ŠARŪNAS VARNAGIRIS

MODIFICATION OF EXPANDED POLYSTYRENE SURFACE AND BULK CHARACTERISTICS USING SILICON DIOXIDE AND TITANIUM DIOXIDE COMPOUNDS

SUMMARY OF DOCTORAL DISSERTATION

ENERGETICS AND POWER ENGINEERING (06T)

Kaunas
2017

KAUNAS UNIVERSITY OF TECHNOLOGY
LITHUANIAN ENERGY INSTITUTE

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KAUNO TECHNOLOGIJOS UNIVERSITETAS
LIETUVOS ENERGETIKOS INSTITUTAS

ŠARŪNAS VARNAGIRIS

POLISTIRENINIO PUTPLASČIO PAVIRŠIAUS IR TŪRINIŲ SAVYBIŲ MODIFIKAVIMAS PANAUDOJANT SILICIO IR TITANO OKSIDŲ JUNGINIUS

Daktaro disertacijos santrauka
Energetika ir termoinžinerija (06T)

2017, Kaunas

INTRODUCTION

During the last few decades energy efficiency has become an essential issue for the majority of users in the industrial, public and domestic sectors. Increase of energy efficiency and development of sustainable energy are especially emphasized in the EU prepared 2020 Energy Strategy. During recent years the amount of statutes related to energy efficiency has progressively increased. The 2010 Energy Performance of Buildings Directive and the 2012 Energy Efficiency Directive are the EU's main legislation covering the reduction of the energy consumption of buildings. Directives foresee general policies and measures on how to significantly increase energy efficiency in new and existing buildings, which are responsible for roughly 40 % of energy consumption in the EU. It is an essential prerequisite to make improvements in thermal insulation of buildings in order to increase energy efficiency.

Expanded polystyrene (EPS) is one of the most utilized material for the thermal insulation of buildings. EPS is cheap, light non-toxic, non-reactive, floating and relatively easy manufactured material. EPS consumption is growing rapidly every year in the whole world.

However, one of the main disadvantages of EPS is flammability. The association of European Manufacturers of Expanded Polystyrene (EUMEPS) recognizes the importance of EPS behaviour in case of fire and promote to use flame retardant materials during the EPS manufacture process. The most utilized flame retardant materials are halogen based and phosphorus based materials. However, when such materials are in contact with flame, toxic compounds are emitted to atmosphere, which are hazardous for the environment or human health. As an alternative for such materials, non-organic compounds could be used as flame retardant (e. g. SiO_2). Such materials emit significantly lower amounts of toxic compounds in contact with flame. Also, SiO_2 is attributed to group of environmentally friendly materials. However, the analysis of literature review showed that SiO_2 utilization as flame retardant material for expanded polystyrene is poorly discussed and required additional experiments.

Other disadvantage related to EPS utilization for building insulation is moisture absorption. During exploitation time, moisture absorption increased. As a consequence, thermal conductivity of EPS also increased. There are a lot of different EPS moisture absorption measurements. However, information on the reduction of moisture absorption is not provided.

EPS is also widely used in packing industry. Such EPS utilization leads to create packages which minimized ambient temperature influence for packed material. EPS could be used in food, medicine equipment or other sectors, such as packing materials. Sterility and protection against bacterial infection of packed materials is very important in the above mentioned sectors. TiO_2 is one of the most promising materials for photocatalysis reactions and reduction of bacteria viability. EPS with deposited TiO_2 film could be used not only for food

or medicine equipment packing, but also for water cleaning or other areas where bacteria inactivation is required. However, literature analysis showed that there is less information on TiO_2 films formation on the surface of EPS. The main problem which prevents thin films formation on EPS surface is that EPS is a thermal sensitive material with low glass transition temperature. This EPS characteristic limits thin films formation process on EPS surface.

In order to form thin films on the surface of EPS or primary polystyrene beads, specific technologies are required, which lead to form thin films in lower than EPS glass transition temperature. Also in order to achieve better thin films adhesion it is essential to increase EPS surface energy.

One of several methods which could be used to solve this problem is low temperature plasma technologies. Plasma treatment, which leads to increase EPS surface energy and thin films formation at lower than 100 °C could be performed using this method. However, analysis of literature review showed that there is less information on EPS plasma treatment of SiO_2/TiO_2 thin films formation on the surface of EPS. Therefore, in order to effectively apply low temperature plasma technologies for thin films formation on EPS surface, it is necessary to accomplish additional experiments, which could reveal potential of such method.

The object of this research – formation of oxide based thin films on primary polystyrene beads and expanded polystyrene foam.

The aim of the Doctoral Dissertation

To create a new SiO_2 and TiO_2 additives incorporation into the bulk and thin films formation on the surface of expanded polystyrene methods using low temperature plasma technology in order to increase bacteria inactivation, heat resistant and reduce moisture absorption of expanded polystyrene foam.

The tasks of the Doctoral Dissertation

1. To create a method in order to increase oxide-based clusters adhesion on the surface of expanded polystyrene foam using plasma technologies.
2. To create a method for thin films formation on the surface of expanded polystyrene foam and primary polystyrene beads.
3. To deposit SiO_2 thin films on the surface of expanded polystyrene foam with a heat resistant characteristic and investigate it using surface analysis methods.
4. To deposit TiO_2 thin films on the surface of expanded polystyrene foam with a photocatalytic characteristic and investigate it using surface analysis methods.

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5. To deposit SiO$_2$ thin films on primary polystyrene beads expand and mould them into one-peace foam and investigate its resistivity to compression and moisture absorption characteristics.
6. To deposit TiO$_2$ thin films on primary polystyrene beads expand and mould them into one-peace foam and investigate its resistivity to compression and moisture absorption characteristics.

Scientific novelty

Created and patented method based on low temperature plasma technology is suitable for plasma treatment and thin films deposition on the surface of primary polystyrene beads and expanded polystyrene foam. This method leads to improve bulk or surface polystyrene characteristics and expands scientific knowledge in thin films deposition on temperature sensitive substrates.

Practical value

Accumulated information is relevant for plasma treatment or oxide-based thin films deposition on the surface of temperature sensitive polymers. Expanded polystyrene foam with SiO$_2$ thin film could be used where short time high temperature impact is possible. Expanded polystyrene foam with TiO$_2$ thin film could be suitable for bacteria decomposition process. Expanded polystyrene with incorporated SiO$_2$ or TiO$_2$ particles could be applied, where lower moisture absorption or higher resistance to compression characteristics are required, compared to conventional expanded polystyrene.

Statements of the Doctoral Dissertation

1. Plasma treatment is a suitable method for expanded polystyrene surface characteristics changes from hydrophobic to hydrophilic. Reached superhydrophilic characteristics could be kept about 48 hours in ambient atmosphere.
2. Magnetron deposition using pulsed DC magnetron sputtering is a suitable method for oxide-based thin films deposition on the surface of temperature sensitive polymers.
3. Deposited SiO$_2$ film which is distributed uniformly on the surface of expanded polystyrene increase its resistivity against high temperature impact (160 °C).
4. Deposited TiO$_2$ film on the surface of expanded polystyrene has photocatalytic and antibacterial characteristics.
5. SiO$_2$ additives incorporated into the bulk are not suitable for expanded polystyrene protection against high temperature impact (160 °C).

6. Resistivity of moisture absorption and compression of expanded polystyrene could be improved by incorporating SiO_2 or TiO_2 additives into the bulk.

Approval of the Doctoral Dissertation

The subject of the dissertation has been discussed in 7 publications: 4 of them published in clarivate analytics web of science database with a citation index, 3 of them published in peer-reviewed journals. The topics covered in the dissertation presented at 7 international conferences. Also, two patents were published based on the subject of the dissertation.

Scope and structure of the dissertation

The dissertation is comprised of introduction, 3 chapters (literature review, methodology and results), conclusions, a list of references and a list of the author's publications related to the dissertation. The dissertation contains 114 pages, 59 illustrations, and 20 tables. The list of references has 178 items.

1. LITERATURE REVIEW

This chapter provides an overview of the literature review related to manufacture of expanded polystyrene, physical characteristics, flammability, applications, reuse, market and other related areas. Also it includes plasma treatment, additives incorporation and thin films formation methods on the surface of expanded polystyrene. Finally, this chapter ends emphasizing the information on the author's achievements in the research of expanded polystyrene modification using low temperature plasma technologies.

2. METHODOLOGY

Before all experiments, combined plasma treatment and thin films deposition system using magnetron sputtering was created in Lithuanian energy institute, Center for hydrogen energy technologies. This system leads to form oxide-based thin films with good adhesion characteristics on the surface of expanded polystyrene (EPS) or primary polystyrene beads (PPB) without extraction to the atmospheric pressure.

