Emission of additives and degradation products from commercial polypropylene, polyethylene and their composite packages

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Migration is a known phenomenon defined as the partitioning of certain chemical compounds from plastic food packaging into food and has been intensely investigated in recent years. Due to outstanding chemical and physical properties plastics are used in many fields. Polypropylene and polyethylene are extensively used polymers because of their chemical resistance, high tensile strength and low density. To improve the properties of the plastics, additives such as plasticizers, stabilizers, antioxidants, lubricants, pigments and others are required to be added. However, they can migrate from the plastics into the food and contaminate it during production or storage. Therefore, the aim of this study was to investigate commercial polypropylene and polyethylene packages to determine what most often used additives and degradation products of the food packages can migrate to food. After the initial identification of plastics by Fourier-transform infrared spectrometry, the determination of cadmium, chromium, lead and mercury was carried out by atomic absorption spectrophotometry. To evaluate possible volatile and semi-volatile organic compounds thermal desorption gas chromatography coupled with mass spectrometry was used. The results revealing the presence of different potential organic compounds and metals emitted during the degradation process of different types of food contact materials are discussed.

Keywords: food contact materials, polymer additives, gas chromatography-mass spectrometry, thermal desorption, atomic absorption spectrophotometry

INTRODUCTION

Plastics have become an integral of our daily life, permeating various industries and applications due to their versatility, durability and affordability. One of the most prevalent uses of plastics is packaging, which accounted for 40% of all plastic consumption [1]. The benefits of employing plastics in packaging are numerous, including protection against damage from microorganisms, light and other external factors, while preserving food quality. Additionally, plastic packaging facilitates convenient storage and transportation, and is as a source of information about the contained food products.

Due to their advantageous properties and ease of modification, plastics have emerged as the dominant material for food packaging. In their raw form, plastics are rarely used, and the manufacturing process often involves the addition of various additives to modify the plastics. The polymer, however, partially retains the additives, production process residues and break-down products since on average non-fibre plastics contain 93% polymer resin and 7% additives by mass [2]. What is more, a huge amount of chemicals that are not used during the manufacturing chain are formed, for

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example, all kinds of derivatives between additives and residues or additives and monomers, etc.

A wide variety of additives, including lubricants, plasticizers, adhesives, stabilizers, antioxidants, pigments, fillers, polishers, and more, can be added to packing materials. The characteristics of the plastic materials are improved by these additions [3]. Unfortunately, plastics used in a direct contact with food are not completely inert. Compounds present in the packaging material can migrate into food through the functional barrier, which separates the food from the rest of the packaging [4]. Most of the additives tend to migrate because of their low molecular weight [5]. There is a growing concern over the potential health effects associated with this migration. Numerous studies have been conducted to investigate the migration of volatiles, semi-volatiles, additives, monomers and oligomers from plastic packaging materials into food [5–9]. However, a great deal of scientific data uncertainties persists in this topic. This migration poses considerable risks, especially as the market continues to expand exponentially and an increasing number of novel additives are used to produce the desired compounded plastic materials.

Plasticizers are a group of additives most used in plastic materials. Phthalic acid esters, known as phthalates, are used as additives to gain the flexibility and durability of polymer materials. Because phthalate additives are not chemically bound to the polymeric matrix, some of them are released slowly into the external environment from the materials [10]. There are many published studies describing the role of phthalates, such as dimethyl phthalate (DNP), diethyl phthalate (DEP), di-n-propyl phthalate (DPrP), diisobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), di-n-pentyl phthalate (DPP), di-n-hexyl phthalate (DHP), butyl benzyl phthalate (DBP), di (2-ethylhexyl) phthalate (DEHP), di (n-octyl) phthalate (DNOP), dinonyl phthalate (DNP) and diphenyl phthalate (DPhP) in food packaging materials [5, 7, 10, 11]. Not only phthalic acid esters are used as plasticizers but also butyl stearate, acetyl tributyl citrate, alkyl sebacates and adipates are used widely as they are assessed as less toxic than phthalates [6]. On the other hand, previous studies have reported that they might be carcinogenic [12]. Apart from plasticizers, thermal stabilizers are the most used additives in plastics as they prevent polymer material from thermal degradation. The mostly investigated stabilizers are different metal soaps like lead, cadmium, barium, calcium, and zinc carboxylates, some di- and mono-alkyltin compounds, e.g. maleates, carboxylates, mercaptides, and epoxy compounds [13–16]. Other well-known additives are antioxidants. They are used to prevent plastics from the oxidation processes. Oxidation processes can be caused by light, heat, radiation, mechanical effects, or even because of the other chemicals that are in the plastic material. In recent years, there has been an increasing amount of literature on Irganox 1010 and Irgafos 168 as they are the most used antioxidants in food contact materials [17–20]. They can be used in a variety of applications, have a good compatibility, a high resistance to extraction and a low volatility. Also, they are odourless and tasteless. What is more, according to the manufacturers, the effectiveness of the blends of Irganox 1010 with Irgafos 168 is particularly noteworthy. Therefore, in most cases, manufacturers use mixtures of different antioxidants. UV radiation is another factor that causes the degradation of polymers. The so-called hindered-amine light stabilizers (HALS) are used as additives to prevent them from UV radiation. Because of the polymeric structure of HALS, they are of a high molecular weight and have a restrictive movement. As a result of that, the migration through the functional barrier of plastics might be inconsequential. L. Coulier et al. investigated migration into food simulants from commercially available polypropylene and high-density polyethylene samples and the concentrations that were detected were significantly lower than the requirements according to the Directives [18]. Lubricants as well are used as additives as they permit the forming process and reduce the adhesion of food components to the packaging. Waxes, paraffin, fats and oils, acylglycerols and fatty acid amines are frequently used as lubricants during the manufacturing processes of plastics. A. Schaefer et al. confirmed the presence of lubricants in coatings of a commercial epoxy-anhydride coating containing carnauba wax and partial acyl glycerol on tinplate strips [21]. Also, stabilizers, antioxidants, UV stabilizers, biocides and fillers are used as metal additives during the manufacturing processes [22].

