

# Sulfonation of Expanded Polystyrene Post Consumption, Structural Analysis and Its Application in Chemical Enhanced Oil Recovery

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In this study, we selected two kinds of polystyrene (PS) from a whole solid waste mass, expanded (EPS) and extruded (XPS). These polymers were degassed in ethyl acetate (AcOEt) and sulfonated through of two different methods. The sulfonated polystyrene (SPS) was characterized by IR and NMR techniques verifying its structure and reaching until 80 % of sulfonation degree. Finally, both PSS were used in simultaneous static adsorption test as potential sacrificial agent (SA) in chemical enhanced oil recovery (cEOR). The adsorption achieved for SEPS and SXPS were 73.002 mg/g and 131.208 mg/g, giving a 66.3 % and 37.0 % of adsorption reduction, respectively. Our sulfonated polymer results to be better than references SA's, polyacrylate and sodium tetraborate.

## 1. Introduction

Plastics are present daily in our life necessities and widely used in different activities. One of the most representative plastic is the polystyrene (PS), very useful, especially in packaging process (Choi and Ohama, 2004). Its mechanic resistance to compressive stress and heat non-conductive properties, make it a necessary plastic in our life (Eskander and Tawfik, 2011). However, PS short useful lifetime allow it to convert easily in a solid waste and it can be easily accumulated in several places (Derraik, 2002), contaminating natural resources as water (Shin, 2005) and soil (Taguchi and Tanaka, 2001) and due to its nil biodegradability became a real trouble in our environment (Kan and Demirboğa, 2009). Therefore, scientific community have recognized these polymers as persistent in marine ecosystems (Browne et al., 2008) and as toxic material in aquatic species (Gregory, 1991). On the other hand, monomer, styrene, can be released from the main polymer chain because the environmental factors, sun light, rain and total solids (Eskander and Tawfik, 2011); affording a potential carcinogen effect in humans (Vodicka et al., 2006).

Due to the above stated, researchers are looking for strategies to reduce the PS negative environmental impact. In that sense, to reuse the PS through physical transformations could be one of these ways. Therefore, PS has been used in concrete to strengthen it and reduce the permeability (Amianti and Botaro, 2008), mixed with fibers to form filters (Shin and Chase, 2005) and introducing the PS to the production process again (Teo et al., 1997). On the other hand, chemical recycling has been emerged as an attractive strategy (Bajdur et al., 2002), transforming the PS in a new material with a new application and reducing the solid waste pollution. The most common PS chemical transformation is toward the preparation of a polyelectrolyte (PEL) with a sulfonate group as anion and sodium as counterion. The sulfonation process has been widely described by Kučera (2001) (Kučera, 2001). Sulfonated PS (SPS) has been widely employed as ion exchange resin to adsorb dyes (Herrera-Sandoval et al., 2013), in sewage water purification (Sułkowski et al., 2009), in catalysis (Harmer and Sun, 2001), among others applications. More recently the SPS (sulfonated polystyrene) has been used as SA in cEOR (chemical enhanced oil recovery), an important procedure to

increase the oil production stage (Sheng, 2013), showing successful results, reducing the surfactant and polymers adsorption on the mineral surface (Budhathoki et al., 2016). Despite of the SPS use in cEOR bench experiments have yielding good results, real minerals and PS waste have not been used in static adsorption tests. Therefore, in our research we wanted to use EPS and XPS obtained directly from municipal solid waste (MSW), submit it to a sulfonation process and used it as SA in static adsorption assays on a real mineral.

## 2. Materials and methods

All reagents were commercially obtained (synthesis degree) and were used without previous purification. Lumex Infracum FT-02 spectrophotometer was used to measure the IR spectra in KBr discs. NMR (1D and 2D) spectra were recorded on Bruker Avance-400 spectrometer. Gas Chromatograph interfaced to an Agilent Technologies MSD 5963 Selective Detector (MSD) was used for MS identification at 70 eV using a 60 m capillary column coated with HP-5 [5 %-phenyl-poly(dimethyl-siloxane)].

