ABSTRACT

Hazardous compounds emitted during the plastic melting process were analyzed to indicate potential air pollution issues associated with recycle plants for waste plastics. These hazardous compounds might be not only from polymer degradation but also from additives and print ink. To confirm what are emitted from them, melting experiments were conducted (150, 200 and 250°C, in air or N2) and volatile organic compounds (VOCs) emitted from samples were trapped by Tenax/Carboxen adsorption tubes and analyzed by TD-GC/MS. In the present study, virgin polymers such as low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and reproduced plastic were tested. As a result, higher temperature caused more emission of VOCs. Moreover, less VOCs and less oxygenated organic compounds which were said to be hazardous to human and the cause of bad odor were emitted in N2 atmosphere than in air. Based on these results, lower temperature and lower oxygen level are preferable to reduce hazardous compounds during the plastic melting process of mechanical recycling.

KEYWORDS
Waste plastics, Recycle, Melting, Emission, Hazardous compounds
oxidative products such as aldehydes and/or ketones are formed. To date, many studies were conducted to investigate emissions of volatile compounds from the plastics during the melting process\textsuperscript{2-6}. Almost all reports indicated that the compounds from the process are products by polymer degradation. When waste plastics were melted, other compounds originated from various factors such as additives besides the polymer degradation would be emitted.

In this study, virgin plastic pellets including low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS) and waste plastic pellets were investigated. Besides the polymer degradation, the effects of additives and other materials in these plastics were also investigated. The aims of this study are to clarify the species and the amount of compounds emitted in air or N\textsubscript{2} atmosphere and at several temperature during the melting process of plastic mechanical recycling and to suggest using an anoxic atmosphere to reduce emission of these compounds.

**EXPERIMENTAL**

**Sample**

Three kinds of commercially available virgin plastic pellets were used: LDPE (NOVATEC Injection grade LD802, Japan Polyethylene Corporation), PP (NOVATEC Injection grade MA3, Japan Polypropylene Corporation) and PS (GPSS HF77, PS Japan). These are three major dumped polymers in Japan\textsuperscript{7}.

The waste plastic pellets obtained from the containers and packaging facility (Kashiwa Ecoplaza) were also used.

**Experimental apparatus**

The experimental apparatus is shown in Figure 1. The sample pellets were placed in a tubular furnace (Ceramic Tubular Furnace ARF Series, Asahi Rika Corporation) with a temperature controller (Digital Temperature Controller AMF-N, Asahi Rika Corporation) and heated at the controlled temperature in air or N\textsubscript{2}. The gas flow was 300 mL/min. At the downstream of the furnace, the line was branched into 2 directions, and an ATD tube (referred to hereinafter) was connected to one of the following lines. VOCs contained in the out gas were collected via the tube pumped at 100 mL/min (Pocket Pump 210-1002, SKC) for 10 min. Prior to sampling, 2-min preheating was conducted.

**Adsorbents**

ATD tubes (PerkinElmer) filled by 100 mg of Tenax TA (Tenax TA 60/80 mesh, Analytical Columns) and 70 mg of Carboxen 1000 (Carboxen 1000 60/80 mesh, SPELCO) were used for sampling. The tubes were preheated at 320°C for 3 hr in N\textsubscript{2} flow.
Experimental condition
In this study, we aimed to qualitatively and quantitatively clarify the volatile compounds from the polymer. To investigate the effect of temperature on emission of volatile compounds, LDPE was heated at the temperature of 150, 200 and 250 °C. This temperature range was set on the assumption of operational conditions. The species of volatile compounds emitted from LDPE, PP, PS and waste plastics in both air and N₂ atmosphere at the temperature of 200 °C were characterized. 0.3 g of plastic pellets were tested. The corresponding number of virgin plastic pellets was 12, 14 and 14 for LDPE, PP and PS respectively, whereas heterogeneous waste plastic pellets were tested around 0.3 grams. Triplicate measurements were performed for each plastic and experimental condition.

Analytical method
The ATD tubes after sampling were analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). An analytical condition is shown in Table 1. The substances trapped by adsorbents are desorbed by TD (TurboMatrix650, PerkinElmer) and then analyzed by GC (6890Series GC System, Agilent) and MS (5973 Network Mass Selective Detector, Agilent).

Table 1 Analytical condition of TD-GC/MS

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption instrument</td>
<td></td>
</tr>
<tr>
<td>Primary desorption</td>
<td>300 °C, 15 min</td>
</tr>
<tr>
<td>Secondary desorption</td>
<td>5 °C - (40 °C /min) - 300 °C, 45 min</td>
</tr>
<tr>
<td>GC/MS</td>
<td></td>
</tr>
<tr>
<td>Column</td>
<td>HP-1 Methyl Siloxane Capillary, 60.0 m×250 μm×1.00 μm</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He (1 mL/min)</td>
</tr>
<tr>
<td>Column temperature</td>
<td>40 °C, 4 min - (7 °C /min) - 280 °C, 10 min</td>
</tr>
<tr>
<td>Detection mode</td>
<td>Scan</td>
</tr>
</tbody>
</table>

Data processing
All the peaks in chromatogram were converted in toluene equivalent as TVOCs. As to a qualitative and quantitative analysis the following data processing procedure was adopted: First, the detected compounds having matching ratio larger than 70 % via searching through a library (Enhanced Chemstation G1701 CA Version C, Agilent) were selected. Next, these compounds were classified, calculated according to the functional group and quantitated. The means and standard deviations (SD) of the amounts of all compounds per 1 g sample were shown as toluene equivalent in the figures.

