calculated according to:

$$Z = (x - \mu) / \sigma$$

Where x is the measured concentration of a given element, μ represents the consensus mean and σ the consensus standard deviation. Absolute Z-scores ($|Z|$) were used to evaluate the magnitude of deviation independently of sign. According to commonly accepted proficiency-testing criteria, $|Z| \leq 2$ was considered indicative of acceptable analytical agreement, whereas values exceeding this threshold were classified as outliers.

X-ray Powdered Diffraction (XRPD)

Prior to analysis in XRPD, polymer samples were cryo-milled to improve homogeneity and reduce particle size as seen in appendix A. Milling was performed using a Retsch MM400 mixer mill: approximately 10 mL of sample, pre-cooled in liquid nitrogen for 3 minutes, was milled at 30 Hz for 3 minutes. Also, to test the accuracy of the results, some samples were analysed both as the bulk pellet/flake and the powdered sample. This analysis was to determine which sample form produced better patterns for interpretation. XRPD measurements were carried out using a Philips X'Pert Pro diffractometer (PANalytical, Almelo, The Netherlands) configured in parafocusing Bragg–Brentano geometry. The instrument was equipped with a long fine-focus cobalt (Co) X-ray tube, operated at 40 kV and 40 mA, and a Real-Time Multiple Strip (RTMS) X'Celerator detector, ensuring high detection efficiency and rapid collection of

diffracted intensities. Samples were prepared using two types of sample holders depending on the material:

- (i) Circular stainless-steel holders (27 mm diameter, 2 mm depth) filled by back-loading, and
- (ii) 27 mm circular silicon zero-background holders, prepared by front-loading for improved signal-to-noise in low-intensity regions.

A spinner mounted on a vertical axis was used during acquisition to minimise preferred orientation and improve powder statistics. The diffractometer was configured with $1/4^\circ$ divergence slits, 1° anti-scatter slits, and 0.04 rad Soller slits to optimize resolution and beam conditioning. Diffraction patterns were acquired over the range $3\text{--}85^\circ 2\theta$ in continuous-scan mode, corresponding to a total acquisition time of 1 hour, with a virtual step size of $0.017^\circ 2\theta$ (equivalent to ~ 100 s per step). Qualitative phase identification was performed using the HighScore Plus software package (v. 4.9, PANalytical B.V., Almelo, 2020), supported by the ICDD PDF-4+ 2020 database. The software description follows the recommended citation: Degen, T. et al., The HighScore Suite, Powder Diffraction, 29(S2), S13–S18 (2014). (Degen et al., 2014). The interpretation of the diffractogram was based on the polymer halo for amorphous samples and Bragg peaks for crystalline or semi-crystalline samples. Also, the PDF database was used to match and identify the phases present in the analysed samples.

Scanning Electron Microscopy (SEM)

SEM-EDX analyses were obtained using an Environmental Scanning Electron Microscope (ESEM, model Quanta 200, FEI Company, Hillsboro, OR) with a thermionic emission gun and with an EDX detector (model Xplore 30, Oxford Instruments, Abingdon, UK). Images and analyses were collected in low vacuum mode (0,53 torr of pressure), with an accelerating voltage of 20 kV. The EDX analyses and maps were performed with the Aztec Live lite 6.0 sp2 software package ((Oxford Instruments, Abingdon, UK). The beam current, working distance (around 10mm) varied from photo to photo. The detector used was the Large Field Detector for low vacuum (LFD). SEM micrographs were acquired to analyse morphological features, while EDX was used to assess elemental composition of inorganic additives and eventual contaminants. Low vacuum ESEM conditions were selected to minimise charging on polymer surfaces and avoid conductive coating, preserving the native morphology and enabling subsequent EDX point analysis on the same regions.

3.2.2.2 Ageing Experiment

Accelerated photo-ageing experiments were carried out using a Xenon (Xe) arc lamp system (Spectra-Physics Oriel, USA) equipped with a universal arc lamp housing (models 66901–66912 series) and an Oriel arc lamp power supply (model 69907). The system is designed to operate with high-intensity Xenon lamps in the 50–500 W range and is fitted with internal ignitors and UV-grade fused silica condensers, ensuring efficient transmission of ultraviolet radiation. Xenon arc lamps are widely recognised for their ability to closely simulate the full solar spectrum, including the UV-A (315–400 nm), UV-B (280–315 nm), and visible regions, making them particularly suitable for accelerated weathering and photodegradation studies of polymeric materials. The spectral emission of the Xenon lamp was characterised prior to ageing experiments, and the resulting emission profile is shown in figure 11. The spectrum exhibits a broad and continuous distribution from approximately 200 to 800 nm, covering the UV-B, UV-A and visible regions, which closely approximates the solar spectral distribution. The high emission intensity in the UV-A and UV-B ranges confirms the suitability of the lamp for inducing photo-oxidative degradation mechanisms in polymeric materials.

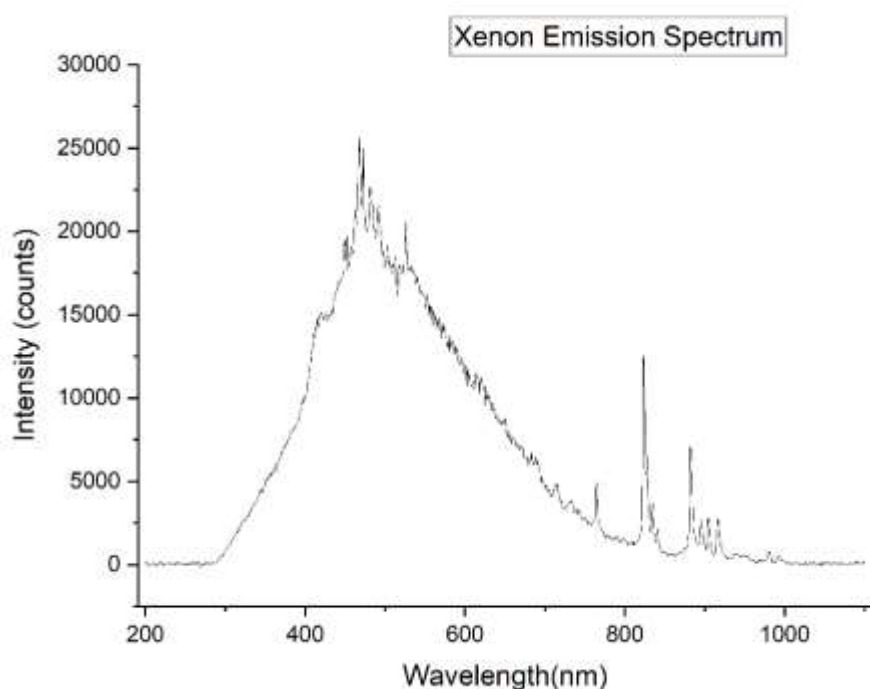


Figure 11: Emission spectrum of the Xenon arc lamp used for accelerated ageing experiments, showing broadband radiation from the UV to the visible region. The strong emission in the UV-A (315–400 nm) and UV-B (280–315 nm) ranges confirms the suitability of the source for inducing photo-oxidative degradation in polymeric materials

05 recycled plastics used for testing. These samples were composed of virgin polypropylene (PP), polyamide (PA), polypropylene + polyethylene (PP+PE), Polystyrene

(PS) and Acrylonitrile Butadiene Styrene (ABS) recyclates. Prior to irradiance, all these samples were cryo-milled to obtain powdered samples to improve homogeneity and increase exposed surface area used as seen in appendix E. Milling was performed using a Retsch MM400 mixer mill: approximately 10 mL of sample, pre-cooled in liquid nitrogen for 3 minutes, was milled at 30 Hz for 3 minutes. The recycled plastic samples were exposed to Xenon lamp irradiation for two exposure durations: 30 minutes and 60 minutes. The powdered samples were placed directly at the centre of the illumination spot as seen in appendix D, where irradiance was highest and most stable. The irradiance at the sample plane was repeatedly measured and maintained at approximately 640 mW, centred on the illuminated area of a diameter of approximately 1cm, corresponding to an irradiance of about 8.2KW/m². These exposure times were selected to simulate accelerated photo-oxidative ageing, under high intensity artificial solar radiation from the Xe lamp. The high intensity of the Xenon lamp enables the induction of photo-oxidative reactions within a short experimental time, including chain scission, formation of carbonyl and hydroxyl groups, and surface embrittlement, which are characteristic of long-term environmental ageing of polymers. After exposure, the samples were analysed by FTIR to assess potential changes in polymer chemical structure, including the persistence of diagnostic polymer bands and the emergence of oxidation-related functional groups. In parallel, the same samples were observed by SEM-EDX to evaluate possible irradiation-induced modifications in surface morphology, such as increased roughness, microcracking, or changes in filler-matrix interfaces. This combined approach allowed assessment of both sensitivity of the analytical techniques to ageing-induced changes and the response of the recycled polymer matrices to accelerated photo-oxidative stress.

3.3 Methodological approach

As mentioned in the methodology, the literature review permitted to shortlist some analytical techniques to be tested and used for analysis of the recycled plastics. These techniques are: Micro-Raman spectroscopy, FTIR, XRF, ICP-OES/ICP-MS, XRPD and SEM. For each technique a specific approach was adopted based on the quality of result and sample preparation.

Micro-Raman Spectroscopy

Micro-Raman spectroscopy was the first technique used as test for identification of polymer matrices and additive characterisation due to its high spatial resolution and widespread application in plastic analysis. Figure 12 below shows representative Raman spectra acquired at 632nm for selected samples (MMPS11 and MMPS12). In this figure, the vibrational features

of polymeric materials can be seen in certain regions, but the spectra are dominated in several cases by a strong and broad fluorescence background, which masks the diagnostic Raman bands and reduces spectral interpretability.

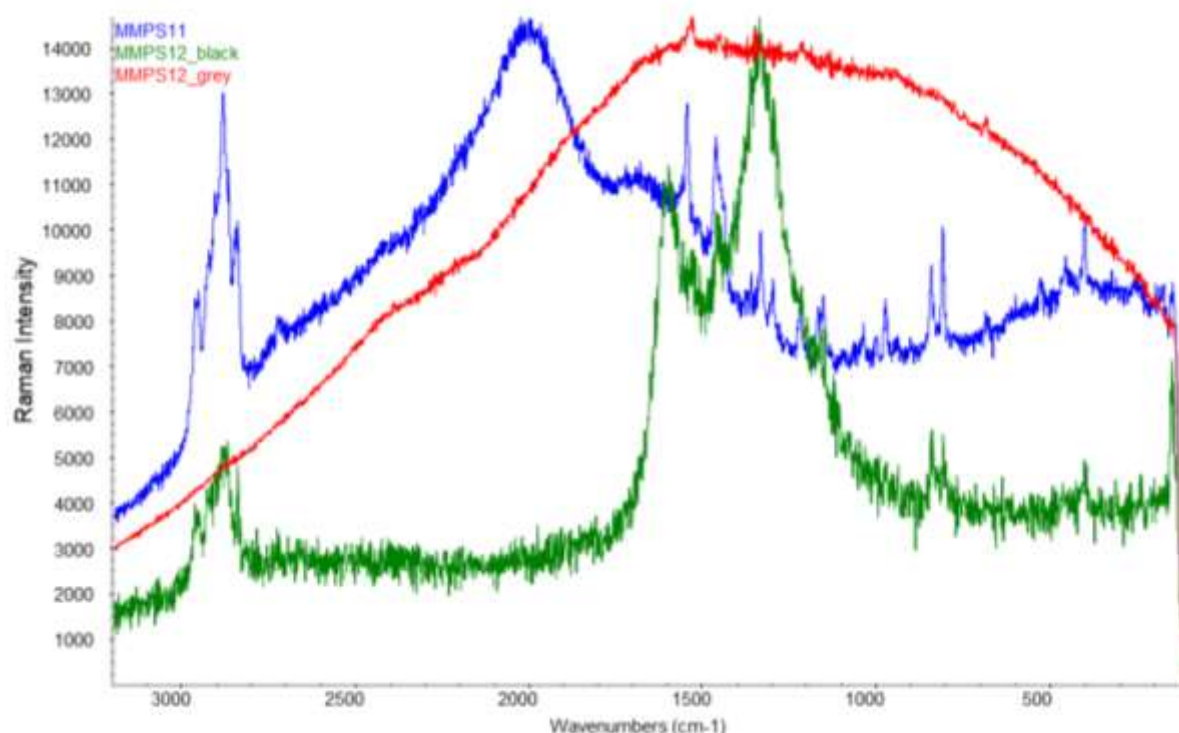


Figure 12: Raman spectra of MMPS11 and MMPS12 showing fluorescence and bands.

The intensity and variability of the fluorescence signal are more evident in the MMPS12 samples. This behaviour is characteristic of fluorescence emission from chromophoric species commonly present in recycled plastics, such as carbon black pigments, organic dyes, stabiliser residues, and degradation by-products. Carbon black is well known to induce strong fluorescence and light absorption in the visible range, leading to poor signal-to-noise ratios and suppression of Raman scattering. In heterogenous recycled plastics, where pigment content, filler distribution and degradation state vary, this effect is increased resulting in inconsistent spectral quality between different points on the sample.

This fluorescence observed using the 632nm, limited the reliability of polymer identification and did not enable the detection of minor phases and additives. Although the use of alternative excitation wavelengths (like 785nm) could, sometimes mitigate fluorescence, such optimisation was beyond the scope of this screening phase and doesn't guarantee a better performance across highly heterogenous, pigment rich recycled plastic. From these

observations, the option of FTIR spectroscopy which from literature provides reproducible, high-quality spectra and minimal fluorescence interference was tested.

Fourier Transform Infra-Red (FTIR) Spectroscopy

In contrast to Micro-Raman spectroscopy, FTIR spectra of the analysed samples exhibited good signal-to-noise ratios and stable baselines, enabling reliable identification of the polymer matrices. The recorded spectra showed well-defined absorption bands characteristic of the respective polymers, allowing unambiguous assignment through comparison with reference spectra. Polymer identification obtained from FTIR analysis was consistent with the material information provided in the corresponding technical datasheets supplied by the manufacturers. Spectral interpretation was supported by library matching within the FTIR software; however, identification was primarily based on the presence and relative intensities of diagnostic functional group vibrations. Figure 13 presents representative FTIR spectra of polypropylene sample, illustrating the characteristic absorption features used for polymer identification.

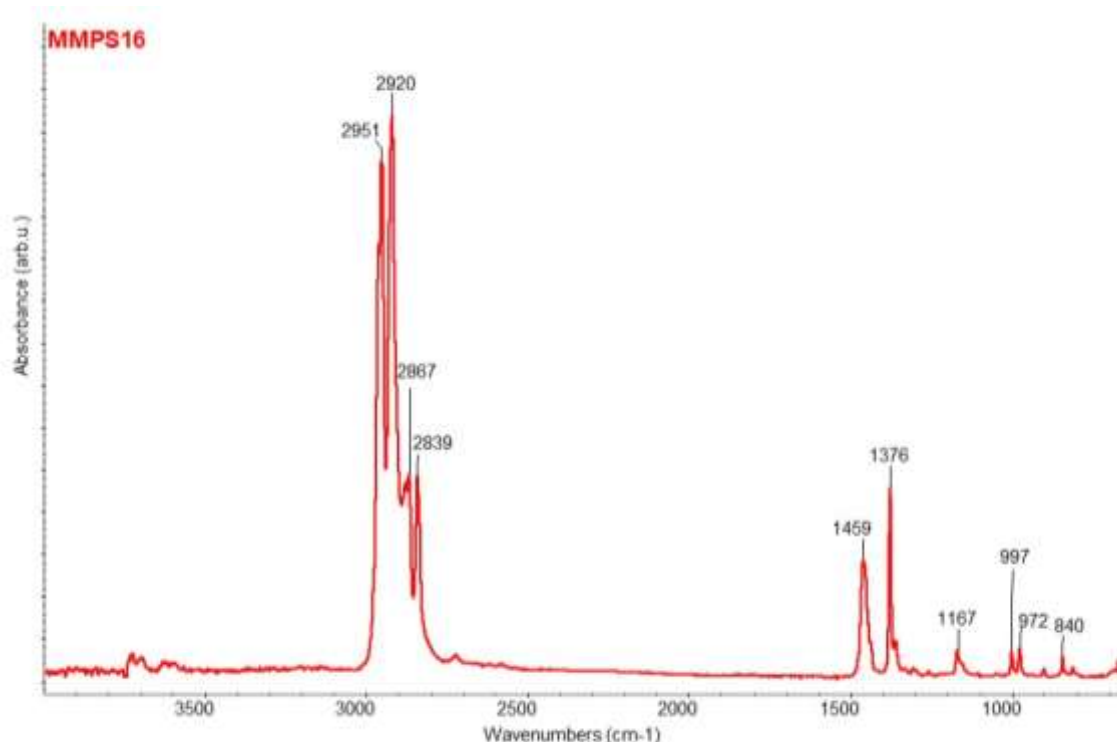


Figure 13: MMPS16 spectra showing PP absorption bands.

X-ray Fluorescence (XRF)

XRF analysis was initially performed to obtain a rapid overview of the elemental composition of the recycled plastic samples. Elemental concentrations were first reported as

oxide equivalents, which yielded plausible values for major elements typically associated with mineral fillers and glass phases (Si, Al, Fe, Mn, Ti, Mg, Ca, Na, K, and P), the results are reported in appendix F. These oxides ranged from 0.02 wt.% (K₂O in MMPS3) up to 97.24 wt.% (CaO in MMPS8), consistent with the presence of carbonate- and silicate-based fillers. In contrast, concentrations calculated for trace elements and heavy metals showed pronounced inconsistencies, with values ranging from 56 ppm for Ga in MMPS4 up to 58,000 ppm for Zn in the same sample. Such elevated concentrations are not consistent with the known formulation or expected contamination levels of recycled polymers. Further evaluation indicated that these discrepancies arose from the use of geological reference materials for calibration, which are not matrix-matched to polymer-rich samples and therefore introduce significant matrix and absorption effects. As a consequence, XRF results for trace and heavy elements as reported in annex section, were considered semi-quantitative at best and unsuitable for reliable interpretation within this study. For this reason, XRF was not retained for detailed chemical characterisation, and quantitative elemental analysis was instead carried out using ICP-OES and ICP-MS following controlled digestion procedures.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

As XRF showed it's in efficiency it was necessary to have the alternative technique for quantitative elemental composition of the samples. The test on ICP-OES and ICP-MS was then adopted. This test was performed in two different labs as stated in the methodology, with Lab L having the ICP-OES instrument and Lab G having the ICP-MS instrument. In Lab L the sample preparation was the same but the heating vessel used was a Castle device, whereas in Lab G the heating vessel was a simple heating plate. The difference in sample preparation heating procedures permitted the test of two different sample preparation (digestion methods) and two different instruments for analysing and getting the elemental composition of the samples. For this test, 10 most contaminated samples were chosen based on the prior XRF results (biased). The samples were prepared in both labs (10 in lab G and 10 in Lab L), all the 20 prepared samples were analysed using both instruments. The schematic workflow is represented in figure 14 below.

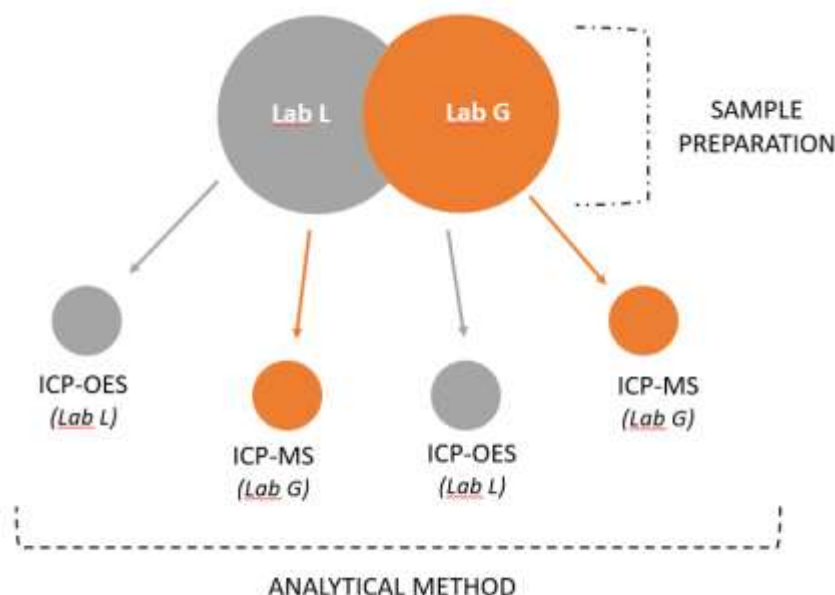


Figure 14: Schematic of different workflows adopted for evaluation of the best analytical protocol.

For ICP-OES the results varied from 1ppm – 21065.36ppm, from ICP-MS the results varied from 0.01ppm - 26171.49ppm. For the samples prepared in Lab G the concentration varied from 0.01ppm - 21.065.36ppm and for the samples prepared in Lab L the concentration varied from 0.07ppm - 26171.49ppm these concentrations are reported in appendix G. To evaluate and the analytical workflow (sample preparation and analysis), Z-score analysis was adopted as the primary metric for evaluation. The Z-score analysis simultaneously captures accuracy relative to consensus values and robustness across samples and elements. The Z-score boxplots as shown in figure 15, reveals that Castle device-based protocols (Lab L sample preparation) exhibit narrower interquartile ranges than hot-plate digestion (Lab G sample preparation) indicating more predictable analytical behaviour due to improved sample preparation. This behaviour indicates that the central 50% of measurements show limited and consistent deviation from consensus values, reflecting robust and predictable analytical performance. It also brings forward the role of improved sample preparation and more complete digestion in reducing method-dependent variability. In contrast, workflows involving ICP-MS (L+G and G+G) exhibit a higher number of outliers, which is attributed to the better sensitivity of ICP-MS combined with the intrinsic heterogeneity of recycled plastics, particularly for trace and heavy metals. These outliers therefore reflect chemically meaningful variability rather than analytical instability. The combination of both the narrow interquartile range of castle-based protocols and the enhanced detection capability of ICP-MS supports the selection of L+G workflow as the most robust and informative reference method for ICP analysis.

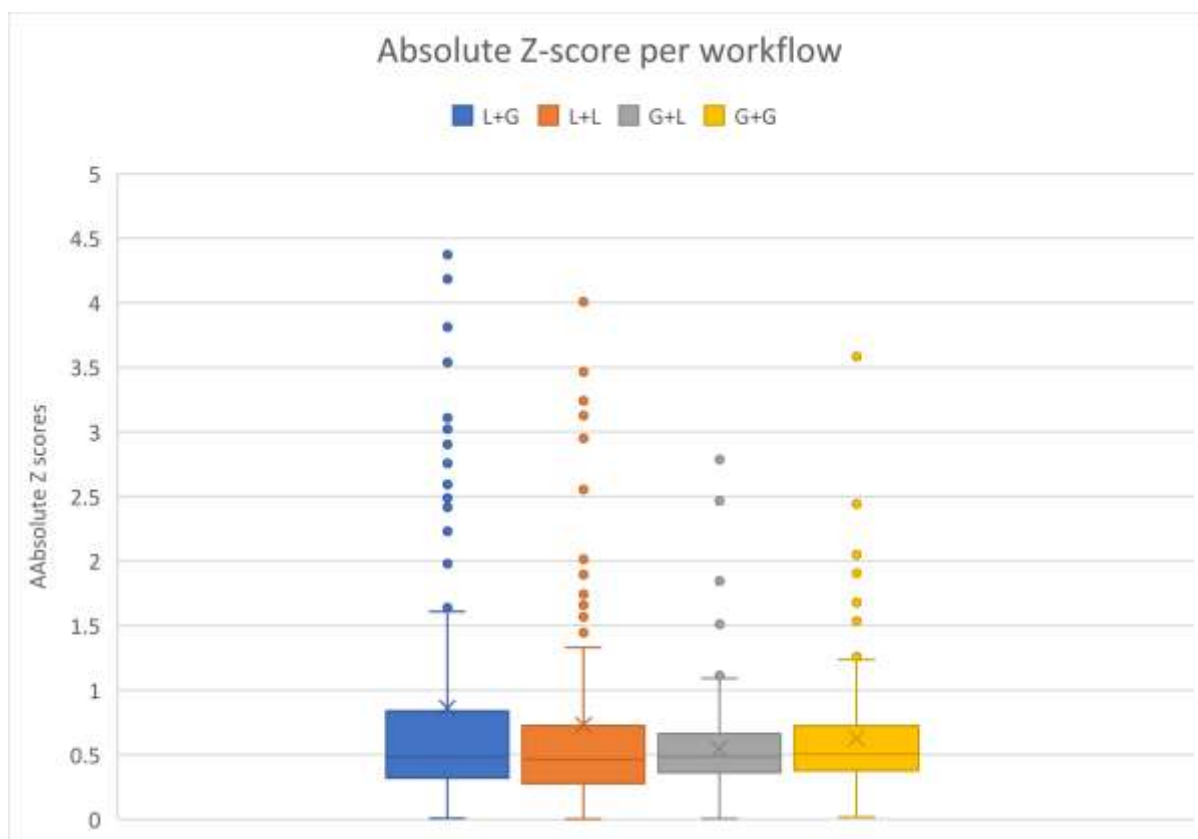


Figure 15: Boxplot of absolute Z-score distributions for the four preparation-analysis workflows (L+G, L+L, G+L and G+G). The interquartile range represents the 50% of the normalised deviations from consensus values, while whiskers and individual points indicate dispersion and outliers.

X-ray Powdered Diffraction (XRPD)

The XRPD analysis permits the identification of inorganic filler phases within the polymer matrices. Reliable phase identification by XRPD requires adequate powder statistics, which are strongly influenced by particle size, sample homogeneity, and crystallite orientation. For the recycled plastic samples, bulk pellets or flakes often exhibit preferred orientation and limited irradiated volume, masking the weak diffraction features associated with low abundance fillers. To evaluate the influence of sample preparation on XRPD data quality, selected samples were analysed both in their original pellet/flake form and after cryogenic milling. 03 samples and their corresponding cryo-milled powders were systematically examined using identical acquisition and processing parameters. This comparative approach allowed assessment of the extent to which cryo-milling improves diffraction peak definition background reduction and the detectability of crystalline filler phases within heterogeneous recycled polymer materials.

The cryo-milled samples peak positions and distribution of peak intensities were better than bulk samples. Also, their peak positions were found to be closer to the reference from pdf files

in the software, so identification would be more accurate. For sample MMPS1, cryo-milled powder revealed some peaks that are not present in the bulk samples as shown in figure 16 (A) below.

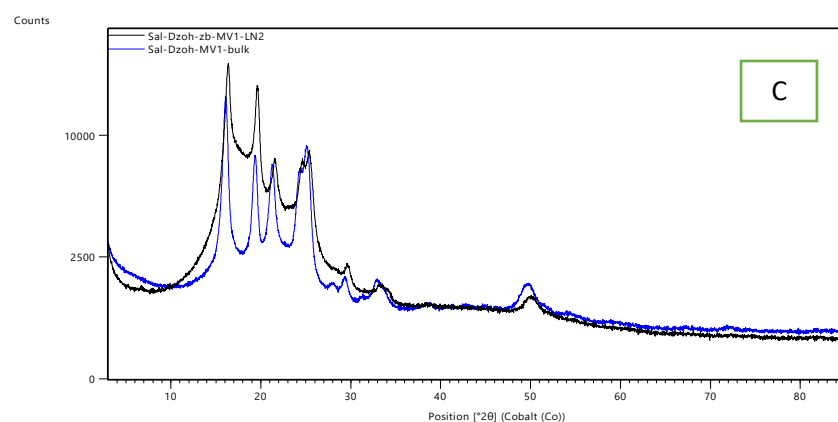
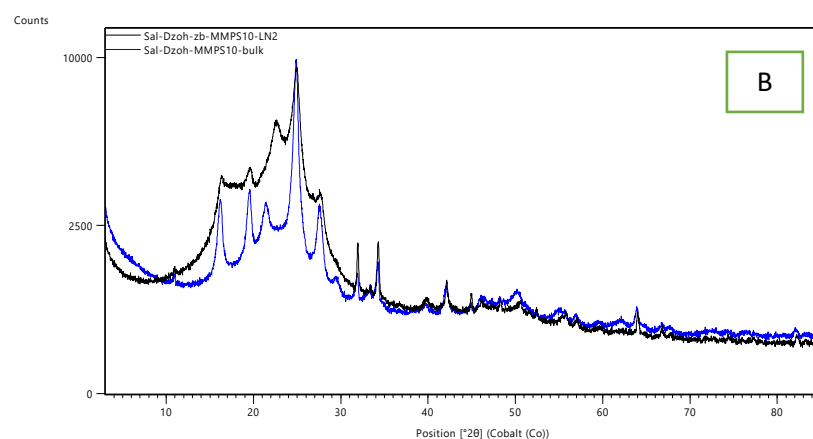
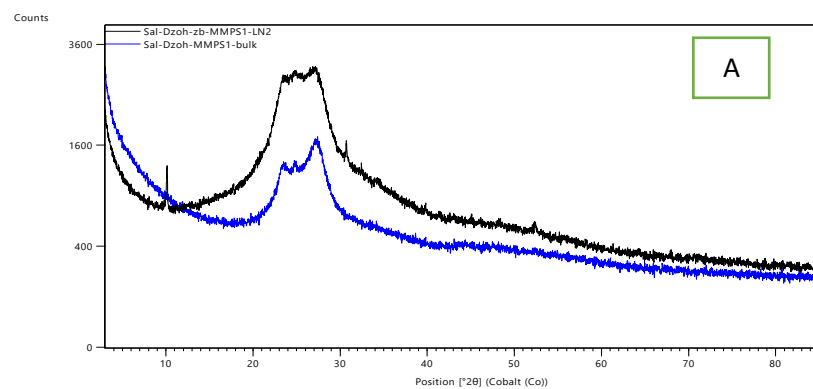


Figure 16: The comparison of the three samples using XRPD. The blue diffractograms represent the bulk sample, whereas the black is for the cryo-milled sample. The addition of peaks is seen if (A) and the intensities vary throughout all the samples.

The choice of cryo-milling all samples before performing XRPD was then adopted as the best analytical pathway for XRPD analysis.

Scanning Electron Microscopy (SEM)

For SEM analysis, no additional sample preparation was applied in order to preserve the native surface features of the recycled plastics. Samples were analysed directly in their original flake or pellet form to enable direct observation of surface morphology, including defects, inclusions, and heterogeneities induced by processing and recycling. Conductive coating was not applied, as the instrument was operated under low-vacuum conditions, allowing effective imaging of polymeric materials while minimizing surface charging. Secondary electron imaging was employed to characterise surface topography, while localized elemental composition was investigated by EDX point analysis on selected surface features. Representative SEM micrographs illustrating the morphological characteristics of the analysed samples are presented in figure 17.

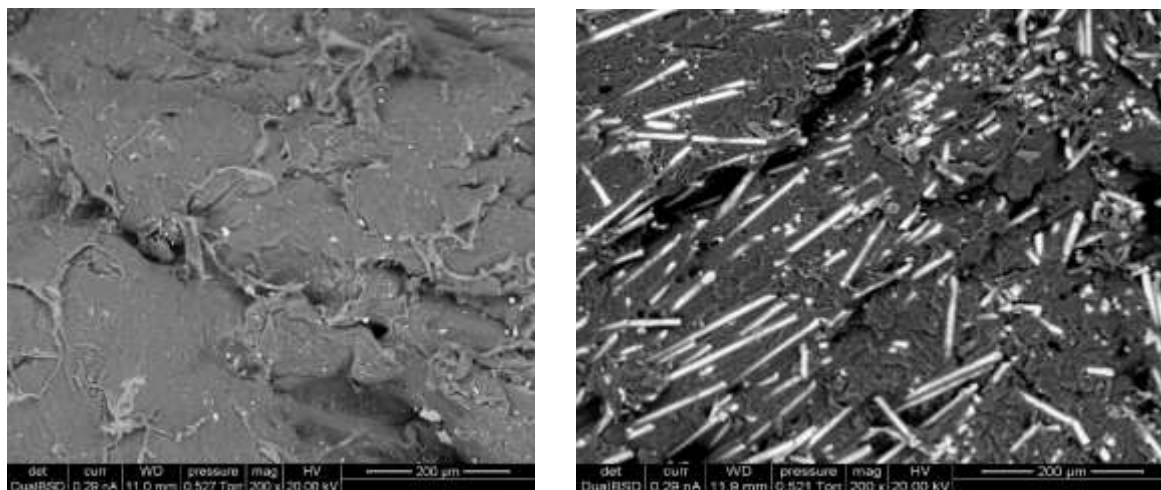


Figure 17: A – Polypropylene + Polyethylene sample showing rough incomplete mixture of two polymers. B- Polyamide showing glass fibres used as reinforcement fillers in the polymer matrix.

