Adsorption Effect of Added Powder Graphite on Reduction of Volatile Organic Compounds Emissions from Expanded Polystyrene

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Volatile organic compounds (VOCs) were evaluated with application of a thermal load of thermal insulation boards made of expanded polystyrene (EPS). Samples of commercially produced polystyrene EPS 100S and EPS GreyWall were tested at 60 °C. For qualitative and quantitative analyses, headspace gas chromatography mass spectrometry (HS-GC-MS) was used. To reduce VOC emissions, the chemically non-bound powder graphite was added to the EPS 100S in experiments. The aim of this research was to analyse the effects of graphite bound in EPS structure and of added free powder graphite on the VOC emissions, especially styrene. The research revealed that the graphite bound in the GreyWall EPS structure had an effect on the reduction of VOCs emissions, and reduced styrene emissions by 14.6%. The addition of powder graphite resulted in a reduction in VOCs emissions below the detection limit.

Keywords: Buildings; Polystyrene; Indoor environment; VOCs; HS-GC-MS terms

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INTRODUCTION

Expanded polystyrene (EPS) can be included in many construction applications. It is used, for example, to insulate the perimeter walls, roofs, floors, and ceilings, as a component of underfloor heating systems, sound insulation systems in floating floors, various sandwich panels, drainage boards, etc. (INEOS Styrenics Netherlands BV 2013). Its application is recommended in the construction of green and energy-passive buildings (low thermal conductivity, low density, water resistance, insect resistance, low cost) (Hassan et al. 2017; Siswosukarto et al. 2017; Němec et al. 2019). Also, the economical and spatial aspects (the use of polystyrene reduces the thickness of the partition structure) are common reasons for its use (Raj et al. 2014). The use of EPS in construction applications must be in compliance with (EC) Regulation no 305/2011 of the European Parliament and of the European Council on construction products (Regulation EU No 305/2011). Annex 1 to this regulation provides that the construction works must be designed and built in such a way that they will, throughout their life cycle, not be a threat to the hygiene or health and safety: workers, occupants, neighbours. Buildings during their construction, use and demolition shall not have an extremely large impact on the environment. In particular, the materials should not result in emissions of dangerous
substances, volatile organic compounds (VOC), greenhouse gases, or dangerous particles into indoor or outdoor air.

The European Committee for Standardization also focuses on emissions from tested construction products into the indoor environment of buildings; this is important because people, in some countries, spend up to 90% of their time in the indoor environment of buildings (Oppl 2014; Cincinelli and Martellini 2017). The assessment of the quality of the indoor environment of buildings and its impact on the incidence of respiratory illnesses and human health have been addressed by several authors (Nakai et al. 1999; Wang et al. 2007; Ferreira and Cardoso 2014; Loreti et al. 2016). They suggest in their studies that the level of pollutants is higher in the indoor environment than in the outdoor environment and that the air pollutants mainly include nitrogen oxides (NOx), carbon oxides (CO and CO₂), and volatile organic compounds (VOCs) from different sources. Depending on the type of used construction materials, furniture, or floating floors, various substances, such as formaldehyde, phenol, styrene, benzene, xylene, toluene, benzaldehyde, pinene, and furfural, may be released into the indoor environment of buildings (Brown et al. 2013; Ye et al. 2014). Two groups of VOCs are recognized in polymeric materials. The first group consists of different additives that are added to improve properties of the material, such as cyclopentane, which is used as a blowing agent for polyurethane foam. The second group of VOCs includes substances present as residues from polymerization processes. In EPS, it is styrene, a monomer for the production of polystyrene. The emission of VOCs from polymeric materials is a process involving the diffusion through the material and the surface emission (Choczynski et al. 2011).

Graphite in the form of carbon nanoparticles, carbon black, or graphene is added to the polystyrene with the aim to improve thermal and insulation properties (Tran et al. 2016). The graphite particles reflect and absorb the radiant energy, thus enhancing the insulation ability of materials while all their performance properties are retained. That is why these polymer composite materials have received increased attention in recent years as a source of new generation of EPS (Lakatos et al. 2018). Due to the interfacial interaction between the graphite nanolayers and the polymer, the graphite/polystyrene nanocomposite exhibits higher glass transition temperature and higher thermal stability when compared to polystyrene (Xiao et al. 2002).