Prior to TiO_2 or SiO_2 thin films deposition samples were treated by argon gas plasma. This step is essential because it is well known that plasma treatment of polymers removes organic contaminants from the surface, introduces polymer chain cross-linking, creates radicals and other effects which synergistically increase free-surface energy of the polymer and significantly improves film adhesion (Larrieu et al., 2005; Sasai et al., 2008). Gas pressure during plasma treatment was set to 10 Pa, plasma was generated using 400 V voltage supplied by pulsed DC power source (combination of Advanced Energy MDX-1K and Sparcle-20 units), distance between sample surface and high temperature stainless steel cathode (made from Alloy 600) was 40 mm (Fig. 1), activation time - 40 s. The described set of EPS foam activation parameters was pre-selected experimentally, finding optimal conditions when EPS surface becomes strongly hydrophilic and at the same time is not melted or otherwise damaged by the interaction with plasma.
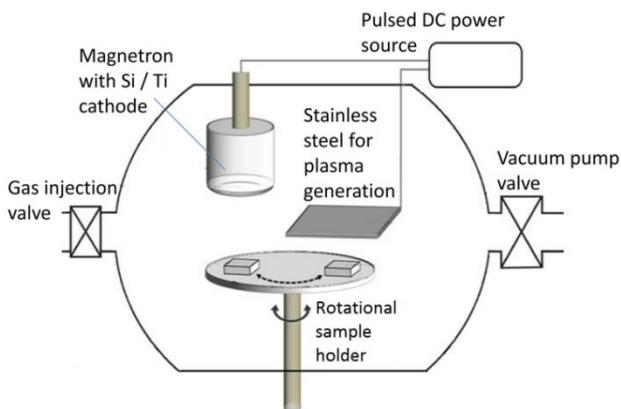
Fig. 1. Scheme of the vacuum system experimental set-up and sample positioning during plasma treatment and SiO_2/TiO_2 deposition on the polystyrene samples

Surface energy changes initiated by plasma treatment were evaluated by laboratory made water contact angle measurement equipment. When the suitable surface energy was reached (the water contact angle was ~8 °), SiO_2 or TiO_2 thin films were deposited on the samples.

After plasma treatment sample holder was rotated by 180 degree and samples were placed directly under the magnetron. Conventional 76 mm diameter magnetrons (balanced K.J. Lesker Company Torrus 3) were used for the SiO_2/TiO_2 deposition in reactive Ar+O_2 gas atmosphere (purity of Ar and O_2 gas was 99.999 %). The main deposition process parameters are shown in Table 1.

Table 1. The main parameters of thin films formation on the surface of expanded polystyrene or primary polystyrene beads

Sample	Cathode	Gas ratio Ar:O_2	Distance, mm	Current, A (power, W)	Deposition time, min
EPS	Ti	4-5.25:1	70	0.7 (240)	360
EPS	Si	3:1	40	0.5 (140)	40*
PPB	Ti	4.5:1	70	0.7 (240)	540**
PPB	Si	3:1	70	0.45 (105)	540**

* - 5 min deposition, then 5 min cooling in order to do not overheat. The cycle is repeated 8 times.

** - 180 min deposition, then polystyrene beads are extracted from the vacuum chamber, mixed and transferred back for further deposition process. Mixing process is repeated in every 180 min.

In all cases during thin film deposition process pulsed-DC power source (v=20 kHz) was used. Pressure during thin films formation was 6×10^{-1} Pa.

Deposited thin films on expanded polystyrene or primary polystyrene beads were analysed by surface analysis methods (scanning electron microscope,

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energy dispersive X-ray spectroscope, X-ray difractometer, X-ray photoelectron spectroscope) in order to evaluate films morphology, thickness, elemental composition, chemical bonds, etc.

Primary polystyrene beads with SiO_2 or TiO_2 films were expanded and moulded into one-peace foam after the above mentioned surface analysis processes. Beads expansion and moulding processes were done collaborating with a company UAB „Modernios E-technologijos".

Practical application adapted experiments were done for expanded polystyrene with SiO_2 or TiO_2 films and expanded polystyrene with incorporated SiO_2 or TiO_2 particles into the bulk. Photocatalysis and antibacterial experiments were done for polystyrene with TiO_2. Resistance of torch induced head experiments were done for polystyrene with SiO_2. Additionally resistance to compression and moisture absorption experiments were done for expanded polystyrene with incorporated particles.

Photocatalysis and antibacterial experiments were performed collaborating with Vytautas Magnus University department of biochemical science. Resistance of torch induced head experiments were done using laboratory made equipment. Resistance to compression and moisture absorption experiments were performed collaborating with Lithuanian energy institute Laboratory of Material Research and Testing.
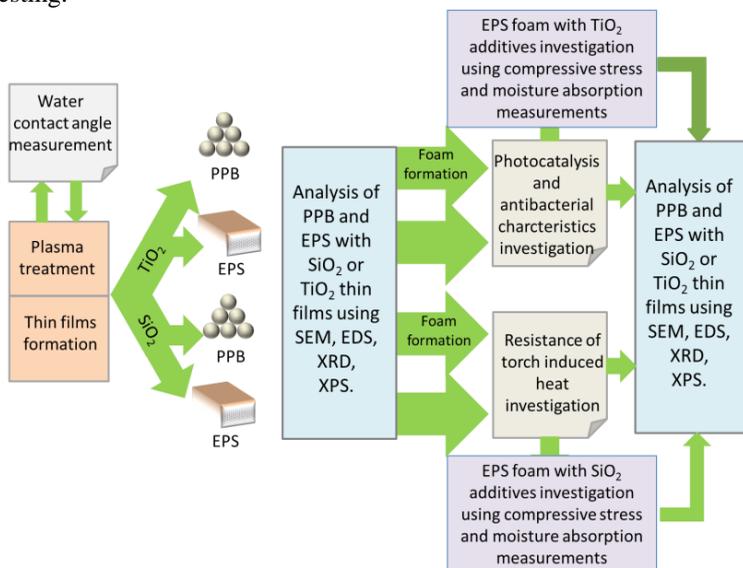

Fig. 2. General scheme of all the experiment sequence during this work

All the samples were analysed again using surface analysis methods in order to evaluate thin films changes after practical adapted experiments. The general scheme of this work is shown in Fig. 2.

3. RESULTS AND DISCUSSION

3.1. Low pressure influence to expanded polystyrene foam

First of all, it was important to understand vacuum influence on expanded polystyrene foam because a lot of experiments during this work were done in vacuum conditions. Two types (based on ASTM C 578-10 (ASTM C578-10, 2010)) of polystyrene, I (14.5 kg/m^3) and II (22 kg/m^3) were used for this test. Both type polystyrene samples were placed into the vacuum chamber, where samples were left for 9 hours in 9.6×10^{-6} Pa pressure. Initial dimensions of the samples were $20 \times 30 \times 10$ mm (volume - 6×10^{-6} m^3). Results showed that I type sample after extraction to atmospheric pressure changed its dimensions to $18 \times 26 \times 9$ mm (volume – 4.2×10^{-6} m^3). It is almost 30 % of volume reduction. II type sample remain stable (Fig. 3). These dimension changes mean that physical characteristics of polystyrene also might be changed.

Also it was observed that I type polystyrene does not change its dimensions during storage in vacuum. Polystyrene started to shrink when air was injected into the vacuum chamber after the test. Moreover, when such shrinked polystyrene was transferred to vacuum condition, it expanded again till it reached initial dimensions.
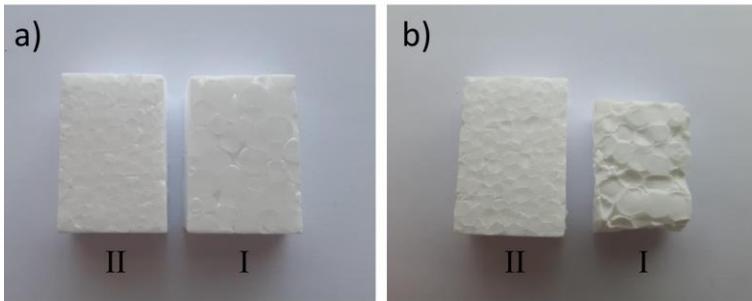
Fig. 3. Comparison of I and II type expanded polystyrene before (a) and after (b) 9 hours 9.6×10^{-6} Pa pressure vacuum test

This phenomenon is related to polystyrene elemental composition and density. It is known that expanded polystyrene consists of 98 % air while the rest part is carbon. Expanded polystyrene has a relatively low density. When such a material is transferred to vacuum, air is extracted from the bulk of polystyrene due to entropy. Expanded polystyrene lost its stability but dimensions did not change. When air is injected into the chamber, pressure increased several times of magnitude. Expanded polystyrene started to shrink.

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Therefore I type expanded polystyrene is not suitable for experiments which requires vacuum conditions. II type polystyrene has higher density and it is much more stable in vacuum conditions. It was decided to use only II type expanded polystyrene for further experiments.

