

Solid-Phase Microextraction (SPME) in Polymer Characterization—Long-Term Properties and Quality Control of Polymeric Materials

Minna Hakkarainen, Mikael Gröning, Ann-Christine Albertsson

Department of Polymer Technology, The Royal Institute of Technology (KTH), SE-100 44, Stockholm, Sweden

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ABSTRACT: Solid-phase microextraction (SPME) in combination with GG-MS was applied to quality control polyamide 6.6 collected for recycling and to study the long-term properties and degradation of nitrile rubber, polyethylene, and polyamide 6.6. The migration of plasticizer and other additives reduces the service-life and changes the properties of the material. It is also a possible health hazard, for example, legislation against the use of brominated flame retardants in plastic materials, is under discussion, and fast and reliable methods are required to detect such compounds in plastic materials collected for recycling. SPME rapidly and effectively extracted several brominated compounds from in-plant collected polyamide 6.6. Migration of tris(2-butoxyethyl)phosphate plasticizer and its degradation products

from nitrile rubber during long-term thermal ageing at 60 and 80°C was shown by SPME-GC-MS, while the plasticizer was not volatile enough to be detected by traditional HS-GC-MS. In accordance the number of degradation products extracted from thermo-oxidized PE by HS-SPME was three times larger than the number detected after HS-GC-MS analysis. SPME-GC-MS could also detect early signs of degradation in thermo-oxidized virgin and in-plant recycled polyamide 6.6 before any signs of degradation were observed by, for example, tensile testing or FTIR. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 867–873, 2003

Key words: chromatography; mass spectrometry; additives; degradation; SPME

INTRODUCTION

As a result of increased environmental consciousness, the interaction between plastic materials and environment has become an important scientific issue. This interaction is mainly determined by the low molecular weight compounds migrating from polymers during manufacture, use, and after disposal. These low molecular weight compounds include monomer residues, oligomers, solvent residues, additives, and degradation products. Many additives including, for example, phthalates and brominated flame retardants, are hazardous, and their migration to the surrounding environment is a point of concern. The migration of additives also changes the properties and reduces the lifetime of the product. Besides the environmental impact, the degradation product patterns give information of, for example, the degree of oxidation in the polymer matrix,¹ they can be used to predict degradation mechanisms² or to differentiate between biotic or abiotic degradation.^{3,4} As recycling of polymers is coming more and more important and the recycled materials are used for more demanding applications, the analysis of degradation products and additives is,

in addition to the commonly employed mechanical characterization, a valuable tool to quality control the plastic materials collected for recycling.

Solid-phase microextraction (SPME) is an inexpensive, rapid, and solvent-free extraction technique. It is based on a typically 1-cm long, thin-fused silica fiber coated with a polymeric stationary phase mounted in a modified syringe. For sampling an aqueous or solid sample containing organic volatiles is placed in a vial that is closed with a cap that contains a septum. The sheath of the SPME syringe is pushed through the septum and the fiber is immersed directly into aqueous samples or in the headspace over the liquid or solid sample matrix. During extraction the analytes are adsorbed or absorbed by the fiber, depending on the type of stationary phase used.⁵ After the completed extraction the SPME fiber is placed in the injection port of a GC where the analytes are thermally desorbed and transferred to the capillary column. SPME is an equilibrium technique, and therefore, the analytes are not completely extracted from the matrix. Nevertheless, the method is useful for quantitative work, and excellent precision and linearity have been demonstrated. The sensitivity and time required to reach adsorption equilibrium depends on the partition coefficients between the fiber and the analytes and the thickness of the phase. Several external factors influence the extraction efficiency of which the most important are temperature (for headspace extraction)

Correspondence to: A.-C. Albertsson (aila@polymer.kth.se).

and pH, salting, and agitation (for solution extraction). For reproducible results consistent timing is more important than full equilibrium. Limits of detection and quantitation are often below 1 ppb. There are several commercially available fiber materials with different polarities and fiber thicknesses and selectivity of the extraction can be altered by changing the fiber material. The theory of SPME is thoroughly described in a monograph by Pawliszyn.⁶ Several examples of SPME applications in analytical chemistry are given in a book edited by Pawliszyn.⁷

We have earlier developed methods to extract and identify low molecular weight degradation products migrating from polymeric materials in different environments.⁸⁻¹² SPME has been applied to extraction of oxidation products from environmentally degradable polyethylene¹³⁻¹⁵ and polyamide 6.6.^{2,16} During this work the potential of SPME in polymer characterization is further evaluated in the quality control of polymeric materials collected for recycling and in studies of long-term behavior of polymers.

