Migration from plastic food packaging during microwave heating

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Abstract

Microwave heating of food has increased rapidly as a food processing technique. This increases the concern that chemicals could migrate from food packaging to food. The specific effect of microwave heating in contrast to conventional heating on overall and specific migration from common plastic food storage boxes was studied in this work. The purpose was especially to determine the interaction effects of different plastics in contact with different types of foods during microwave heating. The study focused on polycarbonate (PC), poly(ethylene terephthalate) (PET), polypropylene homo-polymer (PP), *co*-polymer (PP-C) and random *co*-polymer (PP-R) packages. The migration determinations were evaluated at controlled times and temperatures, using a MAE device. The migrants were analyzed by GC-MS and HPLC. ESI-MS was evaluated as a new tool for migration determinations. Food/food simulant absorption and changes in degree of crystallinity during heating were also followed.

Significant degradation of antioxidants Irgafos 168 and Irganox 1010 in PP packages occurred during microwave heating of the packages in food simulants containing ethanol, resulting in the formation of antioxidant degradation products. Degradation of PC by Fries chain rearrangement reaction leading to formation of 9,9-dimethylxanthene, and transesterification of PET leading to formation of diethyl terephthalate, were also observed after microwave heating the packages in ethanol and 90/10 isooctane/ethanol. These reactions were not observed during conventional heating of the packages at the same temperature, or after microwave heating of the packages in liquid food (coconut milk). The microwave heating also significantly increased the migration of cyclic oligomers from PET into ethanol and isooctane at 80 °C. Migration of compounds into coconut milk was slightly lower than calculated amounts using the EU mathematical model to predict migration of additives into foodstuffs. The results thus show that the use of ethanol as a fat food simulant during microwave heating can lead to a significant overestimation of migration as well as degradation of polymer or the incorporated additives.

Some other detected migrants were dimethylbenzaldehyde, 4-ethoxy-ethyl benzoate, benzophenone, m-tert-butyl phenol and 1-methylnaphthalene. All identified migrants with associated specific migration limit (SML) values migrated in significantly lower amounts than the SML values during 1 h of microwave heating at 80 °C. The antioxidant diffusion coefficients in PP and PP *co*-polymers showed larger relative differences than the corresponding degrees of crystallinity in the same polymers and PP-R showed by far the fastest migration of antioxidants.

Keywords: migration, food packaging, microwave, degradation, food simulant, antioxidant

Sammanfattning
Mikrovågsuppvärmning av mat har ökat markant under de senaste åren. Detta ökar risken för att ämnen i plast migrerar från matförpackningar till mat. Den specifika effekten av mikrovågsvärmning i kontrast till konventionell värmning på total och specifik migrering från vanliga matförvaringslådor av plast studerades i denna avhandling. Syftet var i huvudsak att bestämma interaktionseffekter mellan olika typer av plaster och olika typer av mat under mikrovågsvärmning. Studien fokuserades på förpackningar av polykarbonat (PC), polyetentereftalat (PET), polypropylen homopolymer (PP), copolymer (PP-C) och random copolymer (PP-R). Migreringstesterna utfördes under kontrollerade tider och temperaturer genom att använda MAE. Migranterna analyserades med hjälp av GC-MS och HPLC. ESI-MS-analys utvärderades också som ny analysmetod för migreringstester. Absorption av mat- och matsimulanter samt förändringar i kristallinitetsgrad följdes också.

Signifikant nedbrytning av antioxidanterna Irgafos 168 och Irganox 1010 i PP-förpackningar inträffade under mikrovågsvärmning av förpackningarna i etanol-innehållande matsimulanter, vilket resulterade i bildning av nedbrytningsprodukter från antioxidanterna. Nedbrytning av PC genom en Fries omfördelningsreaktion, vilket orsakade bildning av 9,9-dimetylxanten, samt transesterifikation av PET, vilket orsakade bildning av dietyltereftalat, observerades också efter mikrovågsvärmning av förpackningarna i etanol och 90/10 isooktan/etanol. Dessa reaktioner observerades ej efter konventionell värmning av förpackningarna under samma temperatur och ej heller efter mikrovågsvärmning av förpackningarna i riktig mat (kokosmjölk). Mikrovågsvärmningen ökade också betydelsefullt migrering av cykliska oligomerer från PET till etanol och isooktan under 80 °C. Specifika ämnens migrering till kokosmjölk var alla något lägre än migreringsvärden beräknade m. h. a. EU's officiella matematiska modell för förutsägelse av migrering från matförpackningar till mat. Dessa resultat visar att användandet av etanol som matsimulant för fet mat under mikrovågsvärmning kan leda till betydande överestimering av migrering, samt nedbrytning av polymer och additiv i polymeren.

Andra detekterade migranter var till exempel dimetylbenzaldehyd, 4-etoxy-etylbenzoat, benzofenon, m-tertbutylfenol och 1-metylnaftalen. Alla identifierade migranter med tillhörande 'specific migration limit' (SML)-värden migrerade i betydelsefullt mindre mängder än ämnenas tillhörande SML-värden under 1 h mikrovågsvärmning under 80 °C. Diffusionskoefficienterna för antioxidanterna i PP-förpackningarna visade större relativa skillnader än förpackningarnas motsvarande kristallinitetsgrader och migrering av antioxidanter var snabbast från PP-R.
Nyckelord: migrering, matförpackning, mikrovågor, nedbrytning, matsimulant, antioxidant

List of papers
This thesis is a summary of the following papers:

I Alin, J. & Hakkarainen, M. (2010), 'Type of polypropylene material significantly influences the migration of antioxidants from polymer packaging to food simulants during microwave heating', *Journal of Applied Polymer Science* **118**(2), 1084-1093.

II Alin, J. & Hakkarainen, M. (2011), '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', *Journal of Agricultural and Food Chemistry* **59**(10), 5418-5427.

III Alin, J. & Hakkarainen, M. (2012), 'Migration from polycarbonate packaging to food simulants during microwave heating', *Polymer Degradation and Stability* **97**(8), 1387-1395.

IV Alin, J. & Hakkarainen, M (2013), 'Combined chromatographic and mass spectrometric toolbox for fingerprinting migration from PET tray during microwave heating', *Journal of Agricultural and Food Chemistry* **61**(6), 1405-1415.

The contribution of the author of this thesis to these papers is all the experiments and most of the planning, evaluation of data and writing. This thesis also contains unpublished work. The author has also contributed to:

V Bor, Y.; Alin, J. & Hakkarainen, M. (2012), 'Electrospray Ionization-Mass Spectrometry Analysis Reveals Migration of Cyclic Lactide Oligomers from Polylactide Packaging in Contact with Ethanolic Food Simulant', *Packaging Technology and Science*, **25**(7), 427-433.

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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
ACN	Acetonitrile
BPA	Bisphenol A
DMB	Dimethylbenzaldehyde
DSC	Differential scanning calorimetry
ESI-MS	Electrospray ionization mass spectrometry
EU	European union
FS	Food simulant(s)
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
HFIP	Hexafluoroisopropanol
HPLC	High performance liquid chromatography
I168	Irgafos 168
I1010	Irganox 1010
LOD	Limit of detection
LOQ	Limit of quantification
MAE	Microwave assisted extraction
MHE	Multiple headspace extraction
MHS-SPME	Multiple headspace – solid phase microextraction
OML	Overall migration limit
PC	Polycarbonate
PET	Poly(ethylene terephthalate)
PP	Polypropylene
PP-C	Poly(propylene-*co*-ethylene) block *co*-polymer
PP-R	Poly(propylene-*co*-ethylene) random *co*-polymer
PVC	Poly(vinyl chloride)
SML	Specific migration limit
SPME	Solid-phase microextraction
THF	Tetrahydrofuran
T_m	Melting temperature
UV	Ultraviolet
X_c	Degree of crystallinity (%)

1 Purpose of the study

Plastics are frequently used in our society for packaging different everyday articles, such as foodstuffs. Migration of chemical compounds, such as additives, monomers, catalysts or degradation products, from plastic food packaging materials to food could both introduce bad taste, odors or harmful effects to humans and limit the lifetime of the package. Food is often heated inside plastic packages in microwave ovens and during such usage the food could be contaminated by the migrating compounds. The toxic effects of all the compounds that have been identified in common plastic packages have not been fully evaluated yet. Also, new compounds could be found due to degradation of the additives or polymers, during for example microwave heating, which could produce new degradation products. Therefore it is important for the consumer safety to study migration from packaging materials during microwave heating and high temperature conditions to gain more knowledge on the factors governing migration during such usage, and to obtain realistic estimates of exposure to chemicals during microwave heating of food.

Several migration studies from plastic packaging into food or food simulants involving microwave heating in ordinary microwave ovens have been reported in the existing scientific literature in the past few years. A more systematic study evaluating the effect of both heating time, temperature, microwaves and food/food simulant type on the migration during microwave heating is, however, missing. Also included into these aims is the evaluation of the specific effects of microwaves on polymer-food interactions, and it was therefore not the purpose of the study to exactly simulate real use in a commercial household microwave oven. Minor factors that could affect migration in a real-world scenario such as volatilization/condensation were disregarded and experimental focus was only on the transfer of migrants from package directly to food during microwave heating. Another point was to investigate long-term or repeated use of the packaging, therefore longer microwaving times were also evaluated. Also, the EU commission recommends that overall migration determinations for packages intended for high temperature applications are conducted during at least 1 h at the higher temperature [1]. Temperatures are typically in the range 61 – 121 °C when re-heating ready-prepared foods in a microwave oven [2].

This thesis had the following specific objectives:

- To systematically evaluate the effect of food and package type on the type and amount of compounds migrating from reusable polymer food packaging during microwave heating at different temperatures.
- To evaluate the effect of microwave heating in comparison to conventional heating

at the same temperature on the formation or migration of compounds from the packaging.

- To investigate if the migration to food simulants during microwave heating correlates with the migration to real food and with the values predicted by mathematical models.
- To monitor possible alterations of the packages, such as changes in crystallinity and sorption of food/food simulants after the microwave heatings.
- To further develop and evaluate extraction/analysis techniques for identification and quantitation of migrants in foods or food simulants.

The study focuses on commercially available packages of the polymer types that are most frequently used for microwave heating of food. These are polypropylene, polypropylene-ethylene *co*-polymers, bisphenol A polycarbonate (commonly referred to as polycarbonate) and poly(ethylene terephthalate). Migration into food simulants during microwave heating from polypropylene and polypropylene *co*-polymers are studied in Paper I and II, from polycarbonate in Paper III and from poly(ethylene terephthalate) in paper IV.

2 Introduction

2.1 Background

Additives such as antioxidants, ultraviolet (UV) stabilizers or plasticizers are necessary to protect packaging from UV, mechanical or oxidative deterioration or to increase softness or to improve the overall appearance or quality of the plastic product. The additives are not covalently bound to the polymer and are therefore susceptible to migration during heating or long term storage. Many of the chemical compounds that are common in commodity plastics have been compiled in legislative lists by the European union, and some compounds, with available toxicity data, have been assigned specific migration limit (SML) values for specified test conditions or worst case conditions, which must not be exceeded during the use of the packaging in order to be permitted in the EU market [3]. A large amount of different additives or other constituents of plastic packaging are, however, still not compiled into the lists and/or have unevaluated toxicity. This is especially likely if the compounds are degradation products from additives or polymers. EU has also established regulations concerning the overall migration, which is the sum of all content that migrates from the polymer into the food or food simulant without taking the identity of specific compounds into consideration. The overall migration is typically determined gravimetrically, by evaporating the food simulant and weighing the residue, after the migration tests. The overall migration limit (OML) that have been established for all types of plastics intended to be used in contact with food is 10 mg/dm^2, during standard storage conditions such as 10 days at 40 °C or other worst case high temperature usage conditions depending on the package's intended usage.

Because microwave processing of foods in polymer packages is used more and more in the society, there is a need for more systematic studies evaluating the effects of microwaves, temperature and heating time on migration. Another point is the effect of polymer type in combination with different types of food or food simulants during microwave heating. The heat transfer processes occurring during microwaving are different from processes occurring during heating by conduction/convection and may therefore result in unpredictable migration behaviors [4]. During microwave heating high temperatures are often reached in short times. Microwaves can also increase the diffusion rates, cause degradation of migrants or polymer, or cause localized spot heating which would increase the migration to higher levels than would be expected from the bulk heating temperature. Because of the convenience of microwave heating food directly in plastic food packages, it is expected that this type of processing will continue to increase in the future [5].

2.2 Food simulants

Food simulants are liquid or solid standard chemicals used to simulate the most common food types, and some of them are also approved by the EU commission to be used during migration studies. Typical food simulants are water for aqueous, 10% ethanol/water for alcoholic, 3% acetic acid/water for acidic, and olive oil or ethanol for fat foods [6]. These are used primarily because the analysis of migrants in food simulants is much easier than the analysis of migrants in real foods, and to provide reproducible and easily conducted migration testing methods.

2.3 Microwave and conventional heating of polymer packaging

In the scientific literature, migration experiments from food packaging involving microwave heating were usually made in an ordinary microwave oven [7, 8, 9, 10, 11], which leaved the exact heating temperature or the temperature profiles in the foods/packages unknown. A microwave assisted extraction (MAE) system can be used to determine migration during controlled temperature conditions, and the suitability of the system to evaluate migration into food simulants has earlier shown reproducible results with little or no temperature variations among the samples [12]. A study concerning the effect of microwave heating on the sorption of common polar and non-polar solvents into polyethylene, polyvinyl chloride (PVC) and silicone rubber has shown that microwaves have little or no effect compared to conventional heating on the rate of uptake of solvent by the polymer [13]. Overall migration into food simulants from PVC however increased significantly during 3 min of microwave heating at full effect compared to the overall migration during microwave and conventional heating of other polymer types such as polypropylene, polyethylene and polyamide [8]. Microwave heating also increased the diffusion rate of ethylene oxide in PVC [14] and cyclopentanone in an epoxy resin [15] above the rate that would be expected from the temperature alone. Another study found that overall migration into olive oil from a polypropylene package increased after repeated microwave heating to 400% compared to the first heating [16]. There is thus evidence that microwave heating could increase the migration of specific migrants in specific types of polymers. Possibly those migrant or polymer types that are more susceptible to absorption of microwave radiation are more prone to result in increased migration rates during microwave heating.

Overall migration to food or food simulants from different plastics have been determined in the past both during standard test conditions and during heating in microwave oven [8, 9]. It was found that overall migration from polypropylene to aqueous food simulants during microwave heating for 3 min at 800 W was comparable to the overall

migration during continuous heating at 80 °C for 30 min, with results in the range from 0.05 mg/dm^2 to 0.14 mg/dm^2 [8]. Overall migration determinations from poly(ethylene terephthalate) (PET) into food simulants conducted during conventional heating for 1 h at 90 °C revealed overall migration values of <0.1 mg/dm^2 into water, 0.2 mg/dm^2 into 10% ethanol and 1.4 mg/dm^2 into 3% acetic acid [17].

2.4 Additive content and migration behavior of common packaging materials

2.4.1 Polypropylene

Polypropylene (PP) is one of the most commonly used polymer packaging materials for food usage. It typically has a glass transition temperature in the range from -20 to -10 °C. The degree of crystallinity for isotactic polypropylene is approximately 40%. Normally the crystals in polypropylene have a melting temperature of around 160 °C.

Polypropylene has tertiary hydrogens in the polymer chain which makes it more susceptible to hydrogen abstraction, and it therefore requires relatively large amounts of antioxidants to be protected from oxidative degradation during processing or usage. During the inhibition of polymer degradation by antioxidants, additional degradation products could be formed from degradation of the antioxidants during the stabilizing processes. These new compounds would be of lower molecular weight and therefore they would be more susceptible to migration. Known antioxidants in polymers and their migration are well documented in the scientific litterature and they can therefore be used as model compounds to compare different polymers or heating methods. Antioxidants in polymers are primary (radical scavenger) or secondary (hydroxide decomposer). Often a combination of both types is used. Irganox 1010 (primary antioxidant) and Irgafos 168 (secondary antioxidant) are two of the most common examples of primary and secondary antioxidants, and their structures are shown in Scheme 1. These two types of antioxidants are often incorporated together into the polymer in order to obtain a synergistic stabilizing effect [18]. Dopico-García et al. found that most of the commonly available PP packages on the market contained Irgafos 168 and Irganox 1010, sometimes in concentrations as high as 0.1% or above by weight, and some of them also contained Irganox 1076 and smaller amounts of antioxidant degradation products such as 2,4-bis(1,1-dimethylethyl)-phenol (Scheme 1). Altogether they analyzed a large number of commercial PP food packages [19]. A toxicity study on 2,4-bis(1,1-dimethylethyl)-phenol has revealed a no-observed-adverse-effect level (NOAEL) of 5 and 20 mg/(kg day) for newborn and young rats respectively [20].

Polypropylene copolymers are available in different grades or qualities, obtained most

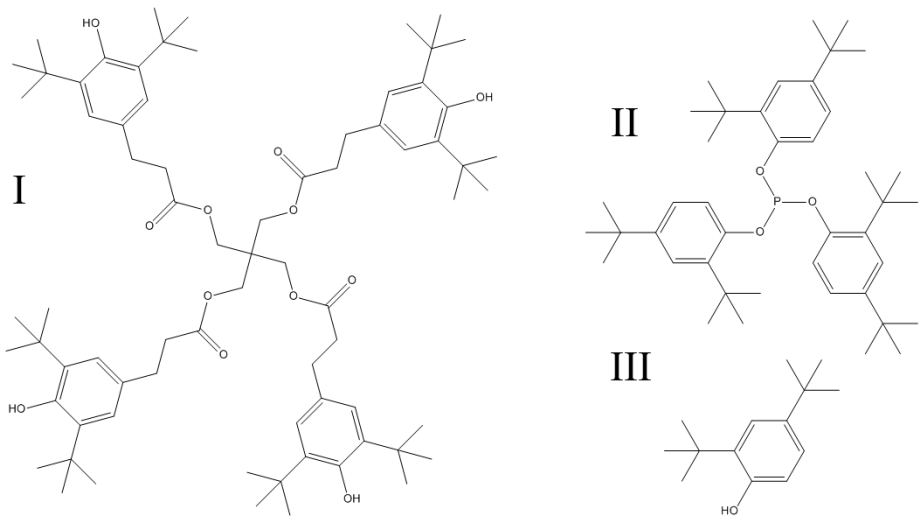
commonly by *co*-polymerization with ethylene in different amounts or orders. This yields different properties, for example different degrees of crystallinity. This can be expected to influence migration rates of additives. Random ethylene *co*-polymers have generally resulted in the highest diffusion rates for antioxidants [21, 22, 23], and this behavior could be related to the often lower degree of crystallinity in the random *co*-polymer. A recent computer simulation study also showed that the amorphous structure of random PP *co*-polymer has more free volume with more inter-connected pores than block *co*-polymers or homopolymers of PP and therefore the random *co*-polymer had a higher diffusion rate for limonene compared to the rate in the other PP types [24]. The initial sorption rates of small penetrants in polypropylene homopolymers were independent of degree of crystallinity at degrees of crystallinity below 50% [25]. The crystal lamellar structure has also been shown to result in unpredictable diffusion rates if the evaluation is done by degree of crystallinity alone [26]. The lamellar stuctures of PP were altered by subjecting the polymers to different thermal histories. When determining the migration of antioxidants from PP packages during conventional heating into different food simulants, Garde et al. found that the food simulant heptane increased the migration of the antioxidants. This increase corresponded to diffusion coefficient increases by factors of 10 at 60 °C [27], and was explained by swelling.

