Investigation of Gas Release from Recycled Plastic Shopping Bags during Melting at Low Temperatures

Friederike Susette Eberhard, Leslie Bowtell, Brian Lenske, and Md Mainul Islam

1Academic Affairs Administration, University of Southern Queensland, West Street, Toowoomba, QLD 4350, Australia
2School of Engineering, University of Southern Queensland, West Street, Toowoomba, QLD 4350, Australia

Correspondence should be addressed to Md Mainul Islam; mainul.islam@usq.edu.au

Received 27 December 2022; Revised 14 March 2023; Accepted 18 April 2023; Published 10 May 2023

Recycling plastic is an excellent way to reduce the environmental impact of its production and use. In a circular economy, recycling of recycled plastic is necessary. Most plastic bags are made of thermoplastic, like high-density polyethylene (HDPE) with a melting point of 130°C, and low-density polyethylene (LDPE). In contrast, recycled plastic bags are made up of many different unknown substances. In this study, the melting of used plastic bags containing 80% unknown recycled material was investigated. FTIR analysis showed that the bags consisted mainly of HDPE. The bags were melted at 160°C, 200°C, and 250°C for 30 min. GC-FID and HP-SPME GCMS analyses showed that the bags released flammable gases (methane, ethylene, and alkane/alkene hydrocarbons) but little acetylene. Aromatic and aliphatic hydrocarbons eluded from the bags at 10% of the gas volume at 250°C. Long-chain alkanes, mostly hexadecane, were the dominant compound, amounting to 28% at 160°C and increasing to 43% at 250°C. On the other hand, alkenes decreased with a rising temperature (23% at 160°C to 3% at 250°C), as they were transformed into alkanes. Methylated compounds, for example, methylated alkanes at 10%, were present at all temperatures. Methane and methylated compounds are released from plastic and contamination of the bags with organic matter. The bags released small amounts of toxic phthalates. The results show that melting recycled plastic bags for remoulding is promising if safety precautions that ensure sufficient ventilation are utilised.

1. Introduction

Plastic waste is an environmental problem worldwide, and the recycling of this waste is problematic as toxic and flammable gases are released into the atmosphere when these materials are heated. Climate change and population growth make it necessary to find sustainable and environmentally friendly methods of recycling and to find new applications for used plastic [1]. Undas et al. [2] found that 368 Mt of plastic was produced globally. According to Hopewell et al. [3], 4% of gas and oil produced worldwide is used to make plastic products discarded within a short period, and shopping bags form a large part of this waste. In 2019, worldwide plastic production was 460 t [4]. The OECD reports that only 9% of plastic worldwide is recycled [5], and in Europe, 9.4 MT was recycled in 2018 [6]. Achillias et al. [7] state that 17% of the total plastic consumed in Western Europe is LDPE, whereas 11% is HDPE and 16% polypropylene (PP). LDPE has a lower density (0.917–0.930 g/cm³), is softer, and has more branching, whereas HDPE (density 0.944–0.965 g/cm³) is harder and has better heat resistance. Most virgin plastic bags are made from LDPE. Seventy-eight percent of all consumed plastics in Western Europe are thermoplastics. HDPE is a thermoplastic that can be melted and moulded many times. HDPE melting often involves high temperature pyrolysis in an oxygen-deprived atmosphere in reactors and the use of catalysts, which produce middle distillates like gasoline, kerosene, and diesel [8]. According to Achillias et al. [7], the total hydrocarbon fraction of waste HDPE after pyrolysis at 450°C was 3.28% weight on polymers, as shown in Table 1. The highest compound was nC₄ (butane), followed by isopentane (iC₅),
then propylene, and the aromatic C₆ hydrocarbon fraction. Pyrolysis, however, is not suitable if the material is destined for remoulding.

Currently, only a small percentage of the used plastic is recycled and reused, for example, as recycled plastic bags. In the European Union, companies that produce plastic shopping bags must now include at least 70% polyethylene waste [9]. In this study, low-temperature melting to remould them to other useable products was investigated. Recycled plastic poses additional challenges for recycling, as the components of these recycled items are a mix of different, often contaminated, substances, which are often also additionally soiled during their use. It was investigated whether melting at a lower temperature reduces the overall risk by reducing the release of toxic, flammable, and greenhouse gases formed during the process. Aguado et al. [10] found that heating plastic at low temperatures results in three fractions: high calorific value gas, condensable hydrocarbons, and waxes. In other studies of lower temperature fractions: high calorific value gas, condensable hydrocarbons, and waxes. In other studies of lower temperature fractions.