RESULTS AND DISCUSSION
Effects of temperature
Figure 2 shows the amounts of TVOC emitted from LDPE in air at 150, 200 and 250 °C. Higher temperature caused higher emission of TVOC. Figure 3 shows the amounts of VOCs classified by functional groups. This result indicates that at the higher temperature the degradation of polymer chain proceeds more rapidly and higher amount of oxidative compounds are generated. Then, higher amount of volatile compounds will be made and outgas contains higher amount of TVOC. Of course, if a compound in the melted LDPE is exposed higher temperature, more amounts should be vaporized.

At the higher temperatures, larger quantities of compounds with each functional group were emitted while the emission of "Others" showed no significant differences. A large part of "Others" was found to
be composed by butylated hydroxytoluene (BHT), a kind of antioxidants. It suggests that BHT will diffuse independently of temperature in this range. Because melting point of BHT is 69-71 °C and boiling point is 265 °C, BHT in LDPE polymer would also evaporated without reaction with other compounds.

**Effects of atmosphere**

The amounts of TVOC from PP and PS had no significant differences between the atmospheres (data not shown). A large part of these VOCs emitted from these plastics are likely originated from the degradation of the polymers. By comparison of VOCs classified by functional groups, however, larger amounts of oxygenated compounds were emitted from PS in air than in N2.

A clear difference was observed in the results of LDPE and waste plastics between the atmospheres. As shown in Figure 4, the number of the peaks obtained in N2 was considerably smaller than that in air. Compared to the chromatogram obtained in air, the peak heights observed in the early retention time were negligible small in N2. According to the temperature condition of GC, these peaks correspond to the compounds with lower boiling points than 180 °C. Because most of VOCs were produced in the degradation of polymer, it is suggested that N2 inhibits the degradation procedure and therefore prevents production of lower molecular weight compounds.

Comparison of the groups of VOCs emitted from LDPE in both the atmospheres is shown in Figure 5. Larger amounts of oxygenated organic compounds such as aldehydes, ketones and carboxylic acids were produced in air than in N2. The ratio of the amounts of these matters produced in N2 to in air was only 2.5 %. In this case, a large part of "Others" was occupied by BHT. As mentioned above, these BHT were considered to be emitted from the polymer by evaporation without reaction with other compounds.

It indicates that the diffusion of BHT isn't predominant by atmosphere.

The same result was observed in the case of waste plastics. N2 atmosphere prevented the emission of VOCs with the lower boiling point than 250 °C (Figure 6). The larger amounts of oxygenated compounds were detected in air than in N2 (Figure 7). The amount of oxygenated productions detected in N2 was 38 % of that in air.
Compounds excluding the degradation products

In the case of LDPE, BHT was the largest component of VOCs classified as the group “Others” compounds.

BHT is one of the most used antioxidants in polymers\(^1\).

Several aliphatic hydrocarbons were also included in VOCs emitted from PS. It seems to be unlikely
that aliphatic compounds were generated from the thermal degradation of PS polymer. Since some oil including aliphatic hydrocarbons is used in the molding process (personal communication with the company which produces the PS pellets), the oil vaporized or reacted with oxygen and then emitted as VOCs from PS.

In the case of waste plastics, many compounds unlikely originated from virgin PE, PP or PS were detected. For example, chlorinated hydrocarbons and phthalates were detected in the case of waste plastics, which indicates that polyvinyl chloride (PVC) was contained in the waste plastics. Limonene, caffeine, siloxane and several nitrogen compounds likely generated from food residue attached to waste plastics were also detected. Since these residues may be not only the cause of coloring but also the source of malodor, washing process is very important to overcome these problems.

CONCLUSION

The result showed the higher temperature caused more TVOC emission. VOCs emitted from virgin plastics were likely to be polymer degradation products as written in literatures. Besides the polymer degradation, additives were emitted from melting LDPE. Furthermore, VOCs which were likely to be derived from food residue attached to waste plastics and unseparated plastics such as PVC were emitted from waste plastics. More TVOC and more oxygenated organic compounds considered to be hazardous to human health and the cause of malodor were emitted in air atmosphere than in N2.

Based on these results, lower temperature and lower oxygen level is recommended to reduce hazardous or malodor compounds during the plastic melting process of mechanical recycling.

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