

An Investigation into Possible Sources and Health Risks of Phthalic Acid Esters in the Iranian Laminated Flexible Films

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ABSTRACT: Phthalates are esters of phthalic acid, mainly used as plasticizer in polymeric packaging materials. The main objective of this research was to determine the exact roots of the phthalate esters in the Iranian flexible/laminated packaging films commercially used for food products such as ketchup, spaghetti, mayonnaise, black tea and snack foods. This investigation was carried out by analyzing the layer by layer constituents of the commercial packaging multi-layer films. Twenty samples have been provided by three different known Iranian companies and analyzed by GC/MS/SIM method. The possibility of film contamination passing through the processing line and the risk of transferring of the phthalate esters from printing inks during winding the printed film (set-off migration) have been also studied. Four different types of phthalate compounds were found in all of the film samples in the range of 1.58-120.99 ppm. No serious phthalate contamination source was distinguished in the film processing line and no set-off migration was observed. The results showed that the total amounts of phthalates in the printed films were higher than the specific migration limit regulatory established for this group of compounds and it may be concluded that the main origin for phthalate esters in the Iranian laminated flexible films are the printing inks.

Keywords: *Laminated Films, Migration, Phthalates, Plasticizer, Printing Inks.*

Introduction

Phthalates are esters of phthalic acid, produced from orthophthalic and terephthalic acid reacted with an appropriate alcohol. On basis of the molecular weight, these chemical compounds may be classified into two groups: low and high phthalates (Wypych, 2013). Phthalate esters are mainly used as plasticizer in vinyl and also non-PVC polymers where the second group of application may be considered as the major

source of these chemical compounds in food packaging materials. A plasticizer is a liquid that is added to a material (usually a resin) making that material softer, more flexible and easier to process. According to a new study published by Market Research Future in July 2017, the global market growth for plasticizers will reach USD 18, 594.07 million by 2022 with CAGR¹ of approximately 3% between 2016 and 2022 (Transparency Market Research, 2017).

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¹ Compound Annual Growth Rate

Since the early 1980s there have been concerns about the effect of phthalates on human health. Phthalates may be potential carcinogens and also endocrine disruptors, and as such could affect reproductive development. Toxicological data of some types of phthalates are presented in Table 1 (Danallo, 2010a; Danallo, 2010b; Bang *et al.*, 2012; Carlson, 2011; Erickson, 2015).

The REACH, Regulation, concerning the “Registration, Evaluation, Authorization and Restriction of Chemicals” is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry.

Phthalate compounds included in the REACH SVHC¹ list because these substances are (ECHA, 2017 a, b):

- Substances meeting the criteria for classification as carcinogenic, mutagenic or reprotoxic (CMR) category 1 or 2;
- Persistent, bio-accumulative and toxic (PBT) substances; or
- Very persistent and very bio-accumulative (vPvB) substances;
- Substances for which there is evidence for similar concern, such as endocrine disruptors.

In recent years, risks of the migration of toxic compounds from the packaging materials into food products have been concerned and discussed as a hot subject in the most of the researches. Therefore the main objective of this research was to determine the exact roots of the phthalate esters in the flexible/laminated films produced by Iranian manufacturers through the following steps:

1- Selecting the commercial flexible food packaging materials for analyzing by GC-

MS system and identifying and quantifying of the phthalate compounds

2-Detecting the main sources of phthalate compounds in each type of the analyzed film sample 3-Presentation and implementation of practical solutions for reducing and or eliminating the risk of phthalate contamination of the Iranian laminated food packaging materials.

Materials and Methods

- *Materials*

Twenty samples of the commercial flexible films (plain monolayers, printed films, metallized films, printed metallized films and printed metallized laminated films) have been provided by three different known Iranian packaging companies and coded as presented in Table 2. The constituent layers of each type of the commercial laminated flexible films have been analyzed in order to detect the main sources of the phthalate compounds.