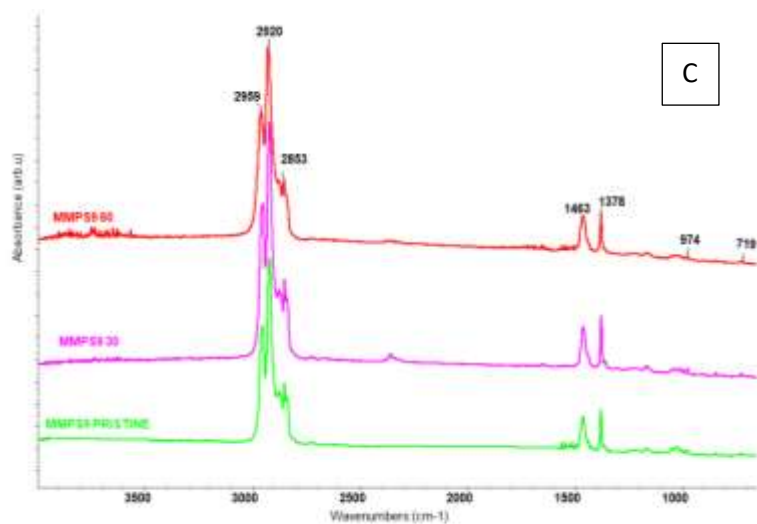
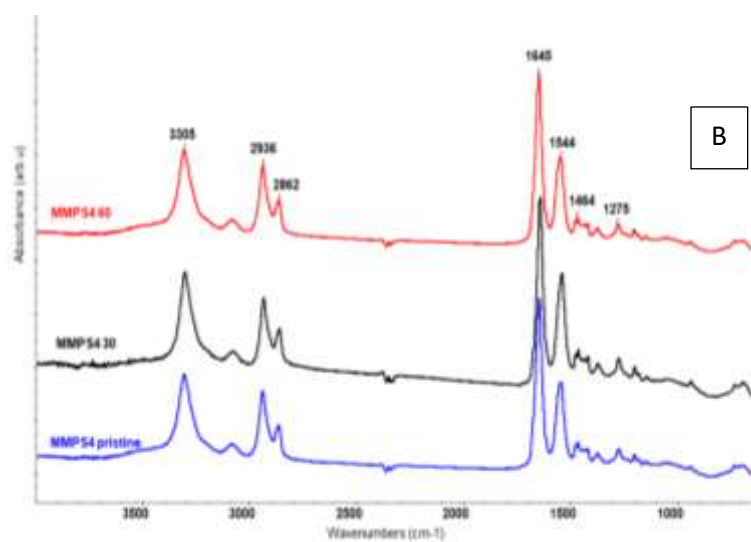
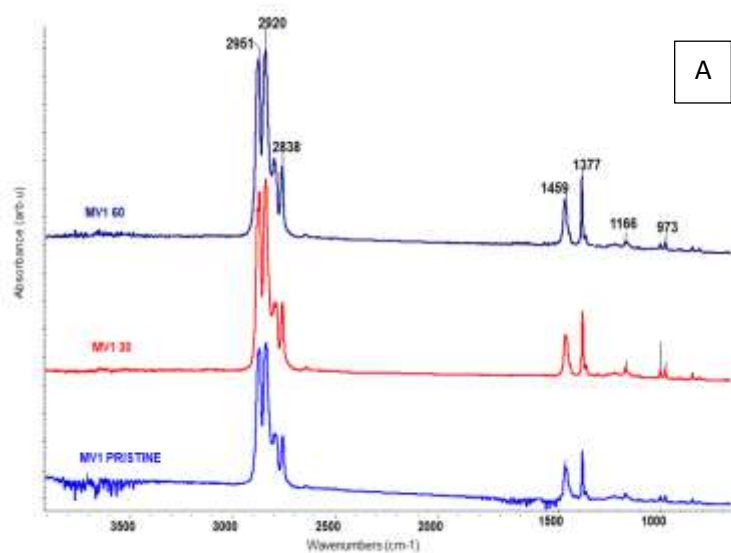
Accelerated UV ageing Experiment: FTIR and SEM Evaluation

1. FTIR Assessment of Photo-Oxidative Ageing

The five representative recycled plastics used for the experiment were exposed to the high intensity Xe lamp irradiation for 30 and 60minutes, in triplicate, to simulate the photo-

oxidative ageing. FTIR spectra acquired after irradiation were systematically compared with those of the pristine materials in order to detect chemical modifications such as chain scissions, oxidation and the formation of carbonyl or hydroxyl functionalities.

For the five samples, FTIR showed no significant changes relative to their pristine counterparts as seen in figure X. The characteristic absorption bands used for polymer identification remained unchanged in both position and relative intensity. In figure 18a the polypropylene sample, MV1 the diagnostic C-H stretching bands ($2951\text{-}2838\text{cm}^{-1}$), CH_2 and CH_3 bending modes (1459 and 1377 cm^{-1}), and skeletal vibrations in the $1166\text{-}973\text{ cm}^{-1}$ region were preserved. No emergence of carbonyl bands in the $1710\text{-}1730\text{ cm}^{-1}$ region or hydroxyl broadening around $3200\text{-}3600\text{cm}^{-1}$ was observed, indicating the absence of detectable oxidative degradation within the applied exposure times. This same observation is made in figure 17c for the PP+PE sample, MMPS9 but with difference in band position 719cm^{-1} the principal PP+PE signature. In figure 18b the PA sample (MMPS4) also kept its amide bands (1645cm^{-1} , 3305cm^{-1} and 2936 cm^{-1}) with no evidence of additional oxidation products. The PS (STMPS27) spectra remained dominated by the aromatic C=C stretching ($1601, 1493\text{ cm}^{-1}$) and out of plane C-H bending modes ($757\text{-}700\text{ cm}^{-1}$), while the ABS sample (STMPS31) preserved the combined styrenic, nitrile (2237cm^{-1}) and the butadiene related features. No increase in carbonyl absorption or nitrile band distortion was detected as seen in figures 18d and 18e.



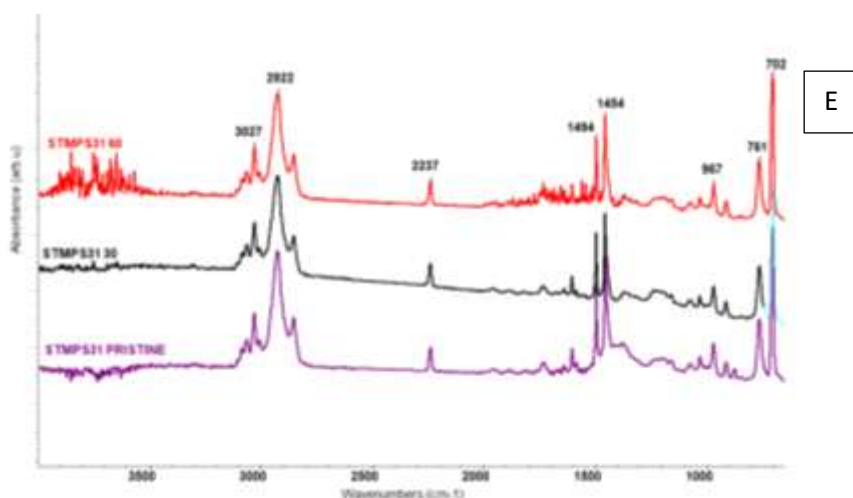
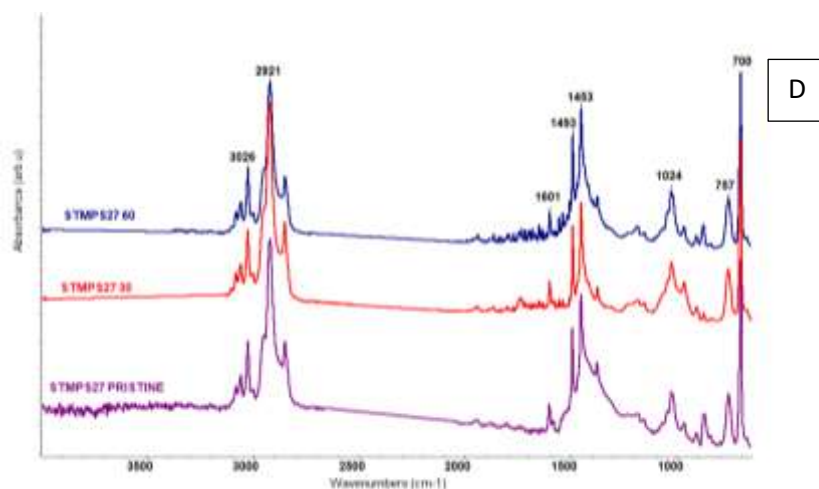


Figure 18: A- MV1 (PP) pristine, 30min and 60min irradiance spectra. B- MMPS4 (PA) pristine, 30min and 60min irradiance spectra. C- MMPS9 (PP+PE) pristine, 30min and 60min irradiance spectra. D- STMP537 (PS) pristine, 30min and 60min irradiance spectra. E.

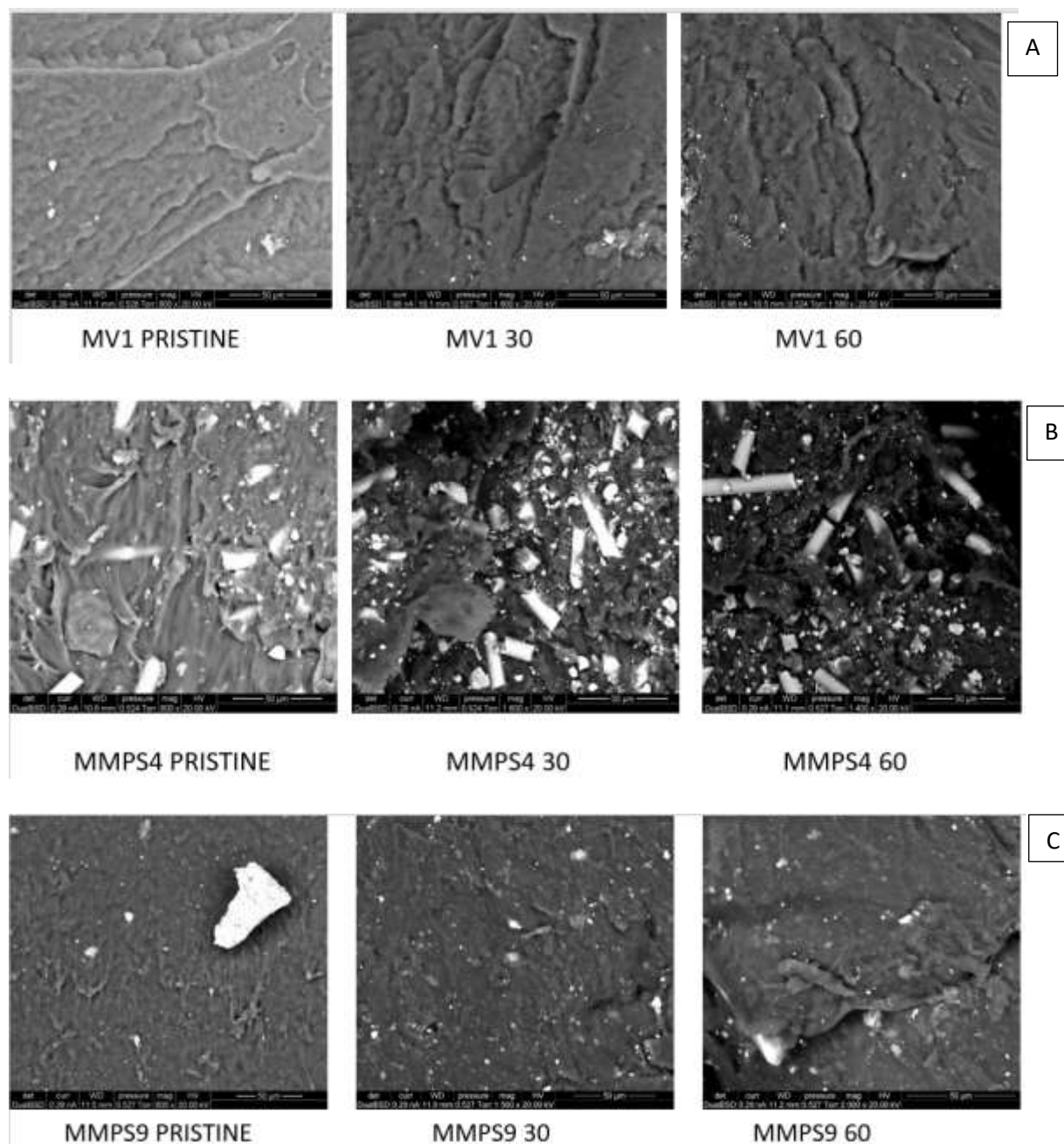
The FTIR results indicate that, under the applied experimental conditions (high irradiance for 30 and 60minutes), the extent of photo-oxidative degradation was below the detection limit of FTIR. This is consistent with the relatively short exposure durations and the intrinsic resistance of these recycled polymers to rapid photo-oxidation. The most important aspect, is the demonstration from the experiment that FTIR remains fully effective for recycled polymer identification even after intense UV exposure, confirming its robustness for the analysis of weathered recycled plastics.

2. SEM evaluation of Surface Morphology After UV exposure

After acquisition of FTIR spectra, the SEM micrographs of the pristine, 30minute irradiated and 60minute irradiated samples were compared for each sample to assess any

potential morphological change induced by photo-ageing. Across all five polymers, no significant cracking, pitting, embrittlement or erosion was observed after either exposure times.

The MV1 and MMPS9 retained their characteristic slightly rough structure as seen in figure 19a and 19c. The PA sample with glass fibres in its polymer matrix, did not show any observable additional surface fragmentation after irradiation (figure 19b), the PS and ABS samples which are generally susceptible to UV-induced embrittlement, also did not display detectable morphological degradation at the SEM scale, figure 19d and 19e.



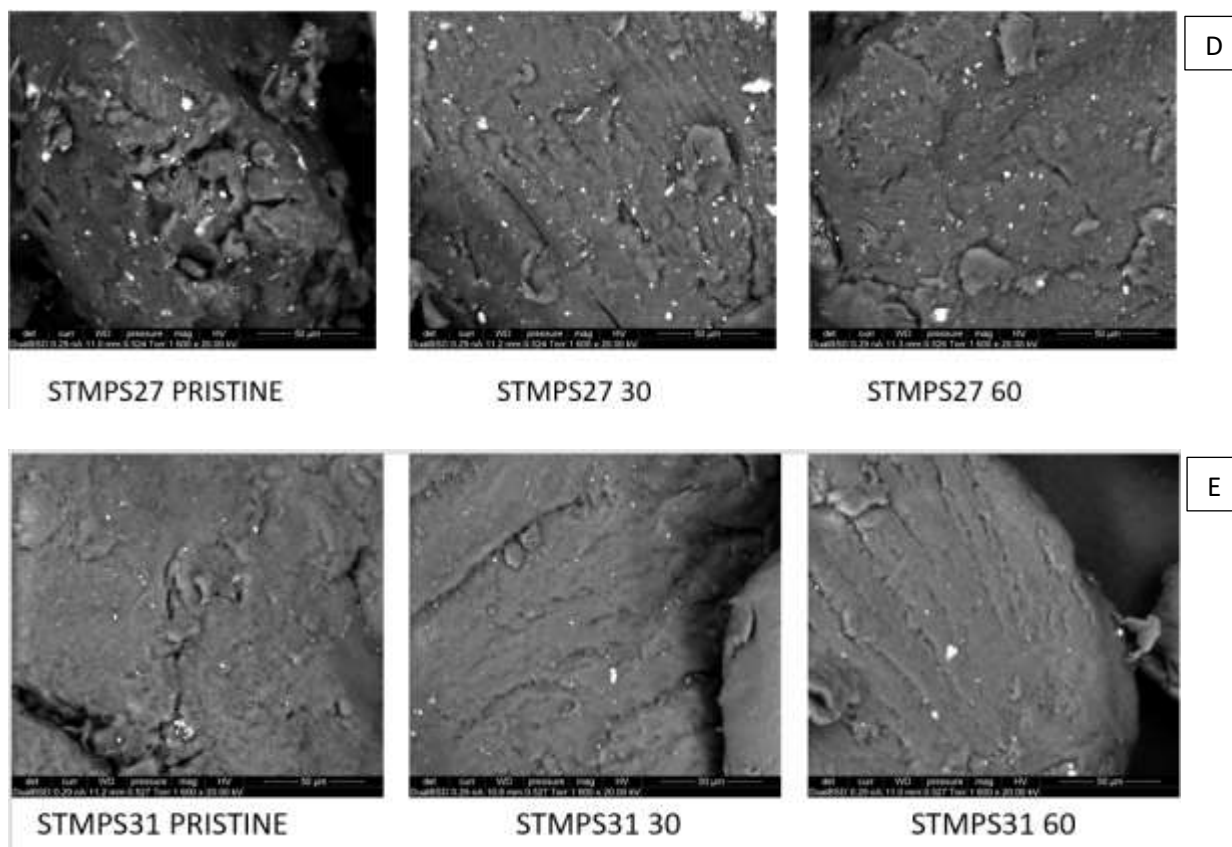


Figure 19: SEM surface images of accelerated UV exposure on the samples.

As for FTIR, the absence of visible surface damage indicates the insufficiency of UV to damage the sample at the applied experimental conditions with the high irradiance. These observations highlight an important methodological point: accelerated ageing conditions must be carefully calibrated, as very short high-intensity exposures may not replicate the cumulative effects of long-term environmental weathering. Nevertheless, SEM permitted the effective visualisation of inorganic fillers and inclusions within the polymer matrices, even after exposure. The Crushed mineral particles, angular fragments, and dispersed filler domains were clearly identifiable in all samples, confirming that SEM-EDX remains a good tool for filler characterisation irrespective of polymer ageing state.

3.4 Final Selected Analytical Techniques

This experimental screening and comparative evaluation of Micro-Raman, FTIR, XRF, ICP-OES, ICP-MS, XRPD, and SEM-EDX permitted an evidence-based selection of the most suitable pathway for the characterisation of heterogeneous recycled plastics. The selection was driven not only by literature recommendations but, crucially, by experimental performance under real sample conditions, including polymer heterogeneity, filler complexity, and contamination levels.

Micro-Raman spectroscopy, XRF and ICP-OES, although theoretically appropriate for polymer identification (Micro-Raman), rapid bulk elemental screening (for XRF and ICP-OES) showed their limitations in the context of the recycled plastics. Micro-Raman spectra had fluorescence dominating the spectra as seen in figure 19, XRF produced inconsistent and unreliable results for trace and heavy metals due to calibration limitations arising from the use of geological standards on polymeric materials and ICP-OES was less suitable compared to ICP-MS.

Based on this integrated experimental validation, the final analytical pathway adopted in this study consists of:

- **FTIR** for polymer identification and mixture detection because it was not affected with fluorescence and required minimal sample preparation. Also, it showed its effectiveness in accelerated ageing experiment for effective polymer identification.
- **SEM-EDX** for morphological analysis and filler/inclusion visualisation, due to its ease to permit the observation of filler agglomerates, mineral fragments and surface morphology. It was also very helpful in the experiment.
- **XRPD** (with cryomilling) for inorganic filler and crystallinity identification.
- **ICP-MS** (with CASEL digestion) for trace and contaminant quantification. This technique was validated after a cross-laboratory and cross-preparation design. The statistical evaluation using Z-score demonstrated superior sensitivity, consistency and lower dispersion for ICP-MS.

This multi-technique combination as shown in figure 20 below ensures comprehensive coverage of chemical, structural, morphological and physical aspects of recycled plastics.

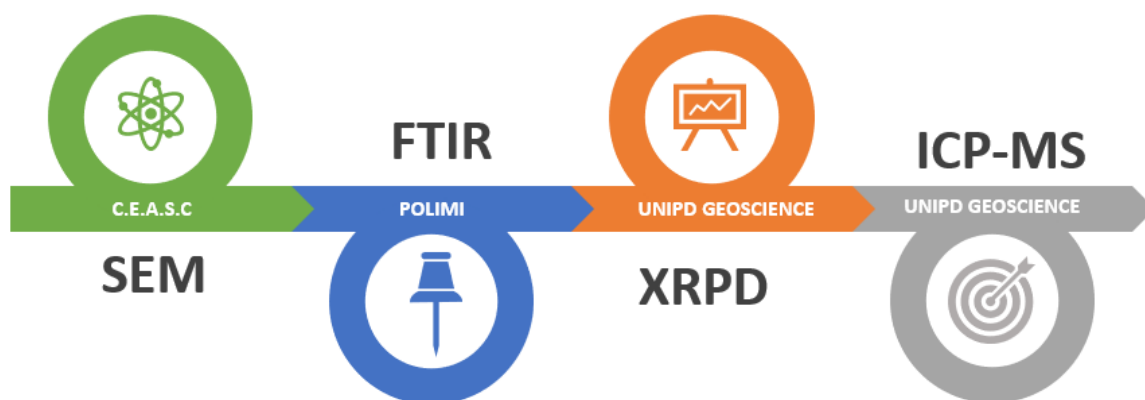


Figure 20: The combination of chosen analytical techniques and corresponding laboratories where the analyses were carried for characterisation of the recycled plastic samples.

3.5 Conclusion

This chapter established a rigorous, experimentally validated methodological framework for the characterisation of heterogeneous recycled plastics. Rather than relying solely on literature review, a systematic screening and testing approach was adopted to evaluate the performance, limitations, and applicability for multiple analytical techniques under realistic conditions.

A literature-driven screening enabled the selection of complementary analytical techniques (micro-Raman spectroscopy, FTIR, XRF, ICP-OES/ICP-MS, XRPD, and SEM) suitable for the multi-scale characterisation of recycled plastics. Systematic experimental evaluation revealed that Micro-Raman and XRF measurements were affected by calibration limitations for heterogeneous polymer matrices and were therefore not retained for quantitative interpretation meaning that not all theoretically suitable techniques perform adequately on complex recycled matrices. Comparative assessment of ICP-OES and ICP-MS, combined with different digestion strategies, demonstrated that sample preparation using the CASEL system followed by ICP-MS analysis provided the most reliable and informative elemental data, particularly for trace and heavy metals. For XRPD analysis, cryogenic milling was shown to significantly improve diffraction quality by enhancing powder statistics and reducing preferred orientation effects, resulting in clearer diffraction features and more reliable phase identification of inorganic fillers. The ageing experiment validated the stability and applicability of FTIR and SEM under high-intensity UV exposure conditions.

Overall, this methodological framework demonstrates that rigorous optimisation of sample preparation and analytical technique selection is essential for capturing the intrinsic chemical, structural, and morphological heterogeneity of recycled plastics. This methodological framework underpins all subsequent analytical results presented in this thesis and provides a robust basis for assessing material quality, contamination, and recyclability, thereby supporting informed decision-making in circular economy and end-of-waste applications.

Chapter 4: MULTI-TECHNIQUE

CHARACTERISATION OF RECYCLED PLASTICS: ASSESSING POLYMER MIXTURE, FILLER COMPOSITION AND ELEMENTAL CONTAMINATION

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ABSTRACT

This work presents a comprehensive multi-technique characterisation of end-of-waste recycled plastics aimed at assessing polymer identity, polymer mixtures, inorganic filler composition, and elemental contamination as indicators of material quality and recycling history. A total of 34 recycled polymer samples originating from different industries were investigated using an integrated analytical framework combining Fourier Transform Infrared (FTIR) spectroscopy, Inductively Coupled Plasma-Mass spectrometry (ICP-MS), X-ray powder diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX). This approach enabled the correlation of chemical, structural, morphological and physical information across multiple length scales. FTIR allowed unambiguous identification of polymer families, revealing the presence of Polypropylene (PP), Polyethylene blends (PP+PE), polyamide (PA), Polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and polyoxymethylene (POM). FTIR, also provided evidence of polymer mixtures. ICP-MS analysis quantified both filler related elements and metal

contaminants, revealing strong variability among samples and polymer types. Calcium rich fillers dominated polyolefin recyclates while talc and glass-fibre related signatures were prominent in engineering polymers. Elevated concentrations of Fe, Cu and Zn were attributed to mechanical abrasion during recycling, whereas Sb and Pb reflected legacy additives and flame-retardant formulations. XRPD enabled differentiation between semi-crystalline and amorphous polymer matrices and allowed identification of crystalline mineral fillers, including calcite, talc and rutile. The technique also highlighted misinterpretations arising from fillers-induced diffraction features, particularly in glass-fibre reinforced polyamides. SEM-EDX provided direct visualisation of surface morphology, filler dispersion, fibre fragmentation, and contamination hotspots, corroborating XRPD and ICP-MS findings at the microscale. The combined results demonstrate that recycled plastics exhibit pronounced heterogeneity arising from mixed polymer streams, filler carry-over and cumulative contamination across multiple lifecycles. Overall, this work demonstrates that only through the integration of complementary analytical techniques can the complexity of recycled plastics be fully resolved. The findings underscore the limitation of single-parameter quality assessments and support the need for multi-dimensional characterisation frameworks to reliably evaluate recyclate quality, regulatory compliance and suitability for reintegration into circular economy value chains.

Keywords: Recycled plastics, multi-technique characterisation, polymer mixtures, mineral fillers, heavy metals, material quality, circular economy

4.1. Introduction

In order to accurately interpret the analytical results obtained for recycled polymers, it is essential to establish a reference baseline corresponding to virgin materials. Virgin polymers exhibit well-defined chemical, structural, morphological, and elemental characteristics, which serve as references for identifying deviations induced by recycling processes. In this context, the reference analytical signatures of the main polymer families investigated in this study (PP, PP+PE, PA, PS, ABS, PC and POM) are presented below using complementary techniques (FTIR, XRPD, SEM-EDX, and ICP-MS). These reference profiles provide the basis for distinguishing intrinsic polymer features from changes related to degradation, filler incorporation and contamination.

Reference Characterisation of Virgin Polypropylene (PP) :

To provide a consistent baseline for interpreting physicochemical properties of recycled polypropylene, a reference description of virgin polypropylene (PP) is essential. Virgin PP is a semi-crystalline polyolefin characterised by a well-defined chemical structure, controlled molecular weight distribution, and minimal presence of inorganic additives or contaminants (Juan et al., 2021). From a spectroscopic perspective, FTIR analysis of virgin PP exhibits characteristic absorption bands dominated by characteristic aliphatic vibrations, including asymmetric stretching $\nu_{as}(\text{CH}_3)$ at $\sim 2950\text{--}2955\text{ cm}^{-1}$ and $\nu_{as}(\text{CH}_2)$ at $\sim 2915\text{--}2920\text{ cm}^{-1}$, as well as symmetric stretching $\nu_s(\text{CH}_3)$ at $\sim 2870\text{--}2875\text{ cm}^{-1}$ and $\nu_s(\text{CH}_2)$ at $\sim 2838\text{--}2840\text{ cm}^{-1}$ (Bian et al., 2025). Bending modes are observed at $\sim 1455\text{--}1460\text{ cm}^{-1}$ ($\delta(\text{CH}_2)$, scissoring) and $\sim 1375\text{--}1380\text{ cm}^{-1}$ ($\delta(\text{CH}_3)$, symmetric deformation), while the fingerprint region displays diagnostic bands at $\sim 1167\text{ cm}^{-1}$ (C–C stretching coupled with CH bending), $\sim 998\text{--}1000\text{ cm}^{-1}$ and $\sim 973\text{--}975\text{ cm}^{-1}$ (CH rocking modes associated with isotactic crystallinity) (Anshari et al., 2025). Notably, the absence of absorption bands in the carbonyl region ($1700\text{--}1750\text{ cm}^{-1}$) and hydroxyl region ($\sim 3200\text{--}3600\text{ cm}^{-1}$) confirms the lack of oxidative degradation (Gopanna et al., 2019). XRPD analysis further reveals a semi crystalline structure dominated by the monoclinic α -phase, with well-defined reflections at $\sim 14.1^\circ$ (110), 16.9° (040), 18.6° (130), 21.2° (111), and 21.9° (041) (2θ , Cu-K α equivalent), indicating a high degree of crystallinity and ordered chain packing (Papajani et al., 2013)

Morphological observations by SEM show a homogenous and continuous matrix, with ductile fracture features and no evidence of inclusions, agglomerates, or phase separation, consistent with the intrinsic semi-crystalline nature of the polymer (Bitter & Lackner, 2021). Complementary ICP-MS analysis confirms extremely low concentrations of inorganic

elements, with only trace levels of Ca, Ti, or Zn occasionally detected due to minor additives, and heavy metals such as Pb, Cr, Ni and Sb generally below detection limits (Klingenberg et al., 2024a). Collectively, these features define the analytical signature of virgin PP as a chemically intact, structurally ordered, and compositionally pure material.

Reference Characterisation of Virgin Polypropylene + Polyethylene (PP+PE).

PP+PE systems represent commonly a class of polyolefin blends frequently encountered in post-consumer and post-industrial plastic streams. Due to their similar chemical composition but distinct crystallisation behaviour, PP and PE are generally immiscible at the molecular scale, resulting in a two-phase system. FTIR spectra of PP+PE mixtures are dominated by overlapping aliphatic vibrations, with characteristic asymmetric stretching bands $\nu_{\text{as}}(\text{CH}_2)$ at $\sim 2915\text{ cm}^{-1}$ and $\nu_{\text{as}}(\text{CH}_3)$ at $\sim 2950\text{--}2955\text{ cm}^{-1}$, alongside symmetric stretching $\nu_{\text{s}}(\text{CH}_2)$ at $\sim 2848\text{ cm}^{-1}$ and $\nu_{\text{s}}(\text{CH}_3)$ at $\sim 2870\text{--}2875\text{ cm}^{-1}$ (Soliz et al., 2024). The coexistence of CH_2 and CH_3 vibrations confirms the presence of both polyethylene and polypropylene. A key diagnostic feature is the $\delta(\text{CH}_3)$ bending band at $\sim 1375\text{--}1380\text{ cm}^{-1}$, which is prominent in PP but absent in PE; in PP+PE systems, this band appears with reduced intensity, reflecting the relative proportion of PP within the blend. In the fingerprint region ($1000\text{--}800\text{ cm}^{-1}$), overlapping contributions from both polymers are observed, often limiting phase discrimination by FTIR alone (Moldovan et al., 2012). XRPD analysis provides clearer structural differentiation, with polyethylene exhibiting orthorhombic reflections at $\sim 21.5^\circ$ (110) and $\sim 23.8^\circ$ (200), and polypropylene showing α -phase reflections at $\sim 14.1^\circ$ (110), 16.9° (040), 18.6° (130), and $\sim 21\text{--}22^\circ$ (111/041). The resulting diffractogram is characterised by a superposition of these peaks, confirming the coexistence of two independent semi-crystalline phases and the absence of co-crystallisation.

Morphologically, SEM observations reveal a heterogeneous two-phases structure, where one polymer phase is dispersed within the other as spherical or irregular domains embedded in a continuous matrix, reflecting the intrinsic immiscibility of PP and PE. Differences in mechanical behaviour between phases may be observed in fracture surfaces, although well-processed virgin blends remain free of defects, inclusions, or interfacial degradation (Bata et al., 2022a). SEM-EDX analysis confirms that the observed heterogeneity is purely polymeric, with spectra dominated by carbon and minor oxygen signals and no detectable inorganic elements. ICP-MS analysis further supports this, showing extremely low concentrations of filler-related elements (Ca, Mg, Ti, Ba, Al) and trace metals (Fe, Cu, Zn, Cr, Ni, Pb, Sb), typically near detection limits (Klingenberg et al., 2024b). Collectively, these features define

the analytical signature of virgin PP+PE blends as a superposition of polyolefin-specific chemical and crystalline characteristics, combined with a phase-separated but compositionally pure morphology.

Reference Characterisation of Virgin Polyamide (PA).

Virgin polyamides (PA), PA6 and PA66, are semi-crystalline engineering thermoplastics characterised by repeating amide linkages (-CONH-), which confer strong polarity and extensive intermolecular hydrogen bonding. This structural feature governs their spectroscopic and crystallographic behaviour and differentiates them significantly from non-polar polyolefins (Tummino et al., 2023a). FTIR spectra of virgin PA are dominated by amide-related vibrations, including a broad $\nu(\text{N-H})$ stretching band centred around $\sim 3300\text{--}3310\text{ cm}^{-1}$ associated with hydrogen bonding, the amide I band ($\nu(\text{C=O})$) at $\sim 1630\text{--}1650\text{ cm}^{-1}$, and the amide II band ($\delta(\text{N-H})$ coupled with $\nu(\text{C-N})$) at $\sim 1530\text{--}1550\text{ cm}^{-1}$ (Tummino et al., 2023a). Additional contributions in the $1200\text{--}1300\text{ cm}^{-1}$ region correspond to $\nu(\text{C-N})$ stretching, while CH_2 stretching vibrations appear at $\sim 2930\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{CH}_2)$) and $\sim 2860\text{ cm}^{-1}$ ($\nu_{\text{s}}(\text{CH}_2)$) (Tummino et al., 2023a). The sharpness and position of these bands reflect the degree of crystallinity and hydrogen bonding within the polymer. XRPD analysis further confirms the semi-crystalline nature of PA, with polymorphic behaviour depending on processing history. The α -phase, typical of PA66 and highly ordered PA6 structures, exhibits characteristic reflections at $\sim 20^\circ$ and $\sim 23\text{--}24^\circ$ (2θ), associated with hydrogen-bonded chain sheets, while the γ -phase, often observed in PA6, shows a dominant reflection near $\sim 21\text{--}22^\circ$ (2θ) (Murray et al., 2022). The presence of relatively sharp diffraction peaks, together with a moderate amorphous halo, indicates a well-organised crystalline structure with strong intermolecular cohesion (Yap et al., 2024b).

