Type of Polypropylene Material Significantly Influences the Migration of Antioxidants from Polymer Packaging to Food Simulants During Microwave Heating

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ABSTRACT: Three different polypropylene materials, polypropylene homopolymer (PP), propylene-ethylene random copolymer (PP-R), and propylene-ethylene copolymer (PP-C) are commonly used in plastic containers designed for microwave heating of food. Migration of antioxidants, Irganox 1010 and Irgafos 168, from PP, PP-R, and PP-C during microwave heating in contact with different food simulants was investigated by utilizing microwave assisted extraction (MAE) and high performance liquid chromatography (HPLC). The polypropylene material significantly influenced the migration rate, which decreased in the order of increasing degree of crystallinity in the materials. PP homopolymer was the most migration resistant of the studied materials especially in contact with fatty food simulants. The use of isooctane as fatty food simulant resulted in rapid depletion of antioxidants, while migration to another fatty food simulant, 96% ethanol, was much more limited. Migration to aqueous and acidic food simulants was in most cases under the detection limits irrespective of microwaving time and temperature. The diffusion coefficients were similar to what have been found previously under similar conditions but without microwaves. The effect of swelling was shown by the large increase in the calculated diffusion coefficients when isooctane was used as food simulant instead of 96% ethanol. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1084–1093, 2010

Key words: polypropylene; antioxidants; chromatography; diffusion; packaging

INTRODUCTION

Plastic food packaging should be designed to minimize the migration of additives and degradation products from the packaging material to food. Migrating substances can cause undesirable flavors in the food or even promote toxicity. Understanding the parameters that govern the migration is important for the selection and development of packaging materials. Migration from food packaging is often established as global migration, which is the total amount of substance released from the packaging. Chromatographic techniques together with suitable extraction method are ideal for identification and quantitative determination of migrants from plastic materials[1] and are increasingly being used to quality control for polymeric materials inclusive food packaging, recycled materials, and medical materials.[2–4] Mathematical models have also been developed to predict migration rates.[5] In a recent study, overall migration methodology was developed to test for food-contact substances with specific migration limits.[6] Migration of common additives, such as antioxidants, can be established by high performance liquid chromatography (HPLC) analysis with ultraviolet (UV) detection because many additives absorb light in the UV region. Microwave assisted extraction (MAE) followed by HPLC-UV analysis has been successfully used to extract Irgafos 168 and irganox 1076 from low density polyethylene (LDPE) with dichloromethane as the extraction solvent.[7] Migration of common antioxidants from polymers to foods and food simulants has been investigated in several studies,[8–13] often under standard conditions (e.g. 10 days at 40°C). Commonly used antioxidants are therefore good model compounds to make comparisons between different studies.

Food is often heated inside a plastic container in a microwave oven. When microwaves are used to heat substances relatively high temperatures can be reached in a short time, which facilitates migration. Food packages are often reused repeatedly after washing, which could cause unpredictable migration behavior due to polymer degradation. Migration

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from food packaging[14–16] from carton board[17] and from susceptor packaging[18] during microwave heating has been studied in previous works. Global migration from polypropylene to aqueous food simulants during microwaving for 3 min at 800W maximum power was comparable to migration during continuous heating at 80°C for 30 min. The effect of microwave heating on the migration from poly(vinyl chloride) (PVC) was significantly higher compared to conventional heating.[14] However, the microwave induced nonthermal effect of increasing diffusion of various polar and nonpolar low molecular weight substances in polyolefins was insignificant.[19] Another study found that global migration into olive oil from a polypropylene package was increased after repeated heating in a microwave oven to 400% compared to the first heating.[20] No study so far systematically compared microwave and nonmicrowave heating effects on migration of common additives from food packaging to food simulating liquids or foods under controlled temperatures. Migration during microwaving at controlled temperatures could be established with a MAE system, which has also shown potential in migration studies to food simulants.[21]

Polypropylene is the most commonly used material in reusable food containers for microwave oven. Three different polypropylene qualities are frequently used, polypropylene homopolymer (PP), random propylene-ethylene copolymer (PP-R) and propylene-ethylene copolymer (PP-C). The type of food simulant affects the migration of antioxidants from polypropylene.[9] However, the type of polypropylene material could also significantly influence the migration of low molar mass compounds from the food container to food because of, for example, different degrees of crystallinity. The specific migration of two antioxidants, Irgafos 168 and Irganox 1010, from PP, PP-R, and PP-C food containers was determined at different temperatures and in contact with different food simulants to evaluate the effect of polypropylene material on the migration of antioxidants during microwave heating of food. This was done under controlled conditions by utilizing a MAE device.