Standard substances from Sigma-Aldrich used in this research were as follows: Diisooctyl Phthalate 99% (DIOP, CAS No: 27554-26-3), Benzyl Butyl Phthalate 98% (BBP, CAS Number: 85-68-7), Dibutyl Phthalate 99% (DBP, CAS Number: 84-74-2) and Bis (2-Ethyl Hexyl Adipate) 99% (DEHA, CAS Number: 103-23-1).

Four following types of standards have been selected and purchased from Sigma-Aldrich: Diisooctyl Phthalate 99% (DIOP, CAS No: 27554-26-3), Benzyl Butyl Phthalate 98% (BBP, CAS Number: 85-68-7), Dibutyl Phthalate 99% (DBP, CAS Number: 84-74-2) and Bis (2-Ethyl Hexyl Adipate) 99% (DEHA, CAS Number: 103-23-1). The main criteria considered in selecting these standards were: availability, posing a high risk for human health, and being used as a commercial plasticizer by the Iranian film manufacturers.

¹ Substances of Very High Concern

Table 1. Toxicological data of some types of the plasticizers

Phthalate Compounds	CAS no.	LD ₅₀ (mg/Kg)	ADI (mg/Kg _{bw} .day)	NOAEL (mg/Kg.day)	SML (mg/Kg)
Dibutyl Phthalate	84-74-2	Dermal >20000	0.2	50	0.3
Diethyl hexyl adipate	103-23-1	na ¹	0.3	28	3
Diisooctyl phthalate	27554-26-3	Oral >22000	0.15	na	-
Benzyl butyl phthalate	85-68-7	Oral >20000	0.2 (TDI)	20	30

¹ na: not available,

Table 2. Specifications of flexible film samples

Type of the Packaged Product	Type of the Film	Constituent Layers of Multilayer Films	Thickness(mm) ¹	Sample Code no.
Ketchup	PET	Plain outer layer	0.0042±0.0047	1
	Printed PET	Printed outer layer	0.0150±0.0050	2
	Printed PET/Metallized PET	Laminated outer/middle layers	0.0175±0.0043	3
	Metallized PET	Middle layer	0.0075±0.0043	4
	Printed PET/ Metallized PET /LDPE	Laminated outer/middle/inner layers	0.0550±0.0050	5
Black Tea & Herbal tea	Printed PET/Metallized PET	Laminated outer/ middle layers	0.0425±0.0083	6
	Printed PET/Metallized PET/LDPE	Laminated outer/middle/inner layers	0.0975±0.0043	7
Snack Foods	Polypropylene(PP)	Inner layer	0.0225±0.0043	8
	Metallized PP	Outer layer	0.0525±0.0034	9
	Printed Metallized PP/PP	Laminated outer/ inner layers	0.0375±0.0043	10
Fruity Ice Cream	Pearlized BOPP	Inner layer	0.0225±0.0043	11
	Printed Pearlized BOPP	Outer layer	0.0450±0.0050	12
General Purpose	Printed PET	Monolayer	0.0075±0.0043	13
Spaghetti	Printed PP	Outer layer	0.0350±0.0050	14
	PP	Inner layer	0.0275±0.0043	15
Salad Dressing	LDPE	Inner layer	0.0600±0.0000	16
	PET	Outer layer	0.0100±0.0000	17
	AL Foil	Middle layer	0.0100±0.0000	18
Mayonnaise	Printed PET/Metallized PET/LDPE	Outer/Middle/Inner /layer	0.0775±0.0043	19
Ketchup	Printed PET/Metallized PET/LDPE	Outer/Middle/Inner /layer	0.0750±0.0034	20

¹ Thickness of the film samples were measured by digital caliper.

- Phthalate Compounds Extraction Procedure

A small piece of each film sample (8x8 cm²) was cut, weighed and immersed overnight into 10 ml of chloroform in order to extract the phthalate compounds. Then the sample extract was dried under a stream of nitrogen and finally re-suspended in 2 ml of chloroform.

