Gas chromatography–mass spectrometry and high-performance liquid chromatographic analyses of thermal degradation products of common plastics

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ABSTRACT

The thermo-oxidation of five commonly used materials, namely low-density polyethylene, retarded polyethylene, paper with a polyethylene foil, a milk package and filled polypropylene, was studied. Capillary gas chromatography and gas chromatography–mass spectrometry were used to analyze the volatile degradation products, while high-performance liquid chromatography was employed to measure polycyclic aromatic hydrocarbons. The results are discussed from the point of view of toxicity of the products.

INTRODUCTION

A great variety of products is formed by thermal degradation of polymeric materials. Many of the degradation products are toxic to living organisms. Carbon monoxide and hydrogen cyanide are among the most important products, but many other compounds are produced during combustion at high temperatures, e.g. organic nitriles, dioxanes, polycyclic aromatic hydrocarbons (PAHs), etc. Detailed analysis of these products is, therefore, of great importance [1–7].

The composition of the product mixtures formed during combustion of various materials depends strongly on the experimental conditions. Therefore, standard methods must be used for the evaluation of the toxicity of the products. The thermal degradation process can be studied in a combustion chamber [1,2] with a constant volume, enabling precise control and measurement of the temperature. In this way, reproducible reaction conditions can be realized, yielding degradation product mixtures of constant composition. Samples of different sizes can be used, and the equipment allows experiments with mice for biological tests.

Volatile products are best analyzed by capillary gas chromatography (GC), especially in combination with mass spectrometry (GC–MS) [3–7]. Modern fused-
silica columns are very well suited for the separation of complex mixtures of substances, and the retention indexes measured on standard stationary phases can be useful for the identification of unknown products \[8,9\].

PAHs are formed during incomplete combustion of organic materials, especially at higher temperatures. PAHs represent the largest known group of chemical carcinogens with mutagenic and teratogenic effects \[10\]. Although capillary GC and GC–MS can be applied to the analysis of PAHs \[11–13\], high-performance liquid chromatography (HPLC) is the method of choice \[14–19\]. Either UV photometric or fluorimetric detection can be applied, the latter being more sensitive and selective \[18,19\].

The present paper reports on the results of the analyses of the thermal degradation products of five materials which are used in every day life. Capillary GC and GC–MS were employed to analyze the volatile products, while HPLC was used for the analyses of PAHs. The results of biological tests \[20,21\] are included, and the toxicity of the combustion products is evaluated.

EXPERIMENTAL

Combustion chamber

The combustion chamber \[1–3\] consisted of separate compartments for the sample combustion (volume 1.8 l) and for biological tests with mice (volume 2.3 l). In the combustion compartment, the sample was placed in a crucible that was electrically heated to the required temperature. A ventilator forced the combustion products into the smoke compartment, from which samples were taken by syringe and directly injected into a gas chromatograph or were swept by an inert gas into vessels placed in solid carbon dioxide. The frozen-out samples were diluted with methanol before analysis. The overall volume of the chamber was 4.2 l; the void volume was 0.1 l.

Analyzed materials

Low-density polyethylene (sample 1), retarded polyethylene (2), paper with a polyethylene coating (3) and milk packages (4) were burnt at temperatures below and above their flash points. Sample 5, filled polypropylene (Taboren), was heated for 35 min at 260°C. The manufacturer did not grant permission to publish the composition of the filler.

Analytical equipment

A CHROM 4A gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) was used with a flame ionization detector. A 25 m × 0.22 mm I.D. fused-silica column coated with 0.32-μm OV-1 stationary phase, was temperature programmed from 50°C, after a 3-min hold time, at 5°C/min up to 300°C. A 50 m × 0.2 mm I.D. stainless-steel capillary column, coated with squalane and operated isothermally at 70°C, was used additionally for the analysis of sample 5. Nitrogen was the carrier gas. Of the gaseous products, 100 μl were injected with a split ratio of 1:100.

For GC–MS analyses an HP 5970A MSD quadrupole instrument was directly coupled to an HP 5790A gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA). A 25 m × 0.22 mm I.D. HP-UP column, coated with 0.32-μm OV-1 stationary phase, was employed with helium as carrier gas. The frozen-out samples, dissolved in
methanol, were injected splitless in 1-μl portions (samples 1–4) or with a split ratio of 1:100 (sample 5, 0.1 μl). The column was temperature programmed as described above.