EXPERIMENTAL

Materials, aging, and the extraction procedure

Silica-based SPME fibers coated by nonpolar polydimethylsiloxane (PDMS), polar carbowax-divinylbenzene (CW-DVB), mid-polar PDMS-DVB fiber, or polar polyacrylate fiber were used to extract additives and degradation products from different polymeric materials. The film thicknesses of the fibers were 100, 65, 65, and 85 μm , respectively. The extractions were done from the headspace above the samples. The extraction time was 30 min and the extraction temperature was 80°C. The thermal desorption time of the fibers in the GC injector was 5 min.

Brominated flame retardants in recycled polyamide 6.6

In-plant collected polyamide 6.6 scrap from various polyamide 6.6 processing plants in Europe was analyzed for Tetrabromobisphenol A. The scrap was re-extruded and granulated when received using an Axon (Nyvång, Sweden) extruder and a Moretto granulating mill. The temperature was 285°C during the extrusion. The granules were dried for 8 h at 90°C in a Piovan granulate dryer and subsequently compression moulded into 100 \times 100 mm \times 80 μm films using a Schwabenthan Polystat 400 S hot-plate press. During the compression molding the temperature of the plates was 285°C and the pressure was 0 bar for 1 min, 20 bar for 2 min, and 50 bar for 2 min. The films were cut into 10 \times 10-mm pieces and 1.00 g of polyamide 6.6 pieces were closed in 20 mL headspace vials sealed

with PTFE-silicone septas. The low molecular mass compounds were extracted onto a 65 μm PDMS-DVB.

Nitrile rubber (NBR)

Commercial-grade compounded NBR, without carbon black, was supplied by SKEGA AB, Ersmark, Sweden. NBR was a mixture of two NBR rubbers with acrylonitrile contents of 18 and 33%, resulting in an average of 28% acrylonitrile. A tributoxoethanol phosphate, KP-140, was used as a plasticizer. The nitrile rubber also contained following additives ZnO, Stearic acid, alkylated diphenylamine (Octamine), trimethyl dihydroquinone (Flektol), sulfur (Struktol SU105), dimethyldiphenylthiurame disulfide (Vulkacit I), and tetramethylthiurame disulfide (TMTD). The nitrile rubber was cut into small pieces, of which 100 mg was weighed and sealed into each vial. The vials were then aged at 60 and 80°C. The ageing times varied from 0 to 24 weeks. The volatile products migrating from the material during the ageing were extracted by polyacrylate SPME fiber.

Polyamide-6.6

A commercial-grade polyamide 6.6., Zytel 101L from DuPont (Stockholm, Sweden), was used to study low molecular mass degradation products from virgin and recycled thermo-oxidized polyamide 6.6. The material was extruded for up to three times into 0.2-mm thick and 100-mm wide sheets using a Brabender DSK 35/9 counterrotating twin screw extruder. The temperature of the three heating zones of the extruder was 285°C, and the screw speed was 30 mm/min. Between the extrusions part of the material was granulated in a Moretto granulating mill. Prior to extrusion the granules were dried for 8 h at 90°C in a Piovan granulate dryer. Strips of 10 \times 100 mm were cut from the sheets and 1.00 g of strips were sealed in 20-mL headspace vials with PTFE-silicone septas. The samples were thermo-oxidized at 100°C for 1200 h in a conventional circulating air oven. The low-molecular mass degradation products were extracted using a 65 μm PDMS-DVB fiber.

Low-density polyethylene (LDPE)

Low-density polyethylene (LDPE) films (30 μm) were made by a conventional blown film process using a Betol extruder with a 25-mm diameter screw of L/D 20 : 1, a blow-up ratio of about 2.5 : 1, and a die temperature of 185°C. The LDPE granules were acquired from ATO (France) and contained a conventional thermal stabilizer of undisclosed composition. The polyethylene films were subjected to 100 h of UV radiation in an Atlas UVCON weatherometer equipped with UV-lamps (FS-40 fluorescent sunlamp)

giving radiation at wavelengths between 280–359 nm to surpass the induction period. During the irradiation the temperature increased to a mean value of about 50°C. After the UV radiation the samples were thermally aged for 5 weeks at 80°C in sealed vials to collect the volatile degradation products (100 mg of polymer in each vial). PDMS and CW-DVB fibers were used to extract the volatile products.

