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Light heat-resistant polymer concretes based on oligooxyhydridesilmethylensiloxysilane and hollow spherical fillers

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Abstract. Novel type of light heat-resistant polymer concretes was developed on the basis of oligooxyhydridesilmethylensiloxysilane with hollow glass or ceramic microspheres. Adding hollow glass and ceramic microspheres being waste products from thermal power plants operating on solid fuels allowed developing reasonably priced materials and reducing potential environmental pollution. For optimization of production technology, the curing and molding conditions of materials were studied. According to impact strength changes, the optimal curing mode for the composites was at 480–515 K for 4.25–4.5 hours depending on the filler type and binder content. It was stated that used organic-silicon binder provided thermal resistance and high strength characteristics of the composite material. In comparison with traditional silicone resins, the compressive strength value of the developed materials increased by almost two times and the modulus of elasticity increased by almost an order of magnitude. Due to the interaction of aluminum hydroxide groups of ceramic microspheres with organosilicon polymer, Young's modulus of the materials filled by ceramic microspheres was higher by 20–30 % than that of the concretes with glass microspheres. Consequently, enhanced physical and mechanical properties expand possibilities of using these materials under exposure of significant external static loads.

1. Introduction

Many recent studies have focused on physical, mechanical and thermal properties of different types of concrete [1–4]. Fiber reinforcement is commonly used in order to increase strength and tensile-deformation properties of concretes [5]. Introduction of hydrosilicates additives [6] allows to increase the water and frost resistance of materials. Lightweight concretes containing fillers or pores are characterized by improved heat-insulating properties [7, 8].

The filling of mineral binders with hollow microspheres with particle ranging in size from units to several hundred micrometers has been known for a relatively long time. Despite low density and acceptable thermal conductivity, they are characterized by low impact strength. In addition, a major drawback of such materials is their low chemical resistance to aggressive natural and technogenic factors, such as acid rain and carbon dioxide, which limits their use in construction. The polymeric binders can be a promising alternative to the mineral binders.

Light polymer concretes (LPC) comprised of hollow microspheres fastened by mineral or organic bindings are promising materials for thermal insulation with enhanced physical-mechanical properties, in particular, increased impact strength. Most polymeric materials are resistant to acid and alkaline reagents,

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characterized by high adhesive characteristics to the filler particles surface. However, they have several disadvantages, such as low thermal stability and susceptibility to degradation by ultraviolet radiation. In this regard, much attention is drawn to the polymer concretes based on siloxane binders.

The composites based on the hollow inorganic microspheres and silicone polymeric binders with a siloxane main chain were described in the previous works [9–12]. The weaknesses of these thermal insulation materials are their relatively low tensile strength and low thermal stability. The long-term operation temperature of composites with the most common polymethylphenylsiloxane binder does not exceed 250°C, after which a catastrophic loss of tensile strength is observed [13–15]. Fundamentally, new silicon-organic binders containing siloxane and carbosilane units in the main chain are used to increase tensile strength and thermal stability of ceramic microspheres (CM) [16–18]. Under heating, such polymer changes into the ladder structure characterized by the increased tensile strength and thermal stability up to 400°C. Considering that the initial polymer contains a heat-resistant filler, as a result of heat treatment a composite material with high strength characteristics is formed.

This work was devoted to the novel light polymer concretes based on a novel class of silicon-organic polymer oligooxyhydridesilmethylenesiloxysilan (OHSMS) with hollow glass and ceramic microspheres. Based on the fact that ceramic microspheres are the products of smoke emissions of solid-fuel power plants, using waste products as the fillers for the composites under investigation allowed to develop a reasonably priced material and to reduce potential environmental pollution. The materials of this type can be used in the construction of facilities operating at elevated temperatures under aggressive environment and exposure of ionizing radiation, for example, in the construction of conventional and nuclear power plants, chemical production facilities.

The main goal of this research was to study the mechanism of interaction of the binder and the polymer, as well as to examine the physical-mechanical properties and behavior of the developed materials under deformation. The results of this research can be used for developing a new group of polymer concretes with high strength characteristics and resistance to shock loads, thermal effects, chemicals and all types of radiation.