The negative effects of intentionally added substances to food packages on human health are

nowadays well known and concern several aspects from disrupting the thyroid system to allergies [23, 24]. Unfortunately, it is thought that non-intentionally added substances (NIAS) could cause even more issues than intentionally added substances as NIAS are not investigated enough. With that in mind, to protect consumers from the migration of potentially harmful substances from packaging to food a lot of institutions are working on legislation on food packaging materials and public education.

Until now, many researchers have investigated the occurrence of phthalates [5, 7, 10, 25], antioxidants [17–19, 26–35], volatile organic compounds [23, 36], heat stabilizers [37, 38], lubricants [21], light stabilizers [39], slip agents [40] and other additives. A variety of methods are used to identify potential migrants in food simulants or extracts of plastic materials – gas chromatography coupled with mass spectrometry, Fourier-transform infrared spectrometry, UV spectroscopy, liquid chromatography, atomic absorption spectrophotometry, inductively coupled plasma optical emission spectroscopy and other methods. Each has its advantages and drawbacks. The main disadvantages of those methods are that the analysis of the migrant in a food simulant or extract can be very time-consuming and expensive because of the extraction methods and low concentrations of migrants. According to the disadvantages of extraction, the degradation of polymers was investigated by thermal desorption. It is an environmentally friendly method as there is no need for solvents or other reagents. Also, the preparation of the sample is much faster as only cutting of the samples is needed.

All things considered, food packaging is a complex chemical material, and the challenge is figuring out what is in that mixture and what chemicals are possible migrants. Identifying potential migrants probably is the only way we can get knowledge and make decisions in manufacturing processes and assess potential health risks related to the additive and degradation product migration to the food media. Therefore, the aim of this work was to verify and investigate different forms of food contact materials made of polyethylene (PE) and polypropylene (PP) as they take the largest parts in production, 36 and 21%, respectively [2]. Due to the immense work required for migration studies, the scope of this work was limited to non-targeted screening identification by thermal desorption gas chromatography coupled with mass spectrometry of potential migrants, and quantitative analysis of heavy metals by atomic absorption spectrophotometry.

EXPERIMENTAL

In order to compare the different migrants between different plastics, it was decided to analyze samples of PP and PE as they are mostly used for food packaging [41]. Light and dark-coloured samples of PP were chosen for analysis (films for food packaging, candy trays, food preservation bags, plastic jars, etc.). Most of the light-coloured samples were films for bread, cheese, crisps, etc. packaging, and the dark-coloured packages mostly were candy trays, jars and bottles, and intended to be used with chocolate, soft drinks, milk products, and others. The samples of PE included films for packets, food preservation bags, plastic cups, lids, etc., and most of the PE samples were light-coloured. Also, a few samples of PP/PE composite packages were tested for metal analysis. A total of 52 samples were chosen to analyze, 20 of them were PE, 20 PP and 22 PP/PE composites. None of the samples were used for food packaging prior to analysis.

Polymer identification was carried out using the Attenuated Total Reflectance FTIR (ATR-FTIR) (Agilent Technologies Cary 630). The spectra were identified by comparison to the spectra database MicroLab FTIR Software. ATR performed a total of 4 scans with a 2 cm⁻¹ resolution in the 4000–600 cm⁻¹ spectral range; the background was air (4 scans, 4000–600 cm⁻¹). The plastic samples of PP and PE were cut into pieces of 0.2×0.2 cm.

For volatile and semi-volatile organic compound analysis approximately 0.1 g of polypropylene and polyethylene samples was cut into small pieces of 0.2×1.0 cm and inserted into glass thermal desorption tubes (Figs 1b, c). Plugs of annealed glass wool were inserted into the thermal desorption tubes to hold the sample material in the tube. The tubes were sealed with metal caps lined with Teflon, loaded into an autosampler and analyzed. Two parallels of each sample were tested with the same method. For blank analysis, an empty thermal desorption tube with the plugs of glass wool was tested (Fig. 1a).

Fig. 1. Glass thermal desorption tubes: (a) blank, (b) coloured sample, (c) transparent sample

The samples were analyzed by thermal desorption GC/MS using the GCMS-QP2010 Plus (Shimadzu, Japan) gas chromatography system with a mass spectrometer coupled with a thermal desorption sampler TD20 (Shimadzu, Japan). As the non-targeted analysis was employed, no initial standards were used. Potential migrants were identified with a match probability quality higher than 95% using the NIST MS Search 2.0 mass spectra library. To perform sample thermal desorption, the tubes were heated for 60 min at 80°C and a flow rate of 60 mL/min He carrier gas flow. Gases evolved from the sample were transported to the GC injection port under 2.7 mL/min He carrier gas flow. For the analysis of the samples, a capillary column Restek Rtx®-1 w/Integra-Guard® coated with Crossbond® 100% dimethylpolysiloxane (60 m, 0.32 mm ID × 1 μm df) was used. The column oven temperature was programmed from 50°C (10 min), then 5°C/min to 125°C and finally 30°C/min to 240°C (5 min). The full scan mode within the 40–400 m/z range and electron ionization (EI) at 70 eV were used.

