

Savchuk P. P., Kashytskyi V. P., Malets V. M.,
Udovytska Yu. A., Furs T. V.

ACTIVATION OF PHASE INTERACTION OF EPOXY COMPOSITE COMPONENTS BY PHYSICAL FIELDS



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Authors:

P.P. Savchuk, Doctor of Technical Sciences, Professor;

V.P. Kashytskyi, Ph.D., Professor;

V.M. Malets, Ph.D., Associate Professor;

Yu. A. Udovytska, Junior Research Fellow;

T. V. Furs, Ph.D., Associate professor (Lutsk National Technical University).

Reviewers:

V.M. Anisimov — Doctor of Technical Sciences, Professor, Head of the Department of Applied Material Science and Processing Materials of the National University “Lviv Polytechnic”

K. O. Dyadyura — Doctor of Technical Sciences, Professor, Head of the Department of Applied Material Science and Technology of Structural Materials Khmelnytsky State University;

A. V. Minityskiy — Associate professor of high-temperature materials and powder metallurgy department National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” Ph.D., Senior Research.

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The monography is the basic source of knowledges about composites and powder materials.

It is intended for students of educational qualification levels "bachelor" and "master" of technical specialties of universities. Also, the manual may be useful for teachers-material scientists, engineers, scientists and specialists working in the field of creating and improving the properties of composite materials.

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CHAPTER 1.

STRUCTURING OF POLYMERCOMPOSITES FILLED BY HIGH-DYSPER PARTICULARS AFTER INFLUENCE OF PHYSICAL FIELDS

1.1 Effect of high-density particles on the structure and properties of polymer composites

The development of new polymer-composite materials with high mechanical and exploration characteristics is associated with the use of highly dispersed fillers [1; 2]. Small particle sizes, chemical and diffusion activity, high melting temperatures of highly dispersed powders [3–5] allow obtaining effective protector, antifriction, anti-wear, resource-saving, hydrophobic, self-cleaning and bio-inert polymer composite materials. These materials extend the functional and resource capabilities of engineering, structures, machinery and machinery used in engineering, construction, transport, energy, chemical and nuclear industries, military technology, medicine, and everyday life. Therefore, highly dispersed powders, which are used as fillers for composites with a polymer matrix, provide the creation of new materials with a complex of controlled properties that extend the area of practical application of polymer composites [4–6].

Epoxy and phenol formaldehyde resins, polyamides, polyvinyl chloride, polymethyl methacrylate, polystyrene, and various elastomers are most commonly used for the manufacture of polymer composite materials filled with metal powders [6–8].

The use of epoxy oligomers is promising among the wide range of polymer binders that are used to form composites. The authors [7] proved the efficiency of using epoxy resins as binding agents for the formation of composite materials with fibrous and dispersed additives due to the following advantages:

- epoxy resin is characterized by high adhesion to most disperse fillers and reinforcing fibers;
- a large number of varieties of epoxy resins and solidifiers allows obtaining materials with a wide range of properties;

- the cure reaction is not accompanied by the release of by-products (water, plasticizers) or volatile substances;
- shrinkage of epoxy resins in the process of structuring is much lower than other binders;
- the possibility of hardening in the room temperature;
- Composites based on epoxy resins are characterized by high chemical resistance and electrical insulating properties.

A wide range of properties of polymers is due to the chemical composition, structure of macromolecules, as well as their structure and mutual arrangement. The structure of macromolecules of polymers is characterized by conformation, molecular packing of chains, which depends on the nature and energy of intermolecular interactions and determines the ordering of macromolecules in space and among themselves. It has been established that the atoms of the main chain of macromolecules are connected by covalent bonds, and in the process of structuring polymer systems, they are interconnected by physical (Van der Waals forces) or by chemical bonds [7]. In the writings of authors [2–4; 6], using electron microscopy and radiographic studies, it was established that macromolecules in polymers are arranged in order, creating supramolecular structures resistant to mechanical influences.

As we known, the main type of supramolecular structure of amorphous polymers is globular formation, typical of linear and mixed polymers. Globules of polymers can be considered as spatial formations from macromolecules or their segments. Only certain areas of the macromolecules can be located in one supramolecular formation, while others interact with other molecules in other supramolecular formations. Segments of macromolecules located between adjacent globules will most often be deformed because these zones have a lower density. Therefore, we can assume that in amorphous polymers globules are connected with each other by separate chains, which provide uniform distribution of stresses and preserve the material's monolithicity [7–10].

It is known that the globular structure of amorphous polymers leads to deterioration of mechanical properties due to fragile destruction at the boundaries of globules. However, during the rise of temperature (additional heat treatment), the globules unfold, resulting in linear structures, which contributes to the increase in the mechanical characteristics

of polymers, the structure of which at the same time remains thermodynamically unstable [3].

As a result of studies of the influence of a solid support on the supramolecular structure of polymers, it was found that on the boundary there appears a continuous grid of secondary, larger globular entities, between which cells are densely packed small globules [6]. The size of the globules and the density of their packaging depend on the grid density, nature and molecular mass of the polymer.

A significant influence on the cohesive strength of polymeric composites is carried out by the adhesion between the polymer and the filler, the reduction of which leads to the detachment of the polymer from the filler for a low load and the formation of defects in the structure. Due to the high adhesion of the polymer to the filler, the formation of cracks in the matrix occurs earlier than the layering of the matrix from the surface of the particles [5–8].

At the interface between the phases of the polymer-filler system, there is a connection between the adhesion and the type of supramolecular structures. The size of the globules and the density of the packaging depending on the area of actual contact with the surface, the number of functional groups and the value of adhesion [11–15].

The nature of the matrix is one of the main factors that determine the temperature range of the use of composites, their chemical resistance, physical and mechanical properties, electrical properties and durability. In turn, the technological properties of the binder determine the process of obtaining composites. The main technological factors are the process of combining the binder with the binder, the effect of energy fields on the processes of phase interaction and temperature-time modes of material formation. The above factors are fundamental to the formation of the structure of composite materials at the micro and macro levels, which determines their performance characteristics.

The development of polymer-composite systems with controllable properties consists in a rational combination of the properties of the system's ingredients and the application of optimal technological regimes for the formation of polymer-composite materials. The process of structuring the composite material encompasses a complex of physicochemical processes of the interaction of the final groups of oligomer

macromolecules with active centers on the surface of the filler, which causes the formation of a new structure on the boundary between the phases of the phases. The degree of structuring and the volume of the phase in the boundary layer depend on the mobility of the macromolecules and supramolecular formations, which can be regulated by changing the nature and dispersion of the filler, modifying the method of thermal action [16; 17].