EXPERIMENTAL

Materials

Tetrahydrofuran > 99.9% was supplied from Merck, Acetonitrile 99.99% from Fisher, Ethanol 96% and Isooctane 99.5% were both supplied from VWR. All of these were of either HPLC or GC grade. Water was obtained from a Millipore MilliQ water purifier system. Irgafos 168 (Tris(2,4-*tert*-butylphenyl) phosphite, CAS: 31,570-04-4) (I168) and Irganox 1010 (Pentaerythritol tetrakis[3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate] (I1010), CAS: 6683-19-8) were supplied from Ciba Speciality Chemicals. All of the commercial food boxes consisted of a container plus lid. Only the containers were used in the migration determinations. Two of the boxes were obtained from Ikea, Sweden. One of these was opaque white and marked 'PP-C', the other was transparent and marked 'PP-R'. The markings were probably indicating a propylene-ethylene copolymer (PP-C) and a propylene-ethylene random copolymer (PP-R) respectively. The boxes were approved by the manufacturer to be used in a microwave oven for heating food up to a maximum temperature of 120°C. The third commercial food box, marked 'PP204' (hereafter referred to as PP), was transparent, harder, and more brittle than the Ikea boxes, therefore it was likely an isotactic polypropylene (PP) homopolymer. It was obtained from Axfood, Sweden, and was approved for microwave heating, but no maximum temperature was specified.

Polymer characterization by DSC and FTIR

The polymer samples were analyzed by differential scanning calorimetry (DSC) to establish the degree of crystallinity and melting temperature. The DSC instrument was a Mettler Toledo DSC 820 STAR^e system with a GC100 gas controller. Approximately 4 mg of each sample were weighted and analyzed. The samples were heated from 25 to 200°C, cooled to 0°C and then heated to 200°C again. The heating and cooling rates were ± 10°C min^{-1} and the samples were under 80 mL min^{-1} nitrogen flow during the analysis. The containers were confirmed to mainly consist of polypropylene by Fourier Transform Infrared (FTIR) surface analysis. The FTIR spectrometry system was a PerkimElmer 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 to eliminate noise and the spectra were compared to a known spectrum of polypropylene.

Migration determinations by MAE device

Sample pieces were cut from the boxes with a scissor using a rectangular template measuring approximately 23 × 30 mm^2 and care was taken to cut them all in a uniform size. Each sample was weighed. The thickness of 16 samples was measured at five points spread out over the sample using a Mitutoyo IDC-112B digital thickness meter and the mean value was noted. The samples were then heated together with different food simulants in a MAE system under different times and temperatures. The MAE

system was a CEM MES-1000, a multimode type microwave oven with a rotating turntable with a maximum effect of 950W. The turntable had place for a maximum of 12 Teflon vessels, which contained the samples for the extraction. The temperature and pressure was measured from only the first vessel in the turntable. For comparison, some samples were also heated without microwaves, in an oil bath on a heating plate set at the desired temperature. The different food simulants used were 96% ethanol, 10% ethanol in water, 10% ethanol in isooctane, 100% isooctane, 3% aqueous acetic acid, and water. The addition of 10% ethanol to isooctane was needed to be able to heat isooctane with microwaves. For the microwave determinations, each sample was immersed in 20 mL of solvent in the MAE's Teflon vessel. For the migration determinations in the oil bath the sample was kept in a sealed glass vial with 20 mL of solvent. The vial was then immersed in the oil. Both sides of the polymer sample were in full contact with the solvent for all of the determinations. The effect setting on the MAE system was 50% using 10% and 96% ethanol as food simulant at 80°C, because full effect on ethanol resulted in a too high heating rate, which made it difficult to maintain a stable temperature. For the 96% ethanol samples at 60°C the effect was further reduced to 25%. In all other cases the effect was set to 100%. Six 20 mL samples were heated simultaneously in the MAE device; two from each polymer (duplicate runs). After each run, the samples were allowed to cool for a few minutes and aliquots from the extracts were removed and injected into the HPLC system. The samples that were heated at different temperatures in isooctane/ethanol and ethanol were weighed before and after heating to determine the solvent absorption. Samples of the polymers were also repeatedly heated for six 10 min intervals at 80°C in 90/10 isooctane/ethanol in the MAE device. The extracts were removed and analyzed after each step. After each 10 min heating, the samples were kept in room temperature for at least one day.

Determination of antioxidant content in polymers

The total amount of antioxidants in the samples was determined by immersing a polymer sample in 90/10 isooctane/ethanol at 80°C for approximately 24 h and thereafter measuring the concentration in the solvent. The heating was then repeated with new solvent for another 24 h to check for completion of the extraction. Peak areas after the second extraction had either decreased to below 2% of the areas after the first extraction, or were undetectable. To check for any possible degradation of the antioxidants during the extraction, a known amount of standard in 90/10 isooctane/ethanol was analyzed with HPLC before and after heating for 24 h at 80°C. No significant decrease in peak areas of the antioxidants could be observed from this procedure.

HPLC analysis

The analysis of extracts and standards was made on a HPLC system with a mobile phase consisting of 90/10 acetonitrile/tetrahydrofuran and the elution was isocratic. The HPLC system consisted of a Hewlett Packard series 1100 auto sampler and UV detector. The pump was a Shimadzu LC-10AD Solvent delivery module. Two HPLC columns were used, one was a Supelco Supelcosil 5 μm LC-18 4.6 × 150 mm and the other was a Supelco Hypersil ODS 5 μm 4.6 × 250 mm. Both columns had C18 (Octadecyl) stationary phase. The mobile phase was degassed by Helium before use. The wavelength setting on the UV detector was 280 nm, the flow rate was 1 mL min^{-1} and the injection volume was 20 μL for most samples but increased up to 100 μL when the analyte concentration in the sample was low. The antioxidants contained in the extracts were identified as I168 and I1010 by spiking some of the extracts with standard solutions of I168 and I1010 and injecting them into the HPLC system.