For metal analysis, the atomic absorption spectrophotometer AA-6800 with a graphite furnace GFA-EX7 and a hydride vapour generator HGV-1 (Shimadzu, Japan) was used. Ar gas of 99.95% purity was used at a pressure of 0.35 MPa. A deuterium lamp was used for the correction of the background and deuterium hollow cathode lamps were used for the analysis. The wavelengths for Pb, Cd, Cr and Hg were 283.3, 228.8, 357.9 and 253.7 nm, respectively. Approximately 0.2 g of PP, PE and PP/PE samples were cut into small pieces and mineralized in the nitric acid (65%) and peroxide solution (30% pure, p.a.) 5:2 (v/v). After the mineralization, the extract was diluted with water to 25 ml. Two parallels of each sample were tested with the same

method. For blank analysis, the nitric acid and peroxide solution 5:2 (v/v) diluted with water was tested. For the method validation the certified reference materials (VWR Chemicals) were used with the certified values 1011.5 ± 4.5 mg/l of Cr, 1016.6 ± 5.0 mg/l of Cd, 991.3 ± 5.5 mg/l of Pb and 1003.3 ± 4.7 mg/l of Hg.

RESULTS AND DISCUSSION

Polymer identification by Fourier-transform infrared spectroscopy working in the attenuated total reflectance mode (ATR-FTIR)

Both PE and PP FTIR spectra display distinct and identifiable bands according to the literature [42–44]. PE is characterized by antisymmetric and symmetric stretching vibrations of methylene ($-CH_2-$) groups within a wavenumber range of 3000–2840 cm^{-1}. Additionally, in-plane deformations of methylene at 1463 cm^{-1} and a rocking vibration at 725 cm^{-1} are typically observed. In the case of PP, the presence of antisymmetric and symmetric stretching vibrations of both methylene ($-CH_2-$) and methyl ($-CH_3$) groups within a wavenumber range of 3000–2840 cm^{-1} can be detected. Also, in-plane deformations of methylene and antisymmetric in-plane deformations of methyl groups at 1459 cm^{-1} along with in-plane symmetric deformations of methylene at 1376 cm^{-1}, rocking vibrations of methyl groups at 1167 cm^{-1}, stretching vibrations of (C-C) bonds at 998 and 973 cm^{-1}, and a rocking vibration of methylene at 840 cm^{-1} can be observed.

In the present study, the FTIR analysis of PE and PP food packages was conducted. In Fig. 2a, the FTIR spectrum of PE revealed four characteristic vibrational absorption bands at 2948, 2914, 1462 and 717 cm^{-1}. These absorption peaks are
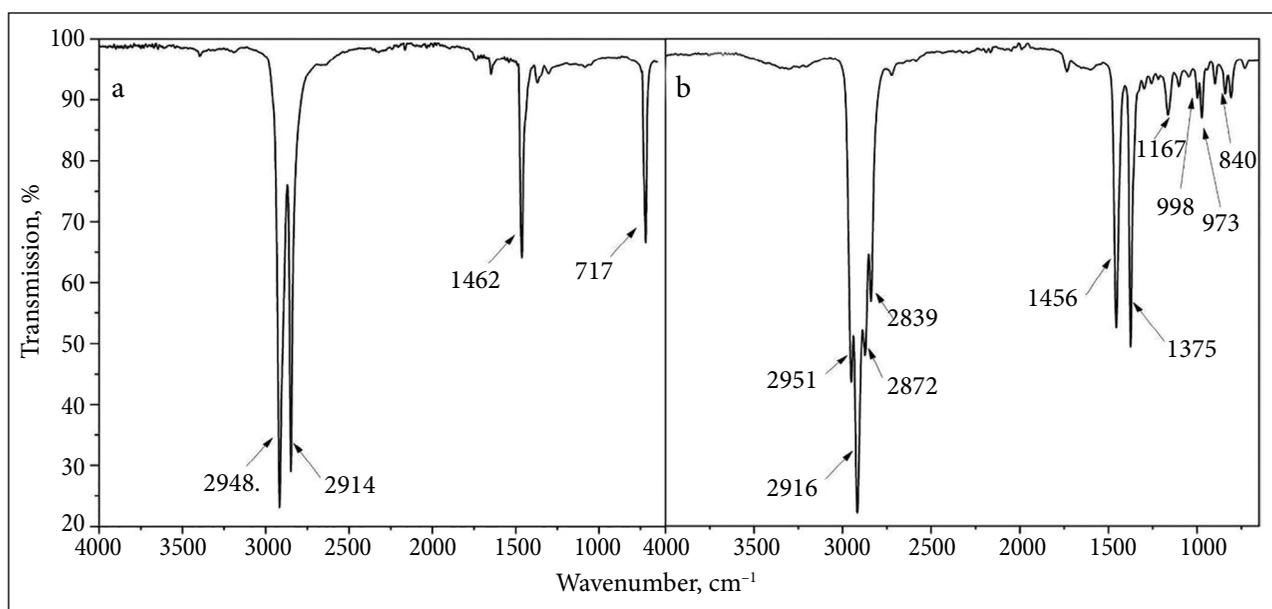
Fig. 2. ATR-FTIR spectra of (a) polyethylene and (b) polypropylene

likely attributable to the antisymmetric and symmetric stretching vibrations of methylene, along with in-plane deformations and rocking vibrations, respectively. These findings are in a strong concordance with data reported in the literature [42–44].

Moreover, the spectra of PP (Fig. 2b) displayed the antisymmetric and symmetric stretching vibrations of both methylene (-CH$_2$-) and methyl (-CH$_3$) groups within the 3000–2840 cm^{-1} range, as well as the in-plane deformation of methylene and antisymmetric in-plane deformation of methyl groups at 1459 cm^{-1}. Other characteristic features included in-plane symmetric deformations of methylene at 1376 cm^{-1}, rocking vibrations of methyl groups at 1167 cm^{-1}, stretching vibrations of carbon–carbon (C-C) bonds at 998 and 973 cm^{-1}, and a rocking vibration of methylene at 840 cm^{-1}.