Gas chromatography-mass spectrometry (GC-MS)

The extractions from polyamide 6.6 samples, both thermo-oxidized and recycled, were analyzed using a GCQ gas chromatograph-mass spectrometer from ThermoFinnigan. The GC was equipped with a wall coated open tubular CP-Sil 8 CB/MS column (30 m × 0.25 mm × 0.25 μm) from Varian. Helium of 99.9999% purity from AGA was used as carrier gas at a constant velocity of 40 cm/s. The temperature of the GC injector was 250°C, and the oven temperature was programmed to be 40°C for 1 min, then raised to 250°C with a heating rate of 10°C/min, and lastly maintained at 250°C for 10 min. The ion-trap mass spectrometer scanned in the mass range of 35–400 *m/z* with a scan time of 0.43 s.

The volatile products from the nitrile rubber were analyzed by Perkin-Elmer 8500 model gas chromatograph coupled to an ITD mass spectrometer. The column used was DB-FFAP from J&W (30 m × 0.32 mm i.d.). The column was held for 3 min at 40°C and then programmed from 40 to 250°C at 10°C/min and lastly held at 250 for 26 min. The injector temperature was 250°C. Helium was used as a carrier gas. The polyethylene extractions were analyzed by a Varian gas chromatograph coupled to a Finnigan SSQ7000 mass spectrometer. The column used for polyethylene was a DB-WAX capillary column from J&W (30 m × 0.32 mm i.d.). The column temperature was held at 60°C for 1 min and then programmed to 240°C at 10°C/min. The injector temperature was 225°C.

Headspace-gas chromatography-mass spectrometry (HS-GC-MS)

To compare the SPME method with a more traditional air sampling method, some samples were also analyzed by HS-GC-MS. A Perkin-Elmer HS 101 autosampler was coupled to a Perkin-Elmer 8500 model gas chromatography and an ITD mass spectrometer. The vials with the aged polymers were thermostatted in the HS unit at 100°C for 30 min in the case of nitrile rubber and at 80°C for 30 min in the case of the polyethylene samples. For the analysis of polyethylene the GC was equipped with a DB-WAX column from J&W (30 m × 0.32 mm i.d.). The oven temperature was first held at 50°C for 8 min and then programmed from 50 to 250°C at 10°C/min. Nitrile rub-

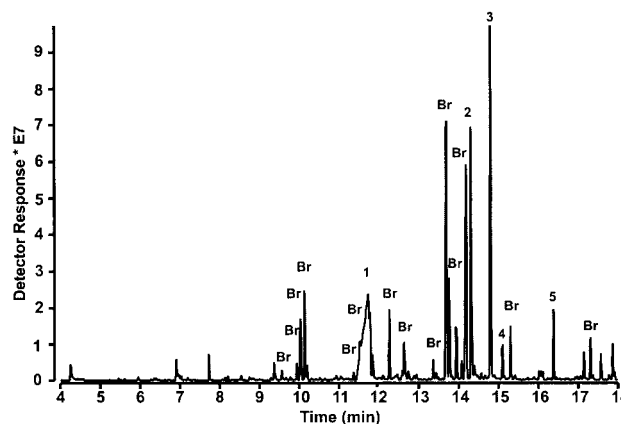


Figure 1 GC-MS chromatogram showing the compounds extracted by solid-phase microextraction from polyamide 6.6 collected from different processing plants in Europe. The identity of the numbered peaks is Br = brominated benzene, peak 1 = caprolactam, peaks 2–4 = hindered phenols from antioxidant, peak 5 = diphenylamine.

ber samples were analyzed with DB-225 column from J&W (30 m × 0.32 mm i.d.). The oven temperature was first held at 40°C for 8 min and then programmed from to 200°C at 5°C/min. Helium was used as a carrier gas.

