Journal of Polymers and the Environment (2021) 29:599–611
https://doi.org/10.1007/s10924-020-01899-1

ORIGINAL PAPER

Investigation of the Presence and Possible Migration from Microplastics of Phthalic Acid Esters and Polycyclic Aromatic Hydrocarbons

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Accepted: 22 September 2020 / Published online: 30 September 2020
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Abstract

The work detailed here examined the presence and possibility of leaching of phthalic acid esters (PAEs) and polycyclic aromatic hydrocarbons (PAHs) from various products in everyday use. Due to the complicated matrix, which is plastic, extraction parameters should be selected separately each time. The properties of both the extractant and the material selected for testing should also be taken into account, which is very difficult in practice. In addition, when designing new methods, it is particularly important to take into account the principles of green chemistry so as not to burden the environment additionally. For this purpose, it is important to know the factors that affect the extraction of impurities. Therefore, the main objective was to assess the impact of selected environmental conditions on the process by which such pollutants in plastics like polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP) and rubber migrate. Analysis *inter alia* addressed the impacts of type of plastic, migration time, temperature and microplastic particle size. It proved possible to note the presence in PVC and rubber of both PAEs and PAHs—as substances posing a particular threat to the environment. One of the former is the commonly-used plasticiser di(2-ethylhexyl) phthalate (DEHP), a listed priority hazardous substance under the provisions of Directive 2013/39/EU as regards priority substances in the field of water policy. As monitoring of this substance in the environment indicates amounts that are increasing steadily, the design of effective removal methods needs to start with initial estimates of amounts appearing in the environment over time. Main sources need to be explored, albeit in the certain knowledge that the ubiquitous microplastics are among these, *inter alia* as influenced by elution mechanisms. An attempt was also made to identify and characterise other auxiliary substances added to plastics as they are being produced. Indeed, chromatograms and GC/MS spectra suggest leaching of many other plastic substances. Relationships between eluted pollutants were also sought.

Keywords Microplastics · Polymers · Migration · PAEs · PAHs

Introduction

The presence of growing amounts of plastic waste in the aquatic environment has long been known about, but the dangers posed by microplastic represent a relatively new issue in need of further research. However, existing data already confirm the serious danger posed to both aquatic organisms and humans. Microplastics are primarily harmful because of their content of various auxiliary compounds. In the plastic production process, substances are added to change the characteristics of the final product, with a view to adequate stability, plasticity, colour, fire resistance or filler function being obtained. Unfortunately, the substances deployed only connect to the polymer matrix in a very unstable way, with the result being release into the environment made contact with, be this water, the air, food or body tissues. Synthetic plastics disintegrate most rapidly in conditions of increased humidity, exposure to solar radiation (mainly UV), or high temperature.

The process by which added substances are released into the environment begins on the surface of the plastic particle. Then steady diffusion of toxic chemicals from the particle core ensures long-term release into the environment. The

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relevant processes of leaching, transfer and diffusion can be described by reference to Fick's second law.

Many of the released plastic auxiliaries have confirmed adverse effects in human beings. Brominated flame retardants, bisphenol A, triclosan, benzene, phenol, polycyclic aromatic hydrocarbons (PAHs), the phthalic acid esters (phthalates) that give polymers plasticity, and lead added to protect against high temperatures, are considered some of the most harmful auxiliaries in microplastics. However, some plastics contain particularly large amounts of added substances, with up to 80% of the content of medical equipment made from PVC (polyvinyl chloride) for example comprising plasticity substances.

In consequence, microplastics that have accumulated in the environment can constitute a constant source of pollution [1–5].

Phthalic acid esters reach the environment both during the plastic production process and in the course of use and storage. Depending on environmental conditions, phthalates can volatilise, precipitate, biodegrade, or adsorb on to organic matter. However, the polymer matrix proves so durable in the environment that the release of phthalates from finished products can continue for many years. Indeed, with an assumed annual emission of 1%, a half-life for DEHP of 69 years has been obtained [6, 7]. According to the US EPA, phthalates are classified as probably carcinogenic among human beings. Therefore, EU Commission Regulation No. 143/2011 of 17 February 2011 [8] on the registration, evaluation, authorisation and restrictions of chemicals (REACH) has included six substances from the list, of which DEHP (bis(2-ethylhexyl)phthalate), DBP (di-n-butyl phthalate) and BBP (butylbenzyl phthalate) meet the criteria, leading to their being classified as toxic for reproduction (Category 1B). In addition, DNA damage has been reported in people exposed to these substances, with some giving rise to genetic aberrations, affecting reproduction and further development negatively, and leading to endocrine disorders.

Polycyclic aromatic hydrocarbons can also be mutagenic and carcinogenic, so their use should be reduced as much as possible. They are introduced into vehicle tyres in the form of aromatic oils, *i.a.* to achieve softening of the rubber. On the other hand, in plastics made of PVC, PAHs are present in soot acting as a dye or filler.

In accordance with the supplement to European Union Directive 76/769 EEC [9], from 1 January 2010, certain types of aromatic oil containing benzo(a)pyrene (BaP), benzo€pyrene (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbFA), benzo(j)fluoranthene (BjFA), benzo(k)fluoranthene (BkFA), dibenzo(a,h)anthracene (DBAhA) may not be present at levels of more than 1 mg/kg BaP, or more than 10 mg/kg where the total for all PAHs listed is concerned. The limit values are considered met if the content of the PAH extract is less than 3% by weight, provided that compliance with the benzo[a]pyrene limits and listed PAHs is checked by the manufacturer or importer every 6 months, or after any major operational change.

The only way to reduce health risks is to reduce the amounts of harmful substances present in plastics. However, some tyre manufacturers are still using significant amounts of polycyclic aromatic hydrocarbons to meet requirements as regards durability and grip.

Progressing industrialisation and the development of various industries represent reasons for the demand for chemical products to go on growing, with the result that new hazards associated with the production, transport, use and storage of hazardous-substances waste continue to emerge. In the case of production activities based on the use of various types of organic solvent (as used widely in the production of paints, varnishes, adhesives and detergents, in chemical industry plants, agrochemicals, polymers and rubber), there is a risk of the environment becoming polluted with hard-to-decompose substances. Solvents such as methanol, ethanol and acetone gain wide use in cosmetics and pharmaceutical products. In contact with plastic, including primary or secondary microplastics, these may enhance the risk of toxic substances leaching, with a consequent polluting effect on the environment involving carcinogens and hard-to-decompose substances.

At every stage of production and use there is a threat of migration of toxic substances, and the identification of plastics proves difficult (indeed impossible unless there is systematic qualitative and quantitative analysis). For this reason, it is necessary to obtain information on the possible leaching of auxiliary compounds in plastics and their quantities, as well as the identification of factors facilitating migration, and decomposition conditions. The research presented here has had this kind of key purpose, though the work is also important in regard to the design of methods by which the impurities referred to might also be extracted from plastics. For knowledge of the composition of microplastics, and of the factors causing toxic substances to leach from them, forms the basis of work seeking their removal from the contaminated environment. It is necessary for integrated measures to be resorted to, in order for further spread of microplastic in the environment to be prevented, and for damage that has already occurred to be rectified. By taking action to combat environmental threats, we will help eliminate or curtail future problems caused by the uncontrolled spread of plastic waste.

