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POTENTIAL MIGRATION OF PHTHALATES FROM DIFFERENT POLYMERS INTO FOOD

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Abstract: *Plastic materials are commonly used for food packaging due to their excellent physical-mechanical, thermal, chemical, and barrier properties. They are also easy to process, can be combined with other materials, and are cost-effective. In order to improve flexibility, transparency, and durability, plasticizers such as phthalates can be added to the chemically stable polymers. The detection and determination of phthalates in articles of general use is crucial as they account for up to 50% of the mass and can easily migrate due to their physical and chemical properties. Exposure to phthalates can lead to various health problems, e.g. allergic diseases, asthma, thyroid dysfunction, fertility issues, endocrine disorders, and cardiovascular disease. There are several factors (temperature, ultraviolet radiation, ultrasound, mechanical forces, etc.) that influence the migration of phthalates. Thus, food products can be contaminated with phthalates by migration from plastic packaging. Therefore, it is important to investigate the migration of phthalates from plastic items and packaging into food. Packaging materials and packaging used in the food industry must be tested to ensure that they do not pose a health risk. The legal framework relating to these materials was created to ensure the safety of food that is consumed and sold.*
Keywords: Phthalates, migration, polymers, food

1. INTRODUCTION

Selecting the appropriate packaging material plays an important role in protecting the packaged product and ensuring its safety and quality. Polymers, which are commonly utilized as food packaging materials, are enhanced with a variety of additives including fillers, colors, plasticizers, softeners, and stabilizers. These additives are usually not chemically bonded to the structure of the basic macromolecular chain which may result in their potential migration into the package contents during transportation, handling, and storage.

Phthalates are a group of semi-volatile organic compounds and most commonly used plasticizers worldwide due to their wide range of industrial applications. [1]. Certain ortho-phthalates, including Di(2-ethylhexyl)phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diisobutyl phthalate (DIBP), may interfere with our hormonal system and are on the candidate list of substances of concern.

These phthalates are extensively used as a plasticizer in many products, especially medical devices, furniture materials, cosmetics, and personal care products, building materials, household furnishings, clothing, cosmetics, pharmaceuticals, nutritional supplements, medical devices, children's toys, glows, modelling clay, food packaging, furnitures, automobiles, lubricants, waxes, cleaning materials and insecticides [2].

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Polymeric (plastic) materials that come into contact with food products can be a potential source of phthalates in food. Therefore it is necessary to examine the health safety of packaging materials and packaging, which is carried out by specialized and authorized institutions and laboratories.

2. POLYMER FOOD PACKAGING

The role of packaging is to protect the product from physical and mechanical factors and external environmental conditions (light, gases, moisture and microorganisms), communicates with the consumer, and serves as a good marketing tool. Food packaging that comes into direct contact with food must be made of a material that does not impair the organoleptic, chemical, and physical properties of the food and must not contain or release any substances that are harmful to health over the quantities specified in the regulation [3]. Polymer packaging accounts for the largest proportion of food packaging, and generally is not harmful to human health. However, some additives found in polymer-based packaging can be harmful if they migrate into food causing adverse effects.
During the production of food packaging, plasticizers are added to serve as softeners and color carriers. Since they have a relatively low molecular weight and are not covalently bound to the polymer, they can potentially migrate from the packaging material into the food and thus become indirect "food additives" [4]. Many additives, solvents, and pigments used in the production of plastic packaging materials are also found in the food product [5], and many can be converted into toxic metabolites, most of which are difficult to identify.
Examples of potentially toxic substances (PoTS) that have been studied for their possible migration from various plastic packaging include phthalates, bisphenol A (BPA), bisphenol A dimethacrylate, lead, tin, and cadmium, as well as formaldehyde and acetaldehyde, 4-nonylphenol, MTBE (methyl tert-butyl ether), benzene, and many other volatile organic compounds [6,7,8,9,10].

