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Microwave Heating Causes Rapid Degradation of Antioxidants in Polypropylene Packaging, Leading to Greatly Increased Specific Migration to Food Simulants As Shown by ESI-MS and GC-MS

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ABSTRACT: Microwave heating of commercial microwavable polypropylene packaging in contact with fatty food simulants caused significant antioxidant degradation and increased specific migration as shown by electrospray ionization−mass spectrometry (ESI-MS) and gas chromatography−mass spectrometry (GC-MS). Degradation of the antioxidants Irgafos 168 and Irganox 1010 was not detected during conventional heating of polypropylene packaging at the same temperature. The migration into aqueous food simulants was primarily restricted by the water solubility of the migrants. Using isooctane as fatty food simulant caused significant swelling and greatly enhanced overall migration values compared to the other fatty food simulant, 99.9% ethanol, or the aqueous food simulants 10% ethanol, 3% acetic acid, or water. ESI-MS spectra clearly reflected the overall migration values, and the number and amount of compounds detected decreased as the hydrophilicity of the food simulant increased. ESI-MS was shown to be an excellent tool for the analysis of semivolatile migrants and a good complement to GC-MS analysis of volatile migrants.

KEYWORDS: polypropylene, antioxidants, migration, food simulant, degradation

INTRODUCTION

Food packaging materials should be designed to minimize migration of additives and other compounds from the packaging into food during storage or processing of food. Food is often microwave heated directly inside the polymer package. Knowledge of the effect of microwave heating on the polymer packaging and especially on the migration of chemical compounds from the polymeric materials into different food types is important for the selection and manufacturing of good packaging materials for microwave use. Plastic food contact materials are a major source of contaminants, many of which are unidentified and have unevaluated toxic properties. Many potential migrating compounds from commodity plastics are listed in European Union Directive 2002/72/EC together with specific migration limits (SML) of these substances migrating into food or food-simulating liquids (FS).[1]

Polypropylene (PP) is one of the most commonly used packaging materials available on the market. Of the different PP qualities, such as PP homopolymer (PP), PP copolymer (PP-C), and random copolymer (PP-R), PP-R generally results in the highest diffusion rates,[2−5] which could be coupled to the lowest degree of crystallinity. However, the initial sorption rate for small penetrants in polypropylenes was shown to be independent of crystallinity at degrees of crystallinity below 50%.[6] There are many studies on migration from food packaging to food or food simulants at elevated temperatures and also some studies on the effect of microwave heating in ordinary microwave oven, which leaves the exact heating temperature unknown. Isothermal microwave heating at known temperature allows the separate evaluation of microwave and thermal effects. A microwave-assisted extraction (MAE) device is ideal for this purpose.[7] Studies on the effect of microwaves on diffusion of common polar and nonpolar solvents into polyethylene, polyvinyl chloride (PVC), and silicone rubber have shown that microwaves have little or no effect compared to conventional heating.[8] In accordance, our previous study on migration from PP food packaging showed that microwaves had no significant effect on the migration of antioxidants.[2] In contrast, overall migration to food simulants from PVC displayed a marked increase using 3 min of microwave heating at full effect over conventional heating compared to other polymer types such as polypropylene, polyethylene, and polyamide,[9] and microwave heating increased the diffusion of ethylene oxide in PVC.[10]

Garde et al. characterized the migration of antioxidants from PP packages during conventional heating into different food simulants and found that the swelling food simulant heptane greatly increased the migration of antioxidants.[11] In accordance, our previous study on migration of antioxidants showed that highly swelling isooctane as food simulant greatly increases the migration of antioxidants during microwave heating at higher temperatures, corresponding to diffusion coefficient increases by factors of 100−1000.[2] A large number of commercial PP food packages have been characterized for their antioxidant and antioxidant degradation product contents. Most of them contained Irgafos 168 and Irganox 1010, and some of them contained smaller amounts of degradation products such as 2,4-bis(1,1-dimethylethyl)phenol.[12] The toxicity of this compound has been evaluated, and studies on rat revealed no-observed-adverse-effect levels (NOAEL) of 5 and 20 mg/(kg·day) for newborn and young rats, respectively.[13] Other potential migrants from PP based packaging are, for example, UV and hindered amine light stabilizers (HALS).[14,15]

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Common instruments often used for the analysis and detection/identification of migrants from polymers are high-performance liquid chromatography (HPLC)[2,12,16,17] or liquid chromatography−mass spectrometry (LC-MS)[15,20] for semivolatiles and gas chromatography−mass spectrometry (GC-MS)[18,19] for volatile substances. The separation of low molecular weight substances from water prior to GC-MS analysis can be achieved by solid phase microextraction (SPME) using multiple headspace extraction (MHE). With MHE the same sample is extracted multiple times and the total amount in the sample is quantifiable from the sums of the peak areas, thus eliminating matrix effects. MHE is generally a convenient technique for the quantification of compounds when standard preparation in an identical matrix is difficult, for example, in heated food simulants. The theory behind MHE has been described earlier.[21,22] Multiple headspace−solid phase microextraction (MHS-SPME) has earlier been used to quantify 2-cyclopentylcyclopentanone in polyamide,[18] and the method also works under nonequilibrium conditions.[23]

Previously, migration of antioxidants Irgafos 168 and Irganox 1010 from PP, PP-C, and PP-R into different food simulants during microwave heating was determined by HPLC.[2] In this case similar migration levels were detected during both microwave heating and conventional heating at 80 °C. However, microwaves could selectively increase the diffusivity of small and polar additives in the polymer. They could further influence the polymer matrix, causing localized spot heating effects and degradation or consumption of incorporated additives. Sorption of food simulants could further promote migration and/or antioxidant degradation during microwave heating. To address these questions, specific and overall migration during microwave heating of polypropylene packaging in contact with different food simulants was determined and compared to migration during conventional heating at the same temperature. Because many of the migrating compounds were anticipated to have low volatility, electrospray ionization mass spectrometry (ESI-MS) was evaluated as a new complementary tool to GC-MS to follow specific migration and also to correlate the migration of higher molecular weight compounds to the overall migration values.

MATERIALS AND METHODS

Materials. Plastic food containers of polypropylene copolymer (PP-C) and polypropylene random copolymer (PP-R) were commercial food boxes suitable for microwave oven heating and purchased from a local supermarket. The PP-C package was nontransparent and white, whereas the PP-R package was clear and transparent. The mean thicknesses of the polymer packages were 0.13 cm for PP-C and 0.12 cm for PP-R. Polymer packages were cut into small sample pieces, and the surface areas of the pieces (approximately 10 cm^2/sample) were calculated from the sample weights, densities, and measured thicknesses.