An LKB 2500 liquid chromatograph (Bromma, Sweden) was employed with a UV–VIS detector, a Rheodyne 7120 sampling valve with a 20-μl loop, an LKB 220 integrator and a 150 mm × 3.3 mm I.D. 7-μm Separon SGX C₁₈ column (Tessek, Prague, Czechoslovakia). The fluorescence was measured with an RF-535 detector (Shimadzu, Japan) at an excitation and emission wavelength of 260 and 430 nm, respectively. The mobile phase consisted of methanol–water mixtures (80:20 or 90:10) and had a flow-rate of 0.3 ml/min and a temperature of 20 ± 2°C.

RESULTS AND DISCUSSION

Five samples of routinely used materials were examined: low-density polyethylene (1), retarded polyethylene (2), paper with a polyethylene foil (3), a milk package (4) and filled polypropylene (5). Samples 1–4 were degraded in the combustion chamber in air under flameless (500°C) conditions. Sample 5 was degraded at 260°C. i.e. the

Fig. 1. Gas chromatogram (OV-1) of sample 3 (polyethylene-coated paper). Compounds identified by GC–MS: A = acetone alcohol; B = trimethoxymethane; C = 2-furfural; D = furanone; E = 5-methoxy-2(5H)-furanone; F = phenol; G, H = cresols; I, J = dimethylphenols; K = trimethylphenol; L = 1,3-diphenylpropane; M = diphenylbutene; N, O = phthalates.
Fig. 2. Gas chromatogram (OV-1) of sample 4 (milk package). Compounds identified by GC–MS: A = trimethoxymethane; B = 2-furfural; C = 5-methyl-2-furfural; D = 1-decene + 2-hydroxy-1-methoxyethyl-1-furan; E = n-decane; F = cresol; G = 1,1-dimethoxyheptane; H = 1-undecene; I = n-undecane; J = 2-dimethoxyethyl-2,3-dihydrofuran; K = trimethylphenol; L = 5-hydroxyethyl-2-furfural; M = 1-dodecene; N = 1,1-dimethoxynonane; O = 1-tridecene; P = 1,1-dimethoxydecane; Q = 1-tetradecene; R, S, T, U, W = 1-pentadecene through 1-eicosene. Inset: exploded view of C_{19} fraction. a = 1,1-Dimethoxy-pentadecane; b = 1,18-nonadecadiene; c = 1-nonadecene; d = n-nonadecane.

Fig. 3. Gas chromatogram (squalane, 70°C) of sample 5 (filled polypropylene). Compounds identified by retention index matching: 1 = methane + ethane + ethene; 2 = propene; 3 = butene + 1,3-butadiene; 4 = acetone + propionaldehyde; 5 = pentane; 6 = 1-trans-3-pentadiene; 7 = 3-buten-2-one; 8 = 4-methyl-1-pentene; 9 = 2,5-dihydrofuran; 10 = 2-butanol; 11 = n-hexane; 12 = 2-pentanone; 13 = acetone alcohol; 14 = 1-heptene.
ANALYSIS OF THERMAL DEGRADATION PRODUCTS

The temperature used for the production of automobile dashboards from this material. The products were analyzed by GC, GC–MS and HPLC. The results are summarized in Figs. 1–5 and Table I.

Biological tests, involving measurements of the lethal dose, LD\textsubscript{50}, the carboxyhemoglobin content (HS value), and calculation of the toxicity index I\textsubscript{Iox}, were carried out at the Biological Departments of Charles University, within the framework of a systematic study of the dangerous effects of the combustion products of various materials [21]. These results are summarized in Table II.

**GC and GC–MS**

Sample 1 yielded the simplest spectrum of products. Compounds typical of the thermal degradation of polyethylene were found, i.e. characteristic gas chromatographic triplets of homologous \(1\)-alkenes (present in the largest amounts) and the corresponding \(\alpha,\omega\)-alkadienes and \textit{n}-alkanes. The only other substance present was trimethylphenol.

Similar degradation products were found in the gas chromatogram of sample 2 (retarded polyethylene). In addition to the hydrocarbons, 1,1-dimethoxyalkanes were present among the products. The origin of these compounds can be explained by the

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**Fig. 4.** Gas chromatogram (OV-1) of sample 5 (filled polypropylene). Compounds identified by GC–MS: A = acetone; B = acetone alcohol; C = 3-penten-2-one; D = diacetone alcohol; E = (tetrahydro-2H-pyran-2-yl)oxyacetone; F = dimethoxymethyl-2,3-dihydrofuran.
reaction of alkylaldehydes with the solvent methanol. The initially formed aldehydes are very unstable and degrade before analysis. They can be stabilized by the formation of methoxy derivatives, as was proven by the analyses of sample 2 with and without methanol added to the sample.