Morphologically, SEM observations of virgin PA reveal a dense and homogeneous matrix, with fracture surfaces often displaying lamellar features and ductile deformation behaviour characteristic of semi-crystalline polymers (Murray et al., 2022). The strong hydrogen-bonding network contributes to cohesive fracture behaviour with limited void formation and no evidence of phase separation or inclusions in unfilled materials. SEM-EDX spectra are dominated by carbon (C), oxygen (O), and nitrogen (N), consistent with the polymer backbone, and show no significant contributions from filler-related elements such as Ca, Mg, Ti, or Ba (Hirschberg & Rodrigue, 2023). ICP-MS analysis corroborates this compositional purity, with inorganic elements present at trace or near-detection-limit levels; heavy metals (Cr, Ni, Pb, Sb) and machinery-related elements (Fe, Cu, Zn) are typically negligible, although minor traces

may occasionally arise from stabilisers or residual catalysts (Pani et al., 2025). Collectively, these features define the analytical signature of virgin polyamide as a structurally ordered, hydrogen-bonded semi-crystalline system with minimal inorganic content.

Reference Characterisation of Virgin Polystyrene (PS).

Polystyrene (PS) is an amorphous thermoplastic characterised by a hydrocarbon backbone bearing pendant aromatic phenyl groups, which strongly influence its spectroscopic and structural behaviour. The FTIR spectrum of virgin PS is dominated by aromatic vibrations, with prominent C=C stretching bands observed at ~ 1600 and $\sim 1490\text{ cm}^{-1}$, accompanied by characteristic C–H out-of-plane bending modes in the $700\text{--}760\text{ cm}^{-1}$ region. These bands provide a clear fingerprint for PS identification (Y. Zhang et al., 2022). The absence of carbonyl (C=O) or hydroxyl (O–H) bands confirms the lack of oxidative degradation in the pristine material.

From a structural standpoint, XRPD patterns of PS exhibit a broad diffuse halo centred around $\sim 19\text{--}20^\circ$ (2θ), reflecting its fully amorphous nature and absence of long-range crystalline order (Xu et al., 2024). This contrasts sharply with semi-crystalline polymers and simplifies phase identification, as no discrete diffraction peaks are expected. SEM observations further confirm this amorphous character, revealing smooth and homogeneous fracture surfaces typically associated with brittle failure behaviour, with limited plastic deformation or fibrillar structures (Xu et al., 2024).

Elemental analysis by SEM-EDX and ICP-MS indicates a highly pure organic composition, with spectra dominated by carbon and negligible contributions from inorganic elements. The absence of filler-related elements (e.g., Ca, Ti, Ba) and trace metals confirms that virgin PS provides a chemically simple reference system (Vilaplana et al., 2007). This simplicity makes PS particularly useful as a baseline for detecting contamination and additive incorporation in recycled styrenic materials.

Reference Characterisation of Virgin Acrylonitrile-Butadiene-Styrene (ABS):

ABS is a multiphase copolymer composed of a rigid styrene–acrylonitrile (SAN) matrix and a dispersed rubbery butadiene phase, resulting in a complex but well-defined analytical signature. Its FTIR spectrum reflects this composition, combining aromatic bands (~ 1600 and $\sim 1490\text{ cm}^{-1}$), a sharp nitrile (C≡N) stretching band at $\sim 2235\text{--}2245\text{ cm}^{-1}$, and weaker features associated with the butadiene phase, including C=C stretching ($\sim 1630\text{--}1650\text{ cm}^{-1}$) and out-of-

plane =C–H bending ($\sim 965\text{--}910\text{ cm}^{-1}$) (Agirre et al., 2022). The simultaneous presence of these features is diagnostic of ABS and distinguishes it from pure polystyrene.

XRPD analysis of ABS reveals an essentially amorphous structure, characterised by a broad halo typically centred between 15° and 25° (2θ), reflecting the lack of crystallinity in both SAN and butadiene phases (Moustafa et al., 2017). No sharp diffraction peaks are expected unless fillers are present. SEM provides insight into the material's multiphase morphology, where rubbery domains may be dispersed within the rigid matrix, although these features are often below the resolution limit depending on preparation conditions (Moustafa et al., 2017). In virgin ABS, the morphology appears uniform and free from defects or inclusions.

SEM-EDX and ICP-MS analyses confirm the low inorganic content of virgin ABS, with only trace elemental signals detected. The absence of mineral fillers and heavy metals ensures that the observed properties are intrinsic to the polymer structure.

Reference Characterisation of Virgin Polycarbonate (PC).

Polycarbonate (PC) is an amorphous engineering polymer distinguished by its carbonate functional groups and aromatic backbone, which give rise to a unique and highly diagnostic spectroscopic signature. In FTIR spectra, the most prominent feature is the strong C=O stretching band at $\sim 1770\text{ cm}^{-1}$, associated with the carbonate linkage, accompanied by aromatic C=C stretching bands in the $1500\text{--}1600\text{ cm}^{-1}$ region and C–O stretching vibrations between $1100\text{--}1300\text{ cm}^{-1}$ (Konarzewski et al., 2022). These features collectively provide a clear identification of PC and distinguish it from other aromatic polymers such as PS.

XRPD patterns of virgin PC exhibit a broad amorphous halo centred around $\sim 17\text{--}18^\circ$ (2θ), consistent with the absence of crystalline domains (Babaremu et al., 2024). Unlike semi-crystalline polymers, no sharp reflections are observed, indicating a fully disordered molecular arrangement. SEM observations reveal a dense and continuous morphology, typically characterised by smooth fracture surfaces with limited microstructural features (Konarzewski et al., 2022)). Depending on fracture conditions, PC may exhibit some degree of ductility, but without the lamellar structures seen in semi-crystalline materials.

Elemental analysis by SEM-EDX and ICP-MS confirms the chemical purity of virgin PC, with minimal inorganic content and negligible trace metal concentrations.

Reference Characterisation of Virgin Polyoxymethylene (POM).

Polyoxymethylene (POM), also known as acetal, is a highly crystalline engineering polymer characterised by a repeating $\text{--CH}_2\text{--O--}$ backbone, which imparts high stiffness and

structural order. Its FTIR spectrum is dominated by strong C–O–C stretching vibrations in the 900–1100 cm⁻¹ region, which serve as a distinctive fingerprint of the acetal structure (Jandric et al., 2024). Additional CH₂-related vibrations are observed in the 2800–3000 cm⁻¹ region, while the absence of carbonyl or hydroxyl bands confirms the lack of oxidative degradation in the virgin state (Berkowicz-Płatek et al., 2024).

XRPD analysis of POM reveals a highly crystalline structure, with sharp and intense diffraction peaks typically observed at ~22–23° and ~34–35° (2θ), corresponding to well-organised chain packing (Liu et al., 2023). The high intensity and narrow width of these peaks reflect a high degree of crystallinity and structural perfection, distinguishing POM from less ordered polymers. Only a minor amorphous contribution is present, confirming the dominance of crystalline domains.

SEM observations of virgin POM show a compact and dense morphology, often associated with brittle fracture behaviour due to its high crystallinity (Konarzewski et al., 2022). The surface appears homogeneous, with no evidence of inclusions, voids, or phase separation. SEM-EDX analysis confirms the absence of inorganic fillers, with spectra dominated by carbon and oxygen signals. ICP-MS results further support this, showing extremely low concentrations of inorganic elements and trace metals.

Overall, the analytical signature of virgin POM is defined by strong acetal FTIR bands, highly crystalline XRPD patterns, and a dense, inclusion-free morphology, providing a clear reference for identifying structural degradation or contamination in recycled POM materials.

Materials And Methods

The materials investigated in this chapter correspond to the same set of recycled plastic samples described in Chapter 3. These samples originate from different industrial recycling streams and comprise a range of polymer families, including polyolefins, styrenic polymers, engineering plastics, and polymer blends. Sample selection, provenance, physical form (pellets and flakes), and preliminary classification as reported in chapter 3 are not repeated here.

The analytical techniques applied in this chapter: FTIR, XRPD, SEM-EDX and ICP-MS were selected following the methodological screening and experimental validation detailed in chapter 3. Also, the descriptions of the instrumentation, operating conditions, sample preparation protocols, and analytical parameters for each technique are provided in the same previous chapter.

In this chapter, these techniques are applied to generate and interpret experimental results aimed at characterising polymer identity and mixtures, crystalline structure and mineral filler phases, surface morphology and additive dispersion, and bulk to trace-level, including potential contaminants. The focus of this chapter is thus placed on the presentation and integrated interpretation of the results, while methodological details are referenced to the preceding chapter.

4.2. Results And Discussion

4.3.1 Results from Analyses

Fourier Transform Infra-Red (FTIR) Spectroscopy

Objectively, the first use of FTIR was to confirm the polymer identity of the samples from different companies by comparing their infrared spectra with those from the literature and from spectral database and comparing with those recorded from the virgin sample (case of PP). To proceed, the identification of each functional group not corresponding to the polymers but as an additive, be it an inorganic filler, plasticizer, stabilizer or flame retardant. All spectra were collected under identical conditions in ATR mode (here reported after correction of the intensities by the ATR correction function), to ensure direct comparability. Amongst the 34 samples a total of 7 different polymers were identified. These polymers were PP, PP+PE, PA, PS, ABS, PC, POM, and PC. The functional groups characterizing these polymers were methylene, methyl, amides, carbonyl and hydroxyl groups.

Functional group and Polymer Identification

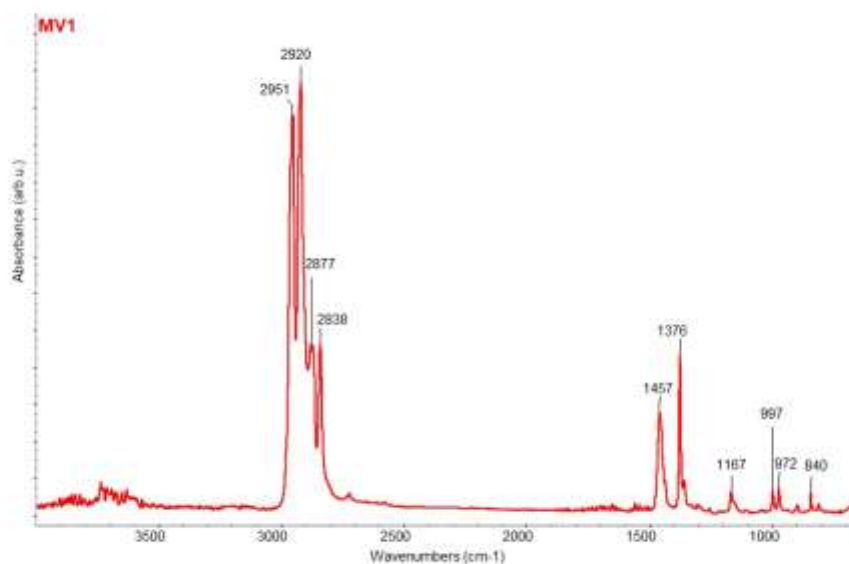
A- Characteristic Polypropylene signature

Across the polypropylene samples, the software detected 4 out of the 34 samples as pure polypropylene based plastics. These samples were MMPS8, MMPS16, MV1 and MMPS 22. MV1 being the virgin propylene sample. All these exhibited the classic vibrational modes of isotactic PP:

- CH₃ and CH₂ stretching region (3000–2800 cm⁻¹)
 - v_{as}(CH₃) at ~2950 cm⁻¹
 - v_{as}(CH₂) at ~2920 cm⁻¹
 - v_s(CH₃) at ~2870 cm⁻¹

- $\nu_s(\text{CH}_2)$ at $\sim 2850 \text{ cm}^{-1}$
- Methyl bending and rocking region
 - $\delta_{\text{as}}(\text{CH}_3)$ at $1455\text{--}1460 \text{ cm}^{-1}$
 - $\delta_s(\text{CH}_3)$ at $1375\text{--}1380 \text{ cm}^{-1}$
 - CH_2 wagging at $\sim 1166 \text{ cm}^{-1}$
 - CH_3 rocking doublet at ~ 997 and 973 cm^{-1}
- Crystallinity/regularity-related bands
 - Band around $841\text{--}810 \text{ cm}^{-1}$ typical of isotactic PP helical segments
 - Intensity ratios between bands at $998/973 \text{ cm}^{-1}$ reflecting ordering.

All these PP peaks (Bian et al., 2025) can be seen in figure 21 which allowed an unambiguous confirmation that all listed samples are polypropylene based plastics.



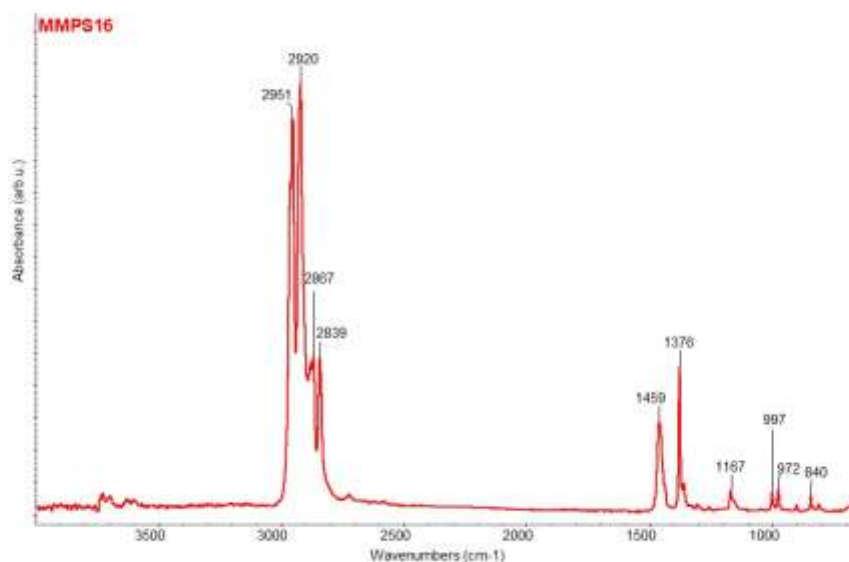


Figure 21: ATR spectra of samples MV1, MMPS10 and MMPS16 showing PP corresponding peaks.

B- Characteristic Polypropylene + Polyethylene (PP+PE) signature

Most samples presented the corresponding PP+PE signals, which exhibits features consistent with polyolefin blends. Their spectra are dominated by C-H stretching and bending vibrations, with some peaks which reveal both PP and PE components.

Common polyolefin features (PP and PE) :

strong CH stretching bands between 3000–2800 cm^{-1}

- $\nu_{\text{as}}(\text{CH}_2)$ ~2920–2925 cm^{-1}
- $\nu_{\text{s}}(\text{CH}_2)$ ~2850–2852 cm^{-1}

CH_2 bending at ~1465–1472 cm^{-1}

Weak overtone/combination bands in the 2000–1700 cm^{-1} region.

PP-specific indicators: as mentioned above in the section on PP characteristic bands, the exact indicator for PP containing samples are the methyl (CH_3) bands:

- $\delta_{\text{s}}(\text{CH}_3)$ at ~1375–1380 cm^{-1} (very characteristic of PP)
- CH_3 rocking and wagging bands around 997 and 973 cm^{-1} (isotactic PP doublet).

As for the confirmation of PE in a spectrum:

- Absence of methyl-specific bands (or much lower intensity of 1375 cm^{-1}).

- CH₂ rocking doublet at ~730 and 720 cm⁻¹, highly characteristic of polyethylene crystallites.

In PP+PE samples, both PP bands: 1375, 997/973 cm⁻¹ and PE rocking doublet bands 730/720cm⁻¹ (Soliz et al., 2024) are present but in varying intensities. This confirms the blends or mixtures of PP and PE. Samples MMPS3, MMPS5, MMPS6, MMPS7, MMPS9, MMPS10, MMPS14, MMPS15, MMPS18 and MMPS20 are those who exhibited these features as seen in the spectra presented in figure 22.

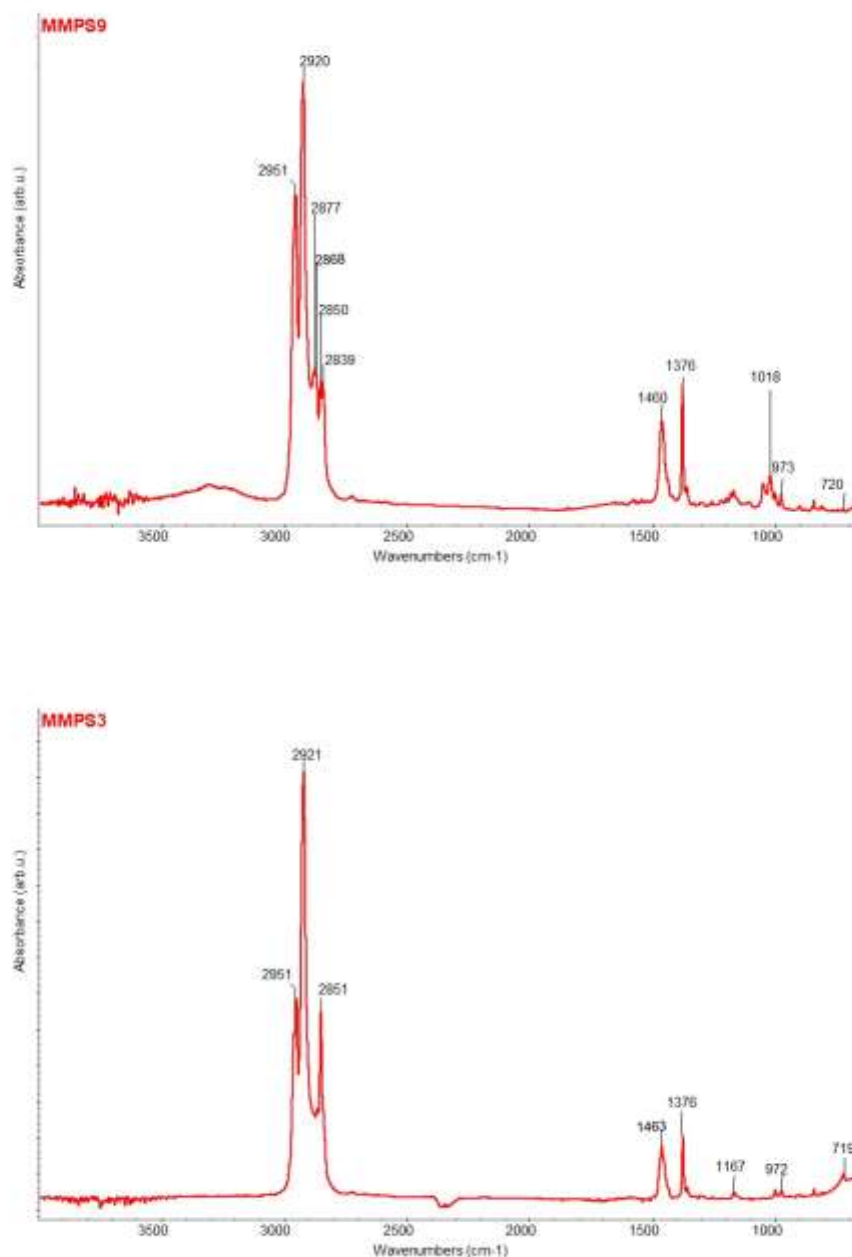


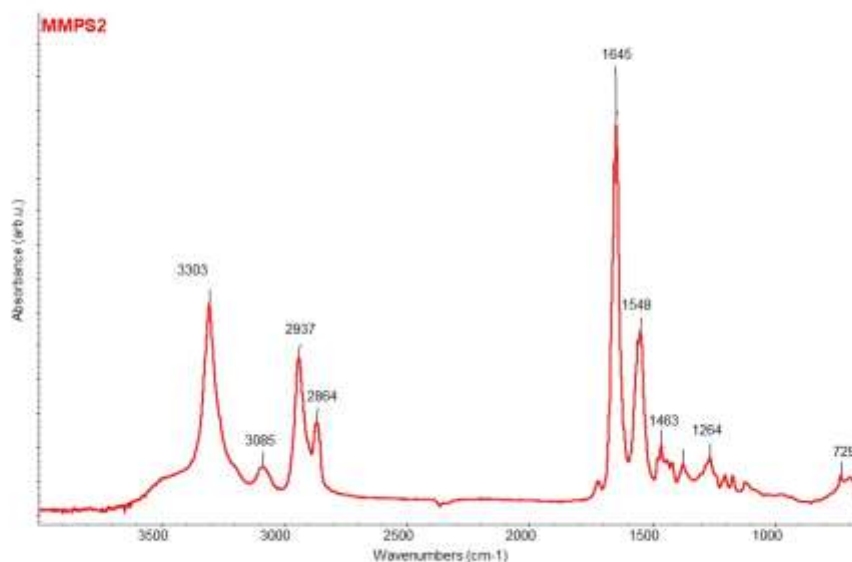
Figure 22: IR spectra of some samples showing the 1375cm⁻¹, 973cm⁻¹, 720cm⁻¹ bands typical of the PP+PE polymer blend or mixture.

C- Characteristics of Polyamide (PA) signature

Samples MMPS1, MMPS2 and MMPS3 spectra showed the typical IR fingerprint of polyamides as in figure 23 with the following bands:

- N–H stretching: broad band in the 3300–3200 cm^{-1} region, often asymmetric and hydrogen-bond broadened.
- Amide I (C=O stretching): strong band at $\sim 1630\text{--}1680\text{ cm}^{-1}$, arising from the carbonyl group of the amide linkage.
- Amide II (N–H bending + C–N stretching): band at $\sim 1530\text{--}1550\text{ cm}^{-1}$.
- Amide III / C–N stretching: features in the 1300–1200 cm^{-1} range.
- CH₂ stretching: $\nu_{\text{as}}(\text{CH}_2)$ at $\sim 2925\text{--}2935\text{ cm}^{-1}$ and $\nu_{\text{s}}(\text{CH}_2)$ at $\sim 2850\text{--}2860\text{ cm}^{-1}$, reflecting the aliphatic segments in the PA backbone.
- CH₂ bending and skeletal modes: bands at 1465–1470 cm^{-1} (scissoring) and $\sim 720\text{--}730\text{ cm}^{-1}$ (rocking), typical of methylene sequences.

Amide I/II bands with N-H stretching bands coexistence with strong CH₂ modes confirms that the samples belong to a polyamide family: PA6/PA66 type (Tummino et al., 2023b).



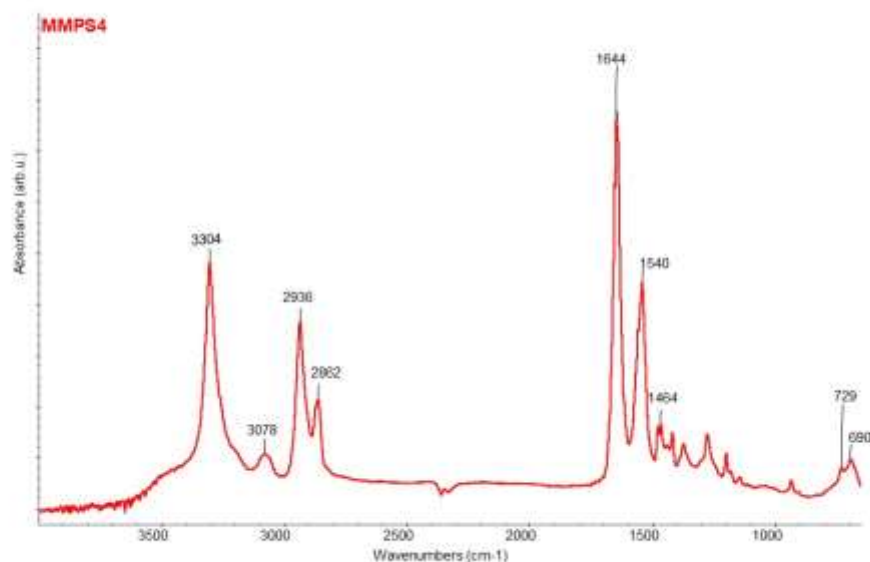


Figure 23: IR spectra of samples MMPS2 and MMPS4, showing the characteristic Polyamide bands.

D- Characteristics of Polystyrene (PS) signature

Polystyrene exhibits a very characteristic FTIR-ATR spectrum dominated by vibrational contributions from the aromatic styrene units. The principal diagnostic markers of PS include:

- Aromatic C–H stretching vibrations ($3100\text{--}3000\text{ cm}^{-1}$)
- Aromatic C=C stretching modes in the $1600\text{--}1400\text{ cm}^{-1}$ region
- Aromatic ring in-plane and ‘breathing’ vibrations ($1200\text{--}900\text{ cm}^{-1}$)
- Out-of-plane aromatic C–H bending ($900\text{--}650\text{ cm}^{-1}$),

key PS fingerprint

PS exhibits a distinctive doublet at:

- 756 cm^{-1}
- $698\text{--}700\text{ cm}^{-1}$

These two intense bands reflect mono-substituted benzene ring wagging and constitute the most recognisable fingerprint region of PS in ATR spectra (Y. Zhang et al., 2022).

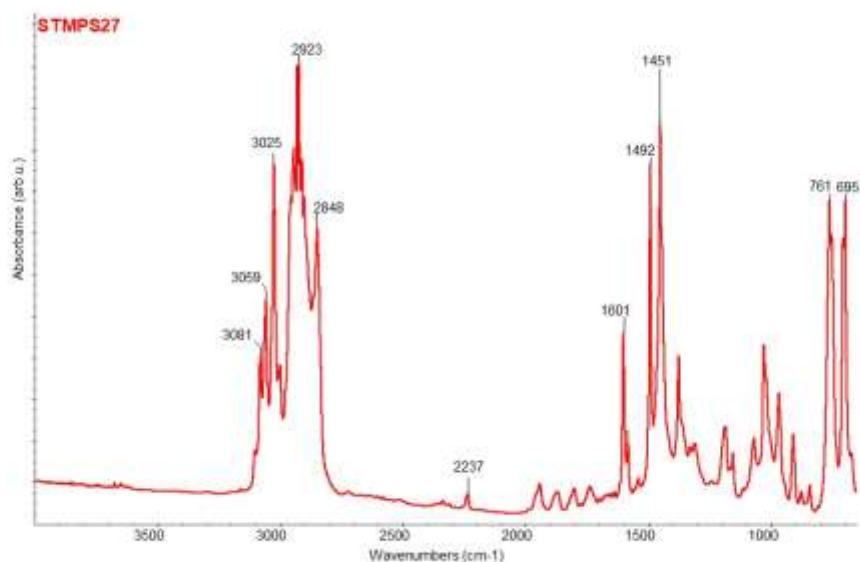


Figure 24: STMPS27 IR spectrum showing the PS signatures.

STMPS27 classified as PS exhibited all these diagnostic aromatic features, without contributions from nitrile stretching ($2235\text{--}2245\text{ cm}^{-1}$) or diene bands. Their strong, well-defined aromatic doublet in the $900\text{--}700\text{ cm}^{-1}$ region, together with the characteristic styrenic C–H and C=C vibrations, confirmed their polystyrene identity.

E- Characteristics of Acrylonitrile-butadiene styrene (ABS) signature

As seen above, ABS share many features with Polystyrene (PS). Their spectra are quite similar but with additional contributions from nitrile stretching ($2235\text{--}2245\text{ cm}^{-1}$) and diene bands (Agirre et al., 2022). The ABS markers are:

- C=C stretching of conjugated dienes in the $1630\text{--}1650\text{ cm}^{-1}$ region (sometimes weak/broadened).
- C≡N stretching: a sharp nitrile band at $\sim 2235\text{--}2245\text{ cm}^{-1}$, the key marker of the acrylonitrile units.
- =C–H out-of-plane bending modes around $965\text{--}910\text{ cm}^{-1}$, associated with trans-1,4 or 1,2-vinyl units.
- Additional CH₂/CH₃ bands reflecting the rubbery backbone.

Samples STMPS21, SIMPS29, STMPS31 and SIMPS32 were confirmed to be ABS but showed slightly more complex low wavenumber regions ($1000\text{--}700\text{ cm}^{-1}$) due to the overlapping contributions from the butadiene and styrenic phase. But the simultaneous

presence of styrenic aromatic, nitrile, and diene-related bands as seen in the spectra of figure 25 confirms the ABS nature of these samples.

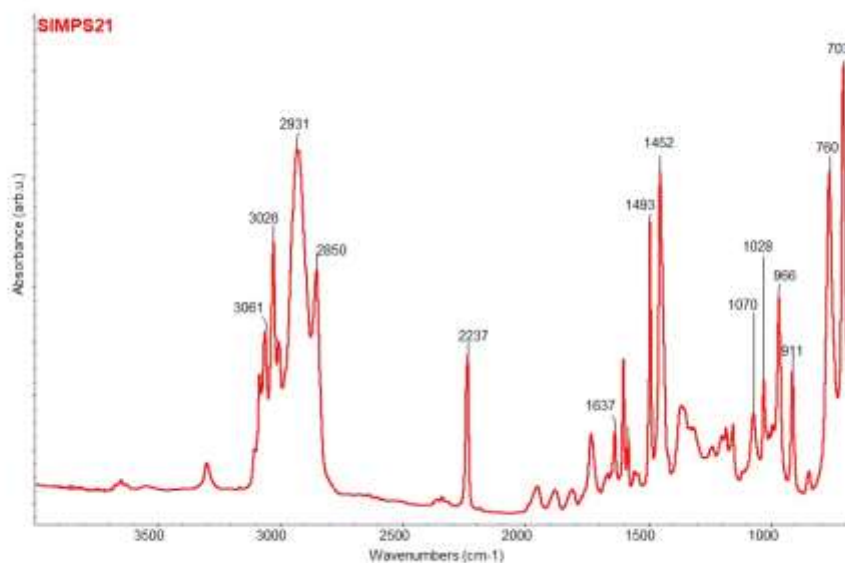


Figure 25: IR spectrum of SIMPS 21. The spectrum shows the marker peaks of ABS at the 1637 cm⁻¹ and 966 cm⁻¹ which are ascribed to the butadiene phase.

F- Characteristics of Polyoxymethylene (POM) signature

SIMPS 25 displays a clean POM (polyacetal) signature by:

- Dominant C–O–C stretching band at $\sim 1100\text{--}1080\text{ cm}^{-1}$, often very intense.
- Additional C–O–C and skeletal modes in the $950\text{--}900\text{ cm}^{-1}$ region.
- CH₂ stretching bands:
 - $\nu_{\text{as}}(\text{CH}_2) \sim 2920\text{--}2930\text{ cm}^{-1}$
 - $\nu_{\text{s}}(\text{CH}_2) \sim 2850\text{--}2860\text{ cm}^{-1}$
- Minimal or absent carbonyl and aromatic bands (Liu et al., 2023).

The figure below shows the SIMPS 25 spectra having the strong ether bands and relatively simple hydrocarbon signature.

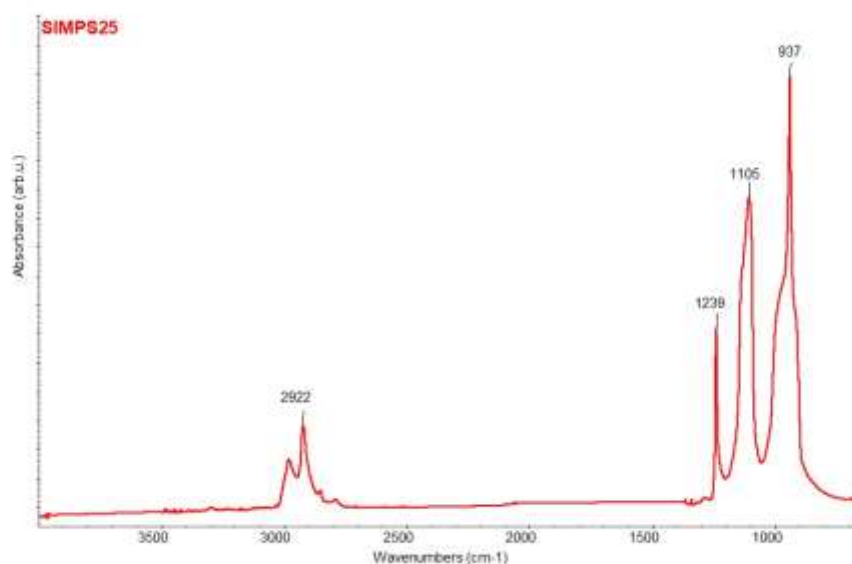


Figure 26: IR spectrum of SIMPS 25, which clearly shows the bands assigned to the C-O-C stretching and skeletal modes, which indicates the presence of POM.