- Experimental Conditions

All measurements have been carried out

using an Agilent 6890A gas chromatography system equipped with a HP 7683 DB-5 auto sampler, J&W Agilent capillary column (30 m x 0.25 mm ID, film thickness of 0.1µ; Model #122-5031) and an Agilent 5973 mass selective detector with a MSD transfer line heater in synchronous full scan/selected ion monitoring (Scan/SIM) acquisition mode to provide high sensitivity of detection of the phthalate esters. The operative gas chromatographic conditions were as follows:

the oven temperature was initially set at 100°C, and then was linearly programmed to increase to a final temperature of 280 °C at 10°C/min. The carrier gas was helium at a flow rate of 1.2 ml/min. one µl of each extract sample was injected in splitless mode. The column maximum temperature was adjusted at 325°C. Analyses were run with full scan data acquisition. Then the mass spectra were compared with the NIST data base for identification and retention time determination and the SIM mode was also used monitoring the major phthalate and adipate target ions at m/z 149,129, respectively. The calibration graphs were plotted by using four different standards of the phthalates, including: Dibutyl phthalate, Benzyl butyl phthalate, Ethyl hexyl adipate and di isooctyl phthalate which were selected as the most hazardous compounds. Based on the phthalates concentrations in different film samples, the calibration curves were plotted in three following ranges: 2-30 ppm, 2-150 ppm and 0.05-0.5 ppm. In order to calculate the phthalate concentration per unit area of each flexible film, the results of phthalate concentrations (ppm) were used in the equation 1:

$$\text{Phthalate Compounds Concentration (mg/dm}^2\text{)} = \frac{\text{Phthalate Compounds Concentrations } \left(\frac{\text{mg}}{\text{L}}\right) \times 0.002(\text{L})}{64\text{cm}^2 \times 0.01 \left(\frac{\text{dm}^2}{\text{cm}^2}\right)} \quad (1)$$

The maximum possible migration of the phthalate compounds (µg/Kg) from each of the analyzed film samples (prepared as a sachet which was composed of two contact surfaces of (5.5x10.4 cm²)) into 20 grams of the packaged food were calculated by the equation 2:

$$\text{Maximum Possible Migration of the Phthalate Esters } \left(\frac{\mu\text{g}}{\text{Kg}}\right) = \frac{\text{Phthalate Compounds Concentrations } \left(\frac{\mu\text{g}}{\text{dm}^2}\right) \times A(\text{dm}^2)}{W_1 (\text{Kg})} \quad (2)$$

A= the film samples are supposed to be used as a sachet with total area of 1.144 dm²

W₁= weight of the packaged food (20gr)

- *Studying the possible contamination sources of phthalate in the processing line of flexible films*

All of the critical points including laminating rolls, printing ink pans and printing rolls were tested. Samples of paper were used for this investigation in order to distinguish certain points of the processing line better which may cause phthalate contamination. Following samples were prepared and analyzed:

- a) Control: The original paper sample
- b) Laminating rolls: The original paper sample that has been passed through the laminating rolls.
- c) Printing rolls: The original paper sample that has been passed through the printing rolls.
- d) Printing ink pans: The original paper that was immersed in ink pans. These samples were prepared from three different colored inks: red, yellow and black.

The above mentioned samples were analyzed by GC-MS according to the previous procedures described earlier.

- *Studying the risk of phthalate esters transfer from printing inks during winding the printed film*

In 1989, Castle *et.al* investigated the possibility of phthalates transfer from the outer printed surface of the films into the unprinted inner surface that would be in direct food contact and therefore might be considered as a contamination risk. In their study, a laboratory printing system has been used that did not present in an actual industrial process. The results showed that some migration might have occurred. In the present research, a commercial printing line used for flexible polyethylene terephthalate film was investigated. After each stage of printing, the film sample was passed (180m/min) from the oven drying step that was accomplished in a set of hot chambers (eight tunnel driers). Each chamber (length: 2m) worked at temperature of 75-80°C with

air velocity of 3800-4000 m³/h and finally was wound around a storage reel. In order to compensate the possible defects of the heating/drying process in curing the printing ink, a hybrid drying process (Park & Rhee, 2010) was accomplished by using an auxiliary IR-drying process as the final stage after the usual oven drying. A digital infrared oven (ASP Co., Iran) was used which operates at 220V and is composed of two IR lamps ($\lambda=1.2-1.8 \mu\text{m}$) with maximum capacity of 1500W. The distances between the lamps and the film and lamps were adjusted at 7.6 cm and 10 cm, respectively. The film sample was heated for 15 seconds. Three following samples were prepared for investigation:

