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Development of the Composition and Study of the Operational and Anti-Corrosion Properties of Composite Polymer Coatings

M. S. Lee, S. M. Turabdjanov, U. A. Ziyamuhamedova

Scientific researcher at Tashkent State Technical University after named Islam Karimov, Tashkent, Uzbekistan
Doctor of Technical Sciences, Professor, Rector of the Tashkent State Technical University after named Islam
Karimov, Tashkent, Uzbekistan

Doctor of Technical Sciences, Professor, Head of "Materials Science" department at Tashkent State Technical
University after named Islam Karimov, Tashkent, Uzbekistan

ABSTRACT: The results of research on the development of composite polymeric materials compositions based on epoxy resin using various industrial grades kaolins are presented. The operational and anti-corrosion properties of the developed coating compositions based on epoxy binder filled with AKF – 78, AKC – 30, and AKT – 10 kaolins were studied. It has been established that compositions filled with AKT – 10 production grade kaolin possess the best protective properties against corrosion in a salty environment but compositions filled with AKF – 78 production grade kaolin possess the best protective properties against corrosion in an acidic environment. The compositions for corrosion protection in salty and acidic environments are proposed.

KEYWORDS: Kaolin, operational ability, aggressive environment, corrosion resistance, coatings, structural modifier, composite materials, protective ability.

I. INTRODUCTION

The use of various materials and coatings based on them to protect against environmental influences is currently promising to protect metals from corrosion. And the most effective are polymeric materials and composites based on them obtained by modifying the components of the composition by various methods. In this case, the study of physicochemical and mechanical phenomena observed at the interface of the bond-filler phase, and ensuring guaranteed properties of the compositions by their targeted regulation, is one of the objectives of research in this area [1, 2].

The particles of minerals subjected to functional modification are widely used in modern composite materials science. At the same time, it is necessary to conduct systematic studies of physicochemical mechanisms, their influence on the structure and properties of matrices, both in the process of obtaining PCM and in creating products from them. Of particular interest are studies of the mechanisms of formation of composite materials by high-energy technology of forming a mechanical mixture of components. Such technology allows forming single-layer or multi-layer composite materials with various combinations of polymer, metal, mineral components, including multi-layer coatings on machine parts and mechanisms. Thermophysical processes in the coolant medium that determine the kinetics of heating, melting of components, thermolysis, thermal-oxidative degradation and the formation of a homogeneous composite layer on a solid substrate require a systematic study. This will allow the development of modern high-tech compositions of composite materials based on various combinations of components and resource-saving technologies for their production and processing into products [3,4]. At the same time, reduction of internal stresses in polymer composite materials, which, due to the difference in linear expansion coefficients of polymers and metals, are concentrated mainly at the interface of their phases, and increase, thus, the adhesion characteristics, fine-dispersed fillers can be used [5, 6] and Moreover, their availability and low cost is one of the main criteria for industrial production. In this regard, in our studies, mechanically activated Angren kaolins of various industrial grades AKF-78, AKC-30 and AKT-10 were used as well as a chemical modifier as a structure-forming agent and the properties of composite coatings were studied with their application. The use of a 1.5% solution of a chlorosulfonated low-molecular-weight polyethylene (XCHIIЭ) Shurtan-gas-chemical complex in toluene as a structural modifier will ensure the chemical stability of the heterogeneous system.



II. KNOWLEDGE OF THE TOPIC AND PRELIMINARY RESEARCH

Corrosion damage to parts of the metal structure and process equipment in most cases begins from the surface and gradually penetrates into deeper layers. As a result of corrosion, chemical compounds of different composition are formed on the metal surface, which either remain in the form of films of salts, oxides and other compounds, or are transferred to the external environment. If the corrosion products are removed from the surface of the metal part, it is possible to detect the destroyed areas in the form of spots, shells and points. As a result of corrosion, the thickness of the part gradually decreases and, if measures are not taken to protect them, the metal structures can be completely destroyed.

Under the anti-corrosion (protective) coatings understand layers of composite materials such as paints, plasterings, linings, etc., with a given layer thickness, which are resistant to aggressive operating environments and the ability to protect the surfaces on which they are applied from destruction during a given period (life).

Protective coatings should ensure the almost complete absence of direct contact of the operating environment with the working surface of the protected structure. Coatings must be made of materials that are sufficiently resistant to external factors in certain environments. Among the chemically resistant materials include polymeric materials [6].