Although the graphite integrated in polystyrene improves its thermal and insulation properties, it does not prevent VOC emissions from EPS (Bednár and Bubeníková 2018). The EPS is generally considered non-toxic, but it may release residual styrene that is toxic, mutagenic, carcinogenic. The International Agency for Research on Cancer (IARC) has classified it in group 2B of possible carcinogens (European Commission (EC) Regulation 10/2011). Research suggests that indoor air quality has a significant impact on human health. Radon and gamma radiation have been identified as the most important factors for human health (Meijer 2007). Studies have shown the presence of VOC (benzene, toluene, styrene, and formaldehyde) in the indoor air of the building. Their concentration is in units of µg/m³ (Marzocca et al. 2017; Danihelová et al. 2018). It is not quantified how these concentrations affect human health. At present, these concentrations are considered as safe. However, it is necessary to note that there is no mechanism to restrict these VOC emissions to the indoor air of buildings and that the research does not take into account the long-term effect of exposure to nor contribution of VOC emissions from other materials used in construction. Similarly, the potential synergistic effect of VOC emissions and other factors that may affect human health in the non-working and working environments are not taken into account (Mečiarová and Vilčeková 2015; Mračková et al. 2016).
In this paper, VOC emissions from two kinds of commercially used EPS (EPS 100S and EPS GreyWall), which is manufactured in the form of thermal insulation boards, are compared. The objective of the present research is to investigate the effects of graphite bound in EPS structure and of added free powder graphite on the VOC emissions.

EXPERIMENTAL

Materials
For testing, the expanded polystyrene samples were obtained from commercially available 100-mm thermal insulation boards made of two kinds of EPS. The first group of samples was prepared from EPS 100S (Isover, Saint-Gobain Construction Products, Trnava, Slovakia) in a self-extinguishing version treated with polymer-based flame retardant (PolyFlameRetardant – PFR). EPS 100S is primarily designated for thermal insulation of floor constructions and flat roofs with common requirements for their loading by pressure. The second group of samples was prepared from EPS GreyWall (Isover, Saint-Gobain Construction Products, Trnava, Slovakia), which is the EPS with the addition of powder graphite bound in the material structure. The EPS GreyWall (EPS GW) is designated for thermal insulation of building claddings with the highest demand on insulation efficiency. According to the manufacturer’s technical data sheet, the long-term heat resistance is declared at 80 °C for EPS 100S and at 70 °C for EPS GW (Saint-Gobain 2019). The third group of samples was prepared from EPS 100S, with powder graphite (samples referred to as the EPS 100S plus G) added to the samples in the same weight ratio as contained in the EPS GW structure.

The weight ratio of bound graphite in the EPS GW was determined by dissolving the EPS GW in tetrahydrofuran followed by filtering (PTFE 0.45 µL), drying, and weighing. The process of determining the weight ratio of graphite was performed on 20 samples. An average weight ratio of graphite in the EPS GW was determined as 0.03% (0.003 g/g).

Granular graphite manufactured by Aces SA (Gdynia, Poland) was used for testing, which is also used for the drinking water purification in urban water treatment stations, catalytic removal of residual chlorine and ozone, sewage purification, organic compound removal: benzene, toluene, ethylbenzene, and xylenes (BTEX) in ground water, and soil remediation processes (Aces 2019). This granular graphite was ground to a powder prior to being added to the EPS 100S.

The EPS samples were disintegrated into “bubbles”, prior to emission testing, which were conditioned for 48 h at laboratory conditions at temperature 20 °C and 60% humidity. The EPS samples with weight of 0.07 g were placed in a 20-mL headspace vial, and the vials were tightly closed with a disposable polytetrafluoroethylene (PTFE) / silicone septum. A total of nine samples were tested in each series.