- **Control:** The original/unprinted polyethylene terephthalate (PET) film
- **Treatment 1:** The unprinted PET film directly kept in contact with the printed side of the printed/oven dried PET film. The two layers were kept in touch under pressure for several days in order to provide conditions for set-off migration (Siegwerk, 2015).
- **Treatment 2:** The unprinted PET film directly kept in contact with the printed side of the printed / oven and IR- dried PET film. The two layers were kept in touch under pressure as explained for treatment1.

Results and Discussion

- Method Validation of GC/MS Analysis

Different parameters of each standard are given in Table3. All calibration curves showed good linearity between different concentrations. The calibration plots revealed good correlation between the response and the standards concentrations, and the regression coefficients were higher than 0.980. Limit of detection (LOD) and limit of quantification (LOQ) were found to be within the range of 0.06–0.11mg/l and 0.19-0.36mg/l, respectively, which indicated that the accomplished method for analysis of the phthalates has good sensibility. The recoveries were in the range of 92-115%.

The concentrations of different identified phthalates in each type of the flexible film samples are presented in Table 4.

The results given in Tables 4 revealed that the phthalate compounds were existed in all types of the plain (unprinted) polyolefin films (code no: 8, 11, 15 and 16). Generally, the polyolefins such as polyethylene and polypropylene do not require any plasticizer like phthalates (Mark, 2014). Therefore, the origin of these compounds may be either the result of contamination during passing the processing line or the polymer production process. The results of analyzing the critical points of the processing line are shown in Table 5.

Table 3. Analytical Parameters of the standard compounds

Analyte	Concentration range (ppm)	Calibration equation	R ²	LOD (ppm)	LOQ (ppm)	RSD (%)	Average Recovery (%)
A	2-30	$Y = 6.99e^{0.005}x + 4.83e^{0.005}$	0.989	0.08	0.25	2.1	92
	0.05-0.5	$Y = 1.45e^{0.006}x + 4.47e^{0.004}$	0.994				
B	2-150	$Y = 1.09e^{0.005}x + 1.88e^{0.005}$	0.997	0.11	0.36	5.2	115.6
	0.05-0.5	$Y = 2.36e^{0.005}x + 8.62e^{0.003}$	0.989				
C	2-150	$Y = 1.07e^{0.005}x + 3.02e^{0.005}$	0.991	0.06	0.19	1.7	96
	0.05-0.5	$Y = 3.25e^{0.005}x + 4.71e^{0.003}$	0.997				
D	2-150	$Y = 1.54e^{0.005}x + 4.44e^{0.005}$	0.990	0.07	0.21	1.3	97
	0.05-0.5	$Y = 4.39e^{0.005}x + 3.36e^{0.004}$	0.996				

A: Dibutyl Phthalate, **B:** Benzyl Butyl Phthalate, **C:** Bis(2-Ethyl Hexyl) Adipate, **D:** Diisooctyl Phthalate

Table 4. Phthalate Compounds Concentrations (ppm) in the Flexible Packaging Film samples

