

Use of dispersive additives to ensure high indicators of physico-mechanical properties of functional polymer coatings

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Abstract

The paper presents a method for improving the properties of protective coatings by injecting an optimal content of additives in the form of manufactured industrial wastes, which reduces the cost of the composition when eliminating the effects of corrosion damage of oil and gas main pipelines. It has been established that it is expedient to use particles of granularity equal to 63 μm for the formation of the adhesive layer of coating. Whilst for the formation of the functional layer of coating it is expedient to use particles of granulated slag dispersion equal to 80 μm . It has been proven that, depending on the degree of filling, the epoxy composites can be characterized by elastic properties and be distinguished by high rigidity. There has been analyzed the structure of epoxy composites by the method of optical microscopy and determined the optimal concentrations of the filler, at which a uniform distribution of particles in volume occurs, and the possibility of agglomeration of disperse particles has been excluded. This allows using materials and coatings based on them for a long-term operation.

Keywords: adhesion, dispersion, fracture structure, granulated slag, IR-spectral analysis, optical microscopy, physical and mechanical properties.

The reliability of oil and gas main pipelines to a large extent depends on the state of anti-corrosion protection, in particular insulation. The material of insulation grows old under the influence of the soil environment, losing its protective properties, gets destroyed and flakes. Therefore, the scientifically-substantiated development of new protective materials of pipes is urgent, in particular, on the basis of epoxy composites with improved properties for extension of main pipelines life. At the same time, it should be noted that the application of cheaper fillers is relevant for the formation of protective coatings for the functional purpose, as it reduces the cost of compositions. At the same time, a significant number of metallurgical enterprises in Ukraine receives a large amount of waste products annually. There are formed special institutions and organizations dealing with the use of such wastes in many countries. The processing and use of slags in different countries varies, which is explained by the specific conditions of industry development in each country. It is necessary to indicate the effective actions of the National Slag Association of the USA, the merits of which include the creation of the slag processing industry. Slag is recognized as a mineral raw material. In the United States, England, Germany and France air-cooled metallurgical slag is mainly recycled to rubble,

which is used as ballast in the construction of railways, and also as a filler for the construction of protective coatings for roads and aerodromes. It should be noted that the surface of such industrial wastes can be both dense and porous. In this case, the porosity of granulated slags is 60–70 %, which is of considerable interest for Polymer Material Science. When filling the epoxy binder with these additives, both the chemical interaction of the developed surface of the particles and also the physical one are possible, due to the formation of a significant number of physical nodes during polymerization. Therefore, the use of such disperse particles in the development of composite materials for corrosion protection of main oil and gas pipelines provides significant improvement of materials properties and, at the same time, reduces their cost and utilization of industrial waste [1–6].

Widespread use of epoxy resins in various industries results from a complex of physical, chemical and mechanical properties of such materials. Optimization of ingredients number during the formation of epoxy composites provides an increase in adhesive strength, improvement of physical and mechanical, thermal and physical properties, the materials resistance to the effects of corrosive media and wear. It is important, from a scientific and practical point of view, to take into account the above-mentioned study of the effects of additives, such as granulated slag, since it is possible to achieve significant improvement in the properties of composite materials (CM) by utilizing waste products [1–3].

The purpose of the work is to study the influence of granulated slag, which is a waste of the processing of

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fire-liquid metallurgical slags, on the properties of epoxy composites for protective coatings for various functional purposes.

Materials and methods of research

The epoxy dyanoic oligomer ED-20 (the State Standard GOST 10587-84), which is characterized by high adhesion and cohesive durability, slight shrinkage and technological ability, when applied on the longitudinal surfaces of the complex profile, is chosen as the main component of the binder during the formation of CM.

For cross-linking of epoxy compositions there has been used a hardener – polyethylene polyamine PEPA (TU 6-05-241-202-78), which allows the materials to solidify at room temperatures. It is known [1–3] that PEPA is a low molecular weight substance consisting of such interconnected components as $[-CH_2-CH_2-NH-]_n$.

The particles of the granulated slag (GS), characterized by the following composition, %: SiO_2 – 38.67; Al_2O_3 – 5.90; Fe_2O_3 – 0.08; FeO – 0.43; MgO – 6.70; MnO – 0.69; CaO – 44.96; S – 1.50; Fc – 0.39 were used as a filler. There was used GS of different dispersion: $d = 80 \mu m$, $d = 63 \mu m$, $d = 40 \mu m$.

An epoxy composite filled with particles of GS was formed using the following technology: preliminary dosage of epoxy dyanoic resin ED-20, heating the resin to a temperature of $T = 353 \pm 2 K$ and holding it at a given temperature during the time $\tau = 20 \pm 0.1$ min; dosage of the disperse filler and its subsequent injection into an epoxy binder; hydrodynamic combination of ED-20 oligomer and dispersed filler during the time $\tau = 1 \pm 0.1$ min; ultrasonic processing of the composition during the time $\tau_3 = 1.5 \pm 0.1$ min; cooling the composition to room temperature during the time $\tau = 60 \pm 5$ min; injection of PEPA hardener and mixing the composition over time $\tau = 5 \pm 0.1$ min. Subsequently, the CM was approved according to the experimentally established mode: the formation of specimens and their ageing during the time $\tau = 12.0 \pm 0.1$ h at a temperature $T = 293 \pm 2 K$, heating at a speed of $v = 3 K/min$ to a temperature $T = 393 \pm 2 K$, CM ageing during the time $\tau = 2.0 \pm 0.05$ h, slow cooling to a temperature $T = 293 \pm 2 K$. In order to stabilize the structural processes in the matrix, the samples were kept at a temperature $\tau = 24$ h in the air at a temperature $T = 293 \pm 2 K$ followed by experimental tests.

The following properties of CM were studied in the paper: adhesive strength as a result of shear and shift, residual stresses, destructive stresses, bending elastic modulus, and the impact strength.

The adhesive strength of the matrix to the metal base was investigated by measuring the destructive stress with a uniform separation of the pair of glued samples in accordance with the State Standard GOST 14760-69. The force of detachment of adhesive compounds of steel samples was measured by means of an automatic bursting strength test machine UM-5 at a loading rate of $v = 10 N/s$. The diameter of the working part of the steel samples at the bursting was $d = 25$ mm.

The residual stresses in the matrix were determined by the console method [7]. The coating with the thickness of $\delta = 0.3-0.5$ mm was formed on a steel base. Parameters of the base were as follows: total length – $l = 100$ mm; working length – $l_0 = 80$ mm, thickness – $\delta = 0.3$ mm.