These attributes were validated by ATR-FTIR analysis of the PP spectrum, which revealed ten distinct vibrational absorption bands at 2951, 2916, 2872, 2839, 1456, 1375, 1167, 998, 973 and 840 cm^{-1}. These bands align precisely with the spectral characteristics of PP as detailed in the existing literature [42–44], thereby underscoring the reliability of our experimental results.

It is noteworthy that despite the different compositions, additives and forms of the PP or PE samples, the spectra presented in Fig. 2 highlight no significant differences between the typical experimental spectra and the ones reported in the literature.

Non-targeted analysis of volatile and semi-volatile organic compounds by thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS)

In this study, a non-targeted screening analysis was carried out to find out what potential volatile and semi-volatile organic migrants could be present in food packaging composed of PE and PP packages. Firstly, the difference between the GC-MS chromatograms of different coloured PP packages was investigated. Figure 3 shows an example of the chromatograms of detected substances (undesignated peaks) of dark and light-coloured PP samples and empty tubes – blanks. As shown in Fig. 3a, the dark-coloured PP packages release more migrants than the light-coloured PP packages (Fig. 3b), but the main groups of migrants are the same (Table 1). The definite reason for this observation is not clear. However, this might result from higher concentrations of degraded oligomers in coloured plastics. Also, it could be because of a considerable number of additives used during the manufacturing process of dark plastic packages.

Secondly, the difference between the GC-MS chromatograms of different plastics – PP and PE – was determined. A typical GC/MS total ion chromatogram of the detected substances (undesignated peaks) of the PE sample is presented in Fig. 3c. Evidently, comparing the results of the GC/MS total ion chromatograms (undesignated peaks) of PP samples (Fig. 3a, b) and PE samples (Fig. 3c)
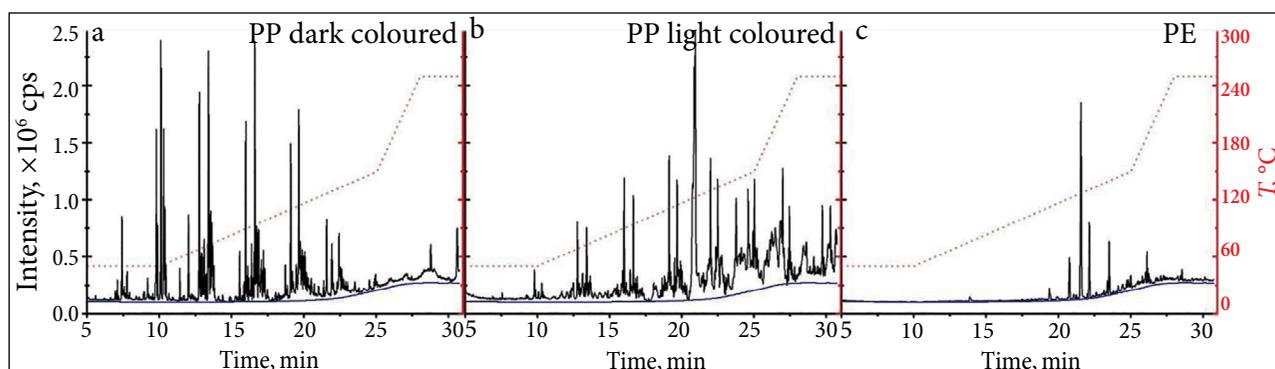
Fig. 3. TD-GC/MS total ion chromatogram of the dark coloured (a) and light (b) PP packages and PE packages (c). A blue line represents the background signals. Dotted red lines mark the temperature during the sample analysis

Table 1. **The possible origin of the identified compounds from the PP and PE samples**

No.	Plastic composition: identified compounds	Groups of compounds – possible origin
1	**PP and PE:** 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester; dodecanoic acid, 1-methylethyl ester; silicic acid, diethyl bis(trimethylsilyl) ester; sulfurous acid, octadecyl 2-propyl ester; 7,9-di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione; bis(2-ethylhexyl) phthalate; bis(tridecyl) phthalate; di-n-octyl phthalate	Esters – plasticizers
	PP: 1,2,4-benzenetricarboxylic acid, 1,2-dimethyl ester; 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,3-cyclohexadiene-1-carboxylic acid, 2,6,6-trimethyl-, ethyl ester; 1,4-benzenedicarboxylic acid, bis(4-butylphenyl) ester; 2-propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester; arsenous acid, tris(trimethylsilyl) ester; benzoic acid, 3-methyl-2-trimethylsilyloxy-, trimethylsilyl ester; benzoic acid, 4-methyl-2-trimethylsilyloxy-, trimethylsilyl ester; benzoic acid, heptyl ester; dichloroacetic acid, decyl ester; oxalic acid, 6-ethyloct-3-yl propyl ester; oxalic acid, bis(6-ethyloct-3-yl) ester; sulfurous acid, 2-ethylhexyl isohexyl ester; sulfurous acid, hexyl pentadecyl ester; 1,3-bis-t-butylperoxy-phthalan; hexanoic acid, 2-ethyl-, hexadecyl ester	
	PE: hexanoic acid, 2-ethyl-, hexadecyl ester; hydracrylic acid, monoanhydride with 1-butaneboronic acid, cyclic ester; cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester; oxalic acid, cyclohexylmethyl isohexyl ester; phosphonic acid, bis(1-methylethyl) ester; phthalic acid, butyl 3-fluorophenyl ester; phthalic acid, bis(7-methyloctyl) ester; phthalic acid, butyl hexyl ester; phthalic acid, cis-hex-3-enyl tetradecyl ester; phthalic acid, ethyl 3-methylbutyl ester; dibutyl phthalate; diethyl phthalate; diisooctyl phthalate; sulfurous acid, hexyl octyl ester; 1-propene-1,2,3-tricarboxylic acid, tributyl ester; 1,4-di-iso-propyl-naphthalene; 1,7-di-iso-propylnaphthalene; bis-(3,5,5-trimethylhexyl) phthalate	
2	**PP and PE:** 1,1'-oxybisoctane; 5-ethyl-2-methyloctane	Compounds of octane – solvents, lubricants, colourant dyes, adhesives
	PP: 1-chlorooctance; 2,3,6,7-tetramethyloctane; 2,4,6-trimethyloctane; 2,7-dimethyloctane; 3,3-dimethyloctane; 4-methyloctane; 2,2,4,4-tetramethyloctane; 4,4-dimethyloctane; 1-methoxy-3-hydroxymethyloctane	

