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МИКРОСФЕРАЛАРМЕН ТОЛТЫРЫЛҒАН ЭПОКСИДТІ КОМПОЗИТТЕРДІҢ ЖЫЛУФИЗИКАЛЫҚ ҚАСИЕТТЕРІ

ТЕПЛОФИЗИЧЕСКИЕ СВОЙСТВА ЭПОКСИДНЫХ КОМПОЗИТОВ, НАПОЛНЕННЫХ МИКРОСФЕРАМИ

THERMOPHYSICAL PROPERTIES OF EPOXY COMPOSITES WITH MICROSPHERE FILLER

Аңдатпа. *Мақалада микросфералардың эпоксидті композиттердің жылуға төзімділігі мен өзгермелі температураға төзімділігіне әсері зерттелген. Микросфералардың химиялық және гранулометриялық құрамы зерттелді. Жылуға төзімділіктің ең үлкен мәнін қамтамасыз ететін оңтайлы композиция (96 °С дейін), құрамында 10 % микросфералар бар үлгілер. Ыстыққа төзімділік Мартенс әдісімен бағаланды. Толтырғыш мөлшері 2-ден 10 %-ға дейін мас. айнымалы температураның әсеріне төзімділікке айтарлықтай әсер етпейді. Айнымалы температураға ұшырағаннан кейін жабын соққыға төзімді қасиеттерін жоғалтқан жоқ. Эпоксидті композиттердің толтырғыш ретінде микросфераларды қолдану айнымалы температураның өзгеруіне және жылуға төзімді композициялық материалдарды алуға мүмкіндік береді.*

Түйін сөздер: *Эпоксидті шайыр; микросфералар; Мартенс бойынша жылуға төзімділік; айнымалы температураның әсеріне төзімділік.*

Аннотация. *В статье исследованы влияние микросфер на теплостойкость и устойчивость к воздействию переменных температур эпоксидных композитов. Изучены химический и гранулометрический состав микросфер. Оптимальный состав, обеспечивающий наибольшее значение теплостойкости (до 96°С), образцы с содержанием 10% микросфер. Теплостойкость оценивали методом Мартенса. Количество наполнителя от 2 до 10% мас. несущественно отражается на устойчивости к воздействию переменных температур. После воздействия переменных температур покрытие не потеряло своих ударопрочных свойств. Применение микросфер в качестве наполнителя эпоксидных композитов позволяет получать теплостойкие композиционные материалы устойчивые к воздействию переменных температур.*

Ключевые слова: *Эпоксидная смола; микросферы; теплостойкость по Мартенсу; устойчивость к действию переменных температур.*

Abstract. *The research paper shows the influence of microspheres on the heat resistance and variable temperature resistance of epoxy composites. The chemical and granulometric composition of microspheres have been studied. The samples containing 10% microspheres have optimal composition which provides the highest heat resistance value (up to 96°C). Heat resistance was measured by the Martens method. The*

filler amount of from 2 to 10 wt.% insignificantly affects the variable temperature resistance. After exposure to variable temperatures, the coating did not lose its impact-resistant properties. The use of microspheres as a filler in epoxy composites makes it possible to obtain heat-resistant composite materials withstand variable temperatures.

Keywords: *Epoxy resin; microspheres; Martens heat resistance; variable temperature resistance.*

Introduction. Creation of heat-resistant polymer composite materials with enhanced physical and mechanical properties is the task of priority in modern science. It is because the most part of polymer composites, including the epoxy resin composites, is fire-hazardous materials, they burn releasing an exceedingly large amount of toxic substances and they are not resistant to high temperatures. High fire hazard of polymeric materials is the main constraining factor in their large-scale introduction in such spheres as aviation, shipbuilding, mechanical engineering, railway transport and construction [1-3].

Application of polymer composite materials in structures operation in elevated temperatures requires studying their thermo-physical properties. Due to this, very effective method for increasing polymer composites heat resistivity is the use of various fillers [4-9].