The destructive stresses and the elastic modulus for bending were determined in accordance with the State Standards GOST 4648-71 and GOST 9550-81, respectively. Parameters of the samples were the following: length $l = 120 \pm 2$ mm, width $b = 15 \pm 0.5$ mm, height $h = 10 \pm 0.5$ mm.

Impact strength was determined by the Charpy method according to the State Standard GOST 4647-80 at the pendulum copper MK-30 at a temperature $T = 298 \pm 2 K$ and relative humidity $d = 50 \pm 5\%$. There were used the samples sized $l \times b \times h = (63.5 \times 12.7 \times 12.7) \pm 0.5$ mm. The distance between the supports was $l = 40 \pm 0.5$ mm.

The deviation of values during the study of the physico-mechanical properties parameters of CM was 4–6% of the nominal value.

To study the chemical bonds in the filler, IR spectral analysis was used. IR spectra were recorded on an IRAffinity-1 spectrophotometer (Japan) in the wave number domain $\nu = 400-2400$ cm^{-1} by the one-beam method under reflected light. The spectrum was expanded in accordance with the wave numbers $\lambda^{-1} = \nu$ at the diagram within 225 mm in the range of the frequencies chosen. The wave numbers, the transmission intensity, the half-width and the absorption band area were determined using the IR solution software. The error in determining the wave number ν is ± 0.01 cm^{-1} , and when determining the accuracy of the peak location, ν is ± 0.125 cm^{-1} . The measurement accuracy was $\pm 0.2\%$ with programmed slit control and integration time $t = 10$ s. The integration step is $\Delta\lambda = 4$ cm^{-1} .

The study of the structure (topology) of materials was carried out on a metallographic microscope of the model XJL-17AT, equipped with a Levenhuk C310 NG camera (3.2 Mega Pixels). Image zoom range from 100 to 1600 times. For the processing of digital images, Levenhuk TouView software was used.

Research results and their discussion

Previously, the chemical activity of granular slag particles was determined by the method of IR spectral analysis, i.e., the presence of active groups on their surface. The presence of Mg-O, Mn-O, S, Ca-O, and mineral admixture compounds was detected in accordance with the IR spectral analysis (Fig. 1) of the particles of GS in the wave number range $\nu = 561.99 - 487.99$ cm^{-1} [8].

The absorption band at a wave number $\nu = 891.11$ cm^{-1} indicates the presence of valence vibrations of the -C-C-, -C-O- bonds. Absorption bands in the range of wave numbers $\nu = 1195.87-1120.64$ cm^{-1} indicate the stretching vibrations of the -C-O- bond and the Si-O₂ compound. A relatively large peak area $S = 91.95\%$ indicates their significant amount (at $\nu = 1120.64$ cm^{-1}) [8, 9].

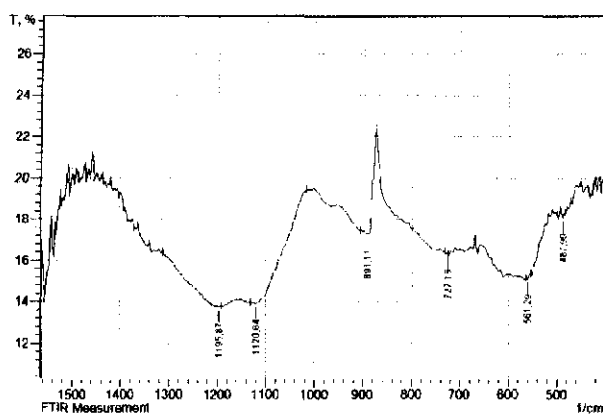


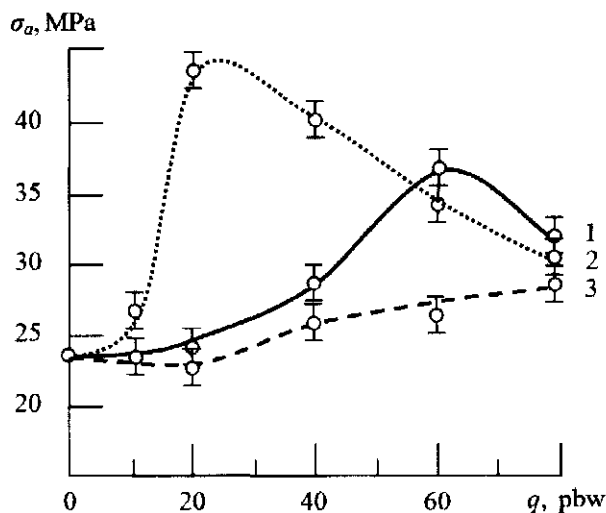
Figure 1 – IR-spectrum of the GS in the range of wave numbers $\nu = 400\text{--}1500\text{ cm}^{-1}$

Thus, IR spectral analysis indicates the activity of the GS filler, which allows us to state about the possibility of physicochemical interaction of particles with side groups and binding segments when the CM is crosslinked.

Then the effect of the GS content upon the adhesive strength at the detachment (σ_a), the displacement (τ) and the residual stresses (σ_r) in the CM were investigated. It should be noted that the kinetic, thermodynamic and chemical activity of the filler affects the physico-mechanical properties of the composites. In addition, an important characteristic of mineral filler, affecting the performance characteristics of the CM, is the specific surface area of dispersed particles. Taking into account that as the size of dispersed additives decreases, their specific surface area increases, the studies have been carried out to determine the effect both of the content and dispersity of granulated slag on the properties of CM.

It was experimentally established (Fig. 2), the injection of particles of the GS disperse filler with a particle size of $80\ \mu\text{m}$ and the content of $q = 10\text{--}20\text{ pbw}$ into the epoxy oligomer leads to an increase in the indices of adhesive strength during the separation of CM from $\sigma_a = 24.8\text{ MPa}$ (for the polymer matrix) to $\sigma_a = 25.0\text{ MPa}$ (Fig. 2, curve 1).

Then the injection of GS at a content of $q = 40\text{ pbw}$ promotes the growth of adhesive strength during the separation up to $\Delta\sigma_a = 27.6\text{ MPa}$. It was considered that the increase in the adhesive strength at $\Delta\sigma_a = 2.8\text{ MPa}$ (relative to the epoxy matrix) was due to the physicochemical interaction of the polymer with the metal substrate (due to the microroughness of the base surface). Further injection of GS disperse filler at a content of $q = 60\text{ pbw}$ leads to the appearance of a maximum on the dependence curve of the adhesive strength versus the content of the additive. Such CMs are characterized by the adhesive strength, which is $\sigma_a = 34.3\text{ MPa}$. In this case, it is advisable to consider the improvement of properties not only due to mechanical interaction, but also the chemical interaction of -C-N-, -C-C-, -C-O-, -NH-, -CH- single bonds (which are present on the surface filler) (Fig. 1) with side groups and segments of macromolecules of ED-20 epoxy oligomer.