The most important feature of the structure of polymeric materials, distinguishing them from low molecular weight substances and metals, is the presence of long chain macromolecules with high flexibility. The ability to transform sections (segments) of a flexible macromolecule as a result of external factors (temperature, pressure, shear stress, tension, compression, etc.) causes an adequate response of the protective composite to operational impacts. This significantly increases the protective life of composite coatings.

The flexibility of polymeric macromolecules depends on the molecular weight, structure and nature of intermolecular interactions. The presence of polar groups in macromolecules and the degree of their branching, the ability to form hydrogen bonds and the size of the side substitutes affects the flexibility. A measure of the flexibility of a macromolecule is the size of a segment — a portion of the macromolecule that participates in thermal motion independently of its other parts. The different flexibility of macromolecules, the unequal mobility of their segments are one of the reasons for the differences in the properties of polymeric materials and compositions based on them.

When forming polymer composite coatings on solid substrates, the flexibility of chain macromolecules is of particular importance. As is known, a solid substrate limits the set of conformations of chain macromolecules located in the boundary layer of the polymer. If coatings are formed from polymers whose macromolecules have hard chains with low flexibility, the inability to move individual segments and slow down relaxation processes can cause such coatings to crack or peel off during the cooling process as a result of high residual stresses.

In addition, the hard chains of macromolecules prevent the achievement of a large area of adhesive contact with the substrate and reduce the likelihood of stable adhesive bonds between the functional groups of the polymer and the active centers of the surface of the substrate. Replacement of non-polar groups in the polymer chains by polar leads, by increasing intermolecular interactions, to an increase in the strength and rigidity of the polymer, a decrease in elasticity, and a decrease in gas and water permeability. Grafting polar groups to the main chain increases the adhesiveness of the polymer coating [7].

One of the main factors determining the performance of polymer coatings is the amount of adhesion of the matrix material to the substrate and its stability under operating conditions.

The adhesion of polymers to metals is usually judged by the adhesion strength of metal-polymer compounds, which is estimated by the work of exfoliation or the time of destruction of compounds by one or another method [8]. However, the work of destruction of metal-polymer compounds only in the case corresponds to the value of adhesion, if there are no defects in the boundary layer.

The production of composite materials with high adhesive strength and resistance to external influences [9, 10] is the most important task in the formation of polymer coatings on metal surfaces. High stability of adhesive joints can be achieved if, in addition to the formation of adhesive bonds with the substrate, the polymer coating has a sufficiently high cohesive strength, provided the maximum possible area of adhesive contact.

Modern theories consider the adhesion of polymers to metals as a result of the specific interaction of the polymer and the substrate, determined by their physicochemical, electrostatic, physical and other processes, with due attention being paid to the mechanical interaction of the adhesive and the substrate, especially when forming coatings of polymers on porous surfaces of various composition.

The strength of composite materials depends on numerous factors that make it difficult to compile experimental data for its prediction. In addition, real polymer coatings are multicomponent systems having a polymer base, various



modifying additives, which in most cases forces us to consider model systems with a limited number of influencing parameters and to use the obtained regularities with certain corrections in real coatings [9,10].

Methods for increasing the adhesion strength of composite systems by modifying polymer matrices are based on changing the chemical composition and structure of macromolecules of polymers, introducing substances that increase their adhesiveness, etc. The presence functional groups. Polymer coatings with a sufficient concentration of polar groups (polyamides, epoxy, phenol-aldehyde oligomers, etc.) have, as a rule, high initial adhesive strength without prior special preparation of the substrate. Increasing the content of polar groups up to a certain limit helps to improve the adhesion properties of polymers and to increase the strength of their combination with metals. The introduction of structuring additives (cross-linking elements) into thermosetting matrices allows an order of magnitude and more to increase the adhesion strength of coatings based on them, significantly increasing the cohesive strength and heat resistance of coatings [11].

Fillers are used to control the physicochemical, mechanical, and other properties of polymer coatings, including adhesive ones, which influence the absolute values of the strength of adhesive joints and the nature of the dependence of adhesive strength on temperature-time formation conditions. The effect of fillers on the adhesion characteristics of polymer coatings is complex, which does not allow general recommendations on the choice of a particular filler to increase the strength of the compounds at the interface and their stability under external influences within the specified limits. In this case, the important role played by the conditions of formation, the individual structural features and properties of the polymer and filler.