2. Materials and Methods

Hollow glass microspheres (HGM) and hollow ceramic microspheres (HCM), referred to cenospheres, obtained by the flotation processing of fume emissions from the thermal power plants operating on solid fuels, specifically on the Kuzbass coal, were used as fillers. The cenospheres had the following composition: 57 % SiO₂, 28 % Al₂O₃, the rest oxides CaO, MgO, Na₂O, Fe₂O₃. In comparison with HGM filler, the fractional composition of HCM is characterized by the larger fractions. Taking into account the low content of HCM float fraction and the necessity of the further utilization of the separated small fractions, the additional fraction separation of HCM is not economically and environmentally justifiable. For this research, HCM were used as a filler without additional fractionation.

Varnish VKL-1 TU 6-05-64-101–85 was used as a binding agent. The main component of this agent is oligooxyhydridesilmethylenesiloxysilan (OHSMS), which contains carbosilane and silane bonds in addition to siloxane bonds. OHSMS was obtained by the esterification reaction of the high-boiling fraction of the direct synthesis of methylchlorosilanes and was used as a solution in the organic solvents [19].

The technology of sample preparation included several stages. At the first stage, in order to achieve the consistency of “wet sand” mixing the binding agent with HGM or HCM was conducted with a rotation speed of 45 rpm by an open low-speed laboratory mixer with a capacity of 0.1 m³ and a frame mixer. In the cases of mixing at elevated temperatures, the mixer with the composite content was placed in an oil bath. Temperature control and adjustments were carried out by the PEX controller REX100. Mixing modes temperature and time are given in Table 1. Then, the composite samples were molded under pressure from 0.05 to 0.5 MPa in the metal molds with an internal sizes of 30×30×30 mm for compression tests and 80×10×4 for impact tests, followed by heat treatment according to the modes indicated by the Box–Behnken design.

The complex of physical and mechanical properties of the obtained composite samples were investigated according to the standard methods. Analysis of compression strength and modulus of elasticity was carried out by a specialized machine Instron Model 4206 (Germany) in accordance with standard ISO 604:2002 at room temperature on cubic samples with a loading speed of 1 mm/min. Izod impact strength of the materials was determined by a pendulum machine GOTECH GT-7045-MDL (Taiwan) in accordance with standard ISO 1268-4:2005.

3. Results and Discussion

The properties of polymer concretes are determined by a set of factors, including chemical composition and structure of polymer matrix (binding agent) [20]. Oligooxyhydridesilmethylenesiloxysilan (OHSMS) used as a binding agent has the following chemical formula:

$$\begin{aligned} & \left[(\text{OH})_{n_1} (\text{CH}_3)_{3-n_1} \text{SiO}_2 \right]_n \times \left[(\text{CH}_3)_{m_1} \text{H}_{2-m_1} \text{SiO}_{m_2} \right]_m \times \left[(\text{CH}_3)_{k_1} \text{H}_{2-k_1} \text{SiCH}_2 \right]_k \times \\ & \times \left[(\text{CH}_3)_{l_1} \text{H}_{2-l_1} \text{SiSiH}_{2l_2} (\text{CH}_3)_{l_2} \right]_l \times \left[\text{O}_{p_2} \text{Si} (\text{CH}_3)_{p_1} \right]_p \times \left[\text{O}_{q_2} \text{Si} (\text{CH}_3)_{3-q_1} (\text{OH})_{q_1} \right]_q \end{aligned} \quad (1)$$

where $n, m, k, l, p, q = 1 \div 4$; $m_1, k_1, l_1, l_2, p_1 = 1 \div 2$; $m_2, p_2 = 1 \div 1.5$; $n_2, q_2 = 1$; $n_1, q_1 = 0 \div 1$.

