Mechanical Recycling of Thermoplastics

Subjects: Polymer Science | Green & Sustainable Science & Technology

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Plastic materials have gathered attention recently due to their omnipresence in the global economy. The transition towards a circular economy is the only way to prevent the environment from landfilling and incineration.

mechanical recycling | sorting technologies | decontamination process | polyolefins | engineering (PET, PA6) and bio-sourced polymer (PLA and PHB)

1. Introduction

Plastic materials have gathered attention recently due to their omnipresence in the global economy. Since last century, plastics have become rapidly one of the most used materials in industry. In 2019, more than 400 million tonnes of plastics (Mt) were produced (**Figure 1**) [1].

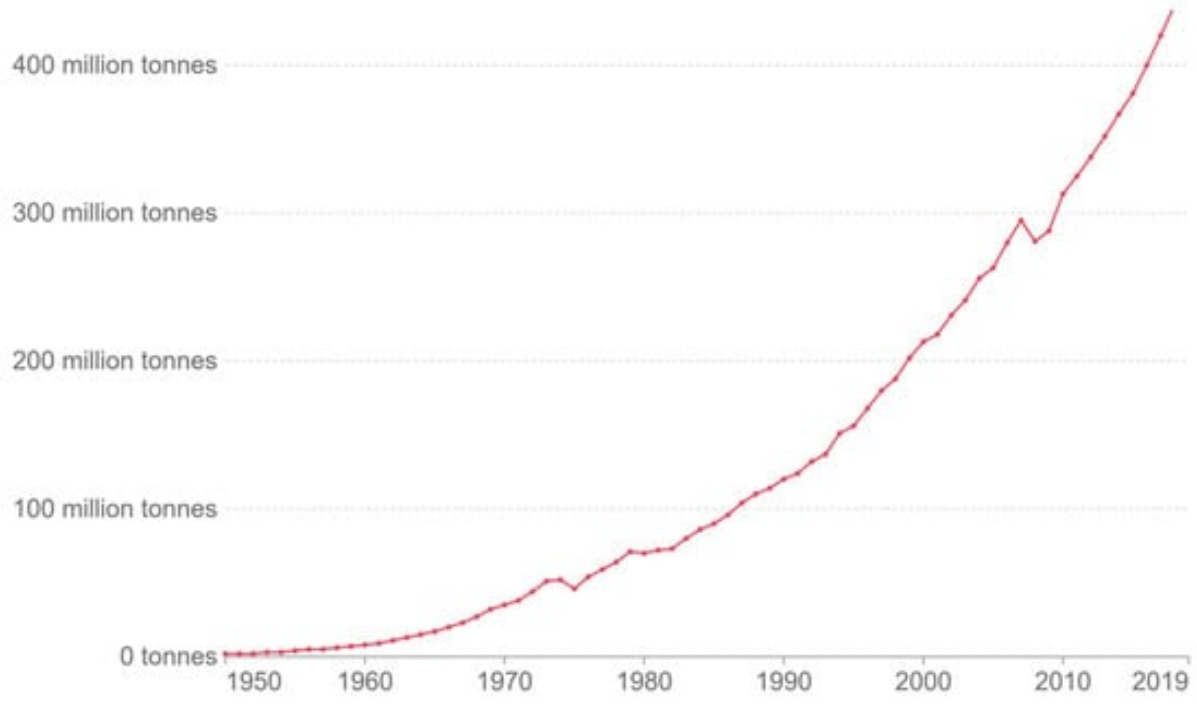

Figure 1. Global plastics production: 1950 to 2019 [1].

If production continues to grow at a similar rate, plastics production will reach 1600 million tons (Mt) in 2050. The rapid growth of plastics production is due to the good properties and low cost of this material. Thanks to its

versatility, this material is used in several fields, such as packaging, textile, transport, and construction. Polymers are widely used, depending on the final application (**Figure 2**).