G- Characteristic of Polycarbonate (PC) signature

For PC, sample SIMPS 23 was consistent with aromatic polycarbonate:

- Carbonate C=O stretching: very strong band at $\sim 1770\text{--}1780\text{ cm}^{-1}$ (higher wavenumber than typical ketone esters or amides).
- Aromatic C=C ring modes: bands at ~ 1600 and 1500 cm^{-1} .
- C–O–C stretching: bands in the $1200\text{--}1150\text{ cm}^{-1}$ region.
- Aromatic C–H stretching: $3100\text{--}3000\text{ cm}^{-1}$.
- Aliphatic CH₃ / CH₂ stretching: $2970\text{--}2870\text{ cm}^{-1}$ depending on specific PC grade.

The most diagnostic feature in the spectrum distinguishing PC from other carbonyl-containing polymers is the high frequency carbonate band around $\sim 1770\text{--}1780\text{ cm}^{-1}$ (Arsyad et al., 2023). This can be seen in the figure below.

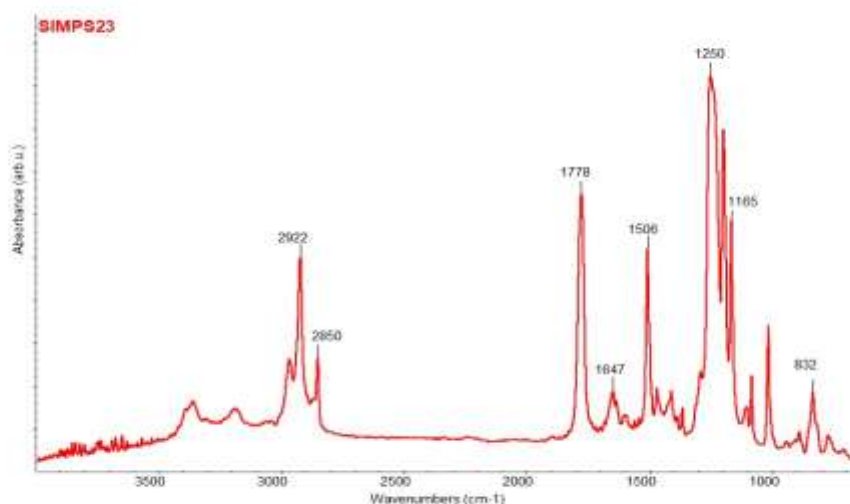


Figure 27: SIMPS 23 IR spectrum showing bands of Polycarbonate.

A summary of all polymers identified using FTIR is presented in table 4 below:

Table 4: Summary of all samples with corresponding polymers.

Polymer	Sample
Polypropylene (PP)	MV1, MMPS12, MMPS13, MMPS16, MMPS17, MMPS22, MMPS19
Polypropylene + Polyethylene (PP+PE)	MMPS3, MMPS5, MMPS6, MMPS7, MMPS9, MMPS10, SIMPS30, SIMPS24, MMPS20, MMPS18, MMPS15, MMPS14.
Polyamide (PA)	MMPS1, MMPS2, MMPS4, MMPS17, SIMPS28
Polycarbonate (PC)	SIMPS23
Polyoxymethylene (POM)	SIMPS25
Acrylonitrile butadiene styrene (ABS)	STMPS31, SIMPS29, STMPS21
Polystyrene (PS)	SIMPS32, STMPS27,
Polyethylene (PE)	SIMPS33

Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) Analysis

Inductively Coupled Plasma-Mass spectrometry (ICP-MS) plays a crucial role in chemical characterisation of recycled plastics due to its unparalleled ability to quantify trace and ultra-trace elements with high sensitivity, broad dynamic range, and multi-elemental detection capability. Unlike other spectroscopic or microscopic techniques, ICP-MS quantifies concentrations down to the microgram-per-kilogram scale, enabling the detection of both intentional additives and non-intentional contaminants embedded within the polymer matrix. In this study, 12 elements (Ca, Mg, Ti, Al, Ba, Cr, Ni, Pb, Sb, Cu, Co, Fe) were analysed using ICP-MS across the 10 selected samples. Their quantification provided insight into filler composition, contamination pathways and the chemical history of the materials. These elements were grouped into two sets: the first containing Ca, Mg, Al, Ba and Ti, representing the key constituents of inorganic fillers such as calcite, talc, glass fibres, barite, and rutile. Although ideal mineral end members such as $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ for talc and SiO_2 for glass might be assumed for filler phases, industrial mineral fillers are chemically heterogeneous. Commercial talc products commonly contain significant amount of accessory minerals, including chlorite, dolomite and calcite, and exhibit complex oxide compositions with Mg, Si, Al, Fe, Ti and other elements, rather than the pure Mg-Si end member alone (Belgacem et al., 2008). Similarly, reinforcing glass fibres such as E-glasses are silicate multicomponent systems containing SiO_2 , Al_2O_3 , CaO , MgO and other oxides rather than pure silica (Hopper, n.d.). These real-world compositional variations are essential for the grouping of filler constituent elements and their interpretation.

The second set (Cr, Ni, Pb, Sb, Cu, Co, and Fe) consists of heavy metals and other metals related to contamination relevant to regulatory assessment in the plastics recycling industry. When examining the concentration of the first set across all samples, Ca emerges as the dominant element, consistent with the widespread use of Ca-rich fillers and reinforcing phases in the plastic industry as seen in table 5 and figure 28. In contrast, the distribution of the second set table 6 shows Fe as the most recurrent metal contaminant, primarily reflecting contamination introduced during mechanical recycling. This is likely associated with wear and abrasion of metallic components in shredding and extrusion machinery, which release Fe-rich particles that become incorporated into the bulk polymer.

Table 5: Filler constituent elements concentration in analysed samples

Element	MMPS9 (mg/kg)	MMPS18 (mg/kg)	MMPS20 (mg/kg)	SIMPS24 (mg/kg)	SIMPS30 (mg/kg)	MMPS4 (mg/kg)	STMPS27 (mg/kg)	STMPS3 1 (mg/kg)	MV1 (mg/kg)	MMPS12 (mg/kg)
Ba	6.11 ± 0.15	13.72 ± 4.01	18.78 ± 0.73	24.07 ± 0.44	9.65 ± 0.422	25.54 ± 0.52	184.32 ± 7.47	169.99 ± 3.14	1.67 ± 0.3	171.04 ± 21.57
Mg	295.86 ± 7.83	233.56 ± 9.64	322.8 ± 12. 59	394.89 ± 7.78	83.79 ± 10.54	1069.44 ± 31.72	364.98 ± 10.56	187.62 ± 9.32	46.3 ± 1.50	1039.81 ± 88.41
Al	236.38 ± 1.83	120.12 ± 13.27	193.75 ± 6.03	1684.02 ± 109.44	134.42 ± 3.76	9715.84 ± 481.64	221.52 ± 4.47	132.15 ± 3.93	6.87 ± 0.28	520.58 ± 34.09
Ti	2.215 ± 0.07	4.291 ± 0.08	13.47 ± 0.44	14.31 ± 1.31	6.42 ± 0.17	120.72 ± 20.53	8.7 ± 0.19	8.40 ± 0.10	0.21 ± 0.01	6.68 ± 0.39
Ca	2048.92 ± 131.65	7907.97 ± 215.87	8907.29 ± 283.92	3750.02 ± 171.66	1580.46 ± 108.12	19140.99 ± 516.20	5015.86 ± 215.30	656.42 ± 36.13	269.78 ± 22.88	706.09 ± 79.61

Table 6: Metal contaminants concentration in analysed samples

Element	MMPS9 (mg/kg)	MMPS18 (mg/kg)	MMPS20 (mg/kg)	SIMPS24 (mg/kg)	SIMPS30 (mg/kg)	MMPS4 (mg/kg)	STMPS27 (mg/kg)	STMPS31 (mg/kg)	MV1 (mg/kg)	MMPS12 (mg/kg)
Sb	89.40 ± 4.38	5.46 ± 2.19	10.16 ± 0.21	1.952 ± 0.57	1.47 ± 0.1	0.99 ± 0.35	165.37 ± 6.94	41.72 ± 1.61	0.28 ± 0.037	0.19 ± 0.01
Pb	1.78 ± 0.05	11.11 ± 0.21	16.36 ± 2.44	5.93 ± 6.44	5.2 ± .23	5.61 ± 0.23	21.83 ± 0.24	19.10 ± 1.59	0.591 ± 0.02	0.83 ± 0.02
Cr	4.58 ± 0.18	6.99 ± 0.17	7.05 ± 0.54	36.4 ± 11.41	1.98 ± 0.14	581.85 ± 18.47	5.44 ± 0.35	4.46 ± 0.19	0.74 ± 0.26	3.97 ± 0.77
Fe	79.89 ± 0.8	133.88 ± 62.08	148.11 ± 9.84	291.69 ± 51.7	44.29 ± 2.04	3147.97± 84.04	196.76 ± 5.71	134.41 ± 4.6	13.73 ± 1.95	266.96 ± 15.88
Co	0.12 ± 0.01	0.26 ± 0.01	0.269 ± 0.01	0.46 ± 0.17	0.07 ± 0.01	6.21 ± 0.21	1.61 ± 0.06	2.89 ± 0.06	0.02 ± 0.001	0.18 ± 0.01
Ni	2.98 ± 0.13	2.65 ± 0.11	2.68949 ± 0.09	11.8137 ± 4.2	0.75 ± 0.1	253.01 ± 6.7	7.17 ± 0.78	9.89 ± 0.43	1.14 ± 0.18	3.26 ± 0.33
Cu	20.42 ± 0.37	6.11 ± 1.11	135.3309 ± 7.81	5.877456 ± 0.22	7.11 ± 0.15	145.48 ± 1.89	10.6 ± 4.66	10.56 ± 0.14	1.79 ± 0.06	9.95 ± 0.62
Zn	32.33 ± 0.4	23.15 ± 1.34	62.59612 ± 5.76	21.51668 ± 1.11	32.94 ± 13.94	114.92 ± 5.94	158.36 ± 3.10	55.78 ± 2.4	10.45 ± 5.8	70.89 ± 9.94

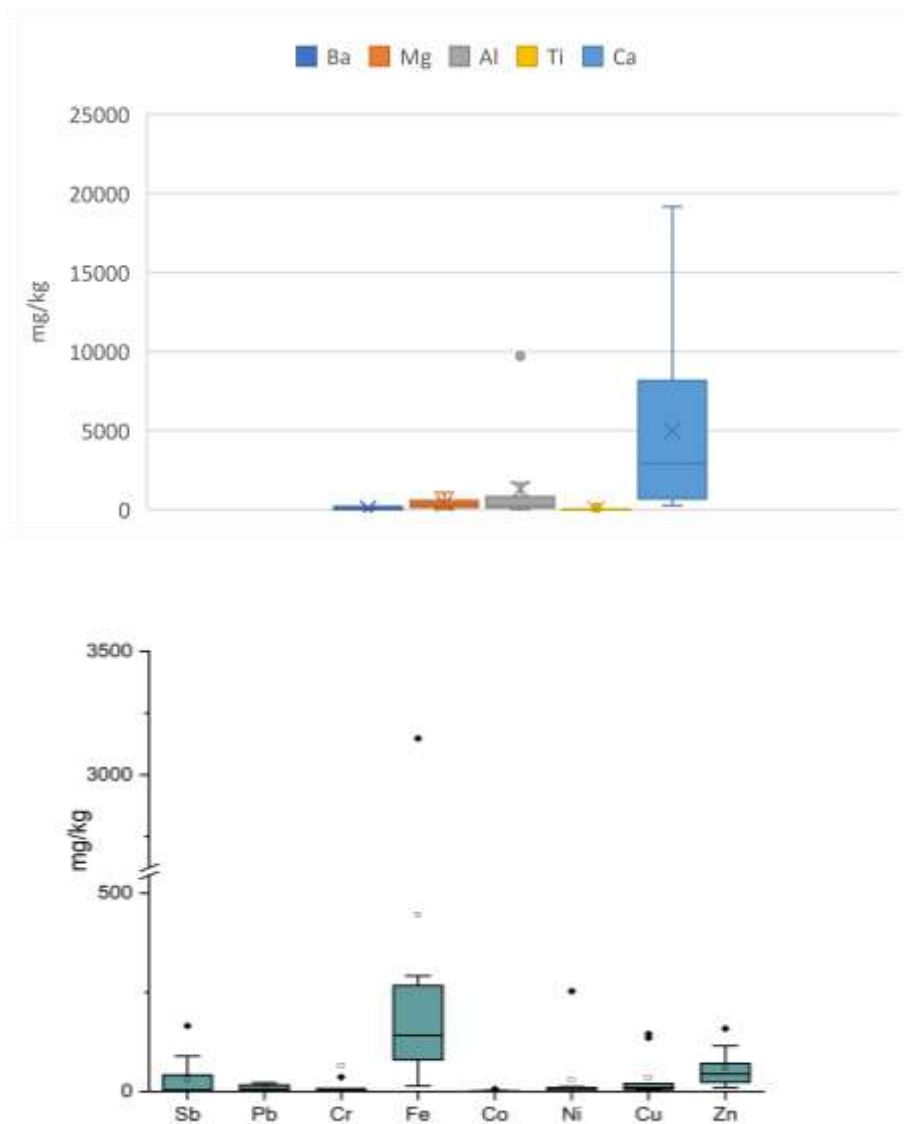


Figure 28: Variation of filler constituent elements and metal contaminants among the analysed samples

Based on the results where the polymers were identified, it will be interesting to see how these elements vary through the different samples. For the selected 10 samples, 5 different polymers were represented: PP, PP+PE, PA, PS, ABS.

Variation of Filler constituent elements in polymers

Polypropylene (PP) Samples

As seen from the graph and table in figure 29 and table 7 below, the polypropylene filler highlights a pronounced compositional difference between the virgin PP (MV1) and the recycled PP samples (MMPS12). This difference reflects the incorporation of mineral fillers

during the material's lifecycle or recycling history. While MV1 exhibits only trace amounts of Mg, Al, Ti, and Ba with Ca present at low background levels, whereas MMPS12 displays dramatically elevated concentrations of Mg ($1039.81 \pm 88.41 \text{ mg/kg}$), Al ($520.58 \pm 34.09 \text{ mg/kg}$), Ca ($706.09 \pm 79.61 \text{ mg/kg}$). This elemental pattern is characteristic of talc-filled polypropylene, where talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) contributes high Mg and Al contents, and Ca appears either as an associated minor phase or due to accidental incorporation of Calcite (CaCO_3). The presence of Ba at moderate levels ($171.04 \pm 21.57 \text{ mg/kg}$) in MMPS12 further suggests cross-contamination with barite containing waste streams or blended polymer residues, which is absent in the virgin material. Ti remains negligible ($6.68 \pm 0.39 \text{ mg/kg}$) in both samples, indicating that rutile (TiO_2) pigmentation was not a significant contributor. Collectively, the enrichment of Mg, Al, Ba and Ca in MMPS 12 provides clear evidence of extensive mineral filler loading and compositional heterogeneity acquired through recycling.

Table 7: Concentration of filler constituent elements in polypropylene samples

	<i>MV1 (mg/kg)</i>	<i>MMPS12 (mg/kg)</i>
<i>Ba</i>	1.67 ± 0.3	171.04 ± 21.57
<i>Mg</i>	46.3 ± 1.50	1039.81 ± 88.41
<i>Al</i>	6.87 ± 0.28	520.58 ± 34.09
<i>Ti</i>	0.21 ± 0.01	6.68 ± 0.39
<i>Ca</i>	269.78 ± 22.88	706.09 ± 79.61

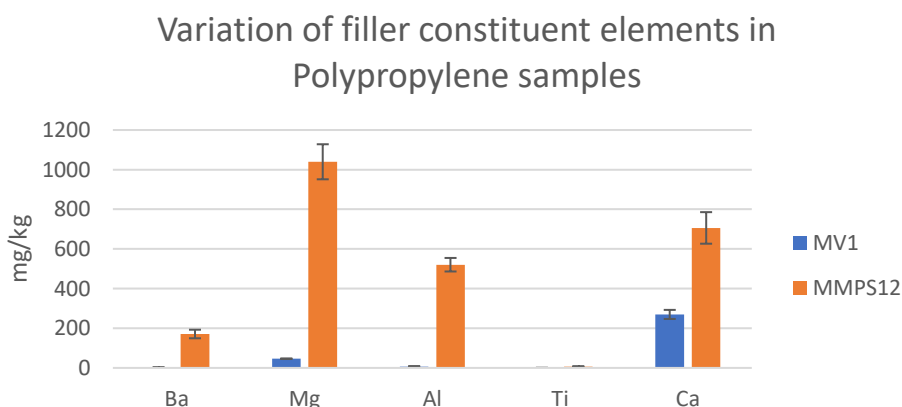


Figure 29: graph presenting the variation of filler constituent elements in polypropylene samples

Polypropylene +Polyethylene (PP+PE) Samples.

The filler element distribution observed PP+PE samples demonstrates a compositional heterogeneity characteristic of mixed polyolefin recyclates, where materials originating from

diverse product streams converge into a single fraction. Across the table shown in table 8, calcium dominates highly, reaching concentrations of 8907.29 ± 283.9 mg/kg in MMPS20 , 7907.97 ± 215.87 mg/kg in MMPS18 , 2049.92 ± 131.65 mg/kg in MMPS9, 3750.01 ± 171.66 mg/kg in SIMPS24 and 1580 ± 108.12 mg/kg in SIMPS30 confirming that calcite (CaCO_3) is the principal filler phase in PP+PE blends. The wide Ca range evident from the large interquartile spread in the graph in figure 30 below indicates that some PP+PE items were originally heavily mineral-filled, while others were lightly filled films or flexible items with minimal inorganic loading. Mg and Al appear at much lower but with co-varying levels as seen in table 9, consistent with the presence of talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) or aluminosilicate additives introduced either intentionally or through contamination from adjacent waste streams as PP or PA. Ti, although present at low concentrations, displays limited variability and likely originates from rutile (TiO_2) pigmentation commonly used for PE-based packaging. Ba remains almost negligible across the dataset, which shows that the Barite fillers are less used in polyolefins. These graphs illustrate that PP+PE recyclates are chemically dominated by carbonate fillers with minor silicate contributions.

Table 8: Concentration of filler constituent elements of PP+PE samples

	<i>MMPS9 (mg/kg)</i>	<i>MMPS18 (mg/kg)</i>	<i>MMPS20 (mg/kg)</i>	<i>SIMPS24 (mg/kg)</i>	<i>SIMPS30 (mg/kg)</i>
<i>Ba</i>	6.11 ± 0.15	13.72 ± 4.01	18.78 ± 0.73	24.07 ± 0.44	9.65 ± 0.422
<i>Mg</i>	295.86 ± 7.83	233.56 ± 9.64	322.8 ± 12.59	394.89 ± 7.78	83.79 ± 10.54
<i>Al</i>	236.38 ± 1.83	120.12 ± 13.27	193.75 ± 6.03	1684.02 ± 109.44	134.42 ± 3.76
<i>Ti</i>	2.215 ± 0.07	4.291 ± 0.08	13.47 ± 0.44	14.31 ± 1.31	6.42 ± 0.17
<i>Ca</i>	2048.92 ± 131.65	7907.97 ± 215.87	8907.29 ± 283.92	3750.02 ± 171.66	1580.46 ± 108.12

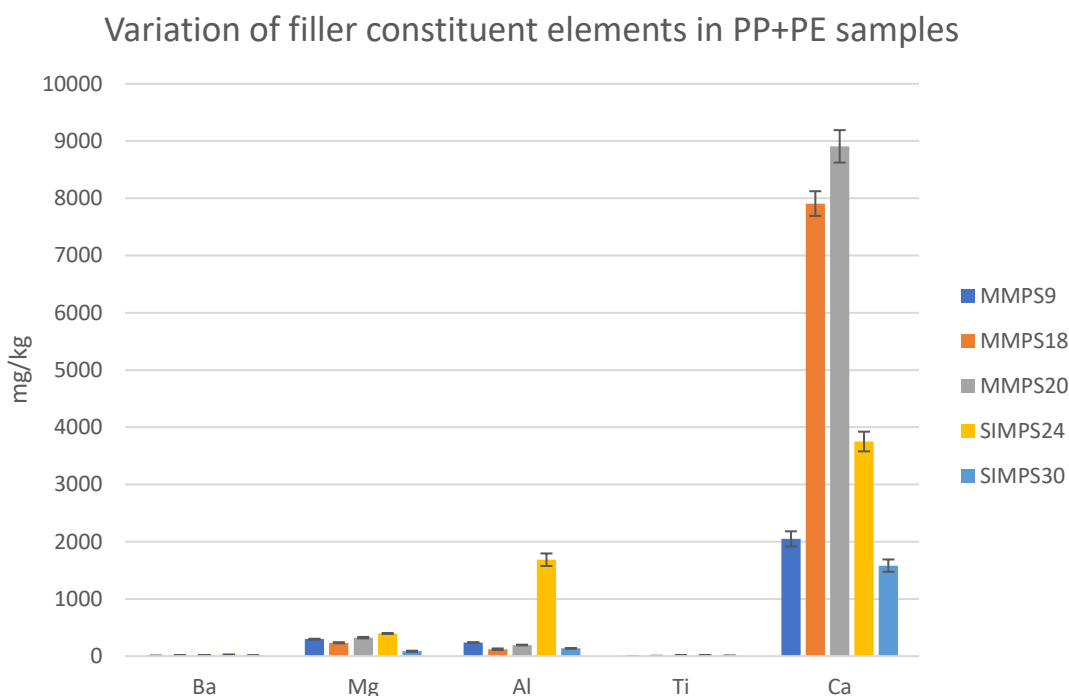
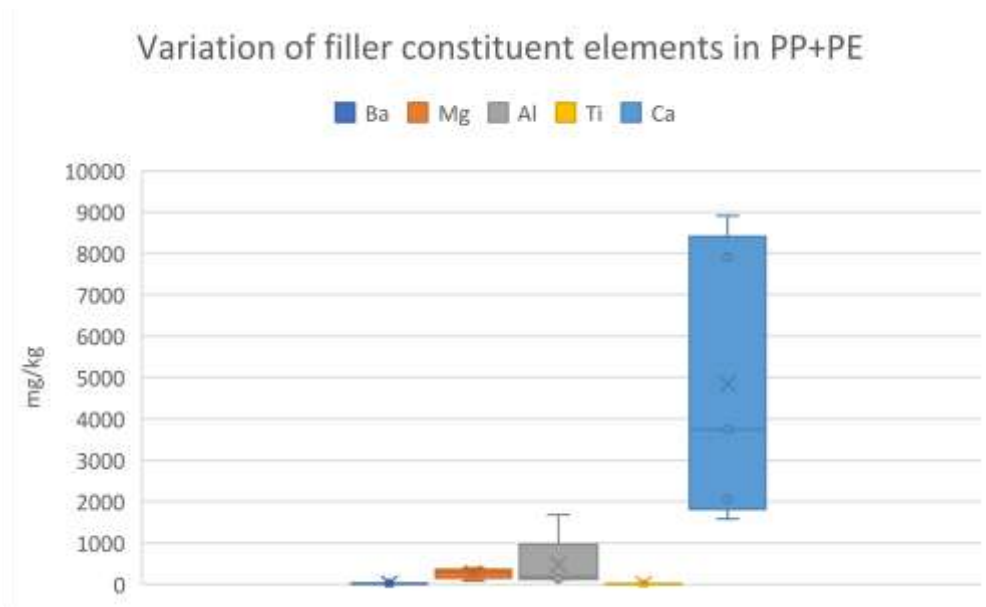


Figure 30: Graphs presenting the variation of filler constituent elements in PP+PE samples.

Polyamide (PA) sample

The elemental composition of the only PA sample (MMPS4) as seen in table 9 and figure 31, reveals a distinctive filler chemistry dominated of a high concentration of Ca (19140.99 ± 516.21 mg/kg) and Al (9715.84 ± 481.64 mg/kg), exceeding levels typically observed in other samples. This dual enrichment indicates the presence of glass fibre reinforcement, most likely E-glass, which is characteristically composed of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--}$

MgO. The moderate concentration of Mg (1069.44 ± 31.72 mg/kg) is consistent with the interpretation of glass fibre as reinforcement. Also the extremely low of Ti and Ba concentrations confirm the absence of rutile (TiO_2) pigments or barite fillers, indicating that the inorganic fraction of MMPS4 is not derived from low cost fillers but from structural reinforcement system used in high-performance PA components.

Table 9: MMPS 4 filler constituent elemental concentration

<i>MMPS4 (mg/kg)</i>	
<i>Ba</i>	25.54 ± 0.52
<i>Mg</i>	1069.44 ± 31.72
<i>Al</i>	9715.84 ± 481.64
<i>Ti</i>	120.72 ± 20.53
<i>Ca</i>	19140.99 ± 516.20

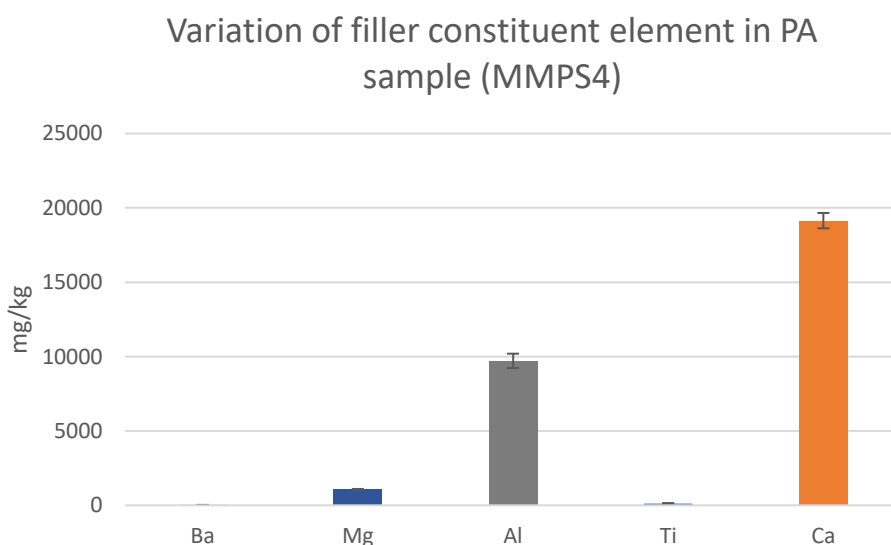


Figure 31: Elemental concentration of sample MMPS4

Polystyrene (PS) sample

The PS sample (STMPS27) presents an inorganic composition dominated by a very high Ca concentration (5015.86 ± 215.31 mg/kg) as reported in table 10 and figure 32, which is a typical for pure PS formulations and therefore strongly suggests significant Calcite (CaCO_3) incorporation or cross-contamination with heavily filled PP recyclates. The moderate presence of Mg (364.98 ± 10.56 mg/kg) and Al (221.52 ± 4.47 mg/kg) suggests minor contributions from talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) or aluminosilicate materials, although the relative

proportions do not match typical talc stoichiometry, implying contamination from mixed plastic feedstock rather than intentional addition. Ba, although present at lower concentrations (184.32 ± 3.93 mg/kg), remains a critical indicator of barite (BaSO_4), a more classical filler in PS systems used in rigid mouldings or E&E (electronic and electrical equipment) housings where enhanced density is required. The negligible Ti (8.7 ± 0.19 mg/kg) levels confirm the absence of TiO_2 pigments in this specific material.

Table 10: STMPS27 filler constituent elemental concentration.

<i>STMPS27 (mg/kg)</i>	
<i>Ba</i>	184.32 ± 7.47
<i>Mg</i>	364.98 ± 10.56
<i>Al</i>	221.52 ± 4.47
<i>Ti</i>	8.7 ± 0.19
<i>Ca</i>	5015.86 ± 215.30

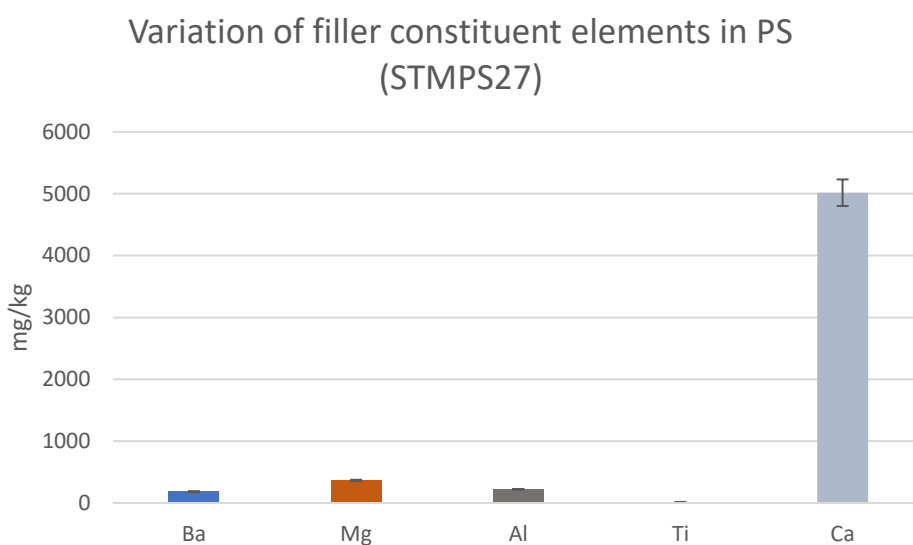


Figure 32: Elemental concentration of STMPS27

Acrylonitrile Butadiene Styrene (ABS) sample

The ABS sample (STMPS31) exhibits a complex but characteristic filler elemental concentration consistent with typical formulations used in mass-market and technical ABS products. The most prominent element is Ca (656.42 ± 36.13 mg/kg), suggesting the presence of calcite (CaCO_3) either as a primary filler or as contamination introduced during recycling with polyolefin streams. Ba (169.99 ± 3.14 mg/kg) is also notable, pointing to the use of barite

(BaSO₄), a common additive in ABS grades designed for improved density, dimensional stability, and acoustic damping. The presence of Mg (187.62 ± 9.32 mg/kg) and Al (132.15 ± 3.93 mg/kg) in moderate quantities indicates either minor inclusion of talc/aluminosilicates or carry-over from adjacent waste streams, especially given the mixed nature of post-consumer ABS. Ti is nearly absent, implying that rutile (TiO₂) pigmentation was minimal or absent in this particular batch, contrary to some ABS formulations where opacity is required. The balanced but non-uniform distribution of Ba, Mg, and Al reflects a heterogeneous filler system.

Table 11: STMPS31 filler constituent elemental concentration.

<i>STMPS31 (mg/kg)</i>	
<i>Ba</i>	169.99 ± 3.14
<i>Mg</i>	187.62 ± 9.32
<i>Al</i>	132.15 ± 3.93
<i>Ti</i>	8.40 ± 0.10
<i>Ca</i>	656.42 ± 36.13

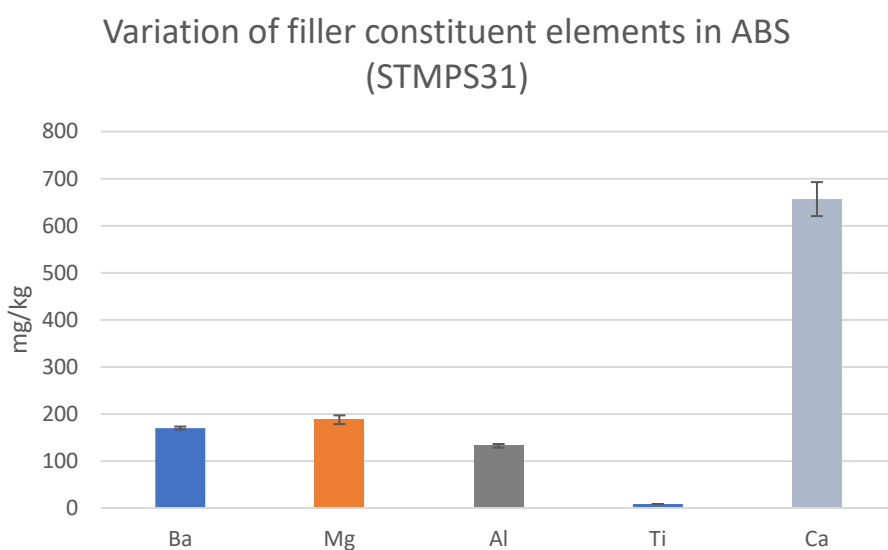


Figure 33: Filler constituent elemental concentration in STMPS31

Variation of metal contaminants and heavy metals in polymers

Polypropylene Samples

ICP-MS permitted the identification of metal contaminant in the polypropylene samples: MV1 and MMPS12, which revealed a straight contrast between the two samples.