To determine the optimal technological conditions of obtaining materials, the processes of curing and molding were studied comprehensively. Curing of OHSMS apparently occurs due to the presence of both reactive hydroxyl groups and hydride radicals. Considering the chemical structure of OHSMS, it can be assumed that intensive processes of oligomer curing take place only under the conditions of increased temperatures. The kinetics of the OHSMS curing was defined by the degree of the oligomer curing.

The degree of OHSMS crosslinking (Figure 1) was determined by a residual amount of the fraction dissolved in organic solvent by means of a Soxhlet apparatus. It was stated that nearly 100 % of the oligomer crosslinking was occurred at a temperature of 513 K and a curing time of 6 hours.

After primary investigation, the selection of optimal processing modes of curing was performed. The scheme of obtaining LPC based on OHSMS as a binder was as follows: mixing of OHSMS and microspheres to the consistency of "wet sand", molding of products under pressure, at which the required packing density of microspheres of approximately 60 % is achieved, and subsequent heat treatment. The developed processing method allows to obtain LPC with a volume fraction of the binder not more than 25 vol.%. This is associated with a sharp decrease in the number of open pores in the material and the subsequent hindered penetration of organic solvent.

Table 1 gives the modes of obtaining products from LPC by molding materials under low pressure. The relatively long time and increased temperature during the process of components mixing were determined by a poor solubility of OHSMS in organic solvents (12.5 %) and by the necessity for their subsequent removal to achieve "wet sand" consistency.

Table 1. Modes of obtaining LPC filled by HGM and HCM (curing temperature 423 K, time 2 hours).

Filler type	Composition (wt.%)		Volume fraction of binding agent (%)	Blending mode		Exposure to air (hours)	Packed density (kg/m ³)
	Filler	Binding agent (solid residue)		Time (min)	Temperature (K)		
HGM	65	35	5	10	289	1	257
HGM	60	40	10	20	333	3	294
HGM	55	45	15	40	353	6	372
HGM	50	50	20	60	353	24	401
HGM	45	55	25	90	353	48	462
HCM	75	25	5	10	289	1	361
HCM	70	30	10	20	333	3	416
HCM	65	35	15	40	353	6	474
HCM	60	40	20	60	353	24	514
HCM	55	45	25	90	353	48	578

As the composition reached the consistency of «wet sand», it was placed in a mold and was subjected to layer-by-layer molding under low pressure until the maximum packed density of microspheres was reached (0.6 for HGM and 0.66 for HCM). The maximum packed density was controlled by the values of constant packed density of the material regardless of the molding pressure (Figure 2).

The results of this study showed that a minimal pressure for achieving the required fullness volume coefficient was 0.4 MPa for the composites with HCM and 0.25 MPa for the composites with HGM. Further increase in pressure could cause destruction of the hollow shells of microspheres.

After molding and before heat treating composite materials were kept in an open mold block in accordance with the modes given in Table 1. This operation allowed to foam concrete during heat treatment due to an excessive unextracted solvent. The preliminary curing temperature of 423 K was not optimal, since it was obviously insufficient for the complete crosslinking of OHSMS.

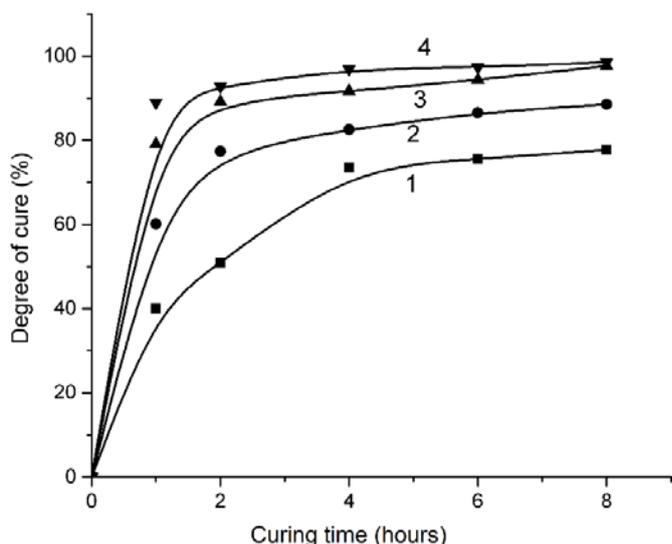


Figure 1. Dependence of the bonding agent (OHSMS) curing degree on the curing time and temperature:
1 – 433 K, 2 – 473 K, 3 – 513 K, 4 – 553 K.