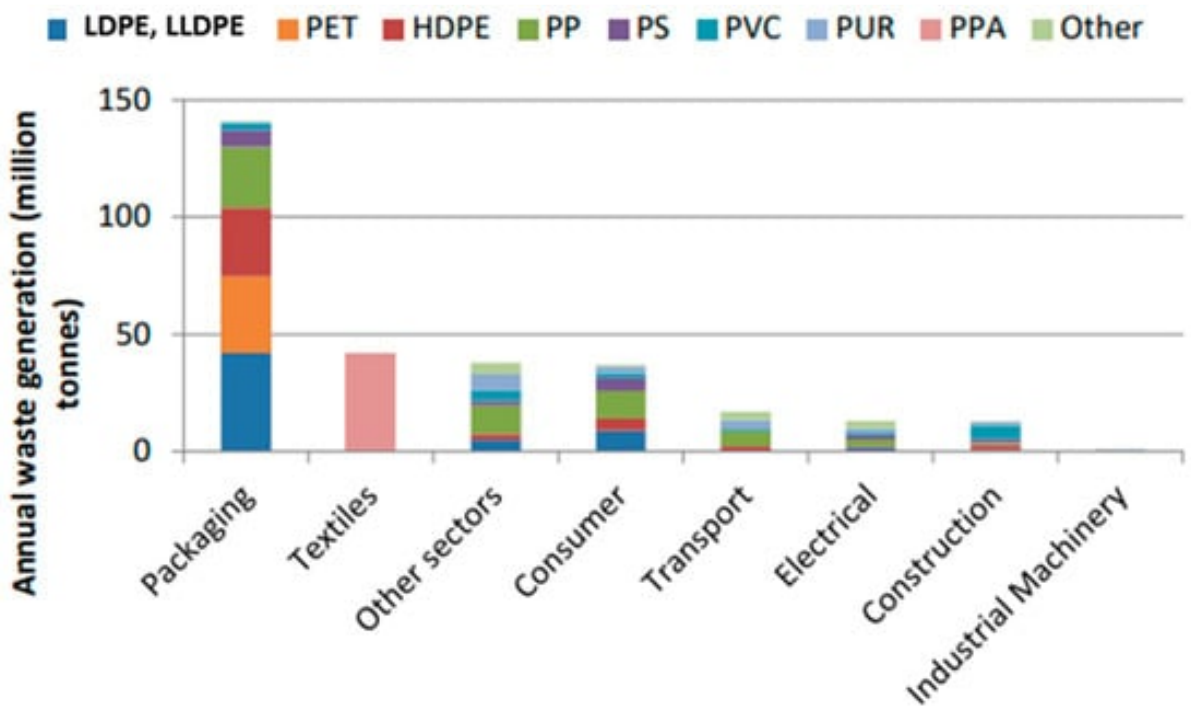

Figure 2. Global plastics use by polymer and sector [1].

The proliferation of plastic production contributes significantly to greenhouse gas emissions and generates pollution in the natural environment. Indeed, the production of virgin plastics requires the transformation of petroleum into monomers. This process is energy-intensive and generated 400 million tons (Mt) of greenhouse gas emissions in 2012 [2].

To protect the environment, some countries adopted a new economic model that aims to revalorize post-consumed plastic and avoid landfilling. The transition toward a circular economy is unavoidable to reduce the plastic footprint and promote recycling. To manage plastic waste, there are different gates that can be classified from the most to the least preferred (**Figure 3**) [3].