3.2. Expanded polystyrene surface characteristics changes using plasma treatment

Plasma treatment was done in order to increase thin film adhesion on the surface of expanded polystyrene. It was important to understand which type of gas is the most suitable for polystyrene plasma treatment. Therefore three types of gas (argon, oxygen and air) were used for plasma treatment. Plasma influence was evaluated by water contact angle (WCA) measurements (Fig. 4).
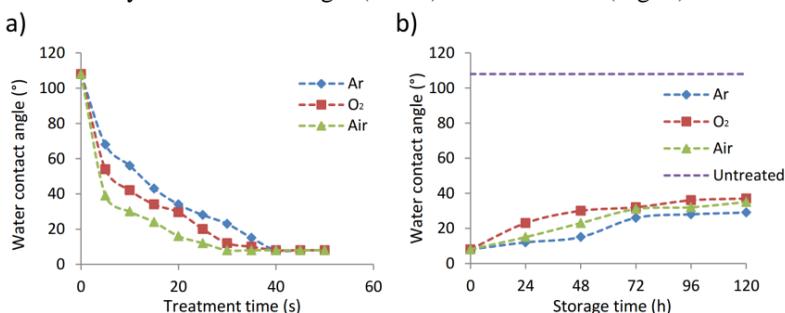

Fig. 4. Plasma treatment: a) water contact angle dependence on treatment time, b) water contact angle dependence on ageing time

Results showed that plasma treatment significantly changed polystyrene surface characteristics (Fig. 4a). WCA of untreated polystyrene was about 108 °, while after 5 s of plasma treatment it decreased to 67 ° and 39 ° using argon and oxygen gas, respectively. Superhydrophilic characteristic (WCA is lower than 15 °) was observed after 30-35 s with all types of gas. Hydrophilic characteristics changes were evaluated by measuring WCA after different storage time (Fig. 4b). Results showed that hydrophilic characteristics decreased during all storage time. However, after approximately 72 hours decrease was negligible: it reached partial saturation. The highest hydrophilic characteristic during all storage time was observed using argon gas plasma. Superhydrophilic characteristic was observed even after 48 hours of storage time, while WCA after 48 hours using oxygen and air gas was 30 ° and 23 °, respectively.

There are two main processes during plasma treatment which fulfil each other: surface cleaning and hydrophilic compounds formation (C–O, C–N, C=O, O–C=O etc.). Hydrophilic compounds formation is the main process for reactive gas plasma (oxygen, nitrogen, etc.). Therefore, it leads to increase oxygen or nitrogen amount on the surface of plasma activated material. During the storage

period in ambient atmosphere these compounds could react with carbon, OH molecules or other compounds. Therefore hydrophilic characteristics could decrease during the storage time. Surface cleaning is the main process for non-reactive gas plasma (argon) treatment. During non-reactive gas plasma treatment, formation of hydrophilic compounds is slower, however, reorientation of very top chain layer is much more intensive compared to reactive gas plasma. Moreover, hydrophilic compounds formation is observed when material is extracted to ambient atmosphere after non-reactive gas plasma treatment. Therefore hydrophilic characteristics using non-reactive gas plasma was observed for longer time in ambient atmosphere compared to reactive gas plasma treatment (Davies et al., 2000; Dhyal et al., 2006; Sasai et al., 2008).

3.3. Investigation of expanded polystyrene with SiO_2 thin film

SiO_2 and TiO_2 thin films were deposited on the surface of expanded polystyrene or primary polystyrene beads after plasma treatment process. Samples were transferred directly under the magnetron without extraction to the atmosphere after plasma treatment process. SiO_2 and TiO_2 thin films were formed using reactive mixture of argon and oxygen gas.

Elemental composition of as deposited SiO_2 thin films and after experiments of flame torch induced heat is shown in table 1.

Table 1. SiO_2 thin film elemental composition before and after flame torch induced heat experiments

Sample	Elemental composition			
	C, atom. %	O, atom. %	Si, atom. %	O/Si ratio
EPS	98.1	1.9	-	-
EPS with SiO_2	10.8	61.7	27.5	2.24
30 s	13.8	59.9	26.2	2.29
60 s	29.1	49.5	21.4	2.31

Results showed that untreated EPS consists of carbon and oxygen. Concentration of carbon decrease to 10.8 atom. % after thin film formation while oxygen concentration increase to 61.7 atom. %. Silicon concentration was fixed at 27.5 atom. %. Theoretical ratio of SiO_2 compound (O/Si) is 2. Experimental measured ratio of O/Si was 2.24. This result is compatible to theoretical SiO_2 compound ratio and confirms its formation. Residual part of measured O/Si ratio (0.24) could be observed due to adsorption of various oxide-based compounds from atmosphere. Elemental composition after experiments of flame torch induced heat showed that carbon concentration increased with longer experiment time (13.8 atom. % after 30 s and 29.1 atom. % after 60 s). This could be related to carbon based compounds formation on the surface of SiO_2 film during the experiment. On the other hand, silicon and oxygen concentrations decrease with longer experiment time (from 27.7 atom % to 21.4 atom. % and from 61.7 atom.

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% to 49.5 atom. %, respectively, after 60 s). This means that SiO_2 compound is consumed when film is in contact with temperature (160 °C). Nevertheless O/Si ratio remains stable during the experiment. These results show that SiO_2 is a stable compound and does not form any other compounds, when it is in contact with high temperature.
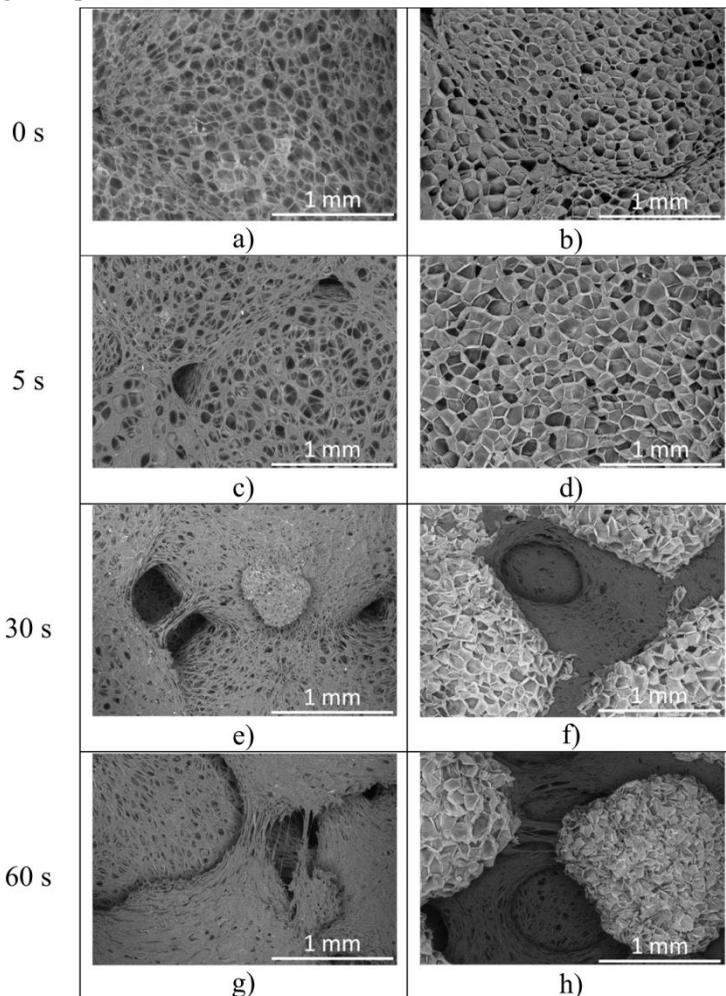

Fig. 5. SEM images of conventional expanded polystyrene surface without and with SiO_2 thin film (a-b), expanded polystyrene surface without and with SiO_2 thin film after flame torch induced heat experiments for different durations: 5 seconds (c-d), 30 seconds (e-f), 60 seconds (g-h)

SEM views of conventional expanded polystyrene, expanded polystyrene with SiO_2 film and expanded polystyrene after flame torch induced heat experiment are shown in Fig. 5. Conventional EPS surface morphology view revealed cellular structure (Fig. 5a) which remains similar after SiO_2 thin film deposition (Fig. 5b). It is seen that SiO_2 thin film replicated EPS surface morphology. Fig. 5c represents surface morphology of non-coated EPS surface after treatment by direct flame torch induced heat for 5 s. The non-coated surface shows clear signs of degradation. Cellular like structure partially disappeared and some of parts of the surface become melted, big (more than 100 μm diameter) open holes appeared. At the same time EPS surface protected by SiO_2 film shows no signs of degradation (Fig. 5d) and remains similar to the as coated sample (Fig. 5b). After direct flame torch induced heat treatment for 30 s non-coated EPS surface material continues to melt (Fig. 5e), the number of holes appeared and holes diameter increases. Most of SiO_2 coated EPS surface remains well protected but surface parts were SiO_2 film erupted from the surface also appeared (Fig. 5f). The areas without SiO_2 film show similar behaviour as in non-coated one: EPS structure melts and formation of holes could be observed. Surface material melting and SiO_2 film eruption becomes more evident with the increase of flame torch induced heating time up to 60 s (Fig. 5g-h).