Calibration curves of I168 and I1010 standards were made by weighing in and dissolving three different amounts of each of the antioxidants in solutions of 90/10 isooctane/ethanol. The obtained calibration curves had a correlation coefficient (R^2) of 0.9991 for I168 and 0.9993 for I1010. All samples run were quantified against these calibration curves. To also determine the variability caused by possible antioxidant degradation, another calibration curve was prepared by dissolving five different concentrations of the antioxidants in 99.5% ethanol. Ethanol was chosen because the antioxidants are prone to degradation in this solvent, as determined by separate tests. These standards were each heated on the heating plate for 1 h at 80°C before injection into the HPLC system. The resulting calibration curves from these standards had correlation coefficients (R^2) of 0.9998 and 0.9985 for I168 and I1010, respectively, and the slopes were equal to the isooctane/ethanol calibration curve's indicating that no significant degradation occurred. To also determine the potential loss of antioxidants in 90/10 isooctane/ethanol from the procedure, a known amount of standard in 90/10 isooctane/ethanol was divided into five parts, 4 were heated for 1 h at 80°C in the MAE, and then analyzed by HPLC and one was analyzed directly. The areas of the heated samples were compared to the area for the unheated sample, showing recoveries of 98% for I168 and 96% for I1010. The areas of the four heated samples had a standard deviation of

TABLE I
Degree of Crystallinity, Melting Temperature, and Antioxidant Content (μg g^{-1}) in the Different Polypropylene Food Containers

Sample	Crystallinity (%) First heating	Crystallinity (%) Second heating	Melting temperature (°C)	Antioxidant content ± SD, $n = 4$ I168	Antioxidant content ± SD, $n = 4$ I1010
PPC	33	40	165	251 ± 26	346 ± 20
PPR	29	34	145	1110 ± 316	312 ± 16
PP	41	48	165	580 ± 116	236 ± 39

1.4% for I168 and 0.6% for I1010 showing good reproducibility in the MAE heating procedure.

RESULTS AND DISCUSSION

Migration of antioxidants, Irgafos 168, and Irganox 1010, from three polypropylene materials, PP, PP-C, and PP-R, in contact with food simulants for aqueous, acidic and fatty food was investigated to assess the effect of polypropylene material on the migration rate. In addition the effect of microwaves, temperature, and heating time were evaluated.

Polymer characterization

Before the migration experiments the total Irgafos 168 and Irganox 1010 contents in the different polypropylenes were determined by HPLC and melting temperatures and degrees of crystallinity were determined by DSC (Table I). As seen from Table I the materials originally contained rather similar amounts of I1010. However, the I168 content in PP-R was about four times bigger compared to PP-C and two times bigger compared to PP. The thickness of the sample pieces was in the range 1.2–1.3 mm and the densities (calculated from sample weight, thickness and area) were in the range 0.87–0.89 g cm^{-3} with no significant difference between the polymer types. The degree of crystallinity values were determined from the integrated melting peak areas with the help of the equation

$$X_c = 100 * \Delta H_f / H_f{}^0 \quad (1)$$

where X_c is the degree of crystallinity, ΔH_f^0 is the melting enthalpy of 100% crystalline polypropylene and ΔH_f is the integrated melting peak area. A value of 209 J/g[22] for 100% crystalline polypropylene was used for the calculations. Because the degree of crystallinity in the packaging materials is expected to affect the migration rate, it was determined from the melting peak of the first heating before it had been affected by the thermal treatment during the DSC analysis. For comparison also the melting peaks from the second heating were integrated and the samples showed even more pronounced differences in the degrees of crystallinity after the second heating with the crystallinity increasing in the order PP-R, PP-C and finally the pure PP showing the highest degree of crystallinity. The melting temperatures for PP-C and PP were in the range typical for pure polypropylene (around 160°C), while the random copolymer PP-R had considerably lower melting point due to the randomly distributed ethylene units.

The effect of different food simulants on the migration of antioxidants

The amount of Irgafos 168 and Irganox 1010 that migrated from the materials during 1 h of microwaving at 80°C to 10% ethanol, 3% aqueous acetic acid, 96% ethanol, and 90% isooctane with 10% ethanol are shown in Table II. The results show large differences in the migrated amount depending on the type of food simulant and the type of polypropylene material. While migration of antioxidants to aqueous and acidic food simulants was in most cases under the detection limit, significant migration occurred to the fatty food simulants. The limit of detection, determined by estimating three times the standard deviation of the baseline noise in the detector signal was 9.3 μg dm^{-2} for I168 and 5.2 μg dm^{-2} for I1010.