### 2.1 PS Sulfonation

The PS was selected from MSW, degassed in ethyl acetate and dried until constant weight. Then, in a two-neck round bottom flask, 5.2 g of PS were dissolved in 25 mL of dichloroethane (DCE), heated up (50 °C) and stirred. At the same time in other reactor were mixed 3 mL of acetic anhydride and 50 mL of DCE, the temperature was down to 5 °C and 1.5 mL of concentrated H<sub>2</sub>SO<sub>4</sub> were dropped until acetyl sulfate formation. Finally, this acetyl sulfate was dropped on the PS-DCE solution and the reaction was heated during 1 h (Kučera and Jancáň, 1996). Sulfonated PS (SPS) was characterized by FTIR and NMR. The sulfonation degree was performed using a volumetric titration and the equation (1) (Unnikrishnan modified formula) (Unnikrishnan et al., 2010).

$$SD = \frac{[0.104M(NaOH) \times V(NaOH)]}{[W - 0,081M(NaOH) \times V(NaOH)]} \times 100 \quad (1)$$

Where: SD: sulfonation degree (%), M: NaOH molarity, V: NaOH volume consumed until neutralization, W: sample mass, 104: PS unit repetitive molar mass and 81: sulfonic group molar mass.

### 2.2 Mineral washed

A mineral pretreatment process was performed to avoid interferences in the surfactant measure. The mineral was obtained from a commercial source as common sand, it was grinded in a ball mill and sieved through 80 net size. Then we followed a modified protocol reported by Mattigod et al. (1985). Briefly a quantity of mineral was dispersed into distilled water (67 g/L) and stirred during 45 min. Afterwards the pH was adjusted to 9.5 with NaOH (0.1 M) and mixture was divided in 50 mL centrifuge tubes. The centrifuged-decanted process was performed five times to remove particles between 2-0.2 μm. Then the mineral was re-suspended in HCl until pH = 3, centrifuged and washed until constant pH = 5.5. Finally, the mineral was dried in an oven to 105 °C and stored in N<sub>2</sub> inert atmosphere to avoid oxidation. This material was characterized by Scanning Electron Microscopy (SEM) combined with X-ray Energy Dispersive Spectrometry (EDS).

### 2.3 Static adsorption test

Static adsorption was performed mixing 1.5 g of mineral and 20 mL of sodium dodecyl sulfate (SDS) solution in a 50 mL centrifuge tube. The mixtures were shaken during 24 h to room temperature (25 °C). Then the samples were centrifuged to 3000 rpm during 30 min and supernatant was filtered through 0.45 μm filter (Azam et al., 2013). The remainder surfactant within the solution was determined by methylene blue active substances method (MBAS) (ASTM D2330-02).

### 2.4 Surfactant quantification through MBAS method

An aliquot was taken (8.3 mL) from filtered supernatant, a drop of phenolphthalein and a drop of NaOH (1 M) were added. The final solution was titrated with H<sub>2</sub>SO<sub>4</sub> (2 M), a methylene blue solution was added (2.3 mL) and 5 mL of chloroform as well. This mixture was vigorously shaken during 30 s and the aqueous phase was separated. Afterwards, the washed solution (H<sub>2</sub>SO<sub>4</sub> 6 N and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O) was added, the mixture was vigorously shaken during 30 s, the organic phase was separated and absorbance was measured to 652 nm (Clesceri et al., 1999).

## 3. Results and discussion

Before to start with the sulfonation process, was necessary to obtain the starting material, in that case, we selected the PS from a whole MSW. Two kind of PS, the EPS and XPS, were separated from MSW and

degassed with different solvents, petroleum ether (PE), dichloromethane (DCM) and ethyl acetate (EtOAc). Both DCM and EtOAc showed good solvent properties, however we used EtOAc because is less toxic. Several sulfonation processes have been reported, including sulfonation by sulfuric acid (Shibuya et al., 1992), silver sulfate (Holboke and Pinnell, 1989), sulfur trioxide (Turbak, 1962), chlorosulfonic acid, silica sulfuric acid (Sułkowski et al., 2009) and acetyl sulfate (Kučera and Jancář, 1998). According to the literature, we compare two common methods for the PS sulfonation, liquid sulfuric acid and acetyl sulfate. In that case the protocol success was determined by the sulfonation degree eq(1) and workup treatment. The acetyl sulfate process showed the best results yielding a white solid easily isolated from the reaction crude and more stable (less hygroscopic).

Therefore, we continue with the sulfonation of both, EPS and XPS solid waste, using the acetyl sulfate process and yielding 68 % SD for XPS and 80 % SD for EPS. Afterward structural characterization was performed for the polymers, identifying main changes on the polymer chain through IR. PS's as same as SPS's, were structurally elucidated observing the main stretching vibration  $\text{SO}_3$  absorption bands at 1342, 1188 and  $1126 \text{ cm}^{-1}$  approximately according to the literature report (Martins et al., 2003). Due to the low water solubility showed by the SEPS (never affects the adsorption assays) and the pronounced vibration bands around  $1200 \text{ cm}^{-1}$ , sulfone cross linker formation ( $\text{Ar-SO}_2\text{-Ar}$ ) could be obtained (Figure 1).