Hindered amine light stabilizers (HALS) are other types of additives that have been found in PP based packaging [28]. HALS have molecular weights as high as 2000 – 4000 amu. Possibly harmful chemicals in PP and PP random *co*-polymer packages were found by Nerín et al. who detected various aromatic hydrocarbons such as ethylbenzene, methylbenzene, xylene and styrene and showed migration from the packages during conventional heating [29].

2.4.2 Polyethylene terephthalate

Polyethylene terephthalate (PET) is commonly manufactured by polymerization of ethylene glycol and dimethyl terephthalate or terephthalic acid through polycondensation. It has high temperature stability and good water barrier properties. It is often used in food packaging, in the form of trays and dishes for microwave and conventional cooking, and in susceptor films.

While migration of cyclic PET oligomers from PET food contact materials is well documented, migration studies on other low molecular weight compounds that could be contained in PET materials, such as acetaldehyde, monomers, catalysts or degradation products, often showed very low or no detectable migration [30, 31]. One study found that PET contents could be genotoxic when they studied growing salmonella strains in water in PET bottles. It could not be determined what compound in the bottle that



Scheme 1: Common antioxidants in polyolefins, Irganox 1010 (I1010) (I), Irgafos 168 (I168) (II) and the Irgafos 168 degradation product 2,4-bis(1,1-dimethylethyl)-phenol (2,4-DTB) (III)

caused the toxicity [32], and a mutagenicity test on non-volatile migrants identified in the study gave negative results [33].

PET often contains cyclic oligomers, ranging from dimers to pentamers, at contents ranging from 0.06 to 1.0% depending on the type of PET material [34]. PET oligomers are of low acute, long or short term toxicity and have no SML [35] but they are still subjected to the OML of 10 mg/dm^2 set by the European commission. A comparison between the effects of microwave and thermal treatment on cyclic oligomer migration from PET roasting bags by López-Cervantez et al. showed that 2.7 – 4.1 mg/dm^2 of PET oligomers migrated into olive oil during 7 min heating in a 850 W microwave oven and 2.7 – 3.5 mg/dm^2 of oligomers migrated during 60 min of heating at 200 °C in a conventional oven [36]. It was estimated that around 65-70% of the oligomers in microwaveable PET susceptor films migrated into corn oil during a 3 min heating period in a microwave oven, while 100% of the oligomers had migrated after a 5 min heating period. The total oligomer content was 3.7 mg/dm^2 [37]. Other conventional studies have found oligomer migration in the range from 1.4 to 4.2 mg/dm^2 into olive oil during a 2 h heating period at 175 °C [38]. An oligomer migration study using

aqueous food simulants established 0.2 mg/dm^2 migration into water and 15% ethanol and 1.4 mg/dm^2 migration into 3% acetic acid during a 1 h heating period at 95 °C of conventional heating [39].

2.4.3 Polycarbonate

Polycarbonate has good mechanical and barrier properties. It is fully amorphous and has a high glass transition temperature of around 150 °C which results in good barrier properties even at higher temperatures. It is widely used in food packaging such as reusable food storage boxes, water bottles and baby bottles.

There have been several scientific studies investigating the release of Bisphenol A (BPA) from polycarbonate, because in the past few years it was shown that this compound could have endocrine disrupting or estrogenic properties. Polycarbonate is polymerized from the sodium salt of BPA and phosgene and sometimes unreacted BPA is left in the polymer. More recent studies have, however, concluded that in most cases the release of BPA from polycarbonate is not a result of migration of residual BPA in the polymer, but rather a result from the depolymerization during hydrolysis reactions under certain conditions [40] *e. g.* when the polymer is in contact with highly alcalic water [41], which produces BPA from the polymer chains. Ehlert et al. found that BPA migrates into boiling water during microwave heating of water in polycarbonate baby bottles in an ordinary microwave oven. However, the migration values were lower than the SML. No correlation could be found between the residual BPA in the bottles and the migrated amounts [42].

There are not many studies available concerning the migration or potential migration of other migrants from polycarbonate. Exceptions are for example studies by Nerín et al. who identified phenol, bisphenol A, 2,4-bis(1,1-dimethylethyl)-phenol, Cyasorb UV5411, bis(2-ethylhexylphthalate), Irganox 1076 and Irgafos 168 [43], and several volatile aromatic and aliphatic hydrocarbons and chlorinated hydrocarbons [44] in commercial polycarbonate food containers intended to be used in microwave ovens. Petersen et al. also determined the migration of 2-butoxyethyl acetate from polycarbonate infant feeding bottles [45].

2.5 Analytical techniques used to identify and quantify migrants

2.5.1 Solid phase microextraction with gas chromatography-mass spectrometry

A common analytical instrument used for the identification and quantification of low molecular weight compounds migrating from polymers is gas chromatography-mass spectrometry (GC-MS) [46, 47]. The determination of migrants in food simulants using GC-MS is often straight-forward and simple. However, additional extraction/separation procedures are usually necessary because aqueous samples cannot be injected directly into a GC-MS instrument. Solid phase microextraction (SPME) can be used to extract trace amounts of migrants from water. This separation/extraction technique was introduced by Arthur and Pawliszyn in 1990 [48] and it is operated by holding a fused-silica fiber coated with a polymeric stationary phase in the liquid (immersion mode) or in the headspace of a liquid solution or solid sample. With this technique, analytes are extracted from the gas or liquid phase by adsorption to the fiber. The adsorbents are then desorbed and analyzed by injecting the fiber into an injection port of a gas chromatographic system. SPME has for example been applied for extraction of thermo-oxidation [49] and hydrolysis products from polymers [50]. SPME by immersion mode was used to extract common plastic migrants such as styrene, phenol and benzophenone from crosslinked polyethylene pipes in water and detection limits around 5 µg/L were achieved [51]. Various fiber materials having different polarities exist and were tested, but the polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber material was found to be the most efficient for the analyzed compounds.

2.5.1.1 Multiple headspace – solid phase microextraction SPME is an efficient extraction technique for low concentrations of analytes because pre-concentration is achieved when the analytes are adsorbed by the fiber. The liquid/fiber, gas/fiber or liquid/gas partition coefficients of the analyte governs the adsorption efficiency during extraction from a liquid sample. These coefficients are in most cases unknown or complicated to determine because they are also dependent on the sample matrix composition. Therefore, a standard matrix having the exact same composition as the samples must be used in order to obtain a valid linear calibration by the analytes in standard solution for quantification. This can be hard to achieve in practice for extraction samples, because many unknown compounds are often extracted simultaneously with the analyte(s) of interest which would alter the partition coefficient of the samples compared to that of the standard. Standard addition is one procedure which eliminates these effects. However, the SPME fiber can be rather easily saturated, having often a relatively narrow

linear range.

One alternative to standard addition to overcome matrix effects is multiple headspace – solid phase microextraction (MHS-SPME). This extraction or quantification technique was originally developed for ordinary headspace analysis by Kolb and Pospisil in 1977 [52]. In this case it is called multiple headspace extraction (MHE) and it is suitable for liquid or solid samples as well as for food simulants. Using this technique, the same sample is extracted multiple times. The chromatographic peak areas, corresponding to the amount of the analyte adsorbed to the fiber during each extraction follow the exponential relationship [52]

$$A_i = A_1 \exp(-q'(i-1)) \tag{1}$$

where A_i is the area for the i:th extraction and A_1 is the area for the first extraction. i is the extraction number in sequence and q' is a constant related to material specific and mass transfer parameters, such as partition coefficients, sample/headspace volume etc. This relationship holds because during each extraction, the amount of extracted analyte is always a constant proportion of the remaining analyte in the sample, provided that the material specific parameters are kept constant during the extractions. The infinite sum of these areas correspond to the total amount in the sample. The infinite sum of the terms in equation (1),

$$\sum_{i=1}^{\infty} A_i = A_1 + A_1 \exp(-q') + A_1 \exp(-2q') + A_1 \exp(-3q') + \ldots \tag{2}$$

can be expressed as

$$\sum_{i=1}^{\infty} A_i = \frac{A_1}{1 - \exp(-q')} \tag{3}$$

which means that after derivation of q' a single extraction would be enough to calculate the total amount in the sample. The derivation of q' can be easily achieved by performing a series of extractions and fitting the obtained areas as function of extraction number to the logarithmed version of equation (1), which is a linear equation of the type $y = kx + m$:

$$\ln A_i = -q'(i-1) + \ln A_1 \tag{4}$$

q' can thus be obtained from the slope of the fitted equation. If the resulting linear correlation coefficient is high enough, the assumptions in the underlying theory are correct and a calibration can be performed relating the area sum to concentration of

analyte by performing MHE/MHS-SPME on a standard as well as on samples. The standard could be kept in a different matrix than the sample because the extraction is assumed to be exhaustive and matrix effects are thus eliminated. If the resulting fit is non-linear, disturbances could be present such as adsorption or partitioning effects. It is important that these are avoided, by for example adding water to the sample as a displacer [53]. The MHS-SPME technique has previously been used to quantify 2-cyclopentylcyclopentanone in polyamide [46] and to simultaneously quantify several volatile phenols in wine [54]. More detailed information on the theoretical aspects/validation of MHE can be found in literature [55].

It has also been shown that MHS-SPME can be performed even if equilibrium in the analyte extraction is not reached [56]. Steady-state conditions in the extraction of analyte to fiber from headspace or solution is then assumed, so that the concentration gradient of the analyte at the fiber/liquid interface is linear. The amount of extracted analyte during one extraction (here describing a liquid/fiber immersion extraction but a treatment could also cover headspace extractions similarly) is then described by [57]

$$n = [1 - \exp(-At)][\frac{KV_fV_s}{KV_f + V_s}]C_0 \tag{5}$$

where n is the amount of analyte adsorbed to the fiber, A is a term composed of mass transfer rate coefficients, partition coefficients and fiber/sample volumes which are constant during the extractions, t is time, K is the fiber/liquid partition coefficient, V_f is the fiber volume, V_s is the sample volume and C_0 is the concentration of the analyte in the sample prior to extraction. The second bracket term can also conveniently be expressed as another single parameter, because it also remains constant during the extractions. Equation (5) describes an extraction approaching an equilibrium value, n_0, asymptotically when t approaches infinity. Equation (5) can in other words be expressed as [57]

$$\frac{n}{n_0} = 1 - \exp(-at) \tag{6}$$

where a is a term that is composed of the constant term A and the constant fiber/volume parameters in the second bracket in equation (5). Therefore, if the extraction time is equally long during each extraction, the extracted amount is a constant proportion of the concentration prior to extraction, C_0, and the peak areas obtained during the extractions could also be fitted to equation (4) obtaining a new value for q'. This allows MHS-SPME to be performed equally well during non-equilibrium conditions, which is positive with respect to analysis time because equilibrium time can be long especially for solid samples.

2.5.2 Electrospray ionization mass spectrometry

Liquid chromatography coupled to a mass spectrometric detector (LC-MS) is a common technique used to identify un-volatile migrants or polymer additives that have too high boiling points to be detectable by GC-MS, such as UV stabilizers [28, 58, 59]. An ion source that is often used in LC-MS for analysis of both un-volatile and thermolabile compounds is electrospray ionization (ESI). This interface coupled to a mass spectrometer can also be used directly on liquid samples without chromatographic separation for rapid analyses of higher molecular weight compounds in aqueous solutions, then called electrospray ionization mass spectrometry (ESI-MS). Because ESI-MS is a soft ionization technique giving very little or no fragmentation, it can be used for the direct identification of migrants, with the possibility to use MS-MS techniques to reveal fragment ions.

ESI-MS has previously been used to determine degradation products from polyesters [60, 61] and for analysis of the total oligomeric fraction in PET [62], but to best of our knowledge it was not used for additive migration determinations from polymers before. It has been described as a promising system for polymer analysis with the potential to detect relatively broad ranges of product abundances [63].

As in the case with GC-MS, separation techniques must sometimes be applied before ESI-MS analysis. For example the ESI-MS interface is very sensitive to contamination of the solvent, requiring a solvent of at least LC-MS grade purity. The only solvents that are commonly available in LC-MS grade purity are water, acetonitrile and methanol.

2.5.3 High performance liquid chromatography

Many of the higher molecular weight additives present in polymers, for example antioxidants, contain chromophores and can therefore be analyzed by using high performance liquid chromatography (HPLC) with UV detection. This is a common technique often used during the analysis of polymer additives [64, 19, 65, 66] and has for example been used to follow the migration of cyclic oligomers from PET packaging into olive oil [36]. HPLC-UV analysis has also been used to analyze Irgafos 168 and Irganox 1076 extracted from low density polyethylene (LDPE) [66].

2.6 Mathematical models used to predict migration from packaging into food

As has also been stated in the Background section, the European legislation requires verification of compliance for migration of substances from polymeric food contact ma-

terials with existing specific and overall migration limits. Numerous scientific investigations have also demonstrated that migration from food contact materials into food or food simulants are predictable physical processes, bound by Fick's laws of diffusion. Modeling of migration is recognized both by the Food and Drug Administration (FDA) and the European Union as a tool to assist in making regulatory decisions [67].

Fick's second law of diffusion in one dimension states that

$$\frac{\partial c(t,x)}{\partial t} = D\frac{\partial^2 c(t,x)}{\partial x^2} \tag{7}$$

where *c(t,x)* is the concentration at time t and position x and D is the diffusion coefficient. This equation has several analytical solutions given typical initial and boundary conditions [68] which for example can be integrated from the values of x representing the top surface, to the value representing the bottom surface, of the polymer package side in contact with the food. Thereby one obtains an expression that gives the total amount in the polymer section as a function of time, or the amount of additive having left the polymer as a function of time. Equation (8) is one such derivation and it is the one that is used in the mathematical model recommended by the European commission to predict migration into foodstuffs [67]. It gives the migrated amount of additive per area unit from a polymer section with uniform thickness, having homogenous initial distribution of additive. After leaving the polymer, the diffusant is immediately without resistance entered into a medium of limited volume where it is homogeneously distributed at all times.

$$\frac{m_{f,t}}{A} = C_{p,0}\rho d_p\left(\frac{\alpha}{1+\alpha}\right)\left(1-\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n}\exp(-Dt\frac{q_n^2}{d_p^2})\right) \tag{8}$$

$C_{p,0}$ is the initial weight fraction of additive in polymer, ρ the density of the polymer and d_p the thickness of the polymer package. α equals $(1/K_{pf} \times V_f/V_p)$ *i. e.* the food simulant/polymer volume ratio divided by the diffusant's polymer/food partition coefficient. q_n are the roots of the transcendent equation 'tan q_n = -αq_n'. Even though the number of the roots is infinitive, the terms in the equation in most cases converge quite rapidly to zero so that a large number of roots is not necessary to obtain adequate accuracy, typically 10 roots are more than enough. However, in some cases where the diffusion coefficient is very low the equation can give erroneous results at short time values even if a large number of roots is used. If however α is sufficiently large (for example a low polymer/food partition coefficient and/or a large external phase volume) and the migrated amount is less than around 60% of the initial amount in the polymer, equation (8) can conveniently be approximated by equation (9): [68]

$$\frac{m_{f,t}}{A} = 2C_{p,0}\rho\sqrt{\frac{Dt}{\pi}} \tag{9}$$

Some limitations with mathematical modeling exists, for example the often unknown diffusion and partition coefficients are tedious to determine. To predict diffusion coefficients, an empirical equation has been derived from a large number of diffusion experiments into liquid and solid food simulants with additives of different molecular weights, constructed to give the confidence interval high limit at 95% significance level of those experimentally determined coefficients, the so called 'upper bound' diffusion coefficients, D'_p (cm^2/s): [69, 67]

$$D'_p = 10^4 \exp(A_p - 0.1351M_r^{2/3} + 0.003M_r - \frac{10454}{T}) \tag{10}$$

where

$$A_p = A'_p - \frac{\tau}{T} \tag{11}$$

T is temperature, M_r is relative molecular weight of the additive, τ is a polymer specific activation energy parameter and A'_p is a polymer 'conductance' parameter with lower values for more dense and less permeable polymers. Equations (10) and (11) are otherwise known as the Piringer model. Parameter values of the most common food packaging polymers exist and are summarized [67]. The activation energy parameter implies that the diffusion coefficient follows Arrhenius' reaction rate law temperature dependence, but in addition the coefficients could also increase with the thermal expansion of the polymer or uptake (swelling) of liquid food/food simulants by the polymer. There are several other theoretical treatments of interest for the diffusion coefficients of molecules in polymers that for example describe the variation of the coefficient with temperature, taking both free volume and an activation energy barrier into account [70]. The Piringer model uses much simpler approximations, yet it has been found that it is adequate so far for the purpose of modeling additive migration from polymers into foods and food simulants. On the other hand, if significant swelling occurs, so that the diffusion coefficient becomes concentration dependent with respect to the swelling liquid, only numerical solutions to the diffusion equation would be able to accurately describe the migrant release. Therefore the model described above is not suitable for highly swelling food simulants.

3 Experimental

3.1 Materials

Tetrahydrofuran (>99.9%) and ethanol (99.9% chromatography grade), 1-methylnaphthalene (>98%) and isooctane (2,2,4-trimethylpentane) (99.0% LC grade) were supplied from Merck. Acetonitrile (99.99%), chloroform (100% HPLC grade), hexafluoroisopropanol (98%) and methanol (99.9%, LC-MS grade) were supplied from Fisher. Ethanol (96%) was supplied from VWR. Acetic acid (99.5%), 2,4-dimethylbenzaldehyde (90+%), 2,4-bis(1,1-dimethylethyl)-phenol (97%), m-tert-butyl phenol (99%) and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (98%) were obtained from Acros. 4-ethoxy-benzoic acid ethyl ester (98%), 9,9-dimethylxanthene (96%), 4-ethoxy-benzoic acid ethyl ester (98%), 1,1'(1,3-propanediyl)bis-benzene (100%) and diethyl terephthalate (1,4-benzenedicarboxylic acid, diethyl ester) (95%) were obtained from Alfa. Acetophenone was obtained from Polyscience (Niles, IL). Benzophenone (>99.9%) was obtained from Fluka. Bisphenol A (99.0%) was obtained from Aldrich. Water was obtained both from Fisher (LC-MS grade) and from a Millipore MilliQ water purifier system. Irgafos 168 (tris(2,4-tert-butylphenyl) phosphite) and Irganox 1010 (pentaerythritol tetrakis[3-(4-hydroxy-3,5-di-tert-butylphenyl)propionate]) were supplied from Ciba Speciality Chemicals (now BASF).

Mean thicknesses of the PP packages were 1.3 mm for PP and PP-C and 1.2 mm for PP-R. The PP-C package was non-transparent and white, while the PP-R and PP packages were transparent. The PP-C and PP-R packages were approved by the manufacturer for microwave use and to be heated up to a maximum temperature of 120 °C. The PP package was obtained from a different manufacturer than PP-C and PP-R packages and had no heating designations listed.

The plastic food container of polycarbonate (PC) was a new reusable commercial food storage box suitable for microwave oven, approximately 1.7 mm thick and it was purchased from local supermarket. It was wrapped in a cardboard package and was designed for heating up to 130 °C.

The poly(ethylene terephthalate) (PET) trays were commercial black trays intended for food usage during microwave heating. The thickness of the trays was approximately 0.35 mm.

Coconut milk was bought preserve-canned from a local supermarket and had a designated fat content of 17% by weight.

3.2 Instruments and methods

3.2.1 Microwave assisted extraction

To determine migration from the packages during microwave heating, a microwave assisted extraction (MAE) system was utilized. It was a CEM MES-1000, a multimode type microwave solvent extraction system with a rotating turntable having a maximum effect of 950 W. It had place for up to 12 sample vessels where the samples to be extracted from are put together with the extraction solvent. The vessels are closed gastight during an extraction. The temperature of solvent and the pressure in the container are constantly monitored. Both the time, temperature and pressure were programmable.