Among the means of anti-corrosion protection paints and varnishes (paintwork materials) remain the most common. The thickness of coatings of paint can vary from tens to hundreds of micrometers, depending on the destination. The paint coating is a solid film of organic substances deposited on the metal surface by spraying an emulsion (suspension) followed by drying. The main components of the paint coating are film-forming substances, curing components, dryers, pigments and fillers.

The most common binders for polymer composites, including paints and varnishes, over the past 40 years include epoxy oligomers. On their basis, receive protective coatings with high adhesive strength, chemical resistance and impermeability for aggressive media [12,13].

Work in the field of creating polymeric functional composites with mineral fillers has been developing intensively. Recently, interest in the use of natural substances such as clays, zeolites, mica, quartz, tuff, marble and other minerals in the creation of composite polymeric materials has increased [14-16]. However, systemic research into the mechanism of the modifying action of silicate-containing mineral particles on polymer matrices of various compositions is clearly not enough. This does not fully satisfy the demands of industrial enterprises in effective functional materials available for large-scale use [17].

However, the compositions proposed in these works are rather complicated, and most of their components are scarce, so their use requires large investments.

III. OBJECTS AND RESEARCH METHODS

As objects of study were used compositions based on epoxy resin ED-20, which have high physicomechanical properties and adhesion strength to metal bases, from which technological equipment and structures are made, high anticorrosion and wear-resistant properties when interacting with various media. In addition, the binding of ЭД-20 with the structurant ПЭПА allows to obtain coatings in natural conditions without special heat treatment, which is very important for large-sized products and structures. In this regard, composite coatings based on thermoplastic ЭД-20 were investigated by introducing various fillers, including mechanically activated Angrene kaolins, of different dispersity, the chemical composition of the basic compounds of which are given in Table 1, and the hardener of polyethylene polyamine (ПЭПА). For a uniform distribution of the filler across the coating thickness, a 1.5% solution of chlorosulfonated low molecular weight polyethylene (XCHПЭ) of the Shurtan gas chemical complex in toluene, obtained from studies [18], was used as a structural modifier. In order to increase the physico-chemical activity of substances at the interface, as well as to achieve maximum homogeneity (homogeneity) of the mixtures being mixed, especially when mixing and compacting multicomponent systems to increase the intensification of processes in order to drastically reduce their duration, the mixing of the filler and modifier was carried out on a dismembrator unit. When this occurs, the activation of the filler, that is, the excitation of molecules, atoms, bringing the latter into a state in which they easily form dense interlayer structural bonds at the interface of the filler-binder phase.

Disperse analysis of mineral fillers was carried out on the instrument of the particle size analysis system on the SediGraph 5100 instrument.

Table 1. Composition of AKF – 78, AKC – 30, AKT – 10 kaolin

Chemical composition, %	Kaolin marks		
	AKF – 78	AKC – 30	AKT – 10
a) Mass fraction of alumina, %	Up to 35	30-32	Up to 25
b) Mass fraction of iron oxide, %	0,4-0,6	0,5-0,55	0,6-0,9
в) Mass fraction of silicon dioxide, %	47,0-48,0	52-53	49,0-58,0
г) Mass fraction of titanium oxide, %	0,5-0,55	0,4-0,6	0,5-0,65

IV. RESULTS AND ITS DISCUSSION

As a result of the research, various formulations were developed.

As an anti-corrosion coating, the compositions shown in Table 2, applied to metal plates, were investigated.

Table 2. Compositions for corrosion resistance testing

Composite № 1	Composite № 2	Composite № 3	Composite № 4
According to the technological regulations of production	Epoxy resin ED-20 –100 wt.h.; dibutyl phthalate DBP +XCHΠЭ–20 wt.h; ΠЭПА –10 wt.h; AKC–30–30 wt.h.	Epoxy resin ED-20 -100 wt.h.; dibutyl phthalate DBP +XCHΠЭ–20 wt.h; ΠЭПА –10 wt.h.; AKF–78–30 wt.h.	Epoxy resin ED-20 –100 wt.h.; dibutyl phthalate DBP +XCHΠЭ–20 wt.h.; ΠЭПА –10 wt.h.; AKT–10-30 wt.h.

