Identification of Odor-Active Compounds Resulting from Thermal Oxidation of Polyethylene

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Thermal processing of synthetic polymers in the presence of oxygen into food-packaging materials can result in the formation of byproducts which impart off-odors or raise toxicological questions. Volatiles from the thermal oxidation of polyethylene were collected and analyzed by gas chromatography/ olfactometry (GCO; CharmAnalysis). Fourteen odor-active compounds, most of which occurred in amounts that were too low to be detected instrumentally, were present. Overall odor was waxlike but individual components were fruity, herbaceous, rancid, metallic, waxy, pungent, or orange. Eight of the 14 compounds were identified and confirmed by matching mass spectra to those of standards. All were C_6–C_9 saturated or unsaturated aldehydes and ketones. Approximately 46% of the aroma from oxidized polyethylene resulted from hexanal, 1-hepten-3-one, 1-octen-3-one, octanal, 1-nonen-3-one, nonanal, trans-2-nonenal, and diacetyl. α-Unsaturated aldehydes and ketones are responsible for much of the off-odor associated with thermally oxidized PE.

INTRODUCTION

While offering advantages for packaging food products, plastics are not inert and involve direct and indirect interactions with food (Risch and Hotchkiss, 1991). For example, plastic packaging materials can absorb aroma compounds from orange juice (Marin et al., 1992). Contact with plastics can also result in the migration of packaging components such as residual monomers, plasticizers, and additives to foods, resulting in flavor defects or toxicological concerns (Risch, 1988).

Polyolefins are often processed into packages at temperatures well above their melting point and in the presence of oxygen and substantial shear stress. This can result in oxidation and thermal degradation of the plastic to form residual byproducts (Kim and Gilbert, 1989). These byproducts can impart undesirable odors to foods. Because of the complex composition of packaging materials, volatile compounds could arise from many sources including residual monomers and oligomers, residual solvents from printing inks, adhesives, coatings, breakdown products of polymers and additives, etc.

Kim and Gilbert (1989) and Kim-Kang (1990) have reviewed the literature on volatiles from packaging materials and methodology for testing polymer odor. Most odor quality studies of plastic materials involve sensory evaluation of intact plastics and correlation with an integrated instrumental response. Fales et al. (1983) correlated resin odor as quantified by a panel with GC–MS analysis by plotting major peak areas against overall odor intensity. However, the aroma was not separated into its components, and specific odor-active compounds were not identified. Fernandes et al. (1986) analyzed the volatile products formed during ionomer extrusion at 280–300 °C by headspace concentration techniques. By using a splitter in the GC-FID an aroma profile of the ionomer headspace was produced, and descriptors were given to individual peaks but they were not correlated to specific compounds. Koszinowski and Piringer (1986) proposed methodology to investigate off-odors in packaging materials by splitting of the GC effluent between a sniffing port and a mass spectrometer. However, they did not

report results from applying this method to packaging materials. Identification by GC–MS of a limited number of volatiles produced during polyethylene degradation has been reported, but the odor activity of the compounds has not been investigated (Barabas et al., 1976; Hoff and Jacobsson, 1981).

Our objective in the present work was to identify several of the specific compounds responsible for the off-odor resulting from the thermal oxidative degradation of polyethylene (PE). To accomplish this, we used a gas chromatography/olfactometry (GCO) technique known as CharmAnalysis (Acree et al., 1984). This technique produces a dimensionless measure of odor intensity based on odor detection thresholds rather than psychological estimations of stimulus intensity and is capable of associating flavor descriptors with specific chemical constituents. The technique is sensitive enough to detect odor-active compounds whose concentrations are too low to be detected by mass spectrometry. We have previously identified 84 compounds produced during the thermal oxidation of PE (Bravo and Hotchkiss, 1992).

MATERIALS AND METHODS

Polyethylene [approximate MW 50 000; density 0.92 g/cm³; $n^{25/D}$ 1.51; melt index 0.8; soluble (above 60 °C) in aliphatic, cycloaliphatic, and aromatic hydrocarbons] was acquired from Scientific Polymer Products, Inc. (Ontario, NY). The apparatus for trapping volatiles has been described in detail (Bravo and Hotchkiss, 1992). Granular PE samples (0.5 g) were heated in a glass vessel inside a specially designed oven at 250 °C for 15 min. Volatiles escaping the polymer melt were swept out of the vessel by a 20 mL/min air flow and condensed in two glass traps cooled in liquid N_2. No flow was detected leaving the apparatus and, thus, all sweep gas was trapped. Air was used in place of an inert gas to provide opportunity for thermal oxidation to occur. Trapped volatiles were dissolved in 4 mL of ultrapure Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), sealed in glass vials, and stored until analysis at 5 °C.

