TECHNICAL TRANSACTIONS | CZASOPISMO TECHNICZNE
CHEMISTRY | CHEMIA
1-Ch/2015

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MODIFICATION OF EXPANDABLE POLYSTYRENE BEADS

MODYFIKACJA PEREŁEK EKSPANDOWANEGO POLISTYRENU

Abstract

This paper presents the effect of modification of expandable polystyrene beads (PSB) with an additional amount of physical blowing agent and the addition of ethylene wax on their properties. Three different sizes of PSB beads were analyzed. The bulk density and thermal properties – thermogravimetric and differential scanning calorimetry were evaluated.

Keywords: expandable polystyrene, bulk density, DSC, TG

Streszczenie

W artykule przedstawiono wpływ modyfikacji perełek ekspandowanego polistyrenu (PSB) za pomocą dodatkowej ilości poroforu fizycznego oraz dodatku wosku etylenowego na ich właściwości. Analizie gęstości nasypowej oraz właściwości termicznych – termograwimetrycznej oraz skaningowej kalorymetrii różnicowej poddano 3 różne wielkości perełek PSB.

Słowa kluczowe: polistyren ekspandowany, gęstość nasypowa, DSC, TG

DOI: 10.4467/2353737XCT.15.107.4055

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1. Introduction

Polystyrene (PS) is one of the earliest discovered synthetic thermoplastics. It is obtained by free radical polymerization of styrene (Fig. 1) [12]. Polystyrene can be obtained by bulk, suspension, emulsion and solution polymerization.

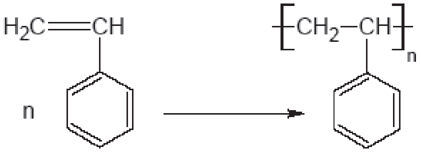

Fig. 1. Styrene polymerization reaction scheme

PS is a hard, brittle, transparent, easy-to-form material. In a commercial form, this material is known as a granulate, which is generally used for injection molding [12]. Additionally, the PS is one of the most commonly used plastics for the preparation of porous materials. In order to give it a cellular structure, foaming agents are used. Depending on the method of homogenizing of a polymer with blowing agent, there are two basic types of porous PS – expanded polystyrene (EPS) and extruded polystyrene (XPS).

Basic raw materials used for the preparation of a porous PS are monomeric styrene and blowing agents. Blowing agents suitable for the production of this material comprise of organic or inorganic substances, solid, liquid, or gaseous [8]. Currently, low-boiling, non-solvent polymer liquid having a high vapor pressure, such as isomers of pentane and hexane, are the most commonly used for the preparation of EPS. They are added in an amount of approx. 6% by mass. The use of liquid blowing agent is more effective than solid blowing agents because they can be uniformly distributed in the polymer. Through the use of low-boiling liquid, it is possible to obtain products with a low density and a uniform structure. However, the use of pentane isomers also has drawbacks. Pentane plasticizes the PS matrix, thus lowering its glass transition temperature [15]. The biggest disadvantage is its flammability and volatility. Therefore, in order to reduce the flammability of EPS, it is necessary to use flame retardants.

In literature of the subject, there is also a suggestion to replace pentane with water as an ecological blowing agent. EPS expanded by water (WEPS) can be prepared by a two-step suspension polymerization. The addition of 2–10 wt. % of water with a suitable surfactant is enclosed in the solid PS in the form of small droplets [6]. So far, WEPS has not been widely used and is not obtained on an industrial scale. It requires the use of special foaming conditions due to the small difference between the boiling point of water and the glass transition temperature of PS [11, 15].

A wider range of physical blowing agents is used in the preparation of extruded polystyrene. Generally, organic or inorganic inert gases are preferred [9]. The first blowing agents used for the preparation of XPS were chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) [4]. Later, they were replaced by new and more environmentally friendly blowing agents hydrofluorocarbons (HFCs) such as HFC-245 fa [16] or HFC-134a [5]. Carbon dioxide [9], and nitrogen [7] are also very often used.