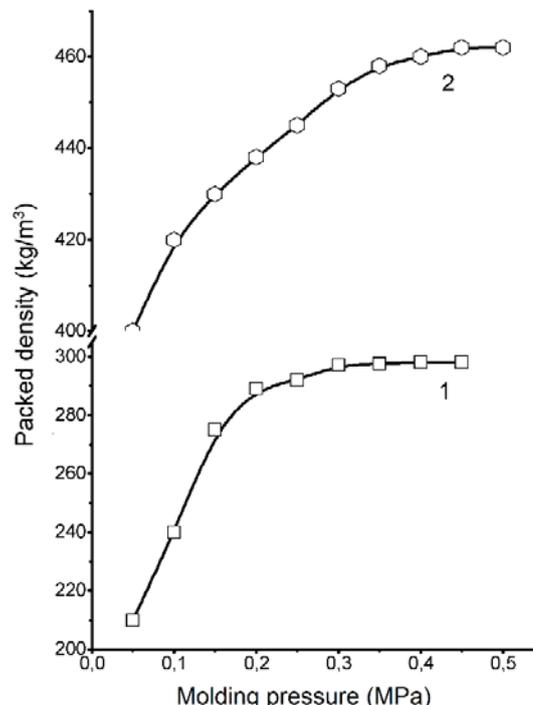


Figure 2. Dependence of the packed density of LPC on molding pressure:
1 – glass microspheres filler (HGM);
2 – ceramic microspheres filler (HCM).

Determination of the optimal temperature conditions of heat treatment is a considerable task, since many factors have an effect on the final performance properties of LPC. However, the dominant factors are temperature, curing time and binding agent content [21]. Therefore, in this study the full three-factor experiment planning was conducted in order to select the optimal modes (Table 2).

The impact resistance was used as a response function, since with increasing temperature and time LPC can completely lose plastic properties and resistance to impact, which is extremely undesirable for protective materials. The impact strength value depends on the degree of macromolecules crosslinking and it can decrease at a certain stage, when a certain crosslinking frequency is exceeded [22]. The purpose of Box–Behnken design was to find the corresponding optimal technological parameters, in particular temperature and time. Figures 3 and 4 show lines of equal levels of impact strength values depending on time and temperature of heat treatment for LPC filled by HGM and HCM with a binder content of 10 vol.% and 20 vol.%, correspondingly.

Table 2. Box–Behnken Design.

No.	Trial No.	Input data of experiment					
		Coded variable levels			Natural variable levels		
		X_1	X_2	X_3	X_1 (Time, hours)	X_2 (Temperature, K)	X_3 (Binding agent, %)
1	6	+	+	0	8	553	15
2	2	+	-	0	8	473	15
3	5	-	+	0	2	553	15
4	1	-	-	0	2	473	15
5	10	+	0	+	8	513	20
6	12	+	0	-	8	513	10
7	11	-	0	+	2	513	20
8	9	-	0	-	2	513	10
9	8	0	+	+	5	553	20
10	7	0	+	-	5	553	10
11	4	0	-	+	5	473	20
12	3	0	-	-	5	473	10
13	13	0	0	0	5	513	15
14	14	0	0	0	5	513	15
15	15	0	0	0	5	513	15
16	16	0	0	0	5	513	15
17	17	0	0	0	5	513	15