The temperature of the structuring of the oligomeric composition is determined by the temperature of the external environment and the thermal effects and affects not only the speed of chemical reactions but also the physical state of the composition and the depth of the chemical reactions. The effect of the thermal effect of the chemical-physical reactions on the temperature of the composition is determined by the volumes and conditions of heat exchange. When heating polymeric compositions to the temperature of structuring, there is a thermal expansion of a system with a high thermal coefficient, which results in thermal shrinkage of materials. In the structured form, the important characteristics of polymer composites, which determine their ability to operate, is the coefficient of thermal expansion, mechanical and electrical properties, sorption, diffusion, absorption of gases and vapors. Rational selection of ingredients should ensure the formation of strong and reliable composite systems at the expense of an optimal correlation between stiffness and viscosity [18, 20–22].

Experimental studies [7–11] of the filled polymer systems confirmed the promising use of highly dispersed metal powders, in particular nickel, aluminum, iron, gold, molybdenum, zinc, tin alloys, germanium and gallium as the fillers. The introduction of the data of the fillers changes the electrical conductivity and thermal conductivity of the polymeric materials, as well as increases the mechanical characteristics [12].

Synthetic inorganic compounds are widely used fillers-silicates Al, Ca, Mg, Br, ash, soot. They are characterized by high purity, high dispersion and high homogeneity in particle size compared with natural fillers [4; 12].

In systems consisting of a polymer matrix in which randomly distributed nanoparticles or clusters (agglomerated nanoparticles), the polymer matrix acts as a dispersion medium, and the nanoparticles are in a polymeric shell in the form of capsules [11].

The list of important requirements for disperse fillers includes compatibility with the polymer or the ability to disperse in it, the high wettability of the melt or polymer solution, lack of susceptibility to agglomeration of particles, homogeneity of sizes and low water absorption [16].

Typically, powder particles in the wide range of particle sizes (from 2–10 microns to 200–300 microns) act as disperse fillers, and in the case of nanocomposites, particle sizes of less than 1 microns with quantum-sized scales are used [15–17] The classification of fine particle size (Table 1.1) is a very important characteristic, since morphology substantially affects the physical, chemical and physical and mechanical properties of polymer composites [16].

Table 1.1.– Classification of highly dispersed particles by dimension

Characteristics of particles	The number of measurements is more than 100 nm	Types of nanoscale solids
The three dimensions (length, width, and height) are less than 100 nm	0 – dimensional object	Fullerenes, quantum dots, colloidal solutions, microemulsions
Transverse dimensions less than 100 nm	1 – dimensional object	nanotubes nanofibers nanocapillaries nanopores
One size (thickness) less than 100 nm	2 – dimensional object	nipples and nanolayers
Three dimensions exceed 100 nm	3 – dimensional object	ordinary macrolate

Properties of polymer composites modified with highly dispersed fillers depend on the volume content of particles, the size and form of inclusions (particles or their agglomerates), contact phenomena between phases, the presence of interphase interactions in the “polymer-filler” system, the structure of the spatial polymer matrix, the spatial distribution of the particles of the filler, technological and operational modes of formation, etc. [20–23].

Properties of polymers filled with metal powders to some extent depend on the conditions of the interaction of polymers with the particles of these metals in the solution, that is, from the shape of the polymer chain, the conditions of the formation of the solution and the conditions of formation of the surface layer. Wetting and interaction of solid surfaces with polymers are largely determined by the conformation of molecules in solution [22].

The density of the packaging of macromolecules is one of the important structural characteristics of a polymer, which determines its physical, chemical and physical and mechanical properties. The interaction of the polymer with the filler leads to the restriction of the mobility of the polymer chains, which is associated with the formation of additional physical nodes of the polymer mesh [24]. In general, the change in intermolecular interaction in the system leads to a change in the packing density of macromolecules. At the boundary of the phase separation of the “polymer-filler” system, initially, there is a decrease in the density of the packaging of macromolecules since the introduction of the filler leads to an increase in the specific surface and pore volume [22; 24].

Polymer composite materials with fine particles distributed uniformly in the volume of the matrix are characterized by an isometrics of properties whose extreme values are achieved at an optimum filling level, which ensures the adsorption of the polymer binder throughout the surface of the filler particles. The use of highly dispersed fillers can significantly improve the mechanical characteristics (flexibility, elasticity, hardness, durability) of polymer composites in the case of low filling, and in some cases enhance the new properties (reduction of permeability, increase of optical transparency, fire resistance), which can not be achieved through the use of traditional fillers and modifiers [17]. However, composite materials with highly dispersed particles have a mainly isotropic structure that is difficult to control, which limits their use in certain industries technique [25–28].

The relaxation processes in polymers at the interface between the phases of the polymer-filler system represent theoretical and practical interest. It is established that the presence of the boundary of the phase distribution leads to a significant change in the relaxation behavior of the polymer in the interphase layer, the change in the temperature of the

glass, the change in the mean relaxation time, and other properties of the heterogeneous polymer system. This is due to the change in the density of the molecular packaging, as well as the decrease in the mobility of the segments of the polymer chains and larger kinetic elements due to their interaction with the solid surface [27]. The change in mobility refers not only to directly contacting the surface of the layers, but also extends to rather large distances from the surface, although the effect itself is non-linearly dependent on the effective thickness of the phase layer. In the surface layers, compared with the volume, there is a noticeable increase in the change in the entropy of activation, while enthalpy decreases by a small amount. Properties of heterogeneous systems are determined by the part of the polymer, which is in the boundary layer [23; 27; 29–31]. These results indicate the dominant role of conformational effects in changing the molecular mobility of chains near the interphase boundary [28]. The thermophysical properties of polymers depend on the structure of the chains and the peculiarities of the course of molecular-kinetic processes on the molecular and supramolecular levels [24].

The mechanical properties of polymer-composite materials depend on the strength of the filler particles, the structure and properties of the phase-layer at the interface between the phases in the matrix-filler system. A strong interphase interaction between the matrix and the filler provides high stability of the composite to deformation, and much weaker – high shock strength [29–34]. In polymer-composite materials filled with fine particles, the main load perceives a matrix in which the particles of the filler form a heterogeneous structure that can effectively resist plastic deformation.

Deformation of the body under the influence of external mechanical forces is due to change in interatomic distances and conformations of macromolecules, the displacement of macromolecules relative to one another. The introduction of solid particles into polymeric compositions reduces the ability of polymer matrices to conformational transformations and the relative displacement of macromolecules. As a result, the resistance of the polymercomposites to the deformation increases and the magnitude of the limiting deformation decreases, which is explained by the presence on the surface of the particles of the filler of the adsorbed macromolecules of the polymer, part of which completely loses mobility

at a certain distance [35]. The closer the segment of the adsorbed macromolecule is to the solid surface, the less the number of degrees of freedom it has, resulting in a layer of polymer with reduced mobility on the surface of the filler. With the distance from the solid surface, the mobility of segments of adsorbed macromolecules increases. Due to the very high specific surface of some fillers (200–400 m²/g), the volume of polymer with reduced mobility can be quite significant. The presence of a limited part in the displacement of macromolecules complicates deformation and promotes increased elasticity, hardness, and viscosity of polymer composites; therefore, with the increase of the specific surface of the filler, the resistance of polymer-composite materials to deformation increases. Also, as a result of the formation of a spatial coagulation grid with dispersed particles, which is similar in structure to the frame structure, the composite system makes an additional resistance to deformation. The formation of this continuous grid is possible only if the specified percolation concentration of the filler in the polymer is reached. The degree of influence of this factor increases with increasing concentrations of filler [36; 37].