Sample Code no.	Film Samples	Sample weight(g)	Phthalate Compounds concentration (ppm)			
			Dibutyl Phthalate	Benzyl Butyl Phthalate	Bis(2-EthylHexyl) Adipate	Diisooctyl Phthalate
1	PET	0.091	1.69	2.95	2.15	21.53
2	Printed PET	0.108	16.40	3.11	2.35	53.47
3	Printed PET/Metallized PET	0.214	17.56	5.99	4.25	74.81
4	Metallized PET	0.069	1.64	2.94	2.17	21.73
5	Printed PET/Metallized PET /LDPE	0.531	19.30	9.09	6.75	78.21
6	Printed PET/Metallized PET	0.280	7.57	3.13	2.27	4.42
7	Printed PET/Metallized PET/LDPE	0.658	10.53	3.20	2.26	6.38
8	Polypropylene(PP)	0.154	1.66	3.21	2.17	2.39
9	Metallized PP	0.119	1.63	3.22	2.16	2.37
10	Printed Metallized PP/PP	0.300	47.25	3.40	2.40	93.80
11	Pearlized PP	0.160	1.64	3.13	2.16	2.40
12	Printed Pearlized PP	0.305	5.44	3.30	2.42	120.99
13	Printed PET	0.121	12.66	3.03	2.22	27.79
14	Printed PP	0.325	26.41	3.35	2.25	112.72
15	PP	0.295	1.82	3.10	2.16	2.69
16	LDPE	0.234	2.05	3.02	2.55	3.35
17	PET	0.109	3.15	5.85	4.30	4.40
18	AL Foil	0.121	1.58	2.93	2.16	2.30
19	Printed PET/Metallized PET/LDPE	0.693	5.51	3.22	3.30	5.57
20	Printed PET/Metallized PET/LDPE	0.726	3.29	2.95	2.28	6.73

According to the results given in Table 5, no serious contaminating point was found in the laminating and printing rolls. A very small amount of phthalate contamination might be due to the released phthalates from the ester lubricants (Mortier & Orszulik, 1995). These results proved that the plain (unprinted) polyolefin films might not be contaminated during passing through the processing line. Thus, the second origin, the polymer production process should be considered. It is well known that the fourth generations of the Ziegler- Natta (Z-N) catalysts used in the polyolefins polymerization process are prepared from a pre-catalyst mixture containing an internal electron donor which is often a phthalate (Chadwick, 2009; Shamiri *et al.*, 2014; Borealis Group, 2016). Progress towards

non-phthalate donors in Z-N systems, addressing REACH concerns, continues quickly (TCGR, 2017). Some types of these catalysts have been introduced but still not globally commercialized. Therefore the risk of the phthalate- containing catalysts which may be entered in the final polyolefin films should be analytically controlled and compared to the legally established limits. All of the phthalate esters analyzed in the current research are grouped in the REACH SVHC list and considered as high risk compounds. On the other hand, according to the forum established by ECHA (European Chemical Agency) in March 2016, the concentration of the specified phthalates including DIOP, DEHP, DBP and BBP in plastic articles may not exceeded the restricted limit of 0.1% by weight of the

plasticized material. The phthalate concentrations based on the weight percentage of the plastic film samples are given in Table 6. As it may be observed, the phthalate esters concentrations in all of the tested films (Table 6), were far below the established concentration limit (0.1%) and it may be concluded that these plastic films may be safe even if used as a directly food contact internal layer of the laminated packaging materials.

In addition to the polyolefin (PE & PP) film samples, the plain PET films have also shown phthalate existence (code numbers: 1, 4 and 17). It has been previously confirmed that migration of different types of phthalate compounds from the PET containers into food products especially mineral water may be possible (Montuori *et al.*, 2008). These phthalic compounds may be originated from isophthalic acid which is used as the main

co-monomer in polyethylene terephthalate preparation process in order to improve its thermal, mechanical and gas barrier properties (Mohan *et al.*, 2012). However, the amount of each phthalic compound in the analyzed film samples (1, 4 and 17) was not higher than the above mentioned limit (i.e 0.1%) but the total concentration level was near this limit, approximately 0.08 % for sample 4 (Table 6). The results given in Table 4 showed that the phthalates concentrations in the printed flexible films were several times higher than the unprinted films. This increasing pattern is more obviously observable for diisooctyl phthalate and dibutyl phthalate (DBP) by performing a pairwise comparison of the following samples: (1, 2), (1, 5), (8, 10), (11, 12), (14, 15). Therefore the main risk source concerning the phthalates is the printing

Table 5. Phthalate compounds concentrations (ppm) in paper samples passed through the processing line