There was also large difference in the migration of antioxidants into the two fatty food simulants,

TABLE II
Antioxidant Migration (μg dm^{-2}) from Polypropylene Food Containers to Different Food Simulants During 1 h at 80°C with or Without Microwaves

Sample	Microwaving I168	Microwaving I1010	Heating I168	Heating I1010
96% ethanol, 80°C				
PPC	30 ± 4[a]	11 ± 2[a]	35	23
PPR	206 ± 22[a]	19 ± 5[a]	290	31
PP	26 ± 3[a]	[b]	39	[b]
90/10 isooctane/ethanol, 80°C				
PPC	509	502	686 ± 31[a]	726 ± 64[a]
PPR	4735	1283	4955 ± 204[a]	1342 ± 217[a]
PP	615	190	748 ± 85[a]	277 ± 45[a]
Isooctane, 80°C				
PPC	–	–	777	765
PPR	–	–	4909	1477
PP	–	–	780	429
3% acetic acid, 100°C				
PPC	[b]	9	[b]	[b]
3% acetic acid, 120°C				
PPC	[b]	9	[b]	[b]
10% ethanol, 120°C				
PPC	[b]	6	[b]	[b]

[a] Determined from 4 measurements.
[b] Not detected.
– Not determined.

isooctane (with 10% ethanol) and 96% ethanol. The amount of I1010 that migrated from the different polypropylenes into isooctane was approximately 40 times higher and the amount of I168, 20 times higher compared to the amounts that migrated into 96% ethanol. This could be explained by high affinity of isooctane to polypropylene, which causes swelling of the polymer and facilitates migration as well as by the solubility of the antioxidants into the two food simulants. There were also large differences in the amount of antioxidants that migrated from the different polypropylene materials as the amount of I168 that migrated from PP-R to 96% ethanol or to 90% isooctane was almost 10 times larger compared to the amount that migrated from PP-C or PP. In the case of I1010 migration the differences were not as large but still the amount of I1010 that migrated from PP-R was two respectively five times higher compared to PP-C and pure PP. In relation also to the original antioxidant contents pure PP showed to be much more resistant to migration compared to the PP copolymers, PP-C and PP-R.

As no migration was detected at 80°C into the aqueous food simulants, they were also microwaved for 1 h at 100°C and 120°C (Table II). The migration into aqueous food simulants was in most cases under detection limits even when higher microwaving temperatures up to 120°C were applied, which is probably due to the limited solubility of the hydrophobic antioxidants into the aqueous simulants. The applied temperatures were in several cases above the atmospheric boiling points of the food simulants, however, the determinations were made under pressure in closed vessels. In addition, when heating with microwaves the temperature can reach above the boiling point even at atmospheric pressure.[23]

The effect of microwaves on the migration of antioxidants

The effect of microwaves on the migration of antioxidants was evaluated by comparing the amount of antioxidants that migrated during 1 h heating at 80°C with and without microwaving (Table II). In the two fatty type food simulants (96% ethanol and isooctane), there was no increase in the amount of migrated antioxidants when heated with microwaves compared to when heated without microwaves. In fact, migration was slightly lower when heated with microwaves compared to when heated without microwaves. Migration was not detected from any of the polymers when heated at 80°C in 3% acetic acid with MAE. In 3% acetic acid at 100 and 120°C, and in 10% ethanol at 120°C, small amounts of I1010 migrated from PP-C when heated in MAE, but not when heated at oil bath of same temperature without microwaves. In this case, the presence of water could increase the migration under the influence of microwaves because water has a higher dielectric constant and dielectric loss factor than ethanol.[23] 100% isooctane could not be used as food simulant during microwaving because it does not absorb microwaves and 10% ethanol had to be added to make heating by microwaves possible. The effect of this addition on the migration rate was evaluated by aging samples at 80°C in 100% isooctane and in isooctane with 10% ethanol without the microwaves. These results are also presented in Table II showing quite similar migration rates for these two food simulants. The addition of 10% ethanol before microwaving is, thus, not expected to significantly influence the results.

The effect of heating time on migration of antioxidants

Migration of the Irgafos 168 and Irganox 1010 to the 90/10 isooctane/ethanol food simulant during heating by MAE at 80°C for different time periods between 10 min and 6 h is shown in Figures 1 and 2, respectively. The migrated amounts are expressed as weight fractions of the total antioxidant contents in the polymers. They are further plotted against time$^{1/2}$ to show a possible fickian behavior in the migration. An increase from linear relation with $t^{1/2}$ trend can be observed for the two antioxidants, after different time period depending on the polypropylene type. The deviation is observed after 1 h in the case of PP-R, after 2 h in the case of PP-C and after 4 h in the case of PP. This is probably due to increasing swelling of the polymer by the solvent, which lowers the diffusion resistance by increasing the free volume. There were significant differences in the

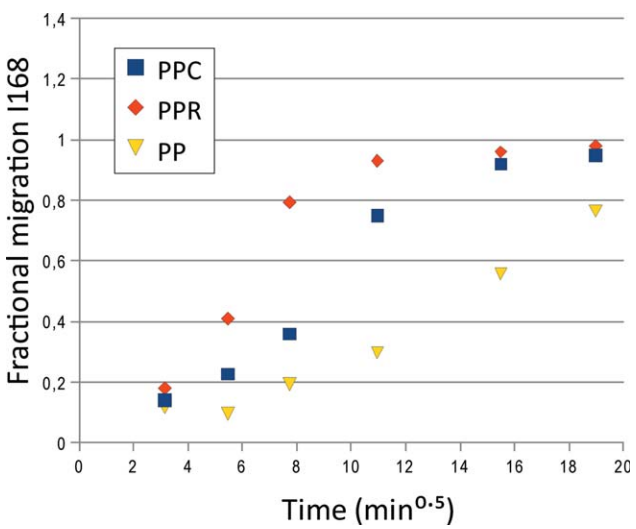

Figure 1 Migration of Irgafos 168 to 90/10 isooctane/ethanol during 10 min, 30 min, 1, 2, 4, and 6 h of microwave heating at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