Increasing the resistance of polymers to deformation and reducing the magnitude of the deformation is also due to the fact that the elastic modulus of the filler particles is much higher than the elastic modulus of the polymers. Replacing part of the polymer with solid particles reduces the ability of the composition to deform and increases resistance to destruction.

The mechanical properties of the filled systems can be influenced by the forces of internal friction on the interface between the phases in the “polymer-filler” system, which arises as a result of shrinkage of the polymer during its hardening. Different types of stresses in the system, which lead to the emergence of nonequilibrium states, reduce the mechanical characteristics of polymercomposites. This applies primarily to the residual stresses that arise at the interface between the phases due to the inhibition of relaxation processes and the differences in the coefficients of thermal expansion of the polymer and the filler [38]. At the same time, increasing the strength of the adhesive bond of the polymer with the filler leads to increased stresses on the surface of the phase separation, which reduces the strength characteristics [32].

Under the influence of the load in the polymer compositions, there are microcracks, the source of which are the defects of the structure, as well as places of overexploited areas. In addition, the formation of primary cracks in the polymer composition contribute to fluctuations in thermal energy, that is, a local sharp growth of internal energy, causing the breakdown of chemical bonds. Since in the composite the particles of the filler practically do not deform together with the polymer matrix due to the large difference in the modulus of the elasticity of the components, therefore, in the process of deformation at the interface between the phases in the polymer-filler system there are overvoltages that cause the appearance of cracks in the matrix [39; 40].

It has been established that over time, adhesion strength decreases under the influence of residual stresses. Adjustment of the relationship between the magnitude of adhesion and residual stresses in polymer coatings can be achieved by the introduction of highly dispersed fillers. In the process of studying the relationship between adhesion and residual stresses, it should be borne in mind that the appearance of this kind of stress is due to differences in the conformational set of chains on the surface, in comparison with the volume of the matrix, determined by the conditions of interaction with the surface of the filler in comparison with the processes in the matrix volume. The residual stresses acting against the forces of adhesion reduce the work of the destruction of adhesion bonds by a value proportional to the given stress [41; 42].

In addition, in the case of low adhesion between the components, a polymer detachment from the surface of the particles can occur during the deformation of the polymercomposite material. Thus, in the process of deformation, the filler particles can be the source of defects and cracks in the polymer. The size of the data is cracks and detachments about.

In addition, in the case of low adhesion between the components, a polymer detachment from the surface of the particles can occur during the deformation of the polymercomposite material. Thus, in the process, the filler particles can be the source of defects and cracks in the polymer. The size of the data of cracks and detachments is proportional to the size of the particulate particles. If the particle size of the filler is less than critical, then also cracking or detachment less critical size, which limits the spontaneous propagation of cracks. Since the energy is expended on

the detachment of the polymer from the filler and the formation of microcracks, therefore, as a result of energy dissipation in the volume of the composite, its strength increases. With the introduction of filler with a critical particle size, large cracks occur in the polymer, which results in the destruction of the material at a lesser load than the destruction of the unpolished polymer. An increase in the particle size causes a decrease in the mechanical properties of polymeric compositions [39, 41–43]. The critical particle size of the filler is within a few hundred nanometers. It has been experimentally established that cracks in the case of meeting fine particles of the filler branch out, which prevents the growth of the crack length to critical size and requires additional energy expenditure to destroy the material.

At high concentrations of the filler in the polymer, there is a decrease in the mechanical characteristics of the composite, regardless of the size of the dispersed particles. Since the deformation of the composite is associated with the displacement of the particles of the filler and the tight packing of the filler particles prevents them from moving, so during deformation of the high-density composite in its matrix, there are large internal strains, which cause a decrease in the strength of the material [44].

The introduction of coarse fillers increases the yield strength of composite materials and reduces the strength limit, resulting in a rise in the temperature of the fragility of polymeric compositions. Highly dispersed fillers increase the strength limit of polymeric compositions, but due to the high specific surface, the yield strength is increased, as a result of which the temperature of the fragility of the polymer increases in this case. The exploitation of polymer composites at temperatures above the brittleness of the temperature allows fine particles to increase strength, however, provided that the limit concentration is reached, the amount of plastic deformation drops sharply. As a result, the fracture work and the impact strength of the polymer composites are sharply reduced in proportion to the limiting deformation [45].

The diffusion coefficients (self-diffusion and heterodiffusion) in epoxy-composite materials with fine particle are, as a rule, at an order of magnitude larger than the corresponding coefficients for systems filled with large-scale powders. These differences are due to the feature of the structure at the interface between the phases and the peculiarity of the

internal diffusion processes. Reducing the size of the filler increases the concentration of physics-chemical bonds, along which the diffusion coefficients are much larger so that the activation energy of diffusion is 2–2.5 times smaller at the interface between the phases of the system “polymer matrix–filler” [46–50].

1.2 Processes of structuring in polymeric compositions containing highly dispersed particles

The high efficiency of the use of highly dispersed fillers is achieved with full mixing of the components, which is largely determined by the ability of the polymer to wet the surface of the filler particles, which is possible due to the interaction of the segments of macromolecules with the active centers of the solid phase [51; 52]. Wetting with polymers in viscous, highly elastic or dissolved conditions is significantly different from wetting with low molecular weight substances. Limited mobility of macro chains and supramolecular formations limits the dispersion of a polymer on the surface of filler particles [53]. The desire of flexible chain molecules to maintain the most convenient conformations leads to the fact that the number of formed bonds is less than expected. Consequently, the creation of conditions for enhancing the interaction between the polymer and the filler is the subject of many studies, since the nature of the interaction between the components in these systems becomes crucial and determines the properties of composites [54].

Under normal conditions of structuring, for the uniform dispersion of the filler in the matrix and the proper wetting of the particles by the liquid phase of the polymer, it is necessary to ensure high compatibility of the components of the composite system. In this case, the physico-chemical processes on the interface between phases are activated in the system of “oligomer-filler” and “oligomer-substrate” [55]. In addition, the physical interaction between the ingredients at the initial stages of the formation of polymercomposite materials complicates the aggregation of the filler particles and promotes the formation in the matrix of layers of considerable density and extent that affects the adhesion and cohesive properties of composite materials [56].