Water (LC-MS grade), chloroform (100% HPLC grade), and methanol (99.9% LC-MS grade) were obtained from Fisher. Ethanol (99.9% chromatography grade) and isooctane (2,2,4-trimethylpentane) (99.0% LC grade) were obtained from Merck. Acetic acid (99.5%), 2,4-dimethylbenzaldehyde (90+%), 2,4-bis(1,1-dimethylethyl)phenol (97%), and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (98%) were obtained from Acros. 4-Ethoxybenzoic acid ethyl ester (98%) was obtained from Alfa. Irgafos 168 (tris(2,4-*tert*-butylphenyl) phosphite) and Irganox 1010 (pentaerythritol tetrakis[3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate]) were obtained from Ciba Specialty Chemicals (now BASF). Isooctane and 2,4-dimethylbenzaldehyde are flammable. 2,4-Dimethylbenzaldehyde is toxic through inhalation, and isooctane and chloroform can cause damage to the eyes and lungs through ingestion, and vapor can cause drowsiness and dizziness. Use eye and hand protection and work in fume hood as much as possible.

Sample Preparation. Samples of PP-C and PP-R were heated in the different food simulants water, 10% ethanol, 99.9% ethanol, 3% acetic acid, and 90:10 isooctane/ethanol. The samples were heated with microwaves and as a comparison at the same temperature on a heating plate.

Microwave Heating. A MAE device was used to heat samples by microwaves. The MAE device was a CEM MES-1000, a multimode type microwave solvent extraction system with a rotating turntable with a maximum effect of 950 W. A sample of the polymer package was cut into a small piece weighing 0.5−2 g and was put into the MAE device's Teflon vessel. Thereafter, 10 mL of food simulant (FS) was added and the vessel closed gastight. Four sample vessels were heated simultaneously in the MAE device, and the temperature was automatically held constant by using a temperature probe measuring the FS temperature. Blank samples of pure food simulants without any polymer samples were also heated for the same durations and temperatures as the samples with polymer. The effect setting on the MAE device was 50% for the ethanol samples, 10% for the ethanol and water samples, and 3% for the acetic acid samples because a higher effect caused the temperature to increase too far above the set temperature for the current sample amount and number of vessels heated simultaneously (four plus blank vessel). Pure isooctane cannot be heated with microwaves due to lack of polarity; for this reason 10% ethanol had to be added to the isooctane samples. Because of this small amount of ethanol, the effect setting on the MAE device had to be 100% on isooctane samples for the temperature to reach 80 °C. After the heating time, the samples were allowed to slowly cool to below 30 °C, and thereafter the vessels were opened and the FS was withdrawn and put into 20 mL glass vials, sealed, and stored for later analysis.

Conventional Heating. For the migration determination during conventional heating, approximately 0.5 g of a polymer sample was put into a 20 mL glass vial, 10 mL of FS was added, and the vial was sealed. The vial was then immersed in a preheated silicone oil bath heated on a heating plate and held at a constant temperature using an electronic temperature regulator probing the oil temperature. Blank samples of pure food simulants without any polymer samples added were also heated for the same durations and temperatures as the samples. After the heating time, the sample vials were removed from the oil bath and allowed to slowly cool to room temperature, after which the vials were opened and the polymer samples were removed. The vials containing only the FS were then resealed and stored for later analysis.

Overall Migration. Some of the heated polymer samples were weighed before and immediately after heating and put into a vacuum oven and left there for several weeks at room temperature to evaporate the absorbed FS. The evaporation of samples under vacuum was periodically checked, and 100% FS evaporation was assumed when the sample weight had stopped decreasing between three consecutive checks.

Sample Preparation for EI-MS. Samples for ESI-MS analyses were prepared by evaporating heated sample and blank FS extracts from the vials with a small continuous flow of nitrogen at room temperature until no liquid remained. One milliliter of 50:50 methanol/water (LC-MS grade purity) mixture was then added to the sample vials, which were sealed and ultrasonicated for approximately 5 min. The solution was then filtered through a 0.45 μm filter-tip using a glass syringe and stored in a refrigerator.

Standard Preparation. *Isooctane and Ethanol Food Simulants.* A standard solution was used to quantify analytes in ethanol, 90:10 isooctane/ethanol, and dissolved/solvent extracted polymers with GC-MS. It was prepared by dissolving identified substances in ethanol to a

concentration approximately within 1 order of magnitude to the concentration in the samples.

Water FS. A 10% ethanol/water standard solution for MHS-SPME analysis to quantitate water migration was prepared by weighing in and dissolving small amounts of all compounds in ethanol, adding an amount of that solution to a 20 mL headspace vial, and then diluting with water until a 10% ethanol solution was obtained with the standard compounds in concentration range from 1 to 20 μg/L.

Degradation of Antioxidants. Standard solutions of degraded antioxidants were prepared by dissolving Irgafos 168 and Irganox 1010 in ethanol, 90:10 isooctane/ethanol, and chloroform and heating them for 1 and 24 h at 80 °C in the MAE and on the heating plate. After cooling to room temperature, the solutions were transferred to glass vials and stored for later analysis. For the ESI-MS analysis of the degraded antioxidant standards, the solutions were evaporated and redissolved using the same procedure as described earlier for the preparation of ESI-MS samples.

Dissolution−Precipitation and Solvent Extraction. Total polymer volatile contents were determined by dissolution−precipitation for PP-R and solvent extraction for PP-C. Approximately 0.1 g of PP-R sample was weighed and added to a small vial, which was immersed in 5 mL of chloroform. The vial was sealed, heated to 80 °C, and shaken for a couple of minutes to dissolve the sample. The polymer sample was then reprecipitated by adding 5 mL of ethanol, stored for at least 1 day in a refrigerator, filtered through a 0.45 μm filter-tip with a glass syringe, and stored for later analysis. PP-C was insoluble in all tried solvents, so approximately 0.3 g of PP-C sample was instead extracted for 24 h at 80 °C in a sealed vial containing 5 mL of chloroform in a silicone oil bath on a heating plate. After the heating, the sample was removed, and the extract was filtered through a 0.45 μm filter-tip and stored for later analysis. The dissolution−precipitations and extractions were carried out in triplicate for each polymer.