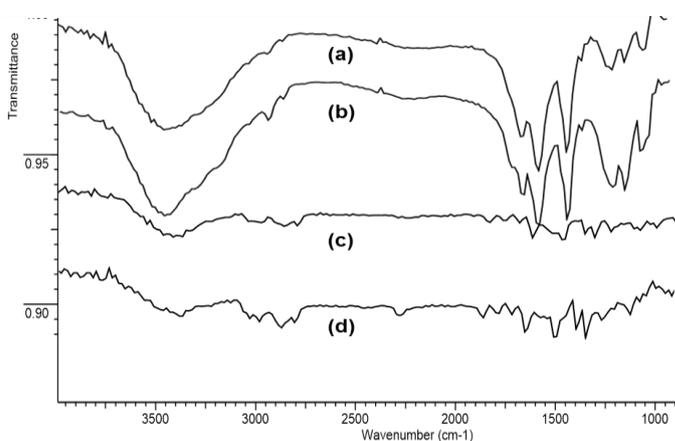


Figure 1: Polymer's Infrared spectra: (a) SEPS, (b) SXPS, (c) XPS and (d) EPS.

The structural change was also checked by  $^1\text{H}$  NMR where the aromatic region was displaced towards high chemical shift frequencies due to the  $\text{SO}_3$  inclusion (Figure 2). On the other hands the main peaks related with the aliphatic and aromatics protons were observed, however as we expected just the aromatic region was altered. An additional decoupling, like a broad signal was observed to down-field for the SEPS maybe because  $\text{SO}_3$  can be include on *para*, *orto* and *meta* benzene position, regarding to C anchored to polymer backbone. Solvent (EtOAc) and water signals were observed as well between 3.5 and 5 ppm.

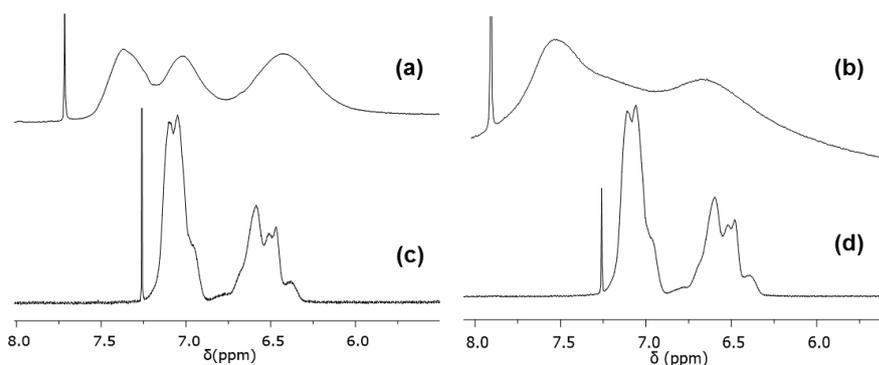


Figure 2: Aromatic region of NMR (400 Hz) spectra for (a) SEPS, (b) SXPS, (c) EPS and (d) XPS.

With sulfonated polymer in our hands we started the mineral pretreatment and the point zero charge (PZC) analysis. Due to the mineral was acquired from a real soil we washed it to avoid interference with another organic compound presents in the soil or another potential surfactant *in situ* formation. More quantity of

surfactant was determined when no mineral washing process was performed. In addition, we wanted to remove potential coating oxides over the mineral compounds and mostly presents colloids into suspension that can interfere in the static adsorption process. After mineral washing we evaluated the morphological structure using SEM experiments and checked the elemental composition by EDS (Figure 3).

