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USE OF MINERAL WASTE IN THE PRODUCTION OF POLYMER COMPOSITES*

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Abstract

The study focuses on the use of aluminosilicate microspheres isolated from ash waste in the polymer industry, which significantly contributes to waste management to produce competitively sought after products. New formulation formulations have been developed and technological parameters have been established for the extrusion production of polymer composites with high physical-mechanical and operational properties.
The main advantages of the new materials are high strength values when filled with 50% by weight, as well as durability during freezing and aging in saline.
The studied composite can be used in various fields as a structural material, since it has a lower cost compared to analogues due to the use of industrial waste up to 50% by weight in the composition.

Keywords: microspheres, ash and slag waste, polymer composite, functional filler

1. Introduction

On the territory of the Baikal region of the Russian Federation there are a number of industrial enterprises that form large-tonnage mineral waste, which occupy vast areas for dumps and tailings. These are mining enterprises, concentration plants, factories for the production of aluminum and silicon, as well as heat power enterprises. In 2017, more than 130 million tons of waste was generated in the Irkutsk region, of which over 17 million tons

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are not subject to use and processing, but are sent for storage and disposal, therefore, another problem arises: land acquisition for waste disposal.

One of the main sources of industrial waste generation in the region is the enterprises of the fuel and energy complex. As a result of the activities of thermal power plants in the Irkutsk Region in 2017, 1300 thousand tons of bottom ash mixtures (BAM) were formed, about 600 thousand m^3 were utilized, while a significant part of BAM is sent for disposal to ash dumps, which are currently close to overflow. Therefore, the issue of bottom ash utilization is very urgent in the region, either new ash dumps are needed, or the capacity of existing ash dumps is increased by increasing the dam, or look for ways to use bottom ash waste as raw materials for the production of commercial products.

Dispersed mineral waste can be used as additives to concrete, clay and bricks; preparation of the foundations of roads; for repair of roads, airfields, bridges; when installing floors resistant to acid, in chemical shops, livestock complexes, metallurgical industries. In addition, fly ash can be successfully used as an effective filler of composite materials based on polymers, for example, polyvinyl chloride (. Composites with a thermoplastic matrix filled with fly ash can be used to produce building materials, automobile parts, railway sleepers, and consumer goods. Together with ash, ash aluminosilicate microspheres isolated from bottom ash waste can be used. Obtaining microspheres is a simple process and inexpensive process. At the same time, the filling of polymers with microspheres allows one to obtain new properties of produced composite materials, such as lower density, better processability during extrusion and molding (Katz and Milewski, 1987). One of the most significant advantages of these materials is their fire resistance, including due to their high filling (Borken et al., 2011; Simonov-Emelyanov et al., 2011, 2012).

The main objective of the study is the utilization of electric power industry waste as a result of their use as a filler in polymer compositions for the production of building materials.

For this, the following tasks were solved:

- The characteristics that are the criteria for the applicability of the material as fillers of the polymer matrix are identified
- Studies have been conducted to study these indicators in industrial waste used as a filler, and their results are presented.
- Tests of a composite material filled with various amounts of industrial waste were completed.
- The potential of using bottom ash waste in composite materials for their disposal were estimated.

This work consists of two main parts:

- determination of the criteria for the applicability of aluminosilicate microspheres as functional fillers of the polyvinyl chloride composition. The character of the size distribution of microsphere particles, particle shape, particle packing density, specific surface area index, weight average diameter, true and bulk density were studied;
- determination of the properties of the obtained polymer composites filled with aluminosilicate ash microspheres. The compressive, tensile and bending strengths of composite materials, their resistance to salt solution, and frost resistance have been established.

2. Materials and methods

The objects of study were dispersed fillers - technogenic waste from the energy industry, as well as rigid polyvinyl chloride compositions filled with them. The following finely dispersed materials were used as fillers:

– aluminosilicate microspheres isolated from bottom ash materials of TPP.

Laboratory studies of the samples made it possible to establish the values of the main characteristics of ash aluminosilicate microspheres that affect the processing of the polymer-mineral composition and the strength properties of the materials obtained. The analysis of the particle size distribution of the material, microscopy, chemical analysis, tests of physical and mechanical properties, studies of the resistance of the material to external influences.