3.2.2 High performance liquid chromatography

The high performance liquid chromatography (HPLC) system consisted of a Hewlett Packard series 1100 auto-sampler and ultraviolet (UV) detector with a Shimadzu LC-10AD solvent delivery module. The columns used were a Supelco Supelcosil 5 µm LC-18 with the dimensions 4.6 × 150 mm, and a Supelco Hypersil ODS 5 µm with the dimensions 4.6 × 250 mm, both having C18 (Octadecyl) stationary phase. The UV detector was set at a wavelength of 280 nm. The mobile phase was composed of 90/10 ACN/THF and eluted at 1 ml/min. It was degassed by helium before use.

FS aliquots from the migration determinations were injected directly after filtration through a 0.45 µm filter-tip into the HPLC system. The antioxidants that migrated from the PP and PP *co*-polymers into the FS were identified by spiking some samples with the standard solutions of I168 and I1010 and then analyzing them with the HPLC system. The samples showed increased peak areas and no peak separation into doublets giving positive identification.

3.2.2.1 Calibration and standard preparation Standard solutions of Irgafos 168 (I168) and Irganox 1010 (I1010) were made by dissolving three different amounts of each of the antioxidants in solutions of 90/10 isooctane/ethanol. The solutions were then injected into the high performance liquid chromatography (HPLC) system. The obtained calibration curves had correlation coefficients (R^2) of 0.9991 for I168 and 0.993 for I1010.

To determine possible antioxidant degradation through hydrolysis with ethanol, another calibration curve was prepared by dissolving different concentrations of antioxidants in 99.9% ethanol. The ethanol standards were heated on heating plate for 1 h at 80 °C before injecting them into the HPLC system. The resulting calibration curves of the ethanol standards had R^2 values of 0.9998 for I168 and 0.9985 for I1010 and the

slopes were equal to the isooctane/ethanol standard calibration curve's indicating that no significant degradation occurred during conventional heating in ethanol.

To determine the repeatability of the antioxidant quantification, after the FS had been subjected to the MAE heating procedure, a known amount of standard in 90/10 isooctane/ethanol was divided into five parts. Four were heated for 1 h at 80 °C in MAE and then analyzed by HPLC and one was analyzed directly. The areas of the heated samples were compared to that of the unheated sample showing recoveries of 98% for I168 and 96% for I1010. Areas of the four heated standards had standard deviation of 1.4% for I168 and 0.6% for I1010 showing good repeatability.

3.2.3 Gas chromatography-massnspectrometry

Volatile migrants in water, 99.9% ethanol, isooctane, 90/10 isooctane/ethanol and chloroform were analyzed on a Finnnigan MAT GCQ system (San José, CA, USA) 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 column from Varian. Helium of 99.9999% purity with a constant linear velocity of 40 cm/s was used as carrier gas.

Volatile migrants in the food sample were analyzed by a Finnigan TRACE Mass spectrometer with a TRACE 2000 series GC oven. Helium of 99.9999% purity was used as carrier gas and the flow rate was 1.5 ml/min. The column was a DB-5MS 30 m × 0.32 mm × 0.25 µm column from Agilent.

The column temperature was held at 40 °C for 1 min, thereafter it was heated at a constant rate of 10 °C/min up to 270 °C and finally it was held at 270 °C for 15 min. The mass scan range of the detector was set at $m/z35$ – 400 and electron ionization (EI) mode was used with an electron energy of 70 eV. The injector temperature was 250 °C.

The ethanol, 90/10 isooctane/ethanol and isooctane FS extracts were injected directly after filtration (0.45 µm filter tip) and the injection volume was 1 µL. Quantification was made by one-point calibration with ethanol standard solution in duplicate and peak integration was carried out on the reconstructed (base peak ion) chromatograms using the most intense fragment ion for respective compound in most cases. The linearity of peak area vs concentraion was checked beforehand, by injecting standard solutions with different concentrations of analytes. The fragment ions used in the quantification of the migrant by the different standard compounds are listed in Table 1.

Solid phase microextraction (SPME) was used to extract migrants from water or real food samples before subsequent GC-MS analysis (see section 3.2.3.1). To quantify migrants in water, multiple-headspace solid phase microextraction (MHS-SPME) was carried out both on the water samples with migrants and on a standard solution in 10%

Table 1: Standard compounds and the fragment masses that were used during GC-MS analysis and quantification of the migrants.

Compound	CAS nr	Quantification ion (m/z)
acetophenone	98-86-2	105
phenol, m-tert-butyl-	585-34-2	135
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	177
2,4-bis(1,1-dimethylethyl)-phenol	96-76-4	191
4-ethoxy-benzoic acid ethyl ester	23676-09-7	121
benzophenone	119-61-9	182
1,4-benzenedicarboxylic acid, diethyl ester-	636-09-9	177
9,9-dimethylxanthene	19814-75-6	195
2,4-dimethylbenzaldehyde	15764-16-6	133
bisphenol A	80-05-7	213

ethanol (see section 3.2.3.2).

Positive migrant identification was assumed when both the unknown analytes and standard compound's mass spectra and retention times were equal. Mass spectra of unidentified compounds were matched against the National Institute of Standards and Technology (NIST) library database using the MS search program v. 1.7 to obtain identification by library reference match.

3.2.3.1 Solid-phase microextraction The SPME fiber was a 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber from SUPELCO (Bellefonte, PA USA). A water and 10% ethanol/water standard solutions for SPME analysis of the migrants in Table 1 were prepared with analytes in concentration range 1 – 20 µg/L.

10 ml of sample or standard solution was extracted in a 20 ml headspace vial sealed with a crimp seal and polytetrafluoroethylene (PTFE) / silicone septum. Extractions of the FS samples were carried out automatically by the Gerstel autosampler by penetrating the septum of the preheated vial with the fiber needle and exposing the fiber to the headspace above the solution under constant vial agitation at 500 rpm. Extraction time was 30 min and temperature was 80 °C. After the extraction, the needle was withdrawn and immediately injected into the GC injection port and left for desorption during 7 min.

SPME of the coconut milk was conducted by pouring 3 ml of the food with potential migrants into a 20 ml headspace vial and thereafter adding a magnetic stirrer and 7 ml of water as a displacer. A standard spiked food sample was also prepared by adding 3 ml of coconut milk into a 20 ml headspace vial. 10 µL of a chloroform solution containing the standard compounds. A magnetic stirrer and 7 ml of water were subsequently added. The vials were thereafter sealed with PTFE/silicone septa. The extractions were carried out manually, with the vial heated in an oil bath holding a constant temperature of 100 °C and a stirring rate of 1000 rpm. The fiber needle was injected into the vial and it was held at approximately 0.5 cm above the surface of the liquid during the extraction. The extraction time was 30 min. After the extraction the fiber was immediately injected into the GC-MS system and left in the injector port during a desorption time of 5 min.

3.2.3.2 Calibration using MHS-SPME Before multiple-headspace solid phase microextraction (MHS-SPME) of the 10% ethanol standard solution, the linearity of extracted amount vs amount in solution was checked by performing SPME on five different standard solutions with increasing concentrations of the analytes, and plotting the obtained peak areas as a function of concentration. All of the compounds were shown to be within linear range of the fiber.

Samples and a standard solution (the one having the lowest concentration of the analytes) were extracted four consecutive times. The standard solution was analyzed in triplicate and samples in duplicate. Mean values of the areas of the three parallel standard extractions were used to determine q' in equation (1) by fitting the logarithmed area values as function of extraction number to a linear function and obtaining q' from the slopes according to equation (4). The migrated amounts from the unknown samples were determined individually from single samples and the two parallel determinations were averaged later. Area sums of the standard and sample compounds were then calculated with equation (3) and the migrated amounts were calculated by

$$m_{sample} = \frac{A_{s,sample}}{A_{s,standard}} C_{standard} V_{standard} \tag{12}$$

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

3.2.4 Electrospray ionization mass spectrometry

Electrospray ionization mass spectra were acquired with a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). 50/50 methanol/water sample solutions were

directly infused into the mass spectrometer with a continuous flow rate of 5 µL/min with a syringe pump set at constant speed. Scanning of mass spectra was performed in positive ion mode and the ion source was operated at 5 kV. Capillary temperature was 175 °C and nitrogen was used as nebulizing gas and helium as damping and collision gas.

3.2.4.1 Sample preparation Samples for ESI-MS analysis of the migrants from the PC, PET and PP packages were prepared by evaporating 10 ml of analyte/migrant and blank FS solutions contained in 20 ml headspace glass vials using a small continuous flow of nitrogen in room temperature until no visible liquid remained in the vials. 1 ml of a 50/50 methanol/water mixture was then added to the sample vials which were sealed and ultrasonicated for approximately 5 minutes. The solutions were then filtrated (0.45 µm filter-tip) using a glass syringe and stored for later analysis.

3.2.4.2 Standard preparation Standards of degraded antioxidants for ESI-MS analysis were prepared by dissolving I168 and I1010 in 90/10 isooctane/ethanol, 99.9% ethanol and chloroform and heating the solutions for 1 h and 24 h at 80 °C in MAE and on heating plate before solvent evaporation and re-dissolution for ESI-MS using the procedure described in section 3.2.4.1.

3.2.5 Differential scanning calorimetry

Degree of crystallinity (X_c) of the original and microwave heated samples, as well as the melting temperatures of the samples, were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 820 STAR^e system with a GC100 gas controller. Sample amounts of 3 – 4 mg were heated first from 25 to 300 °C at a rate of +10 °C/min, then cooled from 300 to 0 °C at a rate of -10 °C/min and then finally heated from 0 to 300 °C again at a rate of +10 °C/min. The samples were kept under 80 ml/min of constant nitrogen gas flow during the whole analysis. The degree of crystallinity (%) was calculated with the equation

$$X_c = \frac{100 \times \Delta H_f}{\Delta H_f^0} \tag{13}$$

where ΔH_f is the integrated melting peak area from the thermogram divided by the sample amount and $\Delta H^0{}_f$ is the melting enthalpy of a 100% crystalline polymer sample. The melting enthalpy value used for 100% crystalline PP, PP-R and PP-C material was 209 J/g [71] and the value for 100% crystalline PET was 144.7 J/g [72].

3.2.6 Fourier transform infrared spectroscopy

The identity of the polymer packages was confirmed by Fourier transform infrared spectrometry (FTIR) surface analysis using a PerkinElmer Spectrum 2000 FTIR system with a Specac P/N 10,500 series single reflection Attenuated Total Reflectance (ATR) diamond accessory. Sixteen scans for each sample were made and averaged to eliminate noise. The sample spectra were then compared to known spectra of polypropylene, polycarbonate and poly(ethylene terephthalate), obtained from the Scifinder database, for identification.

3.3 Migration determinations

3.3.1 Microwave heating

Samples of polycarbonate (PC), poly(ethylene terephthalate) (PET), polypropylene (PP), polypropylene block *co*-polymer (PP-C) and polypropylene random *co*-polymer (PP-R) were heated in different FS as well as in a real food (coconut milk). Sample pieces weighing 0.5 – 2.0 g were put into the MAE device's Teflon vessels and 10 – 20 ml of food or FS was added to each vessel. During overall migration determination from the PET package, 50 ml FS was heated with approximately 3.5 g of PET. One blank sample for each food or FS and time/temperature was also prepared by adding food/FS to an empty vessel. The samples were heated up to the programmed temperature in the MAE which was then held constant for the specified time. Effect settings were 50% for the ethanol, 10% ethanol and 3% acetic acid because a higher effect caused the temperature to increase too rapidly, resulting in a temperature above the programmed temperature. During heating of the real food to 120 °C the effect setting was 100% and during heating to 80 °C it was set at 50%. Due to lack of polarity, isooctane cannot be heated with microwaves; therefore 10% ethanol had to be added. Because of the small amount of ethanol in the isooctane FS, the effect setting was 100% to enable heating of isooctane up to 80 °C and 100 °C. After the heating, the vessels were allowed to slowly cool to room temperature, the polymer samples were removed and the FS was stored separately in glass vials for later analysis.

3.3.2 Conventional heating

To determine migration during conventional heating, sealed glass vials with plastic screw caps containing 10 – 20 ml of food/FS and approximately 0.5 – 2.0 g of polymer sample were immersed in a preheated silicone oil bath heated on a heating plate and held at a constant temperature using an electronic temperature regulator. During overall

migration determination from the PET package, approximately 3.5 g of PET and 50 ml of FS were used. After the heating, the sample vials were removed from the oil and allowed to slowly cool to room temperature after which the polymer samples were removed and the vials were re-sealed and stored.

3.3.3 Overall migration and solvent absorption

Samples were weighed before and after heating to determine the degree of FS absorption. The FS on the surface of the pieces were gently removed before weighing and the pieces heated in the real food were washed with water and surface water droplets were then removed before weighing. PP, PP-C and PP-R samples were put in vacuum oven at room temperature for several weeks to evaporate the absorbed FS. The evaporation of samples was periodically checked and 100% FS evaporation was assumed when the sample weight had stopped decreasing between three consecutive checks. The overall migration from the PP and PP co-polymer packages were calculated from the difference in weight between the original and the heated and evaporated samples.

Overall migration from PET samples were determined by transferring three 10 ml portions of the sample FS extract into three separate pre-weighed 20 ml headspace vials and evaporating them under a gentle stream of nitrogen until no visible liquid remained in the vials. The vials were then weighed again and the overall migration was determined from the weight increase of the vial.

The overall migration values were transformed from mg to mg/dm^2 units by using the sample weights, thicknesses and density of the trays. The density of the PET tray was calculated from the volume crystallinity and the tabulated values for 100% amorphous density (1.33 g/cm^3) and 100% crystalline density (1.46 g/cm^3) of PET [72]. Differential scanning calorimetry (DSC) analysis yielded the weight crystallinity. The weight crystallinity value was re-calculated to volume crystallinity using the tabulated density values, resulting in approximately 20% volume crystallinity. With the same density values and the volume crystallinity, a sample density value of 1.36 g/cm^3 was calculated. Density of the PC package was obtained from literature (1.2 g/cm^3) [72]. The densities of the PP, PP-C and PP-R packages were calculated from measuring weight and dimensions of 16 representative sample pieces and they were in the range 0.87 – 0.89 g/cm^3 with no significant differences between the polypropylene types.

3.4 Total content of migrants in the polymers

3.4.1 Antioxidant content in PP and PP *co*-polymers determined by HPLC

Total amount of antioxidants in the PP, PP-C and PP-R samples was determined by HPLC. Samples were solvent extracted in 90/10 isooctane/ethanol for >24 h and analysis of extract was made with HPLC. The antioxidant contents in the extracts were determined by calibration with antioxidant standard solutions. To check for any possible degradation of the antioxidants during the long extraction procedure, pure antioxidant standards in 90/10 isooctane/ethanol were also heated for 24 h at 80 °C. The HPLC analysis made before and after heating showed no decrease in peak areas, showing that no degradation of pure standards occurred. The solvent extractions were carried out in quadruple.

3.4.2 Volatile content in PC, PET and PP *co*-polymers determined by GC-MS

Total amount of volatiles in PC, PET, PP-C and PP-R were determined by dissolution/re-precipitation and solvent extraction followed by GC-MS analysis of the extracts. Dissolution/precipitation and solvent extraction by chloroform was performed on PC, PP-C and PP-R samples. 50/50 chloroform/HFIP was used as solvent for PET.

0.3 – 0.4 g of PC was dissolved in 3 ml of chloroform and re-precipitated by adding 1 ml of ethanol. Approximately 0.1 g of PP-R was dissolved in 5 ml of chloroform and re-precipitated by 5 ml of ethanol. 0.02 – 0.05 g of PET was dissolved in 1 ml of 50/50 chloroform/HFIP and it was re-precipitated by 5 ml of ethanol. After re-precipitation, the solutions were stored for one night in a refrigerator to fully precipitate the polymer. PP-C was insoluble in chloroform and other tried solvents. Instead, PP-C sample was extracted for 24 h in a sealed glass vial containing chloroform in a silicone oil bath on heating plate set at 80 °C. The dissolution-precipitations and solvent extractions were carried out in triplicate. The extracts were filtrated through a 0.45 µm filter using glass syringe and analyzed by direct injection of the extract on GC-MS.

A standard solution of the antioxidants I168 (0.17 g/L) and I1010 (0.15 g/L) in chloroform was heated on heating plate for 24 h to determine the possible formation of antioxidant degradation products during the extraction procedure. The heated antioxidant standard solution did not reveal any detectable compounds. Because of the higher concentrations of antioxidants in the standard than in the samples, this means no additional volatile compounds or degradation products are likely to have resulted through degradation of antioxidants during the extraction procedure.

4 Results and Discussion

Migration of specific compounds into the food simulants and a real food after microwave and conventional heating were determined by HPLC, GC-MS and ESI-MS. Overall migration into food simulants was also determined. The polymer packages were characterized for degree of crystallinity before and after microwave heating in different food simulants to investigate the effect of microwave heating on the packaging material.

4.1 Polymer characterization and original additive content

Degrees of crystallinity for original and microwave heated samples in the FS are shown in Table 2 and the compounds originally present in the polymer packages and their amounts are shown in Table 3. No compounds were detected in the original PET package.

The PP and PP *co*-polymers show an increase in crystallinity from PP-R to PP-C and finally to PP which had the highest degree of crystallinity. The higher crystallinity from the first DSC scan for PP-R heated in 90/10 isooctane/ethanol compared to the first scan in the original sample indicates that crystallization occurred during microwave heating due to increased chain mobility induced by the isooctane swelling. The PET package had an original degree of crystallinity of 24% which did not change noticeable during microwave heating for 1 h at 80 °C in any of the FS. After heating for 4 h at 100 °C in ethanol a slight reduction was however observed.

Melting temperatures (not shown in table) did not change after heating in the FS and were, for PP-R: 148/147 °C and for PP and PP-C: 168/163 °C as determined from first/second heating scan. The PET package had a glass transition temperature of 79 °C during both the first and the second heating scan and a melting temperature of 254/244 °C during first/second heating scans respectively. The melting or glass transition temperatures of PET did not change significantly during heating in any of the FS. Melting temperatures for PP and PP-C were in the typical range for polypropylene while PP-R had lower melting point due to randomly distributed ethylene units.

All of the PP materials originally contained similar amounts of I1010 (Table 3). However, the I168 contents differed somewhat. In addition, 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) were found in PP-C and 2,4-DTB and dimethylbenzaldehyde (DMB) were found in PP-R. Both 2,4-DTB and 2,6-DTBQ could be degradation products from the antioxidants, I168 and I1010. 2,4-DTB could be degradation product from I168 and 2,6-DTBQ could be degradation/oxidation product from I1010 because of the structural similarities. Hindered phenolic primary antioxidants such as I1010 can undergo oxidation by

Table 2: Crystallinity of the packages before and after 1 h of heating at 80 °C in different food simulants taken from first/second heating scan.

Sample	Crystallinity (%)					
	Original	Isooctane	Ethanol	10% ethanol	3% acetic acid	water
PP-C	38/42	34/38	36/41	36/41	35/41	35/41
PP-R	34/37	38/38	34/38	35/37	34/36	34/37
PP	41/48	-	-	-	-	-
PC	[a]	[a]	[a]	[a]	[a]	[a]
PET	24/24	23/23	24/24	25/23	24/24	24/24

[a] No crystallinity present
- Not determined

reaction with peroxide radicals when preventing polymer degradation [18].