1 – CM with particles granularity equal to $80\ \mu\text{m}$;
2 – CM with particles granularity equal to $63\ \mu\text{m}$;
3 – CM with particles granularity equal to $40\ \mu\text{m}$

Figure 2 – Dependence of the adhesive strength at separation (σ_a) on the content and dispersion of the GS filler

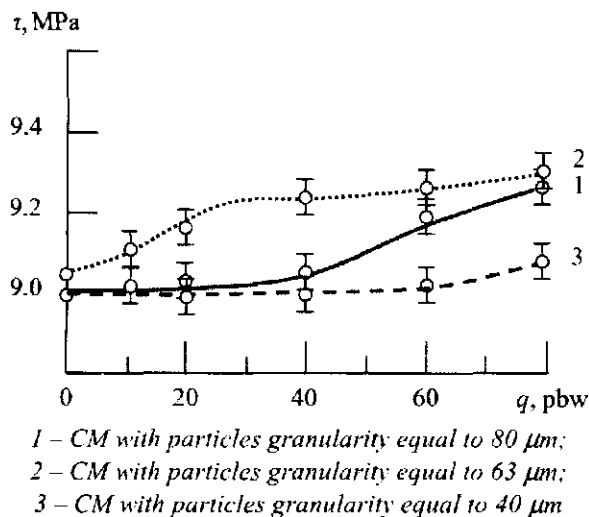
An increase in the filler content to $q = 80\text{ pbw}$ leads to a deterioration of the adhesive strength of the CM. The value of the adhesive strength of such composites is $\sigma_a = 32.0\text{ MPa}$. At the same time, the value of the adhesive strength is quite high relative to CM with a content of GS in the amount $q = 10\text{--}40\text{ pbw}$. This creates conditions for further studies of the structure of CM by the method of optical microscopy. In case of the formation of CM without defects in the structure, the use of materials with the content of GS equal to $q = 80\text{ pbw}$ is quite cost-effective, because by injecting a significant amount of filler, the cost of the composition decreases and the adhesive strength is sufficient.

Concerning the effect of the content of GS particles sized $63\ \mu\text{m}$ on the properties of CM, we can state the following. It was found that the injection of GS particles into the content of $q = 10\text{--}20\text{ pbw}$ provides a monotonous increase in adhesive strength when separated. At the same time, the maximum value of the adhesive strength when separated ($\sigma_a = 44.5\text{ MPa}$) was observed for the content of the additive $q = 20\text{ pbw}$ (Fig. 2, curve 2). Further injection of GS particles ($q = 40\text{--}80\text{ pbw}$) leads to a decrease in the values of the adhesive strength of CM to $\sigma_a = 30.2\text{--}40.0\text{ MPa}$.

Comparing the study results of adhesive strength during the separation of epoxy composites with particles sized $80\ \mu\text{m}$ and $63\ \mu\text{m}$, it is possible to state clearly the influence of the specific surface area on the properties of materials. It has been proven that the decrease in the particle size, and, consequently, the increase in their specific area, provides effective wetting of the surface and, as a result, the adhesive strength of the "binder – filler", "polymer – base" systems is improved.

The analysis of the adhesive strength of CM during the injection of GS particles sized $40\ \mu\text{m}$ made it possible to reveal the following (Fig. 2, curve 3). The

injection of GS particles with a content of $q = 10\text{--}20$ pbw provides stable values of adhesive strength relative to the epoxy matrix ($\sigma_a = 24.4\text{--}24.8$ MPa). The injection of GS particles with more than $q = 20$ pbw causes a monotonous increase in the adhesive strength during the separation of the developed CM. At the same time, it should be noted that the adhesive strength of CM filled with GS particles at the maximum content ($q = 80$ pbw) is $\sigma_a = 28.0$ MPa. It exceeds the value of the adhesive strength of the epoxy matrix at $\Delta\sigma_a = 4.4$ MPa. Further injection of particles is not rational, since an effective mechanical combination of the composition is not ensured due to a high viscosity value of the polymer system. Theoretically, a reduction in the GS particles size to $40\ \mu\text{m}$ should ensure an increase in the adhesive strength during the separation, as the specific surface area of the particles increases. But the results of the study indicate an opposite trend. It was considered that as the dispersion decreases, the distance between the filler particles in the CM decreases, as their amount increases per unit volume at the chosen degree of filling. This enhances their ability to form agglomerates, which are stress concentrators. Obviously, this can explain the insignificant values of the CM adhesive strength during injection of GS particles sized $40\ \mu\text{m}$ into the epoxy binder.



1 – CM with particles granularity equal to $80\ \mu\text{m}$;
2 – CM with particles granularity equal to $63\ \mu\text{m}$;
3 – CM with particles granularity equal to $40\ \mu\text{m}$

Figure 3 – Dependence of the adhesive shear strength (τ) on the content and dispersion of the GS filler

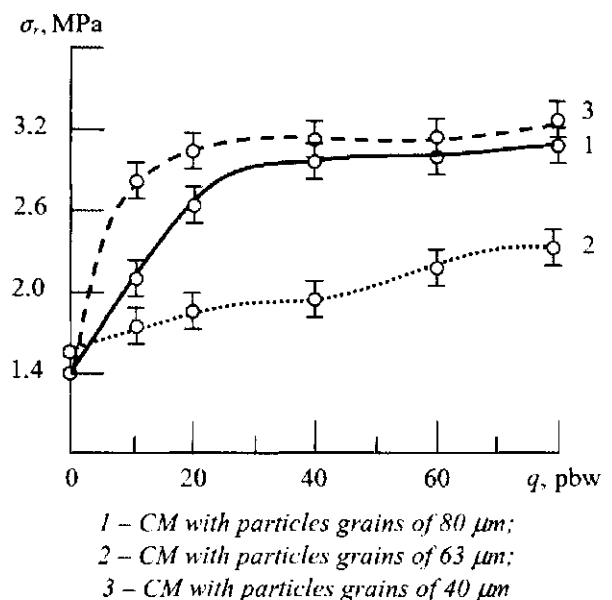
Further, the effect of GS particles ($d = 80\ \mu\text{m}$) on the adhesive shear strength was investigated. It was experimentally established (Fig. 3, curve 1) that there was observed a monotonic increase in the adhesive strength when dispersed particles were introduced into the binder. The maximum value of the adhesive shear strength ($\tau = 9.1\text{--}9.3$ MPa) was observed when GS particles were injected into a content of $q = 60\text{--}80$ pbw.