Ta b l e 1. **(Continued)**

No.	Plastic composition: identified compounds	Groups of compounds – possible origin
3	PP and PE: dodecane; 3,5-dimethyldodecane; 2-bromo dodecane; dodecane, 2,6,10-trimethyl-; dodecane, 4,6-dimethyl-; dodecane, 4-methyl-; hexadecane; hexadecane, 1-iodo-; hexadecane, 2-methyl-	Compounds of dodecane and hexadecane – solvents, lubricants
	PP: dodecane, 2,5-dimethyl-	
	PE: hexadecane, 2,6,10,14-tetramethyl-	
4	PP and PE: 1-tetradecene; 5-(2-methylpropyl)-nonane; 5-methyl-5-propyl-nonane; undecane; 3-methyl-undecane; heptadecane; 2,6,10,15-tetramethyl-heptadecane	1-tetradecene and compounds of heptadecane, nonane and undecane – lubricants
	PP: 2,5-dimethylnonane; 3-methylnonane; 5-butylnonane; 2,4-dimethylundecane; 2,5-dimethylundecane; 2-methylundecane; 3,7-dimethylundecane; 3-methylundecane; 4,6-dimethylundecane	
	PE: 5,5-diethylheptadecane; 7,7-diethylheptadecane	
5	PP and PE: pentane; 2,2-dimethylpentane; 2-methylpentane; 3-methylpentane	Compounds of pentane – solvents, lubricants, colourants, adhesives
6	PP and PE: heneicosane	Compounds of heneicosane – stabilisers
	PE: 3-methyl-heneicosane	
7	PP and PE: 1-tridecene; tridecane; 3-methyl tridecane	Compounds of tridecane – solvents
	PP: 1-iodo tridecane; 2,5-dimethyl tridecane; 2-methyltridecane	
	PE: 5,5-dimethyl tridecane	
8	PP and PE: di-n-decylsulfone	Mixed – antimicrobials, adhesives and curing agents
	PP and PE: 2-hexyl-1-decanol	Mixed – dispersion agents, plasticizers, lubricants and monomers
	PP and PE: D-limonene	Mixed – plastic polishers, hardeners, lubricants, fillers, colourants and adhesives
	PP and PE: acetone	Mixed – adhesion promoters, antistatics, catalysts, polishers, seal materials, solvents, stabilisers, lubricants, hardeners
	PP and PE: tetrahydrofuran	Mixed – adhesives, dispersion agents and solvents
	PP and PE: nonanal	Mixed – plastic polishers and lubricants
	PP and PE: decanal	Mixed – plastic polisher
	PP and PE: nonanoic acid	Mixed – antimicrobial, lubricant, colourant and adhesive
	PP: 4,4-dimethyl-1,3-dioxane	Mixed – filler, colourant and adhesive

it is clearly seen that the PE samples release far less migrants than the PP samples, but the main groups of migrants or degradation products are the same (Table 1).

Table 1 illustrates the groups/compounds of potential migrants that were identified using the NIST MS Search 2.0 spectra library with a match probability higher than 95% in the PE, PP, and in both PE and PP samples. The identified compounds in the samples were grouped into 9 compound groups regarding the functional groups and possible origin. One group is called 'mixed' as it consists of single compounds. These compound groups were comprised of esters, compounds of octane, dodecane and hexadecane, 1-tetradecene and compounds of heptadecane, nonane and undecane, pentane, heneicosane, tridecane, mixed group (Table 1), identified compounds that were listed as additives for food contact or other plastic materials, but the function was not determined (Table 2). Most of the migrants identified are not regulated in the EU and, therefore, have no legal limits in place. The origin of the volatile and semi-volatile potential migrants or degradation products is not clear, but it is possible to draw the tendencies based on the literature.