Upon receipt of composite materials, the concentration of the filler in the composite material is particularly important. Low-filled composite materials are more prone to viscous fracture, while highly filled to brittle [9]. One of the main conditions for ensuring the operational properties of the material is a strong adhesive bond at the interface between the filler and the matrix. As noted in [20], if a filler does not adhere to the matrix, its particles cannot bear any load, and the pores that appear during deformation serve as stress concentrators, if an inert filler is present in the composite material, then the dominant influence factor is entropy [21], leading to loosening of the surface layers of the binder. The entropy factor arising under the geometric constraint of the conformation of the polymer chains [22], regardless of the chemical nature of the filler. The entropy factor limits segmental and facilitates group mobility, reduces packing density. This factor manifests itself at any temperature, decreasing with its growth and distance from the interface. Taking into account these phenomena, in order to increase the adhesion between the filler and the binder, the properties of the compositions treated with a 1.5% solution of chlorosulfonated low-molecular-weight polyethylene in toluene were investigated, and the dispersion of the filler was different (from 0.3 μm to 45 μm).

The results of the study of the operational properties of coatings based on the developed compositions of composite materials showed that the coatings filled with Angren kaolin of the AKT – 10 brand have the best performance properties, while the worst ones are observed with the composite coating filled with AKF – 78 (fig. 1, 2), filler grain indicators are shown in table 3.

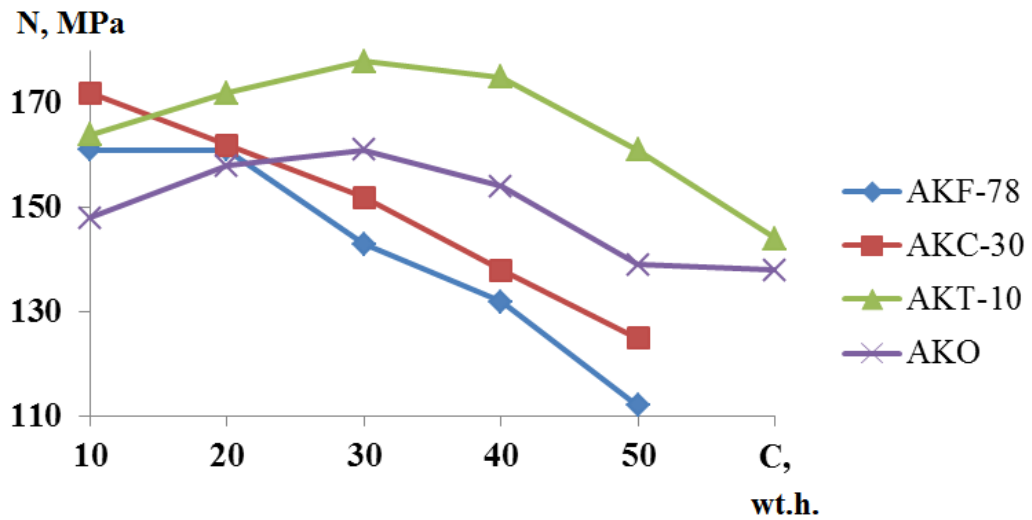


Fig.1. The effect of the type and content of fillers (Angrene kaolin - AKF-78, AKC-30, AKT-10 and AKO) on the microhardness (H) of epoxy coatings.