The high viscosity of polymers reduces the rate of wetting of the surface, which occurs under the action of capillary forces, which ensure

the penetration of the liquid into the free space between the particles of agglomerates of the filler. For the rapid dispersion of the filler, it is necessary to spend work on the destruction of agglomerates or to treat the surface of the particles to reduce the angle of wetting. Unauthorized wetting or wetting by gravity is possible only at an angle = 0° , so all factors that reduce the angle of wetting improve dispersion filler [57–60].

For solid polymer compounds it is expedient to use fillers with a large specific surface, that is, with the smallest particle size. However, when selecting the optimum size of the filler particles, especially when using as a binder, low viscosity oligomers, it is necessary to take into account the tendency of particles to agglomeration, which increases with the increase of the specific surface of the filler, as well as the tendency to sedimentation, which is intensified with a decrease in the specific surface area, increasing the density of the filler and reducing the viscosity of the binder. Introduction of highly dispersed fillers is associated with the emergence of technological problems, as there is a growth of viscosity compositions by absorbing a considerable volume of polymer molecules by the surface of a solid phase [61–65].

During deformation of composites, agglomerates cause the formation of large cracks in the matrix, which reduces the strength of the material. In addition, agglomerates are complexes of low strength, which are the source of the appearance and spread of cracks. Therefore, in the case of the degradation of the dispersion of the filler, a sharp decrease in the strength of the composites occurs [66–69].

Polymer macromolecules in some cases are placed on the surface of metals in the form of fixed adsorption layers, forming chemical (covalent, ionic or coordination) bonds with atoms of the surface metal layer [70]. The connection between the macromolecules of the polymer and the metal is also explained by the action of physical forces of any type (orientation, induction, and dispersion). The adhesion of polymers to metals occurs due to the formation of hydrogen bonds between the individual links of the polymer macromolecules and the oxide film, which is almost always present on the metal surface [71–73]. The adhesion enhancement occurs when the polymer contains in a predetermined number of polar groups that can intensively interact with the surface metal atoms, for example, to act as a donor of electrons. It is established

that the more clearly expressed electron-donor properties of functional groups of polymers, the higher their adhesion to the metal [74; 75].

Polymers containing carboxy-phenol and hydroxyl groups interact with the metal surface mainly by means of ion-type bonds. In unstructured epoxy resins with a molecular weight of 400...2500, the interaction is carried out using functional hydroxyl and epoxy groups. In the case of perfect packaging hydroxyl groups in the formation of the adhesion bond involved 13...17% oxide ions [67, 75–77]. An increase in the number of epoxy groups in a macromolecule results in a sharp increase in adhesion interaction [71]. The weaker the ionic nature of the interaction of the metal surface with polymer dipoles, the greater the dominant influence of physical forces is on increasing the total energy of adhesion [72].

Structure of polymeric compositions containing highly dispersed particles is possible in the case of the synthesis of a spatial grid, with the subsequent formation of physicochemical bonds. Modern concepts of nanostructural formations make it possible to control the process of polymer structure formation by the influence of external physical fields [71–73]. Fine particles, evenly distributed in the polymer matrix, for small contents in polymeric compositions (up to 5 mass%) are capable of forming additional nodes in a spatial grid and interacting with a polymer matrix, which leads to a change in the strength characteristics of the polymeric composites [77]. Electrothermophysical parameters of polymeric composites are determined by transfer phenomena in a heterogeneous system, in which the electroconductive phase is formed from dispersing filler particles [72]. Dispersed metal fillers can weaken electromagnetic or corpuscular radiation, change the speed and mechanism of thermal and radiated-chemical transformations, provide radio-elaborating composites, increase their thermal and thermal stability [78; 79]. However, with decreasing particle size, their surface energy increases, agglomeration capacity and chemical activity increase, which leads to instability in the free state, ignition, rapid oxidation, and the complexity of uniform distribution in the volume of the polymer matrix arises [80; 81]. An important task concerning the formation of the heterogeneous structure of the composite system in the initial stages is to ensure the spatial placement of structural elements and the patterns of their

distribution in the event of a change in the average macroscopic density of the system [82].

The formation of physico-chemical bonds during the structuring of polymeric compositions is accompanied by a change in the molecular or segmental mobility of macromolecules, by the release of heat and by the change in the volume of the material, which leads to a sharp change in all the physical and mechanical properties of polymer composites. The determining influence on the change in the mobility of polymer molecules during the structuring process is performed by the ratio of the temperatures of the structuring and the composition of the compositions. Due to the peculiarities of the composition and properties of polymers, not all active functional groups of flexible macromolecules interact with active centers on the surface of particles. The irreversible sorption of polymers on the surface of particles is one of the proofs of a strong connection between the components, but the nature of the resulting bonds can't always be established, due to the complexity of their differentiation and identification [82–85].

Adsorption of polymers plays an important role in the formation of the structure of filled polymers, determining the nature of the packaging of macromolecules in the boundary layers, their molecular mobility, and relaxation properties, and ultimately the properties of polymer composites. Adsorption phenomena on the boundary of interphase interaction lead to the fact that the polymer material obtains additional heterogeneity, which is associated with the formation of the surface layer [74; 75].

Analysis of adsorption processes of polymers on solid surfaces showed that saturation of the surface occurs at relatively low concentrations of equilibrium solutions. Concentration decreases with increasing molecular mass, and the thickness of the adsorption layer increases. For example, the limit adsorption of polymethyl methacrylate in iron comes at a concentration of 0.1%, and polystyrene or polyvinyl chloride on silica – within 1% [76].

Adsorption of polymers from solutions on the surface of a solid phase essentially depends on the following factors: the nature of the polymer, the state of the surface of metal particles, the thermodynamic properties of the solvent, the molecular mass of the polymer, the reversibility of the adsorption process, the confirmation of macromolecules [77].

Significant influence on the kinetics of adsorption of polymers is carried out by the state of the surface, which is due to the increase in the number of pores in the fillers, high specific density and a decrease in the rate of diffusion of large molecules to the adsorbent in the event of an increase in concentration [78–80]. After the initial rapid increase in time adsorption, the process continues to slow down, indicating a delay in the adsorption process on the inner surfaces. This change in speed is conditioned by the presence on the surface of an adsorbent of sites of varying activity or associated with a change in the structure of the previously formed adsorption layer of molecules [79; 81].

The adsorption interaction of the polymer chains with the filler and the high degree of dispersion of the fillers can significantly slow down the hardening process, and the critical content of the filler may limit the formation of the spatial grid [84].

The study of the effective density of nodes of network polymers filled with fine dispersed fillers, which are introduced into the polymer at the stage of formation of the spatial grid, showed that in the presence of a filler, a more defective grid is formed than during polymerization in the absence of a filler. This is due to the fact that the highly developed surface of the filler at the initial stage of structuring can lead to an increase in the rate of bond breakage on the surface, resulting in a decrease in the density of the grid and it becomes more defective. In the subsequent stages of polymerization through adsorption of polymer chains, the number of which increases on the surface of the filler, the mobility of the chain segments significantly decreases, which is also reflected in the growth rates and recombination of bonds and the emergence of a more defective structure of the spatial grid [82].