RESULTS AND DISCUSSION

SPME in quality control of recycled materials: screening for brominated flame retardants in recycled polyamide 6.6

Due to the forthcoming legislation against the use of brominated flame retardants in plastic materials, fast and reliable methods are required to detect such compounds in polymeric materials collected for recycling. HS-SPME effectively extracted several brominated compounds, all possible degradation products of the commonly used flame-retardant Tetrabromobisphenol A, from recycled polyamide 6.6. Figure 1 shows a chromatogram of the volatile compounds extracted from the recycled polyamide 6.6. The peaks corresponding to brominated benzenes are marked with Br in the chromatogram. The mass-spectrums of all of these compounds showed the significant ion-patterns of aromatic compounds with electronegative substituents (fragment ions 50, 51, 63, 64, 65, 75, 76, etc.) as well as the characteristic isotope-ratios of one ($A = 100\%$, $A+2 = 97.3\%$) or two ($A = 51\%$, $A+2 = 100\%$, $A+4 = 49\%$) bromine atoms, confirming the mono- or dibrominated benzene structure of the compounds. A quantitative analysis using 1,4-dibromobenzene and bromobenzene as model compounds for the identified Tetrabromobisphenol A degradation products showed that the amounts of brominated benzenes migrating from the recycled polyamide 6.6 ranged from 3 to 10 μg/kg polyamide per analyte.

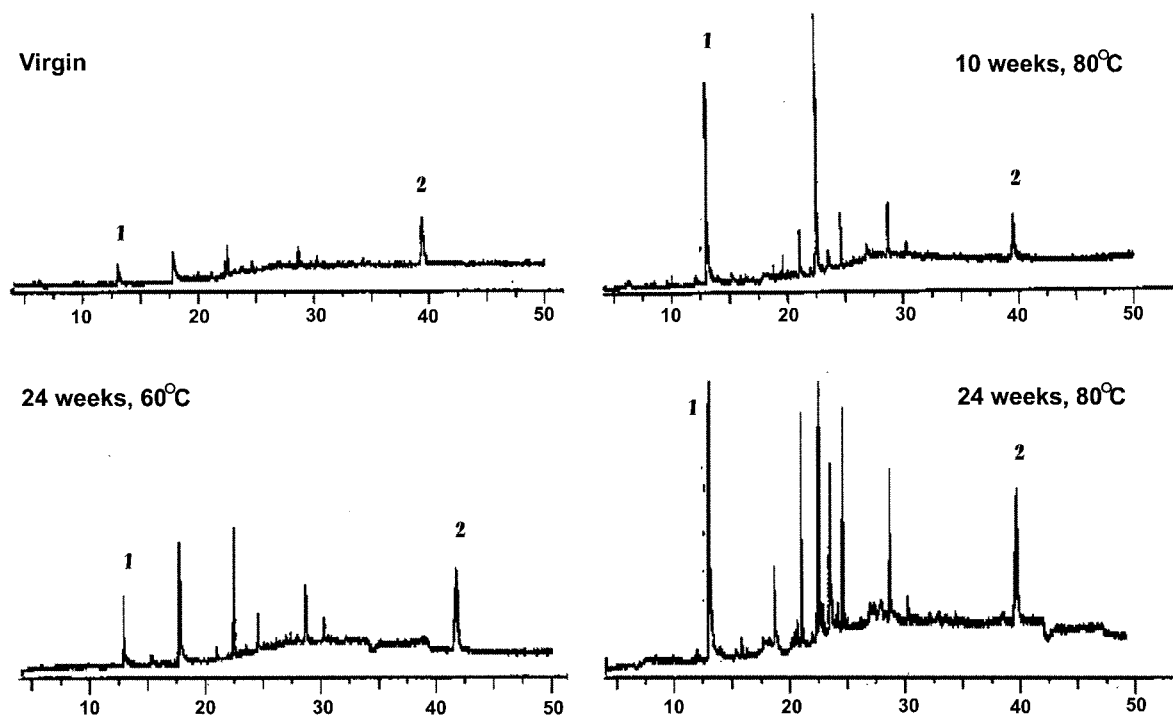


Figure 2 GC-MS chromatograms of the compounds extracted from virgin and thermo-oxidized nitrile rubber by polar polyacrylate fiber. Peak 1 = 2-butoxyethanol, and peak 2 = Tris(2-butoxyethyl)phosphate. Most of the unnumbered peaks are degradation products of TBEP and TMTD.