Fig. 6. An optical images of expanded polystyrene with (a) and without (b) SiO_2 film after 60 s of flame torch induced heat experiment

Fig. 6. shows the difference between EPS with SiO_2 and without SiO_2 thin film after 60 s of flame torch induced heat experiment. It could be seen that EPS without SiO_2 film (Fig. 6b) is much more melted, compared to EPS with SiO_2 film (Fig. 6a). The highest degradation was observed in the middle of EPS without SiO_2 film, due to the highest temperature at this point (160 ± 2.5 °C). On the other hand, EPS with SiO_2 film remain much more stable compared to EPS without SiO_2 film.

3.4. Investigation of expanded polystyrene with TiO_2 thin film

TiO_2 thin films were formed on the surface of expanded polystyrene for photocatalytic and bacteria inactivation experiments. These films were formed

similarly as SiO_2 thin films. On the other hand, it was important to find deposition parameters which would be suitable for anatase phase TiO_2 formation. Results showed that 18 % of oxygen flow (rest part - argon) during deposition process is appropriate to anatase phase TiO_2 (tetragonal, I41/amd, JCPDS No. 21-1272) thin film formation.

XPS survey scan of the as deposited film showed presence of only three elements Ti, O and C. Ti2p electron spectra reveal that there is only one chemical state of Ti (Fig. 7a). Observed Ti2p 3/2 peak energy of 458.7 eV and Ti2p 3/2 and Ti2p 1/2 spin-orbit components separation of 5.72 eV corresponds well with the reported values of TiO_2 oxide (NIST, 2017). O1s peak of can be fitted with three components at binding energies of 530.0 eV, 531.4 eV and 532.3 eV, respectively (Fig. 7b). Binding energy of the foremost component is in good agreement with reported values of TiO_2 (NIST, 2017). The latter two components are attributed C-O/C-OH (I) and adsorbed moisture (II). Both of them are observed due to adventitious contamination when sample was handled in air and contribute just a small fraction of the total O1s peak area.
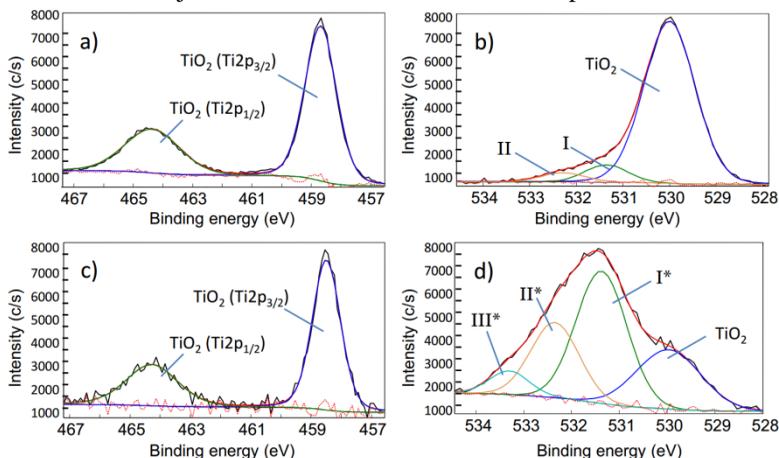
Fig. 7. Ti2p and O1s electron spectra of the as deposited TiO_2 film (a-b) and TiO_2 film after it was used for the *E. coli* vitality tests (c-d)

Results of the aqueous MB solution bleaching in the dark and under UV-B irradiation with and without TiO_2 coated EPS are shown in Fig. 8. It was observed that when generally stable aqueous MB solution is poured over EPS foam and kept in the dark some of the MB molecules are soaked up and trapped in microporous EPS foam structure, therefore MB concentration is slowly decreasing. This assumption is supported by the fact that MB concentration drop during the first hour accounts for nearly 50 % of its total reduction over 8 hours. Exposure to UV-B light initiates MB molecule degradation and significantly

enhances MB bleaching process. The highest MB decomposition ratio was observed using EPS with TiO_2 film, which was irradiated by UV-B lamp (the first order reaction constant k = 1.76×10^{-3} min^{-1}).
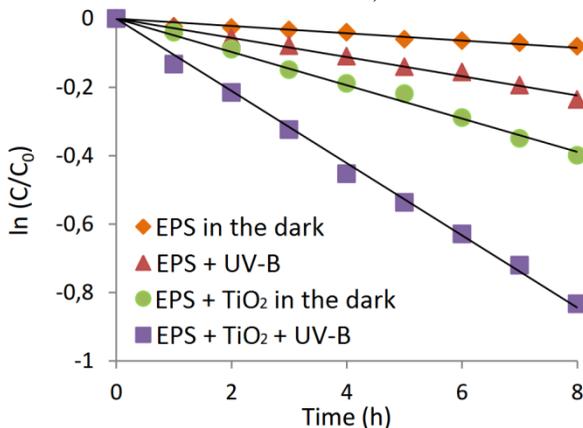
**Fig. 8.** Aqueous MB solution bleaching in the dark and under UV-B irradiation with and without TiO_2 coated EPS

E. coli cell viability tests were performed on several sets of samples with independently grown *E. coli* cultures. Experimental data from all tested samples showed qualitatively similar results and their averaged quantitative values are presented in Fig. 9.

Comparing *E. coli* cell capability to form colonies on agar plates after 30 min UV-B exposure period (Fig. 9), one can notice that the difference between bacteria placed into bare glass vessel and above TiO_2 coated EPS is small (~2.6 %). Furthermore, the viability of these two sets of samples is similar to what was measured for *E. coli* suspensions in bare glass vessel after 45 min of UV-B exposure. On the other hand, after 45 min UV-B exposure viability of *E. coli* bacteria incubated above TiO_2 coated EPS is roughly four times lower. Such trend indicates that there are two mechanisms of *E. coli* bacteria inactivation.

Observations that *E. coli* bacteria inactivation ratio caused by combination of TiO_2 and UV light has synergistic effect and is superior to separate effects of TiO_2 and UV light have been already reported by (Liu et al., 2010) and (Rizzo et al., 2014). *E. coli* cell envelope consists of the inner membrane, lipopolysaccharide (LPS)-containing outer membrane and peptidoglycan layer in between them (Raetz, 1990). Liu et al. demonstrated that UV alone or TiO_2 under daylight lamp irradiation were capable to break down integrity of LPS layer, but were not able to destroy peptidoglycan and consequently *E. coli* cells could still keep the original rod shape (Liu et al., 2010). Based on the obtained results, we assume that relatively fast damage of LPS by UV-B alone is the key

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factor behind nearly equal reduction of the capability of cells to form colonies after 30 min of UV-B exposure with and without TiO$_2$ film (Fig. 9). The same model suggests that further inactivation of *E. coli* bacteria by UV irradiation alone is limited due to inability to damage peptidoglycan. Therefore after 45 min of UV-B exposure we see nearly the same result.


		30 min			45 min	
Time						
Experiment conditions	EPS+TiO$_2$ in the dark	*E. coli* suspension in glass container UV-B	EPS+TiO$_2$ UV-B	EPS+TiO$_2$ in the dark	*E. coli* suspension in glass container UV-B	EPS+TiO$_2$ UV-B
■ Average	100	39.9	37.3	100.0	44.7	11.9 %
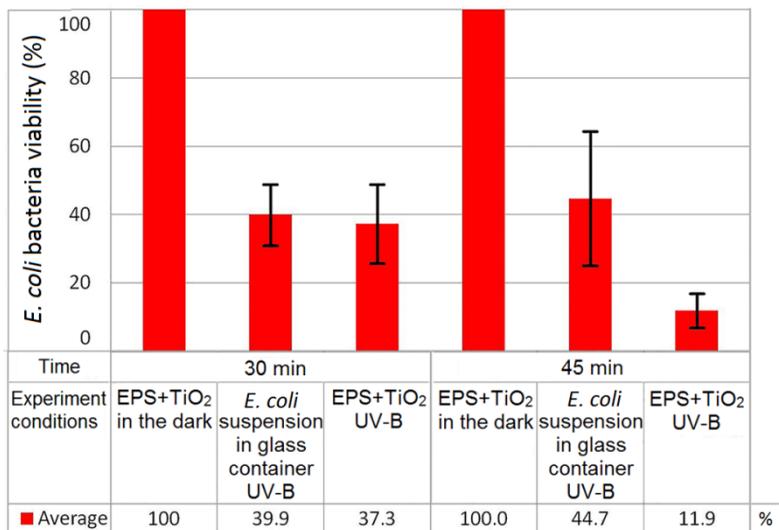
Fig. 9. Comparison of *E. coli* bacteria viability after 30 and 45 min incubation under UV-B radiation with and without TiO$_2$ coated EPS

The second mechanism of *E. coli* inactivation can be invoked only with TiO$_2$ and UV combination. When TiO$_2$ is irradiated with UV pairs of holes in the valence band (h$^+$) and electrons in the conduction band (e$^-$) are produced. Valence band holes react with water or hydroxide ions to produce hydroxyl radicals (HO$^\bullet$), while the adsorbed oxygen molecule reacts with photo-generated electrons to generate active superoxide radical (O$_2^\bullet$) which, in turn, transforms into highly reactive species such as HO$^\bullet$, HO$_2^\bullet$ and H$_2$O$_2$ (Altin et al., 2014; Hu et al., 2010; Karunakaran et al., 2011). These radicals initiate the chain peroxidation of organic molecules, break down peptidoglycan and within 45 min results in nearly 90 % reduction of *E. coli* bacteria viability.