Paper Samples	Sample Weight (gr)	Phthalate Compounds ¹			
		Dibutyl Phthalate	Benzyl Butyl Phthalate	Bis (2-Ethylhexyl) Adipate	Diisooctyl Phthalate
Control	0.518	-	-	-	-
Laminating Rolls	0.518	0.09 (0.0003)	-	-	-
Printing Rolls	0.526	0.05 (0.0002)	-	-	-
Printing ink pans					
Yellow	1.007	122.850 (0.383)	0.101 (0.0003)	0.260 (0.0005)	26.886 (0.084)
Red	1.175	403.025 (1.259)	-	-	344.275 (1.075)
Black	0.938	496.202 (1.551)	0.094 (0.0002)	0.188 (0.0005)	571.242 (1.785)

¹Values in the parenthesis are based on mg/dm²

Table 6. Phthalate compounds concentrations based on the weight percentage of the plasticized films

Sample Code no.	Film Samples	Sample Weight (g)	Phthalate Compounds Concentrations (% , by weight of the plasticized film)			
			Dibutyl Phthalate	Benzyl Butyl Phthalate	Bis(2-EthylHexyl) Adipate	Diisooctyl Phthalate
1	PET	0.091	0.0037	0.0065	0.0047	0.0473
4	Metallized PET	0.069	0.0048	0.0085	0.0057	0.0630
8	Polypropylene(PP)	0.154	0.0021	0.0042	0.0028	0.0031
11	Pearlized PP	0.160	0.0021	0.0039	0.0027	0.0030
15	PP	0.295	0.0012	0.0021	0.0015	0.0018
16	LDPE	0.234	0.0021	0.0026	0.0022	0.0029
17	PET	0.109	0.0058	0.0107	0.0080	0.0081

process especially the printing inks. For making better decision about the risk level, two regulatory factors may be considered: specific migration limit (SML) for each type of phthalate compound and total specific migration limit (SML (T)) (European Commission, 2013). Based on the results given in Table 4 and equation 2, the maximum possible migration of dibutyl phthalate (DIOP) (mg/Kg) and total amount of migrated phthalates from different film samples were calculated and reported in Figure 1. According to the data given in Figure 1, the total amounts of the migrated phthalic acid ester compounds from the most of the printed film samples were higher than the established limit. Since the role of printing rolls and also the possibility of set-off migration were previously checked, it may be concluded that the main origin for phthalate esters in the Iranian laminated flexible films are the printing inks. Phthalates are used as plasticizer in the formulation of the printing inks for plastic films in order to improve ink flexibility, provide better adhesion to polymeric substrate and also to stabilize the nitrocellulose in order to deactivate the hazardous properties of dry nitrocellulose. Generally, the printed film layer is laminated to the other polymeric substrates and therefore it is believed that there is no risk of printing inks because no directly contact with the food product might happen. The alternative and somehow safer method is reverse printing, where the outermost layer is printed on the backside and then laminated to the rest of the multi-layer structure. However diffusion of additives including phthalates through the polymeric substrates has been previously investigated. Theoretical and semi-empirical models were developed and revealed that this migration may be possible especially from polymers with low crystalline structure into fatty food products at high temperatures (Jackson *et al.*, 1968; Limm & Hollifield, 1996;

Piergiovanni *et al.*, 1999). In addition leaching of additives from plastic films was reported that might be considered as another path to encounter the risk of phthalate contamination (Zhang & Chen, 2014). Therefore, in spite of the fact that the printed layer is not directly in contact with the food product but using safe/phthalate free printing inks is an inevitable necessity that should be noticed by the food packaging manufacturers.

Conclusion

The risk of phthalate esters is a rising concern worldwide and most of the countries are taking legislative actions to limit or prohibit their usage in different applications. Concerning the main distinguished roots for phthalate esters in the analyzed flexible films, it may be concluded that the best short term solution is the elimination of the phthalates from printing inks formulations. While, modifications of the polymerization processes of polyolefins and polyethylene terephthalate are time-consuming operations with large investments to be considered as medium term solutions.