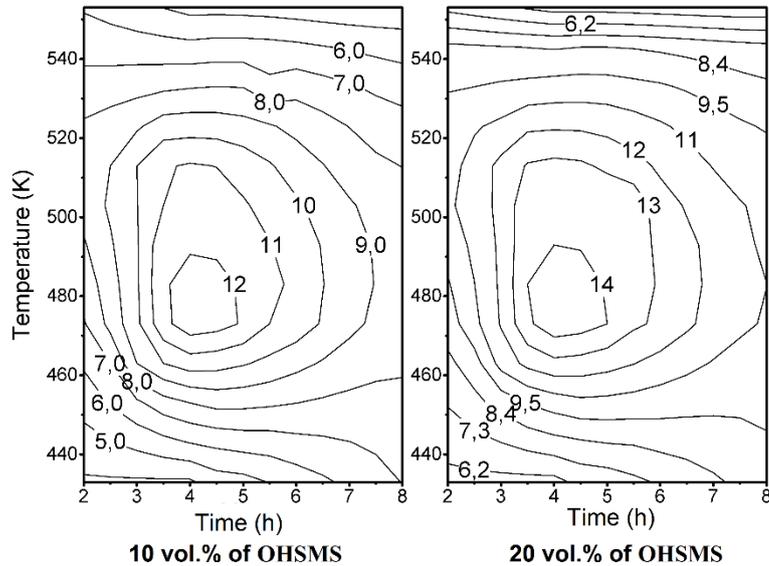


Figure 3. Lines of impact resistance equal levels f or LPC with HGM (10 vol.% and 20 vol.% of OHSMS).

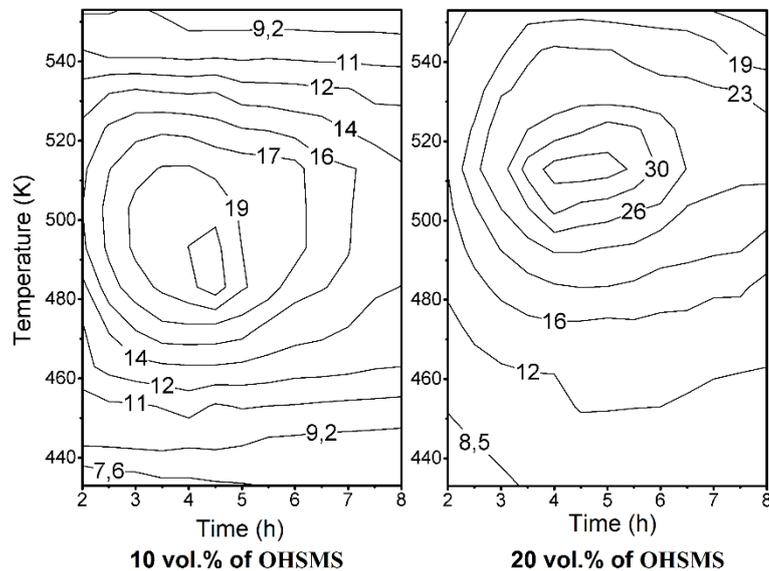


Figure 4. Lines of impact resistance equal levels for LPC with HCM (10 vol.% and 20 vol.% of OHSMS).

According to the obtained experimental data, as the binding content increased, the impact strength value shifted towards higher temperatures. As expected, an optimum impact value zone was found in all the cases. When HGM was used as a filler, the optimum impact strength was achieved at OHSMS content of 10 vol.% at a temperature of 480 K and curing time of 4.25 hours.

With an increase in the binder content up to 20 vol.%, no significant changes in the optimum character were observed. For this composition, the impact strength of the building material increased by no more than 20 %, owing to the low reactivity of HGM surface with OHSMS at the given temperatures.

When HCM was used as a filler, another behavior was observed. For composites filled by HCM, the optimal curing mode was 515 K at the curing time of 4.5 hours (20 vol.% of OHSMS). The impact strength increased significantly to about 36 kJ/m at OHSMS content of 20 vol.%, which is a very significant value for building materials with the similar density.

Automated implementation of the Box-Behnken Design allowed to obtain the following regressions that describe the dependence of impact strength value on curing time, temperature and binding agent content.