Table 12 shows that the heavy metals occur at trace levels (<5 mg/kg) in MV1 (virgin), consistent with the expected purity of virgin polymers. MMPS12 shows a high concentration of Fe (266.97 ± 15.88 mg/kg), which is higher than any other metal, indicating abrasive wear of steel components during shredding which transfers Fe particulates into the polymer fragments. Zn (70.89 ± 9.94 mg/kg) and Cu (9.95 ± 0.62 mg/kg) was present moderately, suggesting secondary contamination from brass and zinc-coated machine parts or from mixed packaging waste. The overall pattern in figure 34 highlights the contamination in MMPS12 as it is contrast to MV1.

Table 12: Metal contaminant concentration in Polypropylene.

	<i>MV1(mg/kg)</i>	<i>MMPS12(mg/kg)</i>
<i>Sb</i>	0.28 ± 0.037	0.19 ± 0.01
<i>Pb</i>	0.591 ± 0.02	0.83 ± 0.02
<i>Cr</i>	0.74 ± 0.26	3.97 ± 0.77
<i>Fe</i>	13.73 ± 1.95	266.96 ± 15.88
<i>Co</i>	0.02 ± 0.001	0.18 ± 0.01
<i>Ni</i>	1.14 ± 0.18	3.26 ± 0.33
<i>Cu</i>	1.79 ± 0.06	9.95 ± 0.62
<i>Zn</i>	10.45 ± 5.8	70.89 ± 9.94

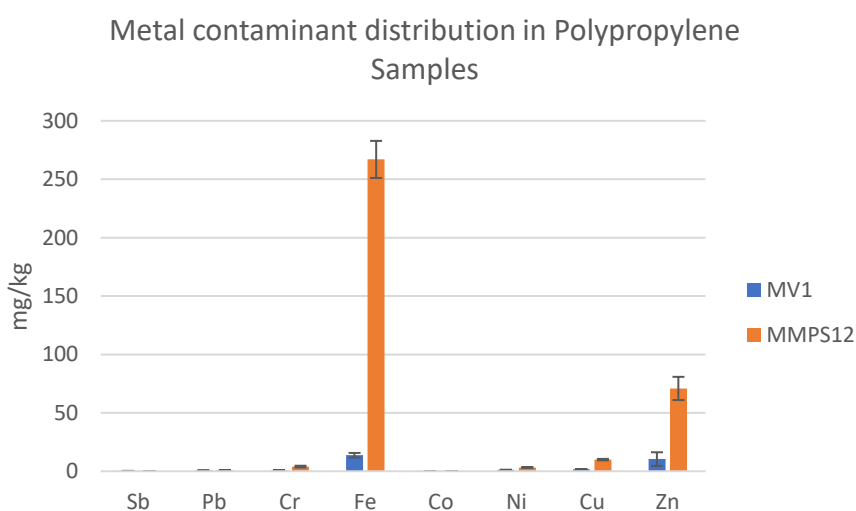


Figure 34: Metal contaminant concentration in Polypropylene samples.

Polypropylene + Polyethylene Samples

In the PP+PE samples the metal contaminant distribution is more heterogeneous than that observed in the PP samples, showing a complex and mix origin of the recycled plastic stream. As in PP, the element with the largest variability is Fe ranging from moderate levels in SIMPS30 (44.29 ± 2.04 mg/kg) to high levels in SIMPS24 (291.69 ± 51.7 mg/kg), signifying a difference in the degree of mechanical wear experienced during processing and in the metallic content of the incoming waste. Sb appears at unexpectedly high levels in some samples like MMPS9 (89.41 ± 4.387 mg/kg), which could be a resultant of the addition of flame retarded materials. Pb and Cr show moderate variability, which may originate from legacy pigments or stabilizers in older packaging or from incorporation of WEEE (waste of electrical and electronic equipment) plastics. Also, some plastics from WEEE, may have high concentration of Cu and Zn due to contamination from parts of the electrical and electronic equipment. This case is clearly seen in sample MMPS20 where the high variability of Cu and Zn reaching up to 135.33 ± 7.8 mg/kg of Cu and 62.59 ± 5.76 mg/kg of Zn compared to the other samples could be indicative of contamination from WEEE. These concentrations are reported in table 13 and figure 35.

Table 13: Metal contaminant concentration across PP+PE samples

	<i>MMPS9</i> <i>(mg/kg)</i>	<i>MMPS18</i> <i>(mg/kg)</i>	<i>MMPS20</i> <i>(mg/kg)</i>	<i>SIMPS24</i> <i>(mg/kg)</i>	<i>SIMPS30</i> <i>(mg/kg)</i>
Sb	89.40 ± 4.38	5.46 ± 2.19	10.16 ± 0.21	1.952 ± 0.57	1.47 ± 0.1
Pb	1.78 ± 0.05	11.11 ± 0.21	16.36 ± 2.44	5.93 ± 6.44	$5.2 \pm .23$
Cr	4.58 ± 0.18	6.99 ± 0.17	7.05 ± 0.54	36.4 ± 11.41	1.98 ± 0.14
Fe	79.89 ± 0.8	133.88 ± 62.08	148.11 ± 9.84	291.69 ± 51.7	44.29 ± 2.04
Co	0.12 ± 0.01	0.26 ± 0.01	0.269 ± 0.01	0.46 ± 0.17	0.07 ± 0.01
Ni	2.98 ± 0.13	2.65 ± 0.11	2.68949 ± 0.09	11.8137 ± 4.2	0.75 ± 0.1
Cu	20.42 ± 0.37	6.11 ± 1.11	135.3309 ± 7.81	5.877456 ± 0.22	7.11 ± 0.15
Zn	32.33 ± 0.4	23.15 ± 1.34	62.59612 ± 5.76	21.51668 ± 1.11	32.94 ± 13.94

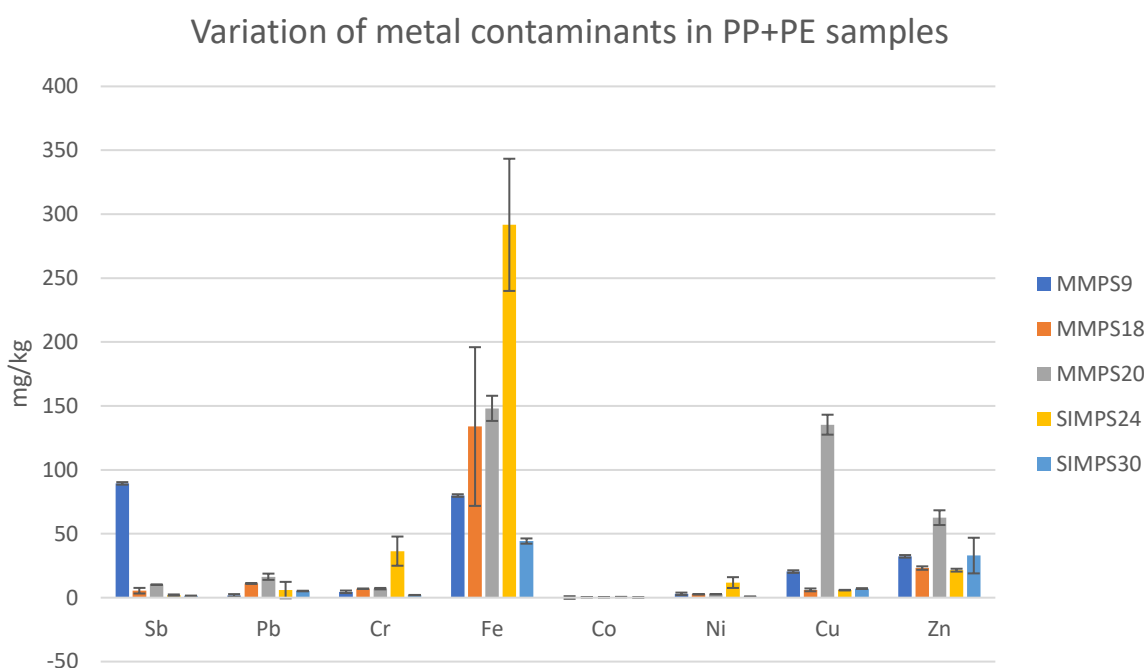


Figure 35: Metal contaminant concentration across PP+PE samples

Polyamide

In the MMPS4 sample, the element with the highest concentration as metal contaminant was Fe (3147.96 ± 84.04 mg/kg) which exceeds any other concentrations measured within the 10 samples. This high Fe enrichment strongly indicates severe mechanical abrasion of steel components during repeated shredding, which is consistent with the processing of polyamides. The second most abundant metal as shown in table 14 is Cr (581.85 ± 18.47 mg/kg) together with detectable Ni (253.01 ± 6.70 mg/kg) form a classic contamination trio (Fe-Cr-Ni) characteristic of stainless-steel alloy abrasion. The presence of Cu (145.48 ± 1.89 mg/kg) and Zn (114.92 ± 5.94 mg/kg) illustrates the contamination pathways of these plastics. Pb and Sb are somehow absent indicating that the original PA was not a flame-retardant grade.

Table 14: Metal contaminant concentration in PA sample (MMPS4)

<i>MMPS4 (mg/kg)</i>	
<i>Sb</i>	0.99 ± 0.35
<i>Pb</i>	5.61 ± 0.23
<i>Cr</i>	581.85 ± 18.47
<i>Fe</i>	3147.97 ± 84.04
<i>Co</i>	6.21 ± 0.21
<i>Ni</i>	253.01 ± 6.7

<i>Cu</i>	145.48 ± 1.89
<i>Zn</i>	114.92 ± 5.94

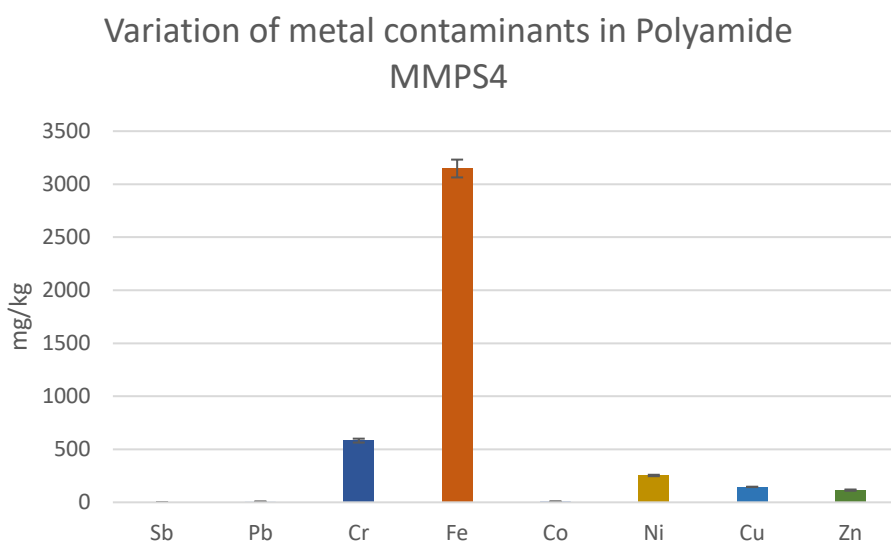


Figure 36: Metal contaminant concentration in MMPS4

Polystyrene (PS) Samples

In STMPS27 the most abundant heavy metals are Sb (165.37 ± 6.94 mg/kg), which represents antimony trioxide (Sb_2O_3) the flame retardant mostly used in the plastic industry. Fe (196.76 ± 5.71 mg/kg) is more abundant than Sb, but the difference is lower than in other polymers, suggesting a high contamination due to flame retardant and some due to mechanical abrasion during shredding, grinding and extrusion of the recycled plastic. The presence of Pb (21.83 ± 0.24 mg/kg) although lower in concentration, suggests legacy pigmentation or stabilizer residual typical of older Electrical equipment products. Zn (158.36 ± 3.10 mg/kg) and Cu (10.66 ± 4.66 mg/kg) suggest additional contamination from brass connectors or other metallic equipment used in the recycling process. Cr and Ni though minor as seen in table 15 and figure 37, reinforce the inference of stainless-steel wear particles entering the recyclate stream.

Table 15: Heavy metal concentration in STMPS27

<i>STMPS27 (mg/kg)</i>	
<i>Sb</i>	165.37 ± 6.94
<i>Pb</i>	21.83 ± 0.24
<i>Cr</i>	5.44 ± 0.35

<i>Fe</i>	196.76 ± 5.71
<i>Co</i>	1.61 ± 0.06
<i>Ni</i>	7.17 ± 0.78
<i>Cu</i>	10.6 ± 4.66
<i>Zn</i>	158.36 ± 3.10

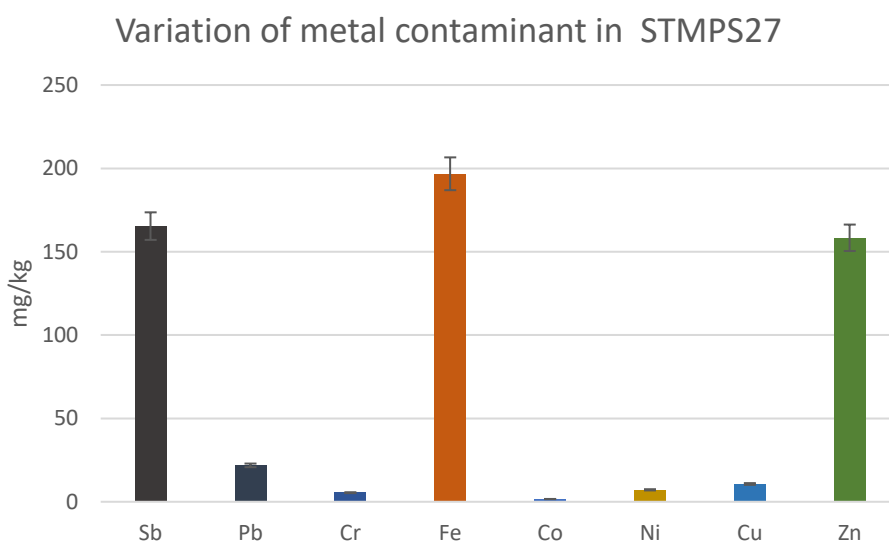


Figure 37: Metal contaminant concentration in STMPS27

Acrylonitrile Butadiene Styrene (ABS) Sample

The ABS sample being STMPS31, showed as other polymers Fe to be the highest concentrated metal with concentration of 134.41 ± 4.6 mg/kg, indicating again a significant mechanical abrasion from steel components during shredding, grinding and extrusion. Sb (41.72 ± 1.6 mg/kg) being the second most abundant heavy metal, suggests the same flame retardant found in PS sample. Pb (19.10 ± 1.59 mg/kg) suggests the presence of some legacy contaminants as in all other polymer. Zn (55.78 ± 2.4 mg/kg) and Cu (10.56 ± 0.14 mg/kg) suggests some contamination to steel but not too sure. The values of Cr and Ni reported in table 16 suggests a very low amount, but could also indicate contamination due to stainless steel in the sample. The overall elemental concentration of STMPS31 reflects a recycle originating from moderately contaminated ABS with contributions from flame retardant residues.

Table 16: Heavy metal concentration in ABS sample STMPS31

STMPS31 (mg/kg)	
<i>Sb</i>	41.72 ± 1.61
<i>Pb</i>	19.10 ± 1.59
<i>Cr</i>	4.46 ± 0.19
<i>Fe</i>	134.41 ± 4.6
<i>Co</i>	2.89 ± 0.06
<i>Ni</i>	9.89 ± 0.43
<i>Cu</i>	10.56 ± 0.14
<i>Zn</i>	55.78 ± 2.4

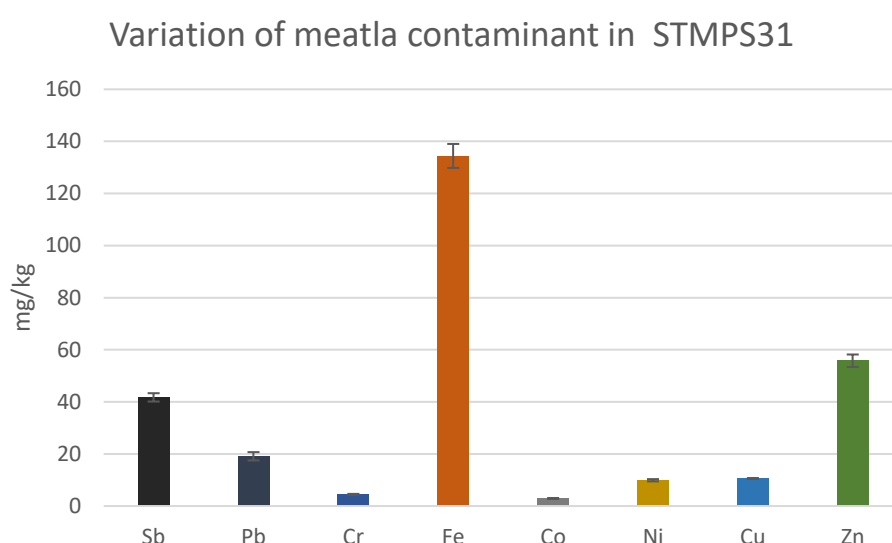


Figure 38: Metal contaminant concentration in STMPS31

X-ray Powder Diffraction (XRPD) Analysis

X-ray powder diffraction (XRPD) is a good technique in probing the structural organisation of polymers and their inorganic fillers. In recycled materials crystallinity could be altered by processing history, or filler addition. In this work, XRPD diffractograms were analysed to firstly distinguish between semi-crystalline polymers and amorphous polymers, later also used for inorganic filler identification in the polymer matrix.

Identification of Semi-Crystalline and Amorphous Polymers by XRPD

XRPD Signatures of Semi-Crystalline Polymers

Semi-crystalline polymers, such as polypropylene (PP), polypropylene + polyethylene (PP+PE), polyoxymethylene (POM) and polyamide (PA) show characteristic sharp Bragg

reflections corresponding to periodic arrangement lamellae (Bitter & Lackner, 2021). These peaks superimposed on a lower-intensity amorphous background as shown by the diffractograms of MMPS12, MMPS9, and SIMPS25 in figure 39 which are PP+PE, PP and POM respectively. In the diffractograms, semi-crystalline samples were identified by:

- Discrete, well resolved reflections typically between $10-20^\circ$ 2θ (Co $K\alpha$) for PP, between $21-35^\circ$ 2θ (Co $K\alpha$) for POM .
- Multiple Bragg peaks with high intensity and narrow full width at half maximum (FWHM), indicative of well-developed crystallites.
- A background that remains relatively flat in comparison to the peak amplitude, confirming that crystalline domains dominate the scattering

Most samples like MMPS9 showed pronounced series of sharp peaks with intensities above 10,000 counts consistent with a highly crystalline polymer matrix possibly combined with crystalline mineral fillers, which is more common in these types of plastics.

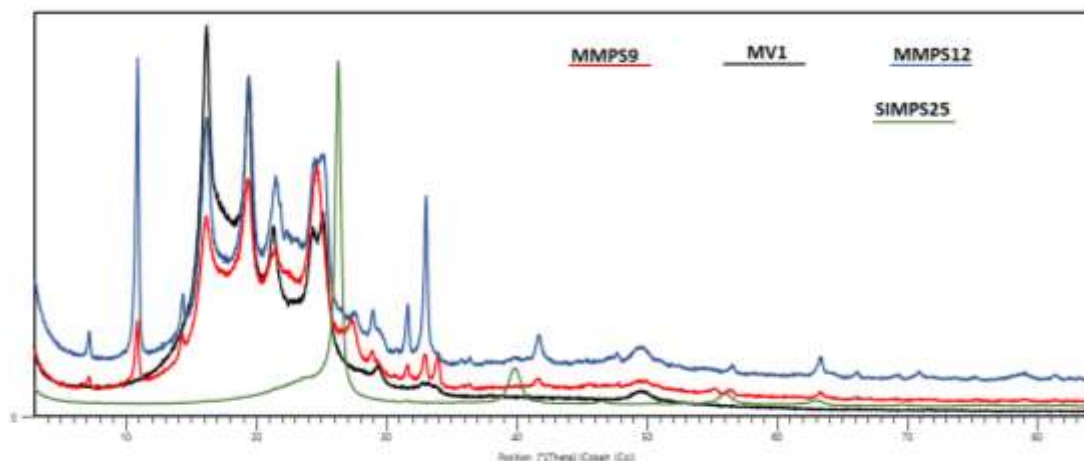


Figure 39: XRPD diffractograms showing the semi-crystallinity nature of samples (PP, PP+PE and POM)

XRPD Signatures of Amorphous Polymers

Amorphous polymers like Acrylonitrile-Butadiene-styrene (ABS), Polystyrene (PS) and Polycarbonate (PC), lack long-range molecular ordering and consequently do not produce sharp Bragg peaks (Fischer et al., 2022) as seen from the STMP27, STMP31 and SIMPS23 in figure 40 which are PS, ABS and PC polymers respectively. Their patterns are dominated by:

- Broad amorphous halos, typically between 20-25° 2 θ (Co K α) for ABS and PS, and 19-22° 2 θ (Co K α) for PC.
- Low overall intensity, with the diffractogram forming a continuous hump rather than discrete peaks
- Absence or near absence of polymer-related crystalline reflections.

SIMPS23, exhibited these features clearly: strong, broad scattering envelopes with only minor peaks corresponding to trace amounts of crystalline fillers. This pattern reflects a polymer structure that is predominantly amorphous or has undergone significant thermal/mechanical degradation leading to reduced crystallinity.

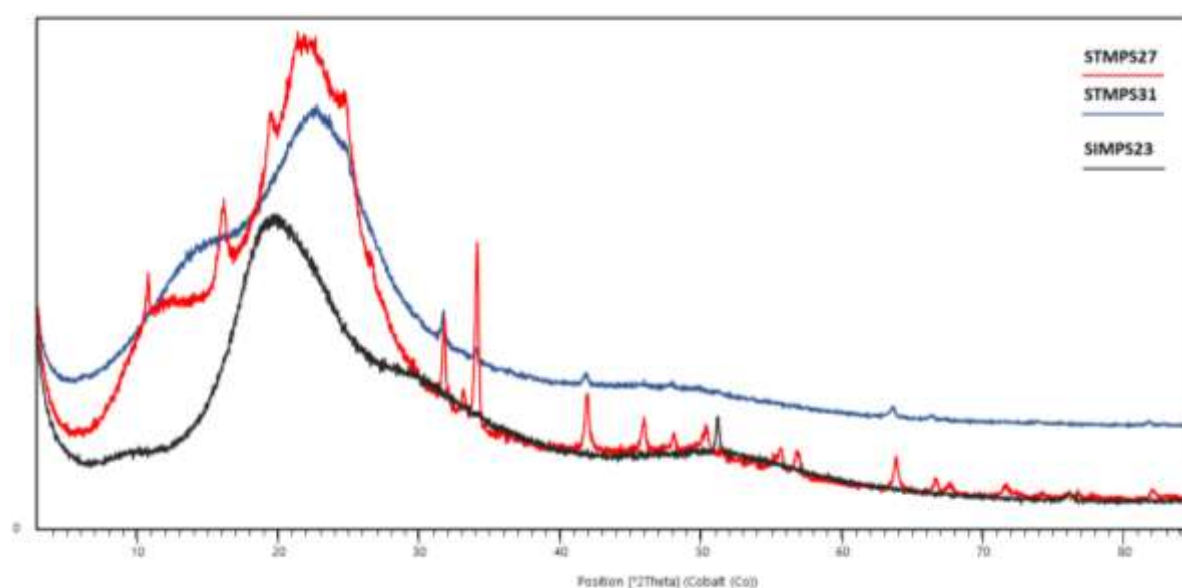


Figure 40: XRPD diffractograms showing the amorphous nature of samples (STMP527, STMP531 and SIMPS23)

One challenge encountered in polymer XRPD analysis, and more specifically in recycled materials is that mineral fillers also produce sharp, intense peaks as seen in figure 41 above which can mask or mimic polymer crystallinity. These fillers are Calcite, Talc, Rutile and Glass fibre (amorphous silicates). Glass fibres produce humps that may overlap with the polymer's own amorphous background creating a pattern which seems amorphous as what was observed in PA polymers (MMPS1, MMPS2 and MMPS4) shown in figure 41 below.

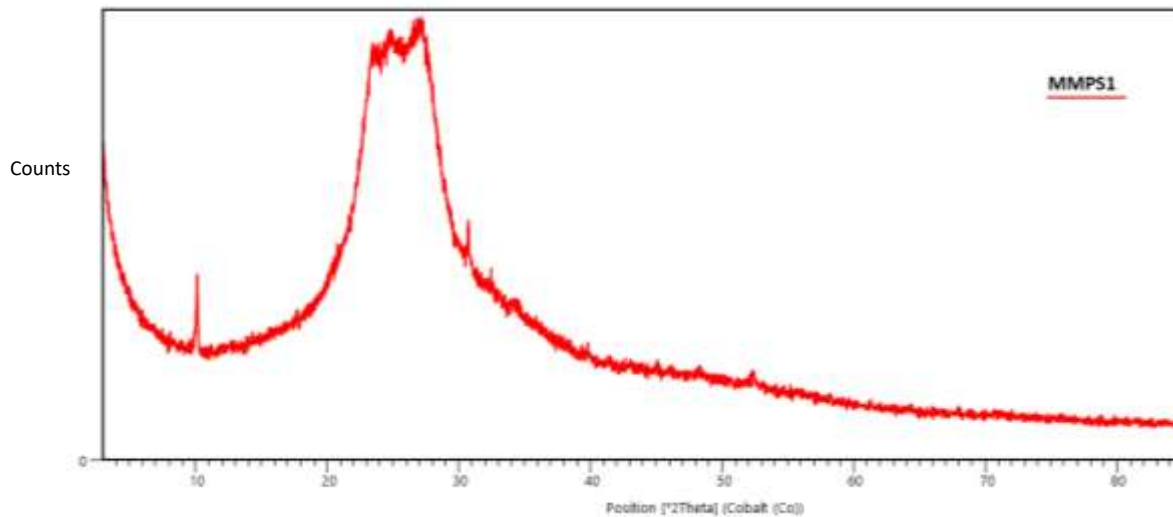


Figure 41: MMPS1 with glass fibre diffractogram, showing how a semi-crystalline PA can be observed as amorphous.

XRPD Filler Identification

Throughout the samples, some fillers were detected using XRPD. These fillers in recycled plastic also acts as markers for prior application, origin of the recycled plastics and degree of processing. XRPD detects these mineral fillers based on their unique patterns they show in a plastic sample. The mineral fillers detected in the course of this works were: calcite (CaCO_3), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), rutile (TiO_2) and glass fibres.

Identification of Calcite (CaCO_3) JCPDS 05-0586.

Calcite was the most abundant and most frequently detected filler in most polyolefins (PP and PP+PE). Its detection was direct due to its strong and characteristics reflections. The peaks of calcite are mostly seen at:

Table 17: Calcite reference peaks at 2 θ Angle (Co Ka)

2θ Angle (Co Ka)	Miller Indices (hkl)	d_{hkl} (Å)
34.3°	(104)	3.035
23.1°	(012)	3.864
31.6°	(006)	2.843
36.3°	(110)	2.5
39.5°	(114)	2.27
43.3°	(202)	2.10
47.6°	(018)	1.87
48.5°	(116)	1.77

These peaks, are highly intense and narrow, differentiating calcite from other carbonates or silicate fillers (Suzana et al., 2024). In many samples (such as MMPS18), calcite peaks as seen in table 18 more dominant. These can be seen in figure 42 where the diffractogram has high calcite peaks indicating high filler loading consistent with the use of CaCO_3 . CaCO_3 is a low-cost reinforcement filler which enhances stiffness and reduce material cost.

Table 18: Observed peak positions for Calcite in MMPS18

Observed Angle	2 θ	Reference Calcite 2 θ	Miller Indices (hkl)	d_{hkl} (Å)
34.39°	34.419°	(104)	(104)	3.035
36.75°	~36.3°	(110)	(110)	2.50
42.29°	~43.3°	(202)	(202)	2.10
50.67°	~50.5°	(108)	(108)	1.87

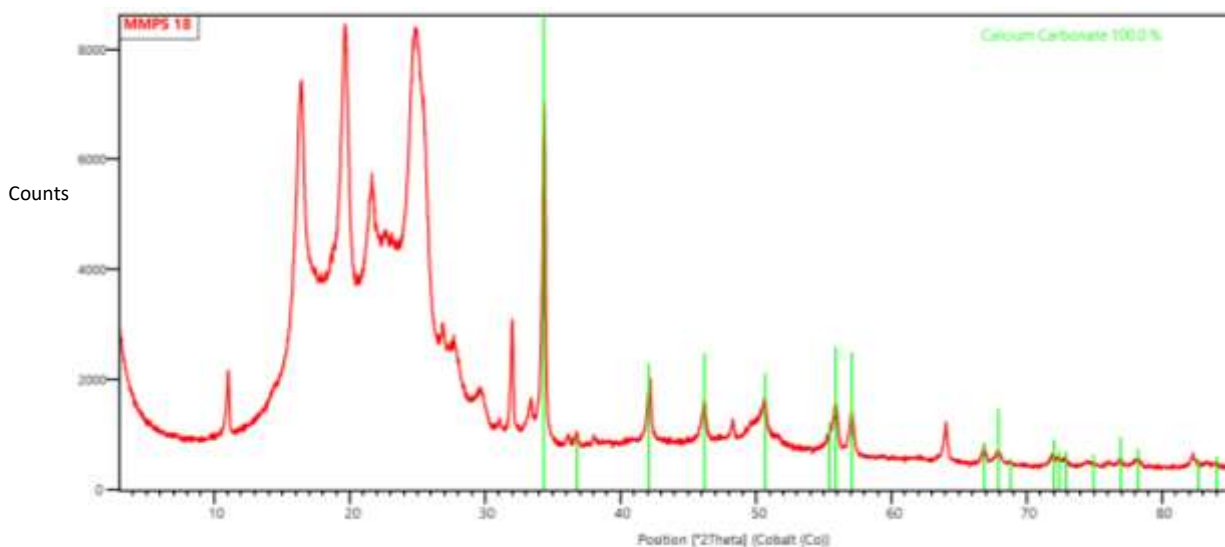


Figure 42: MMPS18 diffractogram showing Calcite phase and polypropylene (as describe earlier)

Identification of Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) JCPDS 21-1493.

The XRPD recognition of talc is based on its characteristic phyllosilicate layered structure, which produces distinct basal reflections. The reference peaks for talc in XRPD depend on the radiation source used. The most common source is copper (Cu) $\text{k}\alpha$ radiation ($\lambda=1.5406$ Å). For Cu $\text{k}\alpha$ radiation which is the one with reference (Shuai et al., 2025), the main characteristic peaks for talc are typically observed at the following approximate 2 θ angles and d-spacings:

Table 19: Reference Peaks of Talc using Cu α radiation.

2θ (Cu α)	Angle	d-spacing (nm)	Relative Intensity	Miller Indices (hkl)	d_{hkl} (Å)
9.5°		0.95 nm	Strongest	(001) or similar reflections	basal 9.3
19.0°		0.45 nm	Strong		
28.6°	-	0.32 nm	Strong		
29.0°					

However, our instrument uses a Co α radiation so we have to convert these reference peaks using the corresponding wavelength of Co ($\lambda=1.789$ Å) and inserting it into the Bragg's law equation. After using this formula, the corresponding reference peaks for talc in Co α radiation are stated in table 20 below.

Talc was identified in some samples by comparing its peaks to the reference calculated peaks, and its presence suggests its origin is from automotive or technical applications where talc is added to improve heat, resistance, rigidity, and dimensional stability. Its peaks are sometimes broader than those of calcite due to plate like morphology and partial disorder within talc lamellae. In the diffractogram of sample MMPS12 in figure 43, talc peaks overlapping with polymer amorphous halos, requiring careful interpretation. These fillers should be further confirmed using other analytical techniques such as SEM and ICP.

Table 20: Showing the observed and reference Talc peaks in sample MMPS12

Observed 2θ (Co α)	Calculated Talc 2θ (Co α)	Miller Indices (hkl)	d_{hkl} (Å)
11.02°	~10.8°	Basal Reflection (001)	9.3
21.66°	~22.2°		
33.36°	~35.6°		

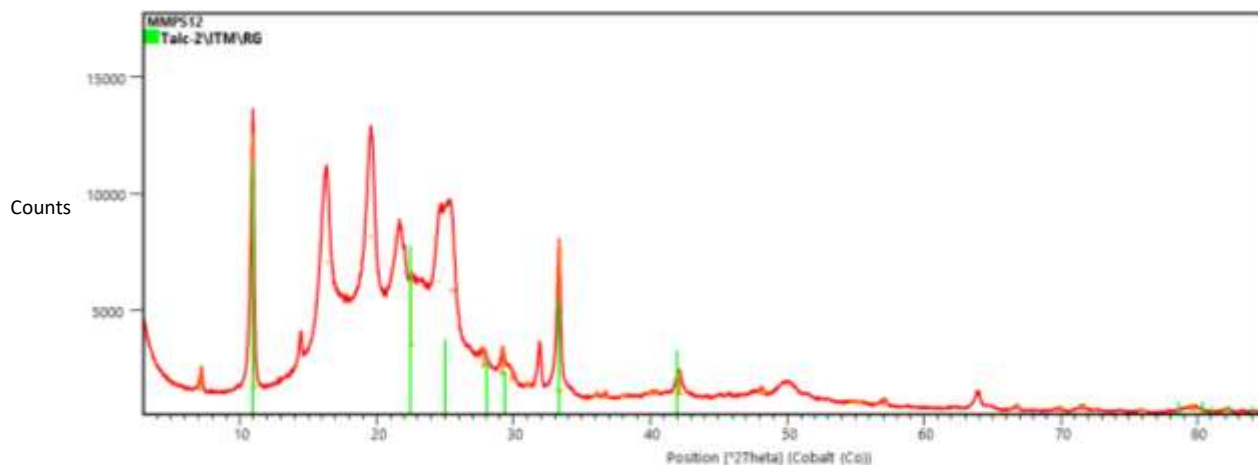


Figure 43: MMPS12 diffractogram showing the corresponding peaks of talc in the sample.

