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The emissions of monoaromatic hydrocarbons from small polymeric toys placed in chocolate food products

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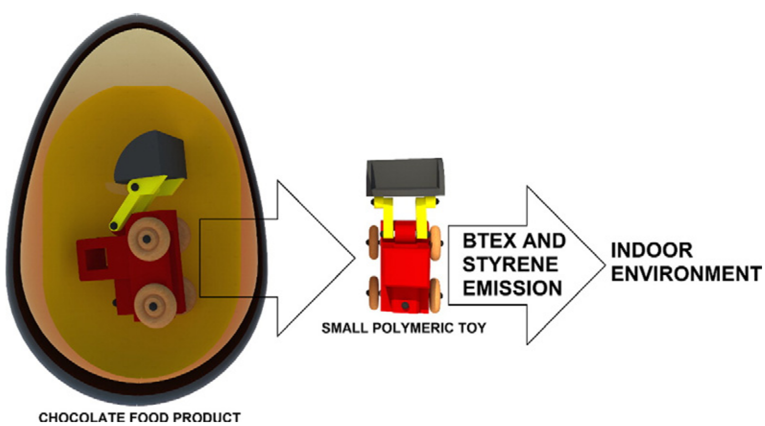
HIGHLIGHTS

- The main type of polymer material used to produce studied toys was determined.
- The microscale stationary emission chamber, μ-CTE™ 250, was presented.
- The emission rate of BTEX and styrene from polymeric toys was studied.
- The differences between emission from polyamide and ABS copolymer toys were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

The article presents findings on the emissions of selected monoaromatic hydrocarbons from children's toys placed in chocolate food products. The emission test system involved the application of a new type of microscale stationary emission chamber, μ-CTE™ 250. In order to determine the type of the applied polymer in the manufacture of the tested toys, Fourier transform infrared spectroscopy and thermogravimetric analysis coupled with differential scanning calorimetry were used. It was found that the tested toy components or the whole toys (figurines) are made of two main types of polymers: polyamide and acrylonitrile–butadiene–styrene copolymer. Total number of studied small polymeric toys was 52. The average emissions of selected monoaromatic hydrocarbons from studied toys made of polyamide were as follows: benzene: 0.45 ± 0.33 ng/g; toluene: 3.3 ± 2.6 ng/g; ethylbenzene: 1.4 ± 1.4 ng/g; p,m-xylene: 2.5 ± 4.5 ng/g; and styrene: 8.2 ± 9.9 ng/g. In the case of studied toys made of acrylonitrile–butadiene–styrene copolymer the average emissions of benzene, toluene, ethylbeznene, p,m-xylene and styrene were: 0.31 ± 0.29 ng/g; 2.5 ± 1.4 ng/g; 4.6 ± 8.9 ng/g; 1.4 ± 1.1 ng/g; and 36 ± 44 ng/g, respectively.

1. Introduction

According to the literature data a wide range of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) can

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be emitted into the indoor environment from various types of equipment elements made of various plastics (Vilaplana et al., 2010). These include: carpet products made of flexible PVC (Lundgren et al., 1999; Wilke et al., 2004), PVC-coated wallpapers (Lim et al., 2014), kitchen utensils (dishes, cups, spoons, forks) (Abe et al., 2014), and covers of electronic devices (TVs, computers, washing machines, etc.) (Jian et al., 2014). Specific groups of products made of plastics, in terms of the type of consumers, and used in residential environments, are children's toys (Noguerol-Cal et al., 2011). As the basic substances in children's toy production various kinds of plastics are applied, such as polypropylene (PP), low or high density polyethylene (LDPE or HDPE), polystyrene (PS), polyamide (PA), and acrylonitrile–butadiene–styrene copolymer (ABS) (Godoi et al., 2011; Abe et al., 2013). The final product, which is a children's toy, is very often made of a single type of polymer, but it may be a product composed of various types of polymers and additives for improving the esthetic and functional advantages, for example fillers, coloring agents (pigments, dyes), and plasticizers. Due to the fact that these products are intended for use by children, and in some cases may come into contact with food, European legislation in the Directive 2009/48/EC describes in detail the requirements and criteria to be met by such products introduced in the market (Noguerol-Cal et al., 2011; Directive, 2009/48/CE).

Due to the dynamic development of related industries connected with the production and distribution of children's toys made of plastics, there is a reasonable necessity to conduct research aimed at evaluating the quality of manufactured products and to obtain analytical information about the type and amount of VOCs emitted from children's toys. According to existing literature, the presence of VOCs in children's toys results from the occurrence of unreacted monomers (1,3-butadiene, styrene, acrylonitrile) and solvents (their purity) used in the polymer production e.g. toluene, ethylbenzene, isopropylbenzene, propylbenzene (Abe et al., 2013, 2014).

