

Microspheres as potential fillers in composite polymeric materials

Anna Magiera^{1,*}, *Monika Kuźnia*¹, *Wojciech Jerzak*¹, *Magdalena Ziąbka*², *Radosław Lach*² and *Bartosz Handke*³

¹AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Heat Engineering and Environment Protection, 30 Mickiewiczza Av., 30-059 Krakow, Poland

²AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractories, 30 Mickiewiczza Av., 30-059 Krakow, Poland

³AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Silicates Chemistry and Molecular Compounds, 30 Mickiewiczza Av., 30-059 Krakow, Poland

Abstract. Microspheres used in our work were acquired from one of Kazakhstan coal-fueled power plant. The size of the microspheres varied between 45 and 400 μm , the median particle size (D_{50}) was 158 μm . Microscopic analysis revealed that the material consisted mainly of cenospheres. The results of elemental and oxide analysis showed that microspheres were composed of aluminosilicates. Identified crystalline phases were mullite (approx. 12 %) and trace amount of quartz (silica). Microscopic observations of the cross-sectional surface of both unmodified PUR foam and foams modified with microspheres showed a well formed, cellular structure of all materials. The observed cells are polyhedron in shape, most of them are closed, microspheres were uniformly distributed within polymer matrix and placed between cells. The apparent densities calculations of the samples showed that when microspheres were added to the polymer matrix, apparent density of the resulting composite materials increased. The results of elemental analysis pointed out the highest content of all three elements in unmodified PUR foam sample. The addition of the microspheres to the system resulted in decrease of the concentration of all three elements.

1 Introduction

The vast majority of the electricity generated in Poland is obtained from coal-fired power plants [1]. Fly ashes produced during coal combustion in conventional block contain microspheres of several morphological types. The amount of microspheres in the fly ash depends on numerous variables, like combustion technology and properties/composition of the fuel. The highest quantities of microspheres are being generated during pulverized coal

* Corresponding author: asocha@agh.edu.pl

combustion. During lignite combustion, fly ash with high calcium oxide content is being emitted.

Fly ash-derived microspheres are characterized by valuable properties from the application point of view including low density, hydrophobicity, thermal and mechanical stability [1-5]. The application of the microspheres in industry is quite common. The popularity of this material is associated with its availability and ease of acquisition. Microspheres were used in architecture, insulating and incombustible materials, composite materials and light concrete.

Considering the diversity in the distribution of elements within the fly ash, the formation of microspheres with different chemical and mineral compositions is highly probable [6-8]. The outer shell of microspheres is composed of aluminosilicates occurring in two phases, amorphous and crystalline. Glassy phase is formed by aluminum and silicon oxides, in a smaller amount by calcium and iron oxides. Crystalline phase is constituted by quartz, mullite, and in lower quantities by hematite and magnetite. The detailed chemical composition of microspheres is related to the type, composition, and quality of the fuel used in the combustion process, parameters of the process itself, type of the furnace and efficiency of the dust removal device used.

Microspheres can be a good source of a modifier of thermal properties and flame-retardant in polyurethanes production [9, 10]. Rigid polyurethane foams have been used as thermal insulation in building industry and in automotive sector [11]. Polyurethane is characterized by low density, low thermal conductivity, high abrasion resistance, good shock absorption. Unfortunately it is also a combustible material, which is particularly problematic in building industry. The use of microspheres as filler in polyurethane foams would enhance the economical aspect of production of this expensive materials.

The aim of this work was to characterize the microspheres derived from fly ash and use them as fillers in composite polymeric material. After characterization, microspheres were utilized as additives in order to obtain composite polymeric material. The polymeric matrix used was the rigid polyurethane foam. Composite foams, containing different amounts of microspheres, were prepared using one-step method, and then analyzed in order to compare the influence of the microspheres on the rigid polyurethane foam structure.

2 Materials and methods

2.1 Microspheres and their characterization

Microspheres used in our work were acquired from one of Kazakhstan coal-fueled power plant and separated from fly ash by flotation method in reservoirs. In this work microspheres were used as received, without prior preparation or sieving.

