Optimization of the composition and properties of heterocomposite materials for coatings obtained by the activation-heliotechnological method

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Abstract. The article presents the results of research on the development of compositions and the study of the properties of heterocomposite materials for coatings used for equipment for the collection, storage and transportation of oil and gas products protected from corrosion and hydroabrasive wear. On the basis of the analysis of the existing devices characteristics for the mechanical activation of mineral particles, the mechanical activator installation “System of running drums” was developed. Using Newton's interpolation formula and Lagrange's method, trigonometric and functional factors were determined, regression equations were derived, which were used to determine the optimal type of filler and the quantitative effect of the compositions and properties of composite coatings and the exploited aggressive environment influence on the properties of the material. Analysis of the results of theoretical and practical research on the rational use of natural minerals can be used as a scientific basis for the targeted use of physicochemical phenomena, in particular priority factors such as the formation of positively and negatively charged particles on the surface of the filler-binder phase division.

1. Introduction

For internal and external coatings of the large-sized items and technological equipment, for example, for underground oil gathering systems and systems for maintaining reservoir pressure, hot and cold water supply, special-purpose pipelines, where it is important to ensure corrosion resistance and wear resistance during at hydro-abrasive wear, it is necessary to develop new materials and technologies, significantly superior to the known ones. Such materials can be created using new scientific and technological methods, effective physical, mechanical and chemical modification methods.

The possibilities of increasing the protective and wear-resistant performance properties of composite epoxy coatings under hydro abrasive action by applying the method of mechanic and chemical modification of local mineral fillers have been investigated. Even better results can be achieved by optimizing the geometric dimensions of nanoparticles from local minerals and technological processes when obtaining special heterocomposite coatings.

The development of new technological principles for the production of highly efficient compositions of multifunctional action using secondary industrial raw materials will solve the problem of reducing the hydroabrasive-corrosion-mechanical wear.

In this regard, it is necessary to conduct research on the choice of the optimal filler and optimization of the compositions and properties of heterocomposites and the technological modes of their preparation.
for their use as coatings. It is also necessary to substantiate quantitatively and qualitatively the expediency of using the mineral kaolin of various grades, and its industrial wastes, which differ significantly in chemical and dispersed composition as fillers for a heterocomposite coating for machine-building purposes.

The choice of the method and means of mechanical activation of heterocomposite materials. Mechanical activation of solids is associated with the destruction of materials [1-3]. To destroy solids to the required size, different methods of mechanical action are used, depending on the requirements for the grinding product (particle size distribution, particle shape, reactivity, etc.), as well as on the properties of the grounded body (cohesive characteristics, features of the crystal structure, mechanical fragility, etc.). Devices used for crushing, as a rule, simultaneously combine various types of mechanical action: crushing (compression), splitting, free and constrained impact, abrasion, rupture, etc. Crushing and impact actions are mainly used in devices for crushing fragile materials. Soft materials are usually dispersed in abrasion machines. For fibrous samples, the most effective devices are of the bursting type. Thus, a large number of devices of different designs and principles of operation are used for dispersion. For example, a multipurpose radial centrifugal mill (RCM), a high-speed separation mill (HSM) of impact action, roller, disc and other grinders. Among these grinders, the most convenient and efficient are the vortex mills. Carrying out special experiments, the authors of work [4-6] note the essential efficiency of the dismembrator installation.

2. Methods and materials

Epoxy resin (ED-20), polyethylene polyamine (PEPA) hardener, plasticizer – dibutyl phthalate (DBP), structure former – chemical modifier gossypol resin (GS), produced by Angren Kaolin brands AKF – 78, AKC – 30, AKT – 10, wollastonite, basalt and glass wool were used as reinforcing fillers (table 1).