### Table 1: Composition of gases from HDPE polymers during catalytic pyrolysis at 450°C (weight % on polymers) [7].

<table>
<thead>
<tr>
<th>Gases</th>
<th>Wt.% on polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen H₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Carbon dioxide CO₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Carbon monoxide CO</td>
<td>0.00</td>
</tr>
<tr>
<td>Methane CH₄</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethane C₂H₆</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethylene C₂H₄</td>
<td>0.02</td>
</tr>
<tr>
<td>Propane C₃H₈</td>
<td>0.05</td>
</tr>
<tr>
<td>Propylene C₃H₆</td>
<td>0.44</td>
</tr>
<tr>
<td>nC₄</td>
<td>1.25</td>
</tr>
<tr>
<td>nC₅</td>
<td>0.37</td>
</tr>
<tr>
<td>iC₅</td>
<td>0.69</td>
</tr>
<tr>
<td>C₆</td>
<td>0.44</td>
</tr>
<tr>
<td>Total</td>
<td>3.28</td>
</tr>
</tbody>
</table>

3. Results

FTIR analysis showed that the sample consisted mainly of HDPE (81% confidence). Other polyethylene compounds were also present, like LDPE, ethylene/propylene co-polymer, calcium carbonate dyes, magnesium stearate, waxes, and ionomers, which are used to cross-link plastics to make them sturdier, for example, in plastic bottles. Figure 2 shows the peaks of the functional groups present in plastic. There also was an additional peak at 872 cm⁻¹, which indicates a group of carbonate (calcium carbonate, often used as an additive to HDPE to provide colour). The different inks showed small differences in transmission (not shown).

Table 2 shows the peaks of the FTIR spectrum of the white area of the shopping bags. The wave numbers 2916.37 cm⁻¹ and 2846.93 cm⁻¹ corresponded to the HDPE library entry, but the peaks at 1458 cm⁻¹ (CH₂ bending), 1458 cm⁻¹, and 1427 cm⁻¹ (CH₂ bending) had lower transmittance, indicating that these functional groups increased compared to the library HDPE spectrum. They also merged, whereas the HDPE peaks were separated.

The quantitative gas analysis for methane, ethylene, and acetylene was conducted against calibration curves prepared from standards; the results for the headspace analysis of the gas are shown in Figure 3.
The highest amount of quantified gas was methane, although, at 160°C, there was a bit more ethylene. The methane emission from the bags at 160°C was 0.0295 mg/g; at 250°C degrees, it was rising to 0.334 mg/g; the ethylene concentration rose from 0.035 mg/g to 0.082 mg/g. In all samples, there was little acetylene (<0.004 mg/g sample).

The qualitative GCMS scan revealed a variety of volatile compounds. These were identified with peak integration and compound searching against the NIST14 library SI > 70. Relative abundance of the gases in the scan in percent was used to report the results. Relative abundance is a common way to report results from a qualitative GCMS scan and is only applicable for the given scan under the set conditions. Many gases were alkenes, alkanes, and fatty acids. This analysis identified 146 peaks across three heating temperatures. The samples contained four phthalates. Figure 4 shows the 10 most abundant gases in the scans at their respective temperature. The most abundant gas at all heating temperatures was hexadecane. At all heating temperatures, eicosane, 1-nonadecene, nonanal, and isopropyl myristate occurred. Other than that, there was little similarity of gases among the 30 most abundant ones across all heating temperatures.