Comparing Fig. 7a and Fig. 7c it is evident that Ti2p spectrum remains the same meaning that chemical state of titania is unchanged. At the same time the shape of O1s spectrum changes drastically: i) TiO$_2$ component (at roughly 530.0 eV) remains but it is no longer the dominant one; ii) components I* and II* are fitted at the same energies as I and II (531.4 eV and 532.3 eV respectively) but have much stronger intensities; iii) new peak at 533.3 eV arise. Based on the elemental composition data it was concluded that component I*

now stands up not only for the C-O/C-OH but it also includes O=N-C (and possibly even C=O) bonds. Component II* in Fig. 7d is naturally stronger than corresponding peak II in Fig. 7b because there are more water molecules due to sample submersion into *E. coli* suspension. It is also considered that fraction of II* peak is caused by presence of C-O-C bonds which have similar energy. Finally, 533.3 eV binding energy of the last (III*) component allows to attribute it the O-(C=O)-C functional group (NIST, 2017). Although XPS analysis was focusing to areas with undamaged TiO_2 film it is also possible that a fraction of the oxidised carbon species detected O1s spectra (Fig. 7d) were detected from the opened up EPS areas.

3.5. Investigation of SiO_2 incorporated into the bulk

In order to incorporate TiO_2 or SiO_2 particles into the bulk of expanded polystyrene, thin films were formed on the surface of primary polystyrene beads. PPB with deposited TiO_2 or SiO_2 films were expanded and moulded into one-peace foam. These films cracked into small fractures during beads expansion process due to its inelastic origin. It is important to mention that fractures do not detach from the surface of polystyrene beads during expansion process.
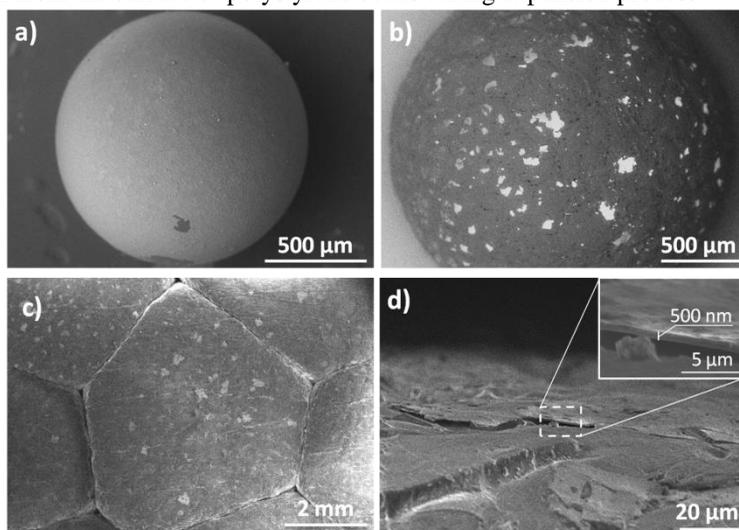
Fig. 10. Expanded polystyrene with incorporated SiO_2 fractures into the bulk: a) primary polystyrene beads with SiO_2 film, b) expanded polystyrene beads with SiO_2 film fractures, c) expanded polystyrene with SiO_2 fractures, d) cross-cutting of SiO_2 fracture on expanded polystyrene

Fig. 10a shows primary polystyrene bead deposited with SiO_2 film. However, small parts without deposited films were observed. These parts could detach due

to friction between PS beads when they were stored after deposition process or due to shadowing effects during films deposition. PPB were pre-expanded after films deposition and moulded into one-piece foam. During pre-expansion, radius of polystyrene beads could increase more than 4 times. Consequently, volume could increase 64 times ($V \sim r^3$). Such expansion of polystyrene beads induces SiO_2 film fracturing process. On the other hand, these fractures distributed relatively uniform in all bulk of expanded polystyrene (Fig. 10b). These pre-expanded beads were moulded into one-peace foam.

Expanded polystyrene with SiO_2 fractures is shown in Fig. 10c. It could be seen that SiO_2 fractures do not detach after moulding process. Dimension measurements of SiO_2 fractures showed that there are no trends related to fractures sizes. Sizes of SiO_2 fractures varied randomly from several tens nanometer to 400 µm. Thickness of SiO_2 fractures was evaluated by cross-cutting measurement using SEM (Fig. 10d). Results showed that averaged thickness was about 500 nm. It is important to mention that real thickness of SiO_2 fractures varied from approximately 100 nm to 1 µm. Such significant difference of thickness could be related to mixing of beads during deposition process and selected deposition parameters. Some of beads could fold on the same side and further deposition increase thickness of film.

Fig. 11. An optical images of expanded polystyrene with (a) and without (b) SiO_2 fractures incorporated into the bulk after 40 s of flame torch induced heat experiment

Expanded polystyrene with incorporated SiO_2 fractures into the bulk was used for flame torch induced heat experiment (temperature during experiment was 160 ± 2.5 °C). Results showed that such polystyrene with incorporated SiO_2 particles in contact with high temperature act very similar as pure expanded polystyrene – it started to melt after the first 5 s of experiment. On the other hand, SiO_2 fractures remain stable, do not decompose or form any other compound in contact with high temperature. Significant melting of polystyrene results was observed after 40 s of experiment. As shown in Fig. 11, melting of expanded polystyrene with SiO_2 fractures is almost the same as conventional

expanded polystyrene. Therefore it could be noticed that SiO_2 fractures incorporated into EPS bulk do not protect polystyrene against high temperature.

3.6. Investigation of TiO_2 incorporated into expanded polystyrene foam

Incorporation of TiO_2 was performed the same way as SiO_2: thin films formation on primary polystyrene beads, expansion and moulding into one-peace foam. Similarly as in SiO_2 case, deposited TiO_2 film cracked during beads expansion process. Also, TiO_2 fractures distributed relatively uniform after beads expansion process. Cross-cutting measurements showed that TiO_2 fracture thickness varied from approximately 100 nm to 1.1 µm with 500-600 nm average.
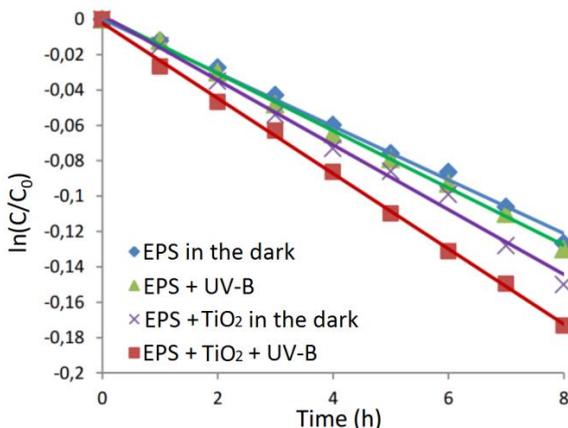

Fig. 12. Aqueous MB solution bleaching in the dark and under UV-B irradiation with and without TiO_2 fractures incorporated into EPS

Expanded polystyrene with incorporated TiO_2 fractures into the bulk was used for decomposition of methylene blue solution (Fig. 12). Aqueous MB solution bleaching experiments showed that decomposition process using such polystyrene is very slow (the first order reaction constant is 0.36×10^{-3} min^{-1}). For the most part MB bleaching process was observed due to MB adsorption on the surface of expanded polystyrene. Photocatalysis covers just a small part of total MB bleaching process. This adsorption process could be approved with the results of elemental analysis. Elemental analysis results showed that carbon and oxygen amount increase after MB bleaching experiment (from 31.9 atom. % to 33.4 atom. % and from 46.8 atom % to 49.6 atom. % respectively). Also small amount of nitrogen (0.1 atom. %) was observed after this experiment. However, such small amount of nitrogen could be assigned to errors, on the other hand, this could be the prove of MB adsorption because chemical formula of MB is $C_{16}H_{18}ClN_3S$ (Fabiyi et al., 2000). Due to very slow decomposition process it

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was decided to stop further photocatalytic process because such decomposition ratio is too slow for practical purposes.