3. PHTHALATES IN PLASTIC MATERIALS

Polymers can be transformed into polymer (plastic) materials by adding plasticizers such as phthalates, citrates, and phosphates. Diesters of 1,2-benzenedicarboxylic acid (phthalic acids), better known as phthalates, are widely used as plasticizers, solvents and additives in the manufacture of plastics [1]. They are commonly used to increase the flexibility, durability, elasticity, and transparency of plastics. For example, rigid polyvinyl chloride (PVC) can be transformed into a wide range of flexible materials and processed more easily by adding plasticizers such as phthalates (up to 40 % w/w), citrates, and phosphates. In addition, phthalates can be used in a variety of general-use products such as toys, personal care and household products, electronics, various solvents, adhesives, glues, pesticides, food packaging, medical devices, pipes, and building materials. Due to their non-polarity, phthalates have a low solubility in water, but dissolve well in a non-polar medium and have a high solubility in oil.
Although phthalates are usually used in the manufacturing of PVC, they are also used as part of the catalyst (Ziegler-Natta catalyst) during the polymerization process of polypropylene (PP), polyethylene (PE), and polystyrene (PS) [11]. Therefore, they have also been found in food packaging materials that are not made of PVC [12].

4. POTENTIAL MIGRATION OF PHTHALATE FROM POLYMERS INTO FOOD

Migration is the transfer of potentially harmful substances from the packaging material and packaging into the food. The legislation on plastic packaging materials that come into contact with food ("food-contact" legislation) has defined two types of migration: specific and general migration. Specific migration refers to the migration of substances that are present even in low concentrations can pose a risk to consumer health and therefore require strict control. General migration refers to the migration of components that do not pose a major risk to consumer health but are still undesirable. Since phthalate are not chemically bound to the macromolecular chain, but are merely attached to the polymer structure, they can leach, evaporate, or migrate from the plastic packaging into the

environment. Various factors influence the migration of phthalates, e.g. temperature, ultraviolet radiation, ultrasound, mechanical forces, or contact with a non-polar environment. It is very important to be aware of these factors and handle plastic products and packaging with care to prevent phthalate migration.

According to the European Union Directive [13], FCM suppliers are required to demonstrate that their materials comply with the relevant limits (EUROPEAN UNION, 2002), which are defined by the following values: Overall Migration Limit (OML), Specific Migration Limit (SML) and Maximum Permitted Quantity (QM). Several studies have shown that phthalates migrate from plastic packaging mainly into fatty foods such as oil, milk, butter, meat, fish, etc. [14]. Food in plastic packaging heated or cooked in a microwave oven is also a source of phthalates, and it was reported that phthalates easily migrate into fatty foods under high temperatures [15]. Monitoring of potential contamination of milk and dairy products with phthalates is important as milk is the main food source for children [16]. It has already been reported that cow's milk can be contaminated by the plastic utensils used in processing. In addition, human milk can also be contaminated with phthalates through the use of breast pumps [17].

The investigation of phthalates in alcoholic beverages revealed a negligible migration of phthalates from plastic packaging into alcoholic beverages. The detected phthalate concentrations were low, although most of the samples in this analysis were packaged in plastic bottles [18]. The study carried out by Del Carlo et al. also showed that the increased phthalate concentration in alcohols is not due to the interaction between plastic packaging and alcoholic beverages, but to the migration of phthalates during the technological process [19]. When comparing the results of phthalate concentration in plum brandy bottled in glass and plastic packaging, it was found that there is no migration of phthalates from plastic packaging into alcoholic beverages, as there is no significant difference in phthalate concentration between brandy in different packaging [20]. On the other hand study with showed extremely high migration of phthalates (350%) in olive oil, from the sealing material of closures [21].

Generally, it is recommended to avoid heating of food in plastic packaging in the microwave as well as washing the plastic material in the dishwasher. It is suggests to use glass packaging as far as possible, and to check the composition of the plastic on the product declaration.

Phthalates in food, beverages, and other products are analyzed using various analytical methods, including liquid and gas chromatography with mass spectrometers or UV spectrophotometers. The most important method for determining phthalates is gas chromatography-mass spectrometry (GC-MS) [16]. However, Fourier transform infrared spectroscopy (FTIR) is also used.

5. TOXIC EFFECT OF PHTHALATES

The annual production of phthalates in 2009 and 2010 was about 230,000 tons per year, of which 210,000 tons were DEHP [22]. Humans are frequently exposed to phthalates, which can enter the human body through the skin, by inhalation, or through food. Due to their lipophilic nature, fatty foods in particular are contaminated with phthalates. When phthalates enter the body, they are rapidly metabolized and excreted in urine and feces. Their half-life is short, and more than 60 % are excreted within 24 hours, the rest in less than 48 hours [23]. However, endocrine-disrupting chemicals (EDCs) which include phthalates can interfere with the synthesis, secretion, mechanism of action, metabolism, and excretion of hormones in humans and animals, with adverse health consequences, including the occurrence of obesity and diabetes mellitus [24, 25].