Scanning electron microscope, SEM (Nova NanoSEM 200; FEI Company, USA) was used in order to characterize the morphology and microstructure of the microspheres. Concentration and distribution of elements within the microspheres were analysed using EDS analysis (EDAX, USA). X-ray fluorescence (XRF) analysis was used in order to perform elemental analysis of the microspheres. The obtained results were converted into concentrations of oxides of the corresponding elements using Omnian software. Mineral phases present in microsphere samples were identified and quantified by X-ray diffraction (XRD) method using corundum as standard. Particle size distribution was performed using the particle size analyzer Mastersizer 2000 (Malvern Instruments, England) according to ISO 565:1990.

2.2 Preparation of rigid foams

Polyurethane rigid foams (labeled PUR) were prepared by hand casting method, using the two-component system EKOPRODUR BF5032 obtained from PCC Prodex (Poland). The adequate quantities of both polyol and isocyanate components (weight ratio 100 : 120) were mixed together and transferred into cylindrical moulds of approx. dimensions 8 × 15 cm and left under fume hood for the reaction to terminate. After 48 h samples were removed from the moulds and left in room temperature and under fume hood for further 5 days in order to eliminate the residual unreacted isocyanate component. After this time the obtained samples were analyzed. When preparing PUR rigid foams modified with microspheres, proportionate amounts (5, 10, and 15 % wt.) of the filler were stirred into polyol component prior to its mixing with isocyanate component. Further preparation steps were the same as for unmodified foams. The acquired composite foams were labelled PUR+M5p, PUR+M10p, and PUR+M15p.

2.3 Characterization of rigid foams

The cellular morphology of the obtained foams was studied using the stereoscopic microscope Keyence VHX-900F (Keyence, Japan). Samples of the materials were cut into slices of approx. thickness 0,5 cm, the optical images were taken from different areas of each sample. More detailed microscopic observations were performed using Scanning electron microscope, SEM (Nova NanoSEM 200; FEI Company, USA). Samples of the materials were cut into cubes of approx. dimensions 0,5 × 0,5 × 0,5 cm, coated with gold, and analyzed using an acceleration of 10 kV. Apparent densities of the samples were calculated based on foams' weight and dimensions. Samples were cut into cylinders of approx. diameter 5 cm and height 10 cm, then weighted using analytical weight. Elemental analysis of the obtained materials was carried as well using LECO CHN628 Series (LECO Corporation, USA). The content of carbon, hydrogen, and nitrogen in the samples were analyzed.

3 Results and discussion

3.1 Structure and composition of microspheres

The results of particle size distribution analysis are presented in the Figure 1(a). The size of the microspheres in the sample varied between 45 and 400 μm. The median particle size (D_{50}) was 158 μm, 90 % of microspheres in the sample (D_{90}) were smaller than 266 μm. Only 10 % of microspheres (D_{10}) had diameters below 90 μm, which indicate they were rather coarse-grained material.