Table 1. Materials chosen for research.

| №  | Materials                        | State standard or tech.condition | Note               |
|----|---------------------------------|---------------------------------|--------------------|
| 1  | Epoxy resin (ED–20)             | GOST10587–72                    | Thermoreactive binder |
| 2  | Dibutilftalat (DBF)             | GOST 8728–76                   | Plastificator      |
| 3  | Gossypol resin                  | Technical conditions 86-38:2001 | Modifying plastificator |
| 4  | Polyethilenpolyamin (PEPA)      | TC 6–02–594–70                 | Hardener           |
| 5  | AKKF–78                         | Uzbekistan standart 1056:2004  | Filler             |
| 6  | AKC–30                          | Uzbekistan standart 1056:2004  | Filler             |
| 7  | AKT–10                          | Uzbekistan standart 1056:2004  | Filler             |
| 8  | Glass wool                      | GOST 319132011                 | Filler             |
| 9  | Basalt wool                     | GOST 4640-2011                 | Filler             |

Physical and mechanical properties were determined by well-known standard methods. Structural changes in the coating surface were studied by optical (MIN – 8, MBI – 6) and electron microscopy (REM – 1002).

Mechanical properties (microhardness) were investigated using PMT-3 and an ME-3 pendulum device, thermo mechanical properties of coating materials - using a Q-102 derivatograph, and adhesive strength - using an F01 tensile testing machine.

Determination of coating thickness. The thickness of the film or coating was measured with an ITP – 1 magnetic thickness meter. The thickness gauge ITP-1 can measure the film without breaking its
integrity. The principle of operation of the device is based on a change in the force of attraction of a magnet to a ferromagnetic substrate, depending on the thickness of the non-magnetic film. The force of attraction is measured by the elongation of the spring on a movable scale. The dependence of the attractive force of the magnet on the thickness of the film is indicated in the nomogram intended for converting the scale readings into micrometers.

To optimize the composition and operational properties of heterocomposite polymer materials and to process the research results, the interpolation formula of Newton and the Lagrange method, specially developed programs [7, 8] were used.

3. Experimental part

Despite the progress achieved in the application of the method of mechanical activation, from our point of view, it is necessary to find effective structure formation on the filler-binder interphase level.

It is known that positive and negative electrostatic charges are generated in any type of friction and abrasion. Charged electrons in natural minerals, especially in kaolins, can be assumed to have a mosaic structure. The resulting electrostatic charges, without accumulating, mutually recombine. Researchers have not studied the positive effect of charged particles of the filler surface on the filler-binder interfacial layer based on the analysis of the mechanism of the nature of grinding.

Based on these considerations, a method of mechanoactivation of fillers with a slight change in geometric dimensions was chosen, in which charged electrons are formed on the surface of activated mineral particles, which have a positive effect on interfacial structure formation.

In this regard, on the basis of studying the methods of mechanical activation, in order to increase the volume of critical filling, which allows saving the consumption of the binder, we have chosen a method of mechanical activation of the filler with a small change in the geometric size of its particles (if possible, retaining their size), with the maximum renewal of the surface of mineral particles in a specially designed mechanical activator consisting of a rotating cylindrical vessel and natural stones approximately 50x50x50 mm in size as a spherical element of a mechanical activator “figure 1” [9]

To consider the energy sources used today, the most relevant is the use of alternative energy. And in this regard, the use of solar energy is really affordable, which has successfully found its application in obtaining new materials and coatings for targeted purposes [10-13].

The process of structure formation of coatings based on thermosetting plastics on the surface of metal structures requires the expenditure of thermal energy or other methods of physical modification during their processing, which is performed in thermal furnaces or in complex installations. For structures used in the collection, storage and transportation of oil and oil and gas products, obtaining a uniform structure that provides the required operational properties in practice is quite difficult and virtually impossible, since there are no such furnace designs or physical modification units operated in practice or in the field production conditions.

In this regard, the use of local energy resources and the use of technology, including the study of the mechanism and patterns of formation of coatings due to direct processing through the use of solar energy, is one of the innovative solutions to the problem of energy conservation [9,14].