The utilization of finely dispersed industrial wastes is a platform to support environment in the issues related to waste disposals.

Microspheres contribute a number of their properties to the composite materials in which they are introduced. These properties are: lightness, chemical inertness, fireproofness and low heat conductivity. When added to various materials exclusive of epoxy resin, they make such materials lighter, scale up their heat properties and sound-proofing properties [10]. Usage of microspheres can reduce the mass [11-12] of the material by 50-60%, what is often employed in ship and aircraft building. Most often, microspheres are added to epoxy resin to increase its fluidity. Smooth, round microspheres move easily relative to each other, this ensures that resin better fills cavities and voids.

In this regard, the purpose of this research paper is to develop compositions and to study the properties of epoxy composites reinforced with microspheres, which enhance the epoxy composites thermo-physical properties.

Materials and methods of research. Compositions based on make ED-20 epoxy-diane resin (GOST 10587-93) were developed. Polyethylenepolyamine hardener (PEPA) (TU 2413-010-75678843-2012), capable of forming a 3D network structure in the absence of heating, was used. Microspheres (originated from Ekibastuz GRES power plant) were used as a filler for polymer compositions. Microspheres are by nature of hollow solid particles of small sizes, that are formed in the ash when coal is burned in power plants.

To determine variable-temperature resistance of the epoxy resin-based and microsphere reinforced composite coatings, test sample substrates indicated in the previous research paper were used [13-14].

The samples used for determining heat resistance, were fabricated in the form of bars as specified in [15].

Microspheres added in epoxy resin in an amount of 2-10 % of mass and thoroughly stirred for 5-10 min until a homogeneous mass generated. Then hardener was added in the ratio of resin: hardener (1:10) and stirred for 2 minutes. The prepared referent sample was made without adding the filler. Curing at ambient temperature was conducted within 24 hours.

The following methods used to research the properties of the epoxy compositions and the filler:

The chemical and elemental compositions determined with the PANalytical X-ray fluorescence spectrometer, model Axios Max (Rh 2.4 kW). The microspheres surface morphology was studied with Auriga Crossbeam 540 scanning electron microscope (Carl Zeiss, Germany) at an accelerating voltage of 5 kV.

The filler particle sizes determined with Mastersizer 3000 laser particle size analyzer with the Hydro MV unit (120 ml) in water dispersion medium.

The Rigaku Corporation SmartLab X-ray diffractometer measured the X-ray diffraction. Variable temperature resistance was determined in accordance with GOST 27037-86 in the BINDER MK series climate chamber designed for testing in the range from -40°C to +60°C for 60 minutes.

The Martens heat resistance was determined according to GOST 21341-75 on sample bar with dimensions of 10x15x120 mm, with temperature rise rate of (50±5)ºC, fixed bar bending stress of 5±0.5 MPa. The essence of the method is to determine the temperature at which the test sample, loaded with a certain static stress, is deformed in such a way that the end of the loaded lever attached to the sample, drops by 6±1 mm [15].

Results and discussion. As a result of the study on the elemental composition of the microspheres, it was found that the microspheres mainly consist of Al, Si, Fe oxides, contain small impurities of Ti, P, K, Ca, Na oxides (Table 1).

Table 1. Chemical composition of the microsphere

Element	Concentration	Unit
Na	0,127	%
Al	12,277	%
Si	24,812	%
P	0,116	%
K	0,706	%
Ca	0,857	%
Ti	0,910	%
V	210,0	ppm
Mn	356,9	ppm
Fe	2,328	%
Sr	713,4	ppm
Zr	417,9	ppm

*1ppm = 0.0001%

The aluminosilicate microspheres are dispersed material composed of smooth hollow microspheres – white and dark spherical particles, shown in Figure 1. Some of the larger spheres were split or even broken into small pieces. In addition, it was interesting to note that some of the larger spheres were filled with smaller spheres, which the authors also observed in their work [10].