3.7. Bulk characteristics of expanded polystyrene with incorporated SiO_2 and TiO_2 additives

Previous results showed that expanded polystyrene with incorporated SiO_2 or TiO_2 fractures into the bulk is not suitable for photocatalytic process of reduction high temperature impact into polystyrene stability. On the other hand, these incorporated fractures could change some of EPS bulk characteristics. Due to this, moisture absorption and resistance to compression measurements were done.
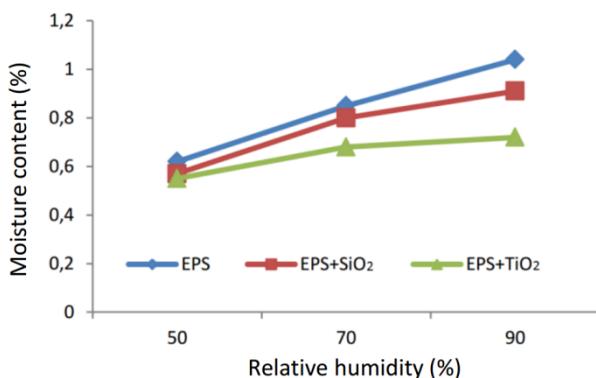

Fig. 13. Absorbed moisture content dependence on relative humidity after 4 hours using EPS with incorporated SiO_2 or TiO_2 fractures

Fig. 13 shows absorbed moisture content dependence on different relative humidity (50 %, 70 % and 90 %) after 4 hours experiment. An absorbed moisture content increases with higher relative humidity using all types of samples. The highest moisture content was observed using conventional expanded polystyrene (1.04 % with 90 % relative humidity). The lowest moisture content with the same relative humidity was observed using expanded polystyrene with incorporated TiO_2 particles (0.72 %). This result invokes presumption that incorporated additives which have hydrophobic characteristics (e.g. SiO_2, TiO_2) could reduce moisture absorption into the bulk of expanded polystyrene. EPS with TiO_2 showed lower moisture content compared to EPS with SiO_2. This result could be related to relatively uniform distribution of TiO_2 fractures after polystyrene beads expansion process. Also TiO_2 fractures have relatively higher thickness compared to SiO_2.

Other measurement which gave additional information about bulk characteristics changes was resistance to compression measurement, which was based on EN 826:2013 standard. The obtained results are shown in Fig. 14.
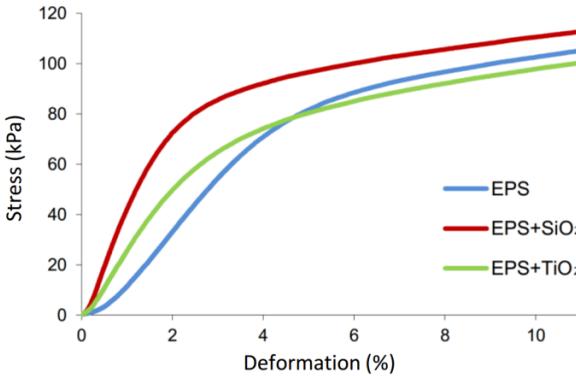

Fig. 14. Compressive stress dependence on deformation of conventional EPS and EPS with SiO_2 and TiO_2 additives

Results showed that EPS with incorporated SiO_2 fractures has higher resistance to compression, compared to conventional EPS or EPS with incorporated TiO_2. Conventional EPS resistance to compression is 104.2 kPa while EPS with SiO_2 resistance to compression is 113.7 kPa with 10 % deformation. This means that incorporated SiO_2 fractures increase EPS resistance by approximately 8.4 %. This resistance to compression change could be related to mechanical characteristics of SiO_2 or TiO_2 fractures. SiO_2 and TiO_2 compounds resistances to compression could vary from 1100 MPa to 1600 MPa (AZOM, 2017a) and from 660 MPa to 3675 MPa (AZOM, 2017b), respectively. The highest values of these characteristics could be observed using totally crystal structures of these compounds. In this case, SiO_2 has amorphous and TiO_2 has very weak crystal structure. Therefore, the lowest values of these compounds (SiO_2 - 1100 MPa, TiO_2 - 660 MPa) should be received. These values showed that SiO_2 has almost two times higher resistance to compression value. This could be the reason for higher EPS with SiO_2 resistance to compression value, compared to EPS with TiO_2.

In conclusion, EPS moisture absorption and resistance to compression values could be changed incorporating TiO_2 or SiO_2 additives into the bulk. EPS with incorporated SiO2 additives has higher resistance to compression while EPS with incorporated TiO_2 additives has lower moisture absorption, compared to conventional EPS.

3.8. Photocatalytic properties of TiO$_2$ deposited on primary polystyrene beads

In previous section, TiO$_2$ deposited on expanded polystyrene or incorporated into the bulk of expanded polystyrene was used for photocatalysis and antibacterial experiments. In both cases samples were cut from expanded polystyrene foam. However, it was observed that primary polystyrene beads could be used as an alternative for foam-based samples. PPB are buoyant, relatively cheap and easily manufactured (Fabiyi et al., 2000; Raps et al., 2015). Also, PPB are spherical material with around 1−3 mm dimensions (surface area: 12.5–113 mm^2). M. E. Fabiyi (Fabiyi et al., 2000) formed TiO$_2$ coatings on primary polystyrene beads using spray coating technology with a 74 °C temperature. However, such method does not confirm good adhesion between bead and coating. I. Altin and M. Sokmen (Altin et al., 2014) formed ZnO coatings on primary polystyrene beads. They used thermal annealing process (162 °C). However, such temperature is higher than polystyrene glass transition temperature. Therefore, polystyrene beads have to undergo physical changes.

PPB with deposited TiO$_2$ thin films were used for photocatalysis (methylene blue bleaching) and antibacterial (viability of Escherichia coli bacteria) experiments. TiO$_2$ films deposition on primary polystyrene beads process is explained in section "Investigation of TiO$_2$ incorporated into expanded polystyrene foam".
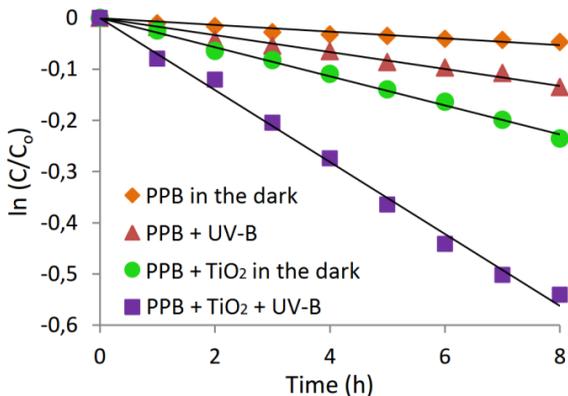
Fig. 15. MB aqueous solution bleaching in the dark (PPB in the dark), pure PPB beads with UV-B irradiation (PPB + UV-B), PS with TiO$_2$ (PPB + TiO$_2$ in the dark) and PS with TiO$_2$ under UV-B irradiation (PPB + TiO$_2$ + UV-B)

Aqueous MB solution bleaching experiment results are shown in Fig. 15. First of all, absorption of MB solution into PPB with TiO$_2$ was evaluated. Beads were mixed with MB solution end kept in the dark for 8 hours. Measurement showed that absorption of MB solution into PPB with TiO$_2$ film is relatively

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negligible. UV-B irradiation influence of MB bleaching was estimated using PPB without TiO_2. Results showed that exposure to UV-B light initiates MB molecule degradation (first order reaction constant $k=4.6\times10^{-6}$ s^{-1}). Bleaching of MB solution measurement using primary polystyrene beads with TiO_2 films under UV-B irradiation showed significant degradation which is more than 4 times higher (the first order reaction constant $k=1.95\times10^{-5}$ s^{-1}) compared to single UV-B irradiation.
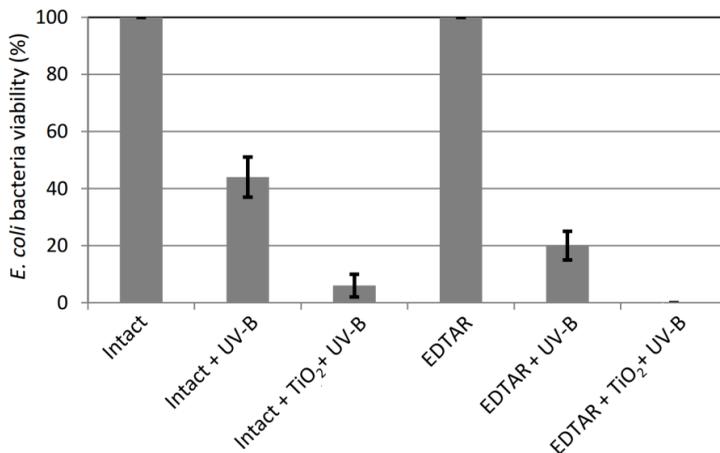

Fig. 16. Viability of intact and EDTA treated *E. coli* bacteria: untreated (Intact / EDTA), under UV-B irradiation (Intact + UV-B / EDTA + UV-B), under UV-B with TiO_2 coated PS beads (EDTA + TiO_2 + UV-B)

E. coli viability test was performed with intact and EDTA treated bacteria under UV-B irradiation and combination of TiO_2 (PPB beads with TiO_2 films) and UV-B (Fig. 16) after 45 min of treatment time. Results showed that UV-B alone can make damage for both intact and EDTA treated bacteria after 45 min of treatment (bacteria viability 44 % and 20 % respectively). Combination of UV-B and TiO_2 can increase decomposition of *E. coli* bacteria more than 7 times (bacteria viability 6 % for intact and 0 % for EDTA treated bacteria). This result indicates that there are two mechanisms of *E. coli* bacteria inactivation. *E. coli* consist of inner (phospholipid chains and proteins) and outer (lipopolysacchride (LPS), phospholipid layer and peptidoglycan (PP)) membranes (Raetz, 1990). P. Liu (Liu et al., 2010) demonstrated that UV-B alone or TiO_2 under daylight irradiation could destroy LPS but were not able to break down peptidoglycan. Therefore further inactivation of *E. coli* bacteria by UV-B irradiation or TiO_2 alone is limited by inability to damage PP layer. On the other hand, combination of UV-B irradiation and TiO_2 could create highly reactive oxygen species (Chen et al., 2017; Pelaez et al., 2016) which able to break down PP layer. This additional decomposition invokes reduction of *E. coli* bacteria viability (Birnie et

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al., 2006; Hu et al., 2010; Karunakaran et al., 2011). The higher decomposition ratio of EDTA treated bacteria is related to EDTA mechanism. Using such method, bonds of LPS layer becomes weaker. Therefore it is easier to treat PP layer using UV-B or combined UV-B with TiO_2.