1.1. The methods of EPS preparation

EPS is a porous material, which is obtained by foaming of PSB containing a blowing agent. The basic method of preparation of PSB is suspension polymerization conducted at elevated temperature and a pressure of approx. 1 MPa. As a result of this process, beads obtain a diameter of 0.3 to 5.0 mm [10].

Producers offer a large selection of PSB for expansion, which differ in size fraction, content and the type of blowing agent and flame retardants. These features of PSB determine their subsequent use (Table 1). The size of obtained granules can be controlled by varying the speed of agitation and the addition of an appropriate amount of suspension stabilizers [13].

Table 1

PSB application according to the size of beads [13]

PSB size [μm]	Size classification	Application
800–2000	Large	Insulation board
500–1000	Medium	Packaging, objects with complex shapes
300–800	Small	Containers with thin walls e.g. cups

PSB processing, in order to obtain final products, involves three-stages: the initial expansion, seasoning and final expansion coupled with the formation of finished products [3]. Pre-expansion can be carried out using hot air, hot water or steam [12] at a temperature of about 100°C. As a result, PS softens and the blowing agent closed inside beads evaporates giving a porous structure [14]. Pre-expanded polystyrene beads (P-EPS) are white, have regular shapes with dimensions up to several millimeters. During expansion, the bulk density of the beads is gradually decreased and after a period of about 5–10 min. reaches approx. 10–20 kg/m^3. The final formation of EPS products takes place in metal molds having perforated double walls. Through the holes in the walls steam is provided to the mold [14]. The steam makes further expanding of P-EPS possible, their sticking together and final forming in the mold shape.

Due to the cellular structure, EPS gains completely new, different properties, and therefore, new applications. The low cost of production and good properties of EPS allow this material to compete with polyurethane foams and mineral wool.

1.2. Properties and applications of EPS

EPS belongs to the group of rigid porous materials. PS foams are characterized by [8] application temperature range from –180°C to 75°C, resistance to fresh and salt water and moisture, resistance to acids, alkalis and alcohols, solubility in esters, ketones, ethers, aromatic hydrocarbons, resistance to microorganisms and lack of photostability – yellowing in the sun.

In Poland, EPS is the most commonly used heat insulating material. The share of EPS is up to 45–50% in the domestic market of thermal insulations [1]. EPS apparent density is in the range of 13–160 kg/m3. Due to the use of EPS as heat insulating material in the construction, mechanical and insulating properties are also important, primarily compressive strength and thermal conductivity. Depending on the EPS apparent density, compressive strength has a value of 100–500 kPa, while thermal conductivity is in the range from 0.032 to 0.045 W/m·K [2]. Thanks to the easy formation even very complex shapes from EPS, all kinds of shock absorbers packaging, containers, trays or cups of different shapes and sizes are produced by the use of it.

The aim of this study was to obtain modified beads with better ability to be expanded than in the case of typical commercial PSB. Such beads may have other applications, e.g. for the preparation of polyurethane-polystyrene composites by co-expansion. Therefore, modification of PSB was performed by increasing the amount of pentane and polyethylene wax. Obtained beads were analyzed and bulk density as well as thermal properties were determined, and compared with the properties of commercial beads.

2. Materials

Owipian® FS is an expandable polystyrene, which is in the form of beads. It is produced by Synthos Sp.o.o. from Oświęcim. Owipian FS contains flame retardants (hexabromocyclododecane in an amount up to 0.5 wt.%) and a mixture of isomers of pentane as a blowing agent (6.0% by weight). Commercial beads were marked with the symbol S. Table 2 presents three EPS commercially available fractions and their characteristics.