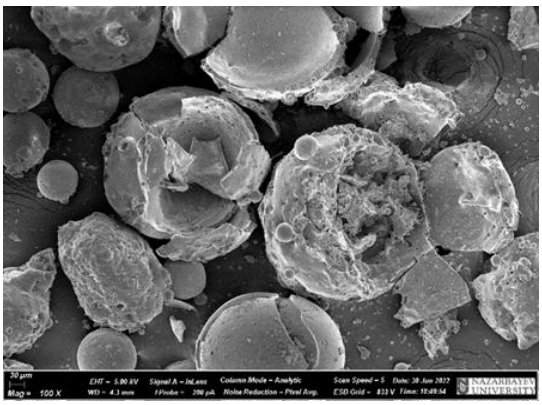

Figure 1. The SEM image of the microspheres x100

According to laser analysis, the average microsphere particle size is 0.1-100 microns (Figure 2).

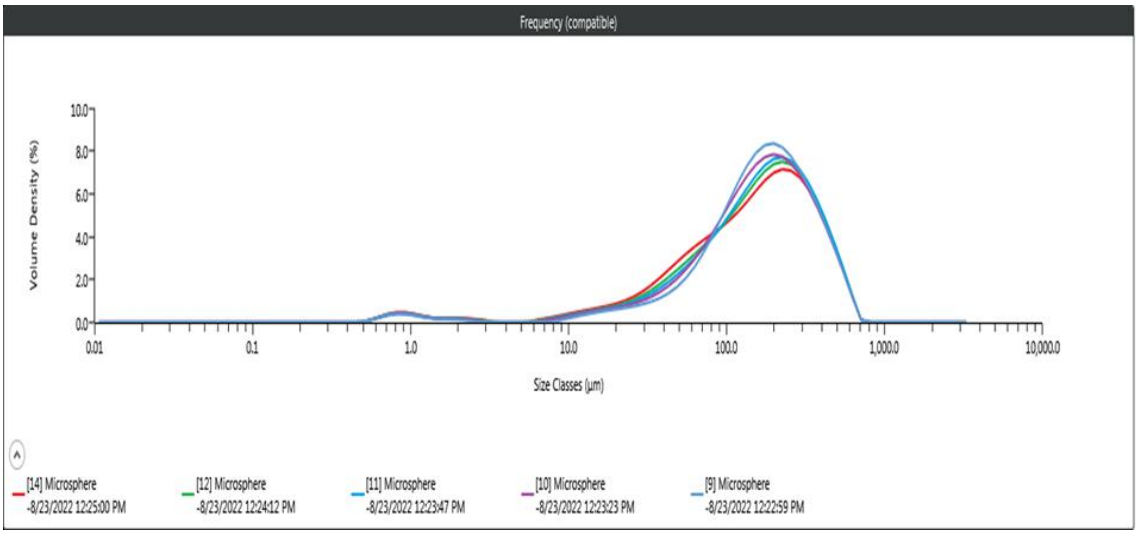

Figure 2. The laser analysis data on the microspheres particle sizes

According to X-ray phase analysis, the studied ash microspheres are represented by a mixture of phases of Aluminum Silicon Oxide (Al2 (Al2.588 Si1.412) O9.706), quartz SiO2 and amorphous glass phase.