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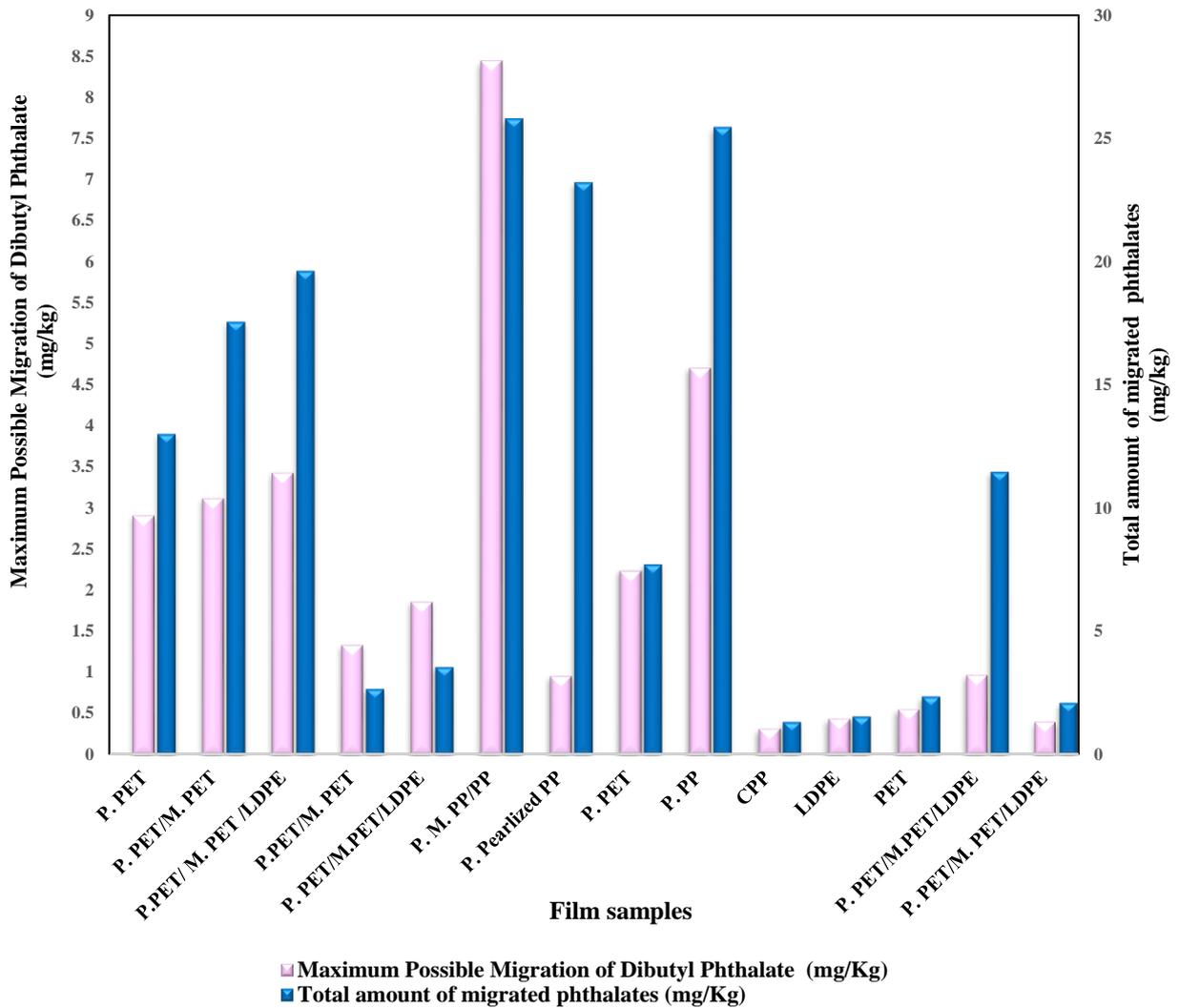


Fig. 1. Maximum possible migration of DIOP (mg/Kg) and total amount of migrated phthalates from different film samples¹

¹The established SML for DBP and SML (T) for phthalic acid esters are 0.3 mg/Kg and 9 mg/Kg respectively (European Commission; 2013).

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