3. Results and discussion

The study of particle shape is important, since this indicator affects the structure, properties and technological parameters of the preparation of polymer composites. The finely dispersed large-tonnage mineral industrial wastes under study are of a different nature, ash-aluminosilicate microspheres were formed as a result of burning coal at a thermal power station. Fig. 1 shows microphotographs of samples made on a double-beam scanning microscope (multi-beam system) JIB-4500 in the research laboratory of electron microscopy of the Irkutsk National Research Technical University (INRTU).

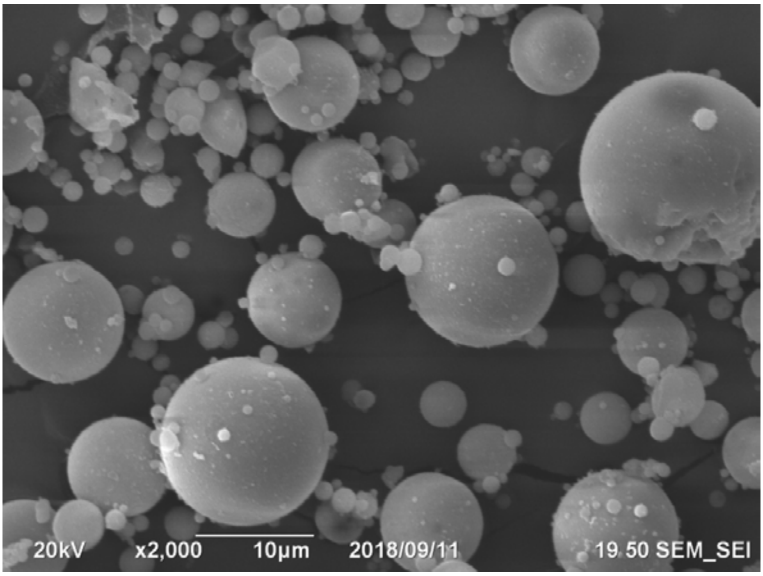


Fig. 1. A sample of aluminosilicate microspheres

In the electron microscope photographs, the particles of the microspheres have a regular spherical shape with sizes from 2 to 10 microns, among which there are destroyed spherical particles with sizes up to 15 microns and a small part of round particles of irregular shape of various sizes. However, the particle size of the microspheres has higher values, which is proved by the analysis of the particle size distribution below. The high packing density of the microsphere particles is also confirmed by their different diameters (Fig. 1).

The particle size distribution of the studied fillers was analyzed on a Fritsch Analysette 22 MicroTec Plus laser granulometer from Germany, Fritsch, manufactured in Germany, at the Research Laboratory of Physicochemical Investigations of Metallurgical Processes at INRTU. The results of determining the particle size distribution of aluminosilicate ash microspheres are presented on Fig. 2.