For the optimum content of the filler, the density of the filled and unpolished polymer grid will become even. In this case, the processes that are associated with the adsorption of macromolecules and lead to the formation of a defective grid are compensated by processes associated with the orientation of molecules on the surface of the filler, which provides the formation of additional nodes of the spatial grid [83]. The effect of the filler on the change in the polymer density may be reduced by heat treatment or under the influence of the solvent in which the polymer is present [84–87].

The effective effect of the filler particles is to streamline the structure formation process. According to the thermodynamic conclusion A. I. Rusanov, the influence of the dispersed phase extends to the total volume of the neighboring, but at a certain distance from the surface, this effect dampens. Compared to the general structure of the matrix in the boundary layer, there is a more dense or porous packing of macromolecules. The density of the boundary layer is determined by the ratio of the energy of cohesion and adhesion, and the nature of the change of properties as far as the distance from the surface is a function of the flexibility of the polymer chain [87–90].

Since the residual stresses are determined by the strength of adhesion bonds, therefore, the processes of structuring filled polymers must be carried out in such a way that the stress relaxation time that arises during the formation of the polymer matrix is proportional to the duration of the process of formation of physico-chemical bonds. In this case, it will allow for high strength adhesion bonding and maximum possible reduction of residual stresses [91].

If the adhesion forces exceed cohesively, then it is more likely that the formation will begin in the part of the polymer, which is located near the boundary surface. Sealing polymer on the surface is associated with the displacement of the polymeric substance in the interphase region, so a porous sublayer appears near the sealed boundary layer. If all segments that have the ability to move to the structuring zone, then they do not have sufficient movement and form a porous zone. In the case of weak adhesion interaction, the resulting mass transfer is directed from the surface, so the boundary layer becomes more porous. In the case of using active filler, the existence of a porous layer is related to the nonequilibrium of the system and the incompleteness of the structuring processes [92].

In filled systems, coagulation structures begin to form, the elements of which are the particles of the filler with the condensed part of the boundary layer. Coagulation structures arise in the case of the connection of particles with weak Van der Waals forces through thin residual layers of the polymeric medium. Coagulation structures appear only in the case of high dispersion and sufficient anisotropy of particles, that is, in the case of a small number of coagulation centers [93]. As the surface

layer becomes thinner, the packing density of the macromolecules in the porous sublayer begins to increase gradually. Therefore, since the formation of dense boundary layers in the spatial grid, a stage of increasing the strength characteristics of the composite occurs [94].

The difference in the surface energy of the fillers also affects the morphological characteristics of the structure of the filled polymers. The structure formed in the presence of particles with high surface energy is more homogeneous [95].

As a result of the introduction of the filler, the molecular weight distribution and the rate of polymerization are changed, and a continuous spatial grid is formed that has highly elastic properties, which is explained by the change in the mobility of molecules in the boundary layers [88; 91]. The reaction rate on the surface of particles is always higher than in the volume of the polymer matrix, which leads to some increase in the ordering of molecules in the boundary layer, as well as the redistribution of intermolecular bonds.

Before the beginning of the formation, homophase fluctuations occur in volume and near the boundary surface. At the initial stage, micro-objects with high density occur and are fixed in zones with an increased level of intermolecular interaction [96]. With the increase in the energy of intermolecular interaction, the temperature at which macromolecules lose mobility, or in which the thermal motion is able to bring a macromolecule from a fixed state increases.

The filler can affect the occurrence of adverse reactions, which leads to changes in the chemical composition of the formed polymeric composition, and also affects the reaction rate, which is due to the difference in the structure of the boundary layer and the intensity of intermolecular interactions in the given layer. The rate constant of the reaction is higher for polymers containing a solvent, which promotes adsorption and, accordingly, the formation of boundary layers of greater thickness. The effect of adsorption on the rate of the structuring process consists in the fact that the part of the activated molecules in the boundary layer increases in comparison with the volume of the given layer. Under the influence of molecules in the boundary layer, the distribution of intermolecular interactions changes. Separate internal and intermolecular bonds in macromolecules are destroyed, resulting in reactive groups bind to the

surface of the particles as they become more active [94]. The surface of the filler particles determines the depth of the boundary layer, which in turn affects the elastic properties of the polymer.

Chemical and structural heterogeneity, which arises as a result of the influence of the interface of phases on the process of synthesis of the polymer network, determines the level of mechanical characteristics. Reducing molecular mobility and tight packaging, the emergence of defects and local stressed areas in the boundary layers, differences in the nature of the interaction of polymers with substances that modify the surface of the filler and a number of other processes determine the peculiarities of the behavior of the filled polymers under the influence of external loads [93].

Deep destruction of polymer chains at the nanoscale is possible under the action of ultraviolet radiation, which is an electromagnetic effect on the nanostructural level and leads to the breaking of bonds in the main chain of macromolecules [89], which causes the aging of the polymer. Changing the molecular structure leads to a change in the physical and mechanical properties of the polymer material and the loss of operational qualities. To protect polymers from photochemical destruction, light stabilizers are used, whose action is based on the absorption of sunlight (UV absorbers) [95]. Active light stabilizers for polymeric materials are inorganic pigments (TiO_2 , ZnO , ZnS), but during their application, there is a problem of uniform distribution of absorbers in the polymer matrix. To solve this problem, special coatings are applied which are applied to inorganic pigments. However, most light stabilizers are opaque and give the surface a white color. ZnO nanopowders are used to create almost transparent materials; however, powder particles can react with each other and lose photoprotective activity [96].

To maintain stable forms of metallic nanosized particles, they are stabilized by organic ligands. One of the most promising and affordable ways of stabilizing the forms of highly dispersed particles is to obtain organometallic complexes that can be introduced and evenly distributed in a polymeric material. In this regard, in the first stage of the formation of nanostructured polymer composites, the actual task is the introduction of new metal-complex compounds, as well as the study of the influence of nanosized particles on the properties of polymer composites [94].

The process of stabilizing nano-sized fillers in the polymer matrix is facilitated by the high absorption capacity of the particles to many high-molecular compounds. As a result of stabilization, a lyophobic core is formed, which is surrounded by a shell of a lyophilic solid layer of solvated polymer chains. The stabilization mechanism is based on the structural and mechanical stability factors of disperse systems and spatial networks of the type of coagulation structures, as well as the formation of adsorption-solvation structured films on the surface of nanoparticles [96].