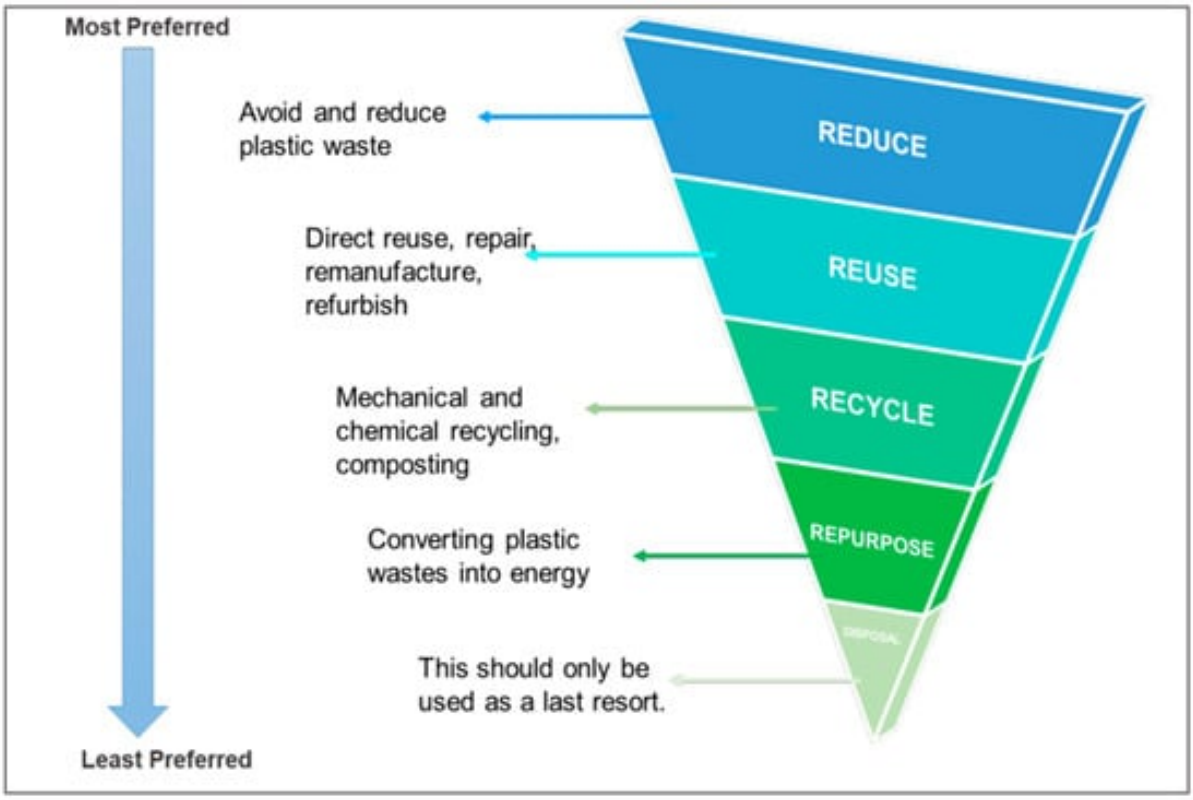

Figure 3. Hierarchy of priority in plastics management [4].

Waste management places reduction as the top priority. The idea is to prevent the unnecessary consumption of resources. Direct reuse of original products is the second-best practice in waste management. The third stage is recycling products to avoid landfilling. Repurpose is about energy recovery. If the material cannot be recycled and recovered to energy, it will be landfilled, but it is the least preferred stage in the waste management hierarchy.

To achieve the goal of 100% recovery of plastics, the waste management system should be extended to all fields using plastics. In the industry, there are four ways to recover plastics: primary, secondary, tertiary, and quaternary recycling (**Figure 4**).

Figure 4. Stages of Recycling.

2. Sorting Technologies

Plastic separation faces a lot of challenges due to the huge quantity of plastics to collect and the complexity of identifying some types of plastics. The sorting is important to remove contaminants from plastics. This section will cover separation techniques that use density, surface charge transfer, and spectral analysis. The most used sorting methods are listed in **Table 1**.

Table 1. Sorting Methods.

Sorting Method	Characteristics	Drawbacks	Reference
Manual	Hand based sorting	Laborious, bad working environment	[5]
Tribo-electric	Based on electrostatic charge	Only for clean, dry, and non-surface-treated products.	[6]
Near-infrared Radiation (NIR)	Fundamental vibration	It is not adapted for dark plastics and is very expensive.	[7]

Sorting Method	Characteristics	Drawbacks	Reference
Flotation	It is related to a specific gravity of material.	It is not applied to High-density Polyethylene (HDPE) and Low-density Polyethylene (LDPE).	[8]
X-ray fluorescence (XRF)	Uses X-rays as a source	It is very expensive	[9]

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3. Recycling Techniques: Overview

In the industry, there are several ways to recover plastics. They are classified into four categories: primary, secondary, tertiary, and quaternary recycling. Each type has its advantages and disadvantages. It depends on the application of recycled polymer. The four ways are listed in **Table 2**.

Table 2. Recycling techniques.

Type of Recycling	Process	Limits	References
Primary recycling (Re-extrusion)	It is a process based on the extrusion of plastics. It does not require too much equipment and high investment.	It is adapted for plastic scrap with less contamination	[10][11]
Secondary recycling (Mechanical recycling)	The technique begins in the sorting center by separating, washing, and grinding plastics. After these steps, plastic materials are processed with extruders and pelletized.	Degradation of thermomechanical properties of plastics	[12][13][14][15][16]
Tertiary recycling (Chemical recycling)	Chemical recycling consists of converting polymer into molecules or monomers that can be used to manufacture new polymers.	It is an expensive process with a negative impact on the environment	[17]

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Type of Recycling	Process	Limits	References
Quaternary recycling (Energy recovery)	Quaternary recycling aims to generate energy heat or electricity from plastic scraps [11].	The emission of toxic gases.	[11]

4. Sources of Contaminations

In general, ballots obtained from sorting centers are composed of three components: the desired polymer, polymeric contaminants, and some residual wastes. Contaminants can be classified into two categories volatile organic contaminants (VOCs) and solid contaminants. This last can be a polymeric contaminant or another material [12].

4.1. Structural Inhomogeneities

Compared to virgin polymers, recycled resin presents heterogeneity due to the attacking environment during its lifecycle. Irreversible structural changes can happen at both molecular and morphological levels. This modification can be induced mechano-chemically or by irradiation. The oxidation of polymeric materials creates free radicals such as carbon-centered (alkyl) and oxygen-centered (alkoxyl). This transformation is enhanced by the formation of crosslinked structures caused by the radical recombination of low molecular fragments [13].

4.2. Impurities

Impurities are present in high concentrations in post-consumed plastics. Some of them are VOCs and depend on the polymer type [14]. They come from additives added during the polymerization, such as phenolic antioxidants, consumed during the stabilization process. Furthermore, residues of titanium and aluminum polymerization generate colored salt. Resin absorbs contaminants, and the migration of some products to the matrix of packaging influences the quality of the material after being recycled [5].