For LPC filled by HGM:

$$\sigma_{sp} = 20.87 + 0.674X_1 + 2.123X_2 + 1.585X_3 - 3.299X_1^2 - 7.844X_2^2 - 2.434X_3^2 - 0.995X_1X_2 + 1.282X_1X_3 + 1.942X_2X_3. \quad (2)$$

For LPC filled by HCM:

$$\sigma_{sp} = 21.44 + 0.701X_1 + 2.122X_2 + 1.559X_3 - 3.561X_1^2 - 7.158X_2^2 - 2.694X_3^2 - 0.994X_1X_2 + 1.23X_1X_3 + 1.942X_2X_3, \quad (3)$$

where X_1 is curing time; X_2 is curing temperature; X_3 is binding agent content in LPC.

The results presented above indicate that there is an active interaction of the filler with the binding agent due to the presence of active functional groups on the HCM surface. By virtue of the chemical composition, there are aluminum hydroxide groups with an increased reactivity on the surface of HCM. The interaction of aluminum hydroxide groups of HCM with functional groups of the organosilicon polymer located along the main chain apparently occurs.

OHSMS used as a binder differs from commonly used organosilicon materials in not only chemical nature (silane and carbosilane bonds in the main polymer chain appear in addition to siloxane bond), but also in a high frequency of OHSMS macromolecules cross-linking limiting their mobility after curing [23]. Thus, the developed composite materials based on OHSMS have lower plastic properties than commonly used LPC. However, the analysis of physical and mechanical properties under compression showed compression strength and modulus of elasticity increased in comparison to these values of commonly used LPC (Figure 5).

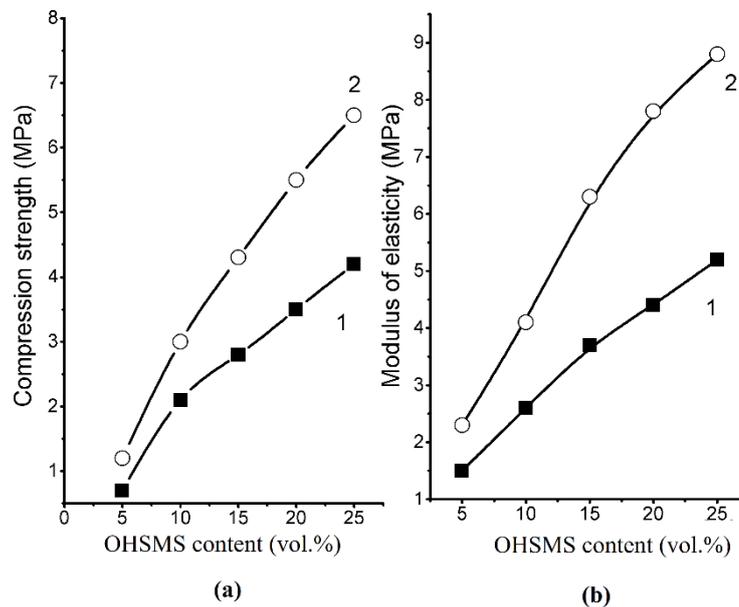


Figure 5. Dependence of mechanical strength characteristics of LPC filled by HGM (curve 1) and HCM (curve 2) on bonding agent content (OHSMS): (a) compression strength, (b) modulus of elasticity.

Apart from the nature and the content of a binder, the chemical composition and the size distribution of fillers have a significant impact on the physical and mechanical properties of LPC. In this study the use of HCM filler led to a significant increase in compressive strength as compared to LPC with HGM filler. The modulus of elasticity of LPC with HCM as a filler is 20–30 % higher than that of LPC with HGM. This could be explained by a difference in the fractional composition and the chemical interaction between the binder and the filler surface. Apparently, chemical reaction occurred between the surface functional groups of HCM and the reactive groups of OHSMS [24]. Moreover, in comparison with traditional silicone resins (polyphenyl and polymethylphenyl siloxane), the compressive strength value increased by almost two times and the modulus of elasticity increased by almost an order of magnitude. The properties of the developed concrete expand possibilities of using the material under exposure of significant external static loads.