GC-MS. The 90:10 isooctane, ethanol, and water FS extracts were analyzed on a Finnigan MAT GCQ system (San Jose, CA) with a Gerstel MPS2 autosampler (Mülheim an der Ruhr, Germany). The column was a wall-coated open tubular (WCOT) CP-SIL 8 CB low bleed/MS 0.25 mm × 0.25 μm × 30 m from Varian. Helium (99.9999% purity) with a constant linear velocity of 40 cm/s was used as a carrier gas. The temperature program of the GC oven was 40 °C for 1 min, thereafter heating with a constant rate of 10 °C/min up to 270 °C, and finally holding at 270 °C for 15 min. The mass scan range of the MS detector was set to 35−400 (m/z). EI mode was used with electron energy of 70 eV. The FS extracts were injected directly after filtration through a 0.45 μm filter with a 10 μL microsyringe. The injection volume was 1 μL. Quantification was made by one-point calibration by the ethanol standard solution in duplicate. Peak integration was carried out on the most intense mass fragment (m/z) ion detector response for a respective compound. The water extracts and the 10% ethanol standards were extracted with SPME before GC-MS injection. Positive identification of compounds in samples was made if the standard and the sample compound's mass spectra were identical and the retention time of the sample compound was within ±0.05 min of the retention time of the corresponding standard compound. Unidentified compounds' mass spectra were matched against the National Institute of Standards and Technology (NIST) library database (MS search program v. 1.7) to obtain the closest match.

SPME. SPME was used to extract the migrants from water samples before the subsequent GC-MS analysis. To quantify the compounds that migrated into water, MHS-SPME was carried out both on water samples and on standard solutions in 10% ethanol. The SPME fiber was a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber from Supelco (Bellefonte, PA). Ten milliliters of the sample and standard solutions was added to 20 mL headspace vials and then capped with crimp seals with PTFE/silicone septa. The extraction was carried out by penetrating the septum of the preheated vial with the fiber needle and exposing the fiber to the headspace above the solution under constant agitation of the vial. The extraction time was 30 min, and the temperature was 80 °C. After the extraction time, the needle was withdrawn and immediately injected into the GC injection port, where the temperature was 250 °C. The fiber was left in the injection port for 7 min to completely desorb all of the analytes from the fiber. Before MHE extraction of the 10% ethanol standard solution, the linearity of the extracted amount versus the amount in solutions for all of the compounds contained in solution was checked by extracting different concentrations of the standard solution, and all of the compounds were shown to be within the linear range of the fiber. Both the samples and the standard solutions were extracted four consecutive times and recapped after each extraction to stop the analyte or solvent vapor to pass through the septum hole during heating. The standard solution was analyzed in triplicate, and the samples were analyzed in duplicate. The mean value of all three areas in each parallel standard extraction was used for the determination of the slopes of ln(peak area) as function of extraction number (q'). For the unknown samples the amounts of the duplicate samples were determined individually and averaged later. The area sums of the standard and unknown sample compounds were calculated with the equation[21]

$$A_s = \frac{A_1}{1 - e^{q'}}$$

where A_1 is the area for the first extraction. The migrated amounts were then calculated by

$$m_{sample} = \frac{A_{s,sample}}{A_{s,standard}} \times C_{standard} V_{standard}$$

where m_{sample} is the mass of migrated analyte, $A_{s,\ sample}$ and $A_{s,\ standard}$ are the area sums of the sample and standard, $C_{standard}$ is the standard migrant concentration, and $V_{standard}$ is the standard solution volume.

ESI-MS. Electrospray ionization mass spectra were acquired with a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). Sample solutions in 50:50 methanol/water were directly infused into the mass spectrometer with a continuous flow of 5 μL/min using a syringe pump. The instrument was set at positive mode, and the LCQ ion source was operated at 5 kV. The capillary temperature was set at 175 °C, nitrogen was used as nebulizing gas, and helium was used as damping and collision gas.

Differential Scanning Calorimetry (DSC). Melting temperature (T_m) and degree of crystallinity of original and microwave heated samples, after complete evaporation of the food simulants, were determined by DSC using a Mettler-Toledo DSC 820 STAR^e system with a GC100 gas controller. The sample amounts were 3−4 mg each, and the samples were heated first from 25 to 300 °C at 10 °C/min, then cooled from 300 to 0 °C at −10 °C/min, and then heated from 0 to 300 °C at +10 °C/min again. The heating scans were performed with the sample under 80 mL/min constant nitrogen gas flow. The crystallinity was calculated with the equation

$$X_c = \frac{100 \times \Delta H_f}{\Delta H_f^0}$$

where X_c is the degree of crystallinity, ΔH_f is the integrated melting peak area from the thermogram, and ΔH_f^0 is the melting enthalpy of a 100% crystalline polymer sample. The melting enthalpy used for 100% crystalline material was 209 J/g.[24]

Fourier Transform Infrared Spectroscopy (FTIR). The identity of the polymer packages was confirmed as polypropylene by FTIR surface analysis. The FTIR system was a Perkin-Elmer Spectrum 2000 FTIR with a Specac P/N 10,500 series single-reflection attenuated total reflectance (ATR) diamond accessory. Sixteen scans were made for each sample, and these were averaged to eliminate noise. The spectra of the

Table 1. Crystallinity of the Polypropylene Samples before and after Microwave Heating in Different Food Simulants Taken from the First/Second Heating Scan[a]

	crystallinity (%)						
sample	original	90:10 isooctane/ethanol	ethanol	10% ethanol	3% acetic acid	H_2O	compounds present ± SD (μg/g)[a]
PP-C	38/42	34/38	36/41	36/41	35/41	35/41	2,4-DTB: 210 ± 117 2,6-DTBQ: 13 ± 7
PP-R	34/37	38/38	34/38	35/37	34/36	34/37	dimethylbenzaldehyde: 54 ± 12 2,4-DTB: 87 ± 41

[a] The volatile compounds detected after dissolution−precipitation or solvent extraction of nonheated samples are also given. Abbreviations: 2,4-DTB, 2,4-bis(1,1-dimethylethyl)phenol; 2,6-DTBQ: 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

samples were compared to a known spectrum of polypropylene to identify them.

RESULTS AND DISCUSSION

Two polypropylene copolymers (PP-C and PP-R) were heated in contact with food simulants for aqueous, alcoholic, and fatty foods to determine the overall and specific migration and the effect of conventional versus microwave heating. Volatile migrants were identified and quantified by GC-MS, whereas ESI-MS was applied as a new tool for following the migration of semivolatiles such as polymer additives.