Only one compound, 9,9-dimethylxanthene was detected in the original PC package at a concentration of 11.3 ± 3.4 µg/g. No bisphenol A was detected, which means that the amount was lower than the detection limit of 0.4 µg/g. Other studies found residual bisphenol A in commercial PC containers at levels ranging from 7 to 58 µg/g [73] or from 10 to 177 µg/g [74].

4.2 Migration from PP and PP *co*-polymers

Migration of antioxidants from the PP packages into FS were determined by HPLC analysis while migration of volatiles were determined by GC-MS analysis. Overall migration determinations in combination with ESI-MS analysis of the unvolatile migrants were also conducted.

4.2.1 Comparison of antioxidant migration during constant time and temperature

The amount of antioxidants I168 and I1010 that migrated from PP, PP-C and PP-R during 1 h of microwave and conventional heating at 80 °C to 10% ethanol, 3% acetic acid, 96% ethanol and 90/10 isooctane/ethanol are shown in Table 4. The migrated amounts were highly dependent on type of FS and type of polypropylene material. Significant migration occurred to the fatty FS while migration into the aqueous FS

Table 3: Content of antioxidants and other volatile compounds in the packages.

	Amount ± SD (µg/g)			
Compound	PP-C	PP-R	PP	PC
Irgafos 168	251 ± 26	1110 ± 316	580 ± 116	ND
Irganox 1010	346 ± 20	312 ± 16	236 ± 39	ND
2,4-DTB	210 ± 117	87 ± 41	-	ND
2,6-DTBQ	13 ± 7	ND	-	ND
dimethylbenzaldehyde	ND	54 ± 12	-	ND
9,9-dimethylxanthene	ND	ND	-	11.3 ± 3.4

ND Not detected
- Not determined

was in most cases under the detection limits. Limits of detection for I168 was 0.09 µg/cm^2 and for I1010 0.05 µg/cm^2. The difference in the migration to the two fatty FS 90/10 isooctane/ethanol and ethanol was large. Migration into isooctane/ethanol was significantly larger probably due to high swelling of PP in isooctane. The high compatibility of isooctane with polypropylene is also shown by the small solubility parameter difference of 3.3 MPa$^{1/2}$ [72]. The sorption degree of PP-R and PP-C in isooctane/ethanol was 15% and 13% during 1 h of microwave heating at 80 °C and 12% and 9% after conventional heating respectively. The sorption of ethanol was only 0.5% after 1 h of microwave heating at 80 °C. In water, there was no detectable I168 or I1010 migration even when heating temperatures up to 120 °C were applied.

Since no migration was detected in aqueous FS after heating to 80 °C, the samples were also microwaved for 1 h at 100 °C and 120 °C (Table 4). Even when these higher temperatures were applied the migration was in most cases under the detection limits which is most probably due to the limited solubility of the hydrophobic antioxidants in the aqueous FS. Applied temperatures were in several cases above the atmospheric boiling points of the FS, however determinations were made in closed vessels under pressure. The temperature could also reach higher than boiling point under atmospheric pressure when microwaves are used for heating [4].

The effects of microwave- versus conventional heating on migration can also be seen in Table 4. In the two fatty FS, 96% ethanol and isooctane, the migrated amounts during microwave and conventional heating were similar, in fact migration was even slightly lower when samples were heated with microwaves compared to when they were

Table 4: Antioxidant migration from polypropylene food containers into different food simulants during 1 h of microwave and conventional heating.

	Microwaving (µg/cm^2)		Conventional (µg/cm^2)	
Sample	I168	I1010	I168	I1010
96% ethanol, 80°C				
PP-C	0.3 ± 0.0[a]	0.1 ± 0.0[a]	0.4	0.2
PP-R	2.1 ± 0.2[a]	0.2 ± 0.1[a]	2.9	0.3
PP	0.3 ± 0.03[a]	ND	0.4	ND
90/10 isooctane/ethanol, 80°C				
PP-C	5.1	5.0	6.9 ± 0.3[a]	7.3 ± 0.6[a]
PP-R	47.4	12.8	49.6 ± 2.0[a]	13.4 ± 2.2[a]
PP	6.2	1.9	7.5 ± 0.9[a]	2.8 ± 0.5[a]
Isooctane, 80°C				
PP-C	-	-	7.8	7.7
PP-R	-	-	49.1	14.8
PP	-	-	7.8	4.3
3% acetic acid, 100°C				
PP-C	ND	0.1	ND	ND
3% acetic acid, 120°C				
PP-C	ND	0.1	ND	ND
10% ethanol, 120°C				
PP-C	ND	0.1	ND	ND

[a] Determined from 4 measurements
ND Not detected
- Not determined

heated without microwaves. This was shown to be due to degradation of the antioxidants during microwave heating (see section 4.2.6). For PP-C samples limited migration of I1010 was detected in 3% acetic acid at 100 °C and 120 °C and in 10% ethanol at 120 °C when heated with microwaves, but not when heated conventionally. In this case presence of water, having higher dielectric constant and dielectric loss factor than ethanol [4], could increase the migration under the influence of microwaves. The effect of adding 10% ethanol to isooctane, to enable heating by microwaves, is also shown in Table 4. Quite similar amounts of the antioxidants migrated to 100% isooctane and to 90/10 isooctane/ethanol, therefore the addition of 10% ethanol to isooctane is not expected to significantly influence the results.

4.2.2 Antioxidant migration as a function of time at constant temperature

Figures 1 and 2 show migration of antioxidants I168 and I1010 into 90/10 isooctane/ethanol as a function of time for the different heating periods, from 10 min up to 6 h, in fractional amounts. The migration during a constant time of 1 h at 80 °C in 90% isooctane was also compared to the migration during six repeated 10 min heatings at 80 °C in 90% isooctane. After each 10 min heating, the package pieces were stored in room temperature during at least one night. It was found that the packages showed fickian diffusion behavior during the repeated heatings and for PP-C and PP the total amount of antioxidants that had migrated during the six 10 min heatings were the same as the amount that migrated when the packages were heated continuously for 1 h. During heating of the PP-R package in isooctane the amount approximately doubled during continuous heating compared to repeated heatings due to the increasing swelling degree of the polymer during continuous heating [75]. The horizontal axis has values expressed as the square root of time to show a possible fickian migration behavior. An increase from linear relation with time$^{1/2}$ trend can be seen for the two antioxidants, after different time periods depending on the polypropylene type. The deviation is observed after one hour in the case of PP-R, after two hours in the case of PP-C and after four hours in the case of PP. The deviations are probably a result of increasing swelling degree by the isooctane which lowers diffusion resistance by introducing free volume. There were also significant differences in migration rates between the different types of polypropylene materials with the rate of migration increasing in the order: PP $<$ PP-C $<$ PP-R for both I168 and I1010. This order coincides with the degree of crystallinity for the samples, which increased in the opposite order, PP-R $<$ PP-C $<$ PP. Diffusion in polymers generally decreases with increasing degree of crystallinity, but in addition the *co*-polymerization probably also affects the morphology of the samples especially in the case of the random *co*-polymer PP-R, which also has a considerably lower melting

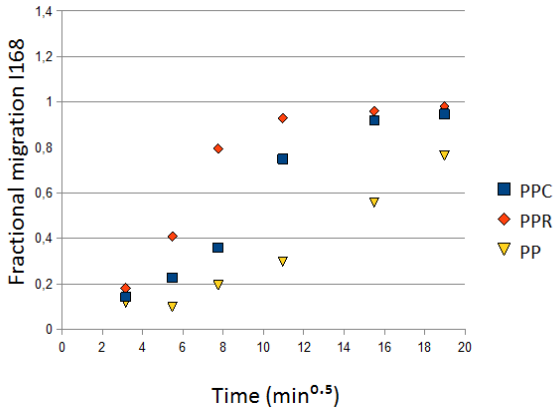


Figure 1: Migration of antioxidant Irgafos 168 to 90/10 isooctane/ethanol from PP packages as function of time$^{0.5}$ during microwave heating at 80 °C.

temperature compared to PP-C and PP.

Migration of antioxidants into 96% ethanol as function of time is shown in Figures 3 and 4. A clear linear relationship with time$^{1/2}$ exists for I168 but for I1010 it is not as clear. Instead the migration increased slightly from linear relation with time which, as in the case for 90% isooctane migration, could be due to the increasing solvent absorption with time. The rate of migration follows the same order, increasing with decreasing level of crystallinity, as during migration to 90% isooctane. It is also here more clearly seen that I168 migrated slightly faster than I1010 which could be expected from the slightly smaller size of I168 (647 g/mol) compared to I1010 (1177 g/mol). Also here, PP was the most migration resistant polymer with detectable I1010 migration first after 2 h in 96% ethanol.

4.2.3 Diffusion coefficients and activation energies for antioxidant migration

The diffusion coefficients for the antioxidant migrations into 90/10 isooctane and 96% ethanol are shown and compared in Table 5. Equation (9) was used for the calculation of the diffusion coefficients because the FS/sample volume ratio was high (~20). The low

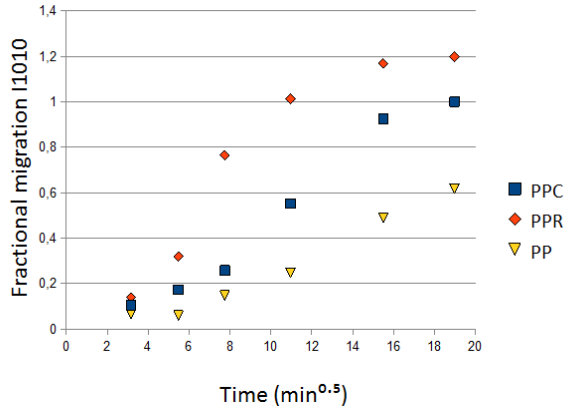


Figure 2: Migration of antioxidant Irganox 1010 to 90/10 isooctane/ethanol from PP packages as function of time$^{0.5}$ during microwave heating at 80 °C.

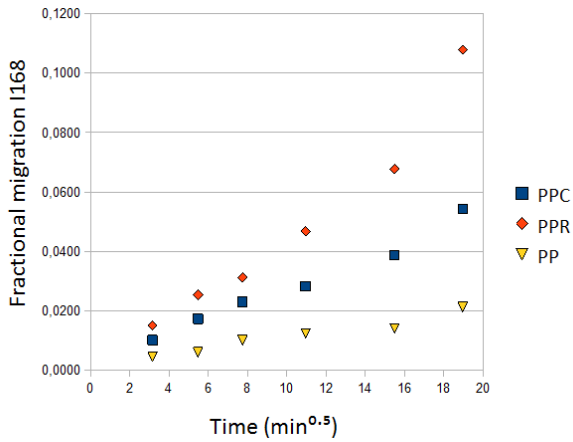


Figure 3: Migration of antioxidant Irgafos 168 to 96% ethanol from PP packages as function of time$^{0.5}$ during microwave heating at 80 °C.

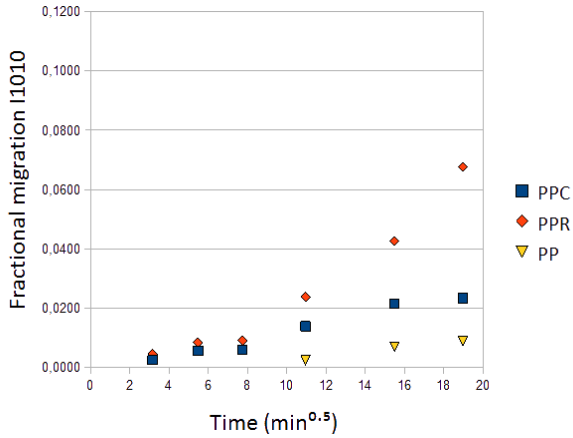


Figure 4: Migration of antioxidant Irganox 1010 to 96% ethanol from PP packages as function of time$^{0.5}$ during microwave heating at 80 °C.

partition coefficients in isooctane were confirmed by the high extraction yield achieved in the total antioxidant concentration determinations, while partition coefficients for some similar antioxidants between 96% ethanol and polypropylene were shown to be reasonably in favor of ethanol at 60 °C, and shifting more towards ethanol with increasing temperature [27]. Similar diffusion coefficients as these, 5×10^{-11} and 1.6×10^{-10} cm^2/s, have been measured for the diffusion of I1010 in PP homopolymer and PP random *co*-polymer respectively, and other values in the range 6×10^{-11} to 1.7×10^{-9} cm^2/s, during conventional heating using the Roe method [21, 23]. Those measurements also resulted in higher diffusion in random *co*-polymer than in the homopolymer. The diffusion coefficients in the 90/10 isooctane/ethanol swelled polymers were similar to a value which was measured during high-pressure solvent extraction of I1010 from PP with cyclohexane at 80 °C: 3.1×10^{-7} cm^2/s [76]. The similarities in diffusion coefficients in swelled/unswelled systems at the same temperature indicate that migration into both 90/10 isooctane and 96% ethanol was diffusion controlled and that there was no mass transfer resistance during the antioxidant migrations. The increase in diffusion coefficients by solvent swelling/interaction was large. An increase in the diffusion coefficient by a factor of 10 at 40 °C for the diffusion of antioxidants from PP packages was earlier observed when heptane was used as FS instead of ethanol [27]. In the present study the

Table 5: Calculated diffusion coefficients and activation energies for antioxidant migration from PP polymers to 90/10 isooctane/ethanol and 96% ethanol at 80 °C during microwave heating

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

- Not determined

effect of FS was even higher due to the higher temperatures used.

Activation energies are also given in Table 5. These were calculated with the assumption of Arrhenius' rate dependence of the diffusion coefficient (D = const × exp(-$\Delta H/(RT)$)) and by data from the fractional amounts migrated during 1 h and 30 min at different temperatures (data not shown). The data showed linear relationships for logarithm of migrated amount versus inverse absolute temperature, indicating that diffusion coefficients changed with respect to Arrhenius' rate law. Only a slight deviation in the case of migration of I168 and I1010 from PP to isooctane/ethanol was observed with a tendency to be concave towards the temperature axis, which could be attributed to swelling saturation at the higher temperatures. The free volume/swelling change is thus expected to influence the calculated activation energies. Calculated activation energies were considerably higher for ethanol migration and also higher for I1010 than I168, especially during migration into ethanol, which could be due to the influence of swelling or constraining effects on the large antioxidant molecules.

4.2.4 Migration of volatiles

The results from the GC-MS analysis of volatiles migrating into 90/10 isooctane and 99.9% ethanol during microwave and conventional heating are shown in Tables 6 and 7. The migration from PP-C and PP-R into 90/10 isooctane/ethanol increased significantly during microwave heating compared to conventional heating. In addition the migration into ethanol increased somewhat during microwave heating. During conventional heating the migration into isooctane/ethanol and ethanol was much more similar. The 2,4-DTB migration in particular was most affected by this; the amount that migrated from PP-C was higher by a factor of 700 when isooctane/ethanol was used and by a factor of 100 when ethanol was used as FS, compared to migration during conventional heating. The swelling isooctane is also expected to increase the migration. The microwave field would affect primarily small and polar molecules by setting them in rotating motion and increasing their diffusion rate.

Dimethylbenzaldehyde that migrated from PP-R had a slightly different retention time value compared to 2,4-dimethylbenzaldehyde standard, but was assumed to be a structural isomer due to the identical mass spectrum.

Results from MHS-SPME – GC-MS analysis of volatiles that migrated into water are shown in Table 8. Also listed are the means of the duplicate R^2 values for the MHS-SPME extractions. R^2 values from the extractions of the standard solution were in the range 0.95 – 0.98. The compounds were quantified only if R^2 was 0.9 or above. Because lower detection limits are achieved when using SPME compared to when using direct injection, compounds present at lower concentrations could possibly be detected in water compared to when analyzing migrants in 90/10 isooctane/ethanol and ethanol. However, the compounds that were detected in all three FS migrated in significantly lower amounts to water compared to isooctane/ethanol and ethanol, most likely due to the limited solubility of the migrants in water. In most cases the migration into water during microwave heating was higher compared to during conventional heating but the differences were not large. 4-ethoxy-benzoic acid ethyl ester, a compound included in the list of additives potentially migrating from plastics [3], was found in low amounts in the water FS, but the migration was far below the listed SML value for this compound.

4.2.5 Comparison of specific migration into food simulants and theoretical migration

Migration of some compounds commonly detected in 90/10 isooctane/ethanol, ethanol and water from PP-R and PP-C during microwave heating is presented graphically together with theoretically calculated migration values and total amount of the com-

Table 6: Low molecular weight compounds that migrated from PP-C and PP-R packages into 90/10 isooctane/ethanol during 1 h of microwave and conventional heating at 80 °C (µg/cm^2). 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.

			Microwaving		Conventional	
RT (min)	Compound[a]	CAS	PP-C	PP-R	PP-C	PP-R
10.8	dimethylbenzaldehyde	-	ND(0.002)	0.14	ND(0.002)	0.011
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	*719-22-2*	0.18	0.29	ND(0.004)	ND(0.004)
14.4	*4-hydroxy-1 h-Indole-3-carboxylic acid 35%*	*24370-76-1*	D	ND	D	ND
14.6	2,4-bis(1,1-dimethylethyl)-phenol	*96-76-4*	6.7	8.8	0.009	0.023
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-tertbutyl-4-hydroxyphenyl) propionate 95%*	*6386-38-5*	D	D	D	D

D Detected but not quantified
ND Not detected
[a] Detection limit of 4-ethoxy-benzoic acid ethyl ester: 6 ng/cm^2 in both ethanol and isooctane/ethanol food simulants.

Table 7: Low molecular weight compounds that migrated from PP-C and PP-R packages into 99.9% ethanol during 1 h of microwave and conventional heating at 80 °C (µg/cm^2). Detection limits are given in parentheses.

RT (min)	Compound	CAS	Microwaving		Conventional	
			PP-C	PP-R	PP-C	PP-R
10.8	dimethylbenzaldehyde	-	ND(0.002)	0.072	ND(0.002)	ND(0.002)
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	*719-22-2*	ND(0.004)	ND(0.004)	ND(0.004)	ND(0.004)
14.4	*4-hydroxy-1 h-Indole-3-carboxylic acid 35%*	*24370-76-1*	D	ND	D	ND
14.6	2,4-bis(1,1-dimethylethyl)-phenol	*96-76-4*	1.2	0.50	0.012	0.010
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-di-tertbutyl-4-hydroxyphenyl) propionate 95%*	*6386-38-5*	D	D	ND	ND

D Detected but not quantified
ND Not detected

Table 8: Low molecular weight compounds that migrated from PP-C and PP-R packages into water during 1 h of microwave and conventional heating at 80 °C (ng/cm^2).