Materials and Methods

Reagents and Materials

A standard solution of phthalic acid esters was obtained from Sigma-Aldrich (Darmstadt, Germany) (with 2000 µg/

mL in methylene chloride of each of the substances bis(2-chloroethoxy)methane, 4-bromophenylphenyl ether, di-n-butyl phthalate, bis(2-chloroethyl)ether, 4-chlorophenylphenyl ether, di-n-octyl phthalate, bis(2-ethylhexyl) phthalate, diethyl phthalate, butylbenzyl phthalate, bis(2-chloroisopropyl)ether and dimethyl phthalate). Likewise, a standard solution of PAHs was purchased from Reagecon (Shannon, Ireland) (with this comprising 500 µg/mL each, in toluene, of acenaphthene, anthracene, benz(a)anthracene, chrysene, fluoroanthene, fluorene, naphthalene, phenanthrene, pyrene, benzo(a)pyrene, benzo(b)fluoroanthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, benzo(k) fluoroanthene, indeno(1,2,3-cd)pyrene and acenaphthylene). Internal standards relating i.a. to benzyl benzoate (1 g/mL), naphthalene-d8 (2000 µg/mL in dichloromethane), phenanthrene-d10 (2000 µg/mL in dichloromethane) and perylene-d12 (2000 µg/mL in dichloromethane) were obtained from Sigma–Aldrich; while analytical grade n-hexane, methanol, and acetone were all purchased from POCH. Finally, ultra-pure water was obtained from Purix CNX-100 (Polwater, Cracow, Poland).

All glassware was submerged in NaOH solution for 24 h, rinsed with ultra-pure water, and dried for 5 h. A further rinse with acetone was applied prior to heating at 280 °C for 5 h.

Sample Preparation

The presence of PAEs and PAHs, and the conditions under which they might leach from microplastics, were tested for in relation to various types of plastic in everyday use. Indeed, it was plastics from products available commercially and likely to be in wide use that were selected for study. This meant analysis of materials such as polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS) and rubber (Table 1). The plastics involved were cut industrially in appropriate devices, with pieces ultimately attaining sizes below 3000 µm. In turn, rubber from used tyres was purchased in various particle sizes, with testing used on those of 600, 1000, 1000–3000, 1000–4000 and 3000–8000 µm, as well as a mixed fraction (combining 0.1 g of each of the above). Individual samples were placed in 40 mL screw-cap glass bottles.

Experimental Migration Conditions

Investigations concerned the possibility of components from the group of phthalic acid esters and polycyclic aromatic hydrocarbons being leached under various conditions. Testing thus considered the influence of temperature (20, 40 and 60 °C), time (1, 2, 4, 12 and 24 h), solid to liquid phase S/L (1:5, 1:10, 1:20), type of solvent (methanol, hexane or acetone) and degree of elution (I or II). In addition, where the rubber was concerned, analyses were carried out for different particle sizes.

0.5 g of each type of microplastic was weighed into a 40 mL bottle and solvent added. Vials were then closed and stored in an incubator under the various different parameters referred to above, and in the dark. Extracts were passed through a 0.45 µm filter (PTFE), with the aid of a glass syringe, before being analysed by way of direct injection of the extract on GC–MS.

Instrumental Analysis

Analysis seeking to quantify PAEs and PAHs was carried out using gas chromatography coupled to a mass spectrometer GC–MS (Thermo Scientific, Waltham, USA) (Table 2). Separation was achieved along a 30 m × 0.25 mm I.D. DB-5MS column (Thermo Scientific, Waltham, USA) coated with 5% phenyl-95% dimethylpolysiloxane (film thickness 0.25 mm). Helium was the carrier gas. Internal-standard quantification was applied, and the method proved to be linear, with regression coefficient (R^2) > 0.99.

Identification of introduced substances and leachates from plastics was achieved by reference to retention times, and fragmentation ions characteristic for reference substances (Table 3). To identify other auxiliary compounds added during the plastic production process, use was made of the spectra library search method in interpreting mass spectra (with a > 90% match to NIST library mass spectra).

Table 1 Plastic products included in the study

Polymer		Product	Color	Size [µm]
Polyethylene	PE	Foil	Transparent	< 3000
Polyvinyl chloride	PVC	Gasket	Black	< 3000
Polyvinyl chloride	PVC	Phthalate foil	Transparent	< 3000
Polystyrene	PS	Insulation material	White	< 3000
Rubber (caoutchouc)	Rubber (caoutchouc)	Tires	Black	600, 1000, 1000–3000, 1000–4000, 3000–8000
Polypropylene	PP	Gloves	Green	< 3000

Table 2 GC–MS system operating conditions

	PAEs	PAHs
Dosing system	Split-splitless injector with an automatic sample feeder	
Sample volume	1 μL	
Injector temperature	300 °C	280 °C
Carrier gas	Helium	
Carrier gas flow rate	1,0 mL/min	1,1 mL/min
Temperature program	40 °C hold for 1 min, 9 °C/min to 300 °C hold for 5 min	40 °C hold for 3 min, 8 °C/min to 300 °C hold for 4 min

Statistical Analysis

Results were analysed with *Statistica 13* and *MS Excel 2013*. Each substance was tested over the concentration range present in at least three independent experiments. Basic descriptive statistics were then defined to achieve a general characterisation of results. Prior to statistical analysis, values below LOQ (1 ng/mL) were replaced by the LOQ/2 value for each compound. Non-parametric statistical analyses were carried out on raw data, given the uneven variances and sample sizes characterising the conducted analyses. Homogeneity of variance was checked for using the Levene and Brown-Forsythe Tests. Hypothesis testing used the criterion of differences significant at $\alpha \leq 0.05$. Nonparametric Kruskal–Wallis ANOVA, post hoc, was used for multiple and steam comparisons of these data. The Kruskal–Wallis test was used to compare differences between concentrations. To assess data structure, and the relationship between the variable and factors contributing to noted differences in the leaching of individual substances, a principal component analysis (PCA) was performed. PCA is a multidimensional statistical tool used to reduce a set of original variables with a view to extracting a small number of hidden factors called main components for analysing the relationships between observed variables.

Results and Discussion

The Influence of Type of Solvent

First-stage checking considered the influence of type of solvent on the leaching of substances from the group of phthalic acid esters and polycyclic aromatic hydrocarbons. Figure 1 shows possibilities for different substances to be leached from different polymers after t = 2 h at T = 60 °C, in line with the type of solvent applied. The degree of leachability of plastic components is seen to depend primarily on the actual polymer matrix and types of auxiliary compounds present within it. Various factors to be taken account of include initial particle size of the material being analysed, analyte stability, interactions between excipient and polymer, solubility of the additive in the solvent, and conditioning of the elution process (as regards temperature, time and pH).

