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THE IMPACT OF STORAGE ON PHTHALIC ACID ESTERS CONCENTRATIONS IN YOGURTS PACKED IN PLASTIC CUPS

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Abstract

Phthalic acid esters are used as plastic softeners and also can be found in food packaging materials. European legislation defines specific migration limits of plastic additives for plastic materials that come into contact with food. This study monitors the phthalic acid ester concentrations in yogurts after manufacturing and then after a 3-week storage. The studied yoghurts were natural yogurt with 1 % of chia flour, natural yogurt with 5 % of chia flour, natural yogurt with 1 % of bamboo fibre, natural yogurt with 5 % of bamboo fibre and natural yogurt. The analysed phthalic acid esters were dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP). The average phthalate concentrations in plastic cups were detected for DBP of 59.5 μg/g and for DEHP of 9.0 μg/g of the plastic material. Higher DBP concentrations than DEHP concentrations were also found in all studied yogurts. The average DBP concentrations in yogurts were detected from 1.8 μg/g up to 5.0 μg/g of the original matter and the average DEHP concentrations were determined from 0.5 μg/g up to 1.0 μg/g of the original matter. No statistically significant difference was found when comparing phthalic acid ester concentrations in yogurts immediately after production and after three weeks of storage. However, in our study in all cases of yogurts, the DBP concentrations were higher than the specific migration limit set by the legislation (0.3 mg/kg) and the DEHP concentrations were in all cases of yogurts lower than the specific migration limit set by the legislation (1.5 mg/kg).

Keywords: DBP, DEHP, contaminant, migration, during storage, yogurt, dietary fibre

INTRODUCTION

Esters of phthalic acid are ubiquitous environmental contaminants due to high production and wide use as plasticizers of plastics. The two most widespread esters of phthalic acid are: dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) (Velíšek and Hajšlová, 2009).

Plastic wrapping for food packaging is widely used. The wraps and also plastic wraps have many functional properties, such as protection against microorganisms, preventing loss of flavour and water from food, etc., but there arises a risk that monomers, oligomers, as well as additives (for example plasticizers) migrate to food. The legislation regulates the amount and kind of migrated substances from wraps to food (Piotrowska, 2005).

Legislative regulation, which deal with plastic food contact materials, is the Commission Regulation (EU) No 10/2011. Specific migration limits (SML) are set for DBP 0.3 mg/kg of food and for DEHP 1.5 mg/kg of food. The term „specific migration limit" means the maximum permitted amount of release substances from a plastic material to a food, this quantity should not pose a health risk for consumers (European Union, 2011).

The human exposure of phthalic acid esters is not only oral intake, for example from packaged food, but also through inhalation, dermal intake and intravenously (from medical tubes and storage bags) (Benson, 2014). The largest of human exposure to phthalates is probably with contaminated food. Maximum daily dietary intake is estimated for dibutyl phthalate 0.48 μg/kg/day, for di-(2-ethylhexyl) phthalate 4.9–18 μg/kg/day (Schettler, 2006). European tolerated daily intake (TDI) is set for dibutyl phthalate 10 μg/kg/day and for di-(2-ethylhexyl) phthalate 50 μg/kg/day (Hines, *et al.*, 2011).

The phthalates cause a negative effect on the respiratory, reproductive, endocrine and digestive systems. And they are also potential carcinogens (Pilka *et al.*, 2012). Experiments on animals exposed to di-(2-ethylhexyl) phthalate are found in males the disrupted development of the reproductive system, reduction of spermatogenesis and reduction in the weight of the androgen-dependent tissue organs (Dalsenter *et al.*, 2006).

MATERIALS AND METHODS

The raw materials for yogurt production were purchased in the Czech Republic, yogurts were produced at the Mendel University in the Department of Food Technology. The milk composition was determined lactose of 4.50%, protein of 3.42%, fat by 3.50%. The milk was first pasteurised (85 °C/5 min), cooled to 36 °C and inoculated with a starter culture of the original Bulgarican yoghurt. The fermentation was carried out for 18 hours at 36 °C. After fermentation, the yoghurt was homogenized and split into groups: the first group was yoghurt with chia flour in the amount of 1% by weight, the second group was yoghurt with chia flour in the amount of 5% by weight, the third group was yoghurt with bamboo fiber in the amount of 1% by weight, the fourth group was yoghurt with bamboo fiber in the amount of 5% by weight and the fifth group was natural yoghurt. All groups of yogurt were stored at 4 °C.