1.3 Structuralization of highly modified particles of polymeric composites under the influence of physical fields

Obtaining composite materials with predetermined high performance characteristics is achieved by direct regulation of the parameters of the structure of the spatial grid of the polymer matrix, providing thermodynamic, kinetic and mechanical compatibility of the system ingredients, scientifically based introduction of structurally active components, as well as effective external energy influence on the system at various stages of its formation. In this case, the energetic physical fields play an important role in changing the structure of the reactoplast and the polymer composites in general. Depending on the stage of the technological process, the energy efficiency can be carried out at the stage of forming the polymeric composites, at the stage of hardening of the polymer matrix or at the stage of product operation.

It has been proved that the preliminary treatment of a polymer matrix in a magnetic field, ultraviolet, radiation, electrostatic, vibrational irradiation or ultrasound allows reducing the residual stresses in the system, increasing the cohesion and adhesion strength of the polymer composite material. Physical fields act at the level of the substructure, changing the conformational set of molecules, which ensures the creation of an optimal spatial mesh of the binding [97].

An analysis of the structures of epoxy polymers processed in a magnetic field indicates changes in the degree of structuring due to the restructuring of globules of molecules and the formation of additional

structural units due to the convergence of reactive groups under the action of an additional magnetic field moment that unfolds the macromolecule and places them along the gradient fields [98].

Due to the processing of compositions by a magnetic field, the temperature of the binder increases, which significantly reduces its viscosity. Accordingly, the polymer composition, having a high wetting factor, better fills the inequalities and defects of the substrate (substrate and filler particles), which is a prerequisite for the formation of a strong bond between the polymer and the solid phase. In addition, the temperature increase leads to the appearance of free functional groups in the adhesive (hydroxyl, carboxyl, carbonyl), which increases the number of physical and chemical bonds between them and the surface of the solid phase [99].

Treatment of epoxy compositions in a magnetic field is effective in the case of the use of fillers of ferro- or paramagnetic nature. In this case, the orientation of the macromolecules of the reactoplast relative to the particles of the filler is due to the interaction of the polymer dipoles with the magnetic field, which ensures the formation of oriented adhesive layers with increased adhesion strength [100].

Particles of ferromagnetic nature, in contrast to diamagnetic materials, have a non-compensated magnetic moment of considerable magnitude. During the overlay of the external magnetic field, the absolute value of the resulting moment increases, and its direction coincides with the direction of the magnetic field strength, which determines the magnetization of the particles. If the macromolecules of the epoxy oligomer are considered as domains, then the structure of the domains of the macromolecules, oriented in the direction of the magnetic field tension, is formed around the ferromagnetic particles during the superposition of the magnetic field [101]. The degree of binding of the binder in the outer surface layers of the particles and the cohesive strength of the composites considerably increase after processing of compositions in a magnetic field. In this case, the adhesion and cohesive strength of the composite materials increase more intensively after the processing of the composition containing ferromagnetic particles.

Ultrasonic treatment positively affects the structure and physical and mechanical properties of epoxy composites, regardless of the magnetic susceptibility of the filler. This processing intensifies the process

of structuring the system as a result of increasing the mobility of the components, which contributes to their even distribution in the volume of the composite. Reducing the viscosity of the ultrasound-treated composition provides better wetting of particulate particles with a high specific surface area. Also, ultrasonic treatment contributes to the intense degassing of the epoxy composition, which provides the formation of defect-free coatings, especially in the case of the formation of high-filled systems with high viscosity of the composition. As a result of the influence of ultrasound, there is an increase in the temperature of the system due to its heating by the absorbed energy [102–105].

Processing of compositions at the stage of formation of electromagnetic waves of the ultraviolet spectrum leads to a partial destruction of the macromolecule chains and the formation of free macroradicals capable of chemical interaction with the surface of the substrate. Irradiation is effective in the treatment of a polymeric composition without fillers, which is a barrier to pass ultraviolet waves. The intensity of the energy absorbed by the system depends on the thickness of the composition, in the case of which the number of generated macro-radicals decreases and the possibility of occurrence of physicochemical bonds is reduced because of the low ability of the reactoplast to pass electromagnetic waves [107; 108].

The newest technologies of mechanical and thermodynamic activation of physicochemical processes, which are associated with the ability to control the processes of polymer structure formation due to the use of external physical fields, are most intensively developed. Depending on the chemical nature and the physical state of the system, the basic ones are determined by transformation [108; 109] at the interface between phases in the system of “binder-filler” and chemical reactions in compositions:

- destruction, which is accompanied by a decrease in the molecular mass and the formation of free radicals, ions, free electrons, active atoms, molecules with intermediate active states;
- activation of chemical processes of destruction, replacement or addition, which is accompanied by a decrease in the activation energy of the components of the system after elimination of the source of radiation;
- chemical processes that are accompanied by destruction and the formation of new chemical bonds after the removal of the external physical field.

Consequently, scientifically grounded application of external physical fields for optimal regimes during the formation of epoxy-composite systems greatly enhances the physical-mechanical and performance characteristics of epoxy composites [110].

CHAPTER 2.

CHARACTERISTICS OF RESEARCHED MATERIALS AND METHODS OF RESEARCHES

2.1 Characteristics and properties of raw materials

As a matrix of polymeric composites, an epoxy resin of the mark ED-20 was used, which is a liquid reactive oligomeric product based on dibilicidyl ether of diphenylpropane. The basic physical and chemical properties of the epoxy resin are presented in (Table 2.1). Resin epoxy-diagonal ED-20 – viscous liquid of light yellow color without visible mechanical inclusions, soluble in toluene. When heating the resin to 873 K and above, a small amount of volatile substances – epichlorohydrin and toluene – is released. Coatings based on resin ED-20 have high adhesion to various materials, high hardness, elasticity, high dielectric properties, resistance to aggressive environments.

Table 2.1. – Physical and chemical properties of the resin of the brand ED-20

Indicator	Indicator value
Density, g/cm ³	1.16–1.2
Molecular weight	390–430
The content of epoxy groups,%	19.9–22.0
The content of volatile substances,%	1.0
The conditional viscosity of a ball viscometer at a temperature of 298 K, p	65
Total chlorine content,%	1.0

The advantages of epoxy resins, which make them irreplaceable astringent for the formation of high-strength composites, is a low linear shrinkage (less than 2%); lack of low molecular weight curing products; high adhesion (determined by high polarity and the ability of epoxy groups to chemically interact with the surface of many materials), which exceeds the adhesion of most other resins; the possibility of obtaining epoxy resins in different starting conditions (from solid to low viscosity), which allows the use of a variety of technological techniques; high mechanical parameters

of epoxy polymers that exceed the values of other mesh polymers; high electrical characteristics in a wide temperature range; the possibility of obtaining products and structures; water and chemical resistance.