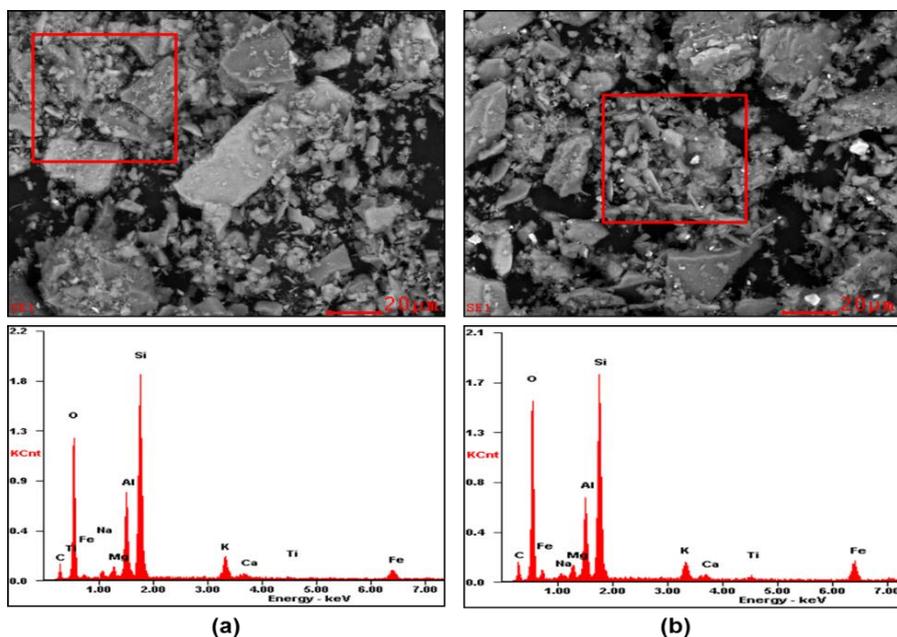


Figure 3: SEM images and EDS analysis for mineral before washing (a) and after washing (b).

According to the composition elemental analysis, percent values change slightly between these two samples, around 1-2 % wt. However, some elements like iron changed from 5 to 9 % on a random selected section. The morphological structure shows small mineral grains more free from the big ones, different than before washing mineral SEM image. In this case the small grains look like stuck on the bigger microstructures. Despite of a DRX analysis was not performed, literature report  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as the major compounds to this kind of sands (Smialek, 1991). The mineral PZC was determined through salt addition method found it around  $\text{pH} = 4.8$  and  $\text{pH} = 12$ . Between this two values the mineral have negative charges but it carries a positive one from the media, therefore it can be attracts anionic surfactants. Below 4.8 value the mineral have positive charge and carries the negative from the media (Figure 4). After pH effect analysis on the mineral surface, we performed the static adsorption test. Mostly surfactant used in cEOR process have anionic features, therefore we used SDS in the static adsorption test. In the same way, we used two SA as reference compounds, the sodium tetraborate reported as excellent SA on berea with high  $\text{SiO}_2$  percent (Azam et al., 2013) and a commercial polyacrylate with 3,500 Da of MW. This last one has showed good behaviour as SA as well, in both static and dynamic adsorption test (Shamsijazeyi et al., 2013).

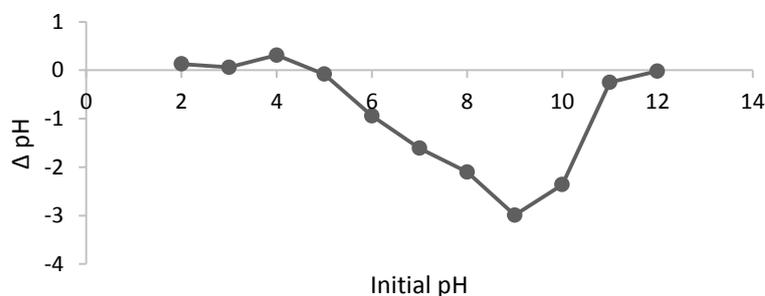


Figure 4: Mineral PZC determination through salt method addition.

SDS concentration was constant, different concentrations of SA were used (0 – 2500 ppm) and the mineral quantity was fixed for a same volume of mixture. The relationship between solution and mineral was 20 mL of

solution per 1.5 g of mineral. In addition, 1.5 % of NaCl was used to activate the mineral surface. The concentration of SDS was determined through MBAS assay before and after adsorption method and the adsorption (mg/g) was calculated employing the eq(2).

$$\text{Ads} = \frac{C_0 \times V}{W} \times (C_0 - C_f) \quad (2)$$

Where: Ads: adsorption (mg/g),  $C_0$ : initial concentration (mg/L), V: volume (L), W: mineral mass (mg),  $C_f$ : final concentration (mg/L). Calculation of adsorption were performed to pH = 9.5 for each SA (SEPS, SXPS, sodium tetraborate and sodium polyacrylate), showing good behaviors in all cases because the adsorption reduction was acquired. Despite of SA and SDS were used simultaneity, was possible to see a mineral preference by SA due to electrostatic interaction. SEPS showed better adsorption reduction than the reference compounds and SXPS. The adsorption achieved for SEPS were 73.002 mg/g, giving a 66.3 % of adsorption reduction. It activity was better than polyacrylate and tetraborate reference compounds. On the other hand, polyacrylate showed an adverse effect due to the adsorption to high concentrations (2500 ppm), probably because free polymer can interact with SDS and afford adsorption (Figure 5). Around 2000 ppm adsorption reduction is better acquired when polyacrylate is used, however, this reagent can result more expensive than PS and tetraborate.