Studies have shown that the heliotechnological method of coating treatment significantly affects the properties of heterocomposite materials. To refine the modes of formation of polymer coatings by processing them with solar radiation, the properties of epoxy coatings were studied depending on the duration of treatment (table 2). The composition contains 12 parts by weight. PEPA, 10 parts by weight DBP and 10 parts by weight of HS and not treated with solar radiation when preparing the composition.

Control coatings were formed in the shade and tested after 24 hours.

As can be seen from the table 2 experimental data, the physical and mechanical properties of epoxy coatings increase depending on the duration of exposure to solar radiation.

In particular, with an increase in the processing time up to 300 minutes, the adhesion strength of epoxy coatings increases from 2.21 kgf / cm (control) to 2.50 kgf / cm, i.e. increases by 13% compared to untreated, tensile strength by 12%, impact strength by 52%, and the microhardness of the coating increases slightly and tends to stabilize with increasing processing time.
Figure 1. Scheme of a mechanical activator using systems of running drums and cylindrical vessel: 1-leading drum; 2-dependant drum; 3-electric motor; 4 – cylinder vessel; 5-belt transmission; 6-polymer and mineral activated components; 7-ballshaped natural mineral stones.

Table 2. Dependence of the properties of epoxy unfilled coatings regarding the duration of exposure to solar radiation.

| Coating property     | control | Duration of processing, min. |       |       |       |
|----------------------|---------|------------------------------|-------|-------|-------|
| 1. Adhesive strength, kgf/ Cм | 2.2     | 2.28                         | 2.45  | 2.50  | 2.37  |
| 2. Tearing strength, MPa    | 120.3   | 120.0                        | 135.8 | 130.7 | 125.5 |
| 3. Crash strength, H*м       | 21.0    | 27.0                         | 30.0  | 32.3  | 33.0  |
| 4. Microhardness, MPA       | 120.0   | 120.5                        | 123.3 | 125.0 | 128.0 |

The improvement of the physical and mechanical properties is explained by the fact that during the direct processing of the polymer coating in the sun, i.e. during the course of the chemical reaction of crosslinking with a curing agent, the polymer mass and the substrate are heated. Reducing the viscosity of the composition increases the mobility of the macromolecular chains of the polymer and improves the orientation of the functional groups of the interacting components.
The study of the effect of mechanoactivation of heterocomposite materials with the activation-heliotechnological method on their structure and properties showed that the density of compositions filled with commercial grades of kaolin obtained by the traditional method (mixing without mechanical activation) is not uniform and tends to increase relative to the substrate surface, i.e. the coating thickness is lower at the top than at the bottom. With the activation-heliotechnological method of structure formation, the density of heterocomposite materials approaches the theoretical one \( (g = 1.45 \, \text{g} / \text{m}^3) \) (figure 2), the time of mechanoactivation of the filler was 50-60 minutes.

![Figure 2. Dependence of the density of organomineral material on the time of mechanical activation.](image)

1-theoretical; 2-experimental

These results are explained by the fact that the charged metal particles of the mineral filler formed during mechanical activation form stable bonds with the active groups of the polymer compound in the polymer-filler interstructural boundaries [10-16], and intermolecular interaction forces prevent the settling of the filler particles under the influence of gravity, while in photographs of the structure obtained by an optical microscope on the surfaces of coatings by mechanoactivation of the filler and the heliotechnological method of structure formation, an improvement in the surface microstructure was observed, explained by a more uniform distribution of filler particles and the absence of agglomerates.

The results of studies of the resistance of heterocomposite polymer coatings to hydroabrasive wear showed that the value of the relative hydroabrasive wear resistance of epoxy compositions filled with AKF-78, AKC-30, AKT-10 kaolin in hydroabrasive media is always higher than the abrasive wear resistance in dry friction. The highest hydroabrasive wear resistance, both in dry and liquid friction, is observed in the samples held in an aqueous medium, and the least in those held in an \( \text{H}_2\text{SO}_4 \) medium (table 3).