Epoxy resins can harden at room temperature or elevated temperature (depending on the chemical properties of the fortress) without the influence of external pressure. Ability to cure these resins without the release of by-products provides a small shrinkage, impenetrability and high density of materials, which is important during the work of structures in difficult conditions of radioactive contamination or vacuum. Properties of products based on epoxy resins depend on the type of hardeners, additives, and plasticizers. Diane epoxy resin ED-20 can be transferred to a non-fusible and insoluble state by the action of various types of cementants-aliphatic and aromatic di- and polyamines, low molecular weight polyamides, di- and polycarboxylic acids and their anhydrides, phenol-formaldehyde resins, and the like.

Polyethylenepolyamine (PEPA) (TU6-02-594-70), which is a low-tensile dark brown liquid, is used to cure epoxy compositions. The hardener is designed for the structuring of epoxy resins at room temperature and lowered temperatures under high humidity conditions. The structuring process consists in the fact that the amine groups that are at the ends of the molecules react with the macromolecules of the epoxy resin. These groups are the most mobile and easy react to polymerization, resulting in a mesh structure of the polymer.

The introduction of highly dispersed fillers into a polymer composition improves the physical, mechanical and operational properties of epoxy composites. Small sizes, high surface energy, chemical and diffusion activity, high melting temperatures of particles allow the use of highly dispersed metal powders or compounds to create new epoxy composite coatings [111]. Pulses of various physical and chemical nature with the dispersity of 0.25–500 μm were used for research.

Powder iron grade PZHR-3 (GOST 9849-86) are obtained by spraying steel melt with high-pressure water jet. The iron contains at least 97% of the basic substance, the dispersion of particles is 30–50 microns. The content of impurities of carbon does not exceed 1.2% by weight, nitrogen – up to 0.9% by weight. and oxygen up to 0.7% by mass, which is in the form of carbides, nitrides, and oxides, respectively.

The carbon-grade iron of the grades P-20(GOST 13610–79) is a finely divided powder of pure iron (the average particle diameter is 2.5–5 microns), which is obtained by thermal decomposition of iron pentacarbonyl, followed by refining in a stream of hydrogen. It has high physical and chemical characteristics: high electrical conductivity, resistance to aggressive media, and also characterized by high ductility.

Contains particles of a spherical shape of a dense structure without sharp projections. Chemical composition: 0.7–0.9% C; 0.6–0.9% N; 0.8–1.2% O₂; 96.9–97% Fe.

The zirconium powder of the brand PCRK1 (TU48–4–234–84) has an average size particles 1–2 microns. Chemical powder composition: 91.447% Zr; 1.847% Si; 5.633% S; 0.171% Fe; 0.902% Hf. Zirconium is plastic and easily exposed to deformation in a cold or heated state. Brinell hardness is 64–67 MPa. The zirconium is paramagnetic, its specific magnetic susceptibility increases during the heating of metals. At a temperature of 346 K, the specific magnetic susceptibility of zirconium is 1.28, and at a temperature of 600 K – 1.41. Zirconium has a high corrosion resistance to atmospheric gases, water, and alkalis, does not react with acids and sulfuric acid (concentration up to 50%) [112–114].

Black Fullerene (TU2166–004–65523364–2010) – fullerene soot after extracting a mixture of fullerenes with nonpolar organic solvents and steamed to remove the organic solvent. Powder black, not soluble, bulk density 0.5 g/cm³, a total content of fullerenes not more than 0.10%.

Fluoroplastic of grade 4PN-20 (GOST 10007–80) is a fluorocarbon polymer that is a product of tetrafluoroethylene polymerization. The mass fraction of moisture is not more than 0.02%. Thermal stability at 688 K to not less than 100 hours. Fluoroplastic has a resistance to all acids, solvents, petroleum products, alkalis (except alkali metals) in the operating range of long-term operation from minus 542 K to plus 533 K, resistant to water vapor, climatic influences, has high strength, high dielectric, antifriction and adhesion properties. The average particle size is 6–20 μm [115; 116].

2.2 Methods of investigation of physical and mechanical properties and structure of epoxycomposites

The study of adhesion strength of epoxy composite coatings was carried out according to the methodology of GOST 14760–69 [117; 118], which is based on the measurement of the resistance of the separation of adhesive joints of the face surfaces of steel rods, with a conical protrusion for self-centering in the grip of a UMM-5 burst machine. The load change speed was 2 mm/min. The area of the end surface at the bonding point of the rods was 2 cm².

The hardness of epoxy composites is determined by the Brinell method(GOST 1786–80) on a hardener of the brand Novotest TC-BRV (Fig. 2.2) [117]. According to the method, a steel ball (indenter) 10 mm in diameter with a load of 2.5 kN for 60 is squeezed onto the material surface. The research was carried out on samples in the form of a bar with a smooth surface thickness of not less than 5 mm and a width of not less than 15 mm.

The boundary of compressive strength is determined by GOST 4651–82. For tests, samples of a cylindrical shape (diameter 5 ± 0.5 mm and a height of 15 mm) were used, in which the ratio of height to diameter (h_0/d_0) make up 1/3, were compressed for a uniformly increasing effort with a speed approaching sites of 2 mm [114].

The impact strength of epoxy composite coatings is determined according to the method of GOST 4765–73 [117], which consists in quantifying the impact energy required for cross-cutting damage to the protective coatings when falling from a certain height of the drummer with a tip of a calibrated size ($d = 8$ mm). The coating was applied on steel plates 60×200 mm in thickness 250–500 microns. The residual stresses are defined by the GOST 13036–67 consolethe method [114], which is based on measuring the deviation from the initial position of the free end of a console fixed elastic metal plate. The deformation of the plate occurs under the action of residual stresses that arise in the coatings (Fig. 2.4).

For measurement of residual stresses, plates of elastic steel of 80×15 mm in size and 0.25–0.3 mm in thickness, on which an epoxy-composite coating was applied with a thickness of 250–500 μm was used. The thick-

ness of the coating Δt is defined as the arithmetic mean of three dimensions along the length of the console.

The degree of structuring of epoxy composites was determined by the contents of the sample gel-sol fraction. The method is based on the ability of the soluble part of the polymer (sol-fraction), which is not bound to a polymeric grid, to be washed away with an organic solvent in the process of research. The amount of sol-fraction was investigated using an extractor Soxhlet, which worked in automatic mode [119]. Extraction of specimens in the size of 25×50 mm in thickness to 0.5 mm was carried out in toluene for 8 hours, followed by drying at a temperature of 393 K to constant weight. The mass of epoxy composites before and after extraction is determined on analytical laboratory scales with an accuracy of 0.0001 g.

To determine the functional groups of epoxy composites with fine particles of carbonyl iron, the spectrum of absorption bands in the region of infrared radiation is analyzed on the IRAffinity-1 spectrophotometer. The research was carried out in the frequency range $400\text{--}4000\text{ cm}^{-1}$ by the single-beam method in reflected light. Wave numbers are determined using the computer program IRsolution. To study the influence of the nature of the binder and the filler on the thermal transformation of composites, a thermogravimetric analysis method was used using the derivative "Thermoscan-2".