Polymer Properties and Volatile Content. The original concentration of volatile compounds in the PP-C and PP-R containers was determined by dissolution−precipitation or solvent extraction, followed by GC-MS analysis. The compounds detected are given in Table 1. 2,4-Bis(1,1-dimethylethyl)phenol (2,4-DTB) and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (2,6-DTBQ) are probably degradation products from the antioxidants Irgafos 168 and Irganox 1010, which are known to be present in the samples.[2] A standard solution of the antioxidants Irgafos 168 (0.17 g/L) and Irganox 1010 (0.15 g/L) in chloroform was heated on a heating plate for 24 h. The heating did not cause any detectable increase in 2,4-DTB or 2,6-DTBQ or other compounds. No additional compounds or degradation products are, thus, expected to be formed during the extraction procedure due to degradation of the antioxidants.

The degree of crystallinity for original samples and after heating in different food simulants is shown in Table 1. The heating in different food simulants did not cause any significant changes in the crystallinity. Only the degree of crystallinity for PP-R microwave heated in 90:10 isooctane/ethanol increased a few percent. This indicates that some crystallinization took place during heating of PP-R in isooctane due to the increased chain mobility induced by the swelling. Melting temperatures (not shown in the table) did not change after heating in contact with food simulants and were, for PP-R, 148/147 °C, and for PP-C, 168/163 °C, as determined from the first and second heating scans, respectively.

Overall Migration and Solvent Absorption. The absorption of different food simulants during microwave and conventional heating can be seen in Figure 1. PP-C and PP-R both absorbed significantly larger amounts of isooctane/ethanol and slightly more ethanol compared to the other food simulants. The less crystalline PP-R absorbed slightly more isooctane than PP-C during both microwave and conventional heating. While the absorption of isooctane/ethanol was profound, the absorption of the aqueous simulants by PP-C and PP-R was in most cases very

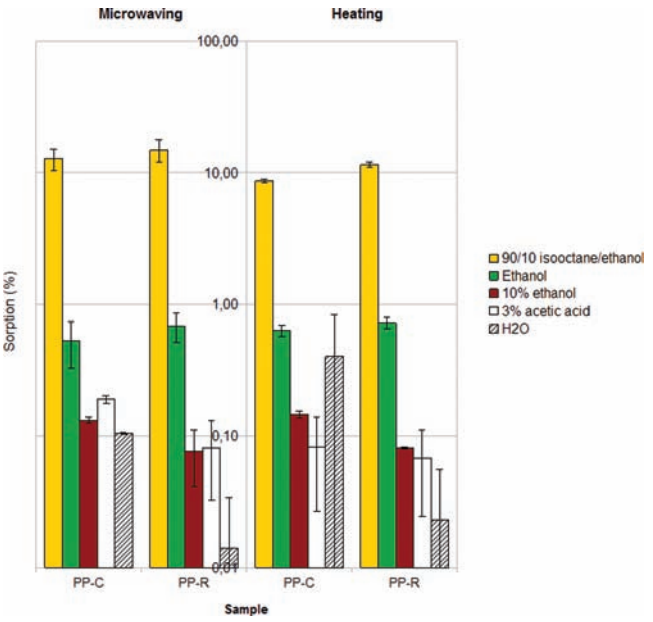

Figure 1. Comparison of food simulant absorption by PP-C and PP-R during 1 h of microwave and conventional heating at 80 °C.

small. Generally, there were no large differences in the solvent absorption during microwave heating and conventional heating. However, the absorption of isooctane by PP-C and PP-R was larger during microwave heating. The calculated solubility parameter for the mixture isooctane/ethanol is 15.5 and that for PP (homopolymer) 18.8 $MPa^{0.5}$, yielding a difference of only 3.3 $MPa^{0.5}$.[25]

Overall migration values for microwave and conventionally heated samples are given in Figure 2. Overall migration from both samples into isooctane was very large during both microwave and conventional heating, probably due to the swelling of polypropylene by isooctane. In accordance, the migration values into isooctane were higher for PP-R compared to PP-C and were further slightly higher for the microwave heated samples compared to the conventionally heated samples. Otherwise, the overall migration from PP-C into ethanol and 10% ethanol appeared to be somewhat higher during conventional heating compared to microwave heating. The overall migration limit (OML) set by the European commission for plastic materials is 60 mg/kg of food, or 100 μg/cm^2.[1] It can be concluded that microwave heating only increased the overall migration into isooctane, probably due to the combined effect of swelling, higher diffusion rate, and antioxidant degradation. Overall migration into

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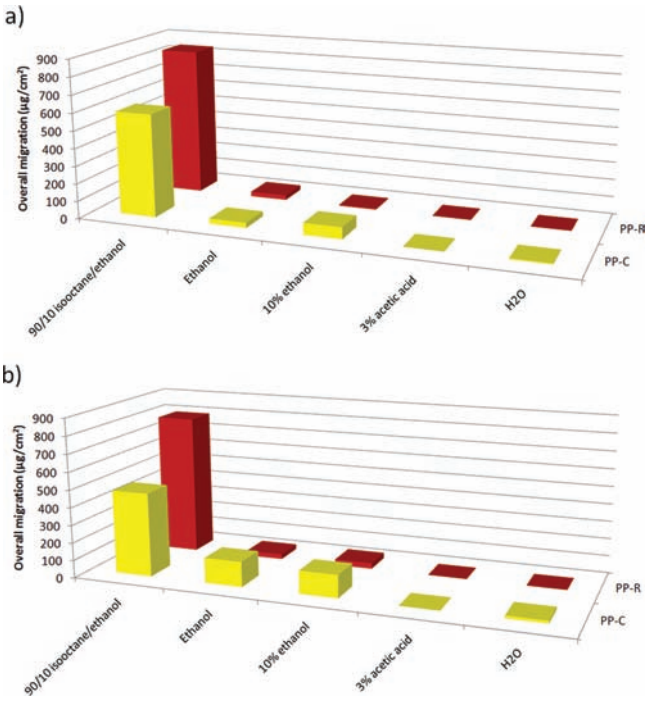

Figure 2. Overall migration from PP-R and PP-C into different food simulants during 1 h of (a) microwave and (b) conventional heating at 80 °C.