RT (min)	Compound	CAS	Microwaving				Conventional			
			Migration		R^2 (Mean)		Migration		R^2 (Mean)	
			PPC	PPR	PPC	PPR	PPC	PPR	PPC	PPR
7.2	*orthoformic acid, tri-sec-butyl ester 60%*	*16754-48-6*	D	D	-	-	D	D	-	-
10.8	dimethylbenzaldehyde	-	b	b	*0.84*	*0.50*	0.44	b	*0.94*	*0.78*
14.1	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	*719-22-2*	0.87	1.1	*0.92*	*0.91*	0.64	0.74	*1.00*	*0.90*
14.4	*4-hydroxy-1 h-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	*0.99*	*0.99*	1.7	2.2	*0.99*	*0.98*
14.9	4-ethoxy-benzoic acid ethyl ester [a]	*23676-09-7*	0.57	0.55	*0.97*	*0.97*	ND	0.8	-	*0.90*
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-tertbutyl-4-hydroxyphenyl) propionate 95%*	*6386-38-5*	D	D	-	-	D	D	-	-

[a] SML: 3.6 mg/kg = 6 µg/cm^2 (6 dm^2 of polymer surface assumed to be in contact with 1 kg of food) [3].
[b] Not quantified due to low linearity of ln A vs extraction number (R^2)
D Detected but not quantified
ND Not detected

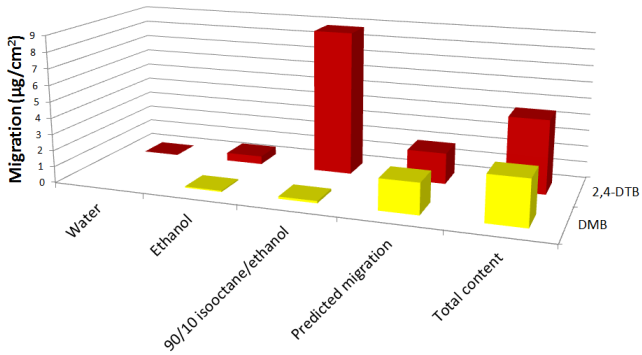


Figure 5: Migration of selected volatile compounds from PP-R to the food simulants water, ethanol and 90/10 isooctane/ethanol during 1 h of microwave heating at 80 °C and calculated worst case migration.

pounds, corresponding to total depletion of all the compounds from Table 3. The theoretical migration values were calculated with equation (8) based on the initial concentrations given in Table 3. Diffusion coefficients were calculated with equation (10) and (11) using data for PP homopolymer [67]. The partition coefficient was set by assuming high FS solubility. This value would lead to almost complete extraction at long times due to the high FS/polymer volume ratio of ~20. The migration of compounds into water was far lower than calculated values, however the migration of 2,4-DTB from PP-R and PP-C was higher than calculated values to 90/10 isooctane/ethanol, and for PP-R even higher than the total amount originally available in the polymer suggesting additional formation of 2,4-DTB.

4.2.6 Antioxidant degradation caused by microwave heating

The amount of 2,4-DTB migrating from PP-C and PP-R into isooctane/ethanol and ethanol (Table 6 and 7) during microwave compared to conventional heating was even higher than the total amount measured in the original sample (Figure 6). Also, smaller amount of I168 and I1010 migrated into 96% ethanol and 90/10 isooctane/ethanol during microwave heating compared to conventional heating (Table 4). This indicates

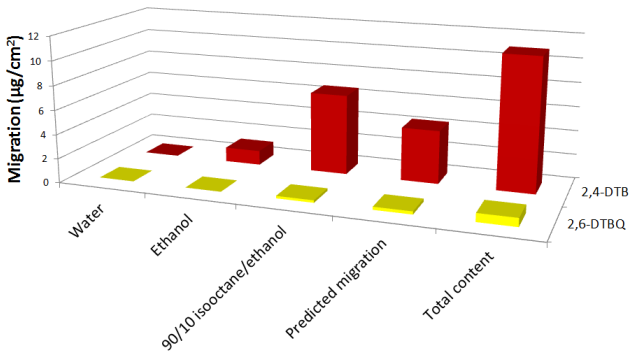


Figure 6: Migration of selected volatile compounds from PP-C to the food simulants water, ethanol and 90/10 isooctane/ethanol during 1 h of microwave heating at 80 °C and calculated worst case migration.

degradation of the antioxidants during microwave heating. This yields lower amounts of antioxidants and larger amount of degradation products *e. g.* 2,4-DTB from I168 and 2,6-DTBQ or methyl 3-(3,5-di-tertbutyl-4-hydroxyphenyl) propionate from I1010, which was experimentally shown by the migration studies.

GC-MS analysis of I168 standard dissolved in ethanol, heated with microwaves and conventionally for 1 h at 80 °C, as well as ESI-MS analysis of degraded antioxidant standards, confirmed degradation of I168 and formation of 2,4-DTB as a degradation product. The GC-MS area corresponded, however, to a very low degree of degradation for the I168 standard (less than 1/100 by weight) and the amount of formed 2,4-DTB was similar during conventional heating for 1 h at 80 °C. No degradation was observed after microwave or conventional heating of pure antioxidants in 90/10 isooctane/ethanol for 1 h at 80 °C. The degradation of pure antioxidants during conventional heating in ethanol could be explained by ethanol induced hydrolysis or trans-esterification of I168 in the standard solution [77].

These results show that antioxidants are consumed and degraded during microwave heating, but not during conventional heating, of the polypropylene packages due to interactions between polymer and antioxidants while no significant degradation occurs during microwave or conventional heating without presence of polymer. Swelling could

also enhance degradation rates of antioxidants directly inside the polymer as well as increase the diffusion of degradation products from the sample.

Some of the other compounds detected in the FS and shown in Tables 6-8 were assigned as degradation or oxidation products from antioxidants, for example methyl 3-(3,5-di-tertbutyl-4-hydroxyphenyl) propionate and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione. The first mentioned compound as well as 2,6-DTBQ were confirmed as degradation products of I1010 by GC-MS analysis of microwave heated 10% ethanol and 99.9% ethanol standards (data not shown). The carboxylic acid analogue of this compound, 3-[3,5-di-tert-butyl-4-hydroxybenzyl] propionic acid, has been shown to be formed during hydrolysis of I1010 in water [78]. The methyl ester found in these samples therefore indicates the occurrence of a different degradation mechanism. The second compound, 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, also has similarities with the antioxidant structure. Both 2,4-DTB, 2,6-DTBQ [79] and 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione [80, 81] have earlier been identified as migrants from polyolefins.

4.2.7 Overall migration

Overall migration for microwave and conventionally heated PP-R and PP-C are given in Figure 7a-b . From both polymers the overall migration into isooctane/ethanol was very large during microwave and conventional heating due to the high compatibility of isooctane with PP that caused swelling and facilitated migration of low molecular weight oligomers and antioxidants from the sample. The overall migration into 90/10 isooctane/ethanol was larger from PP-R than from PP-C and slightly larger for microwave heated samples. The overall migration limit set by the European commission for plastic materials is 10 mg/dm^2 or 100 µg/cm^2 [3].

4.2.8 ESI-MS analysis of semivolatile migrants

ESI-MS spectra from analysis of FS after microwave and conventional heating of PP-C and PP-R in 90/10 isooctane, 99.9% ethanol, 10% ethanol, 3% acetic acid and water were acquired. Figures 8-9 show the spectra of the semivolatiles that migrated into FS from PP-R and PP-C with increasing level of FS hydrophobicity; *i. e.* water, 10% ethanol, 99.9% ethanol and 90/10 isooctane/ethanol. The number of peaks, and the intensities of compounds that migrated were higher in the case of PP-R compared to peaks from PP-C. The peak amounts and intensities also correlated with the overall migration from PP-R during microwave heating (Figure 7a), which increased with increasing hydrophobicity of the FS. The ESI-MS spectra from analysis of the FS after

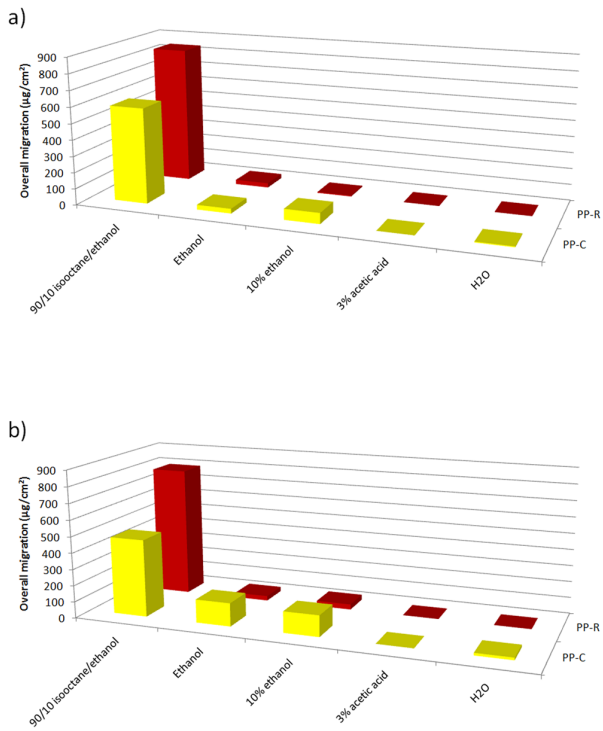


Figure 7: Overall migration from PP-R and PP-C into different food simulants during 1 h of (a) microwave and (b) conventional heating at 80 °C.

migration into isooctane/ethanol and ethanol during conventional heating from PP-C and PP-R showed similar peak amounts and intensities as ESI-MS spectra of microwave heated samples. An exception were the peaks in the low molecular weight range corresponding to degradation products of I168. The spectra showing migration from PP-C and PP-R into 3% acetic acid had very low peak intensities and did not reveal any additional peaks. Series of peaks with mass difference of 44 amu ranging from m/z 551 to 815 were clearly seen in the 10% ethanol PP-R extracts. They were also present in low amounts in the water extract and in ethanol and isooctane/ethanol extracts. They were tentatively identified as poly(ethylene glycol) (PEG) oligomers, which have the characteristic peak series with mass differences of 44 amu originating from the repeating unit (-CH_2-CH_2-O-). PEG is frequently used as plasticizer for other polymers. These peaks were not present in the conventionally heated ethanol samples, indicating accelerated migration due to microwave heating. The ESI-MS spectra of semivolatiles from PP-C also showed slightly more intense peaks for the isooctane/ethanol heated sample compared to the other samples. A peak at m/z 288 present in all of the FS heated with PP-C was not present in the FS heated with PP-R.

4.3 Migration from PET packaging

Migration of unvolatile compounds such as PET oligomers were determined by overall migration determinations in combination with ESI-MS analysis. Migration of volatiles were determined by GC-MS analysis. An ESI-MS method optimization was conducted by evaluating different solvents for direct infusion ESI-MS.

4.3.1 ESI-MS method optimization

The electrospray ionization mass spectrometry analysis of the PET migrants was optimized by evaluating different solvents in order to achieve the highest signal responses for the migrants. The effect of adding acetic acid as protonation agent was also evaluated. ESI-MS analysis was performed on a microwave heated PET ethanol extract, heated for 4 h at 100 °C, and the influence of using the solvent or solvent mixtures 50/50 acetonitrile/water, 100% acetonitrile, 50/50 methanol/water and 100% methanol on detector signal were evaluated.

The PET oligomer peak with the highest intensity was found at m/z 879 and therefore the intensity values for this ion were compared for the different samples. The ion at m/z 1347 was identified as the oxidized antioxidant Irgafos 168 and the intensity values for this peak were also compared. The intensities of oligomer peak at m/z 879 and antioxidant peak at m/z 1347 after analysis in different solvents are shown in Fig-

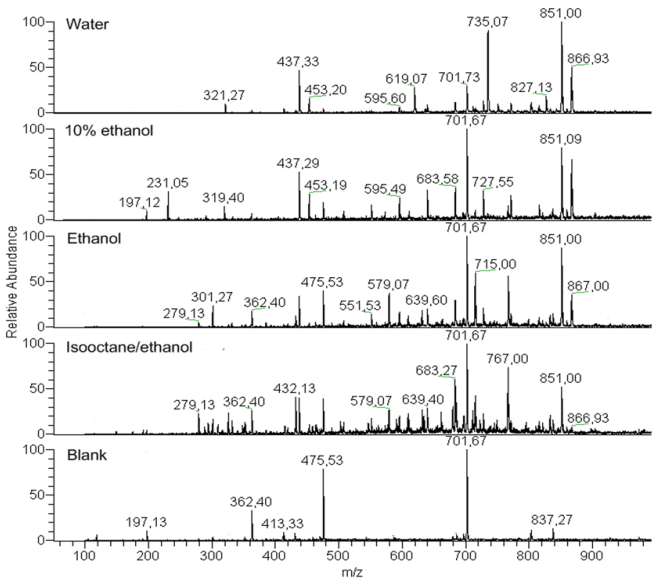


Figure 8: ESI-MS spectra showing the compounds that migrated from PP-R to water, 10% ethanol, ethanol and 90/10 isooctane/ethanol during 1h of microwave heating. The blank sample shown here consisted of same amount of 90/10 isooctane/ethanol microwave heated for 1 h at 80 °C

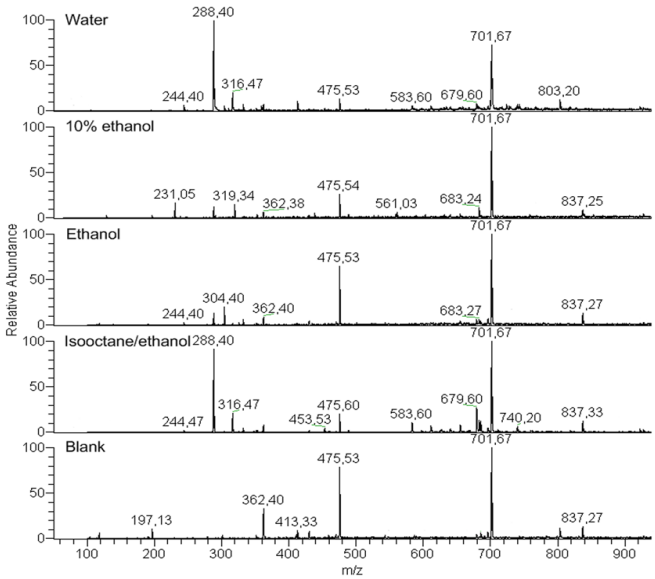


Figure 9: ESI-MS spectra showing the compounds that migrated from PP-C to water, 10% ethanol, ethanol and 90/10 isooctane/ethanol during 1 h of microwave heating.

ure 10a-b. 50/50 methanol/water resulted in the highest peak intensity for the PET oligomer ion when no acetic acid was added. A higher number of other PET oligomers were also visible when 50/50 methanol/water was used as solvent. For oxidized Irgafos 168, 100% methanol gave the highest peak intensity probably due to the hydrophobicity of this compound giving better solubility in pure methanol than in solvent/water mixtures (Figure 10b). In all cases, except with 100% methanol, the addition of acetic acid both decreased the m/z 879 peak and the other PET oligomer peaks. No additional peaks that would correspond to $+H^+$ adducts of the oligomers were detected in the samples with acetic acid.

4.3.2 ESI-MS analysis of PET oligomers and other unvolatile migrants

Summary of the strongest peaks from the ESI-MS analysis of the migration into ethanol is given in Table 9, together with structural assignments of the peaks. The peaks were assigned as cyclic PET oligomers because the m/z values (minus the adduct) correspond to $192n + 44m$ where m and n are integers, 192 is the molecular weight of the repeating unit and 44 is an additional ethylene glycol (EG) unit. Traces of diethylene glycol (DEG) from ethylene glycol units are formed due to high temperature and acid conditions during PET polymerization [82]. The replacement of an EG unit with a DEG unit in the chain results in an increase in molecular weight by 44 amu (one EG). Cyclic oligomers containing DEG are common in PET because the DEG unit, due to increased chain flexibility, promotes cyclization of short oligomers [62]. This series of oligomers has earlier been observed both in commercial PET samples [62], and in bottle grade PET (obtained from manufacturers) [82]. Holland et al. earlier detected oligomer series from monomer to pentamer containing 1 to 2 extra EG units when they analyzed the oligomeric fraction in PET by ESI-MS [62]. The highest intensity peak in their study belonged to the $[PET]_2[EG] + Na^+$ (m/z 451) oligomer adduct. This study also showed that these oligomers migrate to ethanolic FS during heating of PET.

The cyclic trimer usually constituted the largest fraction of the different oligomers present in PET. López-Cervantez determined by semi-quantitative HPLC-UV analysis that the cyclic trimer constituted more than half of the total oligomeric content in PET roasting bags for microwave applications (5.58 mg/dm^2 out of a total of 8.71 mg/dm^2) [36]. In our study no trimers were seen as molecular ions, instead trimer fragments were observed in a few cases after collision induced dissociation (CID) fragmentation.

A large peak was found at m/z 1347 when 100% acetonitrile or methanol were used as solvents and this peak was accompanied by additional peaks at m/z 1342 and 1325 (Table 9). This series probably results from $+H^+$, $+H_2O^+$ and $+Na^+$ adducts of the same compound. From the CID MS-MS fragmentation pattern, this compound was

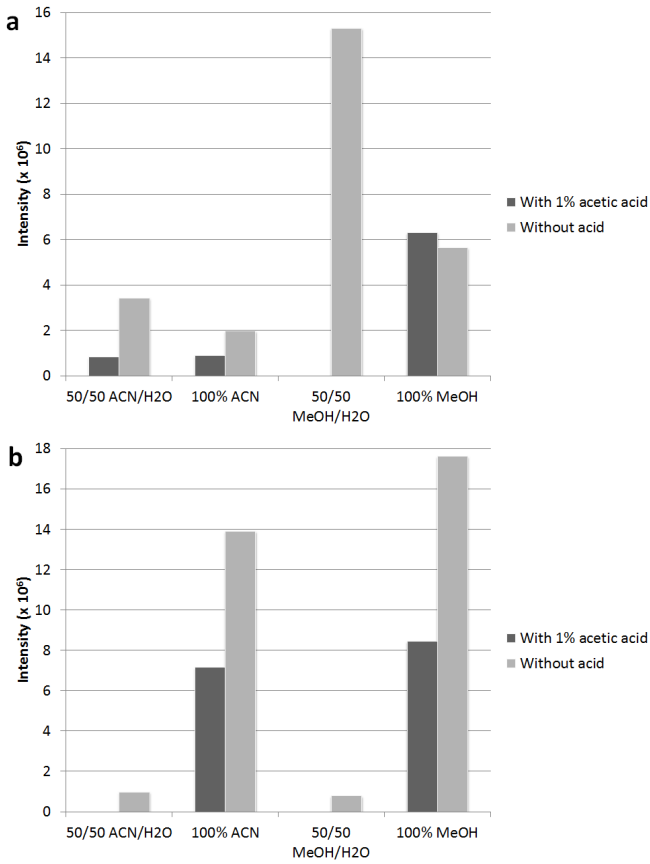


Figure 10: Comparison of ion intensity values for PET oligomer ion at m/z 879 (a) and oxidized Irgafos 168 ion at m/z 1347 (b) in different ESI-MS solvents with and without acetic acid.

Table 9: Peak assignments from ESI-MS analysis of the compounds migrating from PET into ethanol during microwave heating.

PET oligomers (m/z)[a]	**Structure***
446	$[PET]_2[EG] + H_2O^+$
451	$[PET]_2[EG] + Na^+$
490	$[PET]_2[EG]_2 + H_2O^+$
495	$[PET]_2[EG]_2 + Na^+$
879	$[PET]_4[EG]_2 + Na^+$
897	$[PET]_4[EG]_2 + H_2O + Na^+$
923	$[PET]_4[EG]_3 + Na^+$
941	$[PET]_4[EG]_3 + H_2O + Na^+$
1027	$[PET]_5[EG] + Na^+$
1071	$[PET]_5[EG]_2 + Na^+$
1175	$[PET]_6 + Na^+$
1219	$[PET]_6[EG] + Na^+$
Other compounds (m/z)	
647[b]	$[IGF] + H^+$
663[b]	$[IGFox] + H^+$
1325[b,c]	$2[IGFox] + H^+$
1342[b,c]	$2[IGFox] + H_2O^+$
1347[b,c]	$2[IGFox] + Na^+$

* *PET*: polyethylene terephthalate repeating unit (mol weight: 192), *EG*: ethylene glycol unit (mol weight: 44), *IGF* = Irgafos 168 (mol weight: 646), *IGFox* = Oxidized Irgafos 168 (mol weight: 662)

[a] Detected using 50/50 methanol/water as solvent

[b] Detected using 100% acetonitrile as solvent

[c] Detected using 100% methanol as solvent

identified as double-molecular ([2M + adduct]$^+$) ion of oxidized Irgafos 168 (CAS nr: *95906-11-9*) which has the nominal molecular weight of 662 ($C_{42}H_{63}O_4P$). The oxidized Irgafos 168 was previously found to have a MS-MS fragmentation pattern with the same *m/z* values (383, 439, 495, 551, 607, 663) in thermal desorption mass spectrometry [58]. Peaks were also observed at *m/z* 663, assigned as [M+H]$^+$ adduct of oxidized Irgafos 168, and at *m/z* 647, presumably a [M+H]$^+$ adduct of *un*-oxidized Irgafos 168 (CAS nr: *31570-04-4*), using 100% acetonitrile as ESI-MS solvent. The pattern results from the losses of the six tert-butyl groups followed by proton transfer. Further support for the identification of these peaks as oxidized Irgafos 168 is found from GC-MS analysis, which showed the migration of the Irgafos 168 degradation product, 2,4-di-tert-butyl phenol from the PET tray (see section 4.3.4).