Table 2

EPS commercially available fractions

	Fraction symbol		
	0513	0816	1325
Diameter of beads [mm]	0.7–1.0	1.0–1.6	1.6–2.4
Content of fraction [%]	≥ 95	≥ 95	≥ 95
Basic control sieves size [mm]	0.50–1.25	0.80–1.60	1.25–2.50

In this study, commercial PSB (type S) were compared with modified PSB. Modified beads were prepared according to the same formulation as commercial beads (detailed formulation is a company secret), but the concentration of certain ingredients in the formulation was increased. Firstly, PSB recipe was modified by increasing the amount of physical blowing agent. The content of pentane isomers was increased from 6.0 % to 7.5% by weight in the Owipian FS formula. These PSB were marked with the symbol P.

Another modification of PSB was saturating them (during the synthesis) substance capable to loosening of polymer chains cohesion. The synthesis was carried out on the basis of the Owipian FS recipe. The quantity of polyethylene wax increased by five times. These PSB were marked with the symbol W. Solid polyethylene wax has a molecular weight of 1000–2000 g/mol. Polyethylene wax is added to standard beads in order to improve their ability to foam. In addition, polyethylene wax is a nucleating agent substance.

All kinds of PSB (S, P and W) were divided into three fractions and marked with symbols: 0513, 0816, 1325.

3. Methods

3.1. EPS bulk density

The measurements of P-EPS bulk density were carried out according to PN-90/C-89298. This method involves placing a specified quantity of PSB in the heating medium under a given temperature for a specific period of time. Approx. 2.0 g PSB was thrown into water at temperature of 100°C. The beads were left in the water for 1, 2, 3, 5, 7 or 10 min. and then retrieved and dried at room temperature. Then the P-EPS were weighed and transferred into a measuring cylinder to determine the volume. A bulk density was calculated from the formula (1):

$$\rho_N = \frac{m}{V} \left[\frac{\text{kg}}{\text{m}^3}\right] \tag{1}$$

where:

ρ_N – bulk density [kg/m^3],
m – P-EPS mass [kg],
V – P-EPS volume [m^3].

3.2. EPS thermal properties

DSC analysis was performed using the analyzer MettlerDSC 823. Samples were heated at 10°C/min to a temperature of 300°C. The measurement was carried out under an inert atmosphere. The mass of the sample was approx. 5 mg.

Thermogravimetric analysis (TG) was done using a Netzsch TG209. The measurement was carried out in the air. The samples were heated at 10°C/min to a temperature of 600°C.

4. Results

This experiment shows that, with the increase of pre-expansion time, the bulk density of the P-EPS achieves smaller values. This relationship is observed for the 0513 and 0816 fractions. For the largest beads (1325), the bulk density reaches a minimum after expanding time of approx. 3 min. and then increases. PSB remaining at heating medium increase their volume until the break in the outer layer of the PS. After interruption of the layer, blowing agent escapes outside, the beads collapse, and the bulk density of P-EPS increases. It was also observed that then the larger initial size of the PSB then the lower bulk densities of P-EPS and the shorter time in which it is obtained.

It was also found that the modification of PSB affected their bulk density. Regardless of the fraction size the lowest bulk density was reached by the PSB containing an increased amount of pentane isomers (Fig. 2–4). In addition, minimum bulk density of PSB type P is achieved in shorter time than minimum bulk densities of commercial PSB and PSB type W. It was observed that the increased amount of blowing agent in the modified beads allows for a faster and more efficient expansion.