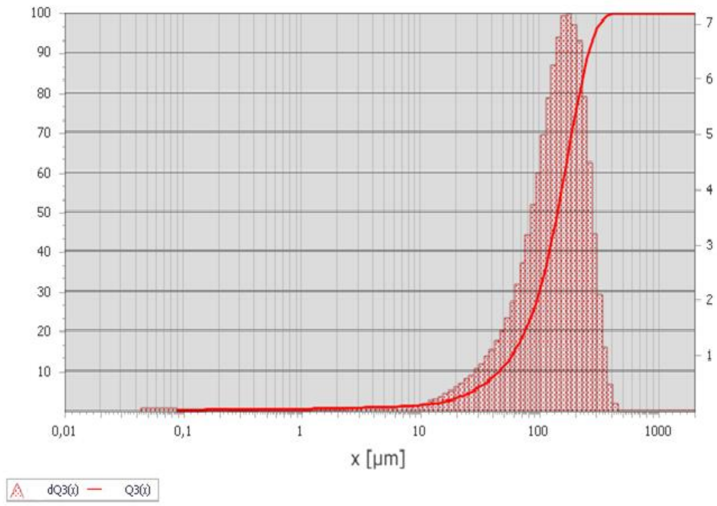


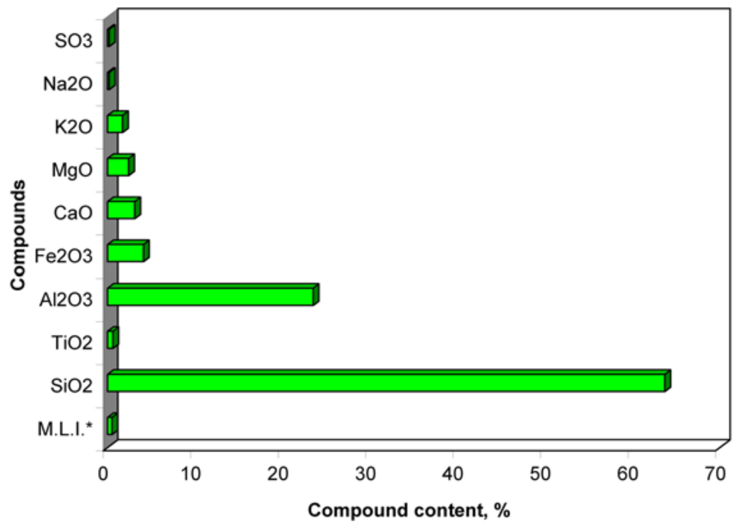
Fig. 2. Particle size distribution of aluminosilicate microspheres

The granulometric characteristic of the sample shows that the microspheres have a less wide range of sizes compared to fly ash (Zelinskaya et al., 2019). This is characteristic of this material under study, since mostly the largest, hollow, spherical particles are distinguished. Aluminosilicate microspheres with a narrower particle size distribution consist mostly of a particle size class of 100-300 microns. The material contains mainly large spheres with a diameter of 100-300 µm, but particles up to 500 µm are also present, which indicates a higher particle size of bottom ash particles of the ash removal channel compared to fly ash removed from the electrostatic precipitators by the dry method.

The studied waste samples have a wide range of particle size distribution and have a suitable particle size distribution, which affects the strength characteristics of the resulting composites. In addition, the studied fillers contain both small and large fractions, therefore, such a particle size distribution will have a positive effect on the rheological properties, as well as on the structure of the resulting material (Duretek, 2015). Since the viscosity of the composition is one of the decisive parameters when choosing a filler, especially for extrusion and injection molding methods, the studied fillers satisfy this criterion (Hesser et al., 2015; Kulkarni et al., 2014).

Chemical analysis: the use of aluminosilicate ash microspheres in the production of building materials in terms of composition is possible if the content of toxic components and radiation safety will meet the requirements of the standards. Chemical analysis of fly ash is shown in the diagram (Fig. 3).

The composition of the studied material is multicomponent and relatively uniform, closest to aluminosilicates, due to the high content of silicon and aluminum oxides up to 90%, of which about two thirds are silicon oxides. Microspheres have almost no unburned particles, in which, as a rule, harmful organic components are concentrated. Known mineral fillers used in polymer compositions do not contain a large number of components, but are mainly represented by one of the minerals: mullite, quartz, kaolin, feldspar, talc, glass, etc. The studied microspheres consist of crystalline (mullite, quartz, feldspars, and some others) and an amorphous phase (glass).



* mass loss ignition

Fig. 3. Percentage of elements in fly ash in terms of oxides

Spectral analysis according to the method (1.80) of NSAM No. 246-C of fly ash was carried out in the Central Control Center of the Baikal branch of Sosnovgeologiya JSC Urangeo. In addition to the above macroelements, the studied material contains only trace concentrations of trace elements or impurity elements (Ni, Co, Cr, Pb, Sn, Zn, Mo, Zr, Ge, Cu, Ag, Zn, Be, Sc, Ga, La, Y, Ba, Sr, Li, B). Chemical analysis of the material did not reveal toxic components, namely, heavy metals (copper, zinc, nickel, lead, chromium, cobalt, cadmium, mercury) and arsenic, or their trace concentrations. In addition, the studied aluminosilicate microspheres consist of minerals that are used as fillers in polymer composites and are suitable for use in chemical composition.