Acetone proved the most effective solvent with which to elute additives from polyvinyl chloride (a gasket), rubber, polystyrene and polypropylene. The exception was PVC phthalate foil, with which methanol leached most. All of the analysed materials were found to leach phthalates, while certain substances of the PAH group were seen to have been lost from the rubber tyres and the PVC gasket. Analysis in relation to the latter revealed the presence of several phthalic acid esters in acetone, such as DMP at 0.59 ± 0.05 mg/kg, DEP—2.08 ± 0.21 mg/kg, DBP—15.50 ± 1.15 mg/kg, and DEHP—10.51 ± 0.35 mg/kg. In addition, the gasket was characterised by the presence of acenaphthylene (ACY 14.30 ± 1.60 mg/kg), phenenthrene (PHE 2.64 ± 0.03 mg/kg), fluoranthene (FLU 10.68 ± 1.24 mg/kg) and pyrene (PYE 55.54 ± 3.05 mg/kg). Rubber tyres were likewise found to contain, not only plasticisers (DBP and DEHP), but also anthracene (ATRH 11.64 ± 1.09 mg/kg), phenenthrene (PHE 5.63 ± 0.10 mg/kg), fluoranthene (FLU 13.30 ± 0.35 mg/kg), benzo(b)fluoranthene (BbFA 12.44 ± 0.75 mg/kg) and pyrene (PYE 28.38 ± 1.41 mg/kg).

However, no migration of phthalic acid esters from polyethylene was observed. The presence of three of the eleven phthalates analysed for was observed in polystyrene, with DEP (0.65 ± 0.01 mg/kg), DBP (12.24 ± 0.19 mg/kg) and DEHP (1.08 ± 0.11 mg/kg) present. In turn, polypropylene yielded only two: DBP (3.12 ± 0.24 mg/kg) and DEHP (3.34 ± 0.31 mg/kg). The phthalate foil was apparently made using a single plasticiser: DEHP at a level of 201.96 g/kg. The main task of these chemicals is to reduce shear during the polymer production's mixing stages, and to improve impact strength. Flaccidity and stickiness properties are also affected [15].

DEHP migration from phthalate foil in the course of the repeat process (with methanol) was at a higher level than with other solvents during the first stage. Repeat-leaching from the remaining plastics revealed contents of individual components between 0 and 80% of those noted in the first stage. In this second stage, it was DEHP that migrated into the solvent in the largest amounts in almost all of the materials tested, while there was practically no leaching of PAH-group substances, especially from the PVC gasket.

A high degree of migration (350%) for plastic phthalates was also observed by Fankhauser-Noti and Grob (2006) [16]. Fasano et al. (2012) [17] likewise studied the migration of phthalates from PE and PS in food packaging into various solvents (with t = 10 d, T = 40 °C). A PE bag for packaging bread released greater amounts of plasticiser than did the

Table 3 Fragmentation ions and the function in plastic of analysed analyte [10–14]

Analyte	Function	Fragmentation ions (m/z)
Bis(2-chloroethoxy)methane	Plasticizer	123, 95, 93, 65, 63
4-Bromophenylphenyl ether	Plasticizer	251, 250, 249, 248, 141, 115, 77
Di-n-butyl phthalate	Plasticizer	223, 205, 150, 149, 104, 93, 76
Bis(2-chloroethyl)ether	Plasticizer	95, 93, 65, 63
4-Chlorophenylphenyl ether	Plasticizer	206, 205, 204, 169, 141, 84, 77, 75, 70, 51
di-n-octyl phthalate	Plasticizer	279, 150, 149, 71, 69, 57
Bis(2-ethylhexyl)phthalate	plasticizer	279, 167, 149, 69, 57
Diethyl phthalate	Plasticizer	222, 177, 149, 121, 113, 71, 70, 57, 55
Butylbenzyl phthalate	Plasticizer	206, 149, 132, 123, 104, 91, 76, 65
Bis(2-chloroisopropyl)ether	Plasticizer	123, 121, 79, 77
dimethyl phthalate	Plasticizer	194, 164, 163, 135, 133, 92, 77, 76
Acenaphthene	Component of dye and filler	154, 126, 102, 87, 77, 63, 50
Anthracene	Component of dye and filler	178, 152, 126, 89, 76, 63
Benz(a)anthracene	Component of dye and filler	228, 200, 150, 113, 88, 63, 50
Chrysene	Component of dye and filler	228, 202, 176, 150, 113, 101, 63
Fluoroanthene	Component of dye and filler	202, 174, 150, 122, 101, 87, 74, 50
Fluorene	Component of dye and filler	166, 139, 115, 83, 63, 50
Naphthalene	Component of dye and filler	128, 115, 102, 87, 75, 63, 51
Phenanthrene	Component of dye and filler	178, 152, 126, 111, 99, 89, 76, 63, 50
Pyrene	Component of dye and filler	202, 174, 150, 101, 88, 74, 50
Benzo(a)pyrene	Component of dye and filler	252, 225, 161, 126, 74
Benzo(b)fluoroanthene	Component of dye and filler	252, 224, 174, 150, 126, 113, 86
Benzo(g,h,i)perylene	Component of dye and filler	276, 248, 225, 207, 191, 138, 125, 97, 73
Dibenz(a,h)anthracene	Component of dye and filler	278, 248, 225, 207, 191, 138, 125, 83, 73, 57
Benzo(k)fluoroanthene	Component of dye and filler	252, 224, 198, 150, 126, 74
Indeno(1,2,3-cd)pyrene	Component of dye and filler	276, 248, 225, 207, 191, 138, 111, 97, 73, 57
Acenaphthylene	Component of dye and filler	152, 126, 98, 87, 76, 63, 50
Propanoic acid	Flavoring agent, mold prevention	74, 73,57, 56, 55
Decanedioic acid	Plasticizer, masking (reducing or inhibiting the basic odour of the product), plasticizers, lubricants, corrosion retardants	135, 125, 98, 97, 84, 83, 60, 55
Benzenediamine	Stabilizer	185, 184, 183, 182, 167, 166, 92, 91, 80
Cyclohexamine	Rubber accelerator, corrosion inhibitor, rubber antioxidant, antistatic agent	203, 202, 161, 160, 146, 117, 115, 104, 91, 77
Neodecanoic acid	stabilizer	102, 88, 87, 57, 55
9-Hexadecanoic acid	Modifying agent, slip agents, antiblocking agent, lubricants	97, 83, 67, 56, 55
Phenol	Precursor or intermediate	126, 108, 97, 80, 79, 53, 52, 51, 50
2(3H)-benzothiazolone	Antimicrobial agent, corrosion inhibitor	153, 152, 151, 123, 122, 96, 70, 69, 61
Benzothiazole	Antimicrobial agent, corrosion inhibitors, ultraviolet light filters	136, 135, 108, 91, 82, 69, 63, 58
Pentadecanoic acid	Modifying agent, slip agents, antiblocking agent, lubricants	129, 73, 71, 69, 57, 55
Benzene	A basic component	79, 78, 77, 76, 74, 52, 51, 50

PE foil. The PS packaging for yogurt showed very limited DMP migration.

In turn, in the research by Barrero-Moreno et al. (2018) [18] involving polystyrene, the presence of 8 analysed PAHs at the level of 12.45 mg/kg (at 40 °C after 24 h) was confirmed, including benzo(a)pyrene present in the greatest amounts (4.52 mg/kg). A similar content of these substances (12.25 mg/kg) characterised material made from low-density polyethylene—LDPE. In contrast, the highest levels of PAHs were found in the car driving wheel cover (internal part), at 332.1 mg/kg.