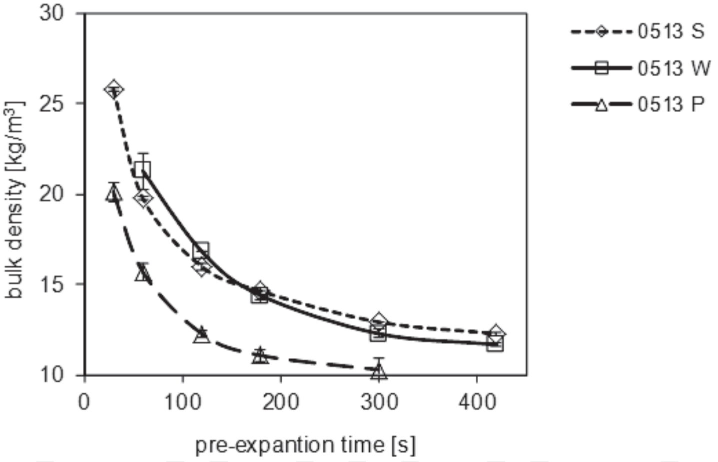

Fig. 2. Bulk density of commercial and modified PSB, fraction 0513 depending on the pre-expansion time

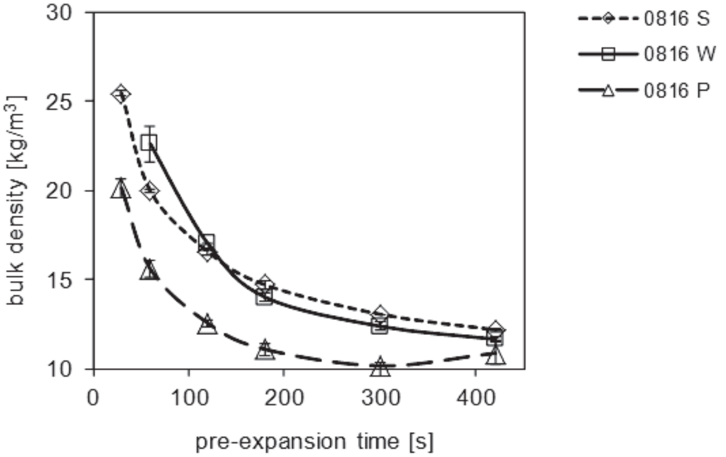

Fig. 3. Bulk density of commercial and modified PSB, fraction 0816 depending on the pre-expansion time

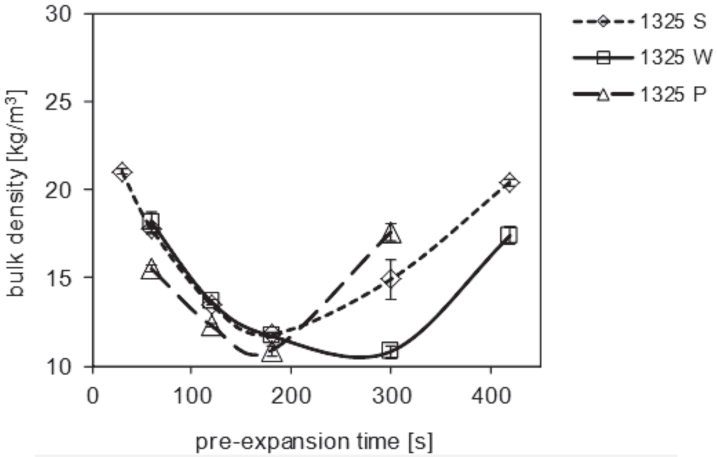

Fig. 4. Bulk density of commercial and modified PSB, fraction 1325 depending on the pre-expansion time

Commercial PSB (0513 and 0816 fractions) and PSB with the addition of polyethylene wax have similar expansion characteristic. In contrast, the expansion curve for fraction 1325 is characterized by a minimum after which the bulk density starts to rise again. Such behavior is observed regardless of the modification type. Commercial beads and beads modified with pentane have reached minimum bulk density after expanding time of approx. 3 min. On the other hand, PSB modified with polyethylene wax achieved minimum bulk density after the time of approx. 5 min. (Fig. 4). Accordingly, it was found that the addition of polyethylene wax in the case of the largest fraction makes it necessary to extend the time of pre-expansion, to achieve the minimum bulk density.

In order to know the phase transitions temperature of PSB, DSC analysis was performed. In all DSC thermograms, for the different fractions, as well as the types of PSB two peaks were observed. The example of the DSC thermogram for the PSB (fraction 1325) is shown in Fig. 5.