The moisture content of the raw materials from which the polymer composites are obtained is an important parameter for processing on an extrusion line, injection molding, calendaring and other methods for producing thermoplastic composites. Ash aluminosilicate microspheres after their extraction from the ash are dried and have a moisture content of up to 1%. The moisture content of the studied mineral fillers meets the technical requirements of the extrusion process. Radioactivity. The radiation safety criterion for the possibility of using building materials is the indicator of the specific effective activity of natural radionuclides (NRN) according to GOST 30108-94 “Building materials and products”. The radiation safety requirement is also included in the standards for raw materials for the production of building materials.

The specific effective NRN activity of fly ash was determined in the above-mentioned SAL of BF “Sosnovgeologiya”. The indicator was measured by a low-background gamma-spectrometric setup based on Gamma-plus № 030 and a detection unit — a scintillation unit based on NaO (Ti) in accordance with GOST 30108-94. The microspheres have an effective specific activity NRN equal to 253 Bq / kg. According to the radiation safety standards of the Russian Federation, this indicator does not exceed the normative 370 Bq/kg, the material belongs to the first class, which makes it possible to use it in the production of composite materials for all constructed and reconstructed residential and public buildings. Thus, the analysis of all the necessary properties of aluminosilicate microspheres confirms the fundamental possibility of their application to obtain polymer composites. Technology for producing composite materials.

Experimental studies on the preparation of polymer composites filled with fly ash and aluminosilicate microspheres were carried out on an extrusion line for the production of polyvinyl chloride profiles (model SJZ55/110YF300, made in China) based on the Technopark FSBEI HE "INRTU". Suspension polyvinyl chloride grade SI-64 manufactured by JSC «Sayanskkhimplast» was used as a binding matrix. This thermoplastic has a relatively low Fikentcher constant, which can make it possible to achieve a higher content of mineral particles, in comparison with other brands of polyvinyl chloride. Technological additives were also used: heat and light stabilizers, processability modifiers, internal and external lubricants, pigments.

Preparation of the dry mixture for the extruder was carried out in a high-speed two-stage turbo mixer, all technological additives, a binder and a filler were simultaneously loaded into the mixer. In the process of producing composites on an extruder, technological parameters were selected: the temperature of the extruder zones to obtain a product of proper quality. In total, over 20 formulations with various contents of technological additives and filler were extruded. For studies, composites were selected whose composition contained 40% and 50% filler by weight. During a series of experiments, optimal parameters were selected to obtain a polymer composite of various formulations. To obtain products, two extruder forming tools (dies) were used, which made it possible to obtain a terrace board for flooring and floor coverings and a lag for its installation (photo of types of products in Fig. 4).

a) b)

Fig. 4. Products from a polymer composite:
a) lag; b) terrace board

Studies of the mechanical properties of the obtained composite materials. Physical and mechanical characteristics of the materials obtained were determined on the basis of the research laboratory for testing building materials and structures at INRTU (Fig. 5). The experiments were carried out on an Instron® 5989 universal electromechanical testing machine; the compressive, tensile, and bending strengths of the samples were tested.

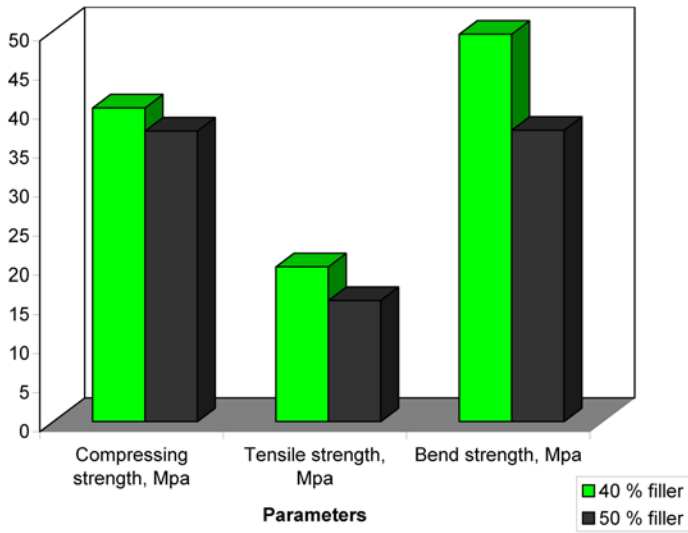


Fig. 5. Average values of physico-mechanical characteristics of composite materials with different contents