The coordination of the study results of adhesive strength as a result of shear and shift indicates that there occur longitudinal and transverse crosslinking bridges (chemical bonds) due to the tight packing of the adhesive, which allows one to resist both tangential and normal stress during shear or shift. The analysis of the

adhesive strength during the shear of CMs filled with GS with a grain size of $63\ \mu\text{m}$ made it possible to reveal the correlation relation between σ_a and τ . Namely: the maximum value of the shear adhesive strength was observed when GS particles were injected in an amount of $q = 20$ pbw, which was $\tau = 9.2$ MPa, and increased by $\Delta\tau = 1.4$ MPa with an additive content of $q = 80$ pbw.

At the same time, an analysis of the adhesive shear strength of CM filled with GS of $40\ \mu\text{m}$ made it possible to reveal an increase in strength comparing with the initial matrix only by $\Delta\tau = 1.4$ MPa. As it was previously noted, insignificant values of adhesive strength were associated with the formation of agglomerates in the volume of the composition. This creates the conditions for the uneven distribution of the disperse filler over the surface of the substrate and causes the formation of an adhesive of different thicknesses, differing in their properties.

When using protective coatings for elements of process equipment, the residual stresses are important, the values of which also affect the adhesive strength. It was found that when GS particles (at a content of $q = 10\text{--}20$ pbw) were injected, residual stresses increased from $\sigma_r = 1.4$ MPa (for an epoxy matrix) to $\sigma_r = 2.0\text{--}2.7$ MPa. Then the injection of GS with a content of $q = 40\text{--}80$ pbw led to an increase in the residual stresses, amounting to $\sigma_r = 3.0\text{--}3.2$ MPa. It should be noted that high residual stresses at the maximum adhesive strength can adversely affect the durability of the protective coating during operation.



1 – CM with particles grains of $80\ \mu\text{m}$;
2 – CM with particles grains of $63\ \mu\text{m}$;
3 – CM with particles grains of $40\ \mu\text{m}$

Figure 4 – Dependence of residual stresses (σ_r) on the content and dispersion of the GS filler

With the injection of GS particles ($d = 63\ \mu\text{m}$) at a content of $q = 10\text{--}20$ pbw, the residual stresses increase from $\sigma_r = 1.4$ MPa (for the epoxy matrix) to $\sigma_r = 2.8\text{--}3.1$ MPa. Then the injection of GS with a content of $q = 40\text{--}80$ pbw leads to an additional increase in the residual stresses, amounting to $\sigma_r = 3.1\text{--}3.3$ MPa.

The lowest values of residual stresses, amounting to $\sigma_r = 1.7\text{--}2.6$ MPa, were observed with the injection of GS particles ($d = 40 \mu\text{m}$). At the same time, the results of the residual stress study are not indicative of the improved performance characteristics of such materials, but only of the insignificant importance of adhesive strength due to the insignificant number of bonds with the base due to the formation of agglomerates.

Thus, the optimal content of GS particles was established for the formation of an adhesive layer of protective coatings:

for CM with GS particles ($d = 80 \mu\text{m}$) – $q = 60\text{--}80$ pbw per 100 parts by weight of ED-20 oligomer; the following values of the adhesive strength of protective coatings were obtained: $\sigma_a = 32.0\text{--}34.3$ MPa, $\tau = 9.1\text{--}9.3$ MPa, $\sigma_r = 3.0\text{--}3.2$ MPa;

for CM with GS particles ($d = 63 \mu\text{m}$) – $q = 20\text{--}40$ pbw per 100 parts by weight of ED-20 oligomer; the following values of the adhesive strength of protective coatings were obtained: $\sigma_a = 44.5$ MPa, $\tau = 9.2$ MPa, $\sigma_r = 3.2$ MPa.

In addition, the physico-mechanical properties of CMs filled with GS particles with a grain size of $80 \mu\text{m}$ were investigated. It was found that the injection of GS filler at a content of $q = 10$ pbw into the epoxy binder leads to an insignificant increase in the parameters of the breaking stresses when the CM is bent relative to the matrix by $\Delta\sigma_{ben} = 1.00$ MPa (Fig. 5, curve 1). When the content of GS particles increases ($q = 20\text{--}40$ pbw), the number of bonds –C-N-, –C-C-, –C-O-, –CH increases in the epoxy binder. Accordingly, the destructive stresses with bending from $\sigma_{ben} = 48.0$ MPa (for an epoxy matrix) to $\sigma_{ben} = 55.0$ MPa also increase. When the content of GS particles increases to $q = 60\text{--}80$ pbw, the stiffness of the formed composite increases, and accordingly the elongation of the molecules under load is restricted because of the considerable compaction of the polymer network. This can explain the decrease in the parameters of destructive stresses during bending to $\sigma_{ben} = 48.0\text{--}50.0$ MPa.

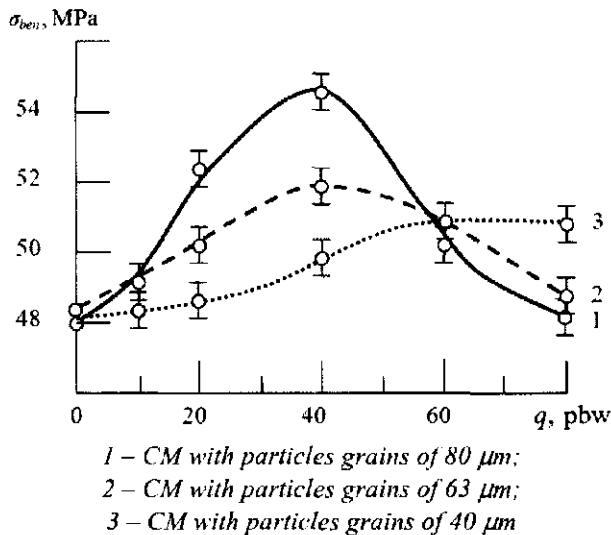


Figure 5 – Dependence of the fracture stress during bending (σ_{ben}) on the content and dispersion of the GS filler

Concerning the effect of GS particles with a size of $63 \mu\text{m}$ on the properties of CM, the following is established. The injection of GS particles at a content of $q = 10\text{--}20$ pbw leads to an increase in the values of fracture stresses during bending from $\sigma_{ben} = 48.0$ MPa (for an epoxy matrix) to $\sigma_{ben} = 49.0\text{--}50.3$ MPa (Fig. 5, curve 2). When the content of GS particles is increased to $q = 40$ pbw in the epoxy binder, the fracture stresses during bending of CM to $\sigma_{ben} = 52.0$ MPa are maximally increased.