Identification of Rutile (TiO₂) JCPDS 21-1276.

As for rutile, it's identification was minor, but important as it could also be used as a pigment in several polymers such as PP, ABS, PC and POM. rutile is widely used a white pigment and UV-stabiliser, making its presence expected in coloured or UV exposed plastics such as MMPS6, MMPS10, MMPS14. Rutile exhibits strong, sharp reflections at:

$$\begin{array}{ll} \sim 31.5^\circ 2\theta \rightarrow (110) \text{ reflection} & d_{hkl} (\text{\AA}) : 3.25 \\ \sim 36.0^\circ 2\theta \rightarrow (101) \text{ reflection} & d_{hkl} (\text{\AA}) : 2.47 \end{array}$$

These peaks as seen in figure 44 are typically narrower and higher in intensity than those of anatase allowing confident discrimination (Huang et al., 2024). In some samples, rutile appeared together with calcite or talc peaks and were smaller relative to them, due to its role as a pigment and not a bulk filler. MMPS6 diffractogram shows how rutile is present with calcite in the same sample. With SEM-EDX mapping the dispersion of rutile can be observed in the sample.

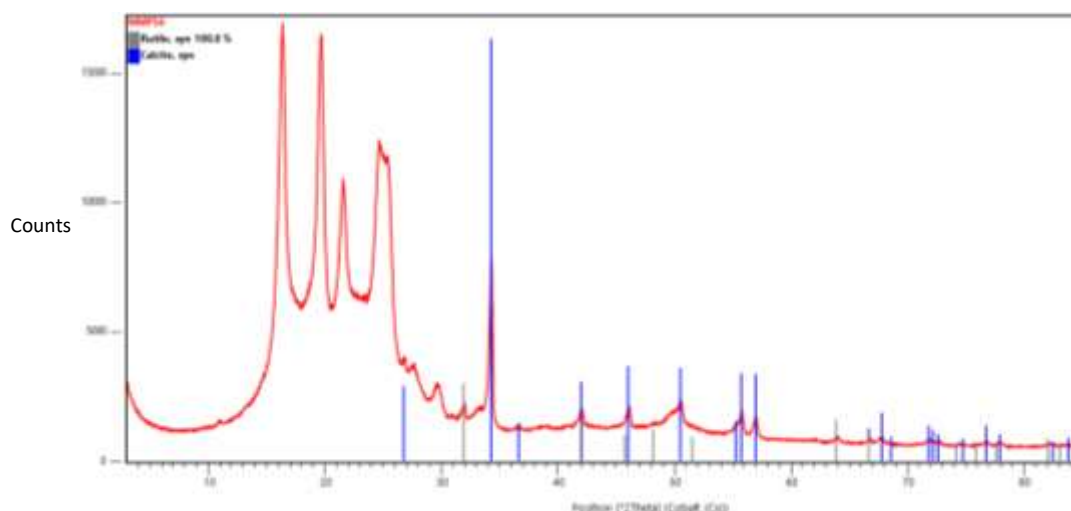


Figure 44: MMPS6 diffractogram showing the corresponding peaks of Calcite and rutile together in the sample

Identification of Glass fibres.

Glass fibres are widely used as reinforcement in engineering polymers such as polyamides (PA) due to their ability to enhance mechanical stiffness, thermal stability, and dimensional resistance. Their detection in recycled polymers is important for the understanding of the plastics origin and previous application. The use of XRPD was attempted but did not reveal discrete diffraction peaks attributable to glass fibres. This outcome is consistent with the intrinsically amorphous nature E-glass which lacks the long-range atomic periodicity required to generate sharp Bragg reflections. E-glass has a disordered, non-crystalline network that diffracts X-rays only as a broad hump, typically centred between 20° and 30° 2θ Co Kα (Shyam et al., 2021) as seen in the diffractogram of sample MMPS4 in figure 45.

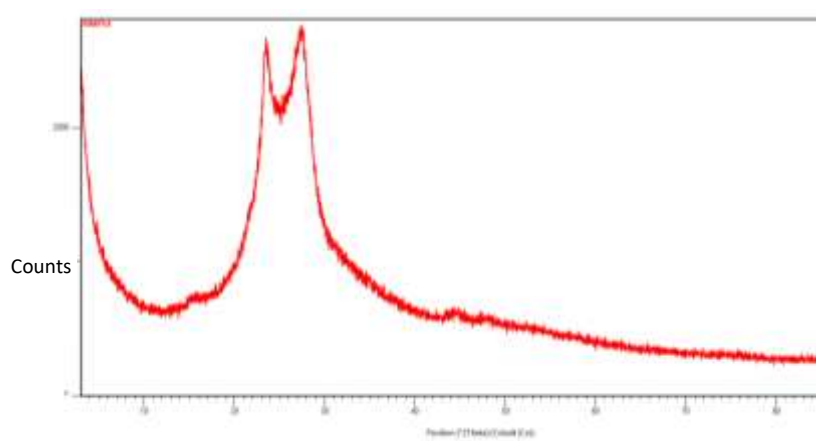


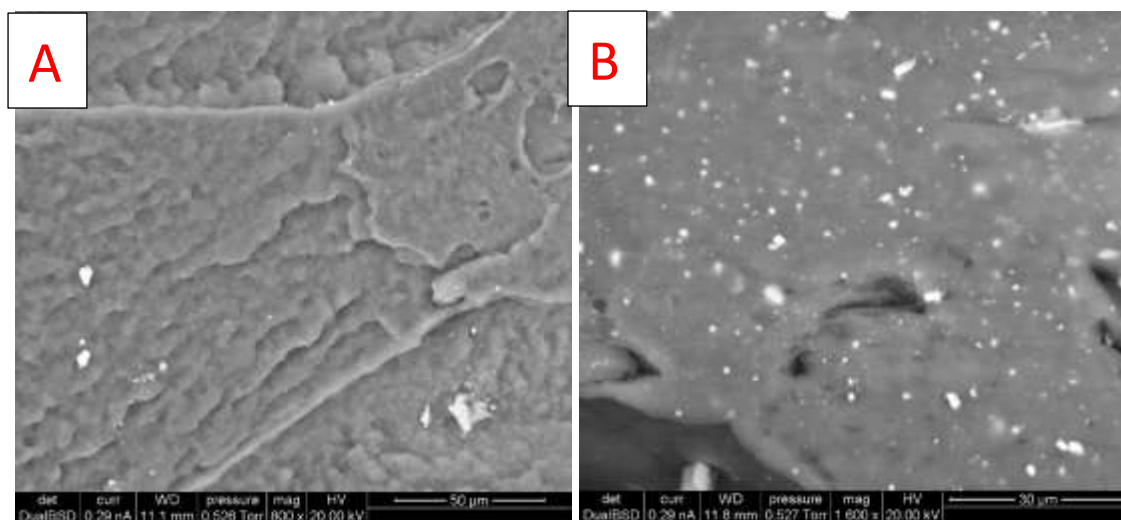
Figure 45: MMPS4 diffractogram, showing the pattern of a sample with glass fibre as filler.

Scanning Electron Microscopy (SEM)-EDX

The micro-structure, surface topography and inorganic inclusions were studied using SEM and EDX on the recycled plastic samples. This combined approach provides direct visual of the chemical evidence of contaminants, fillers and polymer mixtures that complement the XRPD, FTIR and ICP-MS results.

SEM Surface Morphology

SEM micrographs across the analysed samples revealed significant morphological variability that reflects both the polymer type and recycling history. In figure 46(a) the surface morphology of the virgin Polypropylene (MV1) is clearly seen with a lamellar rough surface with no visible filler, additive or mix within the polymer matrix. Figure 46(b) shows the presence of fillers all over the matrix with a smooth surface in sample MMPS5 (PP+PE) .In polyolefin-based (PP, PP+PE) samples, the surfaces displayed heterogeneous roughness, including micro voids in some samples as seen in figure 45(c) . Shear induced fibrillation, and irregular fracture planes could be seen in samples like MMPS12, figure 46(d), which is consistent with repeated melted processing cycles (Bata et al., 2022b). These features are characteristic of mechanical recycling or external conditions exposure which disrupts the continuous plastic metrics. During mechanical recycling, thermal and shear stresses induce local chain scission and disrupt the lamellar arrangement of semi-crystalline polymers (Achukwu et al., 2024). In more degraded fractions as in figure 46(c) representing sample MMPS6, the surface presented microcracks and embrittled regions. Also, most of the fragmented samples (flakes) had a rougher surface, compared to the pelletized ones, which defines a rearrangement of the matrix after cooling and extruding, thereby reducing the degree of degradation.



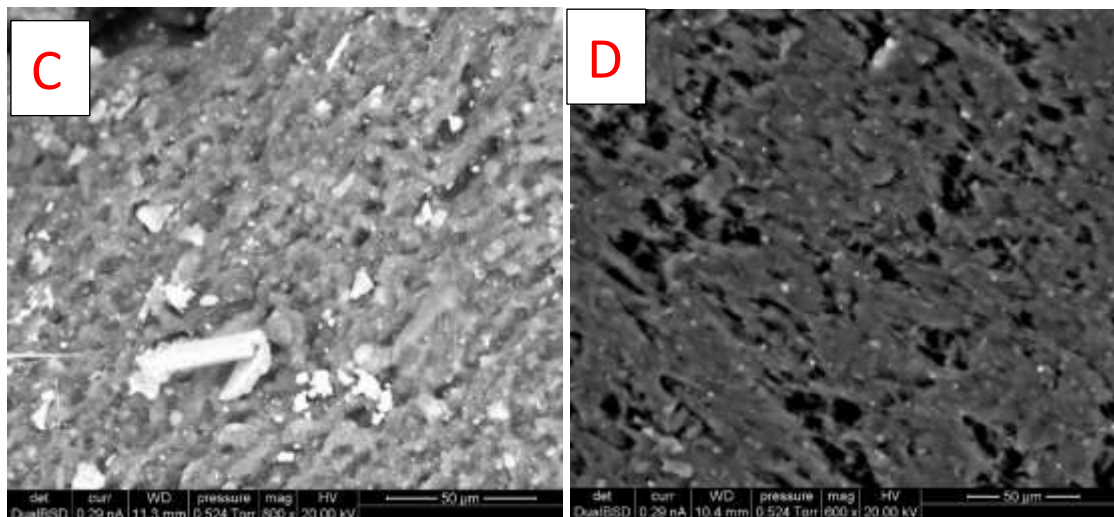


Figure 46: *A- the surface morphology of virgin Polypropylene (MV1) with a lamellar rough surface with no visible filler, additive or mix within the polymer matrix. B- Sample MMPS5 (PP+PE) showing the presence of fillers all over the matrix with a smooth surface. C- MMPS6 surface displays heterogeneous roughness, including micro voids and filler particles on its surface. D- MMPS12 (PP) shows shear induced fibrillation, and irregular fracture planes*

In SIMPS21 (ABS) and STMPS 27 (figures 47a and b) as in all the styrenic polymers, the polymer matrix displays micro-roughness and subtle flow lines, likely formed during melt processing and cooling. These processing-induced striations indicate shear history and may also reflect the thermal degradation of the butadiene phase during repeated recycling, consistent with the diminished impact-modification properties typically observed in aged ABS for ABS samples (Konarzewski et al., 2022). The surface shows a dense distribution of bright particulate inclusions embedded within a darker polymeric matrix. These bright regions labelled as Spectrum 36, 37, 38, 39, and 40 in figure 47(a) and spectrum 37, 38, 39, 40, 41, 42, 43, and 44 in figure 47(b) correspond to areas selected for EDX analysis and are likely associated with inorganic fillers or contaminants. Their strong contrast relative to the organic matrix indicates higher average atomic number, consistent with minerals such as calcite (CaCO_3) commonly used in ABS and PS formulations (Espinal et al., 2022). These morphological signatures could confirm the polymer identification from FTIR, but it is not that clear and sufficient. In polyamide samples (MMPS1, MMPS2 and MMPS4) figure 47(c) and (d), several elongated, rod-like structures are visible across the field of view, many fractured, truncated, or partially debonded from the surrounding polymer matrix. These morphological traits are typical of E-glass fibres subjected to repeated thermal–mechanical recycling cycles. Their broken ends, irregular lengths, and areas of fibre pull-out indicate significant fibre–matrix interfacial degradation, consistent with reduced mechanical performance often observed in recycled polyamides (Csapó & Kovács, 2025). The polymer matrix surrounding the fibres appears relatively rough, with evidence of microcracking, shear marks, and localized voids. Such

features likely originate from mechanical stresses imparted during compounding, shredding, and injection reprocessing, as well as chemical degradation pathways such as hydrolysis, which polyamides are highly susceptible to (Murray et al., 2022). The combination of rough surface morphology and micro voids suggests that chain scission has occurred, weakening the cohesive strength of the polymer. Their orientation and fragmentation suggest fibre-matrix debonding during reprocessing, which explains the levels of Al, Ca, and Mg revealed by ICP-MS.

In most of the samples, smaller bright particulate inclusions are distributed throughout the matrix, appearing with high contrast relative to the polymer. These are likely mineral or metallic contaminants, such as Ca-, Al-, and Mg-rich fragments associated with the glass fibre composition, calcite, talc or Fe-, Cr-, Ni- containing particles derived from abrasion of steel machinery during recycling. This interpretation is consistent with ICP-MS data showing elevated concentrations of Fe, Cr, and Ni in the polymer samples. The clustering of such particles suggests the presence of heterogeneous contamination hotspots, which may arise from insufficient separation in mixed-waste recycling streams.

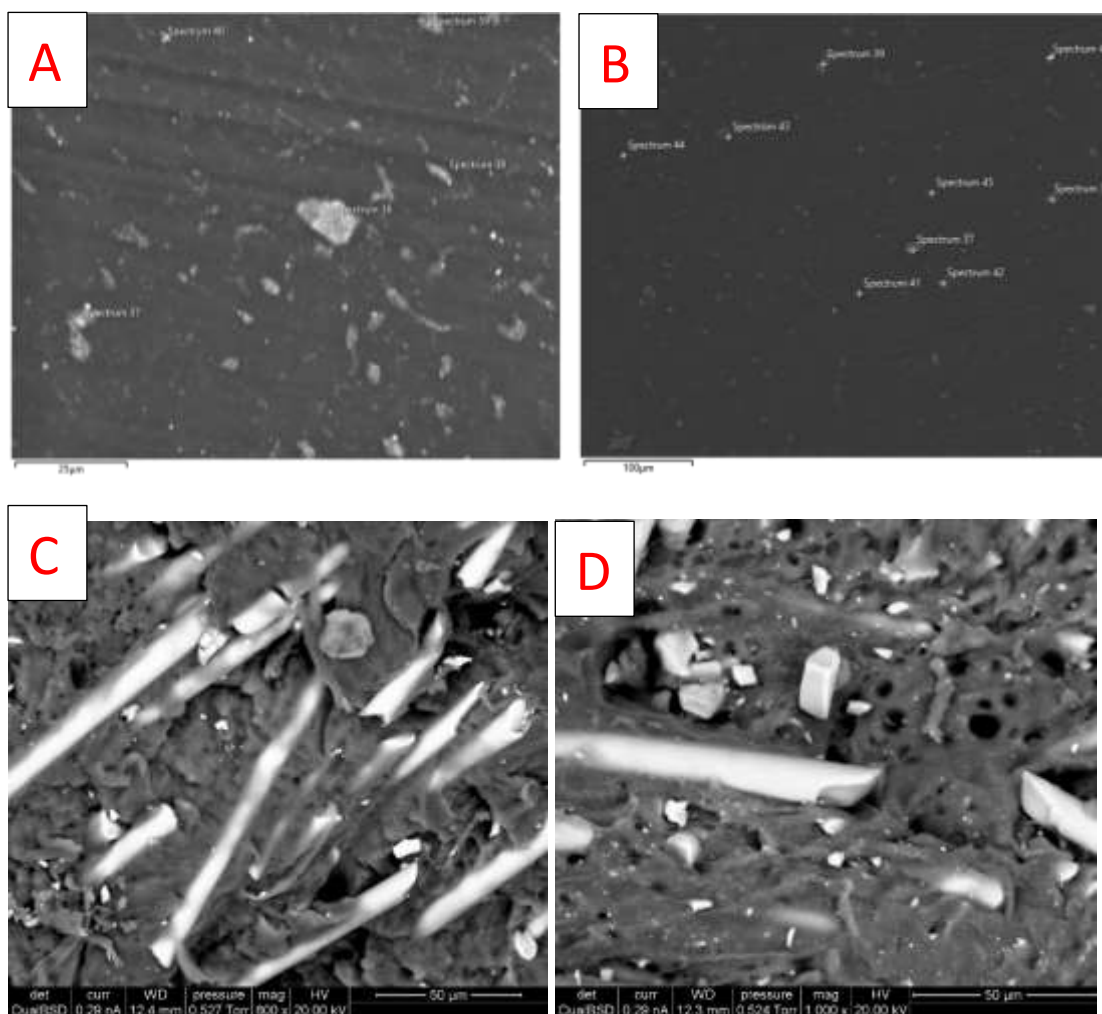


Figure 47: A- STMP21 (ABS) where inorganic fillers can be seen into the smooth polymer matrix. B- STMP27 (PS) showing smooth polymer matrix with inorganic particles incorporated into it. C and D- MMPS1 and MMPS2 respectively, PA matrix full of glass fibres and micro voids.

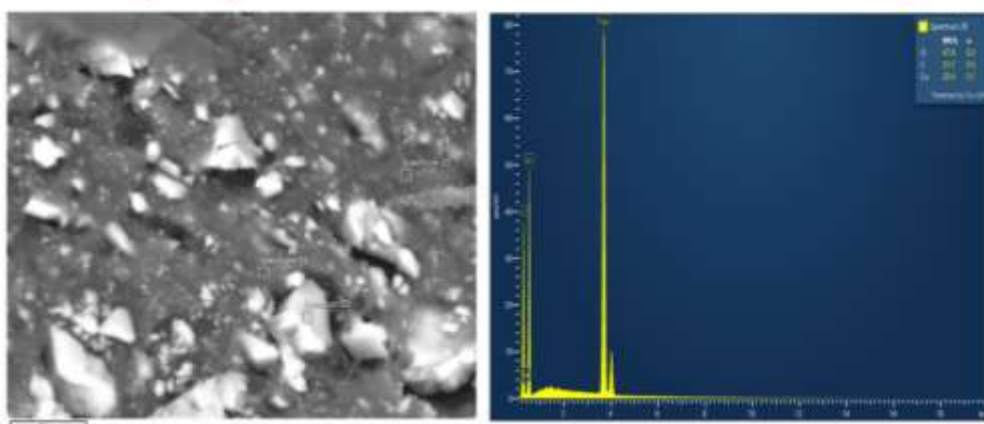
EDX Elemental Mapping and Identification of Inorganic Inclusions

EDX spectra and maps acquired from the point analysis on the SEM micrographs enabled the precise identification of the inorganic phases embedded within the polymer matrices. To confirm the XRPD results, Ca-rich inclusions were frequently detected in the samples, confirming the presence of Calcite (CaCO_3). These inclusions appeared as angular or irregular particles with sharp edges, reflecting the brittle fragmentation of mineral fillers during compounding. EDX spectra from these sites consistently displayed strong Ca and O peaks as seen in figure 48 of the MMPS8 sample.

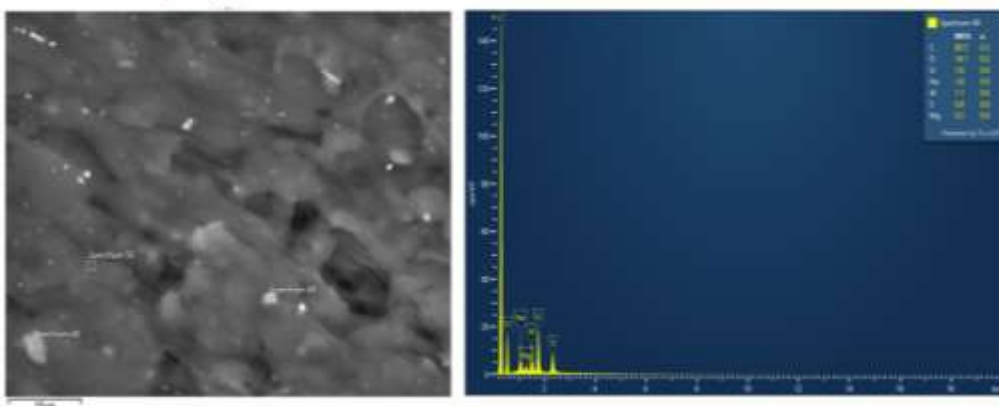
In samples where XRPD indicated the presence of Talc (MMPS12), the EDX mapping revealed lamellar, plate-like structures enriched in Mg and Si, matching the stoichiometry of

$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ as detailed in the EDX spectrum in figure 48. These platy morphologies were typically distributed within the polymer matrix, reflecting talc's function as a nucleating agent and reinforcement in PP. In MMPS6 and STMPS27, rutile inclusions appeared as small, denser nodules with low Ti peaks, demonstrating their role as pigments or UV stabilisers. Their homogenous dispersion as can be seen in the EDX map suggests good compatibility with the polymer melt during compounding. In MMPS18, Ba is seen as a shiny inclusion in the matrix, this should be due to the fact, this element representing the barite filler, a known filler in the past (Kinnunen et al., 2024), still present in the matrix but very low in quantity and its removal has been low during the recycling cycles.

MMPS 8 (PP+PE)



MMPS 12 (PP)



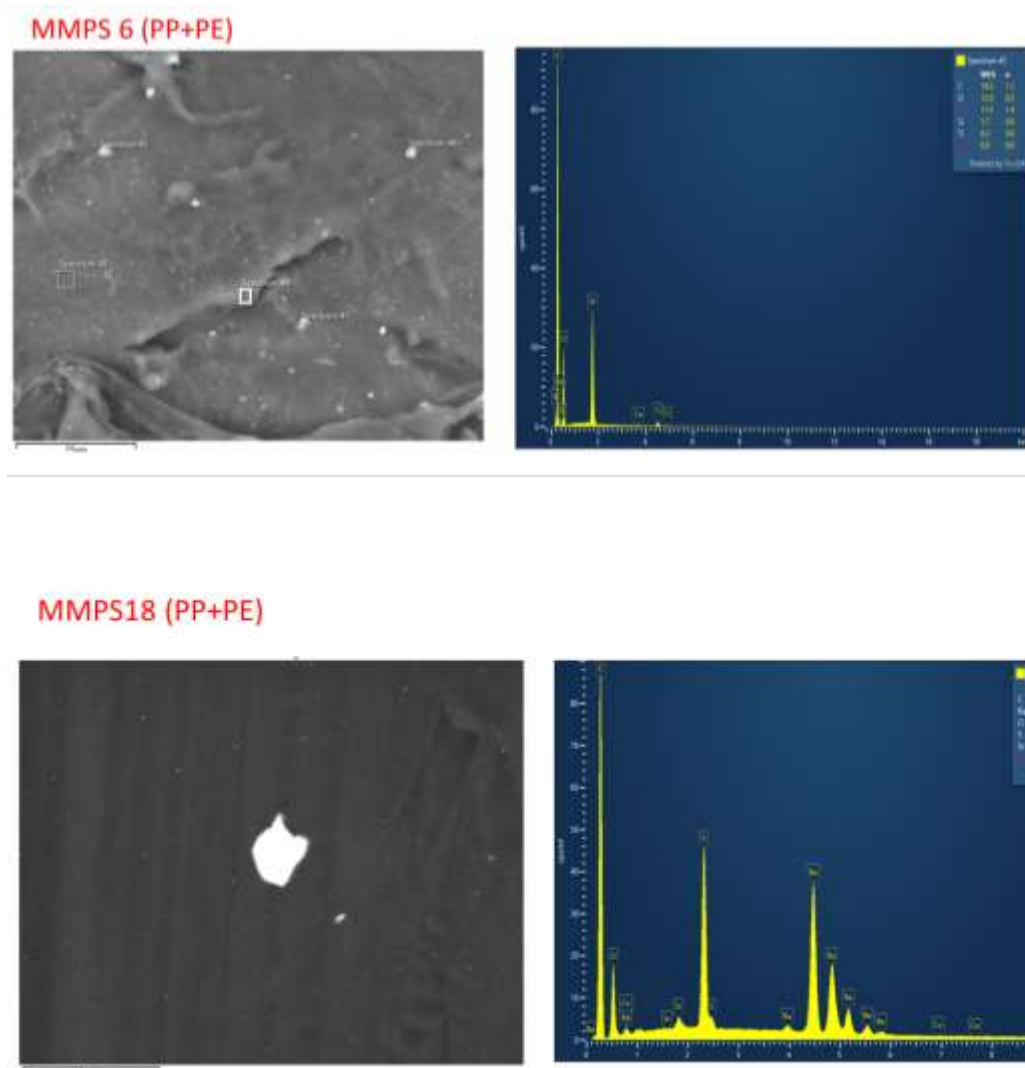
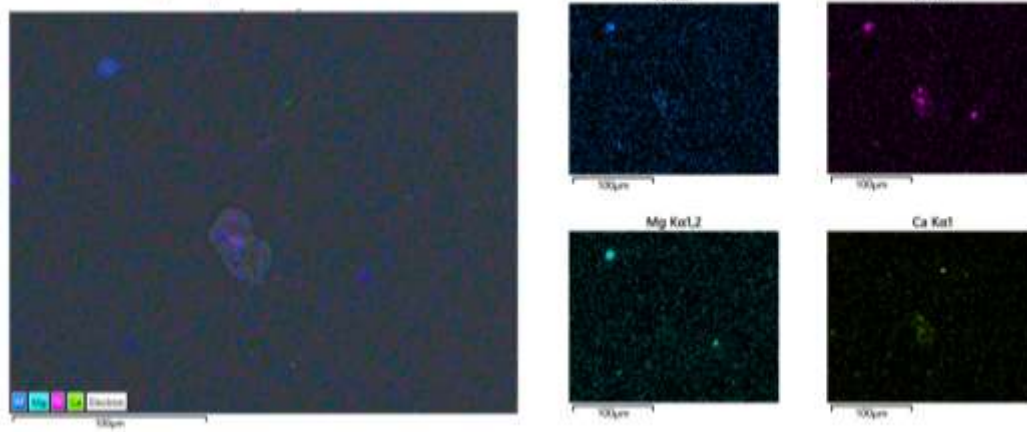


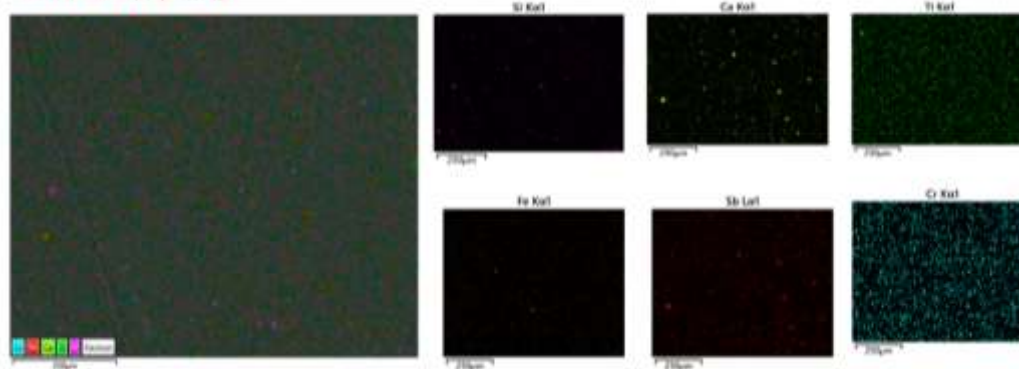
Figure 48: The EDX spectra of the different polymers, showing the chemical composition of each filler in the samples. In MMPS6 we can see the appearance of a low Ti peak, indicating its presence as a pigment in the sample and distributed throughout the matrix. MMPS18 indicating the inclusion of a Barite filler in the matrix of the plastic polymer.

In styrenic samples, the EDX map revealed the presence of fillers like talc (STMPS31), where the elemental map of the talc constituent elements in the filler particles can be seen. Also with the map of STMPS 27, Ti is seen distributed all along the sample which represents rutile inserted as pigment (Turner & Filella, 2017). In polyamide, the EDX was particularly valuable for detecting the glass fibre chemistry, showing peaks of Si, Al, Ca and occasionally Mg. It then revealed the presence of ZnSO_4 , which is usually as a stabiliser in the plastic industry (Borukaev et al., 2021). Although XRPD could not resolve these amorphous reinforcements, their chemical identity and spatial distribution became clear through EDX in figure 49.

STMPs 31 (ABS)



STMPs 27 (SAN)



MMPS2 (PA)

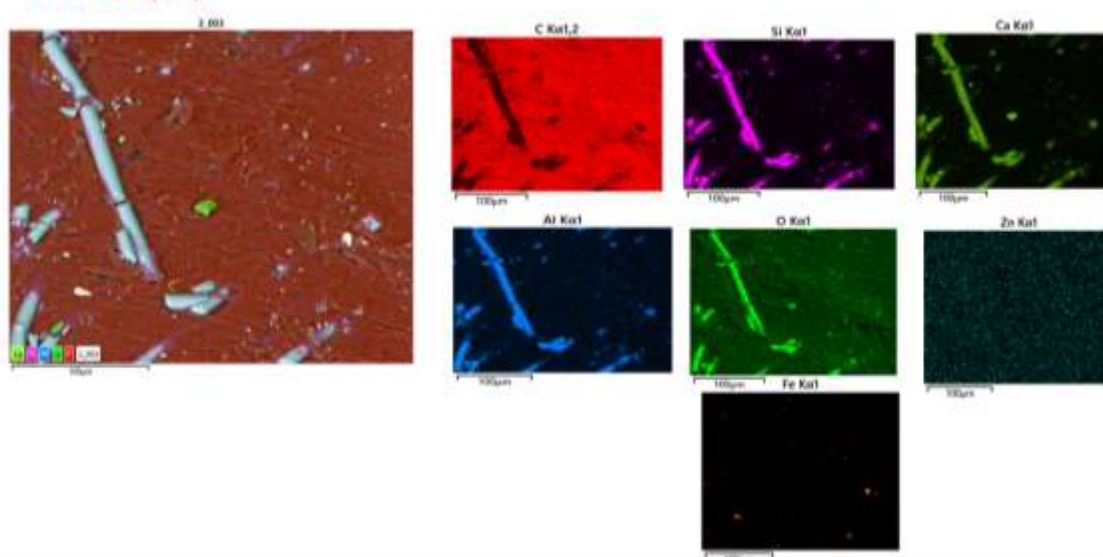


Figure 49: The different EDX maps of some ABS, PS and PA samples, showing their filler composition and heavy metals present in their matrix.

Furthermore, EDX detected sporadic metal-rich inclusions corresponding to Fe, Cr, Sb and Zn in most of these recycled polymers. These metals are associated with processing contamination originating from abrasion of steel components, but as for Sb, it is associated to flame retardants added into the plastic (Chen et al., 2023). Figure 49 illustrates the maps of the samples with these metals. These results correlate with the ICP-MS data, reinforcing the conclusion that mechanical recycling introduces no-intentional metallic impurities into the polymer matrix and flame retardants are still being used in the plastic industry.

4.3.2 Cross analysis of results from complementary techniques.

The heterogeneity and complex nature of recycled plastics requires the integration of these multiple techniques (FTIR, XRPD, ICP-MS and SEM) to achieve reliable material characterisation. The cross analysis of these results enabled robust identification of polymer mixtures, inorganic fillers and metal contaminants, while reducing questions brought up by single-technique interpretations. Together these techniques provide a comprehensive framework for evaluating material quality and regulatory relevance of recycled polymers.