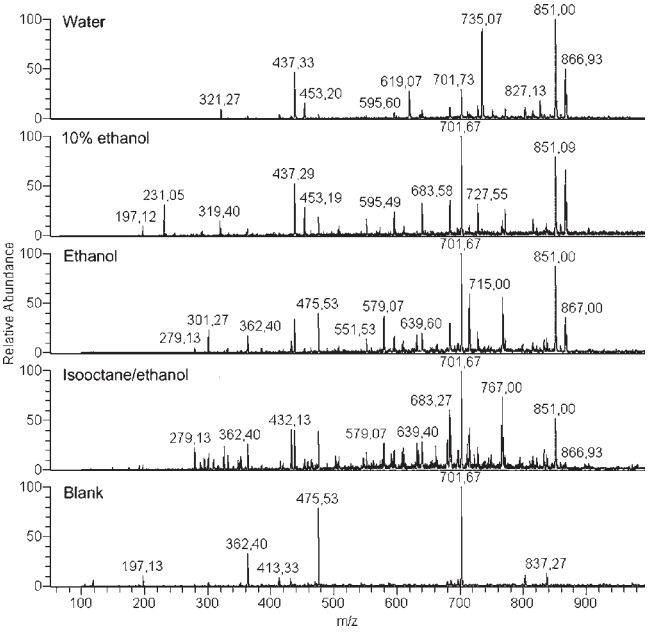

Figure 3. ESI-MS spectra showing the compounds that migrated from PP-R into water, 10% ethanol, ethanol, and 90:10 isooctane/ethanol during 1 h of microwave heating. The blank sample shown here consisted of the same amount of 90:10 isooctane/ethanol microwave heated for 1 h at 80 °C.

the swelling isooctane during both microwave and conventional heating greatly exceeded the overall migration limit of 100 μg/cm^2 during 1 h of heating at 80 °C.

ESI-MS Analysis of Semivolatile Migrants. ESI-MS was evaluated as a new tool for following the migration of less volatile

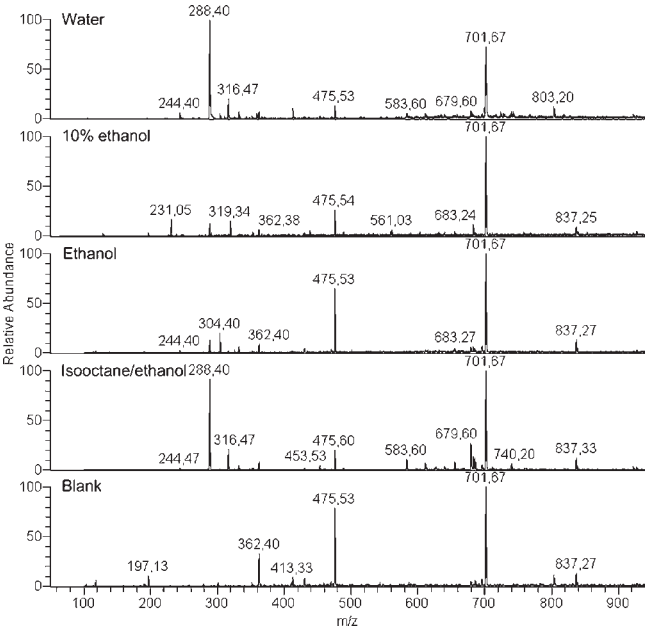

Figure 4. ESI-MS spectra showing the compounds that migrated from PP-C into water, 10% ethanol, ethanol, and 90:10 isooctane/ethanol during 1 h of microwave heating. The blank sample shown here consisted of the same amount of 90:10 isooctane/ethanol microwave heated for 1 h at 80 °C.

migrants. ESI-MS spectra of the compounds that migrated from PP-R and PP-C into different food simulants after microwave heating for 1 h in isooctane/ethanol, ethanol, 10% ethanol, and water can be seen in Figures 3 and 4. The heating temperature was 100 °C for water and 80 °C for the other food simulants. It is evident that larger numbers of semivolatile compounds and in higher concentrations migrated from PP-R compared to PP-C, which for isooctane/ethanol coincides with the higher overall migration during microwave heating (Figure 2). ESI-MS spectra of PP-R and PP-C isooctane and ethanol extracts after conventional heating of samples for 1 h at 80 °C were also acquired, but no clear differences could be seen in the intensities of most of the high molecular weight peaks between microwave and conventionally heated samples. Even though higher heating temperature was used for water samples, it can be seen that for PP-R, the number of peaks and their intensities increase in order of increasing hydrophobicity for the food simulant, which is in correlation with the overall migration from PP-R (Figure 2). The spectra acquired after migration into the acidic food simulant, 3% acetic acid, had very low peak intensities and did not reveal any additional peaks.

In the mass spectra of PP-R showing the migration to water and 10% ethanol (Figure 3), there were two predominant peaks with high masses at m/z 851 and 867. These masses were also large in ethanol extract, but they decreased in isooctane/ethanol. A series of compounds with a mass difference of 44 amu ranging from 551 to 815 was clearly seen in the 10% ethanol extracts. This series of compounds is tentatively identified as poly(ethylene glycol) (PEG) oligomers, which have the characteristic peak series with a mass difference of 44 amu originating from the repeating unit weight ($-CH_2-CH_2-O-$). PEG is frequently used as a plasticizer for other polymers. These oligomers also migrated to water, but to a smaller extent. When ethanol and isooctane were used as food simulants, these peaks were in large

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Table 2. Low Molecular Weight Compounds That Migrated from the Samples into 90:10 Isooctane/Ethanol during 1 h of Microwave and Conventional Heating at 80 °C and Calculated Theoretical Migration Values[a]

			microwaving (ng/cm^2)		heating (ng/cm^2)		calculated migration/total content (ng/cm^2)	
RT (min)	compound [b]	CAS Registry No.	PP-C	PP-R	PP-C	PP-R	PP-C	PP-R
10.8	dimethylbenzaldehyde		ND (2)	137	ND (2)	11		1900/2800
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	184	290	ND (4)	ND (4)	250/700	
14.4	*4-hydroxy-1H-indole-3-carboxylic acid 35%*	24370-76-1	D	ND	D	ND		
14.6	2,4-bis(1,1-dimethylethyl)phenol	96-76-4	6650	8800	9	23	4400/11000	1900/4500
19.2	*7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione 61%*	82304-66-3	D	D	D	D		
19.4	*methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate 95%*	6386-38-5	D	D	D	D		

[a] Detection limits are given in parentheses. The compounds written in italics were only tentatively identified by NIST library, and no positive identification with corresponding standards was performed. D, detected but not quantified; ND, not detected. [b] Detection limit of 4-ethoxybenzoic acid ethyl ester: 6 ng/cm^2 in both ethanol and isooctane/ethanol food simulants.