Different plasticizers [5, 7, 10, 11, 42], such as bis(2-ethylhexyl) phthalate, bis(tridecyl) phthalate, di-n-octyl phthalate, and other esters were identified in all the PP and PE samples tested. What is more, not only plasticizers were identified, but also the non-intentionally added substances such as 7,9-di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione which is the product of well-known antioxidant Irganox 1010 degradation reactions [42, 45–47]. As expected, alkanes were detected among the major compounds. Many alkanes and alkenes were found in this analysis. Linear alkanes together with iso-alkanes originate from the so-called paraffin wax that is used for an external lubricant. Alkanes are also used as a solvent. Alkenes are used as starting compounds for several additives and polymers. Besides that, these alkenes are formed as a by-product in olefin polymerization [48, 49]. According to the database CPPdb Lists A and B [42] compounds of octane are used as solvents, lubricants, colourant dyes, and adhesives. In all the samples tested octane and octane-based compounds were identified. No different compounds of octane were identified in the PE

samples. Also, compounds of dodecane and hexadecane are used as solvents and lubricants. Different methylated dodecane, such as 4-methyl-dodecane, 4,6-dimethyl-dodecane, and hexadecane compounds, such as 2-methyl-hexadecane, were identified in the samples tested. Besides, lubricants, such as 1-tetradecene, heptadecane, 3-methyl-nonane, 3-methyl-undecane, and others were also identified during the analysis. In addition, pentane, pentane-based compounds are used as solvents, lubricants, colourants and adhesives. All these additives were identified in all the PP and PE samples tested and no different compounds of pentane were identified only in PE or PP. Compounds of tridecane, such as 1-tridecane and 3-methyl-tridecane, are used as solvents and they were identified in all the samples tested. 5,5-Dimethyl-tridecane was identified only in the PE samples, while 1-iodo-tridecane, 2-methyl-tridecane and 2,5-dimethyl-tridecane were identified only in the PP samples. Moreover, the stabilizer heneicosane was identified in all the samples tested and 3-methyl-heneicosane was identified only in the PE samples. As well, di-n-decylsulfone, 2-hexyl-1-decanol, d-limonene, acetone, tetrahydrofuran, nonanal, decanal and nonanoic acid were identified in all the PP and PE samples tested. 4,4-Dimethyl-1,3-dioxane was identified only in the PP samples and it is used as a filler, colourant and adhesive.

The possible functions of these migrants according to the database CPPdb Lists A and B [42] are listed in Table 1.

Also, more possible migrants or degradation products, such as compounds of decane, heptane, cyclohexane and 2-propanol, were identified in different samples (Table 2). All the migrants are listed in the database [42] as additives for food contact or other plastic materials but there is no information of possible origin provided.

Analysis of metals by atomic absorption spectrophotometry (AAS)

The function of the heavy metals (Cd, Cr, Hg and Pb) was investigated by searching in the database CPPdb Lists A and B [42] designated for plastics. By their function in plastics, Cd compounds can be used as catalysts, plastics fillers, hardeners, colourants, adhesives, heat or UV stabilizers or pigments (0.01–1% low for, e.g. light beige and high for, e.g. clear war yellow). Cr compounds can be used as raw

Table 2. **The list of identified compounds that were listed as additives for food contact or other plastic materials without a clear function for usage**

Identified compounds			Plastic composition
Eicosane	Heptanal	Tetracosane	
2,2-Dimethylpropanoic acid	3-Ethyl-3-methylheptane	Decane	PP and PE
1-Iododecane	Decane, 3,7-dimethyl-	Decane, 3,8-dimethyl-decane	
Pentadecane	Dodecanal	2-Hexyl-1-dodecanol	
Heptane	2,2,3,3,5,6,6-Heptamethylheptane	2,4,6-Trimethylheptane	
2,3-Dimethylheptane	2,4-Dimethyl-heptane	2,5,5-Trimethylheptane	
4-Methylheptane	2,3,4-Trimethylhexane	2,3,5-Trimethylhexane	
2,4-Dimethylhexane	2,5-Dimethylhexane	n-Hexane	PP
Cyclohexane	1-Ethyl-2-propylcyclohexane	2,6,7-Trimethyldecane	
4-Methyldecane	5,6-Dimethyldecane	2,6,10,14-Tetramethylpentadecane	
1-Cyclopentyleicosane	2,2,4,6,6-Pentamethylheptane	Pentylcyclohexane	
1-(2-Methoxy-1-methylethoxy)-2-propanol	1-(Isooctyloxy)-2-methyl-2-propanol	1-Ethoxy-2-propanol	PE
1-Methoxy-2-propanol	5,6-Dipropyldecane	5-Methyl-6-methylenedecane	

material for plastics production, solvents, hardeners, fillers, colourants, or adhesives. Also, Hg compounds can be used as hardeners, fillers, colourants, adhesives, or catalysts. Lead or its compounds are used as adhesives, antioxidants, oxidants, raw materials, solvents, stabilizer, paint fillers, hardeners, lubricants, colourants, or adhesives.

With the purpose to analyze Pb, Cd, Cr and Hg in PP, PE and PE/PP composite packages, analytical in-house methods were validated, and the main method performance characteristics were estimated: linearity, intermediate precision, repeatability, trueness, limit of quantitation and limit of detection (Table 3). Validation was performed following the guidelines for performance criteria and the val-

idation procedures of analytical methods produced by members of the Eurachem Method Validation Working Group [43], and the uncertainty evaluation was performed following the guidelines of Nordtest [44].

According to the European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging wastes, the sum of concentration levels of Cd, Pb, Cr and Hg present in packaging or packaging components shall not exceed 100 mg/kg by weight. There were no samples tested where the sum of concentration levels of Cd, Pb, Cr and Hg exceeded 100 mg/kg by weight.