4.3.3 Overall migration in combination with ESI-MS analysis

In Table 10 the overall migration values after 4 h of microwave heating at 100 °C in water, 3% acetic acid, 10% ethanol, ethanol and isooctane are listed and it is also noted whether oligomer migration was detected by ESI-MS in the various FS. Figure 11 and 12 show spectra of the migrants after microwave and conventional heating for 1 h at 80 °C and for 4 h at 100 °C in ethanol. As can be seen both from Table 10 and from Figure 11 and 12, oligomers migrated into ethanol and 90/10 isooctane/ethanol during microwave heating for 1 h at 80 °C, but not during conventional heating for 1 h at 80 °C. In Figure 11 and 12 the peaks at *m/z* 451, 879, 923, 1027 and 1071 all result from PET oligomers (see Table 9). After 4 h of microwave and conventional heating at 100 °C oligomers migrated into ethanol and the relative peak intensities of the oligomer peaks were only slightly higher for the microwave heated samples compared to the conventionally heated samples. After 4 h of microwave heating at 100 °C oligomers migrated into isooctane/ethanol 90/10 but only weak oligomer signals at *m/z* 451 and 879 were observed after conventional heating for 4 h at 100 °C in 90/10 isooctane/ethanol. Overall migration values after 4 h of heating at 100 °C were all below the EU commission overall migration limit of 10 mg/dm^2 [1].

The fact that oligomers were detected after microwave heating for 1 h at 80 °C but not after conventional heating for 1 h at 80 °C could be due to a non-thermal "microwave effect" [15] which could increase the diffusion of cyclic oligomers in the polymer. No such effect was earlier observed when the migration of a trimer from PET susceptor packaging was compared to predicted values from the time versus temperature profile during microwave heating [83]. However, the temperatures in those experiments ranged from 120 – 200 °C and at such high temperatures any microwave effect is likely to be insignificant. In our study almost similar overall migration values were measured after

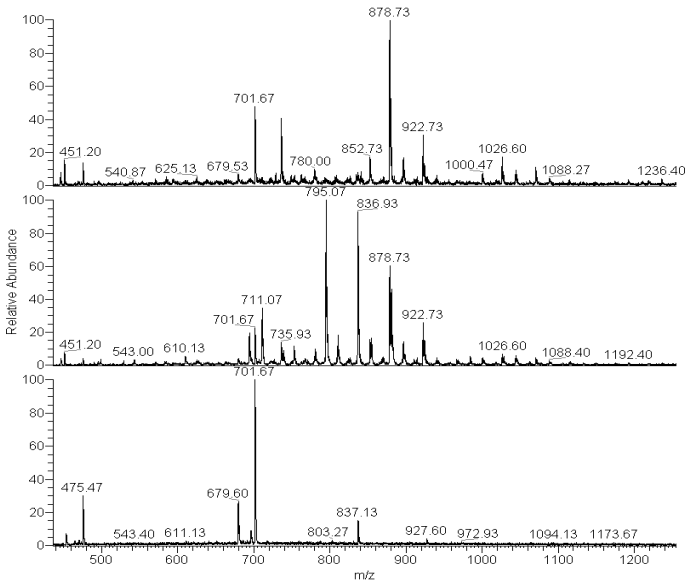


Figure 11: ESI-MS spectra of the migrants from PET microwave heated for 4 h at 100 °C in ethanol (top), PET conventionally heated for 4 h at 100 °C (middle) and blank reference sample microwave heated for 4 h at 100 °C (bottom).

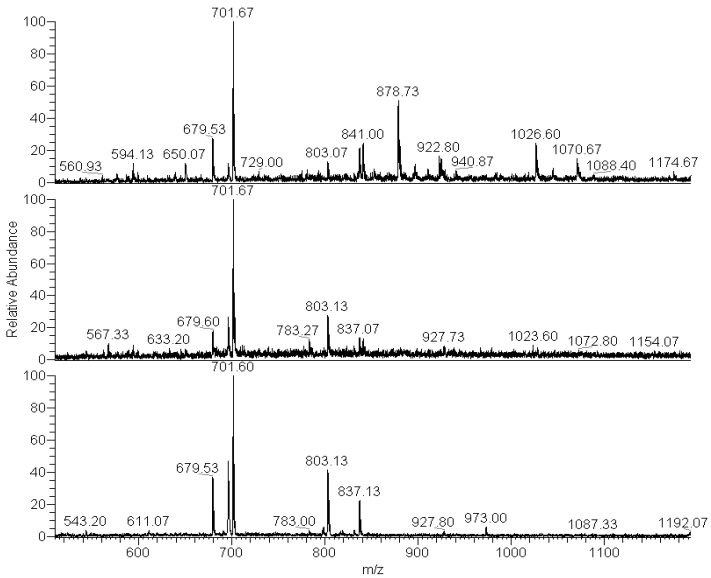


Figure 12: ESI-MS spectra of the migrants from PET microwave heated for 1 h at 80 °C in ethanol (top), PET conventionally heated for 1 h at 80 °C (middle) and blank reference sample microwave heated for 1 h at 80 °C (bottom).

Table 10: Migration from the PET tray into various food simulants during microwave (MW) and conventional (conv) heating. Overall migration values are given as mean ± standard deviation from 3 replicates (mg/dm^2).

	Water	**3% ac**	**10% ethanol**	**Ethanol**		**Isooctane/ ethanol 90/10**		**Isooctane**
	MW	**MW**	**MW**	**MW**	**conv**	**MW**	**conv**	**conv**
1h 80°C								
oligomers	ND	ND	ND	D	ND	D	ND	-
4h 100°C								
oligomers	ND	[a]	[a]	D	D	D	[a]	ND
overall migration	0.13±0.87	0.69±0.91[b]	0.72±0.0	4.8±2.2[b]	4.5±3.4	3.6±1.4[b]	2.0±0.3[b]	3.2±1.1[b]

D Detected
ND Not detected
- Not determined
[a] Only oligomer ions at m/z 451 and 879 were detected with weak signals
[b] significant difference ($p < 0.05$) between the values of sample and reference blank.

microwave and conventional heating at the higher temperature of 100 °C, and oligomers were detected both after microwave and conventional heating at this temperature. These results suggest that the microwave effect is more significant at lower temperatures. Also worth noting is that only weak oligomer signals were observed after 4 h of conventional heating at 100 °C in isooctane/ethanol while all the oligomer peaks were clearly visible after 1 h of microwave heating at 80 °C in the same FS. The fact that migration was larger even after microwaving at the much lower temperature and during a shorter time, suggests a rather significant microwave effect. More visible residues (white precipitate) in the evaporated microwave heated ethanol and isooctane FS samples in comparison with the corresponding conventionally heated samples were also observed.

The cyclic trimer has usually been reported to be the most abundant cyclic oligomer species present in PET [36], while the total oligomer content can be as high as 1% [34]. The initial oligomer concentration was not known in this study, but assuming a rather extreme case of 1% oligomer content, of which the trimer constitutes 80%, and furthermore assuming high solubility in the FS (a polymer/FS partition coefficient of 1), the calculated migration of the trimer after 4 h at 100 °C, using equations (8), (10) and (11) and the material specific conduction and activation energy parameters for PET

[67], is 0.7 mg/dm^2. This figure is quite low compared to the overall migration values determined into ethanol and isooctane, even taking into account the migration of other PET oligomers. The content of other additives in the PET sample is also expected to be low. Interaction with the FS, causing swelling of the polymer, might therefore partly explain the higher overall migration values observed. For example, heating in ethanol was earlier shown to result in higher diffusion coefficient compared to heating in isooctane for the migration of UV stabilizer from PET [84]. This was explained by stronger polymer-FS interaction, and the same phenomenon might also explain the somewhat higher overall migration into ethanol compared to isooctane/ethanol in our study. The PET oligomers are also more soluble in ethanol than in isooctane due to the ester groups.

4.3.4 Migration of volatiles

Migrants detected in water, ethanol and isooctane/ethanol 90/10 after 1 h of microwave heating of PET and FS at 80 °C and in ethanol after 4 h of microwave heating at 100 °C are summarized in Table 11. Increased migration of the diethyl ester of 1,4-benzenedicarboxylic acid (diethyl terephthalate) was observed as a function of longer heating time and temperature. The diethyl terephthalate can be formed by a transesterification reaction between the polymer chains and ethanol, or it could be a side-product formed during polymerization. The stronger interaction between the polymer and ethanol is also shown in Figure 13 showing the sorption degree of PET heated by microwaves and conventionally for 1 h at 80 °C. The migration of 2,4-bis(1,1-dimethylethyl)-phenol also increased with time and temperature. This compound was earlier detected as a degradation product from the antioxidant Irgafos 168 in the PP packages and it was also found earlier together with the antioxidants in PP packages [19]. No compounds were detected in water after 1 h of microwave heating at 80 °C. Diethyl terephthalate had a detection limit of 8 ng/L (0.4 ng/dm^2) and 2,4-di-tert-butyl phenol 0.1 ng/L (0.005 ng/dm^2) in water.

To confirm the origin of diethyl terephthalate migrating from the samples, *i. e.* whether it was formed during heating or if it was originally present in the polymer, a sample was also microwave heated for 1 h at 100 °C in pure methanol. The extract was subsequently analyzed with GC-MS. A large peak for dimethyl terephthalate was observed in the resulting chromatogram but no peak corresponding to diethyl terephthalate could be found. If diethyl terephthalate was originally present in the PET tray, it would have been visible in the chromatogram because the solubility of diethyl terephthalate in methanol is high. It was therefore concluded that the diethyl terephthalate found migrating during the microwave heating in ethanol was formed in a transesterification

Table 11: Migration of volatile compounds from PET into food simulants during microwave heating.

RT (min)	**Compound**	**CAS nr**	**water 1 h, 80 °C (µg/dm²)**	**ethanol 1 h, 80°C (µg/dm²)**	**isooctane/ ethanol 1 h, 80 °C (µg/dm²)**	**ethanol 4 h, 100°C (µg/dm²)**
14.6	2,4-bis(1,1-dimethylethyl)-phenol	*96-76-4*	ND	0.7	ND	16
16.4	1,4-benzenedicarboxylic acid, diethyl ester-	*636-09-9*	ND	ND	ND	33

ND Not detected

reaction with ethanol during the heating.

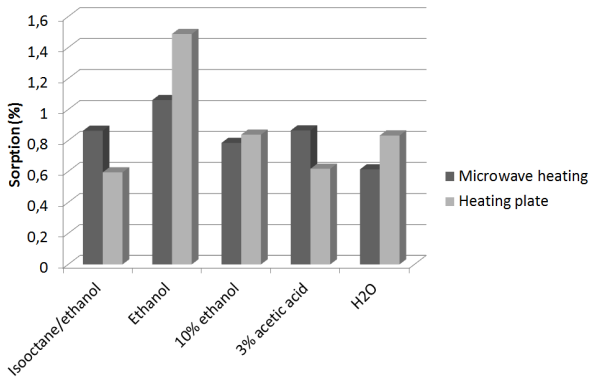


Figure 13: Absorption of the different food simulants by the PET package after microwave and conventional heating for 1 h at 80 °C.

4.4 Migration from polycarbonate

SPME was first performed on water and 10% ethanol standard solutions containing migrants. LOD, LOQ, repeatability and linear range were established. A PLS analysis on the extraction data was also conducted to evaluate the performance of the SPME method. Migration determinations of volatiles in water, ethanol and 90/10 isooctane/ethanol after 1 h of microwave and conventional heating at 80 °C were also conducted by using GC-MS and the SPME method.

4.4.1 Method evaluation

The compounds that migrated into water from the PC package are listed in Table 12 together with repeatability values (% standard deviation), linear ranges and LOD:s and LOQ:s obtained from SPME-GC-MS on standard solutions in water and 10% ethanol. Some of the listed compounds are known constituents of plastics that have been given specific migration limits (SML) by the EU [1]. Benzophenone might originate from the printed cardboard package the container was originally wrapped in. M-tert-butyl phenol was earlier discovered after thermal degradation of PC [85]. 9,9-dimethylxanthene has been found as an impurity in commercial bisphenol A [86]. This compound has also been shown to be influential in the yellowing of PC, and could be formed from the PC polymer by a Fries chain rearrangement reaction [87]. 2,4-bis(1,1-dimethylethyl)-phenol and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione were earlier identified as degradation products from antioxidants Irgafos 168 and Irganox 1010 in the PP materials and these compounds were also included during the method development due to their common occurrence in plastic packaging.

The LOD and LOQ values were established at 3 and 10 times the S/N values, respectively. Repeatability values were established by consecutively extracting three identical samples. Quite low detection limits were obtained, especially in the water solutions. For example, a detection limit for benzophenone was 3 ng/L, 4-ethoxy-benzoic acid ethyl ester 1 ng/L and for 2,4-bis(1,1-dimethylethyl)-phenol 0.1 ng/L. The 10% ethanol standard solution had higher LOD's and LOQ's due to the presence of ethanol in the water. A similar trend of increasing detection limits was observed earlier for various pesticides as a function of increasing ethanol content in water [88].

Table 13 lists the concentrations of standard compounds in the 10% ethanol solution and the parameters (slopes, regression coefficients and area sums) that were obtained from MHS-SPME. The area sums of the integrated MS peaks were calculated by equation (3), individually from each of the triplicate measurements and the mean values together with relative standard deviations are given in the table. For most compounds

Table 12: Retention times, LODs, LOQs, repeatability (relative standard deviation) and linear range for different standard compounds after SPME (PDMS/DVB) extraction of 10% ethanol and water standard solutions.

Compound	RT (min)	10% ethanol				Water			
		LOD (µg/L)	LOQ (µg/L)	Repeat-ability (%)	Linear range (µg/L)	LOD (µg/L)	LOQ (µg/L)	Repeat-ability (%)	Linear range (µg/L)
acetophenone[a]	8.4	0.3	0.8	21	6-18	0.005	0.02	11	0.6-6
m-tert-butyl-phenol[a]	11.8	0.03	0.09	28	1.2-4.8	0.0004	0.001	4	0.1-1.2
1-methylnaphthalene[a,b]	12.2	0.0009	0.003	4	-	0.0003	0.001	3	-
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	14.1	0.01	0.03	18	3.2-6.4	0.004	0.01	18	0.3-3.2
2,4-bis(1,1-dimethylethyl)-phenol	14.6	0.002	0.006	19	1.3-5.2	0.0001	0.0004	24	0.1-1.3
4-ethoxy-benzoic acid ethyl ester[a]	14.9	0.01	0.04	13	6.3-19	0.001	0.005	2	0.6-3.2
benzophenone[a]	16.3	0.02	0.07	15	4.3-17	0.003	0.009	3	0.4-4.3
1,1'(1,3-propanediyl)bis-benzene[a,b]	16.5	0.002	0.006	17	-	0.002	0.008	4	-
9,9-dimethylxanthene[a]	17.0	0.009	0.03	31	2.1-4.2	0.0009	0.003	38	0.2-2.1

[a] Found migrating from the PC package
[b] Not quantified, peak areas in samples close to detection limit

Table 13: Concentration of compounds in 10% ethanol standard solution and MHS-SPME parameters: slopes (q'), peak area sums (A_s) and regression coefficients (R^2) of ln A vs extraction number.

Compound	CAS nr	concentration (µg/L)	R^2	Slope (q')	A_s
acetophenone	*98-86-2*	6	0.943	-0.15±0.04	813000±17%
m-tert-butyl-phenol	*585-34-2*	1	0.981	-0.15±0.06	4430000±40%
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	*719-22-2*	3.2	0.960	-1.08±0.11	3760000±14%
2,4-bis(1,1-dimethylethyl)-phenol	*96-76-4*	1.3	0.983	-0.28±0.01	27100000±3%
4-ethoxy-benzoic acid ethyl ester	*23676-09-7*	6.3	0.972	-0.23±0.04	7530000±16%
benzophenone	*119-61-9*	4.3	0.995	-0.17±0.01	5140000±7%
9,9-dimethylxanthene	*19814-75-6*	2.1	0.995	-0.34±0.004	110000000±1%

high R^2 values were obtained and in most cases the standard deviations in the slopes and area sums were relatively small.

The SPME method was evaluated by calculating enrichment factors by the equation '$S/E \times 1/100$' where S is the peak area obtained for the extracted compounds and E is the area obtained for the compounds by directly injecting 1 µL of an ethanol standard solution of the migrants that was 100 times more concentrated compared to the water and 10% ethanol solutions. This means that for an enrichment factor of 1, the amount adsorbed to the SPME fiber would be equal to that in the drop of a directly injected solution with the same concentration of the migrants. The factors should also be correlated somewhat to the gas phase/fiber partition coefficients, but the relationship could be more complex since the separation in this case is also governed by the gas/liquid distribution. Enrichment factors for the extraction of migrants from the water and 10% ethanol standard can be seen in Figure 14, showing the enrichment factors and the correlation between the factors for PDMS and PDMS/DVB for water and 10% ethanol extractions. The enrichment factors were in most cases very high, for example 25,000 for 2,4-bis(1,1-dimethylethyl)-phenol and 17,000 for 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione extracted from water by PDMS/DVB. The PDMS/DVB fiber gave higher enrichment factors than the PDMS fiber for all the analytes. Correlation coefficients (R^2) of 0.98 for both water and 10% ethanol extraction were obtained.

Partial least squares (PLS) regression analysis was also conducted on the results from the extraction of the standard compounds. The purpose was to explore whether the Y data (enrichment factors for SPME of the standards) could be modeled by the available X data; octanol-water partition coefficient (log K_{ow}), vapor pressure, molecular weight and water solubility of the migrant using a 2-component model, to thereby obtain the

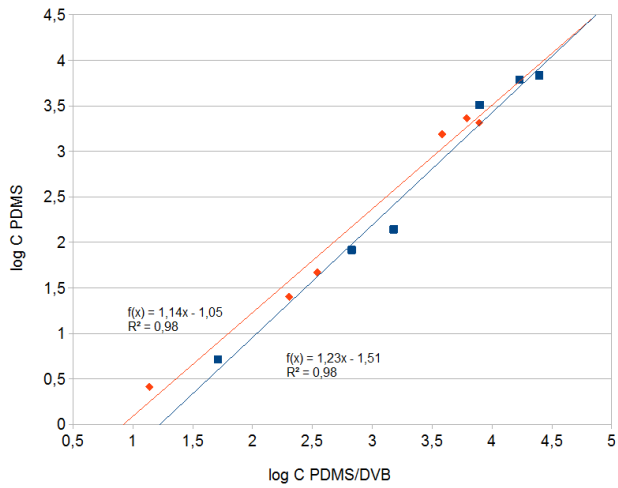


Figure 14: Correlation between logarithm (using 10 as base) of PDMS and PDMS/DVB enrichment factors (log C) for compounds extracted from 10% ethanol (◆) and water (■) solutions.

parameters of the migrant that have most influence on the extraction yield during the HS-SPME method. It was performed using the computer software SIMCA-P+ v. 12.0.1.0 by Umetrics AB, the data was scaled and centered and the vapor pressure and water solubility was further log-transformed before fitting.