4. Conclusions

Novel type of light heat-resistant polymer concrete was developed on the basis of oligooxyhydridesilmethylenesiloxysilan with hollow glass and ceramic microspheres. Organic-silicon binder provided thermal resistance and high strength characteristics of the composite material. Adding hollow glass and ceramic microspheres being waste products from the thermal power plants operating on solid fuels allowed to develop reasonably priced materials and to reduce potential environmental pollution.

The minimum molding pressure of light polymer concrete depends on the type of microspheres: 0.4 MPa for compositions with hollow ceramic microspheres and 0.25 MPa for compositions with hollow glass microspheres. The difference is explained by a more significant deviation of the shape of ceramic microspheres

from a spherical one, which makes it difficult to achieve maximum packing density of the filler. A further increase in pressure is impractical due to the possibility of destruction of the microspheres shells.

For lightweight polymer concrete with oligooxyhydridesilmethylenesiloxysilan content of 10 vol.% and filled with hollow glass microspheres, the optimum curing mode monitored by the toughness function was achieved at a temperature of 480 K and a cure time of 4.25 hours. When using ceramic microspheres with an organosilicon polymer, the optimum temperature and the cure time were increased by about 5 %. This is apparently due to the difference in the concentration of silanol groups on the surface of glass and ceramic microspheres and the difference in heat-conducting characteristics. At the same time, with an increase in the binder content to 20 vol.%, no significant changes in the behavior of the composites were observed.

The compressive strength and elastic modulus of the developed composites significantly exceeds the strength of the materials with traditional organosilicon binders, in particular polymethylphenylsiloxane. This is due to a number of factors, such as the spatial ladder structure of the polymer, the presence of a significant number of reactive groups in the binder, and their interaction with hydroxyl groups on the surface of the filler with the formation of physical and chemical bonds.

The use of hollow ceramic microspheres as a filler led to a significant increase in compressive strength compared to materials with hollow glass microspheres. The elastic modulus of lightweight polymer concrete with ceramic microspheres was 20–30 % higher than that of materials with glass microspheres, which is due to both higher strength characteristics of the filler shells and the difference in the interaction between the binder and the filler surface.

To sum up the obtained results, it could be concluded that using oligooxyhydridesilmethylenesiloxysilan as a binding agent provides the possibility to obtain construction materials, which can be used in various industries, particularly in ferrous and nonferrous-metals industries, conventional and nuclear power industries. Increased physical- mechanical properties, high thermal resistance and resistant to aggressive technogenic and natural factors expand possibilities of using these materials under exposure of significant external static loads.

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Легкие жаростойкие полимербетоны на основе олигооксигидридсилметиленилосилоксисилана и полых сферических наполнителей

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Ключевые слова: полимербетон, армированный бетон, кремнийорганическое связующее, полый сферический наполнитель, стеклянные микросферы, керамические микросферы

Аннотация. Новый тип легких полимербетонов был разработан на основе олигооксигидридсилметиленилосилоксисилана с полыми стеклянными или керамическими микросферами. Добавление полых стеклянных и керамических микросфер, являющихся отходами тепловых электростанций, позволило уменьшить себестоимость материалов и снизить потенциальное загрязнение окружающей среды. Для оптимизации технологии производства изучены технологические условия отверждения и формования материалов. В соответствии с изменениями ударной вязкости был установлен оптимальный режим отверждения для композитов при 480–515 К в течение 4,25–4,5 часа в зависимости от типа наполнителя и содержания связующего. Было установлено, что использованное кремнийорганическое связующее обеспечивает термическую устойчивость и высокие прочностные характеристики композиционного материала. По сравнению с традиционными кремнийорганическими смолами, предел прочности при сжатии разработанных материалов увеличился почти в два раза, а модуль упругости увеличился почти на порядок. Благодаря взаимодействию алюмогидрооксидных групп керамических микросфер с кремнийорганическим полимером, модуль упругости материалов с керамическими микросферами на 20–30 % выше, чем модуль упругости полимербетонов со стеклянными микросферами. Высокие физико-механические свойства расширяют возможности использования этих материалов при воздействии значительных внешних статических нагрузок.

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