Phase transitions during expansion of PSB cause that on the thermogram are two endothermic peaks. The first peak starts at approx. 49°C, ends at approx. 63°C, and the peak falls at a temperature of approx. 54°C. The blowing agent that is enclosed within the PSB is a mixture of pentanes, with a boiling range of 40 to 60°C. Therefore, it was concluded that the first peak on the thermogram corresponds to the evaporation of physical blowing agent.

Despite the phase changes from liquid to gaseous, the blowing agent does not come out from the inside of the PSB. This is evidenced by TG analysis, which results are shown in Fig. 6. The beginning and the end of the weight loss was indicated by dotted lines. The beginning of this process was registered at a temperature of 64°C, while it is ended at 135°C. Upon heating, the sample lost approx. 6% of its weight. This is a value corresponding to the content of the blowing agent in the PSB. However, the loss of weight begins at a temperature higher than evaporation temperature of the blowing agent. This is due to the fact that the first blowing agent is trapped in the solid PS. After exceeding the softening temperature of the PS (about 75°C), the blowing agent may get out.

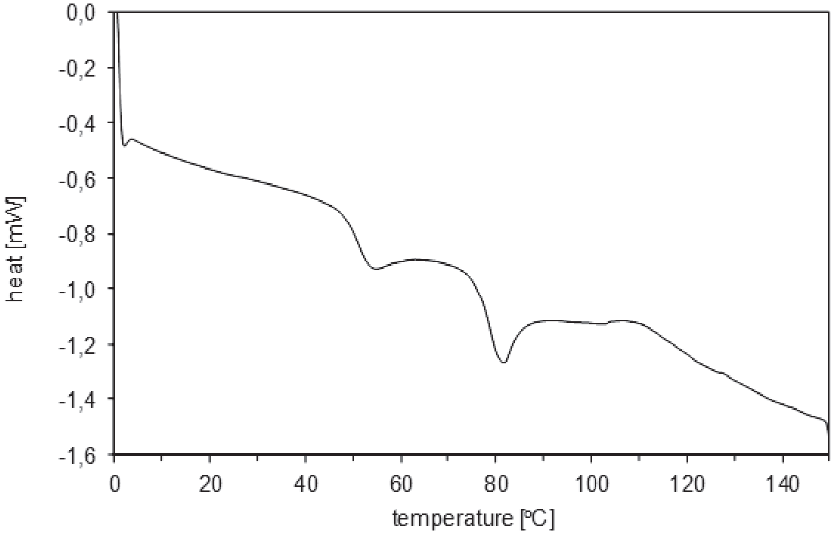

Fig. 5. The DSC thermogram of the PSB, fraction 1325

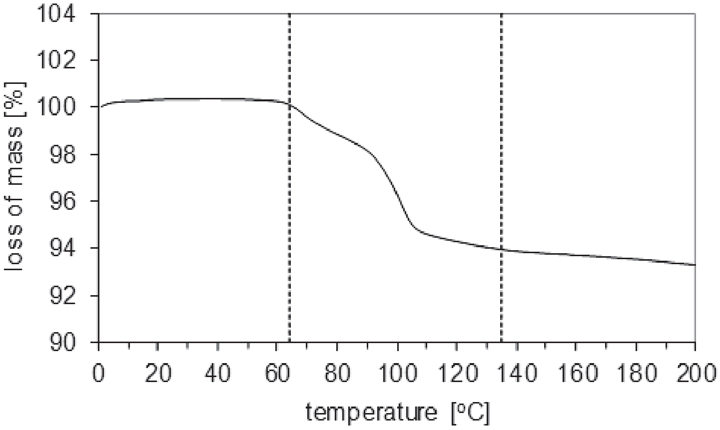

Fig. 6. Thermogravimetric curve of PSB, fraction 1325

The second peak in the DSC thermogram is observed at a temperature of approx. 80°C. The transformation starts at approx. 75°C and ends at approx. 86°C. In order to verify which changes are responsible for the presence of the second peak in the thermogram, DSC analysis was performed for P-EPS. P-EPS was cooled in liquid nitrogen, pressed and cut. In this way, P-EPS without blowing agent was analyzed. The result of the analysis is shown in Fig. 7. In a given DSC thermogram two endothermic peaks were not observed, as it was in the case of PSB with the blowing agent. However, there was a characteristic temperature collapse between 99 and 102°C. Such collapse occurs at the glass transition temperature, which for PS is equal to approx. 100°C.