4.3.2.1 Comparative Framework for Multi-Technique Analysis

To establish a systematic basis for interpreting the analytical results obtained from recycled polymers, a comparative framework was developed using the reference characteristics of virgin materials as baseline. As discussed in the preceding sections, virgin polymers exhibit properly defined chemical, structural, morphological and elemental signatures that reflect their controlled composition and absence of contamination and external effects on the matrix (degradation). In contrast, recycled plastics represent heterogenous, multi-phase systems originating from prior use, processing history and additive incorporation. The integration of complementary analytical techniques; FTIR, XRPD, SEM-EDX and ICP-MS allows for the identification of differences from virgin state, including chemical oxidation, crystallinity changes, filler incorporation, and trace metal accumulation. The following tables summarise these differences across polymer families, providing a structured overview that supports the cross-analysis and facilitates the interpretation of material transformations induced by recycling processes.

Table 21: Comparative analytical signatures of virgin and recycled PP-based materials (PP, PP+PE).

Technique	Parameter	Virgin PP/PP+PE	Recycled PP/PP+PE	Interpretation
FTIR	C-H stretching	Strong CH ₃ (PP) and CH ₂ (PE) bands, well-resolved	Same bands with reduced intensity and slight shifts	Chain scission and structural modification
FTIR	Oxidation (C=O, O-H)	Absent	Present in several samples	Thermo-/photo-oxidation during recycling
XRPD	Crystalline phase	PP α -phase + PE orthorhombic peaks	Reduced peak intensity, Peak broadening	Decrease in crystallinity
XRPD	Additional phases	Absent	Calcite, talc, rutile peaks	Filler incorporation
SEM	Morphology	Homogenous, ductile fracture	Cracks, inclusions, heterogeneous surface	Mechanical degradation + fillers
SEM-EDX	Elemental composition	Mostly carbon	Ca, Mg, Ti detected	Mineral fillers present
ICP-MS	Filler elements	Trace levels	High Ca, Mg, Ti concentrations	Calcite, talc, TiO ₂
ICP-MS	Metals	Negligible	Fe, Cu, Zn detected	Recycling contamination

Table 22: Comparative analytical signatures of virgin and recycled styrenic polymers (ABS,PS).

Technique	Parameter	Virgin PS/ ABS	Recycled PS/ ABS	Interpretation
FTIR	Aromatic bands	Strong aromatic peaks (~1600, 1490 cm ⁻¹)	Maintained but slightly broadened	Structural preservation with ageing
FTIR	Nitrile (ABS)	Sharp band at ~2235cm ⁻¹	Still present but less intense	Possible phase alteration
XRPD	Structure	Fully amorphous	Amorphous + additional peaks	Filler addition
SEM	Morphology	Smooth, homogenous	Heterogeneous, inclusions visible	Multi-phas structure
ICP-MS	Elements	Very low	Ba, Ti, Fe occassionaly high	Additives and contamination
SEM-EDX	Mapping	No inclusions	Localised particles	Filler dispersion

Table 23 : Comparative analytical signatures of Engineering polymers (PA, PC, POM)

Technique	Parameter	Virgin PA/PC/POM	Recycled PA/PC/POM	Interpretation
FTIR	Functional groups	Strong amide (PA), carbonate (PC), acetal (POM)	Same groups + oxidation peaks	Chemical ageing
XRPD	Structure	Semi-crystalline (PA, POM), amorphous (PC)	Reduced crystallinity or added peaks	Structural alteration and filler effects
SEM	Morphology	Compact, homogeneous	Cracks, fibre residues (PA)	Mechanical+ filler effects
ICP-MS	Elements	Low concentrations	Elevated metals (Cr, Ni, Pb) in some samples	Contaminations
SEM-EDX	Inclusions	None	Glass fibres (PA), particles	Reinforcement/ additives

4.3.2.2 FTIR and SEM Observations: Polymer mixture Evidence

The combination of FTIR spectra and SEM images, can reveal many features on the plastic sample. Amongst these features, polymer mixture (either homopolymer, copolymer or polymer contamination) and filler identification within the polymer matrix were confirmed.

The identification of polymer mixtures within recycled plastic samples is crucial and the complementarity of these two techniques enables the discrimination between single polymer matrices and heterogeneous blends arising from mixed waste streams or incomplete sorting. FTIR spectra of several samples exhibited simultaneous presence of characteristic

absorption bands belonging to PP and PE polymers as seen in the results obtained from FTIR. The aliphatic C-H stretching bands at 2920 cm^{-1} and 2850 cm^{-1} are typical of PP and PE. Also, the PE rocking doublet band of $730\text{-}720\text{ cm}^{-1}$ is a clear evidence of PE presence in the Polypropylene matrix. These spectral superpositions suggest physical mixtures rather than copolymerisation, as the individual polymer signature remain spectroscopically distinct. Figure 11 shows the spectrum of MMPS 10 (PP+PE) sample overlapping the virgin polypropylene spectrum to clearly show these bands representing PE.

SEM observations provided direct morphological confirmation of these FTIR-based interpretations. Figure 50 presents the virgin PP (A) and the PP+PE sample (B). Several PP+PE samples displayed phase-separated microstructures, with domains contrasting the surface texture and fracture behaviour. In the PP+PE blend of sample MMPS10, this appeared as a highly heterogenous and fibrillated microstructure. Firstly, displaying a characteristic of mechanically recycled polyolefin blends with limited interfacial compatibility. The fibrils are unevenly distributed and exhibit varying thickness, suggesting the coexistence of polymer phases with different viscoelastic properties, consistent with a polypropylene and polyethylene mixture (PP+PE mixture). The fibrils and stretched ligaments are typical of PE-rich domains which undergo extensive plastic flow and fibrillation under shear due to higher ductility. The broader and rigid feature is attributed to PP-rich domains. The convergence of FTIR spectral superposition and SEM-observed phase separation provides robust evidence of polymer mixtures within several recycled samples. This evidence highlights the heterogeneity of post-consumer recyclates and underscore the importance of cross analysing results of complementary techniques.

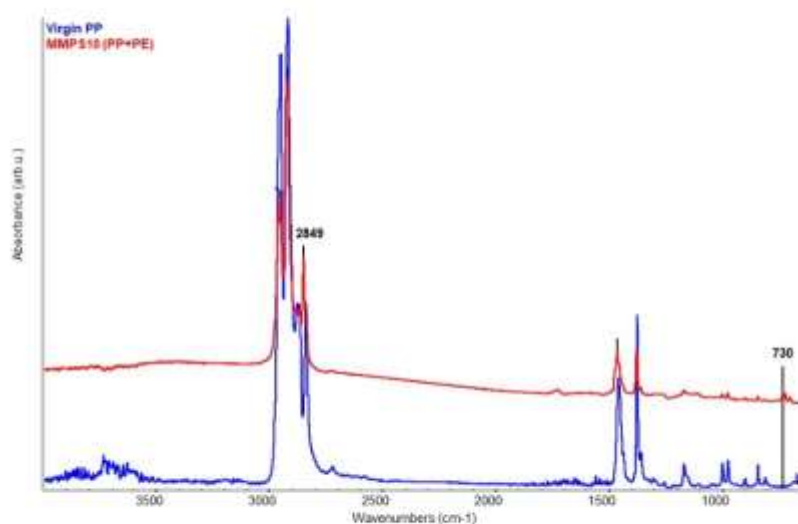


Figure 50: MMPS10 (PP+PE) spectra showing the difference between PP and PP+PE at the corresponding 2850cm-1 and 730cm-1 bands

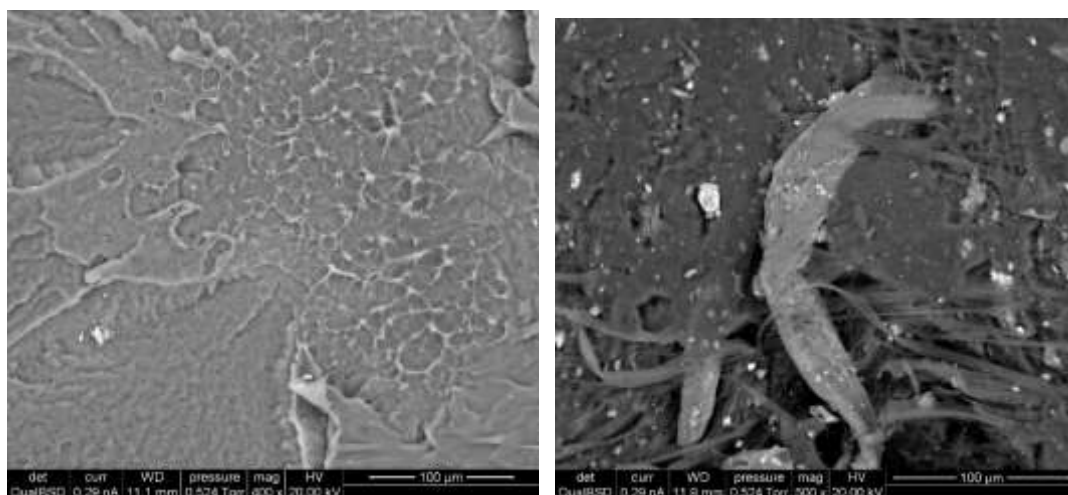


Figure 51: A- MV1 (PP) surface morphology. B- MMPS10 (PP+PE) showing segregation of the different polymers mixed together.

4.3.2.3 XRPD, ICP-MS and SEM Observations: Filler Identification

The analytical strategy used to identify the inorganic fillers in the polymer matrix was the combination of XRPD, SEM-EDX and ICP-MS. This multi-technique was necessary to overcome the limitations inherent to individual methods and to reliably characterise both semi-crystalline and amorphous filler systems embedded in the heterogenous matrices. XRPD provided phase-specific structural information for crystalline minerals, SEM showed direct morphological and spatial evidence of filler dispersion and ICP-MS quantitative elemental data supporting the compositional assumptions.

XRPD revealed the presence of several crystalline mineral phases commonly used in plastic formulations as reported in the XRPD results section. Calcite, Talc and Rutile were all identified, with calcite being the most frequently identified filler. The calcite peaks (34.3° , 23.1° , 31.6° , 36.3° , 39.5° , 43.3° , 47.6° and 48.5° 2θ Angle) were prominent in PP, PP+PE, PS and ABS polymers. MMPS20, with diffractogram shown in figure 52(A), identifies the calcite phase in the sample with observable peaks. Talc, was also identified only in PP and ABS samples. In figure 52 the MMPS12 (PP) diffractogram is shown with the identification of talc as the main inorganic filler in the sample. The talc peaks identified in this sample were: 11.02° , 21.66° and 33.36° . The Talc used in the plastic industry is mostly commercial talc that contains significant amount of accessory minerals. In MMPS12, XRPD identified talc phases accompanied with chlorite in the same sample which is common from commercial talc.

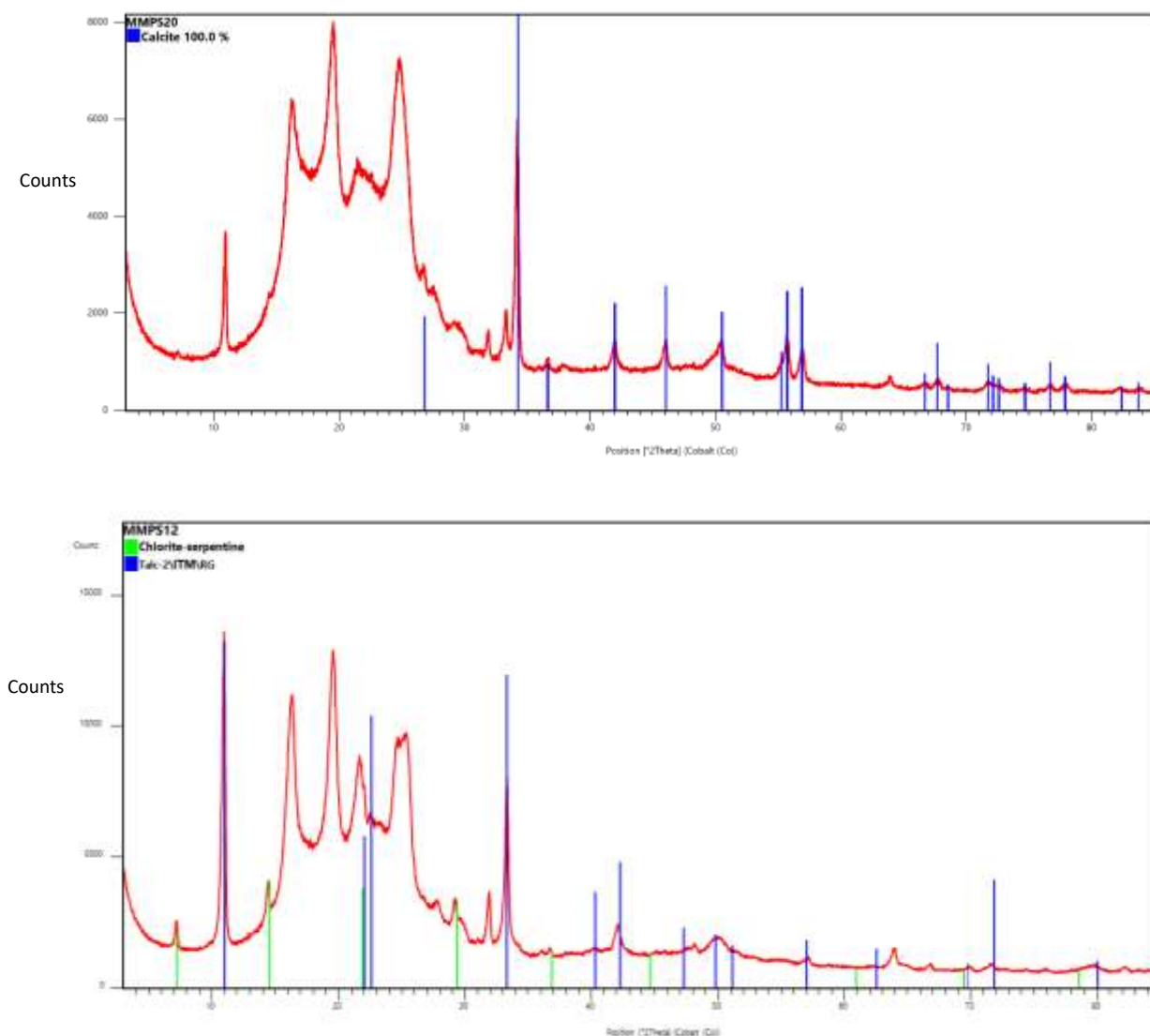


Figure 52: A- Calcite identification in MMPS20 (PP+PE). B- Talc and chlorite identification in the MMPS12 (PP) sample.

SEM observations directly confirmed these XRPD based identifications by revealing the morphology and spatial distribution of the filler particles within the polymer matrices. Using EDX, the spectra and map of the filler crystals were directly identified. Figure 53(a) shows the SEM image and corresponding EDX-spectrum of calcite crystals used as fillers in the MMPS20 sample. In this spectrum we can observe a high percentage of Ca and O with very low Si, Cl and Na content in the crystal, confirming calcite as the mineral identified. Whereas in figure 53(b) the MMPS12 crystal EDX spectrum shows the presence in different percentages of Si, Al, Mg and O in the polymer matrix representing Talc.

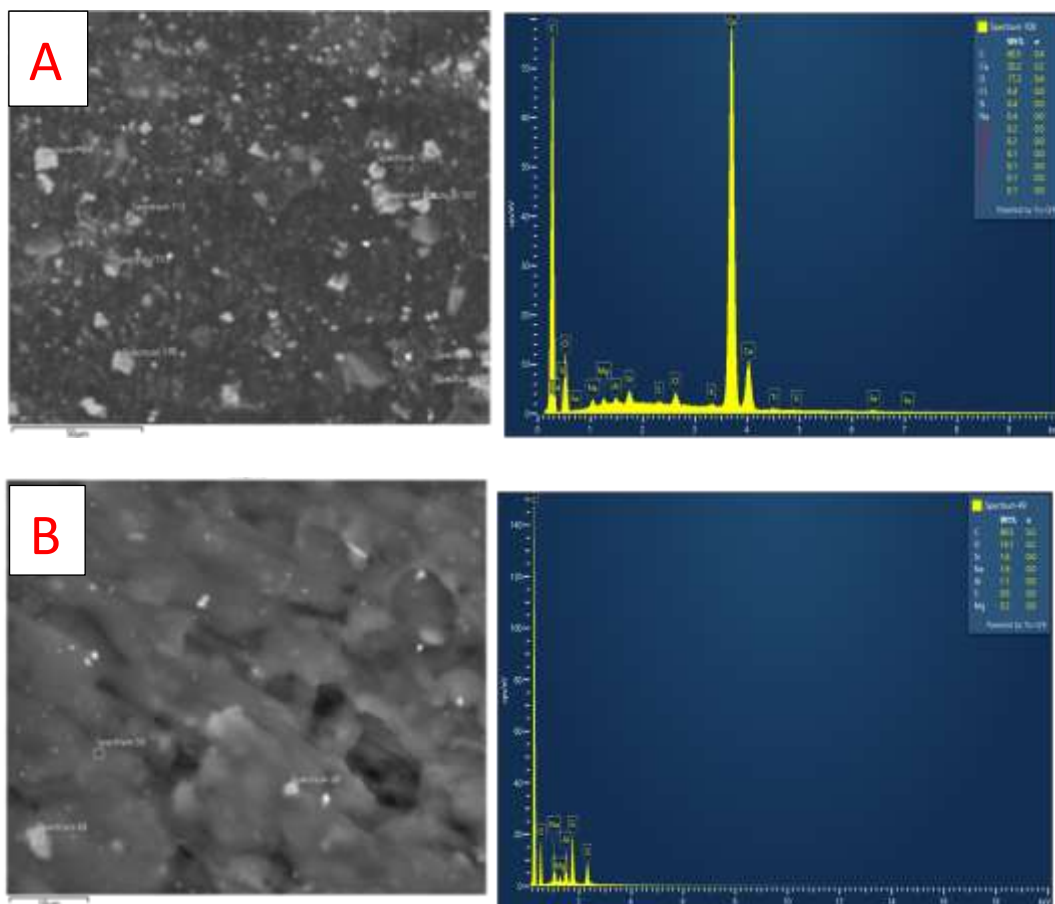


Figure 53: A- EDX spectra of MMPS20 showing the elemental composition of calcite crystals in the PP+PE matrix. B- EDX spectra showing the elemental composition of talc crystal into the MMPS12 (PP) polymer matrix.

As for ICP-MS results to quantitatively confirm the concentration of these fillers in the matrix, some results obtained from MMPS12 (talc containing plastic) and MMPS20 (calcite containing plastic) can be seen in the graphs below in figure 54. The ICP-MS analysis of filler constituent elements of talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) for MMPS12 shows a Mg mean concentration of 1039.82 ± 88.41 mg/kg which is the most element in the sample with a low concentration of Al of 520 ± 34.09 mg/kg often present as a Mg-Si substitute in industrial talc (confirms the

presence of chlorite). In sample MMPS20, the filler constituent element for calcite (CaCO_3) analysis showed a high Ca mean concentration of 8907.3 ± 283.925 mg/kg. The high concentration of these elements brings the backup and confirmation of the fillers identified using XRPD and seen with SEM. The convergence of XRPD phase identification, SEM morphological and elemental composition evidence finally ICP-MS elemental quantification enabled a concise identification of inorganic fillers in the recycled plastics studied.

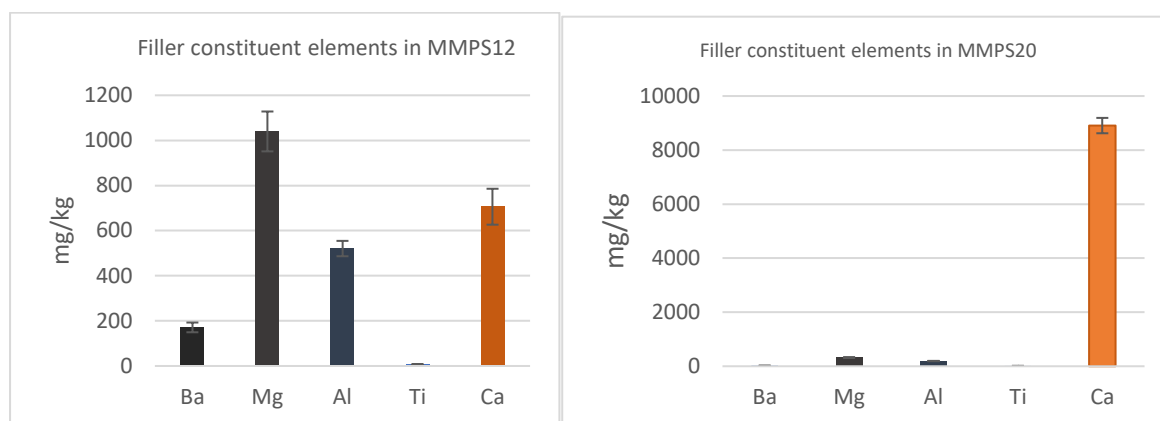


Figure 54: Filler constituent elements quantification in MMPS12 and MMPS20 showing Mg high content and Al content in MMPS 12 (indication of talc) and Ca high content in MMPS20 (indication of calcite).

4.3.2.4 SEM and ICP-MS Observations: Metal contaminants and Heavy metal identification

Metal contaminants and heavy metals were analysed and confirmed in the samples using ICP-MS elemental quantification and SEM-EDX results. This combination enabled the identification and quantitative assessment of metallic species introduced during the previous life cycle of the materials or during mechanical recycling. It also enabled the differentiation between localised particulate contamination and bulk elemental enrichment.

With SEM results, the presence of discrete, high-contrast particulate inclusions embedded within the polymer matrices of most of all the samples. In figure 55, sample STMPS31 SEM-EDX map, Fe inclusions are directly detected as irregular fragments with strong backscattered electron contrast, indicative of an element with higher atomic numbers than the surrounding organic matrix. The Fe inclusions were concentrated particulate on one area and not distributed all over the polymer matrix, meaning it is not an additive from the

polymer formulation but a contamination from abrasion of steel processing equipment due to the contact between the waste sample and machinery parts in the process.

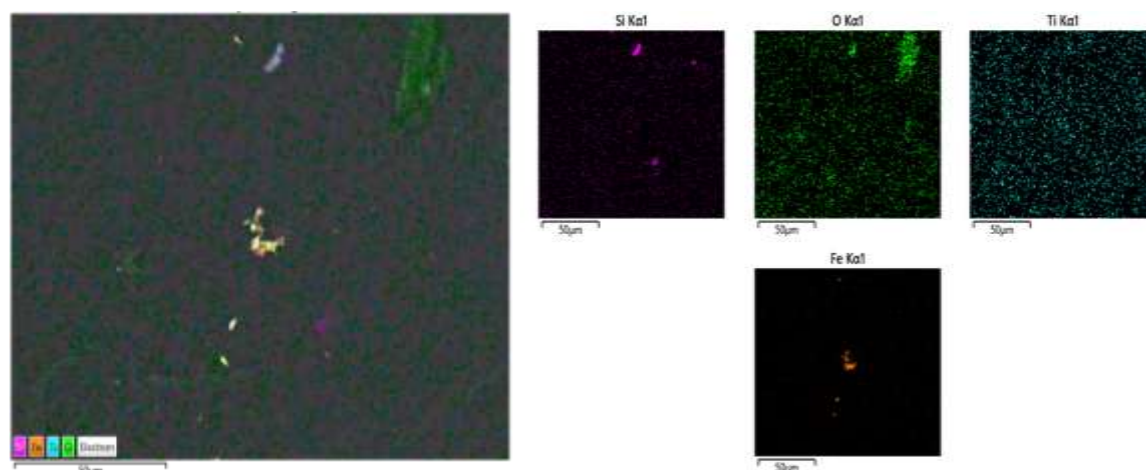


Figure 55: STMP31 (ABS) SEM-EDX map revealing the presence of Fe particles into the sample.

The ICP-MS results of the STMP31 sample as seen in figure 56, presents the quantitative analysis of metal contaminants and heavy metals present in the plastic sample. It is observed that the highest metal concentration is Fe with 134.41 ± 4.6 mg/kg as confirmed with SEM-EDX map. With ICP-MS other heavy metals were identified in the samples which were not really seen with the SEM images. These heavy metals are Zn, Sb and Pb with concentrations of 55.78 ± 2.8 mg/kg, 41.72 ± 1.6 mg/kg and 19.10 ± 1.59 mg/kg respectively. The presence of Zn with Fe confirms the hypothesis of abrasion with machinery parts during the recycling process. The Pb and Sb presence indicates a residual presence of flame retardants and pigments used in the plastic industry. The combined SEM ICP-MS results demonstrate that metal contamination in recycled plastics occurs in two principal forms; (i) micron-scale metallic particles embedded in the polymer matrix, readily by SEM and attributed to mechanical abrasion or residual components, and (ii) homogeneously distributed trace metals detectable only through bulk chemical analysis. This distinction is critical for risk assessment, as particulate contaminants may act as stress concentrators affecting mechanical performance while dissolved or finely dispersed metals are more relevant for regulatory compliance and potential environmental release.

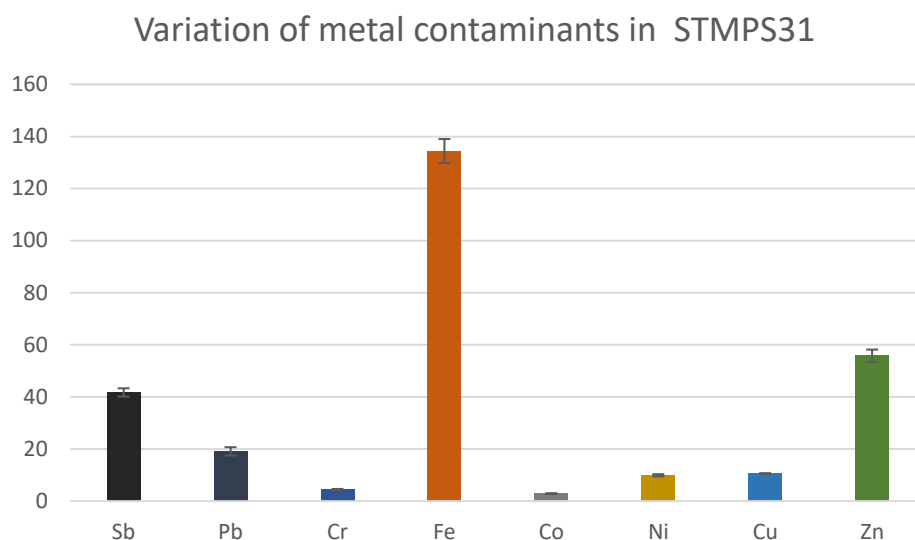


Figure 56: Metal contaminants concentration in STMPS31 (ABS)

4.3. Conclusion

This study demonstrates the reliability of integrated multi-analytical approach in the assessment of recycled plastic quality capturing the chemical, structural, morphological and elemental heterogeneity. The multi-analytical approach is the combination of FTIR, ICP-MS, XRPD and SEM-EDX which shows that the integrity of recycled polymer is primarily controlled by the interplay between polymer mixing, inorganic filler systems, and trace-metal contamination, rather than polymer identity alone. FTIR and SEM jointly revealed that many recycled plastics are physically mixed polymer systems, resulting from incomplete feedstock separation and mechanical blending during recycling. XRPD, SEM-EDX and ICP-MS enabled robust identification of calcite, talc, rutile and glass fibres as dominant fillers, whose reinforcing benefits creates heterogenous polymer-filler interfaces. Finally, SEM-EDX and ICP-MS revealed the persistence of metal contaminants and heavy metals introduced through previous product lifecycles and recycling operations.

Overall, this work establishes a robust diagnostic framework for evaluating recycled plastics, linking molecular identification, microstructural integrity, filler composition and elemental contamination. The results provide practical insights for improving strategies, assessing end-of-waste criteria, and predicting the reliability of recyclates in circular economy applications. By demonstrating the necessity of cross-validated analytical workflows, this study contributes to advancing scientifically grounded quality assessment protocols for recycled polymer materials.

Chapter 5: GENERAL CONCLUSION AND INTEGRATED DISCUSSION

5.1. Overall Scope and Objectives Revisited

This doctoral research was undertaken to address a central and persistent challenge in plastic recycling; the lack of robust, experimentally validated analytical framework capable of capturing the intrinsic chemical, structural, morphological and structural complexity of real recycled polymer materials. While recycled plastics are increasingly promoted as key resources within circular economy strategies, their quality assessment remains largely based on simplified physical and mechanical indicators that fail to reflect degradation phenomena, polymer mixture complexity, filler systems, and trace contamination inherited from multiple life cycles. This discrepancy between material complexity and evaluation methods represents a critical bottleneck for both scientific understanding and industrial implementation of high-quality recycling pathways.

The primary objective of this thesis was therefore to develop and validate a multi analytical characterisation strategy specifically tailored to heterogeneous recycled plastics, with the aim of enabling a comprehensive assessment of material integrity, recyclability, and regulatory compliance. To achieve this goal the work combined a critical literature review, systematic methodological screening, and integrated experimental analysis of industrial recycled polymer samples using complementary analytical techniques. The focus was not on optimising a single measurement method, but rather on constructing a coherent analytical framework capable of resolving polymer identity, mixture content, filler composition, morphological organisation, and trace metal contamination within a unified interpretative context.

Within this framework, particular emphasis was placed on evaluating the real-world performance of analytical techniques when applied to complex, pigment-rich, filler-loaded, and contamination prone recycled materials. This included experimental validation of sample preparation strategies, inter-laboratory comparison of elemental analysis protocols, and targeted ageing experiments to assess analytical robustness under photo-oxidative stress. By systematically testing both theoretical suitability and practical effectiveness, the thesis sought to bridge the gap between idealised laboratory methodologies and the operational realities of recycled plastic characterisation.

Finally, this work aims to contribute to the scientific foundations required for reliable quality assessment of recycled plastics, supporting both regulatory decision-making and industrial material selection within circular economy systems. The following sections of this chapter provide an integrated discussion of the main findings, methodological implications, and broader relevance of the results, synthesising the multi-technique evidence generated throughout the thesis into a unified conceptual interpretation.

5.2. Integrated Discussion of Main Findings

The integrated interpretation of the results obtained from FTIR, SEM-EDX, XRPD and ICP-MS demonstrates that recycled plastics constitute intrinsically heterogeneous and multi-component materials, whose quality and performance cannot be reliably assessed through isolated analytical descriptors. Instead, their properties emerge from the combined effects of polymer identity and mixture content, filler systems, microstructural organisation, and trace elemental contamination, all of which are shaped by complex processing and life-cycle histories.

At the polymeric level, FTIR spectroscopy revealed that a significant fraction of samples classified as single polymer phases. Polyolefin samples frequently exhibited combined spectral signatures of PP and PE, while styrenic materials showed overlapping features between PS and ABS. These findings indicate that industrial sorting processes remain imperfect and that polymer streams often remain incompatible phases even after mechanical domains within individual fragments, further confirming the coexistence of multiple polymer phases. Such heterogeneity is known to compromise melt homogeneity, interfacial adhesion, and mechanical performance, thereby explaining the variability often observed in recycled plastic properties compared to virgin resins.

Beyond polymer composition, the presence and nature of inorganic fillers emerged as a dominant structural feature of recycled plastics. XRPD identified calcite, talc and rutile as the principal filler phases, while SEM-EDX revealed their heterogeneous dispersion and frequent agglomeration within polymer matrices. ICP-MS confirmed these observations quantitatively, showing elevated concentrations of Ca, Mg, Al, Ti and Ba corresponding to these minerals. Importantly, the combined mineralogical and elemental evidence demonstrated that industrial fillers deviate substantially from idealised pure mineral compositions. Talc related phases exhibited Mg-Al substitution patterns, while glass fibres displayed complex aluminosilicate signatures, reflecting the geological origin and industrial processing of these materials. This compositional variability has direct implications for polymer-filler interfacial

behaviour, mechanical reinforcement efficiency, and long-term stability, particularly under repeated thermal and mechanical recycling cycles.

Microstructural analysis further highlighted the role of filler systems governing material integrity. SEM micrographs frequently showed filler agglomerates embedded within polymer matrices, often associated with fracture surfaces and surface irregularities. These agglomerates act as stress concentrators and crack initiation sites, reducing ductility and impact resistance during reprocessing. The problem was particularly pronounced in heavily filled polyolefins and glass fibres reinforced polyamides, where rigid inorganic inclusions disrupted polymer continuity. Such microstructural features cannot be captured by bulk analytical methods alone and underscore the importance of microscopic investigation for understanding recycle performance.

Trace metal analysis provided additional insight into the cumulative nature of contamination in recycled plastics. ICP-MS revealed widespread presence of Fe, Cu and Zn, attributed primarily to mechanical abrasion of recycling equipment, as well as variable levels of regulated heavy metals including Cr, Ni, Pb, Sb and Co. SEM-EDX confirmed the presence of metallic inclusions and contamination hotspots at the microscale, often localised at filler-polymer interfaces or fracture regions. Although most measured concentrations remained below regulatory thresholds, their heterogeneity across samples and polymer types highlights the progressive accumulation of contaminants across recycling cycles. This contamination not only raises regulatory concerns but may also influence oxidative stability, colour, odour, and ageing behaviour, thereby indirectly affecting material quality.