The resulting coefficient values and other parameters from the model and migrants can be seen in Table 14. The high R2Y(cum) and Q2(cum) indicate that the model was good. Both these values are a measure of fit and the R2Y(cum) shows how much of the Y data is explained by the model and the Q2(cum) shows how well the X and Y data correlate, or how well the Y data could be predicted from the X data by the model. In order to be a good model, both of these should be high (close to one). The correlation between the predicted and measured values for SPME of water and 10% ethanol dissolved migrants, obtained from the computer software, were high for both PDMS and PDMS/DVB fibers, with correlation coefficients (R^2) in the range from 0.94 – 0.96. As shown by the values of the coefficients, the most significant variable predicting the SPME enrichment factors was log K_{ow}. Other studies have found strong correlation between analyte liquid phase/fiber partition coefficients and log K_{ow} values of analytes during immersion-SPME when for example PDMS and PA (polyacrylate) fibers were used [89, 90]. The high coefficient values for log K_{ow} during SPME extractions together with the obtained good correlation between measured and predicted values by the model shows that the correlation is strong even for SPME from the headspace. Vapor pressure also correlated positively with the SPME enrichment factors as seen in Table 14 but the coefficients were not significant. A figure displaying the coefficient values for PDMS/DVB extraction from 10% ethanol with error bars is also displayed in Figure 15. A model validation using 20 random permutations of the order of compounds in the original Y matrix while keeping the X matrix intact yielded in most cases much lower Q2(cum) values, indicating that the model was valid.

4.4.2 Migration of volatiles

The migration from PC samples during microwave- and conventional heating for 1 h at 80 °C showed that the compound found originally in the polymer, 9,9-dimethylxanthene (Table 3) and several other volatile aromatic substances migrated to the tested FS. No BPA migrated into ethanol or isooctane above the detection limit of 0.6 µg/cm^2 (SML: 0.6 mg/kg = 1 µg/cm^2) [1]. The amounts of the compounds that migrated during 1 h of microwave and conventional heating can be seen in Figures 16a-b. It can be seen that during microwave heating the migration of individual compounds was in most cases larger than during conventional heating. 4-ethoxy-benzoic acid ethyl ester was detected in ethanol and isooctane after microwave heating but not after conventional heating

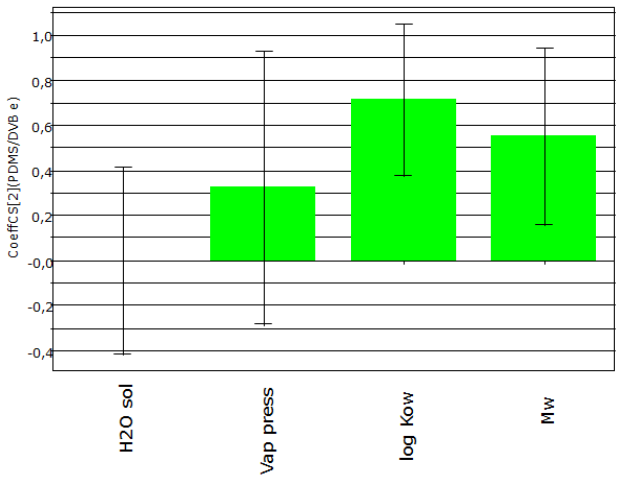


Figure 15: PLS coefficient plot showing the properties that were most influential for the extraction of PC migrants during SPME from 10% ethanol solution.

Table 14: PLS model results and predictor properties. Property values were obtained from the Scifinder database.

R2Y(cum)	0.94			
Q2(cum)	0.85			
Predictors	log K_{ow}	M_w	Vapor pressure	Water solubility
Range	1.67 – 4.64	120 – 220 g/mol	0.08 – 40 Pa	0.002 – 2.4 g/L
Coefficient values				
PDMS/DVB water	0.78[a]	0.59[a]	0.41	0.04
PDMS/DVB 10% ethanol	0.72[a]	0.55[a]	0.32	0.00
PDMS water	0.67[a]	0.52[a]	0.30	0.00
PDMS 10% ethanol	0.66[a]	0.51[a]	0.29	0.00

[a] Significant factor

in these FS. 9,9-dimethylxanthene migrated both during microwave- and conventional heating but the migration during microwave heating was higher by a factor of almost 100. The migrated amount of 9,9-dimethylxanthene into ethanol and isooctane during conventional heating (around 0.001 µg/cm^2) was only a small fraction (1/1000) of the amount that was measured in the sample.

The migration into isooctane and ethanol was as expected in most cases much larger than the migration into water. The migration of most of the compounds into the two fatty FS ethanol and isooctane was similar. Acetophenone which migrated into ethanol but was not detected in isooctane was however an exception. The sorption values of isooctane, ethanol and water were 0.42, 0.48 and 0.29% after microwave heating and 0.22, 0.79 and 0.29 after conventional heating. These values are all quite low and would thus probably not explain the large differences in migration levels between microwave and conventionally heated samples. Benzophenone's SML is listed as 0.6 mg/kg (1 µg/cm^2) and 4-ethoxy-benzoic acid ethyl ester has 3.6 mg/kg (6 µg/cm^2), specified as the highest amount allowed per kg of food in contact with the plastic under worst case or severe usage conditions. The SML values were converted to µg/cm^2 units from a valid conversion factor (assuming 1 kg of food has contact with 6 dm^2 of plastic surface) [1]. The migration of these compounds was much lower than the SML values.

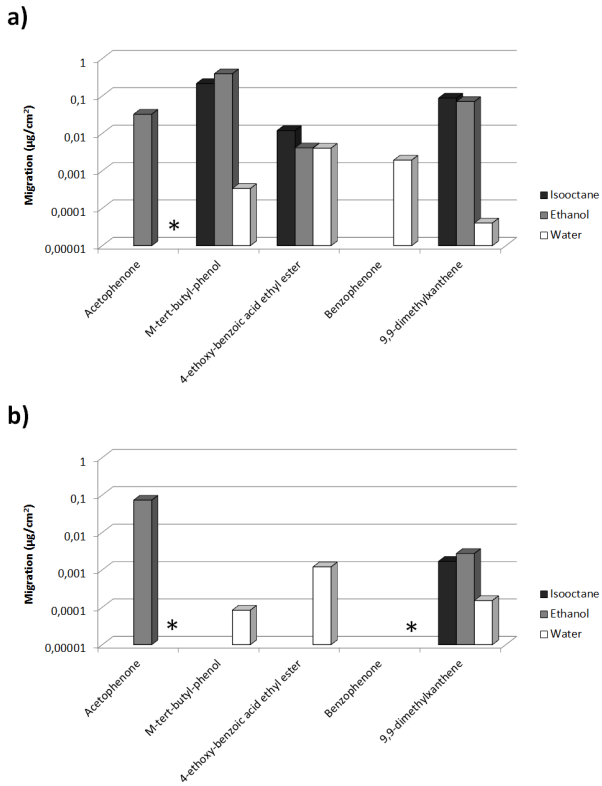
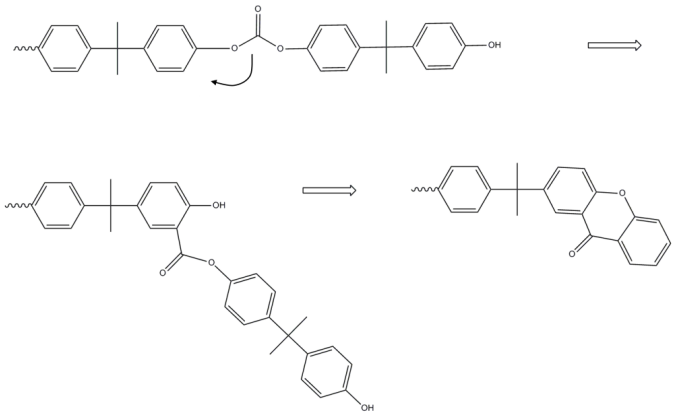


Figure 16: Migration from PC into food simulants during 1 h of (a) microwave and (b) conventional heating at 80 °C. R^2 range for the MHS-SPME determined migrants from water wamples were in the range: 0.92-1.00. (*): detected but not quantified due to low linearity of ln A as function of extraction number.



Scheme 2: 9,9-dimethylxanthene formation from a Fries chain rearrangement reaction [87].

Because the solubility of the 9,9-dimethylxanthene is high in isooctane and ethanol and a large liquid/polymer volume ratio was used in the migration determinations, the diffusion coefficient for 9,9-dimethylxanthene in PC could be determined using equation (9). The diffusion coefficient for 9,9-dimethylxanthene during conventional heating was calculated to be 1×10^{-12} cm^2/s at 80 °C. The corresponding diffusion coefficient calculated with respect to the migrated amount of 9,9-dimethylxanthene during microwave heating was 9×10^{-9} cm^2/s, showing an increase by a factor of 9000 during microwave heating, which is an unrealistically large difference to be explained only by enhanced diffusion by the microwaves. As a comparison, it can be stated that diffusion measurements in earlier work by Antonio et al. showed that the diffusion coefficient of cyclopentanone in an epoxy resin only approximately doubled during microwave heating compared to conventional heating. The temperatures in the study ranged from 60 °C to 95 °C [15]. A more probable explanation to the larger migrated amount could instead be degradation of the polymer chain by a Fries chain arrangement reaction (Scheme 2) [87], which produced more 9,9-dimethylxanthene and resulted in the seemingly higher calculated diffusion coefficient. This explanation also seems plausible given the earlier observed degradation of I168 and I1010 in polypropylene packaging during microwave heating but not during conventional heating at the same temperature.

Table 15: Peak area, concentration, signal-to-noise (S/N) and limits of detection (LOD) for migrants in coconut milk, obtained by SPME and GC-MS analysis

Compound	Area	S/N	Conc (g/L)	LOD (g/L)	LOD PP-R (g/cm^2)	LOD PC (g/cm^2)
acetophenone	ND	-	9.47×10^{-4}	-	-	-
m-tert-butyl-phenol	7807	21	2.80×10^{-4}	4.00×10^{-5}	-	8.16×10^{-8}
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	ND	-	2.60×10^{-4}	-	-	-
2,4-bis(1,1-dimethylethyl)-phenol	4112	71	2.00×10^{-4}	8.45×10^{-6}	1.85×10^{-8}	1.72×10^{-8}
4-ethoxy-benzoic acid ethyl ester	48904	209	7.53×10^{-4}	1.08×10^{-5}	2.36×10^{-8}	2.21×10^{-8}
benzophenone	9092	49	3.00×10^{-4}	1.84×10^{-5}	-	3.75×10^{-8}
9,9-dimethylxanthene	18645	188	2.80×10^{-4}	4.47×10^{-6}	-	9.11×10^{-9}
2,4-dimethylbenzaldehyde	26871	29	5.20×10^{-4}	5.38×10^{-5}	1.17×10^{-7}	-

ND Not detected
- Not determined

4.5 Comparison of specific migration into food simulants and real food

Migration determinations during microwave heating in coconut milk were conducted on PC and PP-R samples to correlate the earlier observed migration of additives or degradation compounds from the packages into FS with migration into a real food. The migration determinations were conducted during 1 h at 80 °C and during 1 h at 120 °C.

4.5.1 SPME of the standard-spiked coconut milk sample

Table 15 shows the GC-MS areas, signal-to-noise values and detection limits of the migrants in coconut milk, obtained from analysis of the spiked food. 9,9-dimethylxanthene and m-tert-butyl phenol had lower detection limits than their earlier migration into ethanol during 1 h of microwave heating at 80 °C.

4.5.2 SPME of the migrants in coconut milk

The specific migration of detected compounds from PC and PP-R, semi-quantified by comparing peak areas to the areas of the spiked standard, are show in Table 16. No migrants were detected after 1 h of microwave heating the packages at 80 °C in coconut milk. Also listed in the table are the predicted migration values using equations (8), (10) and (11) with a polymer/food partition coefficient of 1, the initial concentrations of the migrants in PP-R (Table 3) and material specific data for PP [67]. No polymer-specific material parameters necessary for the estimation of diffusion coefficients in PC exists, therefore no migration values could be predicted for PC by the model.

After 1 h of microwave and conventional heating of PC in coconut milk at 120 °C, m-tert-butyl phenol was detected. Semi-quantification yielded a migration value of 0.14 µg/cm^2 during microwave heating, which is in the same range as the earlier measured value of m-tert-butyl phenol migration after 1 h of microwave heating of PC at 80 °C in ethanol. After 1 h of microwave heating of PP-R in coconut milk at 120 °C dimethylbenzaldehyde was detected and its migration was semi-quantified to be 0.75 µg/cm^2. This value was a bit higher than the semi-quantified value for dimethylbenzaldehyde migration obtained during conventional heating (0.09 µg/cm^2). Earlier 0.072 µg/cm^2 of dimethylbenzaldehyde migrated from PP-R into ethanol during 1 h of microwave heating at 80 °C while no dimethylbenzaldehyde migrated during conventional heating for 1 h at 80 °C (Table 7). Migration of 2,4-bis(1,1-dimethylethyl)-phenol (2,4-DTB) from PP-R was also detected and semi-quantified to be 0.85 µg/cm^2 which is in the same range as the earlier quantified migration value of 2,4-DTB from PP-R into ethanol during 1 h of microwave heating at 80 °C. The migration value into ethanol was significantly increased due to degradation of the antioxidants. The semi-quantified values measured after conventional heating in coconut milk were similar to the migration values measured after microwave heating in coconut milk showing that no significant degradation of antioxidants or polymer occurred during microwave heating at 120 °C, or that the rate of any possible degradation reaction occurring during microwave heating at 120 °C was similar to the degradation occurring during conventional heating at 120 °C in the food matrix. The migrated values were also in the same range, only slightly lower, than the predicted values. The Piringer equation, which is used to predict the diffusion coefficients in the model (equations (10) – (11)), is constructed to give the upper bound coefficients, *i. e.* the confidence interval high limit to give a 'worst case' migration, therefore higher calculated migration values than measured are to be expected. The partition coefficient value of 1 for a mostly aqueous food (17% fat) could also have been a slightly overestimated.

Table 16: Semi-quantified migration values of compounds that migrated into coconut milk during 1 h of microwave (MW) and conventional (Conv) heating at 120 °C in comparison with predicted migration values calculated from the mathematical model.

	MW (µg/cm²)		**Conv (µg/cm²)**		**Predicted (µg/cm²)**
Compound	PC	PP-R	PC	PP-R	PP-R
m-tert-butyl-phenol	0.14	ND	0.13	ND	-
2,4-bis(1,1dimethylethyl)-phenol	ND	0.85	ND	0.6	4.5
dimethylbenzaldehyde	ND	0.75	ND	0.09	2.8

ND Not detected
- Not determined

Other migrants apart from those listed in Table 16 were not detected after 1 h of microwave heating at 120 °C in coconut milk, indicating lower migration than during heating in many of the FS. Since no 9,9-dimethylxanthene was found migrating into coconut milk from PC above the detection limit of 9 ng/cm^2 at 120 °C, the earlier observed degradation reaction was probably not occurring during microwave heating in contact with the food matrix.

The absorption of coconut milk during 1 h of microwave heating at 120 °C was for PC: 0.48% and for PP-R: 2.3%. After 1 h of microwave heating at 80 °C the food absorption was for PC: 0.26% and for PP-R: 0.24%. The food absorption values obtained during 1 h of microwave heating are also compared to the absorption of FS values in Table 17.

Table 17: Food simulant and food absorption by the different package materials after 1 h of microwave heating at 80 °C (%).

Sample	**90/10 isooctane/ethanol**	**Ethanol**	**H_2O**	**3% acetic acid**	**10% ethanol**	**Coconut milk**
PC	0.42	0.48	0.29	0.37	0.37	0.26
PET	0.86	1.06	0.61	0.86	0.78	-
PP-C	12.81	0.53	0.10	0.19	0.13	-
PP-R	14.86	0.69	0.01	0.08	0.08	0.24

- Not determined

5 Conclusions

This thesis has shown the effects of microwave heating on polycarbonate, poly(ethylene terephthalate) and polypropylene food packages heated in different food simulants and foods with respect to the migration of chemical compounds and degradation of the polymer or additives.

Analytical procedures for detection and quantification of the migrating compounds, including SPME-GC-MS, HPLC and ESI-MS were developed and shown to be invaluable for the purpose of determining and fingerprinting migration into food simulants. SPME was also evaluated for the extraction of low molecular weight compounds from real liquid foods.

Significant degradation of incorporated antioxidants Irgafos 168 and Irganox 1010 in PP packages, as well as degradation of PC and PET polymer, occurred during microwave heating of the packages at 80 °C in food simulants containing ethanol. No degradation was observed during conventional heating at the same temperature and no degradation could be observed after microwave heating of the packages in coconut milk. Microwave heating at 80 °C also caused faster migration of cyclic oligomers from PET and migration of poly(ethylene glycol) from PP into ethanol and isooctane, as compared to the migration during conventional heating. The migrants that had SML values migrated in significantly lower amounts than their corresponding SML's during the investigated 1 h of microwave heating at 80 °C. The measured diffusion coefficients of Irgafos 168 and Irganox 1010 in PP and PP *co*-polymers showed larger relative differences than the corresponding degrees of crystallinity for the same polymers. The random *co*-polymer (PP-R) showed by far the fastest migration while the PP homopolymer was the most migration resistant of the PP packages.

Microwave heating of food in plastic packaging could in some situations, in contact with specific foodstuffs, lead to degradation of incorporated additives or the polymer, leading to increased migration of degradation products. Conventional heating methods should thus not be used when testing for potential migration during microwave heating. Above all, this study has shown that the use of ethanol as a fatty food simulant during microwave heating can lead to significant overestimation of migration and degradation of polymers or the incorporated additives. Furthermore, the use of isooctane as a fatty food simulant in contact with polyolefins could lead to overestimation of migration due to swelling.

6 Future work

One important result from this study was that microwave heating can cause degradation of certain compounds such as antioxidants in polymers when heated with certain types of foods or food simulants. Interesting further work would be to determine the possible conditions leading to degradation when heating real foodstuffs in contact with polymers. A small pilot study was already performed in this thesis but further investigations could incorporate other food types such as alcoholic or acidic food.

More detailed studies on the effect of microwave radiation on diffusion of different types of additives in different types of polymers would also provide insights into some of the migration results observed in this thesis. The effect of microwaves on diffusion of molecules or rates of chemical reactions is a relatively unexplored area when connected to the packaging field. Knowledge gained from these studies would also be important for the development of new additives or packages to be used as food contact materials.

Correlating these migration results to those obtained by heating the polymers in contact with food or food simulants in a commercial household microwave oven, and examining the effects of repeated microwaving from all packages, would also be interesting. There exist various other food processing methods that also could produce degradation products from polymers, for example gamma- or steam sterilization techniques, and the effect of those on the formation of migrating compounds could also be investigated in the future.

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Mom, dad and Annica, you have been most encouraging and have always made me feel I could do anything I wanted. So I did. Here is the result.