A method for extraction of Tetrabromobisphenol used as an additive, i.e., mixed with the polymer, has been presented earlier.¹⁷ This method is, however, not suitable for materials where Tetrabromobisphenol A is used as a coreactant, i.e., is covalently bound to the polymeric matrix by, for example, ester-linkages between the phenol group of the flame retardant and the acid group in a polyamide chain. As HS-SPME is able to extract fragments and degradation products of tetrabromobisphenol A, it provides means to indirectly identify coreacted Tetrabromobisphenol A in polyamide 6.6. Furthermore, the high extraction capacity of the PDMS/DVB stationary phase towards aromatic compounds was demonstrated, as the HS-SPME-GC-MS method allowed the extraction and identification of brominated benzenes, from a complex matrix containing only trace amounts of analytes. In addition to the brominated compounds degradation products from a hindered phenol antioxidant were extracted from the polyamides.

Migration of additives during long term ageing of nitrile rubber

Long-term properties of polymers are severely affected and the service life is reduced due to the migration of additives. Figure 2 shows GC-MS chromatograms of the low molecular weight compounds migrating from nitrile rubber during long term ageing at 60 and 80°C. The material contained several additives

e.g. large amount of tris(2-butoxyethyl)phosphate plasticizer (TBEP), which may migrate from the material during use. TBEP, 2-butoxyethanol, a degradation product of TBEP and N-methylbenzylamine were detected already in the virgin material. With respect to release of low molecular weight compounds the material behaved rather well during aging at 60°C. The amount of 2-butoxyethanol and N-methylbenzylamine increased somewhat, but only a couple of new products were formed during 224 days of aging. A large increase in the number and amount of products migrating from the material was, however, seen when the temperature was raised from 60 to 80°C. Most of these volatiles were degradation products of two additives in the material, i.e., Tris(2-butoxyethyl)phosphate and tetramethylthiurame disulfide (TMTD). The identified products include large amount of 2-butoxyethanol and smaller amounts of, for example, N,N-dimethylformamide, dimethylurea, and tetramethylurea. The exact identity of some of the other products seen in the chromatograms was not determined, but they contained characteristic fragments that let us to assign them as degradation products of TBEP and TMTD. The TBEP plasticizer and some of the TMTD degradation products that were extracted and identified in the present study by HS-SPME-GC-MS were not detected in an earlier HS-GC-MS study of the same nitrile rubber even though a higher extraction temperature (100 vs. 80°C) was used during

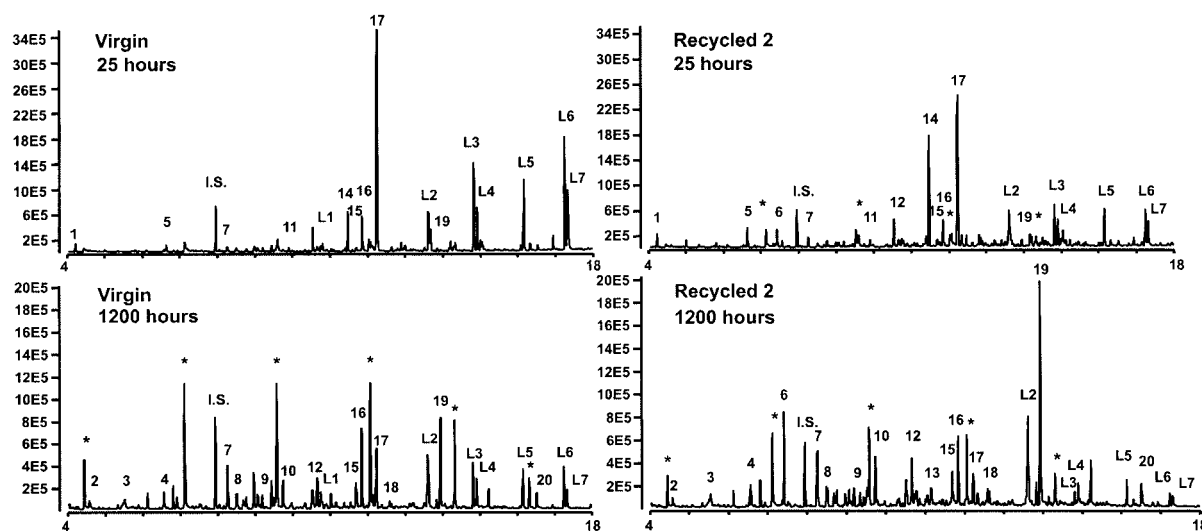


Figure 3 GC-MS chromatograms of the products extracted with SPME from virgin and twice in-plant recycled polyamide 6.6 after thermo-oxidation. The numbered peaks are identified in Table II.

the HS-GC-MS analysis.¹⁸ This shows the ability of HS-SPME to extract even rather nonvolatile compounds present in solid materials.

