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From PP Waste to High-Quality Products: Decontamination of the Material Throughout the Entire Recycling Process Chain Using State-of-the-Art Technologies

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From PP Waste to High-Quality Products: Decontamination of the Material Throughout the Entire Recycling Process Chain Using State-of-the-Art Technologies

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Abstract: Turning waste into high-quality products should be the aim of recycling, but it requires considerable effort to separate specific materials from others, clean them properly, and reconvert them into products. Such a process chain of mechanical recycling of post-consumer polypropylene (PP) from a mixed waste collection was conducted with an advanced combination of state-of-the-art technologies considering the material's decontamination throughout the different process steps. The levels of solid and volatile contamination were analyzed with an optical control system and a gas chromatographic method, respectively, and were found to decrease in varying amounts throughout the process. The results of this study represent the currently achievable qualities of recycled PP in mechanical recycling and, based on these findings, the recycling process can be further improved.

Keywords: Volatile Organic Compounds (VOC), Plastics Recycling, Decontamination, Polypropylene

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Introduction

One of the 17 United Nations Sustainable Development Goals aims to achieve circularity, including recycling plastics [1]. Obtaining a high-quality product from waste material via recycling requires several elaborate steps. In a common mechanical recycling process for plastics, the material is collected, sorted, shredded, and cleaned in the pre-treatment stage, and subsequently heated, filtered, degassed, and granulated in the extrusion stage [2]. Finally, products are produced that can be distributed and used until they are disposed of and collected again. For polyethylene terephthalate (PET), recycling processes to obtain high-quality recyclates are already being implemented [3]. In contrast, polyolefins, such as polypropylene (PP), are usually down-cycled into products with lower specifications, despite holding the highest global market share [4,5]. This results from a detrimental change in the properties, which are affected by mixing different property profiles, contaminations, and material degradation. Solid contaminations, e.g. labels, sand, or other polymer types, have a significant impact on mechanical properties and aesthetics [6,7]. Additionally, volatile contaminations lead to odor or can even be a health hazard, which must be eliminated according to regulations [8,9]. Thus, this study aimed to evaluate how solid and volatile contaminations in PP waste are changing throughout the different stages of a mechanical recycling process. The contaminations were analyzed via optical and gas chromatographic methods to obtain data on the achievable qualities of recycled PP (rPP) with state-of-the-art technologies and to identify potential avenues for further process improvements.

Material and Methods

Post-consumer PP waste from mixed collection of Dutch household waste was separated, sorted in several loops, pre-treated, extruded, and used to produce two types of cups. The detailed recycling process is depicted in Figure 1. While the injection molded cups contained 100% recyclate, the thermoformed cups had a multilayer structure with a middle layer of 60% recyclate content and two top layers of virgin material. Excluding the application stage, all the used technologies were state-of-the-art.