Volatiles Concentration. Samples analyzed by GC-FID were not concentrated. GC–MS samples were concentrated by evaporating the solvent under N_2 at a low flow rate from 1 to 0.2, 0.1, or 0.01 mL. In some cases, condensates collected from several experiments were combined and the solvent was evaporated under reduced pressure using a Buchi RE 111 rotary evaporator and bath (28 °C).

Gas Chromatography/Olfactometry. Odor-active compounds were analyzed by CharmAnalysis (Acree et al., 1984).

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Table I. Standard Compounds Analyzed by GC-MS, GC-FID, and Olfactometry

2,3-butadione	butanoic acid	cyclohexanone
2,4-decadienal	decanal	2-decanone
cis-4-decenal	hexanal	1-hexanol
3-octen-2-one	1-heptanol	4-heptanone
2-heptenal	3-hepten-1-ol	1-hepten-3-one
2,4-nonadienal	2,6-nonadienal	nonanal
1-nonanol	2-nonanol	2-nonanone
3-nonanone	5-nonanone	trans-2-nonenal
1-nonen-3-one	octanal	octanoic acid
1-octanol	1-octen-3-ol	1-octen-3-one
2-hexenal	trans-2-hexen-1-ol	

The solution was diluted by factors of 3–6561-fold, until no odor was detected in the chromatogram. One microliter of each sample concentration was injected into a modified Hewlett-Packard 5890 gas chromatograph containing a 0.32 mm × 12 m fused silica capillary column coated with cross-linked methyl silicone. GC temperature for the injector was 200 °C and for the oven was 35 °C for 3 min, 6 °C/min to 150 °C. The GC effluent was taken up into a sniffer system (Acree et al., 1976), mixed into a stream of humidified air (20 L/min), and passed to the sniffer port through a 10-mm diameter silylated Pyrex tube. All GCO samples were analyzed by a single subject selected for olfactory sensitivity and trained in GCO analysis using a standard compound mixture specifically designed for GCO subject selection (Marin et al., 1988). The subject responded on an Apple MacIntosh Plus computer each time an odor was detected. Odor detection time, duration, and quality were recorded (Acree et al., 1984). Retention times were converted to retention indices (RI) by adjustment to a series of C_7–C_{18} saturated n-hydrocarbons analyzed under identical conditions but detected by FID. Data were displayed as a Charm chromatogram which consisted of a plot of dilution values vs RI. Dilution values can be thought of as the number of dilutions to reach threshold for the subject monitoring the odors. Charm values are the areas under the peaks in the Charm chromatogram and are proportional to the amount of odor-active compound in the most concentrated sample. Thus, Charm values indicate relative aroma potency independent of amount of compound present in the sample.

Gas Chromatography-Mass Spectrometry. Mass spectra were obtained by splitless 1-μL injections into a Hewlett-Packard 5890 gas chromatograph/5970 Series mass selective detector and equipped with a 0.32 mm × 25 m fused silica capillary column coated with cross-linked methyl silicone. Temperatures were as follows: 3-min hold at 35 °C, 4 °C/min to 225 °C; injector 225 °C; ion source, 200 °C. Carrier gas was helium (2 mL/min). Electron multiplier voltage was 2000 eV. Charm peaks (i.e., odor-active compounds) were identified by matching RIs from GCO with GC-MS data and by comparing electron ionization (EI) and selected ion monitoring (SIM) spectra to the NBS Wiley MS data base by computer matching and with spectra from authentic compounds. Compounds were considered identified if the library search gave at least an 80% probability match. SIM mass spectra were obtained as outlined above for full spectra.

Standards. Authentic compounds (Table I; 1–10 μg/mL) were analyzed by GC-MS, GC-FID, and CharmAnalysis to confirm structures. Standards were also co-injected with the unknowns to check retention times in most cases. Compounds were commercially available except for 1-hepten-3-one and 1-nonen-3-one, which were prepared from their respective unsaturated alcohols using the method of Corey and Suggs (1975).