5. Decontamination Techniques

In general, decontamination is performed by a degassing system or/and filtration system that is linked to an extruder. The material is melted at a high temperature, which generates VOCs (Volatile Organic Compounds) [15]. Numerous studies confirmed the effect of extruder profile heating on the extrusion performance. The ratio of VOCs was very high when heating reached 250 °C compared to 150 °C [16].

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5.1. Degassing System

5.1.1. Without Chemical Agent

To remove VOCs contained in plastics, extruders are equipped with a devolatilization system. The vacuum present inside the extruder helps to remove volatile components. Several studies highlight the influence of using single and multidegassing systems in a screw extruder [21]. The concentration of the odor was measured by dynamic olfactometry. The result shows that odor intensity decreases after one degassing step from 373 to 279 OU/m^3 and after the third degassing step to 235 OU/m^3 [22].

5.1.2. With Chemical Agent

The first type of chemical agents are adsorbent agents. They allow the control of polymer emission during extrusion. The addition of 0.30% of adsorbent based on silicate to HDPE virgin pellets reduces the amount of VOCs, and the intensities of odors also decreased [23]. Furthermore, some studies show that the introduction of these particles with post-consumer HPDE in the extruder decreases odor by 50% [21]. The second type of chemical agent is a stripping agent. Their addition to the melt improves the devolatilization of the VOCs contained in the polymer. Their role consists of creating a bubble inside the matrix so the free volume in the melt increases, which helps the diffusion of VOCs in the vapor so that they can easily quit the extruder through the degassing system [23]. The most used stripping agents are water, nitrogen, and air, which enhance the devolatilization of VOCs contained in polyolefins [24]. For example, the use of nitrogen with polyethylene during extrusion reduces VOCs by 50% [25]. In the same context, some researchers developed a mathematical model that showed that the uses of stripping agents such as methanol toluene decrease the time required for degassing, and this number can increase by rising solvent concentration [26].

5.2. Filtration System

A screen changer is an important piece of equipment in a recycling line to remove solid particles from the melt. The most used screens in the extrusion process are manual and hydraulic. The common point between them is the interruption of the melt flow while the screen [illegible] [27]. Large-area filtration systems are available in single vessel-discontinuous or dual vessel-continuous configurations, allowing to change screens without interrupting production [27]. The different types of screens are listed in **Table 3**.

Table 3. Types of filtration systems.

Filtration System	Advantages/Disadvantages	References
Manual screen changers	It helps minimize labor and downtime for screen changes during line shutdown. The compact design eliminates the need for line disassembly and uses a hand lever to manually index the slide plate for screen change.	[27][28]

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Filtration System	Advantages/Disadvantages	References
Hydraulic screen changer	It's used in industry due to its wide range of sizes. It can reach 450 mm. Single screen operation limits filtration area, and the use of seals add to maintenance and the probability of leakage. The mesh size can reach 100 µm in some applications.	[27]
Rotary Disc type filtration system	This system offers high pressure with a lower residence time. System size can reach 250 mm and offer constant pressure operation but relatively high-pressure drops, with a lower residence time. It is a highly automated system with sophisticated controls and a backflush option. Leakage and disc lockup concerns are related to the clamping force of housing plates. It may require attention and to adapt system setup.	[27]

After being extruded, the polymer can be decontaminated by a purifying process such as extraction by supercritical fluid. Cristancho & Guzman [29] studied the supercritical extraction of VOCs using CO_2 and ethane. The process was performed with pressure in the range (7.6–20.7) MPa and two temperatures, 36 and 60 °C (**Figure 5**).