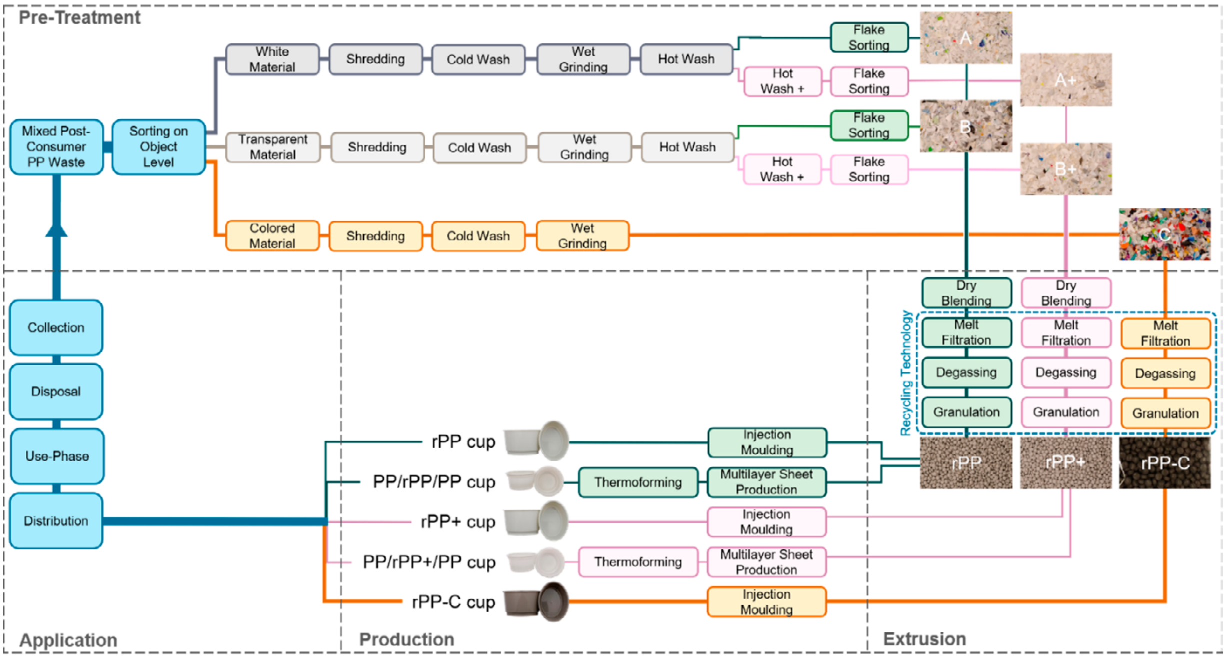

Figure 1. Scheme of the mechanical recycling process. The photographs show the analyzed samples.

For the analysis of solid contaminations in the flakes and granules, a Modular Film Analyzer equipped with a Film Surface Analyzer FSA100 and a Measuring Extruder ME30 (OCS) (OCS Optical Control Systems GmbH, Germany) were used. As the flakes from the pre-treatment stage still contained some PET flakes, they were separated via density in a water bath and dried in a drying and heating chamber at 50°C for 3 h (BINDER GmbH, Germany) before the film extrusion at a processing temperature of 200°C. The solid contaminations were categorized according to size x into those with $x \leq 100$ µm, $100 < x \leq 300$, $300 < x \leq 500$ µm, and $x > 500$ µm. To enable counting of the solid contaminations, the film thickness was reduced to a minimum of about 100 µm, the grey value was set to 219 and the threshold to 15%. An area of 5 m² was analyzed for each sample.

The volatile organic compounds (VOC) were analyzed via a gas chromatograph including a flame ionization detector Clarus 690, which was equipped with a mass spectrometer Clarus SQ 8 T and an analytical thermal desorption unit TurboMatrix 650 (ATD-GC/FID-MS) (PerkinElmer Inc., USA). For separation, an HP Ultra 2 Column with 50 m x 0.32 mm size and 0.52 µm stationary phase (Agilent, USA) was installed. The system was calibrated with an external one-point calibration of a 0.5 µg/µL Toluene (Merck, Germany) solution in Methanol (Merck, Germany). Of this solution, 4 µL were injected into a sample tube filled with the adsorbent TenaxTA (PerkinElmer Inc., USA) under a nitrogen flow of 100 mL/min for 6 min. Pieces of 5 x 40 mm were cut from 250 µm thick film sheets previously produced on the OCS or from the side walls of the cups. A blank was conducted before each sample triplicate. The parameters for the ATD-GC/FID-MS are listed in Table 1.

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Table 1. Parameters of ATD-GC/FID-MS.