The migration potential of the additive put into a polymer depends on several parameters. The polymer itself has a three-dimensional porous structure in which the additives are dispersed. Pore diameter and additive size are then correlated in such a way that smaller (lower molecular-weight)

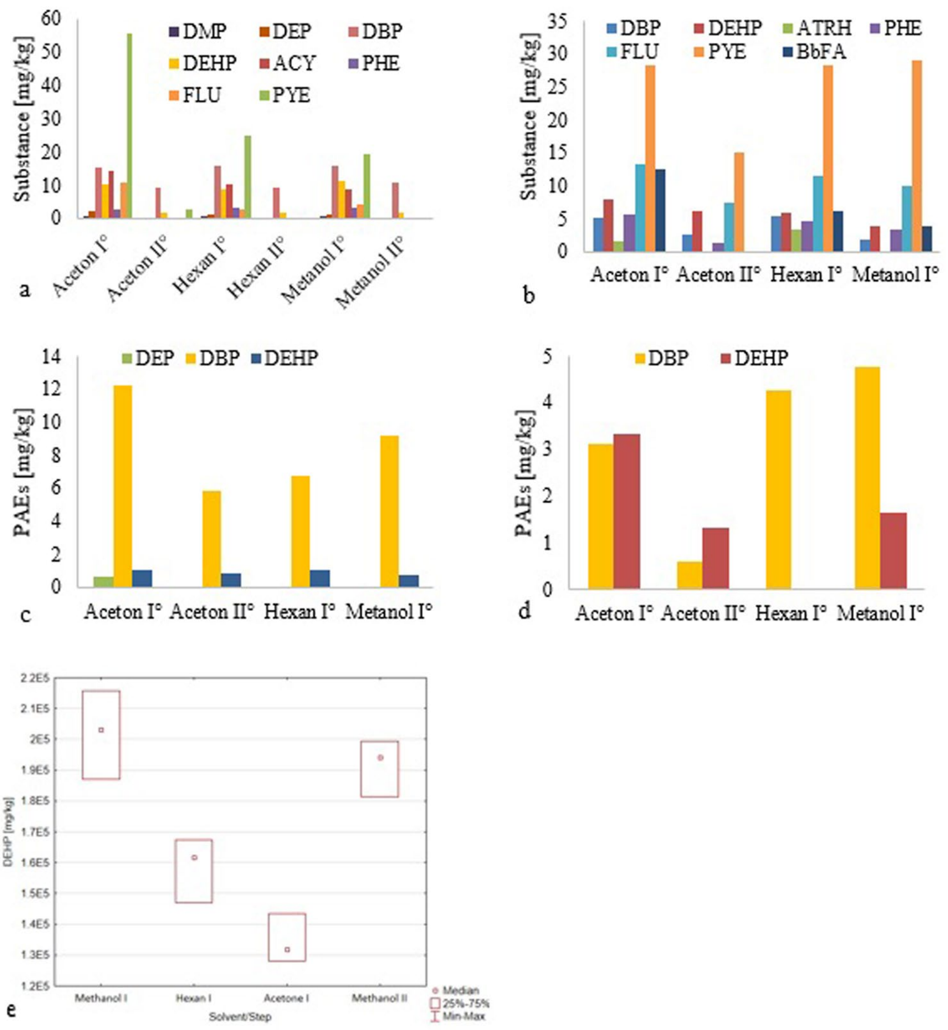

Fig. 1 Impact of choice of solvent (t = 2 h, T = 60 °C) on amounts and types of substances leached from: **a** PVC; **b** rubber; **c** PS; **d** PP; and **e** phthalate foil

additives move more easily through a polymer in which pore size is greater [19, 20]. Plasticisers of relatively low molecular weight (300–600 g/mol) can migrate out of packaging materials into food, thus becoming components thereof, or of the wider environment. However, solvent type and properties often prove crucial in affecting migration from a polymer. The polymer will prove more soluble in the solvent if the solubility parameters are similar.

Acetone, hexane and methanol are different types of solvent [15]. Hexane is an non-polar solvent characterised by the Hildebrand solubility parameter $\delta = 14.9$ MPa$^{1/2}$, acetone is a polar aprotic solvent ($\delta = 20.3$ MPa$^{1/2}$), and methanol is a polar protic solvent ($\delta = 29.7$ MPa$^{1/2}$). Acetone has a solubility parameter closer to that of PS ($\delta = 18.5$–19.8 MPa$^{1/2}$), PVC ($\delta = 19.5$ MPa$^{1/2}$), natural rubber ($\delta = 17.55$ MPa$^{1/2}$), polybutadiene ($\delta = 16.6$–17.6 MPa$^{1/2}$) and polyurethane ($\delta = 18.1$ MPa$^{1/2}$). In contrast, hexane has similar solubility parameters to polypropylene ($\delta = 16.6$ MPa$^{1/2}$). Hexane in fact dissolves the latter, just as acetone dissolves PVC phthalate foil, the principle being that, where solubility parameters are too close, a polymer softens and dissolves. The analysis of polymer additives does not see complete dissolution as desirable. Rather, the solvent should at least swell the polymer by way of diffusion, allowing additives mixed in physically to dissolve. The solvent passes into the plastic, with volume potentially reduced as a consequence. Material swelling can lead to some changes in physical and chemical properties. The fluid in the swollen material allows for attack or reaction of the ingredient in the plastic, which is diffused out [21, 22]. Acetone is shown to increase the desorption of substances like DMP ($\delta = 21.8$ MPa$^{1/2}$), DEP ($\delta = 20.9$ MPa$^{1/2}$), DBP ($\delta = 19.8$ MPa$^{1/2}$), DEHP ($\delta = 18.5$ MPa$^{1/2}$), PHE ($\delta = 20.1$ MPa$^{1/2}$) and ATRH ($\delta = 20.3$ MPa$^{1/2}$) from materials analysed (other than PVC phthalate foil), as compared with hexane or methanol [21, 23, 24].

The Influence of Temperature

Figure 2 presents the influence of temperature on the degree of leaching of the substances analysed. At higher temperatures, the efficiency of leaching of substances from the PAH and PAE groups is seen to be greater, albeit more so for the latter than the former. For example, a higher (60 °C) temperature is not associated with PAH leaching at a significantly higher level, while leaching of DEP from PVC and PP was not noted at the tested temperatures lower than 60 °C.

The scope for greater migration and the moment of its onset are both seen to depend on both the type of plastic and the physicochemical properties of the additive used. Statistical analysis revealed significant differences in behaviour between DEP ($p < \alpha$, $p = 0.0221$), DBP ($p < \alpha$, $p = 0.0390$), DEHP ($p < \alpha$, $p = 0.0265$), PHE ($p < \alpha$, $p = 0.0379$) and PYE ($p < \alpha$, $p = 0.0390$), when it came to the temperature at which components from PVC were leached. The amount of DEHP migrating from the phthalate foil was almost three times as great at 60 °C as at 20, a difference achieving statistical significance ($p < \alpha$, $p = 0.0273$). In contrast, the amounts of DEHP that leached from PVC ($p < \alpha$, $p = 0.0265$) and PP ($p < \alpha$, $p = 0.0390$) were over twice as great, while in the case of PS ($p < \alpha$, $p = 0.0273$) and rubbers ($p < \alpha$, $p = 0.0390$) the figure was almost twice as high.