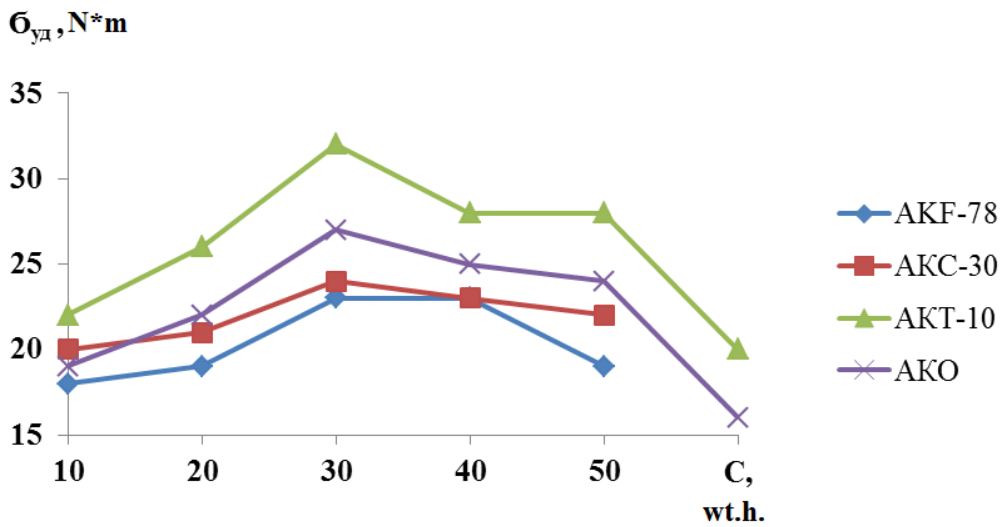


Fig.2. Influence of the type and content of fillers (Angrene kaolin - AKF-78, AKC-30, AKT-10 and AKO) for impact strength (y) of epoxy coatings.

Table 3. Kaolin granularity index

№	Industrial marks of Angren kaolin	Distribution of granularity, %	
		<1 μm	5-45 μm
1	AKF-78	71-73	25-28
2	AKC-30	49-50	47-49
3	AKT-10	25-32	65-72
4	AKO	21-25	72-75

The results obtained can be explained on the basis of technological properties, namely the deterioration of the wettability of the filler particles, which is observed with a sharp increase in the viscosity of the composition with a filler content of 60 wt.h. and more.

From the analysis of the research results presented in Figure 3, it can be noted that for casting materials, the content of the filler is 60 wt.h. not yet the limit.

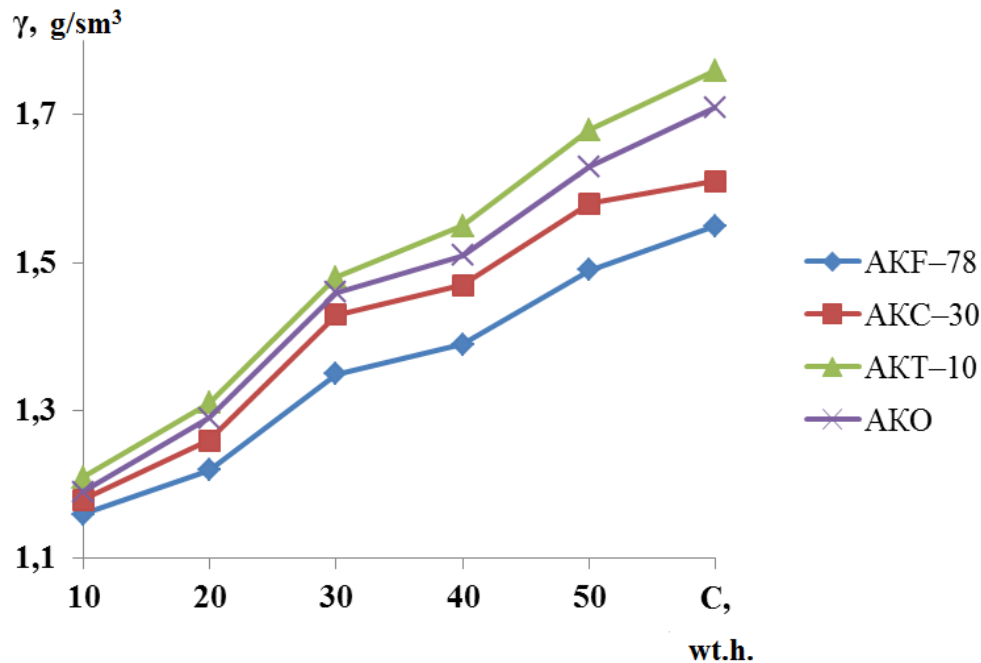


Fig.3. Influence of the type and content of fillers (Angren kaolin - AKF-78, AKC-30, AKT-10 and AKO) for density (γ) coatings based on epoxy composite materials

Since the increase in the content of the filler material density increases, however, with different intensity.

The composition is a dispersed system consisting of a polymer matrix in which solid filler particles are distributed. The properties of such a system are determined not only by the properties of the polymers and the filler, but also by the nature of the distribution of particles in the bulk of the matrix and the interaction processes at the interface.