<table>
<tr><th colspan="2">ATD Parameters</th><th colspan="2">GC/FID-MS Parameters</th></tr>
<tr><td>Mode</td><td>2 Stage Desorption</td><td rowspan="3">Temperature Program:</td><td rowspan="3">60°C, 13min,
6°C/min to 215°C,
25°C/min to 280°C,
12 min</td></tr>
<tr><td>Column Flow [kPa]</td><td>130</td></tr>
<tr><td>Desorption Flow [mL/min]</td><td>40</td></tr>
<tr><td>Inlet Split Flow [mL/min]</td><td>44</td><td>FID Temperature [°C]</td><td>300</td></tr>
<tr><td>Outlet Split Flow [mL/min]</td><td>19</td><td>Hydrogen Flow [mL/min]</td><td>30</td></tr>
<tr><td>Transfer Line Temperature [°C]</td><td>290</td><td>Synthetic Air Flow [mL/min]</td><td>450</td></tr>
<tr><td>Trap Temperature [°C]</td><td>-30 to 280</td><td rowspan="2">Transfer Line Temperature to MSD [°C]</td><td rowspan="2">280</td></tr>
<tr><td>Heating Rate [°C/s]</td><td>99</td></tr>
<tr><td>Trap Hold [min]</td><td>20</td><td>Scan Mode Range [amu]</td><td>29-450</td></tr>
<tr><td>Valve Temperature [°C]</td><td>280</td><td>MS Solvent Delay [min]</td><td>4.5</td></tr>
</table>

Results and Discussion

After the pre-treatment, extrusion, and production stages, we took samples and evaluated them for optical changes, solid contaminations, and volatile contaminations.

Optical Evaluation Results

The separation of white (A) and colored material (C) was good. In contrast, the material intended to be transparent (B) had a lot of white and even some colored mis-sorts. Adding a deinking step (hot wash +) for materials A (A+) and B (B+) visibly removed the color of the residual labels. In the extrusion stage, the white and transparent materials were again blended due to the required amount of material for the recycling technology. This resulted in light grey granules and just slightly brighter granules for the hot washed rPP and for the deinked material (rPP+), respectively. Nevertheless, the color of both was acceptable for a potential new coloration compared to the dark granules resulting from material C (rPP-C).

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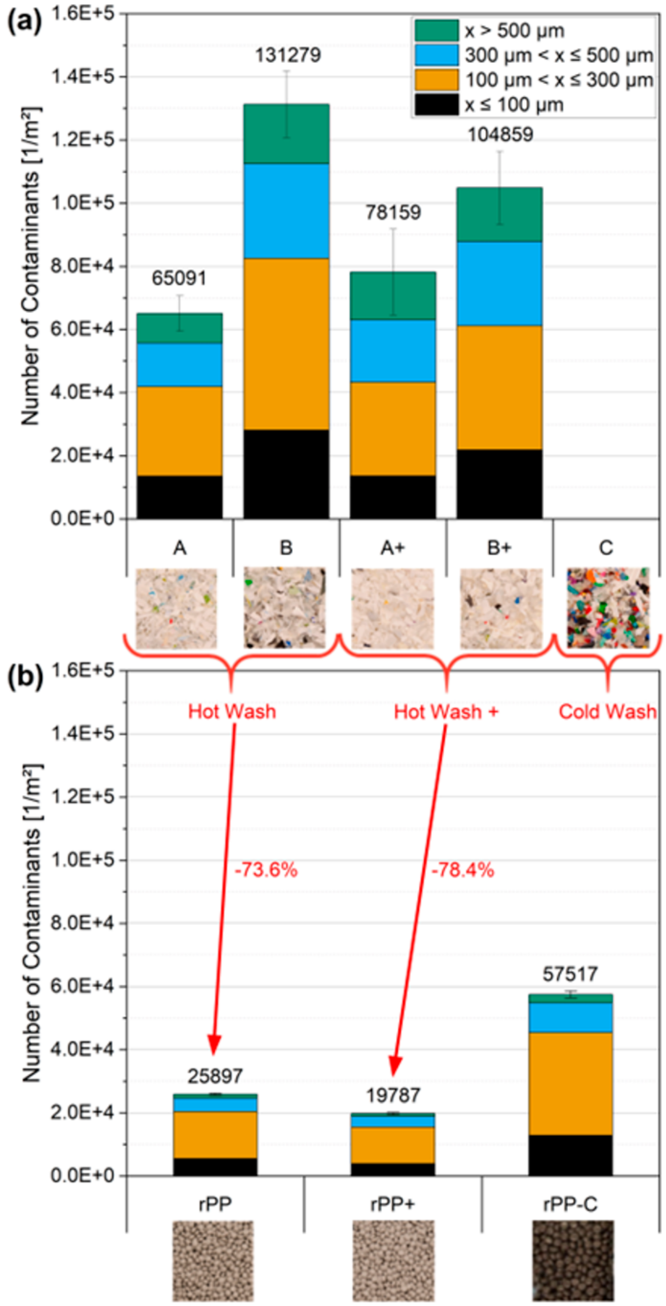

Figure 2. Numbers of solid contaminations that are categorized by size for (a) the flakes after the pre-treatment and (b) the granules after the extrusion.