Taken together, these findings show that recycled plastics cannot be treated as chemically simple or structurally uniform materials. Their properties are governed by intertwined polymer, mineral, and elemental components that reflect both original product design and cumulative recycling history. Only through the integration of complementary analytical techniques can this complexity be resolved in a scientifically meaningful way. The results of this thesis therefore challenge simplified quality assessment paradigms and provide experimental evidence supporting the adoption of multi-dimensional characterisation strategies for reliable evaluation of recycled plastic materials.

5.3. Methodological Implications for Recycled Plastic Characterisation

The methodological results of this thesis show that the characterisation of recycled plastics requires performance-based selection of analytical techniques rather than reliance on theoretical applicability alone. Experimental screening showed that methods widely cited in

the literature, such as Micro-Raman spectroscopy and X-ray Fluorescence (XRF), are limited in practice when applied to heterogeneous, pigment-rich, and additive-loaded recycled materials. Micro-Raman spectroscopy was severely affected by fluorescence phenomena induced by carbon black, pigments, and degradation by products, leading to unstable baselines and loss of diagnostic spectral information. Similarly, XRF suffered from strong matrix effects and calibration incompatibility when geological reference standards were applied to polymer samples, resulting in unreliable trace-element quantification. These findings highlight the necessity of validating analytical methods under realistic sample conditions and confirm that methodological suitability in recycled plastic research must be empirically demonstrated rather than assumed.

In contrast, the integrated use of FTIR, SEM-EDX, XRPD and ICP-MS emerged as a robust and complementary analytical framework capable of resolving the multi-dimensional complexity of recycled polymers. FTIR proved highly reliable for polymer identification and mixture detection, even in aged and contaminated samples. SEM-EDX enabled direct visualisation of surface morphology, filler dispersion, fibre fragmentation and contamination hotspots, providing microstructural context to chemical data. XRPD allowed identification of crystalline filler phases and differentiation between semi-crystalline and amorphous polymer matrices, particularly when cryo-milling was employed to improve powder homogeneity and diffraction quality. ICP-MS, supported by optimised digestion protocols and inter-laboratory validation, offered superior sensitivity, reproducibility, and trace-element detection compared to ICP-OES and XRD, making it the most reliable technique for contamination assessment in complex polymer matrices.

More broadly, this work supports a methodological shift from traditional property-based quality metrics toward structure composition-based material evaluation. Conventional indicators such as melt flow index or tensile strength provide limited insight into the origins of recyclate variability and degradation, whereas multi-technique analytical characterisation enables direct identification of polymer mixtures, filler systems, microstructural defects, and contamination sources that govern material performance. The validated FTIR-SEM-XRPD-ICP-MS work flow developed in this thesis therefore constitutes a transferable methodological template for recycled plastic characterisation, with direct relevance for regulatory compliance, industrial material selection, and the development of scientifically grounded quality assessment strategies within circular economy systems.

5.4. Main Scientific Contributions and Take-Home Messages

The principal scientific contribution of this thesis lies in showing that recycled plastics must be understood as intrinsically heterogeneous, multi-component materials whose quality cannot be reliably assessed through simplified or single-parameter approaches. The integrated analytical evidence shows that polymer identity is frequently ambiguous due to coexistence of multiple polymer phases, even within materials nominally classified as single-polymer streams. Polymer mixtures, filler carry-over, and contamination inherited from previous life cycles are not marginal phenomena but structural features of recycled plastics. This challenges conventional assumptions of material homogeneity and highlights the fundamental difference between virgin and recycled polymers from both a scientific and industrial perspective.

A second major contribution is the experimental validation of a robust, transferable multi-analytical framework for recycled plastic characterisation. By systematically screening and testing multiple analytical techniques, this thesis establishes FTIR, SEM-EDX, XRPD and ICP-MS as a complementary and coherent contamination within a unified interpretative context. The rejection of Micro-Raman and XRF based on empirical performance rather than theoretical suitability further strengthens the methodological originality of this work. The resulting workflow provides a scientifically grounded alternative to fragmented analytical practices and offers a reproducible strategy for addressing the complexity of real industrial recyclates.

Finally, the main-take home message emerging from this research is that recycled plastic quality is not a fixed intrinsic property, but the outcome of interacting structural, chemical, and historical factors that can only be captured through integrated material characterisation. Polymer mixtures, industrial filler systems, and cumulative contamination form an inseparable triad governing recyclate performance, ageing behaviour, and application suitability. Consequently, reliable assessment of recycled plastic requires moving beyond conventional mechanical or physical descriptors toward multi-dimensional analytical evaluation. This shift has profound implication for how recycled materials are classified, regulated, and valorised within circular economy frameworks, and positions analytical science as a central pillar of sustainable material management rather than a purely diagnostic tool.

5.5. Perspectives and Future Work

While this thesis provides a validated analytical framework for the characterisation of recycled plastics, it also opens several perspectives for future research and methodological

development. A first and fundamental step concerns the expansion of the experimental dataset. The present study was performed on representative but limited number of industrial samples, allowing in-depth multi-technique analysis. However, the establishment of a robust and statistically meaningful reference database will require the analysis of a much larger number of recycled plastic samples, spanning multiple recycling streams, geographic origins, product categories, and processing routes. Such a database would enable quantitative classification of recyclate quality levels, identification of systematic contamination patterns, and development of predictive indicators linking analytical signatures to material performance.

A second important direction relates to the integration of analytical characterisation with functional performance testing. While the present focused on chemical, structural, morphological and physical characterisation, future studies should correlate multi-technique analytical data with mechanical, rheological, thermal and ageing properties of the recycled plastics. Establishing quantitative relationships between polymer mixtures, filler systems, contamination profiles, and mechanical behaviour would significantly enhance the industrial relevance of analytical characterisation and support the development of evidence-based quality grading schemes for recycled plastics. This coupling would allow analytical techniques not only describe materials, but also to predict their processing behaviour and application suitability.

From a methodological perspective, future work should also explore the automation and standardisation of multi-technique workflows. The integration of high-throughput FTIR screening, automated SEM image analysis, and machine-learning-assisted interpretation of XRPD and ICP-MS datasets represents a promising avenue for scaling analytical characterisation toward industrial monitoring systems. In parallel, advanced spectroscopic techniques such as hyperspectral imaging, micro-FTIR mapping, and synchrotron-based methods could be employed to further resolve spatial heterogeneity at sub-millimetre scales. Finally, longitudinal studies tracking the same materials across successive recycling cycles would provide critical insight into contaminant accumulation, filler evolution, and long-term degradation mechanisms, thereby supporting the development of dynamic End-of -Waste criteria and adaptive circular economy principles

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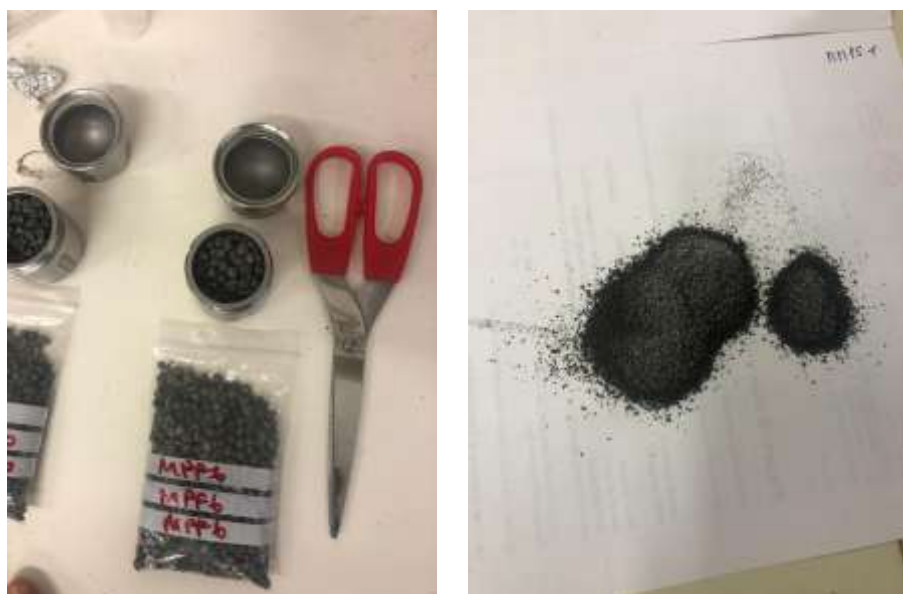
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APPENDIX

Appendix A: Cryomilled product of plastic samples before XRPD, ICP and Ageing Experiment analyses.



Appendix B: Casel device heating apparatus for ICP sample preparation.



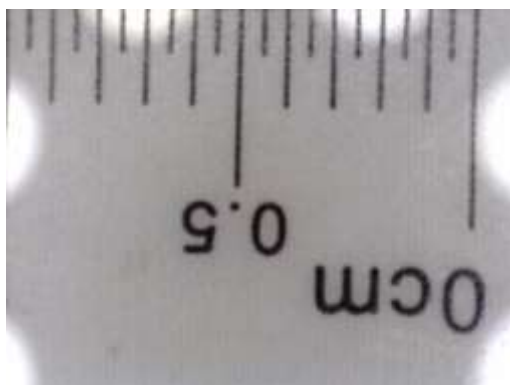
Appendix C: Hot heating plate for ICP sample preparation.



Appendix D: Ageing Experiment Apparatus



Appendix E: Sample MV1 used for Ageing Experiment observed under light microscope.



**Appendix F: XRF results, of oxides percentage in samples and the concentration (ppm)
of metals present in the samples**

%Ox	MMPS 2	MMPS 3	MMPS 4	MMPS 6	MMPS 7	MMPS 8	MMPS 9	MMPS 14	MMPS 15
SiO ₂	42.17		45.99	5.61	5.22	0.55	25.66	9.44	67.48
TiO ₂	0.96	98.35	0.92	25.00	6.18	0.61	20.58	52.03	
Al ₂ O ₃	9.25	0.39	10.36	1.09	0.47	0.14	4.38	2.36	5.32
Fe ₂ O ₃	3.94	0.06	1.01	2.08	5.48	0.19	6.77	9.09	5.77
MnO			0.03						0.86
MgO	1.28	0.02	1.02	0.43	0.48	0.83	12.16	2.53	1.07
CaO	35.55	0.05	37.28	63.67	79.04	97.24	19.51	15.75	8.45
Na ₂ O		0.04	0.38	0.09	0.13		0.28	1.56	0.42
K ₂ O	0.81	0.02	1.08	0.08	0.13		0.48	0.29	
P ₂ O ₅	0.40	0.22	0.06	0.18	0.18	0.02	0.38	0.44	5.42
Tot	94.36	99.15	98.13	98.23	97.31	99.58	90.20	93.49	94.79
ppm									
F			1600	3950			2130		
S	17360	99	305	466	1230	121	4030	8580	7040
Cl	514	503	589	7090	18310	315	13830	11840	42880
V	391								
Cr	836		360	1900	2510		2410	8790	
Ni		121	82	811			552		
Cu	357		1250	1320	1250	905	9800	17400	
Zn	58000		1020	1480	3040	1880	5010	5360	
Ga			56						

As						344			
Br			10560				57750		2290
Rb	109								
Sr	368		895	663		452	249		
Y			73						
Zr	202	115	400						
Nb		601							
Sn			591						
Sb							2530		
I			969						
Ba									
Pb		173	130		643		423	13170	
Bi	1830		89						

Appendix G: Table of elemental results prepared (P) by Casel device (L), heating plate (G) and analysed (A) by ICP-OES (L) and ICP-MS (G).

P= Prepared, A= Analysed.

Samples	P	A	Mg	Al	Cr	Ti	Fe	Co	Ni	Zn	Sb	Ba	Pb	Cu	Ca
MV1 VO	L	G	31.80	5.38	0.85	0.07	11.98	0.10	0.93	5.00	0.11	1.12	0.53	4.72	152.16
MMPS4 VO	L	G	1348.81	10975.48	47.01	248.62	707.92	0.89	21.27	103.22	0.65	26.20	7.91	145.31	23947.51
MMPS9 VO	L	G	254.61	220.49	20.90	1.60	166.76	0.28	10.62	23.69	76.13	3.77	1.43	22.94	1767.77
MMPS12 VO	L	G	1284.85	567.35	4.55	5.61	284.13	0.23	3.18	65.35	0.23	192.77	0.89	13.52	649.24
MMPS18 VO	L	G	256.29	168.95	14.49	2.96	166.3	0.36	6.87	51.31	6.03	31.40	17.11	10.27	6592.47
MMPS20 VO	L	G	358.06	251.61	202.91	10.51	967.45	3.10	111.35	67.14	9.57	19.41	21.93	238.24	9454.58
SIMPS24 VO	L	G	227.66	539.31	69.83	3.20	468.97	0.81	30.56	17.99	1.67	24.08	3.60	9.61	1838.07
SIMPS27 VO	L	G	366.7227	225.06	6.54	6.75	228.58	1.51	7.03	141.39	131.71	143.39	26.52	15.66	6017.69
SIMPS30 VO	L	G	58.98	119.44	1.96	4.53	56.07	0.10	2.88	24.63	1.62	10.83	6.14	7.70	1856.50
SIMPS31 VO	L	G	173.75	137.37	9.17	5.46	163.16	2.60	12.58	52.65	38.84	137.93	21.54	13.73	827.67
MV1 VO	L	L	25.97	6.30	1.00		13.39	1.00	1.00	27.57	1.00	1.00	1.00	37.96	174.83
MMPS4 VO	L	L	1333.50	12303.09	50.05		686.94	1.00	18.05	106.68	1.00	26.62	1.28	146.56	26171.49
MMPS9 VO	L	L	252.23	227.81	22.94		163.85	1.00	8.61	24.33	68.82	3.34	1.00	29.79	1976.17
MMPS12 VO	L	L	1120.59	598.37	3.66		277.67	1.00	1.07	69.02	1.00	201.31	1.00	17.85	703.09
MMPS18 VO	L	L	234.48	168.63	12.37		153.66	1.00	3.75	44.70	4.07	28.44	7.25	13.37	7144.28
MMPS20 VO	L	L	327.38	250.89	212.30		964.29	1.77	107.14	65.97	12.00	19.25	11.71	228.17	10193.45
SIMPS24 VO	L	L	217.48	545.79	80.21		452.91	1.00	29.63	19.45	2.67	25.14	1.00	18.85	2234.64
SIMPS27 VO	L	L	347.09	228.74	5.75		227.75	1.00	4.67	159.12	110.89	149.18	15.32	36.40	6941.82
SIMPS30 VO	L	L	57.27	113.85	1.00		57.67	1.00	1.00	25.74	1.00	9.84	1.87	17.66	1955.70
SIMPS31 VO	L	L	181.76	134.43	8.81		161.79	1.17	10.49	60.82	33.56	147.81	13.08	28.06	884.85
MV1	G	L	3.43	4.29	1.00		5.05	1.00	1.00	5.76	1.00	1.00	1.00	8.02	37.42
MMPS4	G	L	922.04	10142.41	24.65		461.02	1.00	7.70	105.90	1.00	19.72	1.00	139.68	21065.36
MMPS9	G	L	65.32	72.45	1.12		30.83	1.00	1.00	16.87	24.27	1.68	1.00	14.34	1002.81
MMPS12	G	L	558.43	225.90	1.67		125.72	1.00	1.00	53.89	1.00	157.88	1.00	7.41	419.06
MMPS18	G	L	102.77	123.52	2.11		68.02	1.00	1.00	32.49	1.00	14.39	5.13	4.84	4365.27

MMPS20	G	L	156.38	100.72	3.03		86.66	1.00	1.00	49.06	3.15	13.22	6.93	110.77	6916.13
SIMPS24	G	L	186.34	918.72	25.77		206.17	1.00	4.27	13.18	1.00	15.56	1.00	7.26	2269.80
SIMPS27	G	L	163.10	123.42	1.00		95.97	1.00	1.67	57.98	23.37	39.48	6.13	8.61	4415.71
SIMPS30	G	L	16.87	72.88	1.00		14.87	1.00	1.00	12.98	1.00	4.71	1.00	7.25	802.64
SIMPS31	G	L	26.13	64.43	1.00		47.47	1.00	1.30	15.56	1.58	8.98	1.00	8.40	309.17
MV1	G	G	7.93	10.47	0.44		3.81	0.01	0.56	5.21	0.12		0.23	0.96	1.88
MMPS4	G	G	1097.11	9044.05	25.90	208.82	463.04	0.62	10.78	110.91	0.52	21.30	6.89	138.71	18306.50
MMPS9	G	G	54.35	64.36	2.43	0.80	30.13	0.05	2.59	23.51	29.84	2.04	1.04	11.22	940.69
MMPS12	G	G	589.33	235.23	3.11	4.62	128.22	0.19	2.36	57.01	0.18	161.57	0.57	5.52	364.13
MMPS18	G	G	95.47	118.79	3.37	1.81	68.19	0.14	1.76	33.94	1.94	13.80	11.10	3.60	4078.49
MMPS20	G	G	148.854	106.84	4.34	7.31	86.86	0.18	1.78	51.41	4.36	13.11	14.33	123.42	6637.37
SIMPS24	G	G	204.4438	953.94	25.66	21.15	192.88	0.22	6.47	14.86	0.69	15.43	2.68	2.92	2066.61
SIMPS27	G	G	170.0643	125.86	2.30	2.80	92.70	0.78	3.88	59.56	29.38	39.29	13.09	3.11	4019.69
SIMPS30	G	G	20.63	86.89	0.97	2.26	15.44	0.04	0.48	14.38	0.75	4.74	2.61	3.25	691.80
SIMPS31	G	G	28.90	64.49	1.98	0.74	45.44	0.54	3.13	16.52	2.49	8.37	3.89	4.64	260.71

Multi-Technique Characterization of End-of-Waste Plastics: Assessing Degradation, Contamination, and Filler Composition.

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The Circular Economy is a sustainable framework that challenges the traditional linear model of resource consumption based on extraction, usage, and disposal. Instead, it promotes a closed-loop system in which materials are continually reused, recycled, and reintegrated into production cycles. The goal is to reduce waste, conserve non-renewable resources, and minimize environmental impact. Within this model, waste is no longer seen as an endpoint but as a valuable input that must undergo careful assessment to ensure it meets the required standards for reuse. One of the most widely used materials in industrial manufacturing is plastic—particularly polypropylene (PP), which represents 16% of global plastic consumption. As usage increases, so does the generation of PP waste. However, recycling processes such as mechanical recycling often compromise the material's quality due to polymer degradation, including chain scission and loss of molecular weight, which negatively affects performance (Uekert et al., 2023). According to Plastics Europe's 2024 report, only 2% of new plastic products are derived from recycled sources, highlighting both the challenge and the potential for innovation. In Europe, the "End-of-Waste" criteria regulate how recycled plastics can re-enter the market (Johansson, 2023). These standards require that recycled materials are safe, meet market demands, and match the performance of virgin plastics. However, these criteria are not yet fully operationalized, making detailed material characterization crucial for evaluating safety and quality. This study aims to provide a comprehensive evaluation of recycled plastic materials using a multi-technique approach. Analytical tools including; Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-ray Powdered Diffraction (XRPD), and Inductively Coupled Mass Spectroscopy (ICP-MS) were applied to assess chemical degradation, elemental contamination, and filler composition (Dzoh Fonkou et al., 2025). By correlating data from these techniques, the study seeks to develop a robust understanding of the structural and chemical integrity of recycled plastics. The insights gained will support safer reuse, improved quality assurance, and alignment with circular economy goals in plastic waste management.

This study examined 34 end-of-waste recycled plastic samples, including polypropylene (PP), polyamide (PA), ABS, SAN, and POM, collected from industrial partners. The materials included both homogeneous pellets and heterogeneous fragments. For **FTIR**, 100 µm films were prepared by heating samples at 200 °C and analysed in ATR mode to assess chemical degradation. **XRPD** was used to detect crystalline fillers and additives, while **SEM-EDX** provided morphological and elemental surface

information. **ICP-MS** analyses were performed on acid-digested samples using a sequential treatment of HNO_3 , H_2O_2 , and HCl . Each analysis included blanks and replicates for quality assurance. Elements such as Mg, Al, Cr, Ti, Fe, Co, Ni, Ba, Zn, Sb, Cu, Pb and Ca were quantified to evaluate contamination and filler content. Data were assessed for consistency and material compliance with EU standards.

As results, FTIR analysis revealed degradation in several samples through band shifts and intensity changes. Notably, alterations in the C–H stretching region ($\sim 2850\text{--}2920\text{ cm}^{-1}$) indicated chain scission, while new or intensified carbonyl bands ($1700\text{--}1750\text{ cm}^{-1}$) suggested oxidation from photo or thermo-degradation as seen in figure 1. These spectral changes were more prominent in heterogeneous fragments, implying a stronger degradation effect due to mixed composition or past use. SEM imaging supported these findings by revealing surface deterioration, including microcracks and roughness typical of aged polymers.

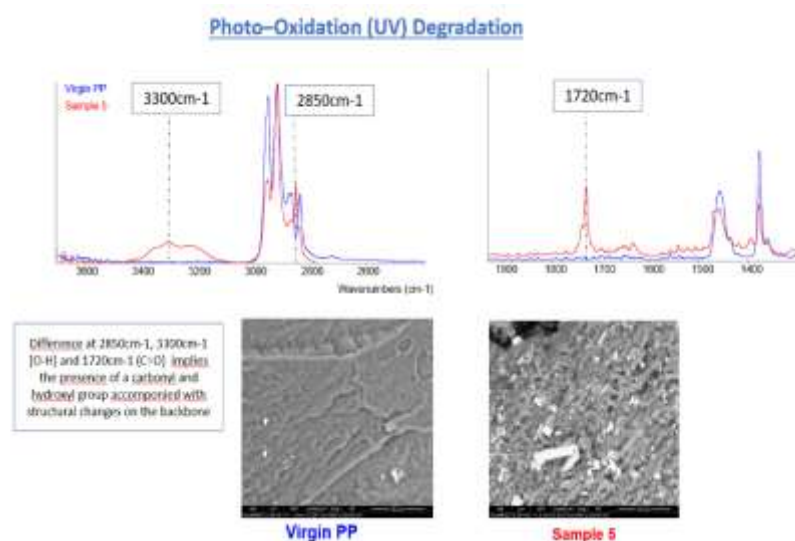


Figure 1: Illustrates the photo oxidation and thermal degradation evidences by FTIR and SEM imaging in the analysed samples.

Elemental contamination was investigated through ICP-MS. Out of 34 samples, 10 representative ones were analysed. Elevated levels of Cr were detected, with some exceeding REACH and other EU thresholds. Differences in contamination patterns were noted between sample types (pellets vs. fragments), reflecting varying histories or additive contents. Filler and additive content were assessed via XRPD, SEM-EDX, and ICP. XRPD revealed common fillers such as calcite, talc, rutile, and barite. Certain samples also showed patterns consistent with glass fibres. These identifications were confirmed by SEM-EDX and supported by ICP results, which quantified relevant filler elements like Ca, Ba, Mg, Al, and Ti.

A multi-technique analytical approach combining FTIR, SEM-EDX, XRPD, and ICP-MS provides a robust and comprehensive assessment of recycled plastic materials. This methodology allows for detailed evaluation of chemical degradation, elemental contamination, and filler composition, revealing that material integrity varies significantly based on polymer type and processing history. The study demonstrates that pellets show better structural and chemical stability than heterogeneous fragments, supporting the need for advanced characterization protocols to ensure the quality and safe reuse of recycled plastics in compliance with regulatory standards and circular economy goals.

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From End-of-Waste to Upcycled Products: Preliminary Results from Characterization of Polypropylene.

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ABSTRACT: Despite great efforts to build a robust circular economy of plastic waste, the worsening of the material quality due to secondary raw material (End of waste) heterogeneity and/or degradation occurring during the recycling process, represents the bottleneck for an effective recycling of polymers. This contribution illustrates some preliminary results we obtained through an in-depth structural characterization of secondary plastic raw materials and the corresponding recycled products. Different techniques (FTIR-ATR, Micro-Raman, XRPD and XRF) have been used to improve knowledge of the chemical composition and physical properties of these materials, with the aim of assessing the quality of upcycled products and suggesting strategies for improving their recycling.

Keywords: Circular economy, end of waste, material quality, upcycling.

1. INTRODUCTION

In recent years, extensive research has been devoted to developing new technologies for managing plastic waste more effectively. Recycling and upcycling techniques have emerged as promising solutions, particularly for polyolefins like polypropylene (PP). Closed-loop (PP-PP) and open-loop (PP-X) recycling processes are widely used (Uekert et al., 2023), encompassing both physical (mechanical) and chemical (production of small molecules from the waste polymer, as raw material for new synthesis) recycling methods.

It is emphasized that while the primary goal of a circular economy is to reintroduce recycled products back into the market, achieving true plastic circularity remains a significant challenge. Currently, only 9% of global plastic waste undergoes recycling (Tan et al., 2023). This low rate can be attributed to several factors, including difficulties in waste collection and sorting, limited access to appropriate recycling infrastructure, and the worsening in material quality with each recycling cycle. Upcycling, a process that upgrades recycled materials into higher-value products, can help address this quality issue.

In Europe, recycled plastic must undergo a specific assessment known as the "End-of-Waste" (EoW) procedure. This legal framework facilitates the transition of waste materials into usable products (Johansson, 2023). According to Article 6(1c) of the Waste Framework Directive (2008/98/EC), a recycled material qualifies for EoW status if it meets the following criteria:

- It is designated for specific purposes and has a well-defined market or demand.
- It fulfils the technical requirements for its intended use.
- It complies with existing legislation and standards applicable to products.
- Its use does not pose any significant environmental or human health risks.

This directive mandates testing recycled plastic products to ensure they meet the same standards as their virgin counterparts.

Usually, the analysis protocols of the re-cycled material focus on the mechanical and rheological properties, which often are adjusted by adding some amount of virgin polymer and/or additives, in order to meet target parameters. Less frequently, characterizations aimed at the knowledge of the chemical composition (i. e. formulation) and of the morphology of the new material are carried out. These characteristics can have a significant impact on the performance of the recycled material and its durability, not immediately evident through standard tests. Moreover, they allow developing structure-property relationships, which can help in the design of optimized recycling procedures.

This study investigates the changes in end-of-life polypropylene (EoW PP) during the upcycling process within the Italian plastic industry. It aims to identify how the material's chemical and physical, characteristics evolve from EoW material to a new upcycled product. The methodology employed depends on several factors, such as the polymer type, the analysis objective, and the material's specific application. These analytical methods can be broadly categorized based on the property they investigate: chemical composition, mechanical, rheological and thermal properties, polymer structure and material morphology. While individual techniques offer valuable insights, a combination of two or more methods is often used to provide a more comprehensive interpretation of the results, allowing for a clearer definition of the investigated properties.

Ataeefard & Moradian,Ataeefard & Moradian,Viora et al. (2023) demonstrated the effectiveness of combining Atomic Force Microscopy (AFM), X-ray Scattering (SAXS), and Dynamic Mechanical Analysis (DMA) to observe changes in crystallinity, microstructure, and several mechanical properties between virgin and recycled polyethylene terephthalate (PET). Conversely, for chemical characterization, two-dimensional gas chromatography time-of-flight mass spectrometry (GC x GC-TOFMS) can be a powerful tool for rapid chemical detection in products(Lowe et al., 2021). For a more detailed comparison of recycled and virgin PET, Bhattarai et al. (2024) employed a combination of X-ray Photoelectron Spectroscopy (XPS), Fourier Transform InfraRed spectroscopy (FTIR) , while Ataeefard & Moradian,(2011) utilized AFM and Scanning Electron Microscopy (SEM) to analyze the surface roughness of polypropylene/organoclay nanocomposites.

2. Materials and Methods

The samples studied in this work have been kindly provided by a plastic recycling company in Italy (Mepol). The samples are mainly composed of polypropylene and consist of three pairs of different materials (a secondary raw material and a material obtained by the corresponding re-cycled product):

1. Secondary raw material (EoW-MMPS12) from post-industrial recycling and the corresponding final product for furniture production (MPF8).
2. Secondary raw material (EoW MMPS13) from post-consumer recycling and the corresponding final upcycled product for furniture production (MPF9).
3. Secondary raw material (EoW MMPS16) and the corresponding final product for commercial large –scale distribution (pallet production) (MPF12).

From the different materials listed above, we prepared samples suitable for the characterization. Some amount of material was heated at 200°C to produce thin films of tens of microns for FTIR analyses in Attenuated Total Internal reflection mode (ATR) and in transmission mode. Additionally, we obtained powdered samples by cryomilling. This technique is more effective than crushing using traditional

grinding methods, because polypropylene being flexible and rubbery, would deform rather than split into smaller particles. With cryomilling, the temperature is brought down to -196 °C with liquid nitrogen well below the PP glass temperature transition, making the sample significantly brittle thus allowing to shatter the plastic to powder suitable for X-ray Powder Diffraction (XRPD) and X-ray Fluorescence (XRF) analysis.

The analyses conducted on the samples were: FTIR-ATR, Micro-Raman, XRPD and XRF.

3. RESULTS AND DISCUSSION

All analyses confirmed that polypropylene was the primary component of the samples.

Sample Pair 1: Secondary Raw Material (EoW-MMPS12) and Final Product (MPF8)

- X-ray diffraction (XRPD) analysis revealed the presence of talc, rutile (TiO_2), and maleic anhydride, along with polypropylene, in the secondary raw material. Talc and rutile are fillers, while maleic anhydride is commonly used as a compatibilizer in plastics. The final product contained only talc and maleic anhydride; rutile was not detected. Furthermore, the XRPD patterns indicated a transition to a more crystalline structure in the final product.
- Spectroscopic FTIR analysis provided further information on the chemical composition of the samples. The final product exhibited an increase in talc content, as evidenced by corresponding characteristic bands at 1014 cm^{-1} and 3700 cm^{-1} in the spectra, which corroborates the XRPD findings.
- Tables 1 and 2 report the results obtained from XRF. In these tables are listed the oxides present in the sample and not the total composition of the sample. This is because XRF has limitations in detecting elements with low atomic numbers like carbon and hydrogen, which are the main components of polymers. For this pair of samples the total oxide content in the secondary raw material was 24.05 wt %, compared to 58.72 wt% in the final product. The main oxides identified in the secondary material were SiO_2 , TiO_2 and MgO . The final product contained primarily SiO_2 and MgO , indicating the removal of rutile (TiO_2) during processing.

Sample Pair 2: Secondary Raw Material (EoW MMPS13) and Final Upcycled Product (MPF9)

- XRPD analysis detected talc, calcite, and maleic anhydride in both samples. The crystallinity remained similar, with both samples exhibiting a semi-crystalline structure.
- Micro-Raman spectroscopy revealed a strong fluorescence emission in the spectra which prevents the chemical recognition of the material. No significant differences were observed between the two samples in the Fourier-transform infrared spectroscopy (FTIR-ATR) spectra, suggesting the presence of polypropylene and a minor amount of polyethylene.
- XRF analysis (Table 1) showed a total oxide content of 12.20 wt% in the secondary material and 22.19 wt% in the final product. The primary oxides were TiO_2 and CaO in both samples, with respective weight percentages of 61.48% and 19.53% in the secondary material and 77.93% and 11.53% in the final product. These results indicate an increase in TiO_2 and a decrease in CaO content.

Sample Pair 3: Secondary Raw Material (EoW MMPS16) and Final Product (MPF12)

- XRPD analysis revealed talc, calcite, and maleic anhydride in the secondary raw material. The final product contained only calcite and maleic anhydride; talc was not detected. The material also exhibited a transition from a semi-crystalline to a more crystalline structure during processing.
- Micro-Raman spectra showed a slight difference between the two samples, with bands at 1081 cm^{-1} and 715 cm^{-1} observed in the final product, which corresponds to calcium carbonate. FTIR-ATR analysis also identified, in the spectrum of the final product, the strong band at 1450 cm^{-1} further confirming the presence of calcite.

- XRF analysis (Table 1) indicated a total oxide content of 0.58 wt% in the secondary material, with SiO₂ and CaO as the primary oxides (20.70 wt% and 18.31 wt%, respectively). In the final product, the total oxide content increased to 56.53 wt%, with CaO accounting for 97.67 wt% of the total oxides.

4. CONCLUSIONS

This study highlights the transformations that occur in EoW PP during the upcycling process within the Italian plastic industry. The analyses using various techniques like Micro-Raman, FTIR, XRPD, and XRF demonstrate significant changes in the material's chemical composition, crystallinity, and microstructure. These findings emphasize the importance of characterizing upcycled materials to guarantee their quality and performance compared to virgin counterparts. Further research can explore the impact of upcycling on the mechanical, rheological and thermal properties of EoW PP and how these properties influence the suitability of upcycled products for different applications within the circular economy.

5. ACKNOWLEDGEMENT

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