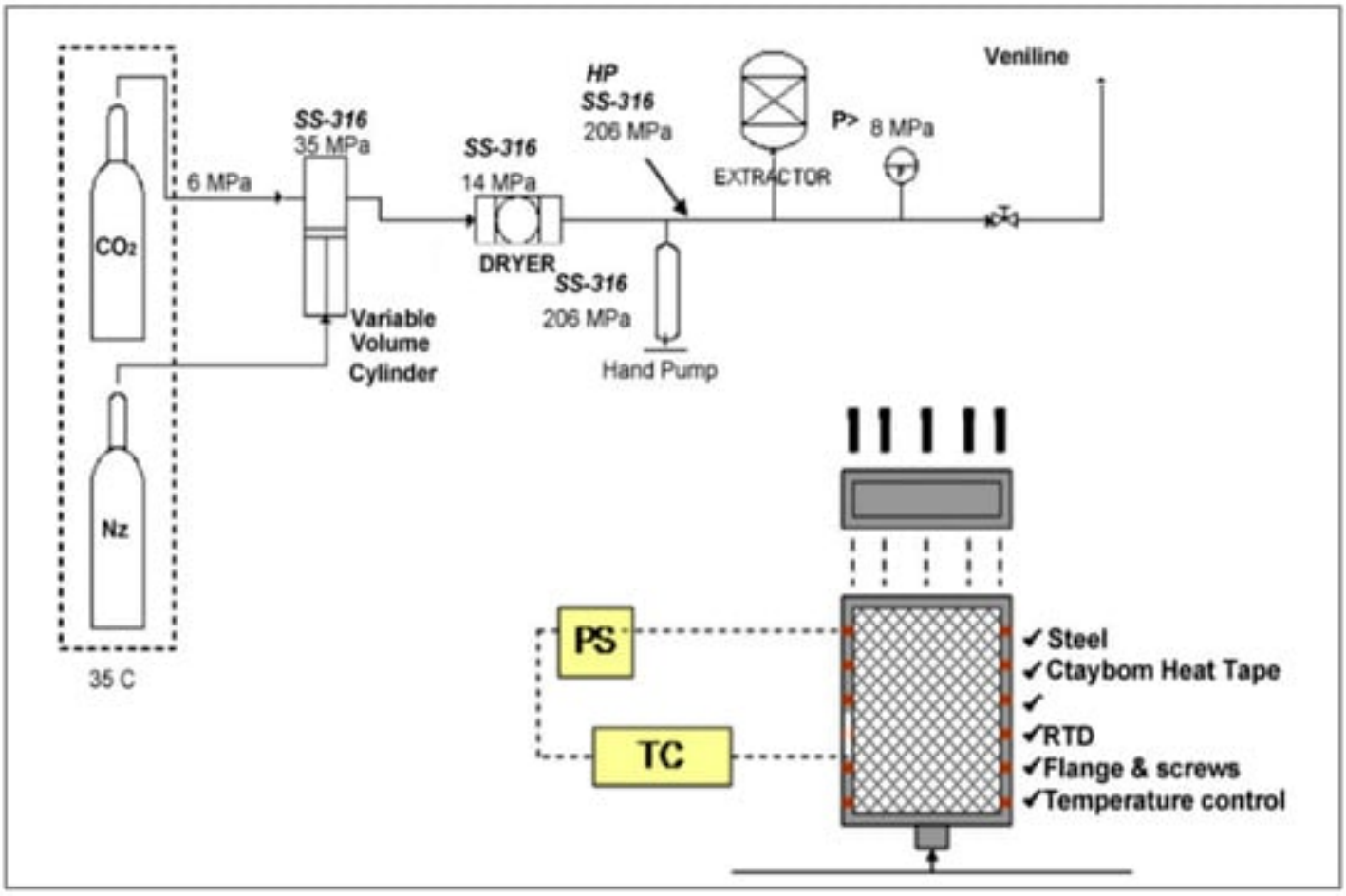

Figure 5. Supercritical extraction apparatus. PS: pressure sensor, TC: temperature control, RTD: resistance temperature detector [29].

The result showed that using ethane was as effective as multiple extractions using CO_2. At a low pressure (7.6 Mpa) and medium temperature 60 °C, the extraction with CO_2 is effective. Higher pressure improves the extraction, but it will increase the operational cost. Both supercritical fluid help to decrease VOC concentration, but CO_2 remain safer and environment friendly than ethane. For this reason, CO_2 is the most used for the extraction of VOCs from polyethylene pellets [29].

6. Identification and Quantification of Contamination Rate

Contaminants can be classified into two categories: polymeric contaminants and volatile organic contaminants (VOCs). To identify and quantify polymeric contaminants present in the blends, Differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR) can be used. Concerning volatile organic compounds, chromatographic methods are the most adapted.

6.1. Differential Scanning Calorimetry (DSC)

This method is adapted to determine the fraction of polymeric contaminants based on the recording of heat exchange during heating and cooling. Nevertheless, this approach is not suitable to identify LDPE/HDPE or even LLDPE/LDPE because of the similarities between their microstructures and melting temperatures. For example, to identify the fraction of HDPE in isotactic polypropylene, we can model the blend with a known ratio of the virgin polymer. These blends are extruded and analyzed by DSC (**Figure 6**) [30].