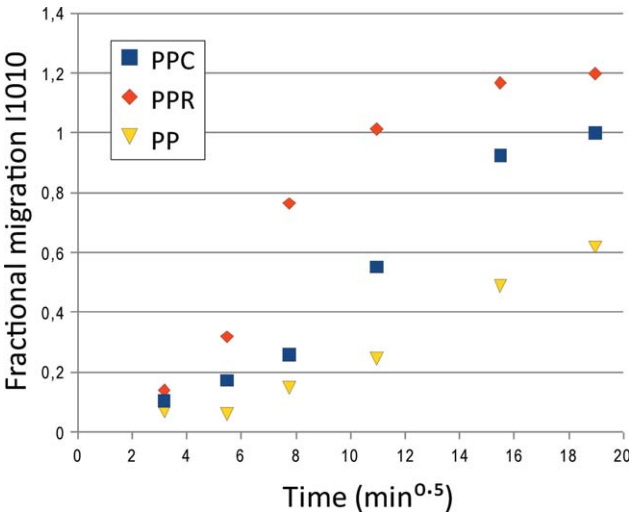

Figure 2 Migration of Irganox 1010 to 90/10 isooctane/ethanol during 10 min, 30 min, 1, 2, 4, and 6 h of microwave heating at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

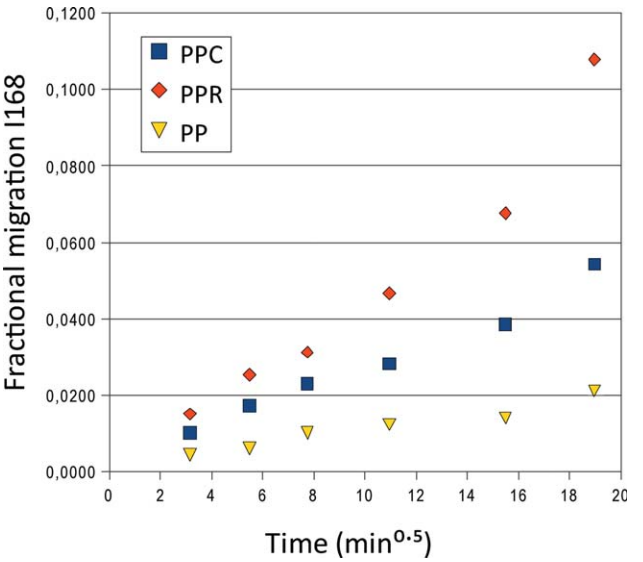

Figure 3 Migration of Irgafos 168–96% ethanol during 10 min, 30 min, 1, 2, 4, and 6 h of microwave heating at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

migration rate depending on the type of polypropylene and the rate of migration decreased in the order: PP-R > PP-C > PP for both of the antioxidants. As could be expected this coincides with the order of increasing degree of crystallinity in the three polymer types (Table I). In addition the copolymerization probably affects the morphology of the samples especially in the case of the random copolymer PP-R, which also has a considerably lower melting temperature compared to PP-C and PP.

The fractional amount of antioxidants that migrated into 96% ethanol as a function of microwaving time can be seen in Figures 3 and 4. For I168 a clear linear relationship with $t^{1/2}$ is seen. For I1010 the linear dependence is not as clear, with the rate of migration from PP-R increasing with time which could be due to solvent absorption. The order of migration rate was the same as to isooctane/ethanol food simulant; i.e. PP-R > PP-C > PP and I168 migrated clearly faster than I1010, with approximately twice the rate. This could be due to the smaller size and higher solubility of I168 (647 g mol^{-1}) compared to I1010 (1177 g mol^{-1}). Again PP was the most migration resistant polymer with detectable I1010 migration first after 2 h in 96% ethanol.

There was large difference between the two fatty food simulants and between the different polypropylene materials. While practically 100% of I168 and I1010 had migrated from PP-R to isooctane after 2 h only a few percent of the total antioxidant content had migrated to 96% ethanol after the same time period. Similar comparison of the different polypropylene materials shows that while almost 100% of I168 had migrated from PP-R after only 2 h in isooctane, after the same time period PP-C had lost 72% of its I168 content and pure PP had only lost 33% of its I168 content. Corresponding figures for migration of I1010 were 100% in the case of PP-R, 53% for PP-C and only 27% in the case of pure PP.