There has been additionally established the influence of GS particles with a size of $40 \mu\text{m}$ on the fracture stresses during CM bending. The maximum growth of fracture stresses during bending ($\sigma_{ben} = 51.0$ MPa) was observed with the injection of GS into the epoxy binder at a content of $q = 60\text{--}80$ pbw.

There was also studied the dependence of the elastic modulus during bending on the GS content (Fig. 6). It was experimentally established (Fig. 6, curve 1) that the monotonic growth of the elastic modulus (relative to the epoxy matrix) $E = 2.8$ GPa to $E = 3.5$ GPa was observed during the injection of GS at a content of $q = 10\text{--}40$ pbw ($d = 80 \mu\text{m}$). The maximum value of the elastic modulus ($E = 3.7$ GPa) was established for CM by the GS in the amount of $q = 60$ pbw, which further confirmed the assumption that the stiffness of such CM increased. The increase in the content of GS particles to $q = 80$ pbw leads to a slight decrease in the elastic modulus during the bending of CM. That is, the supersaturation of GS particles causes the increase of the "binder-filler" system viscosity to a critical value, which leads to the formation of a defective material structure.

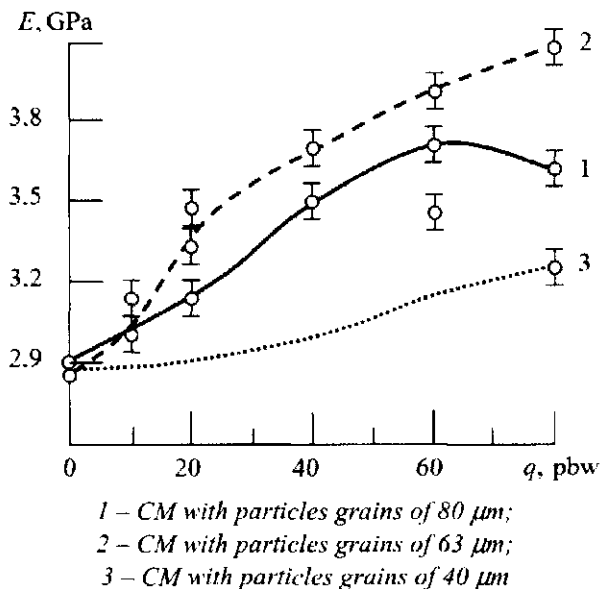


Figure 6 – Dependence of the bending elastic modulus (E) on the content and dispersion of the GS filler

A similar tendency for the growth of the elastic modulus was observed during the injection of GS with a particle size of $63 \mu\text{m}$ and $40 \mu\text{m}$ in the CM. That is, the maximum values of the elastic modulus at bending (for CM with GS particles sized of $63 \mu\text{m}$ is $E = 4.1$ GPa,

and for CM with GS particles sized of 40 μm is $E = 3.3$ GPa), were observed when GS particles were injected at contents of $q = 60\text{--}80$ pbw (Fig. 6, curve 2, curve 3). This indicates a limited mobility of the macrochains of the epoxy binder due to the sealing of the spatial polymer net, which additionally causes an increase in the stiffness of the polymer. At the same time, the analysis of the works [1–3, 10–14] allowed to establish that there are observed the defects in the structure of polymer systems, associated with incomplete wetting of disperse particles by the binder at the maximum filling. This creates conditions for the detachment of the binder from the disperse component and the formation of microcracks, which are stress concentrators in the polymer under the influence of external loading.

Particular attention should be paid to the impact strength of the CM, filled with dispersed particles of GS, because in some cases, when exploiting the applied protective coating, it is necessary to take into account not only the influence of static and dynamic, but also the impact loads.

The correlation connection of physical and mechanical properties indicators (σ_{ben} and W) was established (Figures 5–7, curves 1) when the particles of the GS were injected with a grain size of 80 μm at contents of $q = 20\text{--}40$ pbw. At the same time, the maximum values of impact strength $W = 8.89\text{--}9.00$ kJ/m^2 were observed. Consequently, it can be argued that GS particles form the maximally compacted polymer mesh, capable of counteracting both static and stressful stress, at optimal contents.

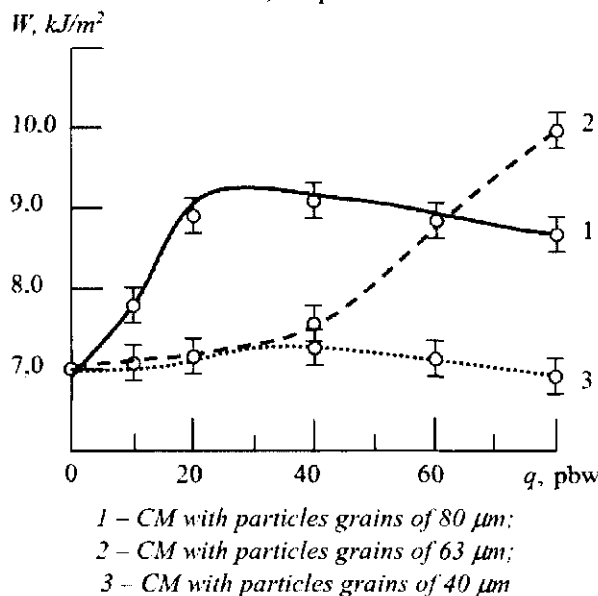


Figure 7 – Dependence of the impact toughness (W) on the content and dispersion of the GS filler

An analysis of the dependence of the impact strength on the effect of the content of GS particles with grain size of 63 μm allowed to establish a monotonous improvement of the CM properties. At the same time, the maximum value of the impact strength ($W = 10.0$ kJ/m^2) was observed when the GS particles were injected into the CM at a content of $q = 80$ pbw.

At the same time, CMs are characterized by the smallest values of impact strength at the content of GS particles with a size of 40 μm . The value of the impact strength of these materials in the whole range of the study is $W = 7.0\text{--}7.2$ kJ/m^2 .

Comparing the results of physical and mechanical properties when injecting GS particles sized in the range of 40–80 μm , it can be argued that the decrease of the filler dispersion affects the degree of polymer crosslinking. It is necessary to take into account the degree of the filler porosity, which reaches 70%. Therefore, reducing the grain size while simultaneously increasing the amount of disperse particles per unit volume causes the formation of agglomerates. At the same time, it should be borne in mind that the pore size of particles with a grain size of 80 μm is larger than that of particles with a granularity of 63 μm and 40 μm . Therefore, in this case, in addition to the formation of a significant number of chemical bonds established by the IR spectral analysis (Fig. 1), physical connections can be formed and also topological, formed by mechanical interweaving of macromolecules (possibly also in the volume of the porous disperse component).