In order to determine the type and quantity of chemicals from the VOC group released from the surface of polymeric materials (including children's toys), various types of analytical tools are used, which include the following techniques and equipment: headspace gas chromatograph/mass spectrometry (HS-GC/MS) (Bart, 2001), headspace-solid phase microextraction-gas chromatography coupled with mass spectrometry (HS-SPME-GC/MS) (Masuck et al., 2010; Lattuati-Derieux et al., 2013), direct thermal desorption/gas chromatography/mass spectrometry (TD–GC–MS) (Mitchell et al., 2014) and stationary environmental (small- or large-scale) emission test chambers (ETCs) (Marć et al., 2012). Depending on the analytical tool used, it is possible to determine the content/emission of a single compound or/and the total content/total emission of all organic compounds (as a TVOC parameter) from a fragment or the full surface of the tested object (Yu and Crump, 1998; Boor et al., 2014).

The article presents findings on the emission of BTEX [ng/g of sample] (benzene, toluene, ethylbenzene and total xylenes) and styrene from the surface of small polymeric children's toys placed in chocolate food products available on the Polish market. For this purpose, a microscale stationary emission chamber, μ-CTE™ 250, was used to release and sample analytes. In order to determine the main type of polymer from which the tested toys were produced, Fourier transform infrared spectroscopy (FTIR) and thermal analysis were performed using thermogravimetry (TGA) coupled with differential scanning calorimetry (DSC).

2. Experimental

2.1. Sample characteristics

The subject of study consisted of 52 randomly selected plastic toys for children, placed in chocolate foods purchased at local grocery stores. The choice of this type of toy for children was conditioned by the fact that they are very well protected against external factors by packaging made of polyethylene, where a toy is placed; the chocolate layer surrounding the polyethylene container, and the packaging of the whole food product (aluminum foil).

Due to this structure of the whole food product, knowledge of its storage time in the grocery store is not important. Toys for children placed in chocolate food products are available for potential customers in two versions: no-assembly toys (figurines), and toys which need to be assembled into the final form from many components.

After purchasing the food products they were transported to the laboratory, where the protective layer of aluminum foil and the layer of chocolate were removed. The polyethylene packaging, wherein the toys were placed, was cleaned of chocolate residue and numbered.

Subsequently, the package was opened and the children's toys were weighed. After weighing, each of the toys was placed in a separate polyethylene bag with an airtight seal to isolate the tested subject from the external environment. The average weight of a single toy for analysis was 6.1 ± 1.3 g.

The children's toys placed in chocolate foods were divided into two main groups: the first group consisted of no-assembly toys (figurines), which had a similar structure and size; the second group consisted of toys that need to be assembled, with the structural elements differing only in color, dimensions and shape. For this reason, to determine the main type of polymer from which the toys were made, 9 representative samples of 52 types of toys (toys with numbers 3, 4, 12, 13, 21, 25, 28, 34, 41) were selected. However, all 52 toys were tested for the determination of organic compound emissions of selected monoaromatic hydrocarbons (BTEX and styrene).

2.2. FTIR, DSC and TGA analyses of small toy samples

In order to identify the type of polymer used in the manufacture of the examined toys placed in chocolate food products, analysis using apparatus for Fourier transform infrared spectroscopy (FTIR) was performed. The study was conducted using a Nicolet iS10 spectrometer (Thermo Scientific, USA). The device had an ATR attachment with a diamond crystal. Measurements were performed with 1 cm^{-1} resolution in the range of 650 to 4000 cm^{-1}.

The thermal analysis of nine selected samples (sample nos. 3, 4, 12, 13, 21, 25, 28, 34, 41) of children's toys, representative of the various types of toys, was conducted using the simultaneous TGA/DSC model Q600 (TA Instruments, USA).

Fragments of small children's toys weighing approx. 10 mg were placed in a corundum dish. The study was conducted in an inert gas atmosphere–nitrogen (flow rate 50 ml/min) in the range from 25 to 700 °C with a temperature increase rate of 15 °C/min.

2.3. Sampling device — Markes' Micro-Chamber/Thermal Extractor™ (μ-CTE™)

In order to determine the amount of organic compounds emitted from various types of toys, the microscale stationary emission chamber – *Markes' Micro-Chamber/Thermal Extractor™ – μ-CTE™ 250* (Markes International Ltd.) was applied. The device (with dimensions 52 cm × 16 cm) is part of 4 microscale emission chamber systems, with an internal volume equal to 114 cm^3 each, a flow control device operating in two ranges of rinsing gas flow rate (10–70 ml/min, and 10–500 ml/min), and a temperature controller (operation range from room temperature to 250 °C). In order to minimize the occurrence of the wall memory effect resulting from the adsorption of impurities on the surface of the device walls, the interior of the miniature emission chambers was made of highly polished stainless steel. Detailed information about the structure, scope of work, and applications of the microscale stationary emission chamber *μ-CTE™* was presented by Schripp et al. (2007).

In each of the four miniature emission chambers one polymer toy was placed and conditioned for 60 min at 40 ± 1 °C. The flow rate of rinsing