Methods
Vials with prepared samples (EPS 100S, EPS GreyWall, and EPS 100S plus powder graphite) were thermally loaded at 60 °C for 60 min in the Headspace Autosampler 7697A (Agilent Technologies, Santa Clara, CA, USA). A temperature of 60 °C was chosen to demonstrate that the emission of VOCs occurs at a temperature lower than the temperature of a long-term heat resistance of EPS (as declared by the manufacturer). Such temperature can also be reached on the building's facade in the summer months or close to
the heaters. The qualitative and quantitative analyses of volatile organic compounds were performed on an Agilent 7890A GC / 5975C MSD system with an Agilent Headspace Autosampler 7697A (Agilent Technologies, Santa Clara, CA, USA).

Experimental HS-GC-MS Conditions

The headspace settings were as follows: The carrier gas was helium (He) with a pressure of 7.5 psi. Oven temperature was set at 60 °C, temperature at loop was 70 °C, and the temperature of transfer line from HS to the GC was 80 °C.

The GC conditions were as follows: The column type was HP-5MS with dimensions (30 m × 0.250 mm × 0.25 μm), the carrier gas was helium with constant flow rate of 1.0 mL·min⁻¹, and the temperature regime was from 40 °C to 220 °C with constant increase at 6 °C·min⁻¹. Temperature regime from 220 °C to 270 °C rose at 15 °C·min⁻¹ and the injector temperature was 150 °C. Split conditions were set to 10:1 and temperature of transfer line to the MSD was 280 °C.

The substances were identified by comparing the measured spectra with the NIST05 mass spectra library, and the retention times of standards from the reference material Aromatic VOC-MIX 3 (Dr. Ehrenstorfer GmbH, Augsburg, Germany).

RESULTS AND DISCUSSION

According to Kruse et al. (2002, 2003), and Woo and Broadbelt (1998), the styrene is already released into the environment from EPS at a temperature of 20 °C, and the amount and variability of volatile compounds increase as the temperature rises. Although the manufacturer declares the long term thermal stability up to 80 °C for EPS 100S and up to 70 °C for EPS GW, emission of a wide range of VOCs occurs already at a temperature of 60 °C. At this temperature, not only styrene, but also toluene, ethylbenzene, xylenes, propylbenzene, and even oxidative degradation products, such as benzaldehyde and acetophenone, were identified among the VOCs. Table 1 shows the list of identified VOCs that occur when the EPS 100S and EPS GW are exposed to a thermal load.

Table 1. VOCs Formed at the Thermal Loading of EPS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Number in Fig. 1</th>
<th>EPS 100S</th>
<th>EPS GW</th>
<th>EPS 100S Plus G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Xylene</td>
<td>2</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Styrene</td>
<td>3</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Benzene, (1-methylethyl)-</td>
<td>4</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Benzene, 2-propenyl-</td>
<td>5</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Benzene, propyl-</td>
<td>6</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>7</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>1-Hexanol, 2-ethyl-</td>
<td>11</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>12</td>
<td>+</td>
<td>+</td>
<td>*</td>
</tr>
<tr>
<td>Alpha-methylstyrene</td>
<td>13</td>
<td>+</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

+ Substance was identified among the volatile products; * substance was not identified among the volatile products
A similar composition of volatile products is also reported by other authors (Kusch and Knupp 2004). They found that toluene, ethylbenzene, xylenes, styrene, cumene, allylbenzene, n-propylbenzene, benzaldehyde, beta-methylstyrene, benzyl alcohol, acetophenone, and other volatile organic compounds were released from EPS at temperatures of 60 and 80 °C.

The formation and composition of volatile degradation products depends on many factors such as material structure, load temperature, or presence of a flame retardant. In the case of EPS, the presence of a flame retardant can cause changes in combustion products such as a reduction in styrene, benzaldehyde, and an increase in phenol contents (Xing et al. 2016).

Some differences in quantity and proportional representation of identified VOCs were detected from comparing the VOC composition of the graphite-modified EPS GW with the VOC composition of the EPS 100S. The qualitative analysis showed a difference in only one case. Alpha-methylstyrene was not identified in the EPS GW. The remaining 12 VOCs were identified in both groups of samples. Figure 1 shows a chromatogram from the analysis of VOCs released from EPS 100S, EPS GW, and EPS 100S plus G at 60 °C.