Two esters of phthalic acid, dibutyl phthalate and di-(2-ethylhexyl) phthalate, were detected. The analyses were performed in yoghurt immediately after manufacture of yoghurt and after three weeks of storage. The new, clean cups, which were used for yoghurt, were also analyzed. Samples of yoghurts and plastic cups were analyzed at six repeats. Analyses were carried out at Mendel University at the Department of Food Technology in the chemical laboratory.

Analyses of plastic cups were performed according to the method by (Gajdůšková *et al.*, 1996), and yogurts analyzes were made according to the method by (Jarošová *et al.*, 1999). The method used to analyze phthalic acid esters in yoghurt is based on the determination of phthalic acid esters in the extracted fat of food. Samples were measured by HPLC with UV detection (wavelength 224 nm), concentrations were determined by software Agilent Chemstation for LC and LC/MS systems. Further processing was done using Microsoft Excel and Statistica 12.

The normality was established by Shapiro Wilk's test. The pair t-test for comparison of phthalic acid esters mean values in week 0 and in week 3 was carried. Furthermore, F-test and subsequently, unpaired t-test was carried out. The unpaired t-test compared the phthalic acid esters mean values in natural yogurt with phthalic acid esters mean values in yogurts with fibres during the same measurement weeks. The significance level was used 0.05.

RESULTS

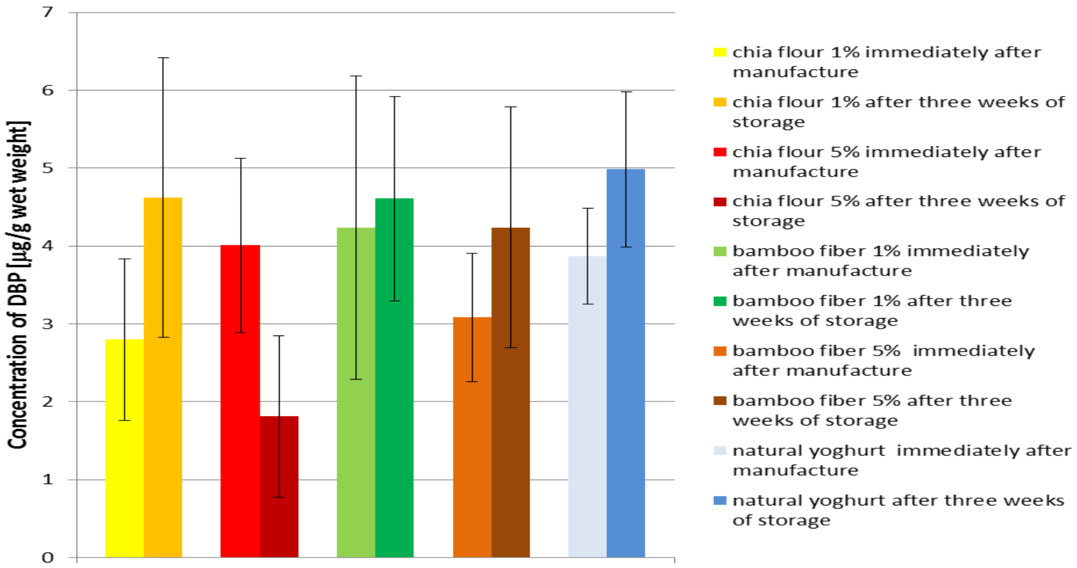
The concentrations of two phthalic acid esters in plastic yogurt cups are listed in Tab. I.

In the case of DBP, the average concentrations in yogurts ranged in total from 1.8 µg/g to 5.0 µg/g of the original matter, from 2.8 µg/g to 4.2 µg/g of the original matter in the case of DBP immediately after manufacture and from 1.8 µg/g to 5.0 µg/g of the original matter in the case of DBP in week 3. In the case of DEHP, the total average concentrations ranged from 0.5 µg/g to 1.0 µg/g of the original matter, from 0.5 µg/g to 1.0 µg/g of the original matter immediately after manufacture and the DEHP concentrations ranged from 0.7 µg/g to 1.0 µg/g of the original matter in week 3 (Fig. 1 and 2).