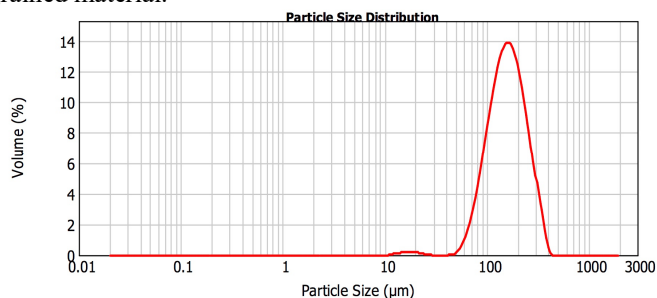


Fig 1 (a) Granulometric analysis of microspheres

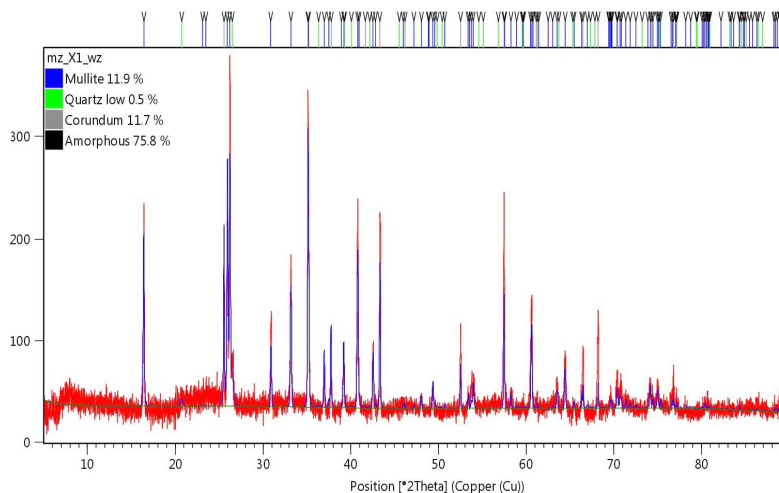


Fig. 1. (b) XRD diffractogram pattern of microspheres' sample.

Scanning electron microscope (SEM) microphotographs (Figure 2) illustrate the structure and morphology of microspheres. It can be seen that the microspheres were mainly cenospheres, some of them contained pores of different sizes. Their surface was therefore coarse. Plerospheres were not observed in the analyzed sample.

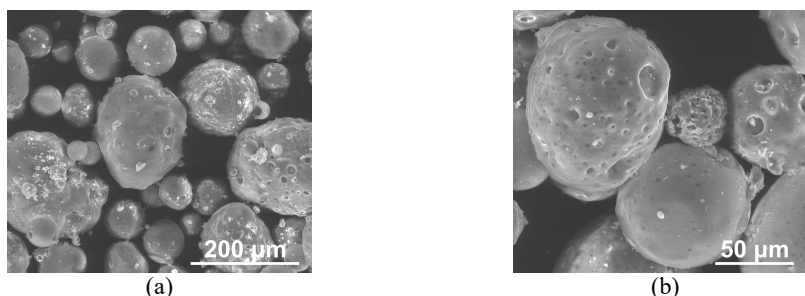


Fig. 2. SEM microphotographs of microspheres. Magnitudes (a) $\times 350$ and (b) $\times 1000$.

The results of elemental and oxide analysis performed using EDS analyzer are given in Table 1. Microspheres were composed mainly of O, Si, and Al, which indicated the presence of aluminosilicates (as was already mentioned in the literature [6-8]). The remaining elements detected were Ti, Fe, Ca, K, and Na. The concentration of none of these elements exceeded 1 % wt. The concentrations of oxides matched the contents of elements, microspheres were formed principally of silica, SiO_2 and alumina, Al_2O_3 .

Table 1. Elemental and oxide analysis of microspheres (SEM/EDS method).

Element	Content, % wt.	Oxide	Content, % wt.
O	45,64	-	-
Si	29,09	SiO ₂	57,20
Al	21,59	Al ₂ O ₃	37,92
Ti	0,93	TiO ₂	1,38
Fe	0,87	Fe ₂ O ₃	1,18
Ca	0,73	CaO	0,93
K	0,64	K ₂ O	0,72
Na	0,52	Na ₂ O	0,67

Microspheres' composition, calculated using XRF technique, is presented in Table 2. They largely correlate with SEM/EDS data, however XRF method is more detailed. The data shown supports the already formulated conclusion that microspheres were mainly composed of aluminosilicates (high Si/SiO₂ and Al/Al₂O₃ content). Other elements and their oxides constituted insignificant addition.

Table 2. Elemental and oxide analysis of microspheres (XRF method).

Element	Content, % wt.	Oxide	Content, % wt.
O	49,30	-	-
Si	24,69	SiO ₂	52,83
Al	21,12	Al ₂ O ₃	39,31
Ca	1,02	CaO	1,42
Fe	0,98	Fe ₂ O ₃	1,41
Ti	0,73	TiO ₂	1,22
P	0,44	P ₂ O ₅	1,02
K	0,42	K ₂ O	0,50
Na	0,34	Na ₂ O	0,46
As	0,25	As ₂ O ₃	0,33
Ba	0,24	BaO	0,26
Mg	0,17	MgO	0,27
Sr	0,10	SrO	0,12

The XRD diffractogram pattern of microspheres' sample is presented in the Figure 1(b). As can be seen, microspheres composed principally of amorphous phase. Identified crystalline phases were mullite (aluminosilicate; approx. 12 %) and trace amount of quartz (silica; below 1 %).