For the maximum rate of migration in the case of a given solvent to be obtained, the process should be carried out under conditions that cause maximum swelling, without actually dissolving the polymer. Greater application of heat can cause a polymer to transition from glassy to rubbery at the glass transition temperature (T_g), with diffusion from the former form as opposed to the latter crystalline form proceeding much more rapidly. A rapid increase in migration rate at T_g is thus to be anticipated, with migration also faster with polypropylene than with PS and PVC, given respective transition temperatures of 10, 95 and 85 °C [21, 25]. The presence of plasticisers is in turn known to decrease glass transition temperature in the case of PVC [26].

Where the leaching of substances is concerned, the density of the plastic involved is also a key parameter. Figge and Freytag (1984) [27] found that the antioxidant they analysed migrated less where polymer density was greater, even as molecular weight was seen to have almost no effect.

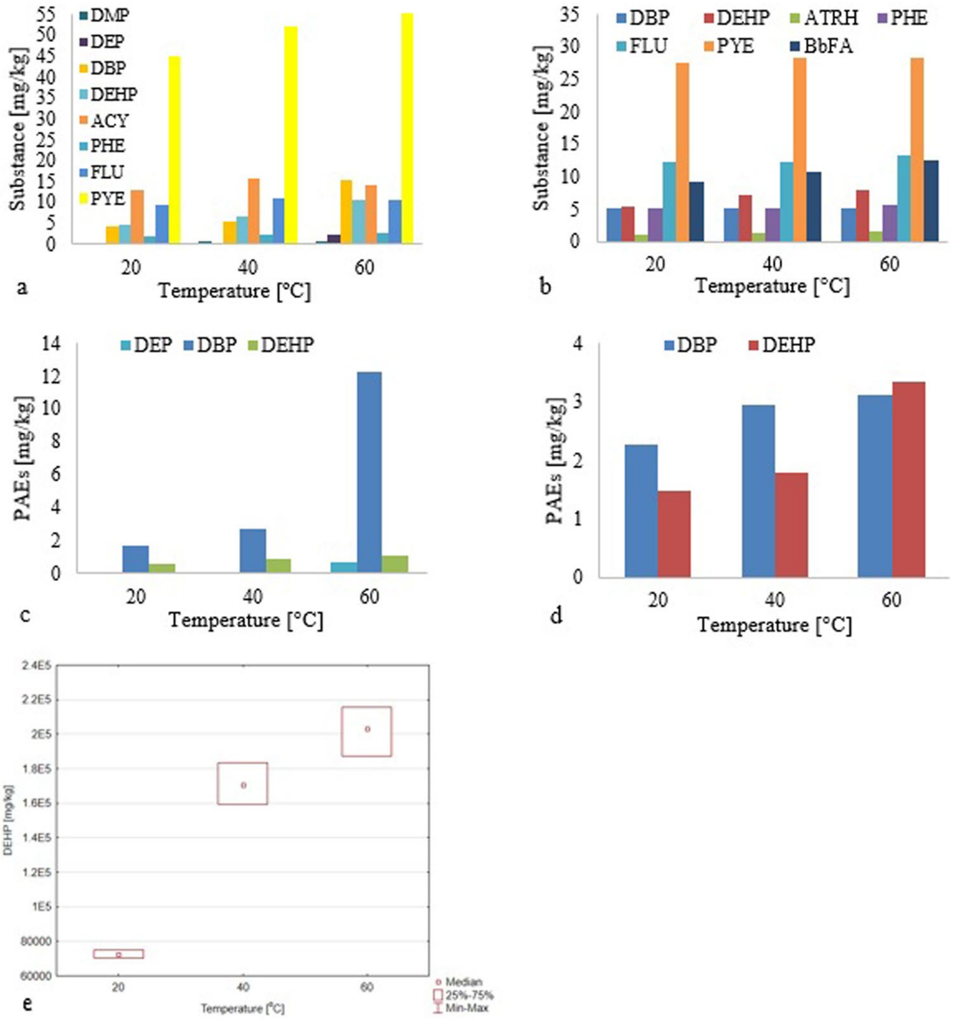

Fig. 2 The effect of temperature ($t = 2$ h, $T = 60$ °C) on amounts and types of substances leached from: **a** PVC; **b** rubber; **c** PS; **d** PP; and **e** phthalate foil

The total amounts of phthalates leaving the PVC gasket at 20, 40 and 60ºC were 10.69, 12.40 and 28.69 mg/kg respectively. In turn, chemical analysis relating to tyres showed a total phthalate content eluted at 20 °C of 8.80 mg/kg, as compared with 12.28 and 13.19 mg/kg at 40 and 60 °C. On the other hand, in PS and PP, higher temperatures were associated with total contents of phthalates eluted in the range 0.0002–0.0014% and 0.0004–0.0006% respectively of the total mass of the material. Similar contents of phthalates were observed in toilet tissue paper by Adjei et al. (2019) [28], who at the same time recall how phthalates are a likely cause of colorectal and skin cancer, among the cancers diagnosed most commonly worldwide, according to WHO reports. Indeed, colorectal cancer is given as the number-two cause of cancer deaths in the world. Toxic substances such as phthalates and PAHs can easily penetrate the lymph following exposure via the skin, and are able to reach other organs from there. The above authors report total phthalate contents in toilet tissue paper in the range 27.06–181.31 mg/kg, depending on the manufacturer [28].

The levels of plasticisers obtained in this study are also comparable with those obtained by Koniecki et al. (2011) [29], in cosmetics and certain personal-care products.

Maia et al. (2016) [30] studied the migration of benzophenone from LDPE foil into different products (again at 20 °C, 40 °C and 60 °C). Diffusion coefficients were greater where the storage temperature was higher, with the 70–700-fold difference noted in liquid foods indicating a much-increased diffusion rate. Almost 100% of benzophenone migrated into high-fat foods, while 70–80% passed into lower-fat foods.

The Influence of Time

The impact of time on the migration of the analysed substances is as shown in Fig. 3. PAHs are introduced into tyres as aromatic oils, used to soften rubber, among other things. However, in PVC they are present in soot filler or dye. After 24 h ($T = 60$ °C), PAHs and PAEs were found to have migrated from the PVC gasket in amounts equal to 112.11 and 38.58 mg/kg, respectively. The total content of PAHs and PAEs eluted from rubber, at 122.60 and 17.11 mg/kg respectively, represents 0.012 and 0.0017% of total product weight. The amount migrating increases rapidly at the outset, before tending to a limit value known as the migration maximum (E_m). The time required to achieve E_m depends on the nature of the system, the thickness of the plastic and the diffusion coefficient. In general, work on the migration of solvent additives shows that amounts are directly proportional to $t^{1/2}$ [25, 31].