RESULTS AND DISCUSSION

Analysis of the trapped volatiles resulting from PE oxidation at 250 °C for 15 min gave a Charm chromatogram containing 14 odor-active peaks (Figure 1). Odor-active peaks were detected between RIs of 655 and 1210 (Table II). As a mixture, the condensate had a strong waxy or burnt plastic odor, but the individual components sniffed after separation had different descriptors (Table II), indicating that no one compound accounted for the waxy-burnt plastic odor.
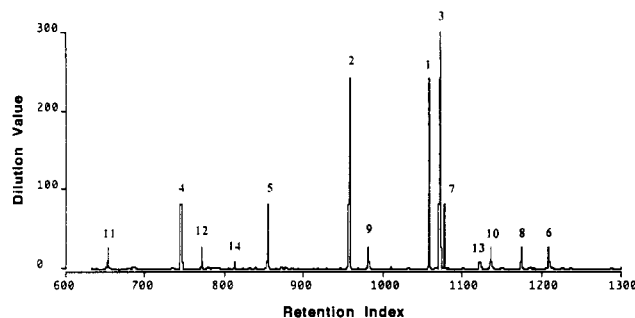

Figure 1. Typical Charm chromatogram of volatiles condensed from the thermal oxidation of polyethylene at 250 °C for 15 min. Peak numbers correspond to the numbers in Table II.

Some peaks were readily identified by comparison of GCO results with GC-MS data and standards. These compounds were hexanal (RI 772), which has been reported to have a powerful, penetrating, fatty-green, grassy odor (Arctander, 1969); octanal (RI 982), which in extreme dilution has been reported as sweet, orangelike, slightly fatty, or honeylike character (Arctander, 1969); nonanal (RI 1079), reported to have a citrusy, waxy odor in concentrations below 5 μg/mL (Arctander, 1969); and trans-2-nonenal (RI 1137), which at high dilution is orrislike (Arctander, 1969).

The first peak in the Charm chromatogram (RI 655) had a rancid/cheesy odor when analyzed by GCO but was not immediately identifiable by GC-MS because it co-eluted with the solvent. On the basis of RI and aroma character, 2,3-butadione (diacetyl) was considered a likely candidate. A 1 μg/mL 2,3-butadione standard gave a similar Charm response at RI 657. Full-spectrum GC-MS analysis of the standard gave the correct retention time, and the spectrum showed two ions, m/z 43 and 86, which are characteristic of the simple spectrum of diacetyl. Full-spectrum analysis indicated the presence of three peaks in the extract between retention times of 2.55 and 2.65 min. The first peak was identified as 2,3-butadione on the basis of a comparison to authentic 2,3-butadione for odor activity, RI, and SIM for ions m/z 43 and 86. The second and third peaks (2.61 and 2.64 min) were identified as butanal and 2-butanone, respectively, by the computer MS library using full-scan data. These C_4 carbonyl compounds have characteristic rancid smells and low odor thresholds. Butanal and 2-butanone have previously been identified as products of polyethylene degradation (Barabas et al., 1976; Fernandes et al., 1986; Hoff and Jacobsson, 1981). Diacetyl (2,3-butadione) has not been previously reported. Larger amounts of each of these compounds were likely produced during degradation, but a portion may have been lost during sample concentration.

The remaining Charm peaks did not produce spectra that could be readily identified with high probability by computer matching. Standard solutions of 1-heptanol, 4-heptanone, 2-hexenal, butanoic acid, cyclohexanone, 1-octanol, 1-nonanol, 2-nonanol, 2-nonanone, 3-nonanone, 5-nonanone, octanoic acid, and 2-decanone were tested, either because they had similar RIs or because of their structure. None correlated with any Charm peak. Tenfold concentration of the PE unknowns failed to produce satisfactory separations.

The unknown Charm peaks with the similar odor descriptors of unpleasant metallic and waxy had common features, and two groups could be distinguished on the basis of RI values:

group I, RI 1073, 1175;   group II, RI 856, 959, 1059

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Table II. Retention Index (RI), Percent of Total Charm, Approximate Concentration, Odor Characteristics, and Structure of Compounds Producing Odor from Thermally Oxidized Polyethylene

peak no.	index	Charm %	μg/g of PE	character	compound	
1	1073	32.33	9	waxy	unsaturated carbonyl	
2	959	18.14	<2[a]	herb/metallic	1-octen-3-one	
3	1059	13.51	<2[a]	pungent	1-nonen-3-one	
4	746	7.25	–[b]	waxy	unknown	
5	856	5.40	<2[a]	herb/metallic	1-hepten-3-one	
6	1210	2.92	–[b]	dusty	unknown	
7	1079	2.82	97	rancid/other	nonanal	
8	1175	2.26	–[b]	waxy	unknown	
9	982	2.21	107	orange	octanal	
10	1137	2.16	11	paper/carton	2-nonenal	
11	655	1.72	–[b]	rancid/cheesy	diacetyl	$CH_3COCOCH_3$
12	772	1.45	177	herbaceus	hexanal	
13	1124	0.98	–[b]	countryside	unknown	
14	814	0.59	–[b]	rancid/cheesy	unknown	