Several polymer additives including, for example, flame retardants and phthalate and phosphate plasticizers, are suspected to cause various health problems. The migration of additives from polymeric materials is, thus, a potential environmental and health hazard. Phosphate esters have been shown to cause acute toxicity of the central nervous system.¹⁹ TBEP is suspected for interference of drug-protein binding,²⁰ and it also inhibited brain and cholinesterases in treated hens.²¹ TBEP and other organophosphates have been identified in industrial and municipal waste water and considerable amounts of TBEP was found, for example, in tap water in Canada (5400 ng/L).²² TBEP has also been detected in indoor air.²³⁻²⁵ In these studies air was sampled in a charcoal tube, the esters were then extracted with ultrasonication or soxhlet and analyzed by GC-MS. In the case of the water samples liquid-liquid extraction (LLE) or solid phase extraction (SPE) were used.

SPME in the analysis of polymer degradation products

In earlier studies SPME was applied to extraction of degradation products from long-term aged virgin and in-plant recycled materials.^{2,13,16} Figure 3 shows GC-MS chromatograms of the products extracted with SPME from virgin and twice recycled thermo-oxidized polyamide 6.6 by HS-SPME. The numbered peaks are identified in Table I. After 25 h at 100°, nine degradation products were detected in virgin material compared to 11 products in recycled material. After 1200 h the number of degradation products had increased to

14 in virgin material compared to 16 in the recycled material. Altogether, 20 compounds were identified. The identified products included cyclic imides, pyridines, chain fragments, and cyclopentanones. Especially the amount of cyclic imides and the different chain fragments increased rapidly during thermo-oxidation. Most of the cyclopentanones, on the other hand, were present already in the unaged material. In addition to the polyamide degradation products,

TABLE I
The Identity of the Low Molar Mass Compounds
Extracted from Thermo-oxidized Virgin
and Recycled Polyamide 6.6

Peak	Compound
1	Cyclopentanone
2	2-methyl-pyridine
3	Pentanoic acid
4	Butanamide
5	2-ethyl-cyclopentanone
6	2,4,6-trimethyl-pyridine
7	Pentanamide
8	3-(1-methylethyl)-pyridine
9	2-butyl-pyridine
10	<i>N,N</i> -hexamethylenebisformamide
11	2-butyl-cyclopentanone
12	Glutarimide
13	1-propyl-2,5-pyrrolidinedione
14	2-pentyl-cyclopentanone
15	Caprolactam
16	Azepane-2,7-dione
17	2-cyclopentyl-cyclopentanone
18	1-butyl-2,5-pyrrolidinedione
19	1-pentyl-2,5-pyrrolidinedione
20	2-butyl-3,5-dimethylethyl-pyridine
I.S.	Internal standard
*	Silicones from rubber septa
L1-L7	Aliphatic compounds from lubricant

some alkanes and alkenes originating from the lubricants were detected. The high sensitivity of SPME-GC-MS as an analytical tool was demonstrated, as it was able to detect changes caused by oxidation considerably earlier than, for example, tensile testing, DSC, or FTIR.¹⁶ Longer oxidation times were required to detect changes in tensile strength, whereas differences in the degradation products pattern could already be seen during the first 100 h using SPME-GC-MS. SPME-GC-MS was also able to clearly differentiate between virgin and recycled material with respect to their degradation product patterns, while both DSC and FTIR failed to show any significant differences. The recorded degradation product patterns correlated well with the simultaneous changes in mechanical properties as the largest increase in the number and amount of degradation products coincided with the time when rapid decrease in tensile strength was detected.

Hydrocarbons, ketones, furanones, and carboxylic acids were the main products extracted from thermo-oxidized polyethylene by polar carbowax-divinylbenzene SPME fiber. Figure 4 compares the products extracted from thermo-oxidized polyethylene by SPME and by traditional HS-GC-MS analysis. The numbered products including hydrocarbons, ketones, furanones, and carboxylic acid are identified in Table II. The number of products detected in thermo-oxidized LDPE was about three times larger when SPME was

TABLE II
Comparison of Products Extracted With SPME and Headspace-GC-MS from Thermo-oxidized Polyethylene