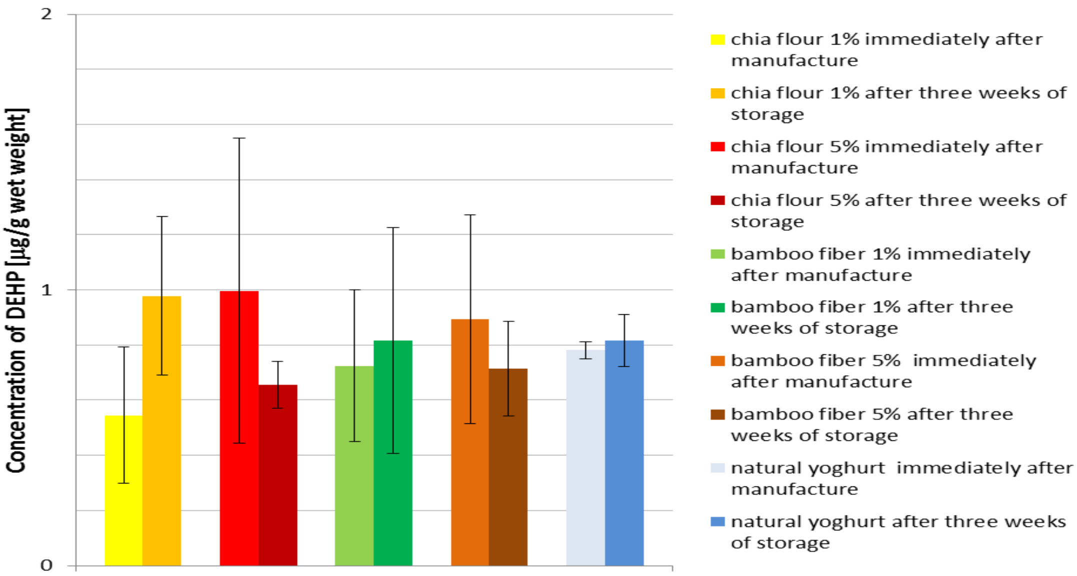
In our study the limit of detection (LOD) was for DBP of 0.11 µg/ml and for DEHP of 0.05 µg/ml and a limit of determination (LOQ) was for DBP of 0.37 µg/ml and for DEHP of 0.17 µg/ml.

I: *Concentrations of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in plastic cups for yoghurt (n=6)*

DBP [µg/g]	DBP [µg/dm²]	DEHP [µg/g]	DEHP [µg/dm²]
59.5 ± 31.7	152.2 ± 80.5	9.0 ± 3.5	23.0 ± 9.0



1: *Concentration of dibutyl phthalate in yoghurts*



2: *Concentration of di-(2-ethylhexyl) phthalate in yoghurts*

The pair t-test showed no statistic difference ($p > 0.05$). Following the F-test, an unpaired t-test was used for comparing equal dispersion. It was showed no statistic difference ($p > 0.05$). Based on the results of the statistical tests, the three-week storage of yoghurts in plastic cups did not affect the change in phthalic acid ester concentrations, so there was no migration of phthalic acid esters from plastic cups to yoghurts.

DISCUSSION

The concentrations of phthalic acid esters determined immediately after production were different for the studied yogurt types. The differences were probably due to the variously contaminated feedstock, whether it was chia or bamboo fiber. Alternatively, contamination could occur during production and filling.

All determined concentrations of dibutyl phthalate in yoghurts, immediately after production and after three weeks of storage, exceeded the specific migration limit given by the legislation (0.3 mg/kg). While the concentrations of di-(2-ethylhexyl) phthalate in yoghurts determined immediately after production and after three weeks of storage were lower than the specific migration limit set by the legislation (1.5 mg/kg).

It can be said from the statistical results that the storage had no effect on the change in phthalic acid ester concentrations and the phthalic acid esters did not migrate during the storage time from the plastic cups into the yoghurts.

In the study (Rastkari *et al.*, 2017) was examined the migration of phthalic acid esters – dibutyl phthalate and di-(2-ethylhexyl) phthalate too – from wrapping to acidic liquids – vinegar, lemon juice, verjuice. The phthalate concentrations in acidic liquids with longer storage time increased.

In the study (Lin *et al.*, 2015) were established concentrations of phthalic acid esters in whole milk products. Higher concentrations of phthalic acid esters were found in whole milk packaged in plastic packaging than in glass or metal containers. In the study was also pointed to the fact that phthalates can be absorbed in solid milk components.

In the study (Jia *et al.*, 2014) were researched esters of phthalic acid, which were the most commonly used plasticizer. They were detected in yoghurts, milk drinks and milk. Almost in all samples was detected di-(2-ethylhexyl) phthalate, the concentrations were ranged from 1 to 936 μg/kg.