The effect of repeated or continuous heating on migration

Figures 5 and 6 show the migration of Irgafos 168 and Irganox 1010 into isooctane/ethanol during

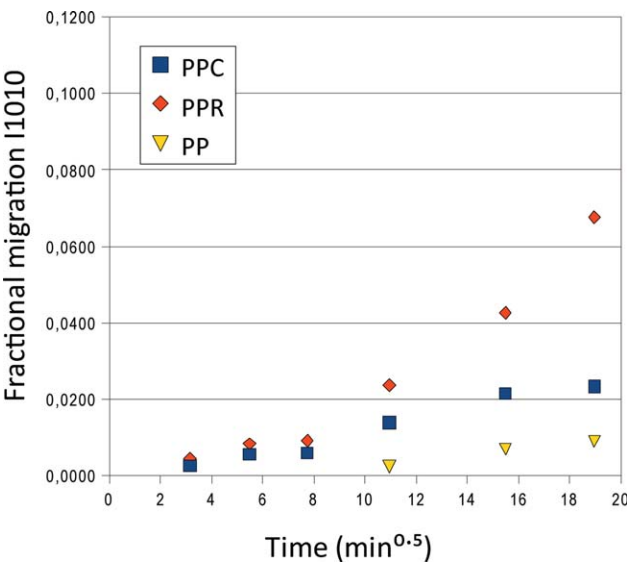

Figure 4 Migration of Irganox 1010–96% ethanol during 10 min, 30 min, 1, 2, 4, and 6 h of microwave heating at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

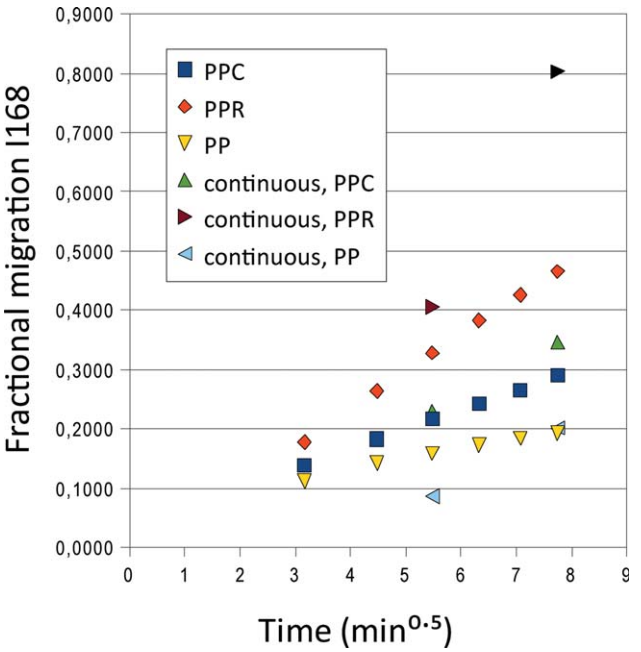

Figure 5 Total amount of migrated Irgafos 168 during repeated microwave heatings in six 10 min intervals, compared to continuous heatings for 30 min and 1 h at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

repeated microwave heating for six times 10 min at 80°C. The figures show the total fractional amount of antioxidant that migrated from the sample starting from the first heating in the sequence. It is evident from the linearity of the data points that the migration was what would be expected from a standard diffusion process with no outer resistance. The lack of scattering in the data in these figures suggests that the reproducibility of the extraction was high and the scattering observed in previous figures was a result of concentration variations between samples, because the previous determinations were performed on different samples pieces. No significant diffusion within the polymer seemed to occur during storage between the heatings at room temperature. When the repeated heatings are compared to continuous heatings during 30 min and 1 h, approximately twice the amount of antioxidants migrated during 1 h continuous heating from PP-R compared to when heated in intervals. The amounts that migrated during repeated heating of PP-C and PP were approximately the same as the amounts that migrated from the samples when they were heated continuously for the same total time. The higher migration rate for PP-R during continuous heating could be explained by swelling of the sample during continuous heating. Between the repeated heatings samples were stored several hours in a well ventilated area resulting in evaporation of the solvents taken up by the materials. However, as shown in Figures 1 and 2, 1 h was not enough to swell PP-C and PP, which resulted in rather similar amounts of migrants during continuous and repeated heating.

The effect of polypropylene type and food simulant on the diffusivity

The migration to fatty food simulants appeared to be controlled by standard (or 'Fickian') diffusion. To quantify the difference between the polymer types and antioxidants in regard to diffusivity, as well as to measure the influence of the simulant type (ethanol or isooctane) on the diffusion in the polymers, the diffusion coefficients satisfying Fick's second law of diffusion of the antioxidants in the different polymers were calculated. The partition coefficient ($C_{liquid}/C_{polymer}$ at equilibrium) between the simulants and the polymer was assumed to be high enough, so that most of the migrant would have been in the liquid phase if the migration was allowed to continue until equilibrium. This was confirmed using isooctane/ethanol as simulant given the high extraction yield achieved in the total antioxidant content determinations. The partition coefficients for some common antioxidants (Irganox 1076, oxidized I168) between 95% ethanol and polypropylene are reasonably high at 60°C and are increasing with temperature.[24] Because the food simulant volume was large compared to the sample volume in these determinations, it should be reasonable