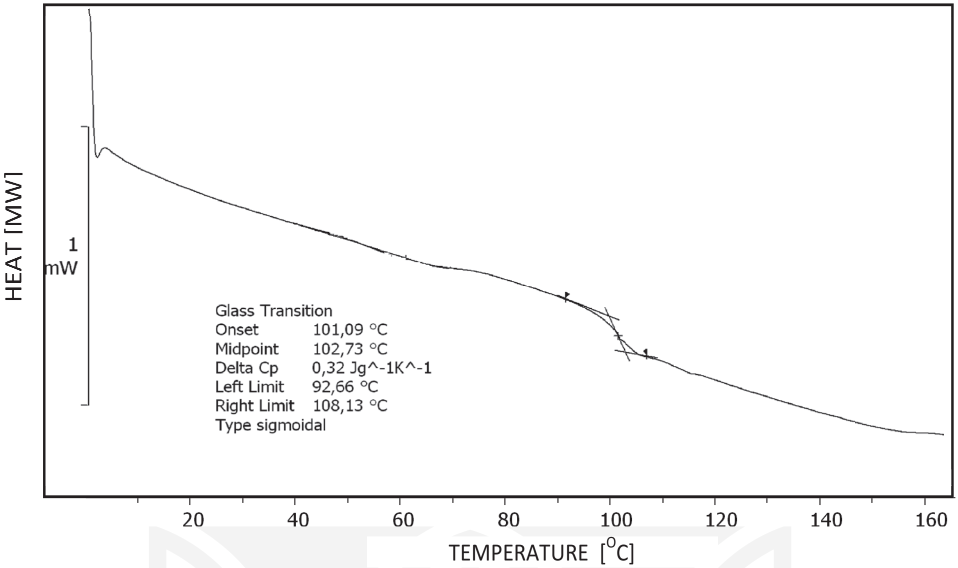

Fig. 7. DSC thermogram of free blowing agent P-EPS

Table 3

DSC analysis results for different fractions of modified and commercial PSB

Type of PSB	I onset temperature [°C]	I peak temperature [°C]	I end temperature [°C]	II onset temperature [°C]	II peak temperature [°C]	II end temperature [°C]
1325 S	49	54	63	76	80	86
0816 S	49	58	65	80	84	90
0513 S	51	62	69	82	86	92
1325 P	54	58	63	77	81	87
0816 P	54	58	63	78	82	88
0513 P	55	59	63	80	84	92
1325 W	55	60	67	80	84	90
0816 W	57	61	69	80	85	91
0513 W	60	66	71	85	90	97

It was found that the second peak appearing in the DSC thermogram of PSB is connected (like the first peak) to the presence of a blowing agent. The endothermic peak in DSC thermogram can be observed during desorption of various substances from different polymers. Therefore, it is possible that second peak in the DSC curve is associated with the release of blowing agent from the PSB. Table 3 shows the results of DSC analysis of commercial and modified PSB.

The analysis shows that the larger the fraction of PSB is, the temperature of the second peak is lower. PSB of 1325 fraction is characterized by the lowest temperature change for all the examined beads, regardless of whether they are commercial or modified. Larger fractions of PSB can contain a higher amount of blowing agent that plasticized PS [6]. Therefore, the higher amount of pentane in large PSB fractions lowers their softening temperature. It was also observed that the fraction size of PSB does not significantly affect the evaporation temperature of blowing agent. The blowing agent within the beads, regardless of fraction size was the same in all fractions and, therefore, the phase transition temperature was the same.