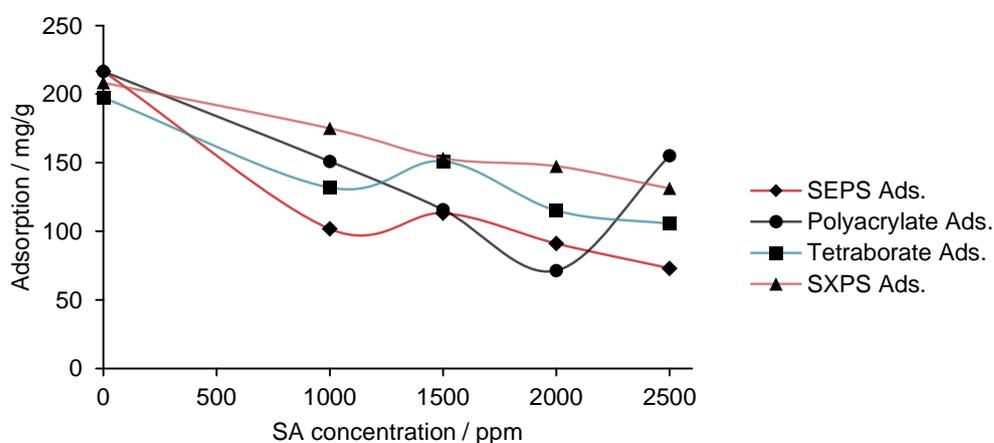


Figure 5: Adsorption curves of sulfonated polystyrenes as sacrificial agents.

#### 4. Conclusion

We obtain a sample of EPS and XPS from MSW whole mass and submit it to sulfonation process through of acetyl sulfate method. It was characterized and used as sacrificial agent in static adsorption test to check its potential application in cEOR. SPSs shown better behavior like SA than recognized tetraborate and polyacrylate, reaching adsorption reduction until 66.3 % to SEPS and 37.0 % to SXPS. It is the first clear evidence about the potential of PS solid waste as feedstock in a sulfonation process towards the synthesis of versatile sulfonated polystyrene.

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#### References

- Amianti M., Botaro V. R., 2008, Recycling of EPS: A new methodology for production of concrete impregnated with polystyrene (CIP), *Cem. Concr. Compos.* 30, 23-28.
- Azam M. R., Tan I. M., Ismail L., Mushtaq M., Nadeem M., Sagir M., 2013, Static adsorption of anionic surfactant onto crushed Berea sandstone, *J. Pet. Explor. Prod. Technol.* 3, 195-201.
- Bajdur W., Pajczkowska J., Makarucha B., Sulkowska A., Sulkowski W. W., 2002, Effective polyelectrolytes synthesised from expanded polystyrene wastes, *Eur. Polym. J.* 38, 299-304.