Table 2: FTIR-ATR peaks taken from the white area of the shopping bag.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Intensity</th>
<th>Corr. Intensity</th>
<th>Base (H)</th>
<th>Base (L)</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>717.52</td>
<td>70.87</td>
<td>21.28</td>
<td>802.39</td>
<td>555.5</td>
</tr>
<tr>
<td>2</td>
<td>871.82</td>
<td>76.49</td>
<td>18.81</td>
<td>902.69</td>
<td>817.82</td>
</tr>
<tr>
<td>3</td>
<td>1427.32</td>
<td>63.48</td>
<td>3.3</td>
<td>1450.47</td>
<td>1095.57</td>
</tr>
<tr>
<td>4</td>
<td>1458.18</td>
<td>64.04</td>
<td>2.06</td>
<td>1666.5</td>
<td>1450.47</td>
</tr>
<tr>
<td>5</td>
<td>2846.93</td>
<td>58.54</td>
<td>26.57</td>
<td>2870.08</td>
<td>2538.32</td>
</tr>
<tr>
<td>6</td>
<td>2916.37</td>
<td>54.52</td>
<td>33.1</td>
<td>3078.39</td>
<td>2870.08</td>
</tr>
</tbody>
</table>

Figure 1: Shopping bag plastic samples subjected to heat treatment at (a) 160°C, (b) 200°C, and (c) 250°C.

Figure 2: FTIR scan transmission results of the original white bag area (a) compared to the HDPE library entry (b). The arrow denotes the calcium carbonate dye used.
compounds was methylated alkanes, which amounted to 10% of the gas volume. Additionally, there were methylated alkenes and esters. In Figure 6, the compound groups which were methylated are shown separately.

Long-chain fatty alcohols amounted to 5% of the gas, decreasing with rising temperatures. The percentage of acids was 5%. They only occurred at 160°C.

The melted plastic bags released different phthalate compounds. Table 3 shows the phthalates in % discovered at different temperatures.

At 160°C, dibutyl phthalate $C_{16}H_{22}O_4$, dibutyl isophthalate, and a phthalic acid ester (phthalic acid, bis (2-ethylhexyl) ester) (DEHP) were found. The most abundant phthalate was dibutyl phthalate (DBP) at 3%. At 200°C, dibutyl phthalate was not found, whereas dibutyl isophthalate and another ester of phthalic acid (DINP) eluded; at 250°C, only DBP and DEHP were found.

Aldehydes and organic compounds created by the oxidation of alcohol were well below 5% and decreased with rising temperatures. Table 4 shows the aldehydes produced. Acetaldehyde was not detected. The detailed results from all gas analyses are provided in Attachments 1 and 2.

4. Discussion

Finding ways to reuse plastic waste safely has a high priority. One of the main contaminants is plastic bags, which are found in oceans [12] and landfills. They are a fire hazard and release toxins into the environment [13], and their degradation contributes to greenhouse gases [14, 15]. In 2016, the U.S. Environmental Protection Agency joined a retail industry campaign which intended to double plastic film recycling to 2 billion pounds by 2020 [16]. Recycled shopping bags are a step in the right direction, but they also need to be recycled when they reach the end of their lifetime. Recycled plastic bags are made up of many different materials and may contain contaminations from unknown sources and therefore pose additional challenges, as the components of these recycled items are a mix of different substances. Heating them for remoulding invariably releases greenhouse gases but less so at lower temperatures. Used plastic may be soiled by organic matter from their use, thereby creating a biohazard. The microbes that grow there, as well as the organic matter, add to the load of greenhouse gases when these bags are heated; however, heating them may also sterilise the material, making it safe for future use, for example, for sealing grain to minimise losses after harvesting [17], for use as hospital gift bags for new mothers [18], or as Tedlar bags for gas storage [19]. Treatments like colouring and plasticisers add another level of uncertainty to the process. In this study, it was investigated whether melting recycled plastic at a low temperature reduces the overall risk of recycling by reducing the release of toxic, flammable, and greenhouse gases formed during the process. We analysed some of the gases released from plastic shopping bags made from 80% recycled material to determine if the process was safe when the bags were melted at 160°–250°C for remoulding purposes. This temperature range falls into the endothermal stage of degradation [11].

FTIR analysis (Figure 2, Table 2) showed that the bags consisted primarily of HDPE and were coloured with ink which contained calcium carbonate. FTIR is a well-established method for the identification of polymers using infrared absorption bands which show functional chemical groups in the material. However, structural isomeric polymers like HDPE and LDPE are often hard to
distinguish. Chércoles et al. [20] and Nishikida and Coates [21] showed that compared to HDPE, LDPE had an additional peak at 1377 cm$^{-1}$, which represents CH$_3$ bending deformation. This peak was not present in our samples. While most shopping bags are made from LDPE, the recycled shopping bags in this study consisted primarily of HDPE, likely because plastic chips from many different hard plastic sources were used to produce these bags.