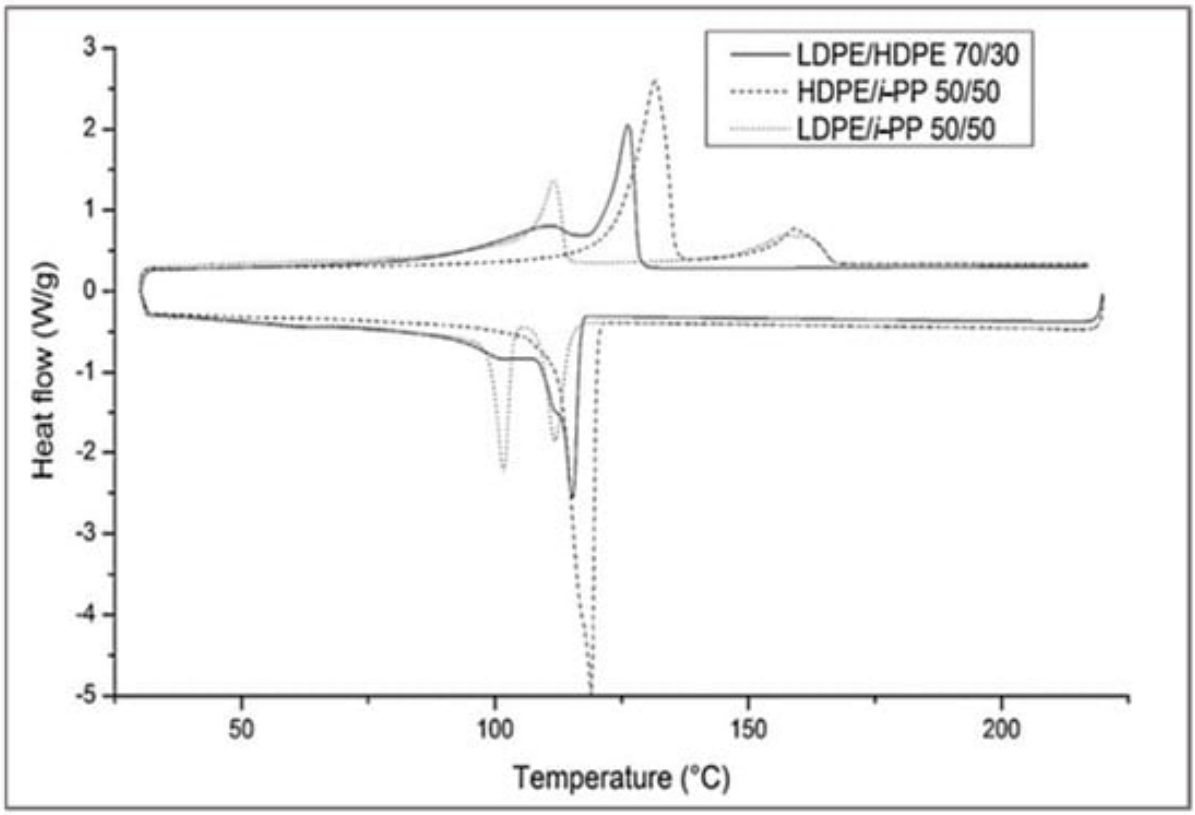

Figure 6. DSC thermograms of a 70/30 LDPE/HDPE blend (solid line), a 50/50 HDPE/i-PP blend (dashed line), and a 50/50 LDPE/i-PP (dotted line) (exo down) [30].

The presence of two melting peaks confirms the immiscibility of these polymers, which has been reported by many other authors [31].

The melting enthalpies were calculated using a linear peak integration and the results for each blend (**Figure 7**). This calibration curve can be used to determine the HDPE ratio in the PP/HPDE blend.