The GC–MS analyses of sample 3 revealed no characteristic polyethylene degradation products. The main components found were phenols, and diphenylalkanes and -alkenes (see Fig. 1).

The largest spectrum of products was obtained when burning sample 4 (milk package). The gas chromatogram of the degradation products of this sample is given in Fig. 2. The characteristic products of burning of polyethylene were formed, i.e. the 1-alkenes, α,ω-alkadienes and n-alkanes. The corresponding alkylaldehydes, and derivatives of furfurals, were present as compounds stabilized by reaction with methanol.

Sample 5, filled polypropylene, was heated to 260°C. During this procedure, this material is partially decomposed, causing an unpleasant smell and irritation of the eyes and skin of the workers. The degradation products were analyzed by capillary GC (Fig. 3) and GC–MS (Fig. 4). The compounds shown in Fig. 3 were identified by comparing their retention indexes, obtained at two temperatures, with values published for standard substances [8]. Many compounds were found, including saturated and unsaturated hydrocarbons, various oxygen-containing compounds, saturated and unsaturated ketones, alcohols, cyclic ethers, ketoalcohols, etc.

Analyses of PAHs by HPLC

The stationary phase and the mobile phase composition were selected on the basis of literature data. The separation conditions were optimized. The best resolution of a standard PAH mixture on a given C₁₈ column was attained with a methanol–water mobile phase at volume ratios between 8:2 and 9:1.

The PAHs contained among the degradation products were identified by comparing the capacity factors of the unknown components with those of standard compounds, measured with two different mobile phases. Fluorescence detection was employed to improve the selectivity and sensitivity of the analyses.

All samples produced the same PAHs, i.e. naphthalene, phenanthrene, anthracene, pyrene, benzo[a]anthracene and benzo[a]pyrene (see Fig. 5), except for sample 4, from which phenanthrene was absent. However, the relative content of individual PAHs in the samples was different (see Table I). Anthracene was present in the highest amount, especially in the degradation products of sample 3, paper impregnated with polyethylene. Similar PAHs were found in refinery effluents [18], environmental dust and grass samples [17,19], and during combustion of polystyrene [12].

Toxicity tests

The toxicity of the combustion products, characterized by the LD₅₀, the carboxyhemoglobin content (HS value) and the toxicity index I₅₀, for the materials studied is given in Table II. The toxicity is not very high, but there are various effects connected with the identified substances.

Aliphatic aldehydes exhibit strong irritating effects, especially on the eyes, and may cause allergies. The same is true of ketones, which also have narcotic properties. Unsaturated ketones, such as 3-buten-2-one (methylvinylketone) and 4-methyl-3-
Fig. 5. Liquid chromatogram of sample 1 (low-density polyethylene). Compounds identified by capacity factor matching: 1 = naphthalene; 2 = phenanthrene; 3 = anthracene; 4 = pyrene; 5 = benzo[a]anthracene; 6 = benzo[a]pyrene.
TABLE I
RELATIVE AMOUNTS OF POLYCYCLIC AROMATIC HYDROCARBONS (%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.4</td>
</tr>
<tr>
<td>Anthracene</td>
<td>91.4</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.7</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>3.0</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>1.2</td>
</tr>
</tbody>
</table>

TABLE II
BIOLOGICAL TOXICITY TESTS

HS = The carboxyhemoglobin content in mouse blood causing death of the animal (%); LD$_{50}$ = lethal dose, i.e. the sample weight in mg/l of the chamber volume causing death of 50% of mice; $I_{ox} = toxicity$ index: $I_{ox} = 10^4/[LD_{50}(1 + HS \cdot 10^{-2})]$.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>HS</th>
<th>LD$_{50}$</th>
<th>$I_{ox}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>58</td>
<td>99</td>
</tr>
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<td>2</td>
<td>54</td>
<td>58</td>
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<td>71</td>
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</tr>
<tr>
<td>4</td>
<td>72</td>
<td>56</td>
<td>105</td>
</tr>
</tbody>
</table>

penten-2-one (mesityloxide), strongly irritate the eyes and skin. Hydrocarbons exhibit narcotic effects that are stronger for unsaturated compounds, and further adversely influence the nervous system, blood production and respiration. The toxicity index of the degradation product mixture of sample 5 was not measured, but the analysis of this mixture confirmed the presence of toxic compounds. Therefore, the original polymer had to be modified to decrease the danger to the workers during its treatment.

Many aromatics, especially PAHs, are proven or suspected carcinogens. Carcinogenic effects of naphthalene, anthracene and phenanthrene are still open to discussion, but pyrene, benzo[a]anthracene and benzo[a]pyrene are definitely carcinogenic.

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