[a] Limit of detection = 2 μg/g of PE. [b] Insufficient peak size or overlapping peaks.
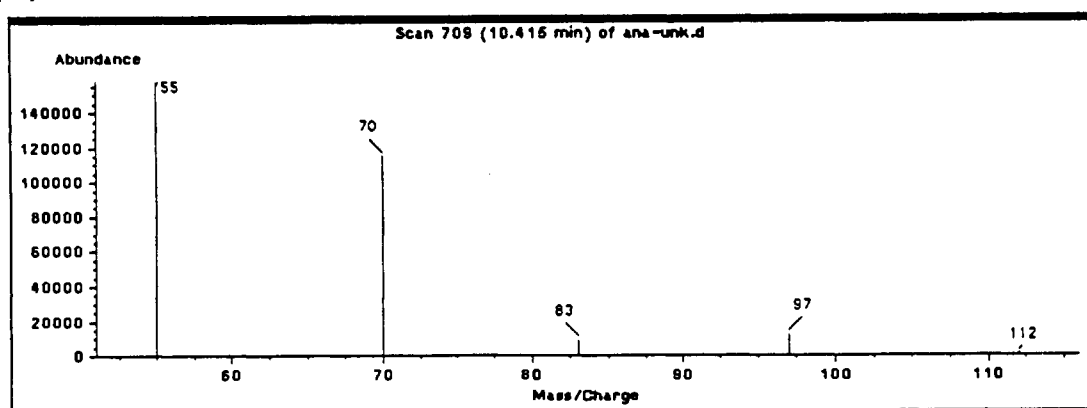
(a)
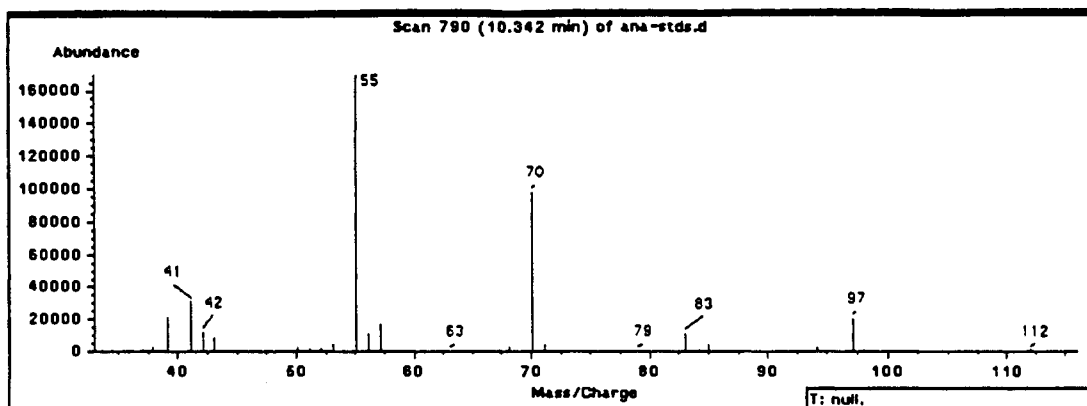
(b)

Figure 2. (a) Full-scan GC–MS(EI) spectra of authentic 1-hepten-3-one and (b) SIM plot for ions m/z 55, 70, 83, 97, and 112 from degraded polyethylene at the same retention time as authentic 1-hepten-3-one.

The similarity in odor character and a 100-increment increase in RI suggested two homologous series of compounds. Typically, each methylene unit introduced within a homologous series results in an increase in RI of 100 units (Evans and Haken, 1989). Preliminary GC-FID and GC-MS analyses showed a repeating pattern of peaks and the presence of a homologous series of compounds (Bravo and Hotchkiss, 1992). Also, the spectra from both groups

had the common feature of having a large ion at m/z 55, which is characteristic of α-unsaturated carbonyls ($CH_2=CH—^+C=O$) (Silverstein, 1981). Conjugated unsaturated carbonyl compounds have been reported to have low odor thresholds and metallic character (Teranishi et al., 1991) and have been discussed but not demonstrated as potentially responsible for off-odors in packaging (Koszinowski and Piringer, 1986). Further, we had already identified and confirmed the presence of one such compound (*trans*-2-nonenal).