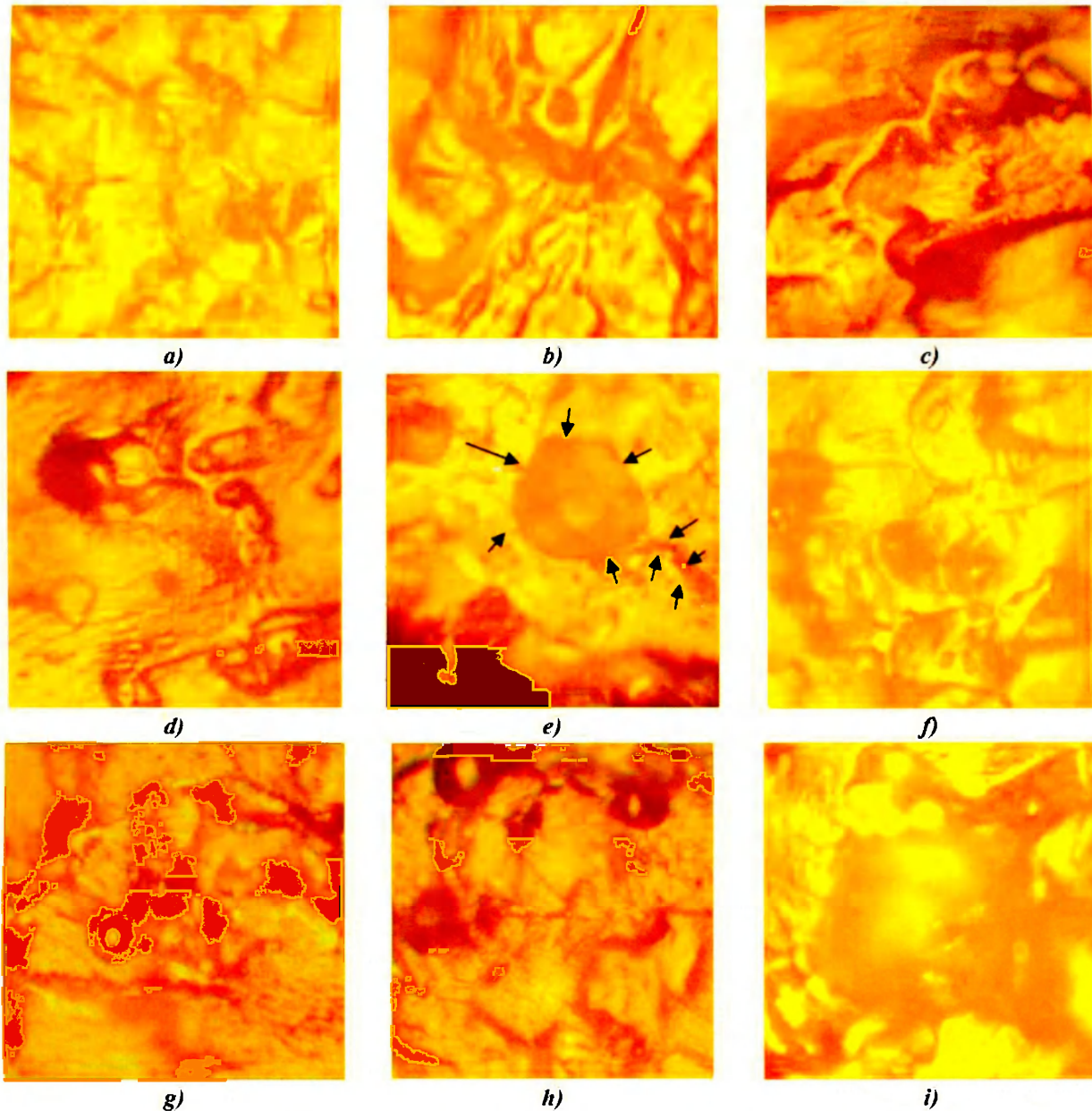
In order to confirm the results of physico-mechanical studies and proposed assumptions, there was studied the fracture surface of composites, filled with GS particles, by optical microscopy (Fig. 8).

Analysis of the CM fracture surface with the content of GS particles in the amount of $q = 10$ pbw (Fig. 8, a) allows us to assert that there are formed materials with a homogeneous structure, in case of this filling, due to the insignificant content of the filler.

During the study of CM fracture surface with the content of GS particles in the amount of $q = 20$ pbw (Fig. 8, b, c) there were observed widespread cracking lines with pronounced cavities characterizing the stress state of the material, and, consequently, high residual stresses.

It is worthy to note the analysis of the topology of the CM fracture with the content of GS particles in the amount of $q = 40$ pbw. The insignificant deepening and the absence of marked changes of the fracture surface testify to the insignificant tense state of the system. At the same time, the 600 time increase allows us to state that the GS particles can inhibit the propagation of cracks in the volume of the polymer (Fig. 8, e). This is confirmed by the absence of cracks (wide, small branched), both around disperse particles and in the volume of the binder. This additionally confirms the physicochemical interaction of GS particles with an epoxy binding compound, resulting in the formation of a seamless spatial polymer net with a maximum degree of stitching.

Analysis of the CM fracture surface with the content of GS particles in the amount of $q = 60$ pbw (Fig. 8, e, f) allowed to detect a defective structure of the polymer, which is expressed by the presence of air inclusions, which may arise due to the excessive viscosity of the binder in the presence of a disperse component. These inclusions are stress concentrators and cells of nucleation of wide branched and fine cleavage lines.



a) 10 pbw; b), c) 20 pbw; d), e) 40 pbw; f), g) 60 pbw; h), i) 80 pbw

Figure 8 – Fractograms of the CM fragment filled with GS particles ($d = 80 \mu\text{m}$), $\times 400$