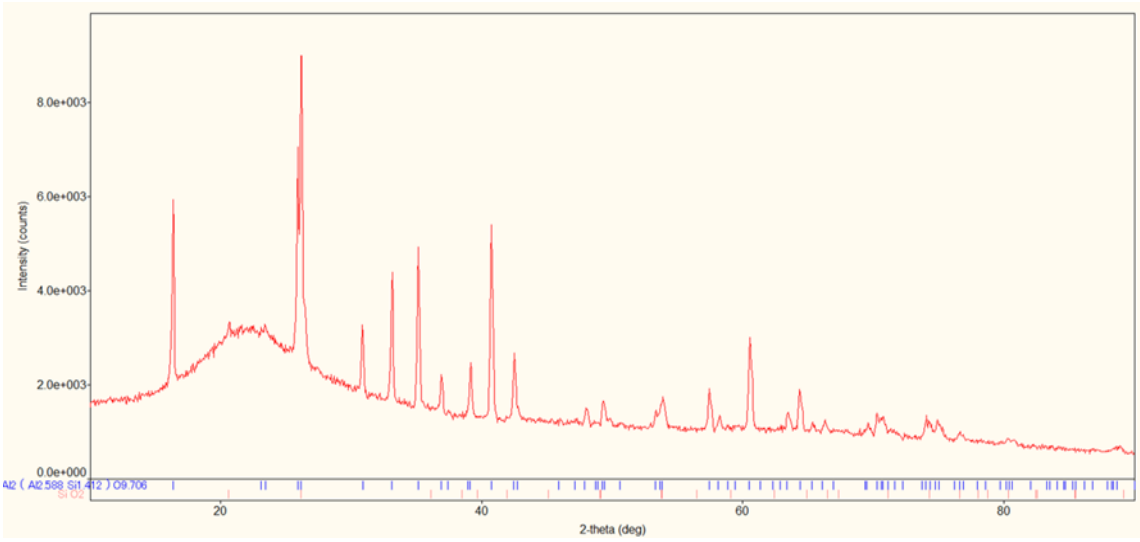

Figure 3. XRD pattern of microsphere samples

Variable temperature resistance was determined in accordance with GOST 27037-86 in the BINDER MK series climate chamber designed for testing in the range from -40°C to +60°C for 60 minutes.

Table 2 presents the resulting indicators on variable temperatures resistance in the epoxy resin-based composite coatings with different mass content of microspheres.

Table 2. The indicators on variable temperatures resistance in the epoxy resin-based composite coatings with different mass content of microspheres

No.	Composition of the composite material	Variable temperature resistance
1	ED-20 (without the addition of microsphere)	Change in gloss, color; delamination from the surface and other defects at the temperature in the range of (-40±2)°C - (+60±2)°C within (60 min.) Not found
2	ED-20+2% microsphere	Change in gloss, color; delamination from the surface and other defects at the temperature in the range of (-40±2)°C - (+60±2)°C within (60 min.) Not found
3	ED-20+5% microsphere	Change in gloss, color; delamination from the surface and other defects at the temperature in the range of (-40±2)°C - (+60±2)°C within (60 min.) Not found
4	ED-20+10% microsphere	Change in gloss, color; delamination from the surface and other defects at the temperature in the range of (-40±2)°C - (+60±2)°C within (60 min.) Not found

The results shown in Table 2 it proves that at visual examination of the samples exposed to variable temperature no changes were found in appearance of epoxy resin samples with different mass content of the filler: the coatings on the substrate were even, no delamination from the substrate, no visible defects and cracks found. The coatings exposed to the variable temperature, did not lose their impact-resistant properties [13].

The ability to reserve hardness at simultaneous exposure to load and temperature, is an important performance property required for polymer composite materials. The most commonly used method for heat resistance measurement is the Martens method.

Martens heat resistance measurement was carried out with a device that consists of a clamping-loading stand, deformation indicator, and the PT-01 heating cabinet with a temperature measurement and control system. Figures 4a and 4b present the device photograph.

After samples installation in the clamping-loading stand and the thermometers putting in the heating cabinet, the temperature control system starts heating. Within one hour, the temperature in the heating cabinet should evenly increase by 323±5 K (50±5°C). The initial test temperature is 298±2 K (25±2°C) [15].

a) *b)*

Figure 4. Martens heat resistance measurement device:
a) clamping-loading stand; b) temperature control PT-01

Martens heat resistance measurement ºC was determined at the moment the bending reached 6±1 mm. Table 3 presents the results on the Martens heat resistance of epoxy composites with different microsphere content.