O. Akhavan in his previous works (Akhavan et al., 2009a, 2009b) demonstrated that bacteria could start to proliferate when viability is higher than 10 %. In common, such decomposition (when viability is still more than 10 %) is useless for practical purposes. Our results showed that 45 min decomposition of *E. coli* bacteria using UV-B with TiO_2 deposited on PPB could be suitable mechanism for practical purposes. On the other hand, further experiments for photocatalysis stability (cycling) are also required.

3.9. Possibilities and recommendations for practical application

SiO_2 and TiO_2 thin films were formed on primary polystyrene beads and expanded polystyrene foam using low temperature plasma technologies (plasma treatment and magnetron sputtering). However it is important to pay attention to several parameters.

First of all, it is necessary to choose suitable type of polystyrene when thin films are formed in low pressure environment (lower than ambient atmosphere). I type polystyrene (density is about 14.5 kg/m^3) is not suitable for operation in low pressure environment. Such polystyrene lose its stability when it is operating in vacuum conditions due to relatively low density. As a result, it is recommended to use harder, II type, polystyrene (density is about 22 kg/m^3) when it is operating in vacuum conditions.

Secondly it is important to do not exceed glass transition temperature on the surface of polystyrene during plasma treatment or magnetron sputtering processes. Temperature on the surface of polystyrene could be controlled by changing some of parameters: distance between substrate and cathode, process current or power, time of plasma treatment or magnetron sputtering.

Also, it is recommended to use vibrating substrate holder when thin films are deposited on the primary polystyrene beads. Using such technology, beads can rotate during the process. This improves uniformity of deposited films on primary polystyrene beads.

Finally, it is important to use plasma treatment before thin films formation on the surface of primary polystyrene beads or expanded polystyrene foam. This step significantly improves adhesion between thin films and the substrate.

From the economic point of view this technology could be relevant. However it is necessary to use industry adapted low temperature plasma technologies (abandon cry pump, use cathodes with significantly higher surface area, etc.). Selective glass manufacture process could be an equivalent for mentioned technology, when thin films are deposited on the glass using magnetron sputtering.

CONCLUSIONS

In this work surface and bulk modification experiments of expanded polystyrene foam were done. This EPS could be used for building insulation or packing industry. SiO_2 and TiO_2 films were formed on the surface of expanded polystyrene or primary polystyrene beads for surface or bulk modification. These films were formed using low temperature plasma deposition technologies. During this work, surface and bulk characteristics, resistance to high temperature, resistance to compression, antibacterial and moisture absorption characteristics of modified EPS were analysed.

1. An increase of expanded polystyrene surface energy was observed using low temperature plasma technologies. Expanded polystyrene surface became superhydrophilic (water contact angle ~8 °) from hydrophobic (water contact angle ~105 °) after argon plasma treatment (voltage - 400 V, distance from electrode to sample - 40 mm, treatment time - 40 s) using pulsed DC power source.

2. SiO_2 and TiO_2 films were deposited on the surface of expanded polystyrene and primary polystyrene beads using magnetron sputtering technique with pulsed DC power source. This method is suitable for oxide based thin films deposition on thermal sensitive substrates. However, it is important to not exceed glass transition temperature on substrate surface during films' formation process.

3. SiO_2 film deposited on the surface of expanded polystyrene increase its resistant to high temperature. Expanded polystyrene with uniform ~500 nm SiO_2 film remain stable about 60 s after high temperature ($160\pm2,5$ °C) impact, while pure EPS started to melt after 5 s of high temperature impact.

4. Deposited TiO_2 films on the surface of expanded polystyrene showed photocatalytic and antibacterial characteristics. Methylene blue bleaching experiments showed that TiO_2 films became photocatalytic active when they are irradiated with UV-B, UV-A or day light irradiation. Antibacterial measurements showed that *E. coli* bacteria viability is 4 times lower after TiO_2 film deposited on EPS and irradiated with UV-B irradiation treatment compared to UV-B irradiation alone.

5. SiO_2 thin films were deposited on primary polystyrene beads. These beads were expanded and moulded into one-peace foam. Results of resistance to high temperature experiment showed that SiO_2 fractures remain stable during high temperature impact ($160\pm2,5$ °C). However, these fractures do not protect polystyrene from melting. Expanded polystyrene with incorporated SiO_2 fractures started to melt after 5 s using $160\pm2,5$ °C temperature impact.

6. Expanded polystyrene with incorporated SiO_2 fractures has better resistance to moisture absorption (0.9 % moisture absorption after 4 hours when relative humidity is 90 %) and resistance to compression (113.7 kPa when deformation is 10 %) characteristics compared to conventional expanded polystyrene (1 % moisture absorption and 102.4 kPa resistance to compression respectively). Expanded polystyrene with incorporated TiO_2 fractures has significantly better resistance to moisture absorption (0.64 %), but lower resistance to compression (98.7 kPa), compared to conventional expanded polystyrene.

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Reziumė

POLISTIRENINIO PUTPLASČIO PAVIRŠIAUS IR TŪRINIŲ SAVYBIŲ MODIFIKAVIMAS PANAUDOJANT SILICIO IR TITANO OKSIDŲ JUNGINIUS

Per paskutinius keletą dešimtmečių energinis efektyvumas tapo esminiu iššūkiu daugumoje industrinių ar namų ūkio sektorių. ES parengtoje 2020 metų energetikos strategijoje ypač akcentuojamas energinio efektyvumo didinimas ir darnios energetikos vystymas. Pastaraisiais metais priimama vis daugiau įstatymų skatinančių energijos suvartojimo mažinimą. 2010 m. ES paskelbtoje pastatų energinio naudingumo direktyvoje (2010/31/ES), kaip ir 2012 m. energijos vartojimo efektyvumo direktyvoje (2012/27/ES) kalbama apie pastatų energinį efektyvumą, kuriuose pabrėžiama, jog apie 40 % Europoje suvartojamos energijos priskiriama naujų, bei senų pastatų reikmėms. Direktyvose skatinama pastatų statybos ar renovacijos metu naudoti termoizoliacinėmis savybėmis pasižyminčias medžiagas tam, kad būtų kuo labiau sumažintos pastatų energinės sąnaudos.

Viena iš pagrindinių termoizoliacinių medžiagų, naudojamų pastatų renovacijos ar statybos metu – polistireninis putplastis (PP). PP yra pigi, lengva, netoksinė, biologiškai inertiška, neskęstanti bei sąlyginai nesudėtingai pagaminama medžiaga. Polistireninis putplastis yra labiausiai naudojama medžiaga tarp visų termoizoliacinėmis savybėmis pasižyminčių medžiagų naudojamų pastatų šiltinimui. Kiekvienais metais, PP suvartojimas ne tik Europoje, bet ir visame pasaulyje yra sparčiai augantis.

Viena iš pagrindinių polistireninio putplasčio neigiamų savybių yra jo degumas. Europos polistireninio putplasčio gamintojų asociacija (EPPGA) pabrėžia degumo problematiką, skatindama PP gamybos metu naudoti liepsnai atsparias medžiagas (LAM). Dabartiniu metu labiausiai paplitusios LAM naudojamos PP gamybos metu yra halogenų pagrindo bei fosforo pagrindo medžiagos. Visgi, kai PP su liepsnai atspariomis medžiagomis yra veikiamas liepsnos ar aukštos temperatūros, į aplinką yra išskiriami toksiniai junginiai, kurie kenkia ne tik aplinkai, bet ir žmogaus sveikatai. Kaip alternatyva tokiems junginiams gali būti naudojamos neorganinių medžiagų pagrindo LAM (pvz.: SiO_2). Tokie junginiai išskiria ženkliai mažiau toksinų esant kontakte su liepsna ir yra priskiriami aplinkai draugiškiems junginiams. Visgi atlikus literatūros analizę paaiškėjo, jog silicio dioksido panaudojimas polistireninio putplasčio atsparumo liepsnai didinimui yra menkai aptartas ir reikalauja papildomų tyrimų.