Table 3. Low Molecular Weight Compounds That Migrated from the Samples into 99.9% Ethanol during 1 h of Microwave and Conventional Heating at 80 °C and Calculated Theoretical Migration Values[a]

			microwaving (ng/cm^2)		heating (ng/cm^2)		calculated migration/total content (ng/cm^2)	
RT (min)	compound	CAS Registry No.	PP-C	PP-R	PP-C	PP-R	PP-C	PP-R
10.8	dimethylbenzaldehyde		ND (2)	72	ND (2)	ND (2)		1900/2800
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	ND (4)	ND (4)	ND (4)	ND (4)	250/700	
14.4	*4-hydroxy-1H-indole-3-carboxylic acid 35%*	24370-76-1	D	ND	D	ND		
14.6	2,4-bis(1,1-dimethylethyl)phenol	96-76-4	1200	504	12	10	4400/11000	1900/4500
19.2	*7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione 61%*	82304-66-3	D	D	ND	ND		
19.4	*methyl 3-(3,5-ditertbutyl-4-hydroxyphenyl) propionate 95%*	6386-38-5	D	D	ND	ND		

[a] Detection limits are given in parentheses. D, detected but not quantified; ND, not detected.

part obscured by other interfering peaks and were, thus, difficult to distinguish. PEG oligomers were, however, not present in the conventionally heated ethanol samples. Of the migrants from the PP-C samples, the most intense ion was found at m/z 288. This compound was detected in all food simulants but in various amounts (Figure 4). Furthermore, the MS-MS analysis on this ion revealed fragments at 88, 106, 244, and 270.

In general, the number and intensity of compounds detected in the mass spectra of PP-C were much smaller compared to the mass spectra of PP-R samples. The number and amount of migrants decreased as the hydrophilicity of the food simulant increased; that is, the highest amount of migrants was found when isooctane was used as a food simulant, in correlation with the overall migration. Many of the compounds that migrated were identical between the two polymers and originated from antioxidant degradation. In addition PEG oligomers were shown to migrate from PP-R. The results show that ESI-MS is an excellent tool for the analysis of semivolatile migrants, such as polymer additives, in food simulants and that it is a good complement to GC-MS analysis of volatile migrants.

Specific Migration into Food Simulants. *Migration into Fatty Food Simulants Ethanol and Isooctane.* The compounds that migrated from PP-C and PP-R into isooctane during microwave and conventional heating are shown in Table 2, and compounds that migrated into ethanol are presented in Table 3. It can be seen that migration from PP-C and PP-R, most clearly the migration of 2,4-DTB, into 90:10 isooctane/ethanol increased significantly during microwave heating compared to conventional heating. In addition, the migration into ethanol increased somewhat. During conventional heating the migration into isooctane/ethanol and ethanol was rather similar, but still, the migration into isooctane/ethanol was somewhat higher compared to the migration into ethanol. Microwave heating mostly increased the migration of 2,4-DTB; for example, the amount that migrated from PP-C during microwave heating compared to conventional heating was higher by a factor of 700 when isooctane/ethanol was used as a FS and by a factor of 100 when ethanol was used as a FS. The significant swelling of PP-C and PP-R in isooctane (Figure 1) is expected to increase the migration of substances as long as the diffusion of solvent into the polymer is at least of comparable speed as the diffusion of migrating compounds from polymer into the food simulants. Also, the microwave field would affect primarily small and polar molecules by setting them in rotating motion and increasing their diffusion rate.

Antioxidant Degradation Caused by Microwave Heating. Figure 5 shows ESI-MS spectra of migrants from microwave and conventionally heated PP-R and degradation products from microwave heated Irgafos 168 standard. The mass spectra clearly show the presence of Irgafos 168 degradation products after microwave heating of PP-R in 90:10 isooctane/ethanol and in ethanol. However, these degradation products were hardly observable after conventional heating of PP-R, which indicates higher antioxidant degradation or consumption during microwave heating of polypropylene compared to conventional heating. Hypothesizing that microwave heating could promote faster degradation of antioxidants compared to conventional heating,

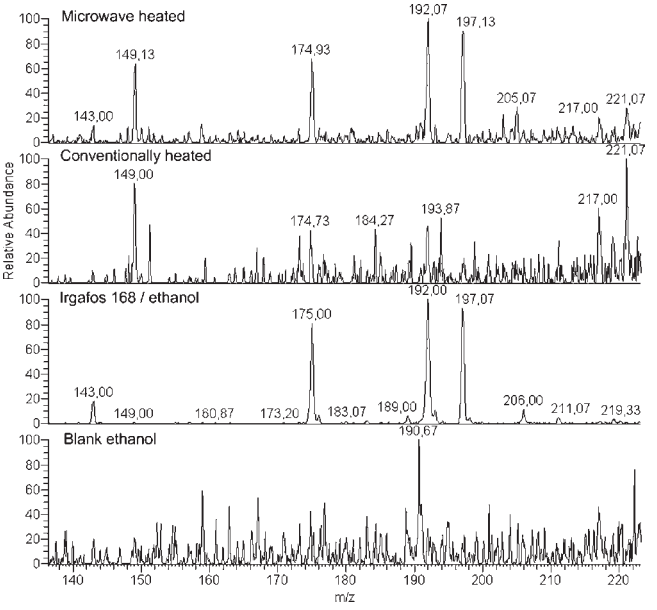

Figure 5. ESI-MS spectra of PP-R microwave heated in 90:10 isooctane/ethanol, PP-R heated conventionally in 90:10 isooctane/ethanol, microwave heated standard of Irgafos 168 (in ethanol), and conventionally heated ethanol blank sample. All of the samples and the standard were heated for 1 h at 80 °C. The spectra of microwave heated PP-R migrants have peaks corresponding to the degradation products of Irgafos 168.