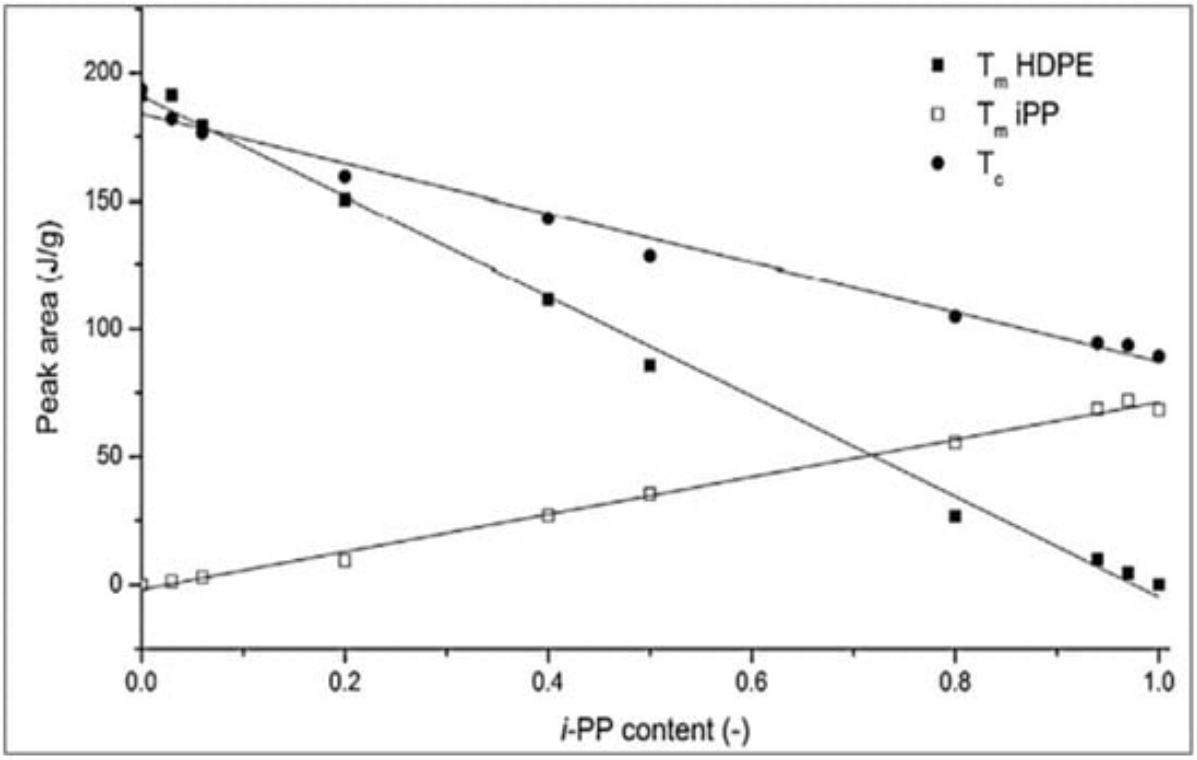

Figure 7. Peak area for HPDE/iPP model blends [30].

6.2. Fourier Transform Infrared Spectroscopy (FTIR)

This technique is used to quantify polymeric contaminants. Light is used to track molecular translations, rotations, and vibrations. The absorbed energy is specific for each chemical bond, and a spectrum is obtained that can be used as a fingerprint to identify polymers [30]. The spectra of the different compositions of blend based on PP and PE are shown in **Figure 8**.

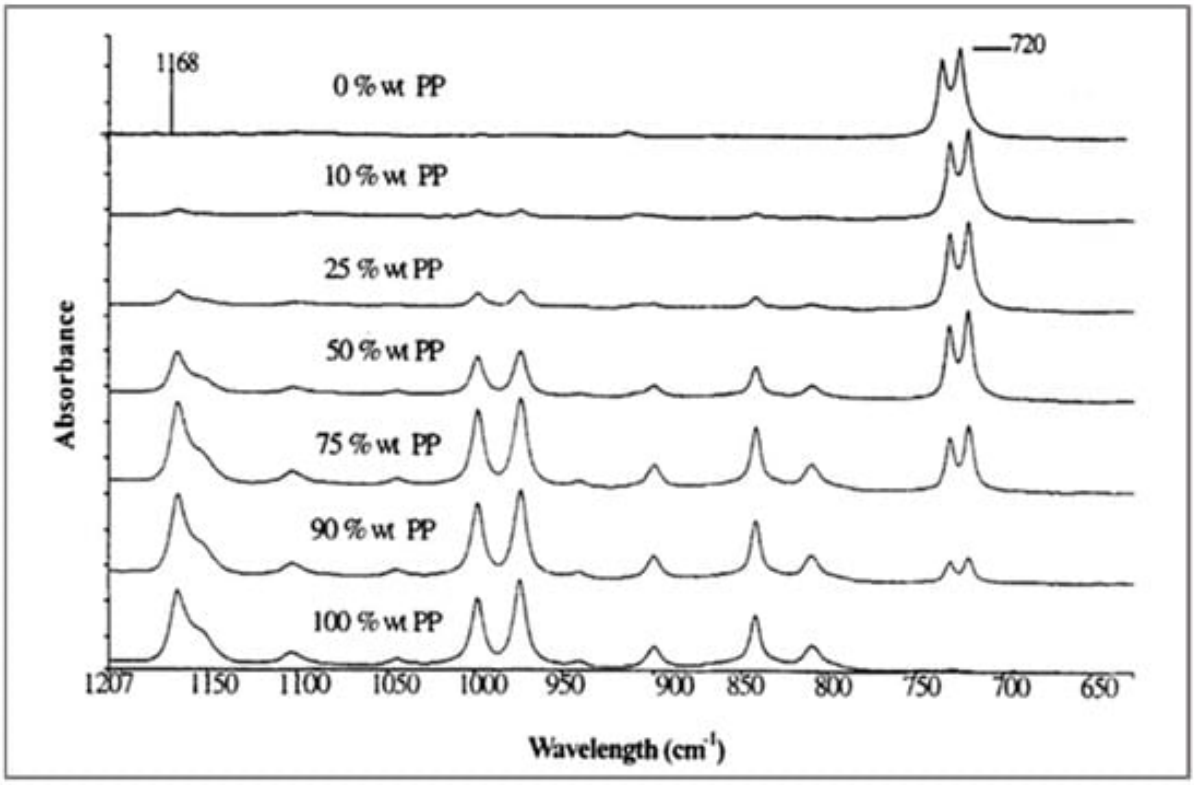

Figure 8. FTIR-spectra of PP/HDPE blends [31].