According to the World Health Organization, individuals can be exposed to phthalates through the daily use of common plastic items. A growing number of studies are investigating the health effects of exposure to phthalates, which have been linked to various conditions such as allergic diseases, asthma, cancer, thyroid dysfunction, fertility issues, endocrine disorders, and cardiovascular disease [26, 27]. Phthalate exposure is associated with cardiovascular risk factors including obesity, lipid metabolism, blood pressure, and atherosclerosis [28]. During the prenatal period, in newborns, and during puberty, human sensitivity is at its highest level. Due to this reason, the European Union has

imposed restrictions on the use of some phthalates in children's toys and products intended for children. The results of the exposure assessment indicate that children are exposed to higher levels of phthalates compared to adults. Based on the latest data from human biomonitoring, it has been established that the intake level considered safe is exceeded in children. In some cases, the excess is up to 20 times the safe level. Due to their chemical properties, exposure to phthalates does not lead to bioaccumulation. However, there are health concerns regarding the developmental and/or reproductive toxicity of phthalates, even at environmental concentrations [29].

6. LEGAL REGULATION

In order to protect public health, various legislative bodies have been established to prohibit or regulate the use of harmful substances. European Union legislation, better known as the REACH Directive [30] (Registration, Evaluation, Authorization and Restriction of Chemicals), created the European Chemicals Agency (ECHA). In 1963, the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) jointly established the Codex Alimentarius Commission (CAC), which is commonly known as Codex and deals with international food standards. The RAPEX system (Rapid Alert System for Non-Food Products) was also established in the European Union to quickly alert authorities and consumers about dangerous non-food products. According to EU regulations, the maximum migration limit for all contaminants from plastics into food is 60 mg/kg of food or 10 mg/dm² of the surface of the food contact material [31]. The specific migration limit is determined individually for each phthalate. Commission Regulation (EU) No 10/2011 establishes specific migration limits (SMLs) for individual phthalates and a limit for a group of phthalates (SML(T)) . The SML values for DnBP, DEHP, and BBP are 0.3, 1.5, and 30 mg/kg of food respectively. Meanwhile, the SML(T) value for the group of phthalates is 60 mg/kg of food [32].

In the Republic of Serbia, there are the National Consumer Organisation of Serbia (NCOS), the Sanitary Border Inspection, and the Public Health Laboratories. The Institute for Standardization of Serbia is the leading authority for the Codex Alimentarius. It is responsible for harmonizing food safety standards and regulations between the EU and Serbia, taking into consideration the differences in tradition and culture. The regulation on health and safety conditions of items of general use that can be placed on the market [33] specifies that synthetic materials used for making tableware and accessories, which come in direct contact with drinking water, milk, milk products, waxed food, foods that contain essential oils, alcoholic beverages, fats, oils, or foods whose outer phase consists of fat, must not contain plasticizers, unless a special regulation expressly stipulates otherwise.

The list of restrictions and prohibitions includes regulations on the production, marketing, and usage of certain hazardous substances, mixtures, or products [34]. Specifically, the list restricts and prohibits the use of phthalates and imposes a limit of 0.1% by weight of the plasticized material in toys and childcare products. Bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diisobutyl phthalate (DIBP) can cause damage to growth hormones and development, and lead to heart disease and obesity.

7. CONCLUSION

Migration is the transfer of potentially harmful substances from the packaging into the food. One of the main sources of phthalates is food packaged in plastic material, especially fatty foods such as oil, milk, butter, meat, fish, etc. Food products can be contaminated with phthalates through migration from polymers and during food processing from production facilities, but also during food storage. Monitoring the contamination of milk and dairy products is of utmost interest as milk is the main food source for children.

According to the legislation, the overall limit for the migration of all contaminants from plastics into food is 60 mg kg^{-1} of food or 10 mg dm^{-2} of the surface of the food contact material. In the EU, the specific migration limit (SML) for the group of phthalates is 60 mg kg^{-1} of food.

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