According to the analysis results, Pb and Cd were not detected in the PP packages (Fig. 4a) as

Table 3. **Method performance characteristics of Cd, Pb, Hg and Cr analytical in-house methods**

|	Cd	Pb	Hg	Cr
Linearity	$r^2 = 0.9982$ (0.2–1.0 ppb)	$r^2 = 0.9972$ (2.0–20 ppb)	$r^2 = 0.9992$ (1.0–15 ppb)	$r^2 = 0.9980$ (1.0–5.0 ppb)
Intermediate precision	3.27%	3.69%	2.63%	2.75%
Repeatability	3.15%	1.76%	0.58%	2.47%
Trueness (bias from certified reference material)	0.0001	0.2500	0.0200	0.0244
Limit of quantitation	0.150 mg/kg	0.150 mg/kg	0.0121 mg/kg	0.025 mg/kg
Limit of detection	0.025 mg/kg	0.025 mg/kg	0.0072 mg/kg	0.0125 mg/kg
Uncertainty ($k = 2$)	4.98%	7.16%	6.42%	7.33%
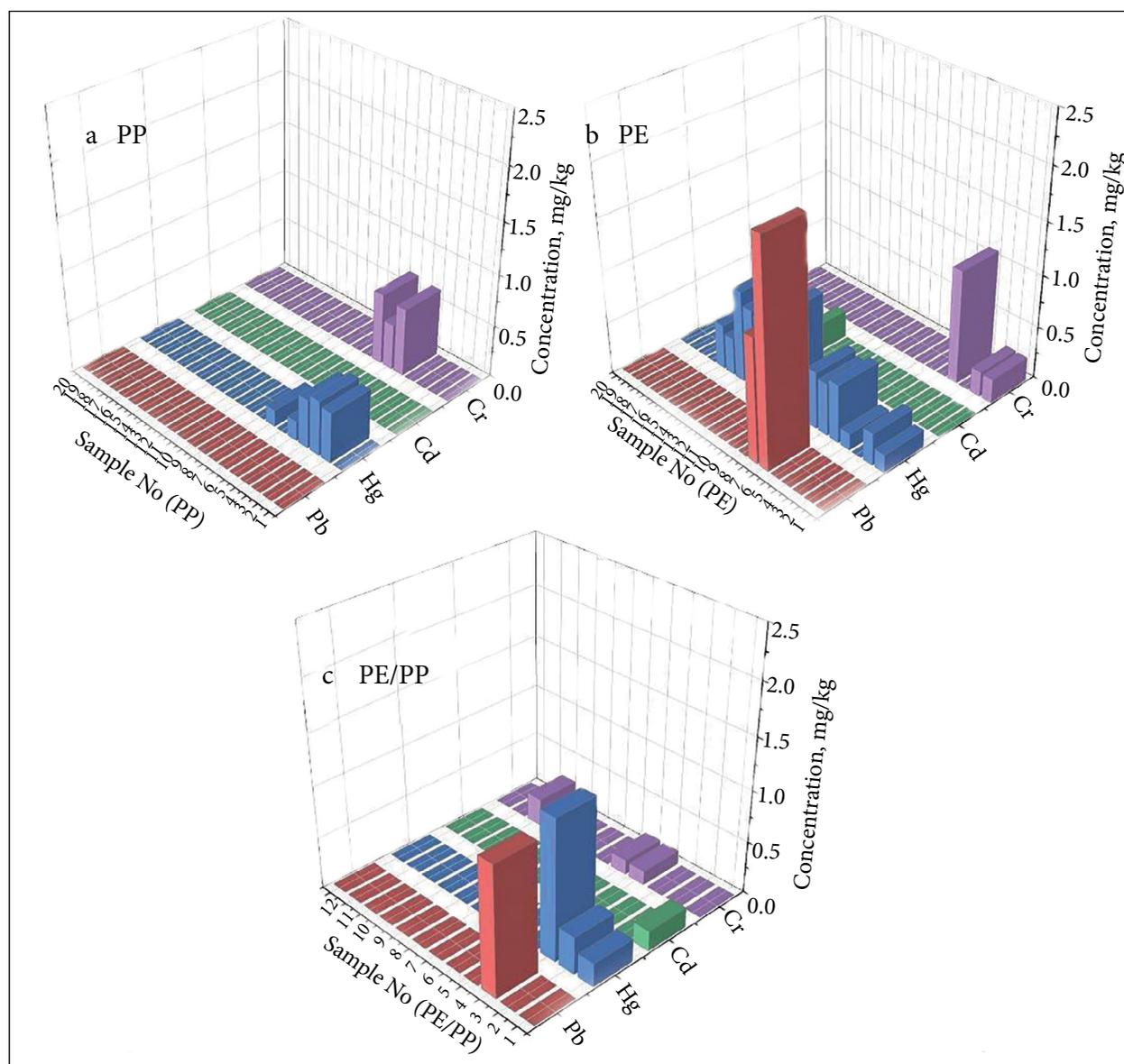
Fig. 4. Concentrations of Cr, Cd, Hg and Pb obtained by AAS in different packaging materials of PP (a), PE (b) and PP/PE composites (c)

T a b l e 4. **The concentrations of Hg obtained by AAS in different packaging materials of PP, PE and PP/PE composites**

Plastic	Sample No.	Hg, mg/kg	Plastic	Sample No.	Hg, mg/kg
PP	2	0.485 ± 0.031	PE	28	0.218 ± 0.014
PP	3	0.527 ± 0.034	PE	30	0.917 ± 0.059
PP	4	0.469 ± 0.030	PE	31	0.340 ± 0.022
PP	5	0.189 ± 0.012	PE	32	0.727 ± 0.047
PP	7	0.160 ± 0.010	PE	33	0.758 ± 0.049
PE	21	0.173 ± 0.011	PE	34	0.881 ± 0.057
PE	22	0.306 ± 0.020	PE	35	0.356 ± 0.023
PE	24	0.158 ± 0.010	PE	36	0.431 ± 0.028
PE	25	0.558 ± 0.036	PE/PP	41	0.227 ± 0.015
PE	26	0.500 ± 0.032	PE/PP	42	0.359 ± 0.023
PE	27	0.547 ± 0.035	PE/PP	43	1.353 ± 0.087