My sister, you deserve a big thank you for simply putting up with having a stupid little brother that miraculously made it this far ☺.

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References

[1] Commission regulation (eu) no 10/2011 of january 2011 on plastic materials and articles intended to come into contact with food text with eea relevance, 2011.

[2] L. Castle, S. M. Jickells, J. Gilbert, and N. Harrison. Migration testing of plastics and microwave-active materials for high-temperature food-use applications. *Food Addit Contam*, 7(6):779–796, 1990.

[3] Commission directive 2002/72/ec relating to plastic materials and articles intended to come into contact with foodstuffs, 2002.

[4] M. Letellier and H. Budzinski. Microwave assisted extraction of organic compounds. *Analusis*, 27(3):259–271, 1999.

[5] B. F. Ozen and J. D. Floros. Effects of emerging food processing techniques on the packaging materials. *Trends Food Sci Technol*, 12(2):60–67, 2001.

[6] Council directive of 18 october 1982 laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs, 1982.

[7] T. H. Begley, J. E. Biles, and H. C. Hollifield. Migration of an epoxy adhesive compound into a food-simulating liquid and food from microwave susceptor packaging. *J Agric Food Chem*, 39(11):1944–1945, 1991.

[8] M. J. Galotto and A. Guarda. Comparison between thermal and microwave treatment an the overall migration of plastic materials intended to be in contact with foods. *Packag Technol Sci*, 12(6):277–281, 1999.

[9] M. J. Galotto and A. Guarda. Suitability of alternative fatty food simulants to study the effect of thermal and microwave heating on overall migration of plastic packaging. *Packag Technol Sci*, 17(4):219–223, 2004.

[10] S. M. Johns, S. M. Jickells, W. A. Read, and L. Castle. Studies on functional barriers to migration. 3. migration of benzophenone and model ink components from cartonboard to food during frozen storage and microwave heating. *Packag Technol Sci*, 13(3):99–104, 2000.

[11] O-W. Lau and S-K. Wong. The migration of plasticizers from cling film into food during microwave heating - effect of fat content and contact time. *Packag Technol Sci*, 9(1):19–27, 1996.

[12] T. D. Lickly, D. W. Harms, and M. G. Nieuwenhuize. The use of a microwave extraction system for high temperature testing of food contact materials. *Packag Technol Sci*, 9(3):131–141, 1996.

[13] J. Y. Jeon and H. Y. Kim. Microwave irradiation effect on diffusion of organic molecules in polymer. *Eur Polym J*, 36(5):895–899, 2000.

[14] C. Gibson, I. Matthews, and A. Samuel. Microwave enhanced diffusion in polymeric materials. *J Microw Power Electromagn Energy*, 23(1):17–28, 1988.

[15] C. Antonio and R. T. Deam. Can "microwave effects" be explained by enhanced diffusion? *Phys Chem Chem Phys*, 9:2976–2982, 2007.

[16] K. Melski, J. Zabielski, and H. Kubera. Model study on intensified migration of volatile substances from food contacting plastic materials during repeated microwaving. *Electron J Pol Agric Univ*, 6(1), 2003.

[17] M. T. De A. Freire, A. P. Damant, L. Castle, and F. G. R. Reyes. Thermal stability of polyethylene terephthalate (pet): oligomer distribution and formation of volatiles. *Packag Technol Sci*, 12(1):29–36, 1999.

[18] M. Chanda and S. K. Roy. *Plastics technology handbook*. CRC press, Taylor and francis group, LLC, New York, 4 edition, 2006.

[19] M. S. Dopico-García, J. M. López-Vilariñó, and M. V. González-Rodríguez. Antioxidant content of and migration from commercial polyethylene, polypropylene, and polyvinyl chloride packages. *J Agric Food Chem*, 55(8):3225–3231, 2007.

[20] M. Hirata-Koizumi, M. Hamamura, H. Furukawa, N. Fukuda, Y. Ito, Y. Wako, K. Yamashita, M. Takahashi, E. Kamata, M. Ema, and R. Hasegawa. Elevated susceptibility of newborn as compared with young rats to 2-tert-butylphenol and 2,4-di-tert-butylphenol toxicity. *Congenit Anom*, 45(4):146–153, 2005.

[21] G. Ferrara, M. Bertoldo, M. Scoponi, and F. Ciardelli. Diffusion coefficient and activation energy of irganox 1010 in poly(propylene-co-ethylene) copolymers. *Polym Degrad Stab*, 73(3):411–416, 2001.

[22] A. O'Brien and I. Cooper. Polymer additive migration to foods - a direct comparison of experimental data and values calculated from migration models for polypropylene. *Food Addit Contam*, 18(4):343–355, 2001.

[23] M. Bertoldo, F. Ciardelli, G. Ferrara, and M. Scoponi. Effect of the structure of reactor poly(propylene-co-ethylene) blends on the diffusion coefficient and activation energy of a conventional antioxidant. *Macromol Chem Phys*, 204(15):1869–1875, 2003.

[24] Z-W. Wang, P-L. Wang, and C-Y. Hu. Investigation in influence of types of polypropylene material on diffusion by using molecular dynamics simulation. *Packag Technol Sci*, 2011. DOI: 10.1002/pts.983.

[25] C. D'Aniello, L. Guadagno, G. Gorrasi, and V. Vittoria. Influence of the crystallinity on the transport properties of isotactic polypropylene. *Polymer*, 41(7):2515–2519, 2000.

[26] W. Vieth and W. F. Wuerth. Transport properties and their correlation with the morphology of thermally conditioned polypropylene. *J Appl Polym Sci*, 13(4):685–712, 1969.

[27] J. A. Garde, R. Catalá, R. Gavara, and R. J. Hernandez. Characterizing the migration of antioxidants from polypropylene into fatty food simulants. *Food Addit Contam*, 18(8):750–762, 2001.

[28] L. Coulier, E. R. Kaal, M. Tienstra, and T. Hankemeier. Identification and quantification of (polymeric) hindered-amine light stabilizers in polymers using pyrolysis-gas chromatography-mass spectrometry and liquid chromatography-ultraviolet absorbance detection-evaporative light scattering detection. *J Chromatogr , A*, 1062(2):227–238, 2005.

[29] C. Nerín and D. Acosta. Behavior of some solid food simulants in contact with several plastics used in microwave ovens. *J Agric Food Chem*, 50(25):7488–7492, 2002.

[30] R. Ashby. Migration from polyethylene terephthalate under all conditions of use. *Food Addit Contam*, 5(sup001):485–492, 1988.

[31] H. J. Park, Y. J. Lee, M. R. Kim, and K. M. Kim. Safety of polyethylene terephthalate food containers evaluated by hplc, migration test, and estimated daily intake. *J Food Sci*, 73(6):T83–T89, 2008.

[32] R. De Fusco, S. Monarca, D. Biscardi, R Pasquini, and C. Fatigoni. Leaching of mutagens into mineral water from polyethyleneterephthalate bottles. *Sci Total Environ*, 90:241, 1990.

[33] S. Monarca, R. De Fusco, D. Biscardi, V. De Feo, R. Pasquini, C. Fatigoni, M. Moretti, and A. Zanardini. Studies of migration of potentially genotoxic compounds into water stored in pet bottles. *Food Chem Toxicol*, 32(9):783–788, 1994.

[34] O-W. Lau and S-K. Wong. Contamination in food from packaging material. *J Chromatogr , A*, 882(1-2):255–270, 2000.

[35] V. O. Sheftel. *Indirect Food Additives and Polymers: Migration and Toxicology.* Lewis Publishers, Boca Raton, FL, 2000.

[36] J. López-Cervantes, D. I. Sánchez-Machado, J. Simal-Lozano, and P. Paseiro-Losada. Migration of ethylene terephthalate oligomers from roasting bags into olive oil. *Chromatographia*, 58(5/6):321–326, 2003.

[37] T. H. Begley and H. C. Hollifield. High-performance liquid chromatographic determination of migrating poly(ethylene terephthalate) oligomers in corn oil. *J Agric Food Chem*, 38(1):145–148, 1990.

[38] L. Castle, A. Mayo, C. Crews, and J. Gilbert. Migration of poly(ethylene-terephthalate) (pet) oligomers from pet plastics into foods during microwave and conventional cooking and into bottled beverages. *J Food Protect*, 52(5):337–342, 1989.

[39] M. T. De A Freire, L. Castle, F. G. R. Reyes, and A. P. Damant. Thermal stability of polyethylene terephthalate food contact materials: Formation of volatiles from retail samples and implications for recycling. *Food Addit Contam*, 15(4):473–480, 1998.

[40] P. Mercea. Physicochemical processes involved in migration of bisphenol a from polycarbonate. *J Appl Polym Sci*, 112(2):579–593, 2009.

[41] S. Biedermann-Brem and K. Grob. Release of bisphenol a from polycarbonate baby bottles: water hardness as the most relevant factor. *Eur Food Res Technol*, 228(5):679–684, 2009.

[42] K. A. Ehlert, C. W. E. Beumer, and M. C. E. Groot. Migration of bisphenol a into water from polycarbonate baby bottles during microwave heating. *Food Addit Contam*, 25(7):904–910, 2008.

[43] C. Nerín, C. Fernandez, C. Domeno, and J. Salafranca. Determination of potential migrants in polycarbonate containers used for microwave ovens by high-performance liquid chromatography with ultraviolet and fluorescence detection. *J Agric Food Chem*, 51(19):5647–5653, 2003.

[44] C. Nerín, D. Acosta, and C. Rubio. Potential migration release of volatile compounds from plastic containers destined for food use in microwave ovens. *Food Addit Contam*, 19(6):594–601, 2002.

[45] J. H. Petersen and K. H. Lund. Migration of 2-butoxyethyl acetate from polycarbonate infant feeding bottles. *Food Addit Contam*, 20:1178–1185, 2003.

[46] M. Gröning and M. Hakkarainen. Multiple headspace solid-phase microextraction of 2-cyclopentyl-cyclopentanone in polyamide 6.6: possibilities and limitations in the headspace analysis of solid hydrogen-bonding matrices. *J Chromatogr , A*, 1052(1-2):61–68, 2004.

[47] E. Hansson and M. Hakkarainen. Multiple headspace single-drop microextraction - a new technique for quantitative determination of styrene in polystyrene. *J Chromatogr , A*, 1102(1-2):91–95, 2006.

[48] C. L. Arthur and J. Pawliszyn. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal Chem*, 62(19):2145–2148, 1990.

[49] M. Hakkarainen, A-C. Albertsson, and S. Karlsson. Solid phase microextraction (spme) as an effective means to isolate degradation products in polymers. *J Environ Polym Degr*, 5(2):67–73, 1997.

[50] M. Hakkarainen. Qualitative and quantitative solid-phase microextraction gas chromatographic-mass spectrometric determination of the low-molecular-mass compounds released from poly(vinyl chloride)/polycaprolactone-polycarbonate during ageing. *J Chromatogr , A*, 1010(1):9–16, 2003.

[51] S. Guillot, M. T. Kelly, H. Fenet, and M. Larroque. Evaluation of solid-phase microextraction as an alternative to the official method for the analysis of organic micro-pollutants in drinking water. *J Chromatogr , A*, 1101(1-2):46–52, 2006.

[52] B. Kolb and P. Pospisil. A gas chromatographic assay for quantitative analysis of volatiles in solid materials by discontinuous gas extraction. *Chromatographia*, 10(12):705–711, 1977.

[53] M. Gröning. Solid-phase microextraction in polymer analysis - extraction of volatiles from virgin and recycled polyamide 6.6. *Doctoral Thesis*, 2004. KTH Royal Institute of Technology.

[54] C. Pizarro, N. Pérez-del Notario, and J. M. González-Sáiz. Multiple headspace solid-phase microextraction for eliminating matrix effect in the simultaneous determination of haloanisoles and volatile phenols in wines. *J Chromatogr , A*, 1166(1-2):1–8, 2007.

[55] B. Kolb and L. Ettre. Theory and practice of multiple headspace extraction. *Chromatographia*, 32:505–513, 1991.

[56] J. Ai. Solid phase microextraction for quantitative analysis in nonequilibrium situations. *Anal Chem*, 69(6):1230–1236, 1997.

[57] P. R. Loconto. *Trace Environmental Qualitative Analysis, Principles, Techniques and Applications*. Boca Raton, FL: CRC/Taylor & Francis, 2 edition, 2006.

[58] S. W. Chen and G. R. Her. Analysis of additives in polyethylene with desorption chemical ionization tandem mass-spectrometry. *Appl Spectrosc*, 47(6):844–851, 1993.

[59] J. D. Vargo and K. L. Olson. Characterization of additives in plastics by liquid-chromatography mass-spectrometry. *J Chromatogr*, 353:215–224, 1986.

[60] A. Höglund, M. Hakkarainen, and A-C. Albertsson. Migration and hydrolysis of hydrophobic polylactide plasticizer. *Biomacromolecules*, 11(1):277–283, 2010.

[61] S. R. Andersson, M. Hakkarainen, S. Inkinen, A. Södergård, and A-C. Albertsson. Polylactide stereocomplexation leads to higher hydrolytic stability but more acidic hydrolysis product pattern. *Biomacromolecules*, 11(4):1067–1073, 2010.

[62] B. J. Holland and J. N. Hay. Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate). *Polymer*, 43(6):1797–1804, 2002.

[63] G. Hart-Smith and C. Barner-Kowollik. Contemporary mass spectrometry and the analysis of synthetic polymers: Trends, techniques and untapped potential. *Macromol Chem Phys*, 211(14):1507–1529, 2010.

[64] B. Marcato, S. Guerra, M. Vianello, and S. Scalia. Migration of antioxidant additives from various polyolefinic plastics into oleaginous vehicles. *Int J Pharm*, 257(1-2):217–225, 2003.

[65] G. Dhoot, R. Auras, M. Rubino, K. Dolan, and H. Soto-Valdez. Determination of eugenol diffusion through lldpe using ftir-atr flow cell and hplc techniques. *Polymer*, 50(6):1470–1482, 2009.

[66] M. S. Dopico-García, J. M. López V., R. Bouza, M. J. Abad, E. González Soto, and M. V. González Rodríguez. Extraction and quantification of antioxidants from low-density polyethylene by microwave energy and liquid chromatography. *Anal Chim Acta*, 521(2):179–188, 2004.

[67] C. Simoneau. Applicability of generally recognised diffusion models for the estimation of specific migration in support of eu directive 2002/72/ec. www, 2010.

[68] J. Crank. *The mathematics of diffusion*. Clarendon, Oxford, 2 edition, 1975.

[69] T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickly, P. Mercea, M. Milana, A. O'Brien, S. Rebre, R. Rijk, and O. Piringer. Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Addit Contam*, 22(1):73–90, 2005.

[70] P. Neogi. *Diffusion in polymers*. Dekker, New York, 1996.

[71] S. C. Tjong and S. A. Xu. Non-isothermal crystallization kinetics of calcium carbonate-filled β-crystalline phase polypropylene composites. *Polym Int*, 44(1):95–103, 1997.

[72] J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, and D. R. Bloch. *Polymer Handbook*. John Wiley & Sons, New York, 4 edition, 2005.

[73] J. E. Biles, T. P. Mcneal, T. H. Begley, and H. C. Hollifield. Determination of bisphenol-a in reusable polycarbonate food-contact plastics and migration to food-simulating liquids. *J Agric Food Chem*, 45(9):3541–3544, 1997.

[74] X-L. Cao and J. Corriveau. Migration of bisphenol a from polycarbonate baby and water bottles into water under severe conditions. *J Agric Food Chem*, 56(15):6378–6381, 2008.

[75] J. Alin and M. Hakkarainen. Type of polypropylene material significantly influences the migration of antioxidants from polymer packaging to food simulants during microwave heating. *J Appl Polym Sci*, 118(2):1084–1093, 2010.

[76] H. J. Vandenburg, A. A. Clifford, K. D. Bartle, S. A. Zhu, J. Carroll, I. D. Newton, and L. M. Garden. Factors affecting high-pressure solvent extraction (accelerated solvent extraction) of additives from polymers. *Anal Chem*, 70(9):1943–1948, 1998.

[77] A. Feigenbaum, D. Scholler, J. Bouquant, G. Brigot, D. Ferrier, R. Franz, L. Lillemark, A. M. Riquet, J. H. Petersen, B. van Lierop, and N. Yagoubi. Safety and quality of food contact materials. part 1: Evaluation of analytical strategies to introduce migration testing into good manufacturing practice. *Food Addit Contam*, 19(2):184–201, 2002.

[78] M. Bertoldo and F. Ciardelli. Water extraction and degradation of a sterically hindered phenolic antioxidant in polypropylene films. *Polymer*, 45(26):8751–8759, 2004.

[79] I. Skjevrak, A. Due, K. O. Gjerstad, and H. Herikstad. Volatile organic components migrating from plastic pipes (hdpe, pex and pvc) into drinking water. *Water Res*, 37(8):1912–1920, 2003.

[80] J. Salafranca, D. Pezo, and C. Nerín. Assessment of specific migration to aqueous simulants of a new active food packaging containing essential oils by means of an automatic multiple dynamic hollow fibre liquid phase microextraction system. *J Chromatogr , A*, 1216(18):3731–3739, 2009.

[81] I. Skjevrak, C. Brede, I. L. Steffensen, A. Mikalsen, J. Alexander, P. Fjeldal, and H. Herikstad. Non-targeted multi-component analytical surveillance of plastic food contact materials: Identification of substances not included in eu positive lists and their risk assessment. *Food Addit Contam*, 22(10):1012–1022, 2005.

[82] K. A. Barnes, A. P. Damant, J. R. Startin, and L. Castle. Qualitative liquid chromatographic-atmospheric-pressure chemical-ionisation mass spectrometric analysis of polyethylene terephthalate oligomers. *J Chromatogr , A*, 712(1):191–199, 1995.

[83] T. H. Begley and H. C. Hollifield. Evaluation of polyethylene terephthalate cyclic trimer migration from microwave food packaging using temperature-time profiles. *Food Addit Contam*, 7(3):339–346, 1990.

[84] T. H. Begley, J. E. Biles, C. Cunningham, and O. Piringer. Migration of a uv stabilizer from polyethylene terephthalate (pet) into food simulants. *Food Addit Contam*, 21(10):1007–1014, 2004.

[85] S-J. Chiu, S-H. Chen, and C-T. Tsai. Effect of metal chlorides on thermal degradation of (waste) polycarbonate. *Waste Manage*, 26(3):252–259, 2006.

[86] E. Nowakowska, Z. Daszkiewicz, and J. B. Kyziol. Studies of some impurities in commercial bisphenol-a. *Pol J Appl Chem*, 40:247–254, 1997.

[87] C. Godinez, A. P. de los Rios, F. J. Hernandez-Fernandez, L. J. Lozano, X. Baraza, and E. Mardomingo. Experimental study of the influence of raw material impurities on yellowness index of transesterification polycarbonate. *J Appl Polym Sci*, 119(3):1348–1356, 2011.

[88] R. Batlle, C. Sanchez, and C. Nerín. A systematic approach to optimize solid-phase microextraction. determination of pesticides in ethanol water mixtures used as food simulants. *Anal Chem*, 71(13):2417–2422, 1999.

[89] R. A. Doong and S. M. Chang. Determination of distribution coefficients of priority polycyclic aromatic hydrocarbons using solid-phase microextraction. *Anal Chem*, 72(15):3647–3652, 2000.

[90] S. T. J. Droge, T. L. Sinnige, and J. L. M. Hermens. Analysis of freely dissolved alcohol ethoxylate homologues in various seawater matrixes using solid-phase microextraction. *Anal Chem*, 79(7):2885–2891, 2007.