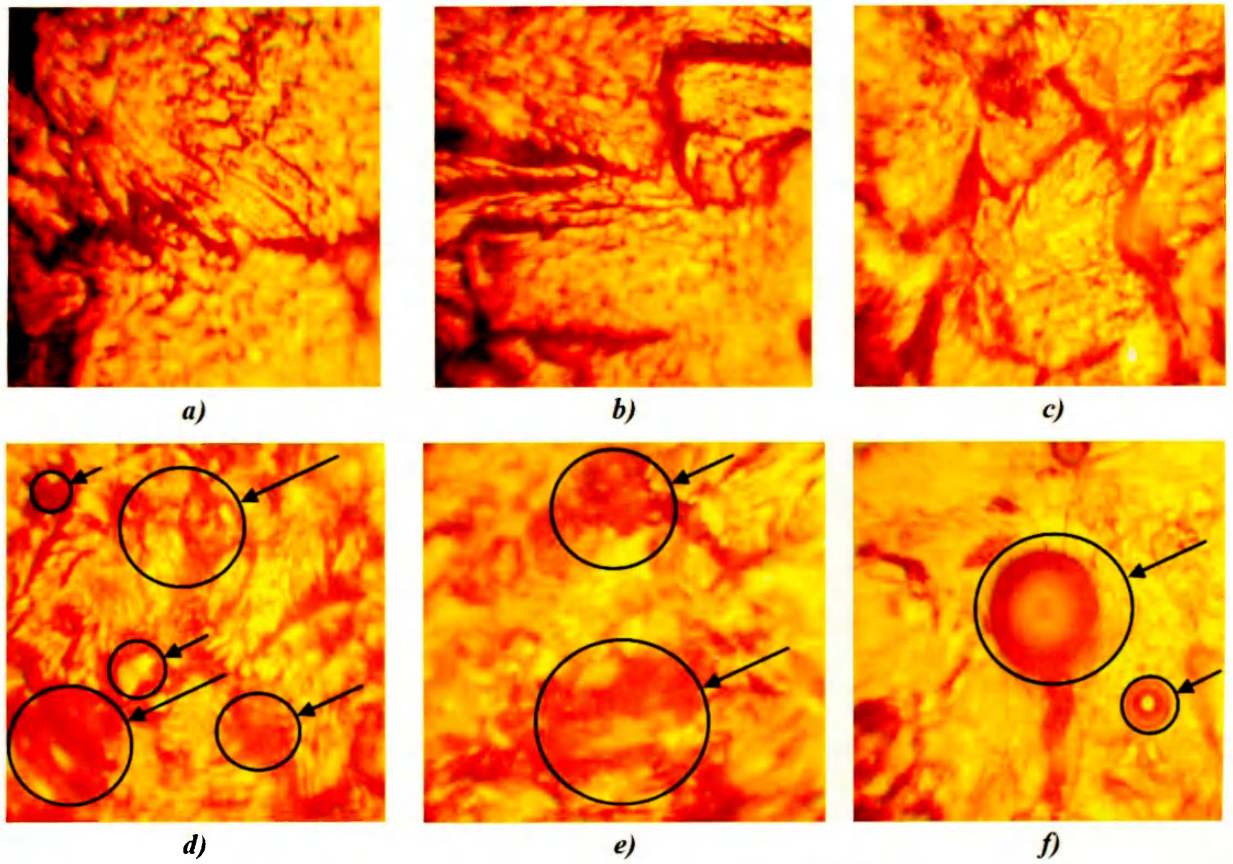
The composites containing GS particles in the amount of $q = 80 \text{ pbw}$ are characterized by the corresponding structure (Fig. 8, g, h).

With an increase in the surface of the fracture ($\times 600$), it was found that fracture of materials gave rise to cracks not only in the volume of the binder, but also around the disperse particles. This provides a defective structure of materials and, as a consequence, the properties of such CMs are unstable in the process of operation. Therefore, the preliminary assumption regarding the use of polymeric adhesives with maximum content of GS particles ($q = 60\text{--}80 \text{ pbw}$) has been refuted, since there are formed materials with defective structure.

In the analysis of the fractograms of the CM fragment with GS particles of grain size $63 \mu\text{m}$ and $40 \mu\text{m}$, the following is found out. The analysis of the

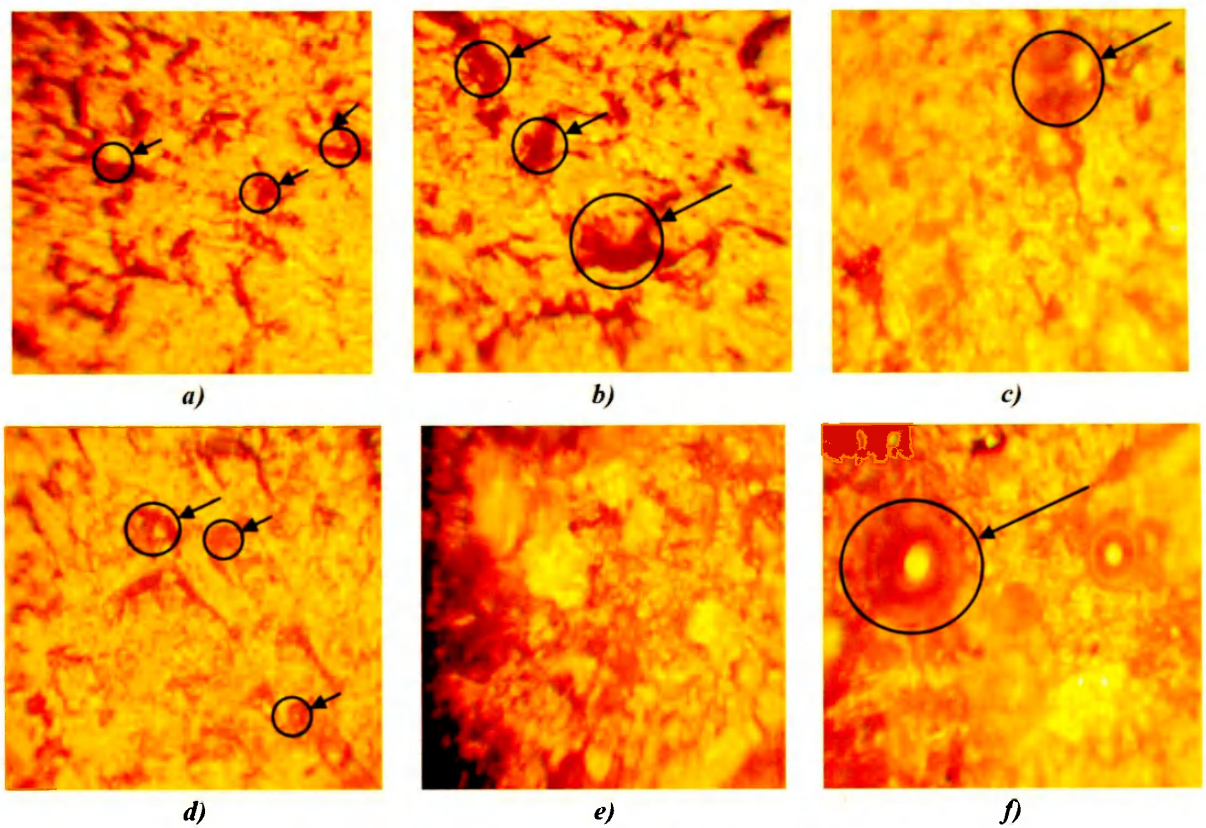
fracture fractograms confirms the preliminary assumption that the decrease in the size of the GS particles causes the formation of agglomerates in the structure of the polymer. The absence of defects in the structure in the form of agglomerates for the CM, filled with GS particles at the contents of $q = 10\text{--}40 \text{ pbw}$ (Fig. 9, a–c), and the viscous nature of the damage, due to wide trunk cleavage lines, indicates the improved properties of such materials. These facts coincide with the results of the study of adhesion (Figs. 2–4) and physico-mechanical properties (Figs. 5–6) of the CM.