Kita problema susijusi su polistireninio putplasčio panaudojimu pastatų šiltinimui yra drėgmės įgertis. Didėjant eksploatacijos laikui drėgmės įgertis taip pat didėja, o tai skatina ir polistireninio putplasčio šiluminio laidumo didėjimą.

Nors drėgmės įgerties tyrimų yra atlikta gana nemažai, visgi būdų šiai problemai spręsti pratiškai nepateikiama.

Polistireninis putplastis yra plačiai naudojamas ne tik pastatų šiltinimui, bet ir pakavimo tikslais. Toks PP panaudojimas leidžia sukurti pakuotes, kurios minimizuoja aplinkos temperatūros poveikį transportuojamiems bei saugomiems daiktams. PP naudojamas maisto, medicininės įrangos ir kt. pakavimui. Būtent šiose minėtose srityse yra labai svarbus pakavimo medžiagų sterilumas apsaugant pakuojamą įrangą ar maistą nuo bakterijų užkratų. Pagrindinis ir labiausiai pasaulyje tyrinėjamas junginys, kurį bandoma pritaikyti bakterijų gyvybingumui mažinti bei fotokatalitiniams procesams inicijuoti yra titano dioksidas (TiO_2). TiO_2 kartu su polistireniniu putplasčiu gali būti panaudojamas ne tik maisto ar medicinos pramonėje, bet ir vandens valyme ar kitose srityse kur reikalingas bakterijų skaidymas. Tačiau atlikus literatūros analizę, kaip ir SiO_2 junginio atveju paaiškėjo, jog informacijos apie TiO_2 dangas ant polistireninio putplasčio yra gana mažai. Pagrindinė problema stabdanti dangų formavimo ant PP tyrimus yra tai, jog polistireninis putplastis yra termiškai jautri medžiaga turinti mažą paviršiaus energiją. Šios savybės riboja dangų formavimo ant PP paviršiaus galimybes.

Norint suformuoti dangas PP paviršiuje ar ant pirminių polistireno grūdelių yra reikalingos technologijos, leidžiančios tai atlikti žemesnėje nei PP stiklėjimo temperatūroje. Be to, norint užtikrinti gerą formuojamų dangų sukibimą su polistireniniu putplasčiu, prieš dangų formavimą būtina padidinti PP paviršiaus energiją.

Vienas iš nedaugelio metodų tinkamų šiai problemai spręsti yra žematemperatūrės plazmos panaudojimas. Naudojant šį metodą galima atlikti PP paviršiaus aktyvacijos procesą, taip padidinant paviršinę energiją, bei dangų formavimą žemesnėje nei 100 °C temperatūroje. Visgi, atlikus mokslinės literatūros apžvalgą paaiškėjo, jog informacijos apie PP paviršiaus aktyvacijos procesą ar SiO_2 / TiO_2 dangų formavimą ant jo paviršiaus yra gana mažai. Taigi, siekiant efektyviai taikyti žematemperatūrės plazmos technologijas dangų formavimui ant termiškai jautrių padėklų, tokių kaip polistireninis putplastis, reikalingi papildomi tyrimai, galintys atskleisti šio metodo potencialą.

Šio darbo tyrimo objektas – oksido pagrindo dangų formavimas ant pirminių polistireno granulių ir polistireninio putplasčio plokščių.

Darbo tikslas ir uždaviniai

Naudojant žematemperatūrės plazmos technologijas sukurti naujas SiO_2 ir TiO_2 priemaišų įterpimo į polistireninio putplasčio tūrį bei dangų formavimo ant paviršiaus technologijas, siekiant pagerinti polistireninio putplasčio atsparumą aukštai temperatūrai, drėgmės įgerčiai ir biologinių objektų poveikiui.

Tikslui pasiekti buvo iškelti šie uždaviniai:

1. Naudojant plazmines technologijas sukurti metodą, leidžiantį pagerinti oksido pagrindo klasterių adheziją prie polistireninio putplasčio paviršiaus.
2. Taikant fizikinio nusodinimo metodą sukurti technologiją, leidžiančią formuoti dangas polistireninio putplasčio ir pirminių polistireno grūdelių paviršiuje.
3. Suformuoti ant polistireninio putplasčio paviršiaus SiO_2 dangas, didinančias atsparumą aukštai temperatūrai, bei ištirti gautų dangų struktūrą.
4. Suformuoti ant polistireninio putplasčio paviršiaus TiO_2 dangas, pasižyminčias fotokatalitinėmis savybėmis, bei ištirti gautų dangų struktūrą.
5. Suformuoti SiO_2 dangas ant pirminių polistireno grūdelių, juos išpūsti, sujungti į vieną plokštę bei ištirti gautų struktūrų atsparumo gniuždant ir drėgmės įgerties savybes.
6. Suformuoti TiO_2 dangas ant pirminių polistireno grūdelių, juos išpūsti, sujungti į vieną plokštę bei ištirti gautų struktūrų atsparumo gniuždant ir drėgmės įgerties savybes.

Išvados

Šiame darbe atlikti polistireninio putplasčio, naudojamo pastatams šiltinti, pakavimui ir kt., paviršinių ir tūrinių savybių modifikavimo eksperimentai formuojant SiO_2 ir TiO_2 dangas ant pirminių polistireno grūdelių ar išpūsto polistireninio putplasčio plokščių. Dangos buvo formuojamos naudojant žematemperatūrės plazmos technologijas. Šio darbo metu ištirtos paviršinės bei tūrinės modifikuoto PP savybės, atsparumas aukštai temperatūrai, antibakterinės, atsparumo gniuždymui bei drėgmės įgerties savybės.

1. Polistireninio putplasčio paviršiaus energijos didinimas atliktas plazminių technologijų metodu. Po plazminio poveikio argono dujomis, plazmą inicijuojant impulsiniu srovės šaltiniu (dažnis – 20 kHz), kai įtampa 400 V, atstumas tarp bandinio ir elektrodo – 40 mm, o poveikio laikas 40 s, polistireninio putplasčio paviršius iš hidrofobinio (drėkinimo kampas $\sim105^o$) virsta superhidrofiliniu (drėkinimo kampas $\sim8^o$). Superhidrofilinės savybės (drėkinimo kampas $\leq15°$) išsilaiko apie 48 val.
2. SiO_2 ir TiO_2 dangos suformuotos polistireninio putplasčio bei pirminių grūdelių paviršiuje magnetroninio dulkinimo metodu, naudojant impulsinį srovės šaltinį. Šis metodas tinka dangoms formuoti ant termiškai jautrių padėklų, tačiau būtina atsižvelgti į proceso parametrus ir juos parinkti taip, kad nebūtų viršyta stiklėjimo temperatūra bandinio paviršiuje.

3. Suformuotos SiO$_2$ dangos polistireninio putplasčio paviršiuje didina atsparumą aukštai temperatūrai. Srityse su tolygia SiO$_2$ danga, kurios storis ~500 nm, polistireninis putplastis išlaiko nepakitusią struktūrą apie 60 s, esant 160 ± 2,5 °C poveikiui. Polistireninio putplasčio be SiO$_2$ dangos lydymasis stebimas jau po 5 s.

4. Suformuotos TiO$_2$ dangos polistireninio putplasčio paviršiuje pasižymi fotokatalitinėmis-antibakterinėmis savybėmis. Metilo mėlio skaidymo rezultatai parodė, kad dangos tampa fotokatalitiškai aktyvios, jas apšvietus UV–B, UV–A ar dienos šviesos lempomis. Antibakterinių savybių tyrimai parodė, kad polistireninis putplastis su TiO$_2$ dangomis po 45 min. poveikio, apšvietus UV–B spinduliuote, sunaikina beveik 4 kartus daugiau bakterijų, palyginti su vienos UV–B spinduliuotės poveikiu.

5. SiO$_2$ dangos suformuotos ant pirminių polistireno grūdelių. Šie grūdeliai buvo išpūsti ir sujungti į vieną plokštę. Atlikti atsparumo aukštai temperatūrai tyrimai parodė, kad įterptos priemaišos išlieka nepakitusios, tačiau jos neapsaugo polistireninio putplasčio nuo aukštos temperatūros poveikio. Esant aukštos temperatūros poveikiui (160 ± 2,5 °C), polistireninis putplastis su įterptomis SiO$_2$ priemaišomis jau po 5 s pradeda lydytis visame poveikio plote, nepriklausomai nuo įterptų priemaišų padėties.

6. Polistireninis putplastis su įterptomis SiO$_2$ priemaišomis pasižymi geresnėmis atsparumo įgerčiai (0,9 % įgertis po 2 val., kai drėgmė 90 %) ir atsparumo gniuždymui (113,7 kPa, kai deformacija gniuždant 10 %) savybėmis, palyginti su standartiniu polistireniniu putplasčiu (atitinkamai 1 % įgertis ir 102,4 kPa deformacija gniuždant). Tuo tarpu polistireninis putplastis su įterptomis TiO$_2$ priemaišomis yra gerokai atsparesnis drėgmės įgerčiai (0,64 % įgertis), bet pasižymi blogesniu atsparumu gniuždant (98,7 kPa), palyginti su standartiniu polistireniniu putplasčiu.