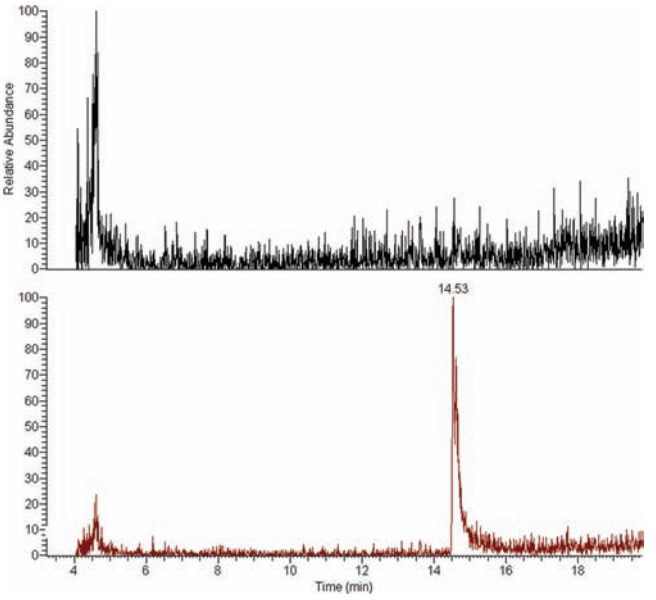

Figure 6. GC-MS chromatograms for Irgafos 168 (0.09 g/L) standard in ethanol (top) and the same standard solution run after microwave heating for 1 h at 80 °C (bottom) showing the degradation of Irgafos 168 to 2,4-DTB (14.53 min). No peak is observed corresponding to nondegraded Irgafos 168 due to low volatility.

Irgafos 168 and Irganox 1010 standards were also heated conventionally in 99.9% ethanol and in isooctane/ethanol for the same time and temperature. GC-MS analysis of heated (1 h, 80 °C) standard solutions of Irgafos 168 and Irganox 1010 confirmed degradation of Irgafos 168 and Irganox 1010 during both microwave and conventional heating in ethanol (see Figure 6). However, no degradation was observed during heating of pure antioxidant standards in isooctane/ethanol. The fact that pure antioxidants even degraded during conventional heating in ethanol could be deduced to ethanol induced hydrolysis or transesterification of Irgafos 168 in the standard solution,[26] whereas the antioxidant in polypropylene matrix could be protected from this effect because it is surrounded by the polymer matrix.

Another interesting finding was that the antioxidant standards did not degrade when heated in isooctane/ethanol solution, whereas the antioxidants embedded in polypropylene matrix degraded during microwave heating. These results, thus, indicate that antioxidants are consumed or degraded during microwave heating of polypropylene packaging due to interactions or reactions between polypropylene and antioxidants. The results also show that the largely increased amount of 2,4-DTB migrating from PP-C and PP-R into 90:10 isooctane/ethanol and ethanol during microwave heating compared to migration during conventional heating could be explained by degradation of Irgafos 168 to 2,4-DTB. Swelling increases the diffusion of larger molecules more compared to smaller molecules because larger molecules are generally more restrained by polymer segments at lower swelling degrees. Because degradation originates from the large antioxidant molecules, the swelling could result in a more pronounced increase in the degradation/migration during heating in isooctane compared to heating in ethanol, as was also seen from these results. The total Irgafos 168 content in PP-R was higher (1000 ppm) compared to that in PP-C (250 ppm),[2] which would also explain the higher amount of 2,4-DTB migrating from PP-R compared to from PP-C. The degree of swelling was also higher during microwave heating compared to conventional heating (Figure 1). According to our previous study the effect of microwaves on diffusion of Irgafos 168 and Irganox 1010 in the polymers was insignificant and the diffusion rate was coherent with the effect of heating temperature only.[2]

Some of the other compounds migrating from PP-C and PP-R could also be degradation/oxidation products of antioxidants, for example, methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate and 7,9-di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione. The first mentioned compound is most likely a degradation product from the antioxidant Irganox 1010 because its molecular structure is identical to a part of the antioxidant molecule. Interestingly, the carboxylic acid analogue of this compound, 3-[3,5-di-*tert*-butyl-4-hydroxybenzyl]propionic acid, has been identified as a hydrolysis product of Irganox 1010 in water.[27] The presence of the methyl ester in these samples therefore indicates that a different degradation mechanism occurred. The second compound also has similarities with the antioxidant structure. 2,4-DTB, 2,6-DTBQ, and 7,9-di-*tert*-butyl-1-oxaspiro-(4,5)deca-6,9-diene-2,8-dione have earlier been identified as migrants from polyolefins.[28] Dimethylbenzaldehyde that migrated from PP-R had a slightly different retention time compared to 2,4-dimethylbenzaldehyde standard, but from the identical mass spectrum it was assumed to be a structural isomer.

Migration into Water. The compounds that migrated into water during microwave and conventional heating are shown in Table 4, which also lists the mean of the duplicate R^2 values for the MHS-SPME extractions. The R^2 values for the standard extractions were in the range from 0.95 to 0.98. Most of the compounds in Table 4 showed high R^2 values, and they were quantified only if R^2 was 0.9 or above. Because of the lower detection limits when using SPME instead of direct injection,

Table 4. Low Molecular Weight Compounds That Migrated from the Samples into Water during 1 h of Microwave and Conventional Heating at 80°C[a]

			microwaving heating				conventional heating			
			migration (ng/cm^2)		R^2 (mean)		migration (ng/cm^2)		R^2 (mean)	
RT (min)	compound	CAS Registry No.	PP-C	PP-R	PP-C	PP-R	PP-C	PP-R	PP-C	PP-R
7.2	*orthoformic acid, tri-sec-butyl ester 60%*	16754-48-6	D	D			D	D		
10.8	dimethylbenzaldehyde		*b*	*b*	*0.836*	*0.500*	0.44	*b*	*0.944*	*0.779*
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	0.87	1.1	*0.915*	*0.910*	0.64	0.74	*0.997*	*0.897*
14.4	*4-hydroxy-1H-indole-3-carboxylic acid 43%*	24370-76-1	D	ND			D	ND		
14.6	2,4-bis(1,1-dimethylethyl)phenol	96-76-4	3.7	4.5	*0.987*	*0.994*	1.7	2.2	*0.985*	*0.981*
14.9	4-ethoxybenzoic acid ethyl ester [c]	23676-09-7	0.57	0.55	*0.971*	*0.965*	ND	0.8		*0.897*
19.2	*7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione 61%*	82304-66-3	D	D			D	D		
19.4	*methyl 3-(3,5-ditertbutyl-4-hydroxyphenyl) propionate 95%*	6386-38-5	D	D			D	D		

[a] D, detected but not quantified; ND, not detected. [b] Not quantified due to low linearity of ln A vs extraction number (R^2). [c] SML = 3.6 mg/kg, 6 μg/cm^2 [1] (6 dm^2 of polymer surface assumed to be in contact with 1 kg of food).