In the study (Fasano *et al.*, 2012) were detected phthalate esters (DBP and DEHP) under limit of detection in yogurt wrappers, but the yogurt wrappers were made from high density polyethylene (HDPE), in our study was made from polystyrene (PS). In the same study was determined too phthalates in polystyrene material, it was polystyrene dish. The polystyrene dish contained DBP under LOD and DEHP from 0.323 to 1.239 μg/L.

CONCLUSION

The phthalic acid ester concentrations in cups, which were used for yogurts, were for dibutyl phthalate of 59.5 ± 31.7 μg/g plastic and for di-(2-ethylhexyl) phthalate of 9.0 ± 3.5 μg/g plastic.

The detected concentrations of dibutyl phthalate in yoghurts in our study, immediately after production and after three weeks of storage, exceeded the specific migration limit given by the legislation (0.3 mg/kg). And the detected concentrations of di-(2-ethylhexyl) phthalate in yoghurts immediately after production and after three weeks of storage were lower than the specific migration limit set by the legislation (1.5 mg/kg).

In our study was found that the 3 weeks of storage had no effect on the change in phthalic acid ester concentrations and the phthalic acid esters did not migrate during the 3 weeks of storage from the plastic cups into the yoghurts.

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REFERENCES

BENSON, R. W. 2014. Hazards of Food Contact Material: Phthalates. In: YASMINE, M., MOY, G. and TODD, E. (Eds.). *Encyclopedia of Food Safety.* San Diego: Elsevier.

DALSENTER, P. R., SANTANA, G. M., GRANDE, S. W. *et al.* 2006. Phthalate affect the reproductive function and sexual behavior of male Wistar rats. *Human & Experimental Toxicology,* 25(6): 297–303.

EUROPEAN UNION. 2011. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*, L12: 1–89.

FASANO, E., BONO-BLAY, F., CIRILLO, T. *et al.* 2012. Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control,* 27(1): 132–138.

GAJDŮŠKOVÁ, V., JAROŠOVÁ, A. and ULRICH, R. 1996. Occurrence of phthalic acid esters in food packaging materials. *Potravinářské Vědy*, 14(2): 99–108.

HINES, C. J., HOPF, N. B. N., DEDDENS, J. A. *et al.* 2011. Estimated daily intake of phthalates in occupationally exposed groups. *Journal of Exposure Science & Environmental Epidemiology,* 21(2): 133–141.

JAROŠOVÁ, A., GAJDŮŠKOVÁ, V., RASZYK, J. *et al.* 1999. Di-2-ethylhexyl phthalate and di-n-butyl phthalate in the tissues of pigs and broiler chicks after their oral administration. *Veterinary medicine*, 44(3): 61–70.

JIA, W., CHU, X., LING, Y. *et al.* 2014. Analysis of phthalates in milk and milk products by liquid chromatography coupled to quadrupole Orbitrap high-resolution mass spectrometry. *Journal of Chromatography A,* 1362: 110–118.

LIN, J., CHEN, W., ZHU, H. *et al.* 2015. Determination of free and total phthalates in commercial whole milk products in different packaging materials by gas chromatography-mass spectrometry. *Journal of Dairy Science,* 98(12): 8278–8284.

PETERSEN, J. H. 2003. Migration of Compounds from Food Contact Materials and Articles. In: D'MELLO, J. P. F. (Ed.). *Food safety: contaminants and toxins*. Cambridge, MA: CABI Pub.

PILKA, T., KOLENA, B. and PETROVIČOVÁ, I. 2012. Anthropopathogenic effect of phthalates on human health [in Slovak: Antropopatogénny vplyv ftalátov na ľudské zdravie]. *Slovenská Antropológia.* 15(1): 45–52.

PIOTROWSKA, B. 2005. Toxic Components of Food Packaging Materials. In: DĄBROWSKI, W. M. and SIKORSKI, Z. E. (Eds.). *Toxins in Food.* Boca Raton, FL: CRC Press.

RASTKARI, N., JEDDI, M. Z., YUNESIAN, M. *et al.* 2017. The Effect of Storage Time, Temperature and Type of Packaging on Release of Phthalate Ester into Packed Acidic Juice. *Food Technology and Biotechnology*, 55(4): 562–569.

SCHETTLER, T. 2006. Human exposure to phthalates via consumer products. *International Journal of Andrology,* 29(1): 134–139.

VELÍŠEK, J. and HAJŠLOVÁ, J. 2009. *Food chemistry II* [in Czech: *Chemie potravin II*]. 3rd Edition. Tábor: OSSIS.

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