3.1 Structure of composite polyurethane foams

Figure 3(a) shows the optical microphotograph of the cross-sectional surface of unmodified PUR foam and presents a well formed, cellular structure. The observed cells are polyhedron in shape, most of them are closed. The high content of closed cells is an important parameter influencing thermal insulation properties of the PUR foams [12-14]. SEM microphotographs of the cross-sectional surface of PUR foam (Figures 3(b) and 3(c)) show slight disruption of the cellular structure, which could be attributed to the coating with gold process or cutting into slices, which was the primary step of preparation of the samples for measurements. Alternative approach of the samples preparation should be considered in future analysis e.g. cryogenic fracturing.

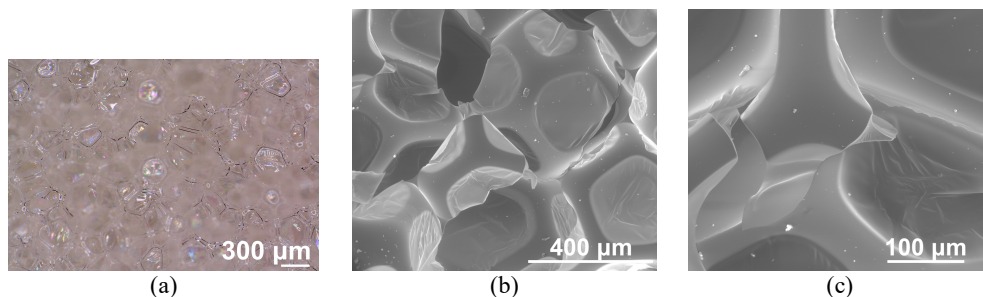


Fig. 3. Optical (a) and SEM microphotographs (b-c) of the cross-sectional surface of PUR foam. Magnitudes $\times 100$ (a), $\times 200$ (b), and $\times 500$ (c).

Optical microphotographs of the cross-sectional surfaces of PUR foams modified with different amount of microspheres are given in the Figure 4. It can be seen that the addition of microspheres did not disrupt cellular structure of the PUR material. The majority of the cells were still closed, however slight decrease in this parameter could be observed when compared to pristine PUR material. The size of the microspheres used varied between 45 and 400 μm, so they were relatively heterogeneous filler. Some bigger elements could impair the PUR cellular structure resulting in cell walls' opening [9, 11]. The shape of the cells remained polyhedron, microspheres were uniformly distributed within polymer matrix (even up to 15 % wt.), and placed between cells (Figure 4 - middle and right column).

The apparent densities of the samples, calculated based on foams' weight and dimensions, are listed in Table 3. The lowest value of density was estimated for unmodified PUR foam. When microspheres were added to the polymer matrix, apparent density of the resulting composite materials increased. The augmentation in this parameter was correlated with microspheres content in the foam. The highest density value (approx. 57 kg m^{-3}) was calculated for sample modified with 15 % wt. of microspheres, which could imply overloading of the system with the filler and hindered foam formation.