PSB modification by the additional amount of pentane also reduced the temperatures at which the phase transitions occur in comparison with commercial PSB. This is also due to the presence of pentane plasticizing PS. On the other hand, the addition of polyethylene wax results in an increase of temperature at which phase changes occur.

5. Conclusions

The analyses show that the changes in the composition of polystyrene beads affects the selected properties of their pre-expanded forms. The bulk density of the pre-expanded beads, and the time at which a minimum value is reached depend on content of physical blowing agent and polyethylene wax.

Due to applied modifications, polystyrene beads were obtained, which may have new applications. The beads modified with the addition of more pentane have lower temperature of phase transformation, so that they are expanding more efficiently at lower temperatures than the commercial polystyrene beads. In contrast, the addition of polyethylene wax increases the permissible exposure time of beads at high temperatures, so that they do not collapse as quickly as commercially available beads.

References

[1] Anonym, *Rynek materiałów izolacyjnych w Polsce 2010, Prognozy rozwoju na lata 2010–2012*, PMR Publications, 2010.

[2] Anonym, *Styropianowe materiały izolacyjne w budownictwie – poradnik projektantów*, Stowarzyszenie Producentów Styropianu, 2005.

[3] Bering M.L., *Plasitcs Engeenering Handbook of the Society of the Plastics Industry*, Springer, 1991.

[4] Chau V., *Advences in thermal insulation of extruded polystyrene foams*, Blowing Agents and Foaming Processes 2011, Confrence Proceedings, 10–11.05.2011, Dusseldorf, Germany.

[5] Chau V., *Blowing agent emission from Styrofoam extruded polystyrene foams a simplified model to calculate the residual blowing agent*, Blowing Agent and Foaming Processes 2010, Confrence Proceedings, 19–20 maj 2010, Cologne.

[6] Crevecoeur J.J., Nelissen L., Lemstra P.J., Polimer, 1999, **40**, 3685.

[7] Faridi N., Dey S., Wan C., Xanthos M., *Use of Polyolefin Additiwes in Inert Gas Extrusion Foaming of Polystyrene*, ANTEC 2000 Plastics: The Magical Solution, Volume 2, Conference Proceedings, 7−11.05.2000, Orlando, USA.

[8] Hertz Z., Krajewski B., Penczek I., Płochocki A., Wiecheć T., Polistyren, Wydawnictwo Naukowo-Techniczne, Warszawa 1962.

[9] Kaemmerlen A., Asllanaj F., Jeandel G., Baillis D., Journal of Quantitative Spectroscopy & Radiative Transfer, 2010, **111**, 865.

[10] Maciaszek S., *Syntetyczne tworzywa porowate*, Wydawnictwo Naukowo-Techniczne, Warszawa 1963.

[11] Pallay J., Kelemen P., Berghmans H., Dommelen D., Macromol. Matter. Eng., 2000, **275**, 18.

[12] Pielichowski J., Puszyński A., *Technologia tworzyw sztucznych*, Wydawnictwo Naukowo-Techniczne, Warszawa, 2003.

[13] Shen J., Cao X., Lee L.J., Polymer, 2006, **47**, 6303.

[14] Sikora R., *Przetwórstwo tworzyw wiekocząsteczkowych*, Wydawnictwo Edukacyjne Zofii Dobkowskiej, Warszawa 1993.

[15] Snijders E.A., *Water expandable polystyrene (WEPS): computational and experimental analysis of bubble growth*, Technische Universiteit Eindhoven, Eindhoven 2003.

[16] Vachon C., *Foaming polystyrene with HFC-245fa and blend sof hfc-245fa and* CO_2, ANTEC Plastics: Annual Technical Conference, Volume 2, Conference Proceedings, 1−5.05.2005, Boston, USA.