After 24 h, DEHP leaching from PVC was recorded at 14.11 ± 0.62 mg/kg, with this comparing with the figures for rubber—11.34 ± 0.82 mg/kg, PS—2.39 ± 0.30 mg/kg, PP—8.15 ± 0.72 mg/kg and PVC phthalate foil—458.62 ± 5.78 g/kg (45.9% of the weight of the product). Some key plasticisers including phthalic esters such as DEHP that are used in PVC formulations account for about 10–60% by weight of flexible PVC [32]. Given their eluted contents of the detected substances could not be used to produce materials in contact with food, as the European Commission (via EC 1282/2011) [33] has set several migration limits for different plasticisers, e.g. 1.5 mg/kg for DEHP and 0.3 mg/kg for DBP. These can only be used as plasticisers in reusable materials and products in contact with non-fat foods, or as a technical support agent in DEHP and DBP concentrations up to 0.1% and 0.05% in the final product, respectively. Under Council Regulation (EEC) No. 793/93 [34], these are classified among the three phthalates most toxic to reproduction (along with BBP).

A statistically significant difference was found for the content of substances migrating from rubber over time, like DEHP ($p < \alpha$, $p = 0.0116$), ATRH ($p < \alpha$, $p = 0.0102$), PHE ($p < \alpha$, $p = 0.0132$), FLU ($p < \alpha$, $p = 0.0118$), PYE ($p < \alpha$, $p = 0.0174$) and BbFA ($p < \alpha$, $p = 0.0157$). Similar results were obtained for the gasket made of PVC, with a statistically significant difference being observed in the content of DMP ($p < \alpha$, $p = 0.0087$), DEP ($p < \alpha$, $p = 0.0137$), DBP ($p < \alpha$, $p = 0.0189$), DEHP ($p < \alpha$, $p = 0.0141$), ACY ($p < \alpha$, $p = 0.0102$), PHE ($p < \alpha$, $p = 0.0090$), FLU ($p < \alpha$, $p = 0$), 0273) and PYE ($p < \alpha$, $p = 0.0262$).

With the passage of time, increased migration of substances from the PAH group was also to be observed. In PVC and rubber it was the highest content of pyrene that was observed. BbFA migration has been recorded from rubber, whose permissible content in extract must be less than 3% by weight. Limit values have been complied with where compliance is checked for at appropriate intervals in accordance with the provisions of Directive 76/769/EEC [9] as amended.

Qualitative analysis for materials subject to migration over 24 h also showed the presence from polystyrene of dibenzene, pentadecanoic acid, styrene and benzene, the latter being one of the most dangerous industrial poisons, due to its high volatility and ability to develop high concentrations in the air. At the International Agency for Research on Cancer (IARC) this compound gains classification in group 1, given benzene's recognised status as a carcinogen for human beings. Furthermore, death results from acute benzene poisoning where concentrations are high (in the range 10,000–65,200 mg/m^3 over a 5–10-min period). Levels of exposure to benzene in various workplaces are given in the range 0.16–266 mg/m^3. A further source of exposure to benzene may reflect its presence in food products and drinking water [10, 35, 36].

Analysis carried out for PVC showed the probable presence of propanoic acid, decanedioic acid and benzenediamine, which acts as a stabiliser. In the case of rubber,

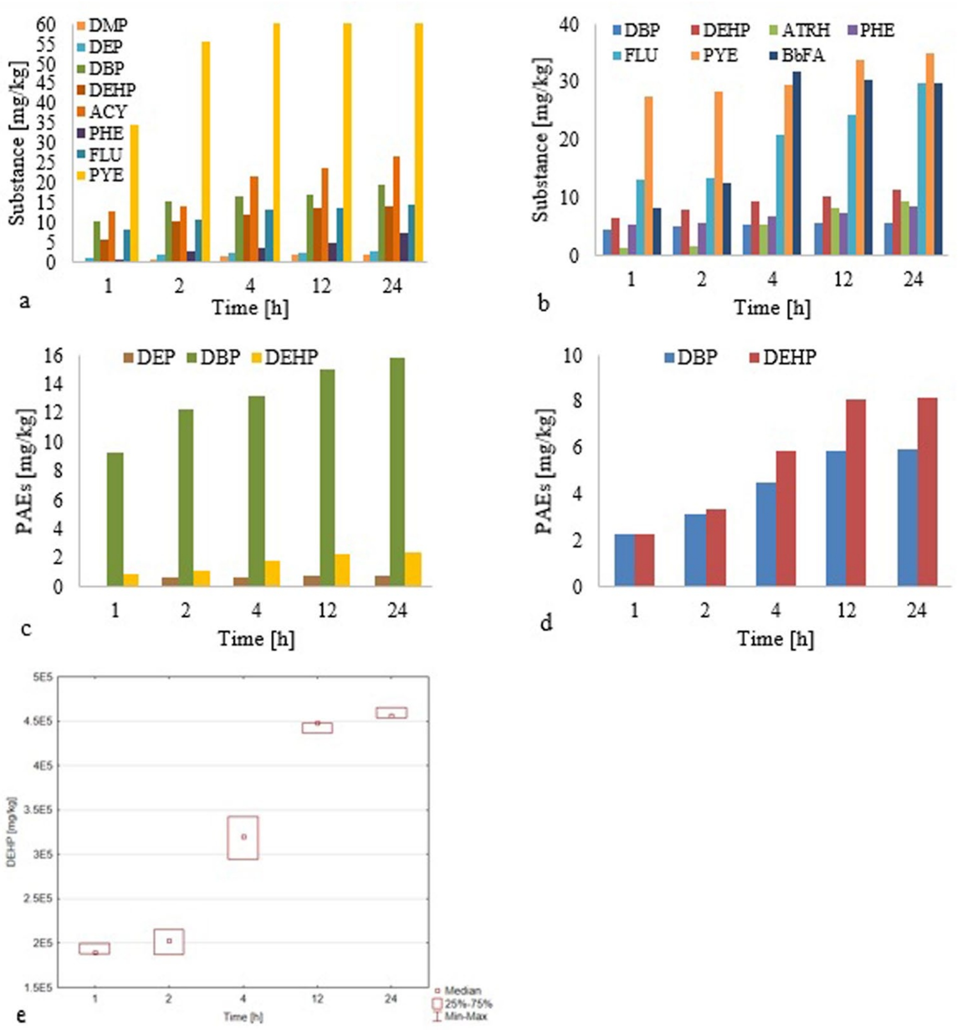

Fig. 3 The effect of time (T = 60 °C) on amounts and types of substances leached from: **a** PVC; **b** rubber; **c** PS; **d** PP; and **e** phthalate foil

the likely presence of cyclohexamine, benzenediamine, neodecanoic acid, 9-hexadecanoic acid, phenol, 2(3H)-benzothiazolone and benzothiazole was indicated. Indeed, more than 200 components are used to make a tyre, with each having its specific role to play. The presence and possibility of migration of 2(3H)-benzothiazolone and benzothiazole from car tyres is confirmed in the latest research by Capolupo et al. (2020) [4]. Additionally, Pośniak et al. (2000) [10] report that, in air samples taken at product preparation stations based on mixtures with the addition of styrene butadiene rubber and acrylonitrile butadiene, ethylbenzene, o-xylene and m-, p-xylene, formaldehyde, acetaldehyde and acrolein were all identified. However, during lining formation in presses, additional tetrachloroethene and dibutyl phthalate were released. In the process of curing brake linings, additional phenol and its derivatives are emitted into the air, as are aliphatic hydrocarbons (pentamethylheptene, tetradecane, pentadecane), di(2-ethylhexyl) phthalate and benzothiazole.