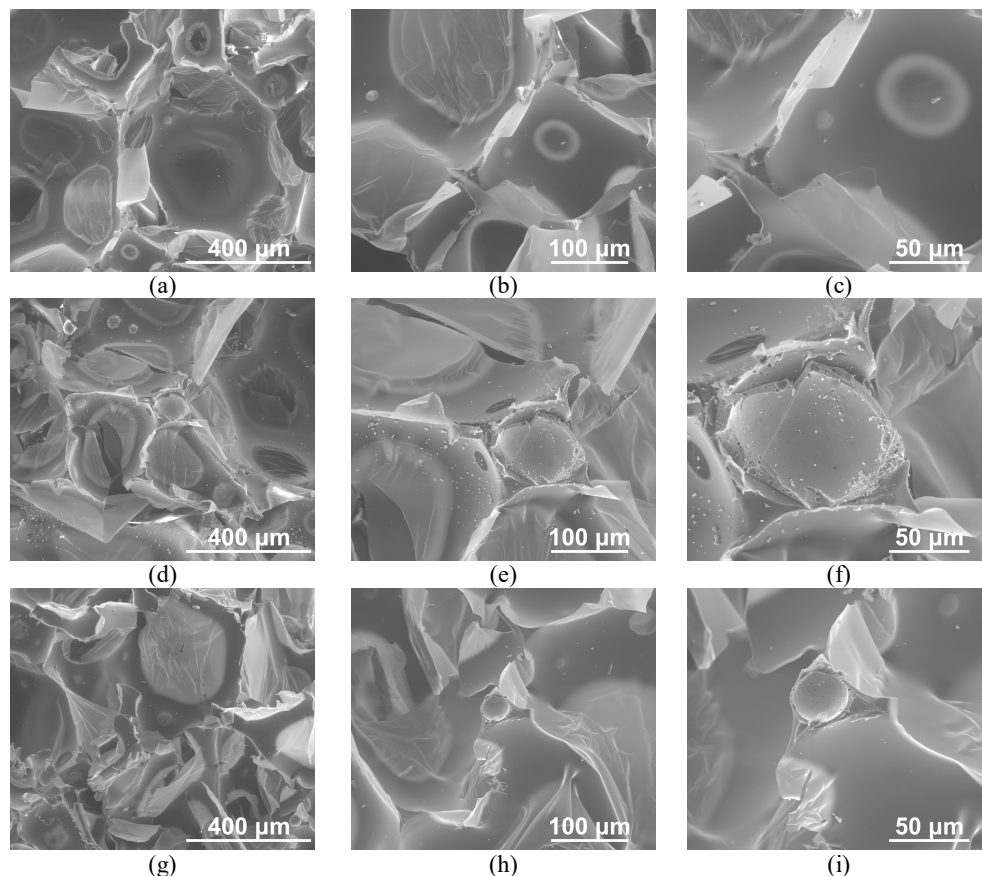


Fig. 4. SEM microphotographs of the cross-sectional surfaces of PUR foams modified with 5 (a-c), 10 (d-f), and 15% wt. of microspheres (g-i). Magnitudes $\times 200$ (left), $\times 500$ (middle), and $\times 1000$ (right column).

Table 3. Elemental analysis and apparent density measurement results of the PUR foams.

Sample name	N content, %	C content, %	H content, %	Apparent density, kg m^{-3}
PUR	5,57	63,70	8,72	46,51
PUR+M5p	4,35	54,17	7,30	47,02
PUR+M10p	4,36	54,60	7,34	49,39
PUR+M15p	4,36	54,42	7,30	57,12

The results of elemental analysis of the obtained materials are presented in Table 3. The highest content of all three elements was measured for unmodified PUR foam. The addition of the microspheres to the system resulted in decrease of the concentration of all three elements. The most significant change concerned the concentration of carbon. However, the change in the amount of microspheres added to polymer matrix did not implied the proportional gradual change in elemental analysis - the concentration of the elements remained practically constant.

4 Conclusions

The aim of this work was to characterize the microspheres derived from fly ash and use them as fillers in composite polymeric material. Our goal would be the enhancement of thermal and flame-retardant properties of the rigid polyurethane foam, used as insulating material in building industry.

The results presented in this paper indicate that polyurethane foams modified with microspheres are promising composite materials with application potential as thermal insulating materials in building industry. Microspheres, composed mainly of aluminosilicates, were uniformly distributed within polymer matrix and did not disrupt cellular structure of the PUR foam. However, more detailed experiments must be carried out in order to support this conclusion. For further examination of the system presented, thermal analysis was to be carried out using differential scanning calorimeter (DSC). What is more, in order to evaluate the thermal stability of the obtained materials, thermogravimetric analysis (TGA) has to be performed as well. Mechanical testing should be performed as well in order to estimate the strength and mechanical handiness of the obtained materials. Thermal conductivity experiments should be carried out as well in order to evaluate the influence of microspheres modification on thermal insulation properties of PUR rigid foam matrix.

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