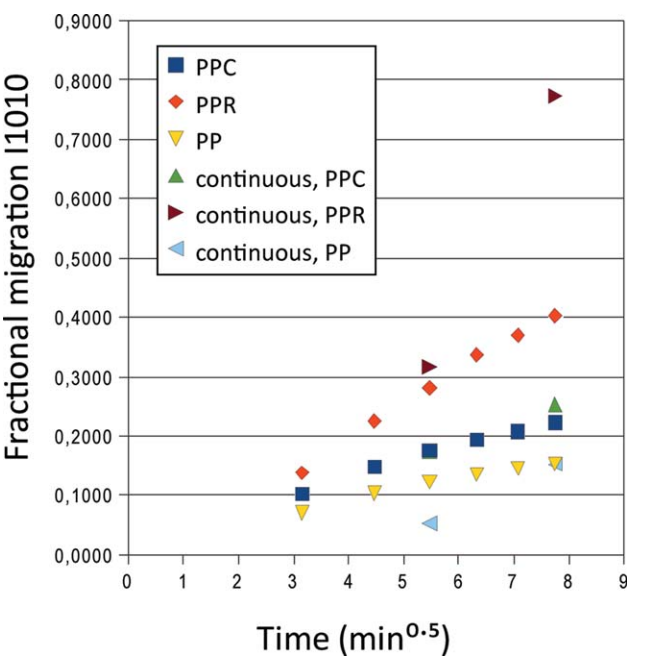

Figure 6 Total amount of migrated Irganox 1010 during repeated microwave heatings in six 10 min intervals, compared to continuous heatings for 30 min and 1 h, at 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Calculated Diffusion Coefficients and Activation Energies for Antioxidant Migration to 10/90 Ethanol/Isooctane and 96% Ethanol at 80°C During Microwave Heating

	Diffusion coefficient ($cm^2\ s^{-1}$)		Activation energy ($kJ\ mol^{-1}$)	
Sample	I168	I1010	I168	I1010
10/90 ethanol/isooctane,				
PPC	8×10^{-8}	5×10^{-8}	53	50
PPR	2×10^{-7}	1×10^{-7}	135	161
PP	4×10^{-8}	2×10^{-8}	127	175
96% ethanol,				
PPC	4×10^{-10}	1×10^{-10}	165	263
PPR	7×10^{-10}	2×10^{-10}	190	281
PP	7×10^{-11}	3×10^{-12}	231	–

to assume that most of the antioxidants in the polymers would have been extracted to ethanol at equilibrium as well. If the above assumptions hold, no external mass transfer resistance exists at the surface and the distribution of migrant is initially homogeneous in the polymer, the migration during short times can be expressed as

$$M_t = 2\, x_0\, \rho (Dt/\pi)^{1/2} \quad (2)$$

where M_t is the migrated amount per total surface area unit, x_0 is the initial weight fraction of migrant, ρ is the density of the sample, t is the time, and D is the diffusion coefficient.[25] The diffusion coefficients obtained by eq. (2) for migration of the antioxidants to isooctane with 10% ethanol and to 96% ethanol are given in Table III. The migrated amount per area unit (M_t) values were in the case of isooctane/ethanol obtained from the linear regression curves calculated from the results from the repeated six times 10 min heatings. The 96% ethanol diffusion coefficients were calculated from the migrated amounts after 2 h because they were in a range linear to $t^{1/2}$ and the later data points deviated too much from linearity. It should be noted that the 96% ethanol diffusion coefficients could be underestimated if the partition coefficient between ethanol and polypropylene is not high enough, or if a significant resistance to uptake of the migrant into ethanol exists at the surface. However, reasonably close diffusion coefficients of 5×10^{-11} and 1.6×10^{-10} $cm^2\ s^{-1}$ have been measured for the diffusion of I1010 in a polypropylene homopolymer and a random propylene-*co*-ethylene copolymer, respectively, and other coefficients in the range 6×10^{-11}–1.7×10^{-9} $cm^2\ s^{-1}$ for diffusion in various polypropylene/polyethylene copolymers, at 80°C during standard heating using the Roe method.[26,27] As with these results, the random copolymer gave a higher diffusion coefficient than the homopolymer. The diffusion coefficients obtained with the isooctane/ethanol mixture are more close to a value achieved with high pressure solvent extraction of I1010 from PP into cyclohexane at 80°C, which was 3.1×10^{-7} $cm^2\ s^{-1}$.[28] These similarities in diffusion coefficients with swelled/unswelled systems at the same temperatures indicate that the migration to both 90/10 isooctane/ethanol and 96% ethanol is diffusion controlled and that there was no enhancing effect from using microwaves, or mass transfer resistance during the migrations. It could further be reasoned that, by immersion in a suitable solvent, the increase of the rate of diffusion in the polymers by solvent interaction/swelling is large. It is not surprising that the magnitude of swelling of polyolefins by hydrocarbons would increase the diffusivity. An increase in the diffusion coefficient by a factor of 10 at 40°C for the diffusion of antioxidants from polypropylene was earlier observed when heptane was used as food simulant instead of ethanol.[24] In this study, the effect of food simulant was even higher due to the higher temperatures used.