The Influence of S/L

The influence of the solid to liquid ratio on the migration of pollutants from polymers is as shown in Fig. 4. The three S/L variants analysed were 1:20, 1:10 and 1:5. Elution differences were observed with different volumes of solvent used. Statistically significant differences were observed for the analysed phthalic acid esters (e.g. for DEHP $p < \alpha$, $p = 0.0265$ from PVC and $p < \alpha$, $p = 0.0273$ from rubber). The volume of solvent may also influence migration. Where volumes are too low, migration goes underestimated. A minimal amount of 50 ml of solvent per square decimeter of contact material is in fact recommended [37]. However, it is when S/L has a 1:20 ratio that the most marked fluctuations in the migration of individual components are noted, as well as their lowest levels of migration. The most suitable solid to liquid ratio was found to be 1:10, with the highest level of migration and lowest coefficients of variation observed where this was

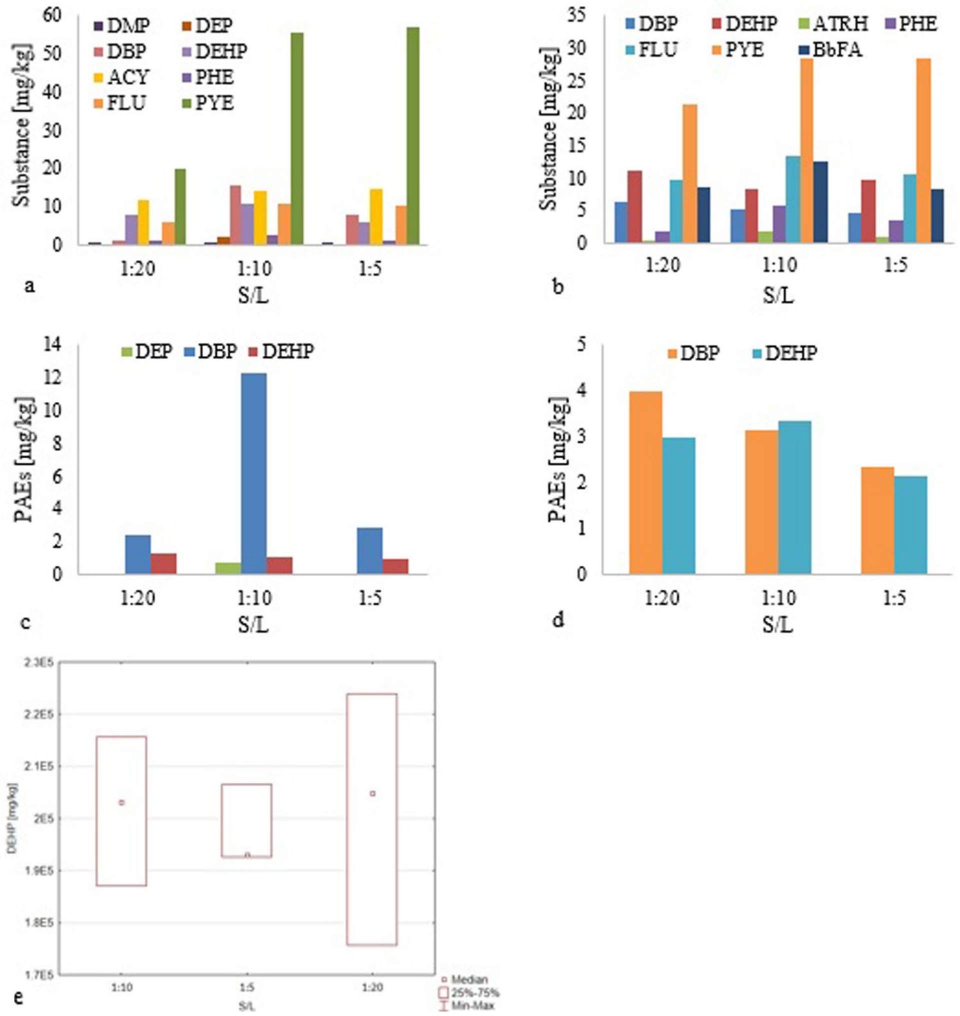

Fig. 4 The effect of S/L (t = 2 h, T = 60 °C) on amounts and types of substances leached from: **a** PVC; **b** rubber; **c** PS; **d** PP; and **e** phthalate foil

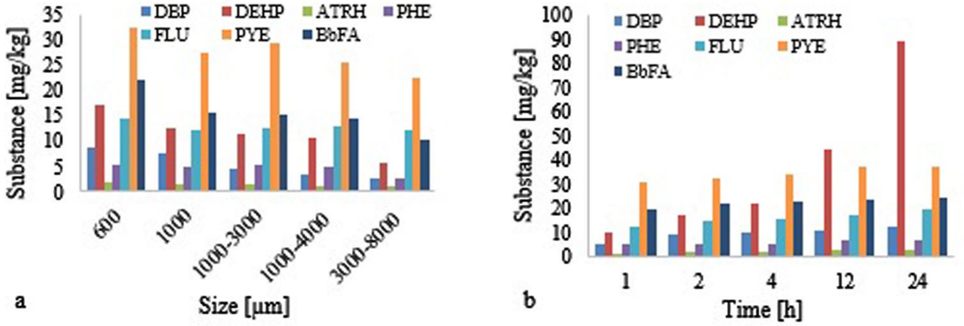

Fig. 5 The leaching of substances from rubber depending on: **a** particle size (t = 2 h, T = 60 °C); **b** time for particle size equal to 600 µm (T = 60 °C)

the study variant. Bejgarn et al. (2015) [20] also tested the migration of pollutants in their research, using an S/L ratio of 1:10. The research methodology was developed in accordance with the guidelines of Swedish standard 12457:2003 [38].

The Influence of Size

Microplastic particle size is an important feature of the process by which contaminants migrate (Fig. 5). The chemical effects are likely to be greater where sizes of microplastic particles are smaller, even as the opposite trend is likely to apply to physical effects. Analysis for 600 µm particles revealed significantly greater migration of DEHP after 24 h. The value was in fact over 80 mg/kg greater than at t = 1 h. Thus, total contents in leachate after 24 h were 101.99 and 89.51 mg/kg in the cases of PAEs and PAHs respectively. Leaching of phthalates from the smallest analysed fraction was more than three times as great as with the largest fraction tested, while a two-fold difference characterised PAHs. Statistically significant differences in relation to time were in fact observed for all analysed components ($p < \alpha$).