The results of the study showed that the best average values of compressive strength and tensile strength have samples filled with microspheres in an amount of 40% by mass, however, even with 50% filling, these values are at a high level for polymer composites. High strength indices are explained by the presence of dense packing of particles in the composite and the stronger interaction of the filler and the polymer binder, due to the high specific surface and the resulting polymer-filler boundary layer. The use of a high degree of filling with microspheres is effective in the case when the obtained mechanical properties of the material are acceptable, and an important indicator is the low density of the composite.

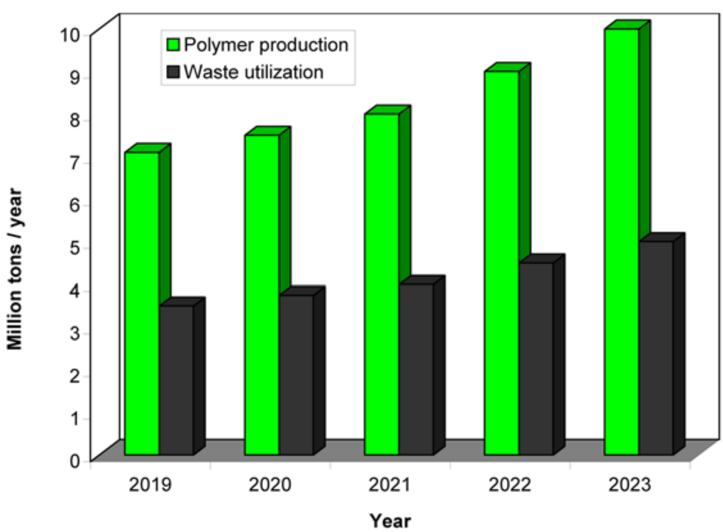


Fig. 6. The volume of possible utilization of bottom ash waste from Russia when they are used as filler for large-capacity polymers produced at 50% content in the composition

In this case, the use of ash microspheres is economically viable, even with a slight loss in the physical and mechanical characteristics of the resulting composites. Studies of the developed polymer-mineral composite material on the effect of UV radiation, resistance to salt solutions, frost resistance were carried out, as a result it was revealed that the material meets the requirements of these tests, this confirms its durability and the possibility of operation in various climatic conditions. Fig. 6 presents a diagram showing the potential use of waste heat from Russia with their 50% use in the manufacture of polymer products.

Fig. 6 indicates the prospects for the use of bottom ash waste accumulated in the Russian Federation in the amount of 80 million tons as functional filler of polymer composite materials. Disposal if used correctly will amount to millions of tons per year. The economic efficiency of using filler based on industrial waste is also important, 50% of the content of almost free material will significantly reduce production costs and reduce the consumption of expensive polymer resins made from hydrocarbons, which will also positively affect the environmental situation. It is estimated that even the use of 15% bottom ash waste by weight in the annual produced amount of polymers in Russia will be able to utilize the annual generated volume of such waste (Tskhovrebov and Velichko, 2014).

4. Concluding remarks

Experimental and laboratory methods have proven the effectiveness of using technogenic energy raw materials - aluminosilicate microspheres isolated from bottom ash waste as functional fillers of polymer composite building materials. This is confirmed both by studies of the characteristics of the dispersed filler particles themselves, and by testing the mechanical and operational properties of the developed materials.

The main advantages of the new materials are high strength values when filled with 50% by weight, as well as durability during freezing and aging in saline. New formulation formulations have been developed and technological parameters have been established for the extrusion production of polymer composites with high physical-mechanical and operational properties.

The use of microspheres in the polymer industry significantly contributes to the disposal of bottom ash waste with obtaining competitively demanded products. The studied composite can be used in various fields as a structural material, since it has a lower cost compared to analogues due to the use of industrial waste up to 50% by weight in the composition.

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