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Solid Contaminations

Figure 2 displays various size categories of detected solid contaminations, with the category of $100 < x \leq 300$ µm exhibiting the highest values across the samples from the pre-treatment stage (as shown in Figure 2[a]) and from the extrusion stage (as shown in Figure 2[b]). Due to the high contamination level of the colored material with a high number of contaminants larger than 500 µm, we were not able to produce films thin enough for light transmission to be analyzed by the OCS. Solid contaminations were reduced by 74 to 78% for material PP and rPP via the laser filter with 90/110 µm in the extrusion stage. We assume similar results for material rPP-C since the same extrusion parameters were used as for the other two materials. Thus, rPP-C has the highest amount of solid contaminations, which is a result of the less extensive washing at the pre-treatment stage. The granules rPP+ showed the lowest amount of solid contaminations, which reflects the additional effect of removing residual inks and labels by multiple washing steps.

Volatile Contaminations

The VOC emitted from the solid samples at elevated temperatures should represent the volatile contaminations trapped in the material. The results are depicted in Figure 3. In the pre-treatment stage, the VOC values were similarly high throughout almost every material except for material C, which was unexpectedly lower (as shown in Figure 3[a]). This may indicate that, compared to the cold washing procedure, surface contaminations are reduced in the hot washing procedures, while volatile degradation products increase with temperature and washing agent. In contrast, the VOC values of material rPP-C are higher than for the other materials in the extrusion stage (as shown in Figure 3[b]). Due to the residual surface contaminations of the cold washed material C, the generation of degradation products during the extrusion may be triggered, and in addition to the residual contaminations result in a high VOC value for rPP-C. Nevertheless, the VOC values of all three rPP samples were still higher than a commercial virgin PP grade for injection molding. In the end, when considering the product level, there was a decrease in VOC throughout the entire mechanical recycling process, but with similar results for the different cups after the production stage (as shown in Figure 3[c]).