- Browne M. A., Dissanayake A., Galloway T. S., Lowe D. M., Thompson R. C., 2008, Ingested Microscopic Plastic Translocates to the Circulatory System of the Mussel, *Mytilus edulis* (L.), *Environ. Sci. Technol.* 42, 5026-5031.
- Budhathoki M., Hari S., Barnee R., Shiao B., Harwell J. H., 2016, Improved oil recovery by reducing surfactant adsorption with polyelectrolyte in high saline brine, *Colloids Surfaces A Physicochem. Eng. Asp.*, 498, 66-73.
- Choi N. W., Ohama Y., 2004, Development and testing of polystyrene mortars using waste EPS solution-based binders, *Constr. Build. Mater.*, 18, 235-241.
- Clesceri L. S., Greenberg A. E., Eaton A. D., 1999, Anionic Surfactants as MBAS. *En Standard Methods for the Examination of Water and Wastewater* (20th ed., pp. 1027-1033). Washington.
- Derraik J. G., 2002, The pollution of the marine environment by plastic debris: a review, *Mar. Pollut. Bull.* 44, 842-852.
- Eskander S. B., Tawfik M. E., 2011, Polymer-Cement Composite Based on Recycled Expanded Polystyrene Foam Waste, *Polym. Compos.* 1430-1438.
- Gregory, M. R. 1991, The hazards of persistent marine pollution: drift plastics and conservation islands, *J. R. Soc. New Zeal.* 21, 83-100.
- Harmer M. A., Sun Q., 2001, Solid acid catalysis using ion-exchange resins, *Appl. Catal. A Gen.* 221, 45-62.
- Herrera-Sandoval G. M., Baez-Angarita D. B., Correa-Torres S. N., Primera-Pedrozo O. M., Hernández-Rivera S. P., 2013, Novel EPS/TiO<sub>2</sub> Nanocomposite Prepared from Recycled Polystyrene, *Mater. Sci. Appl.* 4, 179-185.
- Holboke A. E., Pinnell R. P., 1989, Sulfonation of polystyrene: Preparation and characterization of an ion exchange resin in the organic laboratory, *J. Chem. Educ.* 66, 613.
- Kan A., Demirboğa R., 2009, A new technique of processing for waste-expanded polystyrene foams as aggregates, *J. Mater. Process. Technol.* 209, 2994-3000.
- Kučera F., 2001, Homogeneous and Heterogeneous Sulfonation of Polystyrene. Brno University of Technology.
- Kučera F., Jancář J., 1996, Preliminary Study of Sulfonation of Polystyrene by Homogeneous and Heterogeneous Reaction, *Chem. Pap.* 50, 224-227.
- Kučera F., Jancář J., 1998, Homogeneous and Heterogeneous Sulfonation of Polymer: A Review, *Polym. Eng. Sci.* 38, 783-792.
- Martins C. R., Ruggeri G., De Paoli M. A., 2003, Synthesis in Pilot Plant Scale and Physical Properties of Sulfonated Polystyrene, *J. Braz. Chem. Soc.* 14, 797-802.
- Mattigod S. V., Frampto J. A., Lim C. H., 1985, Effect of Ion-Pair Formation on Boron Adsorption by Kaolinite, *Clays Clay Miner.* 33, 433-437.
- Shamsijazeyi H., Hirasaki G. J., Verduzco R., 2013, Sacrificial Agent for Reducing Adsorption of Anionic Surfactants, *SPE 164061*, (April) 1-16.
- Sheng J. J., 2013, Surfactant-Polymer Flooding. *Enhanced Oil Recovery Field Case Studies*, 117-142, Gulf Professional Publishing, Elsevier, Massachusetts, USA.
- Shibuya N., Porter R. S., Shibuyal N., 1992, Kinetics of PEEK sulfonation in concentrated sulfuric acid Kinetics of PEEK Sulfonation in Concentrated Sulfuric Acid, *Macromolecules*, 25, 6495-6499.
- Shin C., 2006, Filtration application from recycled expanded polystyrene, *J. Colloid Interface Sci.* 302, 267-271.
- Shin C., Chase G. G., 2005, Nanofibers from recycle waste expanded polystyrene using natural solvent, *Polym. Bull.* 55, 209-215.
- Smialek J. L., 1991, *The Chemistry of Saudi Arabian Sand - A Deposition Problem on Helicopter Turbine Airfoils*. NASA, Cleveland, USA.
- Sułkowski W. W., Nowak K., Sułkowska A., Wolińska A., Bajdur W. M., Pentak D., Mięka B., 2009, Study of the sulfonation of expanded polystyrene waste and of properties of the products obtained, *Pure Appl. Chem.* 81, 2417-2424.
- Taguchi Y., Tanaka M., 2001, Preparation of microcapsules composed of waste-expanded polystyrene and paper fiber by semichemical recycle, *J. Appl. Polym. Sci.* 80, 2662-2669.
- Teo M. Y., Yeong H. Y., Lye S. W., 1997, Microwave moulding of expandable polystyrene foam with recycled material, *Mater. Process. Technol.* 63, 514-518.
- Turbak A. F., 1962, Polymer sulfonation without cross linking. The sulfur trioxide-phosphate system, *I&EC Prod. Res. Dev.* 1, 275-278.
- Unnikrishnan L., Nayak S. K., Mohanty S., Sarkhel G., 2010, Polyethersulfone Membranes: The Effect of Sulfonation on the Properties, *Polym. Plast. Technol. Eng.* 49, 1419-1427.
- Vodicka P., Koskinen M., Naccarati A., Oesch-Bartlomowicz B., Vodickova L., Hemminki K., Oesch F., 2006, Styrene metabolism, genotoxicity, and potential carcinogenicity, *Drug Metab. Rev.* 38, 805-53.