The qualitative GCMS scan (Figures 4–6) and (Tables 3 and 4) identified 146 peaks across three heating temperatures. This shows that the bags consisted of many different compounds. The ten most abundant gases are shown in Figure 4. The main gas at all three temperatures was hexadecane (C$_{16}$H$_{34}$), followed by eicosane (C$_{20}$H$_{42}$). When compared to high temperature pyrolysis, longer chained hydrocarbons are much more prevalent. For example, Achilias et al. [7] found that at 450°C, the most common hydrocarbon was nC$_4$ (butane), followed by isopentane (iC$_5$). One explanation for why there are different compounds across the different temperatures could be that at different temperatures, different chemical reactions took place between components. This could be due to the breaking up or formation of bonds, saturation, or methylation. The results showed, for example, that with rising temperatures, unsaturated hydrocarbons (alkenes) were transformed into saturated compounds (alkanes).

The analysis also showed that the plastic bags released methylated carbon compounds, mainly alkanes, alkenes, and esters, as can be seen in Figure 6. In the temperature range analysed, higher methane concentrations did not lead to higher methylation in the gases. Methylation can occur through methane exposure released from HDPE or from methane stemming from organic contaminants. Moulay [22] states that C-methylation with methane is an oxidative process. It would therefore not occur during pyrolysis in oxygen-deprived conditions; however, in this study, melting occurred in ambient air conditions. Microbes may also be present in the bags, producing methane gas from

![Figure 4: The ten most abundant gases in the plastic bags in % at different temperatures.](image-url)
contaminants. According to Ghosh et al. [23], microorganisms can help break down the used plastic; however, this was not the aim of this project. Yamashita et al. [24] state that aldehydes are one of the main flammable components eluding when plastic is melted, but in this study, their concentration was less than 5% of the total gas volume. Seven aldehydes eluded from the heated plastic bags, but acetaldehyde was not detected in the qualitative GCMS scan. According to Ullmann’s Encyclopaedia of Industrial Chemistry, aldehydes are valuable compounds. For example, nonanal, which was detected in the scan, is an essential marketable chemical used as a flavour in food items and is also used in perfumes as it has a citrus-like scent. Food flavours, resins, and rubber accelerators are made from pentanal. It has a nutty and fruity smell of fermented bread [25]. As the quantities of these compounds were very small, commercialisation would be difficult. Acetaldehyde, which was only present in small quantities in the GCMS scan, can easily be reduced to ethane, a gas that could
have been present in larger quantities but was not quantitatively analysed in this scan. Ethane gas is an unsaturated hydrocarbon, the smallest alkene \(\text{C}_2\text{H}_4\), and highly flammable and explosive [26]. Phthalates are commonly used as plasticisers [27] and not present in pure HDPE. Dibutyl phthalate (DBP) was the most abundant phthalate eluded from the bags, eluding at 3% at 160°C and increasing to 3.5% at 200°C. At 250°C, it was not detected (Table 3). Like most phthalates, it has adverse health effects [28]. Surprisingly, dibutyl isophthalate (DBP) and DEHP eluded at a low heating temperature of 160°C, although the volatilisation temperature of phthalates is thought to be higher. This suggests that the actual temperature in the glass vial might have been higher. The elution of different phthalate compounds at different temperatures from the recycled plastic bags leads to the conclusion that the composition of these plastic bags was not homogeneous, as each part of the bags could have contained different recycled plastic pieces or virgin plastic. Other compounds were also present, including calcium carbonate ink, which was detected in the FTIR scan and may also have contained phthalates. This result highlights some of the additional challenges posed by the recycling of recycled plastic.