the concentrations were below the limit of detection, but Hg and Cr were detected in 25% (Table 4) and 15% (0.659 ± 0.048 mg/kg, 0.443 ± 0.032 mg/kg, 0.687 ± 0.050 mg/kg) of the samples, respectively. Also, almost in all the PE packages (Fig. 4b) the concentrations of Cd, Pb and Cr were above the limit of detection and only in 5% (0.264 ± 0.013 mg/kg), 10% (2.113 ± 0.151 mg/kg, 1.184 ± 0.085 mg/kg) and 15% (0.232 ± 0.017 mg/kg, 0.239 ± 0.018 mg/kg, 1.097 ± 0.080 mg/kg), respectively, of the samples Cd, Pb and Cr were detected. Hg was detected in 70% of the PE samples (Table 4). Furthermore, in 8% of the PP/PE composite samples (Fig. 4c) the detected concentrations of Pb (1.247 ± 0.089 mg/kg) and Cd (0.194 ± 0.010 mg/kg) were above the limit of detection, and in 25% of the samples Hg (Table 4) and Cr (0.135 ± 0.010 mg/kg, 0.142 ± 0.010 mg/kg, 0.271 ± 0.010 mg/kg) were detected.

CONCLUSIONS

This study outlines that there is a discernible difference in the migrant composition of PE, PP and PP/PE composite packages. This could be attributed to various factors. One consideration is that PP, due to its rigidity, demands a greater amount of modification agent compared to PE. Additionally, PP's melting point is higher than PE's, which restricts its use in temperatures above 0°C. Also, PP displays less chemical resistance than PE. These properties of PE, including its flexibility, lower melting point and superior resistance, enable the manufacture of packaging materials with fewer additives, making it more cost-effective and practical. This finding was supported by TD-GC/MS results of this study showing that the PP packages released more volatile and semi-volatile organic compounds compared to the PE packages.

TD-GC/MS methods have proven very useful in performing the non-targeted screening analysis of solid plastic samples with no additional preparation steps such as solvent extraction. This method proved effective in identifying migrants and degradation products that could be significant in more comprehensive, targeted migration studies conducted using food simulants.

The analysis of the origin of volatile and semi-volatile organic compounds that were emitted from the tested food contact materials was done according to the latest research and in concord-

ance with the plastics migration research database 'Chemicals Associated with Plastic Packaging' [42]. Although only qualitative analysis of GC/MS has been carried out, the results obtained well agree with the previously mentioned database regarding the PE and PP samples.

In addition, the analysis done by AAS revealed that the plastics contained Cr, Cd, Hg and Pb but their mass concentration in the PE, PP and PP/PE composite plastic samples did not exceed 100 mg/kg. All the tested samples were compliant with the requirements of the European Parliament and Council Directive 94/62/EC of 20 December 1994.

More research on this topic needs to be undertaken before the association between the migrants and their source of origin could be more clearly understood. In order to know if the additives in various tested food contact materials are a relevant health hazard, we need to understand whether all the compounds that were identified could actually migrate to food. Further work with food simulants is required to establish that.

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NAUDOJAMŲ PRIEDŲ IR POLIMERŲ DEGRADACIJOS PRODUKTŲ EMISIJOS IŠ KOMERCINIŲ POLIPROPILENO, POLIETILENO IR JŲ KOMPOZITŲ PAKUOČIŲ

S a n t r a u k a

Dėl išskirtinių cheminių ir fizinių savybių plastikai naudojami daugelyje sričių. Vienas labiausiai paplitusių plastiko naudojimo būdų – maisto produktams ir gaminiams skirtos pakuotės, kurios sudaro 40 % viso plastiko suvartojimo pasaulyje. Paprastai, 93 % plastikinės pakuotės sudaro polimerinė derva ir 7 % priedų, tokių kaip plastifikatoriai, stabilizatoriai, antioksidantai, tepalai, pigmentai ir kt., kurie naudojami siekiant pagerinti plastiko savybes. Tačiau naudojami priedai gali migruoti iš plastikų į maistą ir užteršti jį gamybos ar sandėliavimo metu. Dažniausiai pakuotėms naudojami polipropilenas (21 % viso plastiko gamybos) ir polietilenas (36 % viso plastiko gamybos). Todėl šio tyrimo tikslas buvo ištirti komercines polipropileno ir polietileno pakuotes, siekiant nustatyti, kokie dažniausiai naudojami maisto pakuočių priedai ir pačių plastikų terminio skilimo produktai gali migruoti į maistą. Tyrimo metu plastikai buvo identifikuojami Furjė transformacijos infraraudonųjų spindulių spektrometrijos metodu, Cd, Cr, Pb ir Hg nustatymas buvo atliktas atominės absorbcijos spektrofotometrijos metodu, siekiant įvertinti galimus lakiuosius ir pusiau lakiuosius organinius junginius, buvo naudojama terminė desorbcijos dujų chromatografija kartu su masių spektrometrija.

Terminės desorbcijos dujų chromatografijos kartu su masių spektrometrija metodu nustatyta, kad iš polipropileno pakuočių išsiskiria daugiau pridėtinių medžiagų ir degradacijos produktų nei iš polietileno. Naudojantis literatūra buvo įvertintos pagrindinių išsiskyrusių junginių grupių galimos funkcijos plastiko savybėms gerinti. Atominės absorbcijos spektrofotometrijos validuotu metodu atlikta analizė atskleidė, kad plastikuose buvo Cr, Cd, Hg ir Pb, tačiau jų masės koncentracija PE, PP ir PP/PE kompozitiniuose plastiko mėginiuose neviršijo 100 mg/kg. Visi ištirti mėginiai atitiko 1994 m. gruodžio 20 d. Europos Parlamento ir Tarybos direktyvos 94/62/EB reikalavimus.