The calibration curve was plotted based on the ratio of the absorbance (integrated area) of two peaks, 1168 cm^{-1} for methyl group in PP and a peak of 720 cm^{-1} for methylene in HDPE (**Figure 9**). A1168/(A1168 + A720) was plotted as a function of PP content. The calibration curve can be used to determine the composition of the PP/HDPE blend.

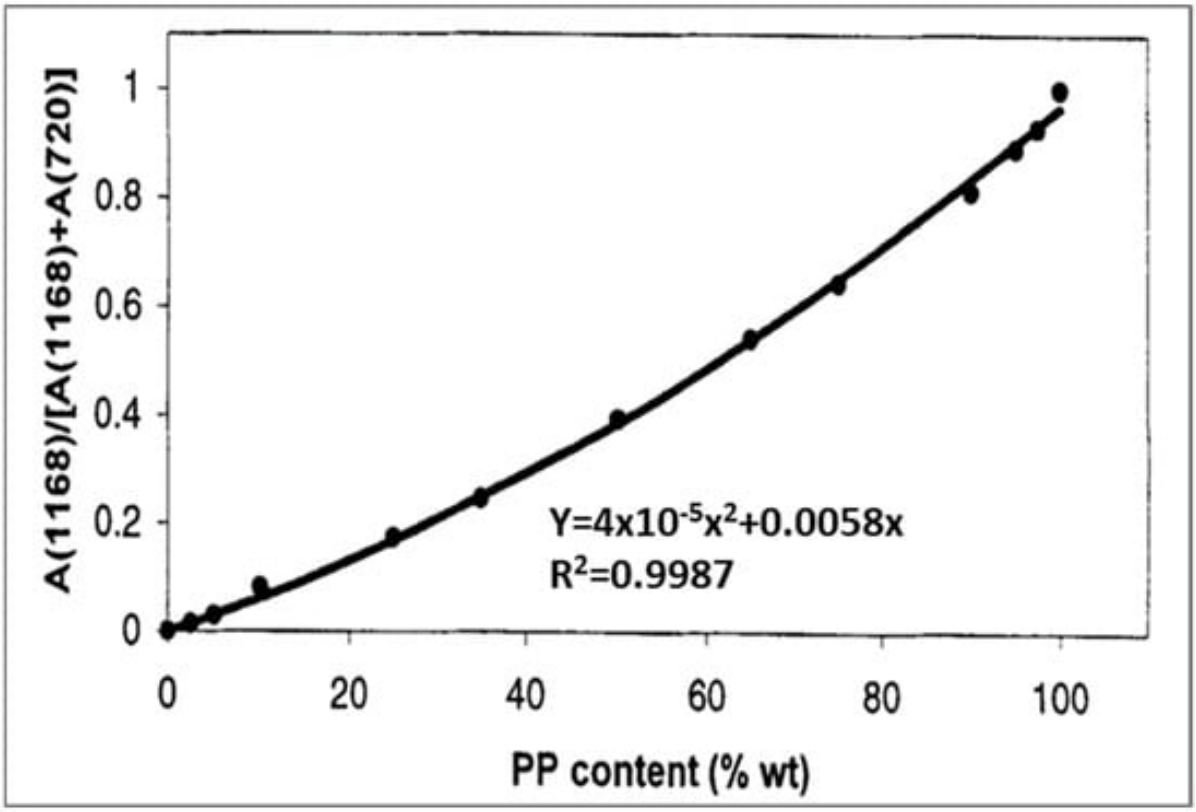

Figure 9. Calibration curve for determination of PP content in PP/HDPE blends [31].

6.3. Chromatography Analysis

For the chemical analysis of recycled plastics, gas chromatography coupled with mass spectrometry (GC-MS) can be used to identify and quantify volatile organic compounds (VOCs). To detect organic contaminants, gas chromatography (GC) is equipped with a mass selective detector (MS). A capillary column with a film can be used for chromatographic separation. The GC oven can be programmed from 40 to 180 °C at 15 °C min^{-1} and then to 300 °C at 5 °C min^{-1}, held for 12 min [32]. Organic contaminants can be identified by consulting the mass spectra libraries. The quantification of the contaminants can be performed by using external and internal calibration curves. The external standard method creates a calibration curve for a standard sample, and unknown samples are quantified using calibration curves. The internal standard method consists of adding a fixed amount of internal standard substance to an unknown sample when creating a calibration curve using a standard sample, and a calibration curve is created with the concentration ratio vs. peak area ratio for quantification [33][34].