Table 3. The results on the Martens heat resistance measurement in polymeric composite material PCM

No.	Composition of the composite material	Heat resistance, ºC
1	ED-20 (without the addition of microsphere)	88
2	ED-20+2% microsphere	92
3	ED-20+5% microsphere	94
4	ED-20+10% microsphere	96
5	ED-20+20% microsphere	91

Due to the fact that microspheres are a heat-resistant material [16-17], its introduction into the epoxy composite leads to an increase in the heat resistance of the Martens from 880C to 960C.

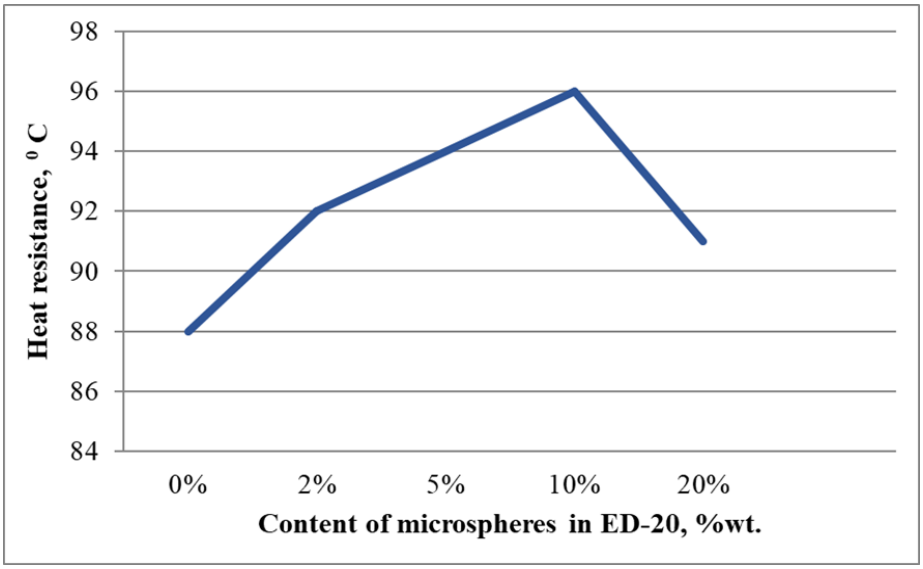

Figure 5. The value of the heat resistance of the samples

The nature of the curve in Figure 5 shows that the introduction of microspheres into the epoxy composition in an amount of 10 wt. % provides an increase in the heat resistance of the PCM to a temperature of 96°C. Heat resistance of samples with additives 2, 5, 10 wt.% the percentage of microspheres increases by 4-9% compared to the control sample. This effect can be ascribed to the high intrinsic stiffness and thick shell of the microsphere particles [18]. A similar trend was noticed with the addition of microsphere in epoxy foams [19].

When the content of microspheres is more than 10 wt.% there is a decrease in the heat resistance index. An increase in the content of microspheres reduces the distances between the particles and reduces the adhesion at the interface between the filler and the epoxy resin. The structuring effect of microspheres is manifested in the effect of small additives. All known polymers are microheterogenic and contain both densely packed, ordered regions and loose more defective zones in which small filler additives are localized. They play a significant structural-

modifying role, contribute to the kinetically stimulated reordering of the polymer and increase the mobility of the pass-through chains, ensuring their denser packaging.

Conclusions. Based on experimental research, it can hereby be concluded, that the microsphere filler positively effects on the thermophysical properties of epoxy composites. The obtained data shows that the samples with 10 wt.% microspheres give better heat resistance performance. In this case, 2 to 10 wt.% filler insignificantly change the variable temperatures resistance. Upon the completion of the variable temperatures resistance tests, no changes in the appearance of the epoxy resin test samples found: the mass is homogeneous; the coating on the substrate is even, no delamination from the substrate, no visible defects and cracks. Therefore, the use of microspheres as an epoxy resin filler makes it possible to achieve not only heat-resistant composite materials withstand variable temperatures, but also solves an environmental problem, since the utilization of fine industrial waste is the main task of implementing environmental policy and solves the problem of their negative impact on the environment, with the aim of their use in polymer composites.

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