The effect of heating temperature on migration of antioxidants

The effect of heating temperature on migration of I1010 and I168 can be seen in Table IV, which shows the migrated amounts to different food simulants during microwaving at different temperatures. The times and temperatures were chosen so that a significant portion of the antioxidants would still be left

TABLE IV
The Effect of Temperature on Antioxidant Migration to Different Food Simulants During Microwave Heating ($\mu g\ dm^{-2}$)

	I168			I1010		
Temperature (°C)	PPC	PPR	PP	PPC	PPR	PP
96% Ethanol, 1 h						
60	[a]	28	[a]	[a]	[a]	[a]
80	30	206	26	11	19	[a]
100	135	1104	217	121	247	55
90/10 Isooctane/ethanol, 30 min						
60	186	616	85	201	103	13
70	218	1249	226	259	257	51
80	322	2443	309	336	535	77
10% Ethanol, 1 h						
100	[a]	[a]	[a]	[a]	[a]	[a]
120	[a]	[a]	[a]	6	[a]	[a]
3% Acetic acid, 1 h						
80	[a]	–	–	[a]	–	–
100	[a]	–	–	9	–	–
120	[a]	[a]	[a]	9	[a]	[a]
Water, 1 h						
120	[a]	[a]	[a]	[a]	[a]	[a]

[a] Not detected.
– Not determined.

TABLE V
Weight Uptake (Solvent Absorption) by the Different Polypropylene Materials During Microwave Heating After 1 h in 96% Ethanol and After 30 Min in 90/10 Isooctane/Ethanol in %

Temperature (°C)	PPC	PPR	PP
96% Ethanol			
60	0.2	0.2	0.1
80	0.5	0.5	0.2
100	1.2	1.5	0.8
10/90 Ethanol/isooctane			
60	2.8	3.0	0.6
70	5.0	7.8	1.4
80	5.9	12.1	2.6

in the polymer after heating so that the results would not be affected by a beginning decline in the available antioxidant. The only detectable migration to 10% ethanol in water was I1010 that migrated from PP-C at 120°C. In 3% acetic acid migration of I1010 from PP-C was detected at 100 and 120°C at practically equal amounts. The rather similar amounts that migrated at the two temperatures could be due to limited solubility of the antioxidant in 3% acetic acid, or degradation of the antioxidant at the higher temperature. Degradation of antioxidants in 3% acetic acid was not tested but in 10% ethanol around 30% of I1010 had degraded after 1 h at 120°C. Degradation of I168 in the same simulant was not significant. Degradation of I1010 in 3% acetic acid and water has also been observed by others.[29,30]

The weight increase, i.e. the uptake of solvent during the microwaving, for the different polypropylene materials can be seen in Table V, showing that the absorption of isooctane/ethanol mixture by the polypropylene samples was much higher compared to uptake of ethanol. The isooctane/ethanol uptake by PP-R was as much as 12% after 30 min at 80°C. The uptake of 96% ethanol by PP-R was at maximum 1.5% after 1 h at 100°C. The uptake of ethanol displayed a rather linear relationship with T^{-1} on a logarithmic-linear scale. The diffusion rate, expressed as the diffusion coefficient, D, from Fick's second law of diffusion, can be described as

$$D = A \exp[-E_a/(\mathrm{RT})] \quad (3)$$

where E_a is the activation energy, R the universal gas constant, T the temperature, and A a constant.[31] If eq. (2) is valid and other diffusivity altering parameters, for example swelling, do not vary significantly with temperature, the activation energy of the different systems can be calculated from eqs. (2) and (3), and from the slopes of the regression curves (fractional migration *vs.* 1/T). The linearity of these regression curves for PP-C and PP-R shows that the diffusion rate changes according to the Arrhenius equation. The deviations from linearity for the migration from PP could be due to other factors, which contribute to the change in diffusion, such as swelling of the polymer only at the higher temperatures, causing increase in free volume. The activation energies calculated from the slopes of the regression curves are listed in Table III. The calculated activation energies for diffusion in samples in 96% ethanol were considerably higher than those obtained in isooctane/ethanol which could be due to swelling or solubility effects mentioned earlier.

CONCLUSIONS

The type of polypropylene material significantly affected the antioxidant migration from packaging to food during microwave heating. There were large differences between the different polypropylene food containers with respect to both the original amount of antioxidants as well as the migration rate. The migration decreased in the order PP-R, PP-C, and PP with respect to both fractional migration and total amount of migrated antioxidants. This coincides with the order of increasing degree of crystallinity in the samples. Almost half of the Irgafos 168 content in PP-R, corresponding to a migration value of almost 3 mg $dm^{-2,}$ had migrated to isooctane after only 30 min at 80°C and after 2 h practically no I168 remained in the material. The migration to the other fatty food simulant, 96% ethanol, was much more restricted and more temperature dependent. Migration of antioxidants to aqueous and acidic food simulants was insignificant even during prolonged heating or at elevated temperature up to 120°C. Migration to the fatty type food simulants did not increase when heated with microwaves instead of conventional heating, while slight increase in the migration was observed in the case of aqueous or acidic food simulants. The amount of antioxidants that migrated to fatty food simulants during microwave heating as a function of time could be predicted from fickian diffusion by the heating effect alone. The diffusion coefficients for migration into the fatty type food simulants during microwave heating were similar to values established earlier during conventional heating. Heating in isooctane could result in significant absorption and swelling with a potential to increase the diffusion coefficient by a factor of 100–1000 at 80°C. The PP homopolymer was by far the most migration resistant polymer in contact with fatty food simulants and is, thus, most suitable of the materials examined to heat foods with high fat content.

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