The quantification of released styrene and other volatile products is presented in Table 2. The EPS 100S, which is largely used in buildings indoors and outdoors to insulate roofs, ceilings, floors, and partitions, released 31.4 mg·kg⁻¹ of styrene and up to 67.96 mg·kg⁻¹ of ethylbenzene. It was assumed that the graphite bound in the EPS (EPS GW) would have an effect on the reduction in quantity of VOCs in addition to its function of improving thermal insulation properties. This assumption was partially confirmed. The EPS GW released 14.6% less styrene, 31% less ethylbenzene, and 41.9% less xylene than EPS 100S. The non-modified EPS is likely to cause faster decomposition of released styrene, which probably also relates to its lower concentrations than in the EPS GW.
graphite integrated in the EPS structure (EPS GW) is likely to affect the chemistry of the formation of degradation volatile products, but it does not completely prevent their emissions (Bednár and Bubeníková 2018). Bednár (2019) reported that styrene was released from EPS GW already at a temperature of 20 °C and that quantity and variability increased as the load temperature became higher.

Table 2. Quantitative Analysis of Selected VOCs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ethylbenzene (mg·kg⁻¹) ± SD</th>
<th>Xylenes (mg·kg⁻¹) ± SD</th>
<th>Styrene (mg·kg⁻¹) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPS 100S</td>
<td>67.96 ± 2.99</td>
<td>3.03 ± 0.04</td>
<td>31.43 ± 1.23</td>
</tr>
<tr>
<td>EPS GW</td>
<td>21.06 ± 1.31</td>
<td>1.76 ± 0.03</td>
<td>26.84 ± 1.27</td>
</tr>
<tr>
<td>EPS 100S plus G</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* Substance was not identified among the volatile products

One of the most effective methods for removing VOCs from the atmosphere is adsorption. Various adsorbents have been studied, including activated carbon (Lillo-Ródenas et al. 2005; Yi et al. 2009; Li et al. 2011; Baur et al. 2015), zeolites (Huang et al. 2006), silica (Hernández et al. 2004; Wang et al. 2011), and polymers (Choung et al. 2001). Graphite appears to be a suitable material, which is characterized by high surface area values (2630 m²·g⁻¹) with active sites for capture of target molecules. Its modification is relatively simple, and it is a promising adsorbent for various contaminants (Kim et al. 2018). Additionally, graphene oxide (GO) has become popular as a potential ecological photocatalyst (Tai et al. 2019).

Due to the above characteristics of graphite, the authors decided to test the emission of VOCs from EPS to which the powder graphite was added. The chromatographic record (Fig. 1), as well as the outcomes presented in Tables 1 and 2, show that such addition of powder graphite to the EPS 100S had a remarkable effect on the elimination of VOCs formed at the thermal loading of EPS. With samples of the EPS 100S plus G, to which the graphite had been added, the volatile products were below the detection limit. The inset in Fig. 1 depicts the styrene peak, where it can be seen that the added graphite effectively sorbs the formed styrene as well as other VOCs. The added “non-bound” powder graphite sorbed the formed volatile organic compounds more efficiently in the same amount as being bound in EPS GW.

CONCLUSIONS

1. Graphite integrated in the EPS structure failed to prevent emissions of VOCs into the environment, but it reduced their concentration. The EPS GW released 14.6% less styrene, 31% less ethylbenzene, and 41.9% less xylene than EPS 100S.

2. The powder graphite added to the EPS 100S had a remarkable influence on eliminating the emission of VOCs, which were below the detection limit.

3. Repeated exposure, even to low concentration of such substances, may have a negative effect on health. A wide range of VOCs is released from EPS into the environment at a temperature of 60 °C. Not only styrene, but also toluene, ethylbenzene, xylenes,
propylbenzene, as well as oxidative degradation products, such as benzaldehyde and acetophenone, have been identified.

4. This research will be tested in real conditions of use of ETICS system to eliminate VOC emissions evolved in to environment.

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