In surface waters, it is above all larger fractions of microplastics (> 630 µm) that are determined, even though, as studies make clear, very fine fractions are much more numerous in such waters [39]. The problem of underestimating amounts of plastic particles is also important due to the greater leaching of impurities where these are smaller, and hence the greater threat posed to the environment. Surface drainage and sewage sludge can also represent potential sources of pollution of surface water. Research indicates that microplastics, e.g. from car tyres, can feed into sewage treatment plants along with road runoff. The efficiency of removal from wastewater increases with particle size. As treatment mainly leads to the accumulation of microplastics in sewage sludge, the use of the latter in fertilising crops makes it likely that a serious threat to the environment will be posed [40].

Research conducted by Klaine et al. (2008) [41], Syberg et al. (2015) [42] and Lead et al. (2018) [43] also suggests that features such as size, as well as form, age and colour, may prove important to interactions between microplastics with impurities and their accumulation in fauna and flora. Small size and large area per unit mass also ensure the relevance of these when it comes to the sorption of organic and inorganic pollutants, with microplastics of 200–250 µm particle size offering very large surface areas. In addition, there may be differences in bioavailability and toxicity. Understanding the impact of particle size on toxicity is an important research goal, as the smallest sizes and shapes are still poorly understood from the point of view of the ecological risk they may represent.

Furthermore, the process by which one substance leaches may depend on the process characterising another substance. Analysis of our results indicated strong relationships between substances migrating from polystyrene and polypropylene (Fig. 6a, b). The large amount of data obtained for PVC and rubber encouraged the use of PCA analysis to achieve a more logical grouping. This analysis showed that substances leached from PVC and rubber differentiated characteristics associated with the first two components (Fig. 6a, b). In the case of PVC, the components accounted for 91.58% of the total variance (i.e. the total, multidimensional variability of parameters eluted from plastics), while the figure for rubber was 87.44%. Where PVC is analysed, the eigenvalue for the first component is 6.12, while the

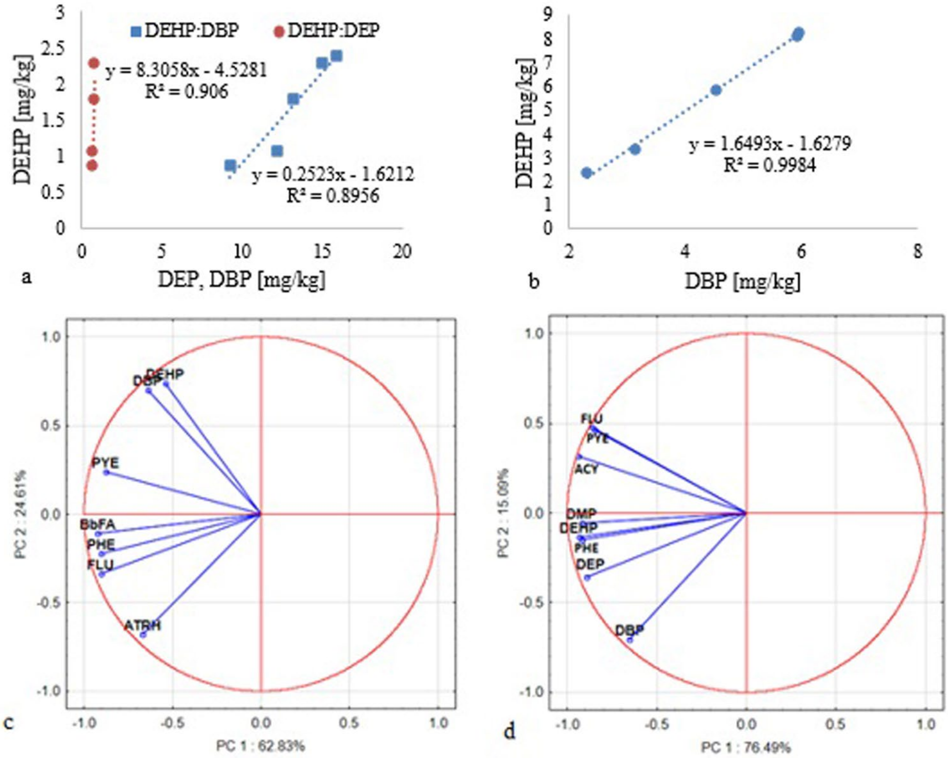

Fig. 6 **a** Dependent relationships between components leached from PS; **b** dependent relationships between components leached from PP; **c** Principal Component Analysis, plot of variables. Location of load vectors towards two principal components for rubber; **d** PCA plot of variables. Location of load vectors towards two principal components for PVC (in a gasket);

percentage of variance it explains is 76.49%. The second component explains much less variance (a mere 15.09%), and its eigenvalue is 1.21.

On the other hand, for rubber, the eigenvalue for the first component is 4.40, and the percentage of variance it explains 62.83%, while the eigenvalue for the second component is 1.72, with 24.61% of the variance explained. In line with the Kaiser criterion, interpretation may be extended to those components whose eigenvalue exceeds 1. In the case of both materials, only the first two main components meet this criterion. Additionally, analysis of the landfill chart shows that the inference is consistent. According to this indication, the first two components provide important information relevant to both materials.

The substances eluted from rubber correlate negatively with the first component, while the second principal component relates to positively-correlated plasticisers and pyrene. Other substances correlate inversely (Fig. 6c). PAHs other than anthracene are represented more by the first component, plasticisers by the second. In addition, a strong observed relationship pertains between DBP and DEHP, while there is no relationship between these substances and anthracene. Pyrene is the subject of a high correlation with DBP, but only a moderate one where DEHP is concerned. In turn, PAHs are characterised by high or very high values for correlations among themselves. The exception is the relationship between anthracene and pyrene, which is only the subject of a limited correlation. Migration of substances from polyvinyl chloride (the gasket) also points to high or very high correlation within the PAH group, but also substances from the group of phthalic acid esters (Fig. 6d). DBP manifests a weakest relationship with substances from the PAH group. The substances analysed are mainly represented by the first component.

Conclusions

Environmental pollution by plastic particles has become a serious problem of global dimensions. The main reason is intensive production of single-use plastics. While such synthetic materials undergo partial deformation over time, they do not degrade, even over periods lasting several hundred years, perhaps even several thousand. However, a change of form is undergone as plasticisers escape from plastics. Scientific data on the migration of such excipients from polymers, and on their biological activity in tissues, are in fact limited, with the topic best-covered involving the effect of BPA on the human body.

Polymers such as polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET), together accounting for about 90% of total world production of plastics, represent the commonest plastics in the environment, and ones that often pose a threat to aquatic ecosystems in nature. This makes it necessary for a number of actions to be taken to check amounts of, and possible leaching from, carcinogenic, hard-to-degrade substances.

Our analyses demonstrated even a low temperature can sustain releases of the studied substances from polymers, while contact time also plays an important role. Furthermore, the smaller the plastic particle, the greater the level of migration occurring. Polymers such as rubber and polyvinyl chloride are found to contain substances from the group of polycyclic aromatic hydrocarbons, as well as amounts of plasticisers that are significantly higher than in polystyrene and polypropylene.

Funding This publication reflects the implementation of Research Project No. 2019/03/X/ST10/01557 funded by Poland's National Science Centre.

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