Peak	Compound	HS-GC-MS	SPME
1	2-heptanone	+	-
2	2-octanone	+	+
3	2-nonanone	+	+
4	2-decanone	-	+
5	2-undecanone	-	+
6	2-dodecanone	-	+
7	formic acid	+	-
8	acetic acid	+	+
9	propanoic acid	+	+
10	butanoic acid	+	+
11	pentanoic acid	+	+
12	hexanoic acid	+	+
13	heptanoic acid	-	+
14	octanoic acid	-	+
15	nonanoic acid	-	+
16	decanoic acid	-	+
17	undecanoic acid	-	+
18	dodecanoic acid	-	+
19	tridecanoic acid	-	+
20	5-methyldihydro-2(3H)-furanone	-	+
21	5-ethyldihydro-2(3H)-furanone	-	+
22	5-propyldihydro-2(3H)-furanone	-	+
23	5-butyldihydro-2(3H)-furanone	-	+
24	5-pentyldihydro-2(3H)-furanone	-	+
25	5-hexyldihydro-2(3H)-furanone	-	+
26	5-heptyldihydro-2(3H)-furanone	-	+
26	5-octyldihydro-2(3H)-furanone	-	+
27	5-octyldihydro-2(3H)-furanone	-	+

The SPME was performed with carbowax-divinylbenzene fiber.

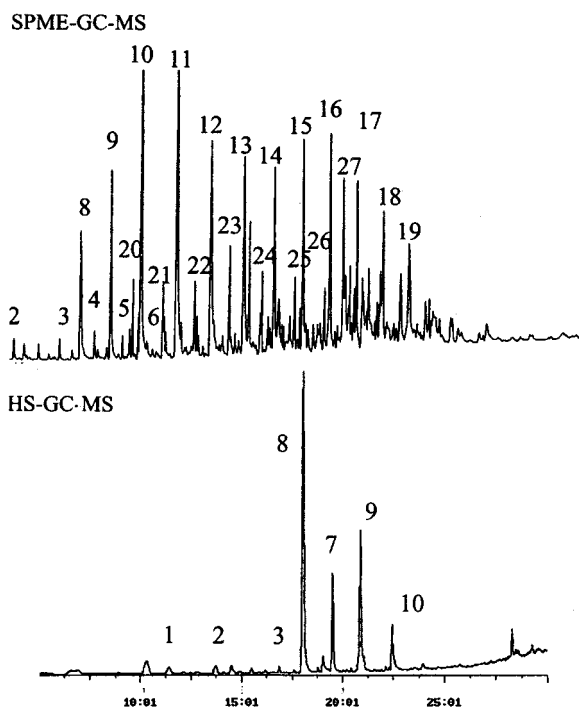


Figure 4 GC-MS chromatograms showing the products extracted from thermo-oxidized polyethylene by SPME, polar carbowax fiber and headspace-GC-MS. The numbered peaks are identified in Table I.

used compared to HS-GC-MS. The SPME method allowed the identification of homologous series of carboxylic acids, ketones, and furanones while only a few carboxylic acids (C1–C6) and traces of a few ketones were detected by HS-GC-MS. In accordance with the results obtained for nitrile rubber, SPME was more effective in extracting less volatile products such as longer carboxylic acids and larger furanones.

CONCLUSIONS

SPME, combined with GC-MS, can be used as a rapid quality control tool to screen for unwanted compounds, for example, different brominated flame retardants in polymeric materials collected for recycling. The developed SPME method extracted several degradation products of brominated flame retardants from polyamide 6.6 scrap and provides, thus, even a way to indirectly identify flame retardants, which are covalently bonded to the polymer matrix. HS-SPME-GC-MS analysis showed that Tris(2-butoxyethyl)phosphate plasticizer and several degradation products of the plasticizer and other additives migrated from nitrile rubber during long-term aging. There was a large increase in the number and amount of products that

migrated from the nitrile rubber when the aging temperature was raised from 60 to 80°C. The ability of SPME to extract products with low volatility was demonstrated as it was able to extract TBEP plasticizer, that was not detected in an earlier study with traditional HS-GC-MS. In accordance, SPME extracted several rather nonvolatile carboxylic acids and furanones from oxidized LDPE, while only the shortest carboxylic acids were detected by HS-GC-MS. SPME was a sensitive tool to detect early signs of degradation in polymeric materials caused by, for example, oxidation or recycling. In conclusion, SPME has a potential to become a valuable tool for polymer characterization equally applicable for predicting long-term properties and degradation mechanisms of polymers as well as for rapid quality assessment of plastic materials.

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