For GC-FID quantitative analysis (Figure 3), the same sample preparation as for GCMS was used. The flammable gases quantified with a standard were acetylene, ethylene, and methane. These gases represent only a small percentage of the total gas released, as the GCMS results, which were not quantified, indicated that there were many other gases present. The gas release from the quantified volatiles was only 0.3 g/kg polymer or 0.03%. The most abundant quantified gas was methane. Methane is considered an asphyxiant at extremely high concentrations, as per Rim-Rukeh [29]. Methane and ethylene are potent greenhouse gases [14, 15], and it is reported that methane emissions are responsible for 25% of the current temperature rises worldwide [30]. Finding ways to reduce its high priority. Royer et al. (2017) [31] discovered that polyethylene produced the greenhouse gases such as methane and ethylene, when exposed to the sun, with the release increasing over time. The methane gas produced could also stem from contamination of the initially recycled plastic pieces or from contamination of the shopping bags during use, as they were not cleaned before analysis. In our experiment, overall methane concentrations were very low. The methane emission from the bags at 160°C was 0.0295 mg/g. At 250°C degrees, it was rising to 0.334 mg/g, eleven times higher; the ethylene concentration rose from 0.35 mg/g to 0.082 mg/g, around twice the initial amount, and acetylene remained at a very low value of 0.004 mg/g (Figure 3). If 1 kg of shopping bags was melted in a room, it would only lead to an air methane concentration of 0.02 ppm. When this methane release is compared to the methane released through pyrolysis at 450°C [7], which was 0.01% weight on polymers, our finding was only lower for the 160°C temperature (0.003%). This result needs further investigation. The American CDC’s National Institute for Occupational Safety and Health (NIOSH) [32] states that the maximum recommended safe methane concentration for workers over 8 hours is 1,000 ppm (0.1%). Melting, however, should only be carried out using safety precautions, for example, an exhaust fan or a fume hood.

4.1. Summary. The recycled bags consisted mainly of HDPE but also some LDPE, ethylene/propylene copolymer, calcium carbonate dyes, magnesium stearate, waxes, and ionomers. During heating at low temperatures, the gas fraction in the headspace consisted of a mix of methane, ethylene, acetylene, and many other, primarily long-chain aliphatic and aromatic hydrocarbons, esters and methylated compounds, aldehydes, and phthalates, as well as many other potentially hazardous and flammable gases. Reuse of nonrenewable fossil fuels is essential. It leads to reduced energy consumption, less landfill, and reduced CO₂ and other greenhouse gas emissions. Overall, melting of recycled plastic at lower temperatures and ambient oxygen levels can help further reduce the environmental impact of plastic production, as it leads to additional useable products, reduces gas emission, and is more energy efficient than high temperature pyrolysis. Although it would be better to first recycle 91% plastic that is not currently recycled, reuse of recycled plastic can help reduce the environmental impact of plastic production even further by supporting a circular economy.

5. Conclusions

(1) Alkanes were the largest fraction of all compounds. Compared to pyrolysis at higher temperatures, more long-chain hydrocarbons were released \(\text{C}_n\). Alkane hexadecane, \text{C}_{16}\text{H}_{34}, a saturated aliphatic hydrocarbon, was the most abundant compound found in the GCMS scan, amounting to 28% at 160°C and increasing to 43% at 250°C. The lower the temperature, the lower the emission of greenhouse gases, which are often short-chain alkanes like methane. For example, the release of shortest alkane methane at 160°C was 11 times lower than at 250°C.

(2) Alkenes decreased with rising temperatures (23% at 160°C to 3% at 250°C), as they were transformed into alkanes.

(3) Methylated compounds, for example, methylated alkanes at 10%, were present at all temperatures. Methane and methylated compounds are released from plastic itself and contamination of the bags with organic matter. Heating the bags may remove some of the biohazard posed by organic matter and microbes, making the new articles safe to reuse.

(4) Potentially useful substances like aldehydes were detected in small quantities.

(5) Potentially toxic substances like phthalates and aromatic hydrocarbons like phenol and benzene were released in small quantities, but at significant temperature, the effect in the studied range could not be established.
(6) Safety measures during melting should include good ventilation and exhaust fans, as well as fire-fighting equipment on hand.

Abbreviations

B: Plastic bag
HDPE: High-density polyethylene
LDPE: Low-density polyethylene
PP: Polypropylene
HP: Headspace solid-phase microextraction
SPME: Headspace solid-phase microextraction
GCMS: Gas chromatography-mass spectrometry
GC-FID: Gas chromatography-flame ionisation detector
DBP: Dibutyl phthalate
DEHP: Phthalic acid, bis(2-ethylhexyl) ester
DINP: Phthalic acid bis(7-methyloctyl ester)
DSC: Differential scanning calorimetry
OECD: Organisation for Economic Co-operation and Development
TGA: Thermogravimetric analysis.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank Dr Nana Satake from the School of Agriculture and Food Sciences Analytical Services Unit, the University of Southern Queensland for funding this study.

References