For example, the smaller the amount of fillers (AKF – 78, AKC – 30), the less intensively the density of the material increases. This indicates the formation of micropores in the composition due to the deterioration of structure formation, due to the large specific surface of the filler.

Thus, the optimum composition of the composite material was established, further studies were aimed at studying their properties for use as anti-corrosion coatings.

Tables 4 and 5 present the results of testing the anticorrosion properties of composite polymer coatings in various environments.

The protective ability was determined by maintaining steel plates in different corrosive environments for 25 days. According to the table it can be seen that the degree of corrosion of steel, applied anti-corrosion coatings is less than that of the control sample. As control samples for testing used plates of steel grade St3.

Table 4. Anticorrosive properties of composite polymeric materials and coatings of them, depending on the type of kaolin grades in salt medium 3% NaCl

Coatings	Stationary potential, Esm, B	Corrosion rate, I, mA	Braking coefficient, γ	Degree of protection Z, %,
No coating	0,78	893	–	–
PCM without filler	0.65	45.3	2.19	84.00
PCM + kaolin	0.50	16.59	53.82	89.00
PCM +AKT-10	0.44	3.89	22.90	99.00
PCM +AKC-30	0.45	13.98	224.30	93.00
PCM +AKF-78	0.48	15.40	5.63	81.00

Table 5. Degree of protection and braking coefficient of kaolin-based compositions in an acidic environment of 3% H₂SO₄

Coatings	Stationary potential Ecm, B	Corrosion rate I, mA	Braking coefficient γ ,	Degree of protection Z %,,
No coating	0,28	1584	–	–
Compound without filler	0,35	876,3	21,19	80,00
PCM + kaolin	0,32	616,59	5,82	83,00
PCM +AKT-10	0,29	36,89	2,90	95,00
PCM +AKC-30	0,31	130,98	4,30	91,00
PCM +AKF-78	0,34	155,40	5,63	86,00

V. CONCLUSION

An analysis of the results of the study comparing the evaluation of anticorrosion ability of the compositions showed (Table 6) that the best protective properties against corrosion in a salt medium are compositions filled with kaolin of the AKT-10 production grade and in an acidic environment — compositions filled with kaolin of the AKF-78 production brand.

Table 6. Comparative indicators of the test and standard paint coating compositions

Indicators	The composition of the applied paint	
	According to the technological regulations of production (bitumen)	Epoxy resin ED20 –100 wt.h.; ДБФ+XCHПЭ–20 wt.h; ПЭПА –10 wt.h; AKT–10–30 wt.h.
The appearance of the film	Black, shines, smooth surface	Dark brown, shines, smooth surface
Elongation by viscometer, 20-25 ⁰ C	18–35	30

Mass fraction of nonvolatile substances, %	39 ± 2	40
Drying time of film to 3-rd stage at 20 ± 2 ^o m.f.	20	20



not more than with 100-110 ⁰ C min. No more (min)		
Film hardness by pendulum device M – 3 conventional units	0,20	0,20
Bending elasticity of the film, mm	1,0	1,0
Resistance of the film to static effect of water at a temperature of 20 ⁰ ± 2 ⁰ m.f., at least	48	48
Resistance of the film to static effect of 3% NaCl solution at a temperature 20 ⁰ ± 2 ⁰ m.f., at least (points)	3	3

Such a difference in the properties of coatings filled with kaolins is explained by their chemical composition (Table 7) and particle sizes. Due to the fact that kaolin AKT – 10 compared to AKF – 78 oxides: iron oxide, silicon dioxide is greater, the predominance of aluminum oxide in AKF – 78 gives an advantage to the coating based on it to predominate anticorrosion properties to aggressively acidic media.

Studies of the properties of coatings have shown that the amount of kaolin fillers in composite polymeric materials influences the physicomaterial properties of materials depending on their grades due to their dispersity, the smaller the dispersion of the filler, the higher the operational properties of coatings at small (10–20 mass.h.) the content of the filler, and at high contents of the filler (30–50 parts by weight), deterioration of the properties of the coatings is observed with a particle size of less than 1 micron in an amount of 50–73% (AKF – 78, AKS – 30).

The optimum amount of Angren kaolin content in potting materials and coatings is 20–30 wt.h. Moreover, from an economic point of view, kaolins with large particles are more beneficial in compositions, which is associated with the consumption of expensive epoxy oligomers.

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