The main operational property of coatings is microhardness, which characterizes mechanical resistance to external influences.

Scientific experiments conducted to disclose a particular phenomenon in science are formed by entering the results obtained in the form of tables, diagrams, graphs characterizing the object under study by a number or a set of numbers and cannot be physical laws. Only a mathematical model of an object in the form of a formula can be a law. Interpolation, the theory of dimensions and the theory of similarity are the scientific foundations of modeling and combine experience and knowledge, experiment and discovery [17].
Table 3. Relative hydroabrasive wear resistance of coatings in different environments.

| Coatings          | 5      | 10     | 15     | 20     | 25     |
|-------------------|--------|--------|--------|--------|--------|
| Without filler    | 0.366  | 0.365  | 0.364  | 0.364  | 0.364  |
| KPM+AKT–10        | 0.389  | 0.388  | 0.388  | 0.387  | 0.387  |
| KPM+AKC–30        | 0.238  | 0.236  | 0.233  | 0.232  | 0.232  |
| KPM+AKF–78        | 0.114  | 0.114  | 0.113  | 0.112  | 0.111  |
| In NaCl (5%) env. |        |        |        |        |        |
| Without filler    | 0.266  | 0.267  | 0.266  | 0.265  | 0.264  |
| KPM+AKT–10        | 0.271  | 0.272  | 0.272  | 0.271  | 0.271  |
| KPM+AKC–30        | 0.182  | 0.178  | 0.172  | 0.168  | 0.167  |
| KPM+AKF–78        | 0.105  | 0.104  | 0.103  | 0.102  | 0.102  |
| In H₂SO₄ (5%) env.|        |        |        |        |        |
| Without filler    | 9.254  | 0.255  | 0.254  | 0.253  | 0.252  |
| KPM+AKT–10        | 0.261  | 0.262  | 0.263  | 0.261  | 0.261  |
| KPM+AKC–30        | 0.152  | 0.151  | 0.150  | 0.149  | 0.149  |
| KPM+AKF–78        | 0.093  | 0.093  | 0.092  | 0.091  | 0.091  |

Each experiment must be carried out on the basis of a specific plan. Interpolation requires the experimenter to know the form of the interpolation function. The fields of application of interpolation are the discovery and clarification of the laws of nature, forecasting, planning and processing of experimental data, modeling, control of various objects, etc. The theory of interpolation together with the theory of similarity and dimensions is the scientific basis of modeling, which is very useful, and in many cases it is simply necessary. Interpolation can serve as a tool for verifying the truth of a law obtained theoretically. There are various formulas that make it possible to obtain an interpolation polynomial, one of which is Newton's interpolation formulas and the Lagrange method [18-20], which we used to determine the quantitative effect of the compositions of composite coatings and the operating environment when processing the experimental results (table 3). In this regard, based on the analysis of the composition of the corrosive medium, the quantitative and qualitative composition of the corrosive medium was selected for further studies of the properties of the coatings.

\[
P(x) = y_0 + \frac{\Delta y_0}{1!X} (x - x_0) + \frac{\Delta^2 y_0}{2!X^2} (x - x_0)(x - x_1) + \frac{\Delta^3 y}{3!X^3} (x - x_0)(x - x_1)(x - x_2) + \frac{\Delta^4 y}{4!X^4} (x - x_0)(x - x_1)(x - x_2)(x - x_3)
\]

In this case, a uniform step is selected:

\[
X = x_1 - x_0 = \varepsilon_{i+1} - \varepsilon_i
\]

Compiling a difference table by values (\(\Delta y, \Delta^2 y, \Delta^3 y, \Delta^4 y\)) for each case, table 3 calculations were made.