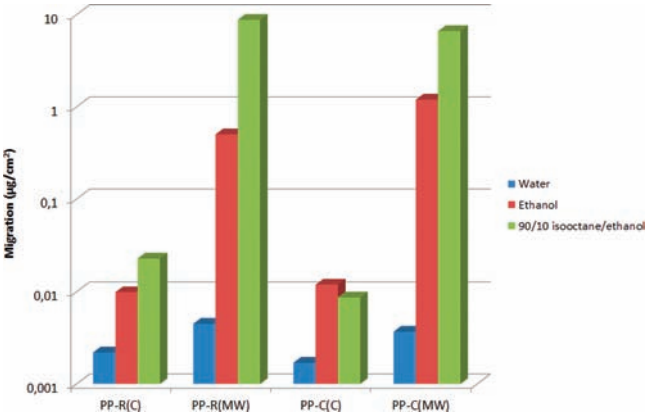

Figure 7. Migration of 2,4-bis(1,1-dimethylethyl)phenol from samples into different food simulants during microwave (MW) and conventional heating (C).

compounds present at lower concentrations could possibly be detected in water compared to analysis of migrants in 90:10 isooctane/ethanol and ethanol. However, migration to water was significantly lower in comparison with migration into isooctane/ethanol and ethanol. This is most likely due to the limited solubility of the migrants in water. In most cases migration during microwave heating was higher compared to conventional heating, but the differences were not large. 4-Ethoxybenzoic acid ethyl ester, a compound included in the list of additives potentially migrating from plastics,[1] was found in low amounts when water was used as a food simulant. Its migration was, however, far lower than its SML.

Effect of Microwave Heating on the Migration of 2,4-Bis(1,1-dimethylethyl)phenol (2,4-DTB). Microwave heating resulted in greatly increased migration values for 2,4-DTB compared to values obtained during conventional heating. The effect of microwave versus conventional heating on the migration 2,4-DTB from PP-R and PP-C is shown Figure 7. A significant increase in migration from both polymers into ethanol and isooctane/ethanol during microwave heating is shown. Migration from PP-R into ethanol was smaller than that from PP-C, probably due to the smaller initial amount of 2,4-DTB in the polymer (Table 1). However, the migration from PP-R into isooctane/ethanol was greater than that from PP-C. This could be due to the degradation of Irgafos 168 in the polymer or the higher degree of swelling of PP-R compared to PP-C or a combination of both factors.

Comparison of Specific Migration between Food Simulants and Theoretical Migration. Migration of selected compounds into water, ethanol, and isooctane/ethanol during microwave heating is presented in Tables 2 and 3 together with theoretically calculated migration values based on the initial migrant concentrations. Values of potential migration at infinite time, corresponding to the total amount in the samples, are also given in the tables for comparison. The mathematical model is described by the EU Commission[29] and is an analytical solution to Fick's second law of diffusion using boundary conditions governed by polymer/FS partition coefficients. Details and further explanation of the equations are also given in refs 30 and 31. Because partition coefficient data were not available, they were set to 1 in all cases, assuming high solubility in the FS. During the present conditions this value would lead to almost complete extraction of analyte at longer extraction times, and the predicted migration is thus the highest possible for a given diffusion coefficient value, due to a high FS/polymer volume ratio of 20. The diffusion coefficients used in the model are estimated high limits at 95% confidence level of experimentally determined coefficients for additives with a broad molecular weight range.[29] It can be seen that migration of all compounds into water and ethanol was far lower than the calculated values. However, the migration of 2,4-DTB from PP-R and PP-C into isooctane/ethanol was higher than the calculated values. In fact, the migration from PP-R was even higher than the total available amount in the polymer. As discussed previously, this could be due to a combination of swelling and antioxidant degradation caused by the heating or ethanol producing more 2,4-DTB.

If the total Irgafos 168 content in the polymer was fully degraded to 2,4-DTB as a worst-case scenario, this would result in an additional migrated amount of 65 μg/cm^2 according to the theoretical worst-case model. With regard to the ability of swelling solvents to increase diffusivity, it must also be taken into account that, although some swelling by food simulants is accounted for in the model's parameters, it is not really suited for highly swelling solvents such as isooctane on polyolefin polymers.[29] More sophisticated models with numerical solutions

to the diffusion equation could be necessary[32] to predict migration in that special case. It can otherwise be seen that migration from the polymer samples during microwave heating was in most cases higher into ethanol and isooctane/ethanol than into water and the experimental migration values were closer to the calculated values. All of the migrating compounds presented in the graphs have relatively high hydrophobicities expressed as octanol−water partition coefficients (log *P* from 3 to 4); therefore, it can be expected that the solubility of the migrants in the polymer is much higher than in water, and it seems evident that solubility is the most significant factor controlling migration of the molecules into water during microwave heating.

During conventional heating the migration into ethanol and isooctane/ethanol was much lower that than the theoretical values, which might indicate that the real partition coefficients were much higher than 1 (i.e., more in favor of the polymer than the FS), which would result in less migration. For the theoretically calculated values to be justified, known partition coefficients should be used whenever possible. The usefulness of the model's ability to evaluate the maximum initial safe concentration of an additive, which is one of its intended purposes,[29] can nevertheless be evaluated. If the real partition coefficients were much higher than 1, the results above indicate that during microwave heating the model has low predictability because microwave heating leads to greatly enhanced diffusion rates, and the model would thus underestimate migration and overestimate the maximum allowable initial concentrations. In addition, the degradation of antioxidants during microwave heating could enhance the migration.

In conclusion, microwave heating of PP-R and PP-C in contact with fatty food simulants caused degradation of antioxidants, which resulted in significantly higher specific migration during microwave heating in comparison to conventional heating. The migration of individual compounds was generally below the established safety limits and theoretically calculated worst-case values. An exception was the Irgafos 168 degradation product 2,4-di-*tert*-butylphenol, which migrated in higher amounts than calculated during microwave heating in isooctane. Due to the further degradation of antioxidants and swelling caused by isooctane, the mathematical model recommended by the EU Commission was limited in its usability to evaluate worst-case migration during microwave heating.

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