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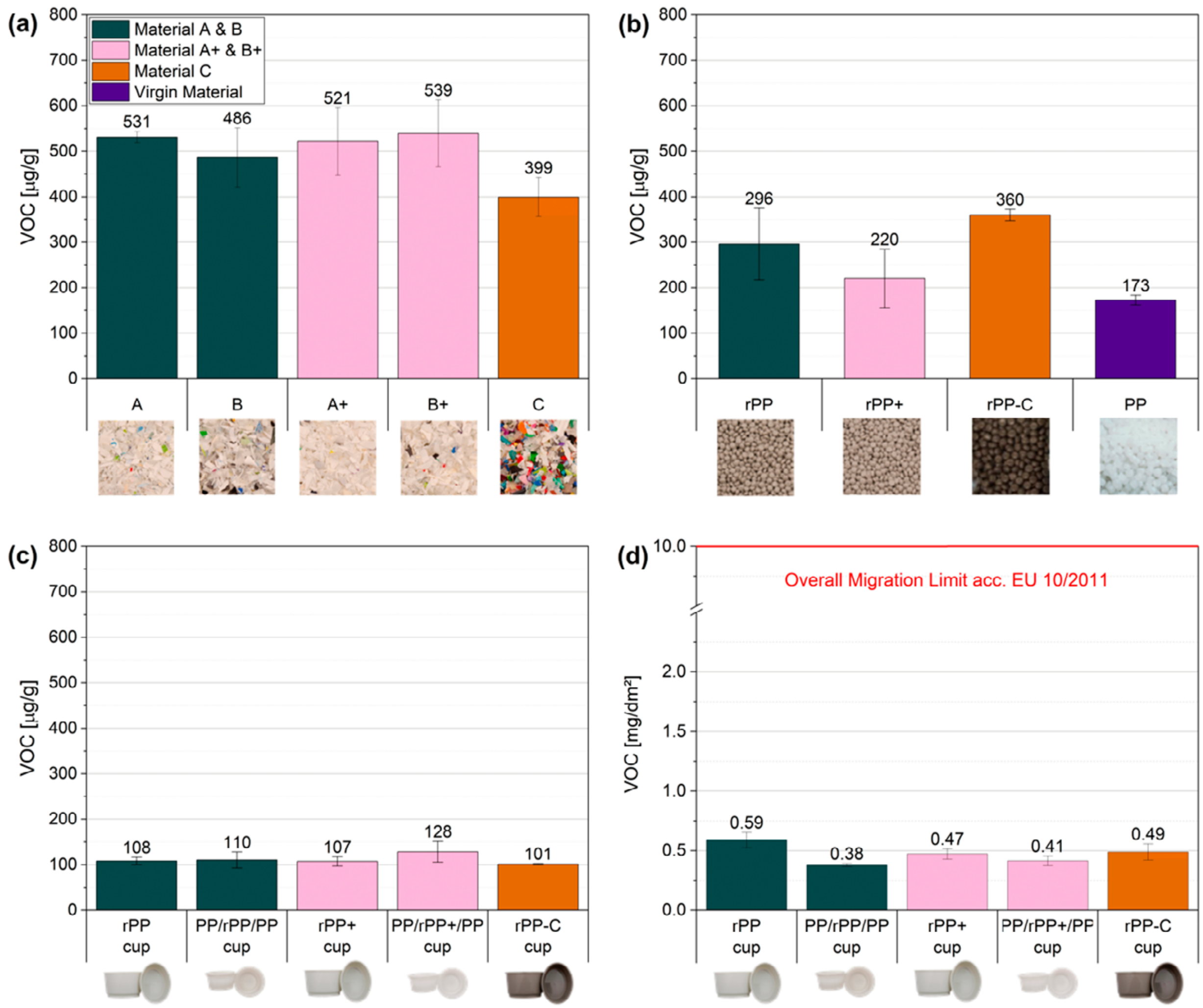

Figure 3. VOC values of (a) the flakes after the pre-treatment, (b) granules after the extrusion, (c) cups after production and (d) overall migration limits set out by the European Commission.

Since cups are usually used as food contact material, we also calculated the VOC values correlated to the contact surface and compared the results with the recent overall migration limits (OML) set out by the European Commission (as shown in Figure 3[d]) [8]. This OML specifies the allowed level of substances that can migrate from the packaging into the food without posing a health risk for the consumer. The resulting values, which were significantly lower than this OML, showed already high purity and high quality of the PP recyclate. Nevertheless, further investigation should be conducted to provide a full picture of the composition of the volatile contaminations.

Conclusion

This study provides an overview of the changes in solid and volatile contaminations throughout the entire mechanical recycling process. The pre-treatment aiming for white material leads to high-quality PP regarding contamination and can be easily colored. In contrast, combining state-of-the-art sorting technologies did not lead to the intended transparent post-consumer recycled PP. Furthermore, choosing the right filter size in the extrusion stage can reduce solid contaminations by around 76%. The OCS can be a helpful method to determine the required filter size. Regarding volatile contaminations, in the end the VOC values of the products did not seem to be affected by the different washing steps, but mainly by the extrusion and processing steps. When removing labels, deinking is efficient but has no significant effect on the VOC values of the end product and only leads to a slight reduction in solid contaminations. Using all the information gathered, there are possibilities to make the recycling processes more efficient by e.g., evaluating the required washing steps for the intended product. In order to do so, we require further information regarding the composition of the VOC. It would be also advantageous to analyze the cold washed references of the white and transparent materials to confirm the decontamination efficiency of the cold washing step. Ultimately, mechanical characterization of the samples should be conducted to obtain a full picture of all the effects on the post-consumer recycled PP throughout the whole mechanical recycling process with state-of-the-art technologies.

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