At the same time, there was observed the formation of agglomerates, which were the centers of origin and distribution of cracks, with the injection of GS particles at the contents of $q = 60 \text{ pbw}$ (Fig. 9, d). The analysis of the fractograms of the CM fragment when the particles of the GS were injected at a content of $q = 80 \text{ pbw}$



a) 10 pbw; b) 20 pbw; c) 40 pbw; d) 60 pbw; e), f) 80 pbw

Figure 9 – Fractograms of the CM fragment filled with GS particles ($d = 63 \mu\text{m}$), $\times 400$



a) 10 pbw; b) 20 pbw; c) 40 pbw; d) 60 pbw; e), f) 80 pbw

Figure 10 – Fractograms of the CM fragment filled with GS particles ($d = 40 \mu\text{m}$), $\times 400$

allowed to identify additional defects in the form of air inclusions. This testifies to the inappropriateness of the injection of a greater amount of filler, since with the increase in the viscosity of the polymer system there are formed significant defects in the structure of the material.

An analysis of fractograms of the CM fragment with GS particles of 40 μm allowed to detect the agglomeration of the filler particles at their minimal content ($q = 10\text{--}20$ pbw) in the epoxy binder (Fig. 10, *a, b*). This also confirms the assumption that reducing the size of the active filler particles increases the amount of the latter in the unit of volume and causes the formation of agglomerates (even with insignificant content).

Subsequent injection of GS particles ($q = 40\text{--}80$ pbw) with a grain size of 40 μm (Fig. 10, *c-f*) leads to an increase in defects in the volume of polymer, and, consequently, reduction of the indicators of physico-mechanical properties, which is consistent with the results of the study above in the work (Figs 2–7, curve 3).

Conclusions

On the basis of the above results of the study it can be stated that the use of metallurgical slags in the form of fillers in the formation of composites is quite effective. At the same time, there is provided not only utilization, but also the improvement of the properties of composite materials and coatings on their basis. The following is set out in the work.

1. An IR spectral analysis of granulated slag particles has been conducted, which allowed to detect a significant number of compounds in the range of wave numbers $\nu = 400\text{--}1500$ cm^{-1} (Mg-O, Mn-O, S, Ca-O, Si-O₂). This allows us to confirm the physico-chemical interaction of granulated slag particles with side groups and binder segments, and, consequently, the improvement of properties of the epoxy composites.

2. Considering that it is necessary to take into account the complex of operational requirements, namely, sufficient rigidity and, at the same time, elasticity of the polymer system in the formation of composites or functional layer of coating, it is necessary to use composites and coatings on their basis with the particles grains of 80 μm at the contents of $q = 40$ pbw. These materials are characterized by destructive stresses during bending $\sigma_{\text{ben}} = 55.0$ MPa, elastic bending modulus $E = 3.5$ GPa and impact strength $W = 9.2$ kJ/m^2 .

3. For the formation of composites with high values of adhesive strength, it is expedient to use GS particles with a grain size of 63 μm at a content of $q = 20\text{--}40$ pbw. The adhesive strength at detachment of such materials is $\sigma_a = 44.5$ MPa, at displacement $\tau = 9.2$ MPa, residual stresses $\sigma_r = 3.2$ MPa.

4. The fracture surface of the developed composite materials was investigated by optical microscopy. It was proved that composites, filled with GS particles with a grain size of 80 μm and 63 μm at a content of $q = 10\text{--}40$ pbw, were characterized by an ordered structure, which provided significant improvements in adhesive and physico-mechanical properties of the

materials developed. Composites, filled with GS particles with a size of 40 μm , even with insignificant additions ($q = 10$ pbw), are characterized by insufficient cohesive strength due to agglomeration of the filler. Therefore, the use of CM with GS particles of 40 μm is possible only with the development of methods to prevent the agglomeration of the additive when cross-linking the polymers.

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Використання дисперсних добавок для забезпечення високих показників фізико-механічних властивостей полімерних покриттів функціонального призначення

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Описано спосіб поліпшення властивостей захисних покриттів введенням оптимального вмісту добавок у вигляді відходів промислового виробництва, що дозволяє зменшити вартість композиції при ліквідуванні наслідків корозійного руйнування магістральних газонафтопровідних мереж. Як основний компонент для зв'язувача при формуванні композитів вибрано епоксидний діановий олігомер марки ЕД-20, який характеризується поліпшеною адгезійною міцністю, незначною усулкою і технологічністю при нанесенні на довговимірні поверхні складного профілю. Для зшивання епоксидних композицій використано твердник полістиленполіамін ПЕПА, що дозволяє затверджувати матеріали при кімнатних температурах. Для дослідження міжфазової взаємодії часток гранульованого шлаку з епоксидним зв'язувачем і твердником використано ІЧ-спектральний аналіз. Встановлено значну кількість з'єднань Mg-O, Mn-O, S, Ca-O, Si-O₂ та коливання одинарних зв'язків -C-N-, -C-C-, -C-O-, -NH-, -CH- на поверхні часток наповнювача. Показано, що питома площа поверхні дисперсних часток гранульованого шлаку впливає на ступінь зшивання полімеру. Встановлено, що для формування адгезійного шару покриття доцільно використовувати частки з зернистістю 60–63 мкм. Тоді, як для формування функціонального шару покриття доцільно використовувати частки гранульованого шлаку з зернистістю 80 мкм. Доведено, що залежно від ступеня наповнення епоксидні композити можуть характеризуватися як пружними властивостями, так і виокремлюватися високою жорсткістю. Методом оптичної мікроскопії проаналізовано структуру епоксидних композитів і визначено оптимальний вміст наповнювача, при якому відбувається рівномірний розподіл часток за об'ємом і нівелюється можливість агломерації дисперсних часток. Це дозволяє використовувати розроблені матеріали і покриття на їх основі впродовж тривалого часу експлуатації.

Ключові слова: *адгезія, гранульований шлак, зернистість, ІЧ-спектральний аналіз, оптична мікроскопія, структура зламу, фізико-механічні властивості.*