1. For coating without filler:

\[
P_{\text{without cover}}(x) = 0.366 - \frac{0.001}{1! \cdot 5} (x - 5) + \frac{0}{2!5^2} (x - 5)(x - 10) + \frac{0}{3!5^3} (x - 5)(x - 10)(x - 15) + \frac{0.001}{4!5^4} (x - 5)(x - 10)(x - 15)(x - 20)
\]

\[
= 0.366 - 0.005x + 0.01 + 0.0000004(x^2 - 15x + 50) \times (x^2 - 35x + 300)
\]

\[
= 0.366 - 0.005x + 0.01 + 0.0000004(x^4 - 20x^3 + 875x^2 - 6250x + 150000)
\]

6
Further, calculations were carried out to assess the hydroabrasive wear resistance of coatings filled with AKC-30 and AKF-78.

\[ P_{KPM+AKF-78}(x) = 0.114 - \frac{0.000}{115} (x - 5) - \frac{0.001}{215^2} (x - 5)(x - 10) + \frac{0.003}{315^3} (x - 5)(x - 10)(x - 15) + \frac{0.006}{415^4} (x - 5)(x - 10)(x - 15)(x - 20) = 0.114 - 0.000002(x^2 - 15x + 50) + 0.000013(x - 5)(x^2 - 25x + 150) - 0.0000066(x^2 - 15x + 50)(x^2 - 35x + 300) = 0.114 - 0.000002x^2 + 0.0003x - 0.001 + 0.00000013(x^3 - 30x^2 + 275x - 750) - 0.00000066(x^4 - 50x^3 + 875x^2 - 6250x + 1500) = 0.1030025 + 0.00446075x - 0.0006014x^2 + 0.0000313x^3 - 0.00000066x^3 \]

\[ P_{KPM+AK-30}(x) = 0.238 - \frac{0.002}{115} (x - 5) - \frac{0.001}{215^2} (x - 5)(x - 10) + \frac{0.003}{315^3} (x - 5)(x - 10)(x - 15) + \frac{0.006}{415^4} (x - 5)(x - 10)(x - 15)(x - 20) = 0.238 - 0.0004x + 0.002 - 0.000002(x^2 - 15x + 50) + 0.000004(x - 5)(x^2 - 25x + 150) - 0.0000004(x^2 - 15x + 50)(x^2 - 35x + 300) = 0.240 - 0.0004x - 0.001 + 0.0003x - 0.0002x^2 + 0.000004(x^3 - 30x^2 + 275x - 750) - 0.0000004(x^4 - 20x^3 + 875x^2 - 6250x + 1500) = 0.239 - 0.0001x - 0.00002x^2 + (0.000004x^3 - 0.00012x^2 + 0.0011x - 0.003) - 0.0000004x^4 + 0.000008x^3 - 0.00035x^2 + 0.0025x - 0.006 = -0.0000004x^4 + 0.000012x^3 - 0.00049x^2 + 0.0035x + 0.230 \]

Graphical images of the research results calculated by equations (1) and (2) are shown in figure 3.
Since it can be seen from the analysis of the results obtained (figure 3) that the best protective properties are possessed by a polyfunctional heterocomposite coating, where AKT-10 filler was used as a filler, to identify the effect of the environment, we performed calculations, the generalized results of which are presented in figure 4.

From the results analysis (figure 4), it can be noted that, regardless of the type of medium, the hydroabrasive wear resistance first increases and having a minimum at points of 10-12 days, in further values of the holding time, its monotonous decrease is observed according to the exponential law. It can be underlined that the highest wear resistance is observed in water (figure 4, a), and the least in acidic environment (figure 4, c).

4. Conclusion

Thus, by mathematical processing of the results obtained using Newton's interpolation formula and Lagrange's method, the quantitative significance of the influence of the compositions of composite coatings and the operating environment were determined, where the most preferable is a polyfunctional coating with AKT-10 filler under conditions of hydroabrasive wear.

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