Several authentic compounds with similar structures were tested for odor activity, RI, and mass spectra including *trans*-2-hexen-1-ol, 3-hepten-1-ol, 1-octen-3-ol, 1-octen-3-one, and 3-octen-2-one. Comparison of RI, mass spectra, and odor activity indicated that group II peaks (RI 856, 959, 1059) had the common feature of containing 1-en-3-one functions, and group I peaks (RI 1073, 1175) were α-unsaturated aldehydes. Standard solutions (1–10 μg/mL) of 1-hepten-3-one, 1-octen-3-one, and 1-none-3-one each had strong herb/metallic odors and RIs of 856, 956, and 1057, respectively, and were indistinguishable from those of group II. The standard compounds coeluted with peaks of RIs of 856, 959, and 1059 from oxidized polyethylene when co-injected. SIM mass spectra of the standards, unknowns, and standards co-injected with unknowns were obtained for ions m/z 55, 70, 83, and 97. Both the retention times and relative magnitude of the ions agreed with standards in all cases, further supporting the C_7, C_8, and C_9 1-en-3-one structures for unknowns in group II. Representative SIM data are given in Figure 2.

The structure of compounds at RI of 1073 and 1175 could not be confirmed although GC–MS data indicated the presence of m/z 55 and 69 ions (m/z 55 + $CH_2 = m/z$ 69) in the spectra of both peaks. *cis*-4-Decenal has a reported RI of 1177 (Jennings and Shibamoto, 1980) and characteristic ions m/z 55 and 69 and, hence, was considered a likely candidate for the unknown peak at RI 1175 in group I. In our system, authentic *cis*-4-decenal had an RI of 1169 which was not different from the 1175 of the unknown. However, *cis*-4-decenal produced a different odor characteristic (described as "sweet") when analyzed by CharmAnalysis at a similar concentration. It is possible that the compound at RI 1175 was the *trans*-4-decenal isomer which was not available to us. Differences in odor and index could be due to the configuration of the double bond. Standard solutions of 2,4-decadienal, 2,4-nonadienal, and 2,6-nonadienal were also tested, but neither the RI nor the odor activity matched those of the unknowns.

The spectrum of the peak with the highest Charm value at RI 1073 could not be matched to any known spectrum with confidence even after the sample was isolated and concentrated by HPLC. The spectrum contained ions m/z 55 and 69 similarly to the peak at RI 1175. As pointed out above, m/z 55 is characteristic of α-unsaturated aldehydes or ketones and m/z 69 is the methylene homolog of m/z 55. These data, the difference in RI of 100, and the fact that the most potent waxy aromas were all produced by unsaturated carbonylic structures suggest that this compound is the C_9 homolog of the peak at 1175 and that both are unsaturated carbonyls.

Unsaturated carbonyls have potent aromas. Swoboda and Peers (1977) have shown that these compounds are responsible for the metallic flavors in oxidized milk. Koszinowski and Piringer (1983) have estimated the odor threshold and aroma character for several unsaturated carbonyl compounds and have proposed that these compounds were responsible for off-odors resulting from PE-

coated paperboard. Many had odor activity at low concentrations. However, no polymers or packaging materials have been assayed for the presence of the compounds.

CONCLUSIONS

Potent odor-active compounds were produced during thermal oxidation of PE. In most cases, these compounds occurred at concentrations that did not produce measurable peaks in the GC–MS total ion current plots and so would not have been normally detected. However, when the samples were analyzed by GCO using CharmAnalysis, they were readily detected. Fourteen compounds were detected by GCO, the most odor active being unsaturated aldehydes and ketones in the range C_6–C_9. In particular, hexanal, 1-hepten-3-one, 1-octen-3-one, octanal, 1-nonen-3-one, nonanal, *trans*-2-nonenal, and diacetyl were identified as responsible for a significant portion of the total odor originating from thermally degraded PE odor. Unsaturated carbonyls such as the 1-en-3-ones, which are present in trace amounts and have low thresholds, are responsible for a significant percentage of remaining off-odors.

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