The method of thermogravimetric analysis consists in measuring the sample weight loss in the process of its continuous heating, which undergoes phase transitions and chemical reactions in the polymer material. Thus, the thermogravimetric dependences $m(T)$ are obtained. Modern studies of thermal effects are based on differential (derivative) thermogravimetry.

The research was carried out in the temperature range $\Delta T = 298\text{--}773\text{ K}$, using quartz crucibles for specimens of volume $V = 0.5\text{ cm}^3$. During the study, the rate of rising of the temperature was $v = 5\text{ K/min}$, with reference substance Al_2O_3 ($m = 0.5\text{ g}$), the weight of the test sample was $m = 0.3\text{ g}$. The temperature error was $\Delta T = \pm 1\text{ K}$. Accuracy of determination of thermal effects 3 J/g. The accuracy of determining the change in the weight of the sample is $\Delta m = 0.02\text{ g}$. The samples were heated to a temperature of 773 K during the conduct of the derivatization analysis [119–121].

The corrosion resistance of epoxy composites was determined by immersing samples in 10% solutions of H_2SO_4 , HNO_3 , HCl , NaCl , NaOH [117].

The size of the samples was $60 \times 10 \times 10$ mm. Samples were weighed before and after exposure in an aggressive environment on analytical grade scales HLR – 200 with an accuracy of 0.0001 g.

In a flask, 50 ml of the investigated solution and weight of the adsorbent were introduced. After a certain period of time (24, 68, 120 h), the samples were taken out and placed on a paper filter. The samples, together with the filter, were placed in a drying oven at a temperature of 80–100 °C.

Determination of the degree of cracking of epoxy composite coatings under the influence of alternating temperatures was to evaluate the length, width, and depth of the cracks in a five-point system and to determine the type of cracks in the standard (Figure 2.5) [114]. The epoxy composite composition was diluted with acetone to a viscosity of 20 s viscosity VZ-246 and applied by a pneumatic spraying method on metal plates made of steel 08 kp in the size $150 \times 70 \times 1.0$ mm. Each layer of the coating was structured at 373 K for 30 min. The research cycle was that the structured coatings were kept at room temperature for 2 hours, then at a temperature of 333 K for 30 minutes in the drying cabinet, and then exposed to negative temperatures in the refrigerating chamber TKS11 at a temperature of 233 K for 1 hour, then 15 min at room temperature. In total, 20 cycles of research were conducted.

The investigation of the macro and microstructure of the material was carried out on an optical microscope MBS-9 with an increase ($\times 30$) and a metallographic microscope of MMP-14C ($\times 100 \dots 1000$). Investigation of the general nature of the structure of the entire surface of polymeric composites and the detailed study of individual areas of the surface at large magnifications were carried out on a raster electron microscope (REM-106I) (Fig. 2.7) for an increase ($\times 100 \dots 1000$).

2.3 Methods for processing compositions and forming epoxy composite specimens

The formation of experimental samples was to obtain a homogeneous composition, which included the necessary components. Depending on the volume of samples, the quantitative content of ingredients in mass fractions was calculated at 100 wt. h. epoxy resin ED-20. The composition was molded as follows: PEPA hardener (12 parts by weight per 100 parts by weight of ED-20) was introduced into the epoxy resin, and the

filler was subsequently injected with the mechanical displacement of the components at each stage to ensure a high uniformity of the system. The formed composition was applied to the prepared surface or poured into special forms. The surface was pre-treated with abrasive to achieve the required roughness and degreased with acetone.

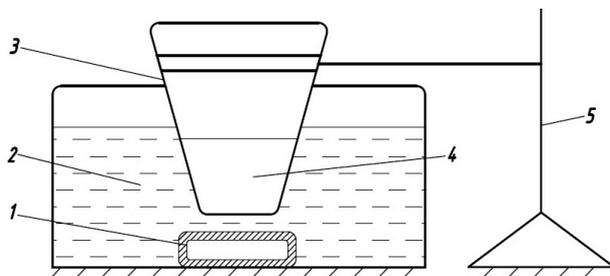


Figure 2.1. Scheme of the device for processing the composition with ultrasound: 1 – radiation source; 2 – medium (water); 3 – container; 4 – composition; 5 – tripod.

To activate the processes of structuring and uniform distribution of a highly dispersed filler in the volume of the polymer matrix after mechanical mixing, the compositions were treated by ultrasound or in an electromagnetic field. Ultrasound treatment was carried out in a laboratory container (Figure 2.1) in a medium of water at a frequency of 20 kHz. The prepared composition in a vessel measuring 6×4 cm was located at a distance of 10 mm from the source of ultrasonic waves. Processing time was 5–10 minutes.

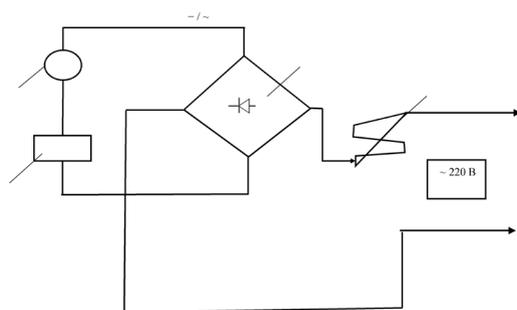


Figure 2.2. Scheme of the installation for processing compositions in the electromagnetic field: 1 – ammeter; 2 – diode bridge; 3 – autotransformer; 4 – electromagnet

To study the influence of electromagnetic treatment, a high-frequency electromagnetic field was used (Fig. 2.2). The treatment was carried out in an air environment. Processing time was 5–10 minutes.

A tissue of epoxy composites under normal conditions lasted 24 hours. Additional heat treatment was carried out in a furnace by step mode: 343 K with 1-year standby, 373 K with 1-year holding, 403 K with endurance 4 hours.

CHAPTER 3.

STUDY OF STRUCTURING PROCESSES OF EPOXY COMPOSITE SYSTEMS MODIFIED BY PHYSICAL FIELDS

Due to the developed raw material base, a complex of high physico-mechanical characteristics and processability, polymer composite materials on the basis of epoxy-dyano resins are widely used in many industries as protective coatings [122], to improve the mechanical characteristics of which introduces a variety of highly dispersed fillers. In addition, to improve the interfacial interaction of components of the system, they are additionally modified by external physical fields [123]. For researches, dispersed fillers of different chemical and magnetic nature are used, which allows us to estimate the influence of physical fields on the processes of the structuring of multifunctional epoxy-composite materials. These fillers are introduced in order to increase the adhesion strength, electrical conductivity, magnetic susceptibility and corrosion resistance of epoxy composite coatings.

3.1 Investigation of the adhesive strength of epoxy composite coatings modified by fine particle

As a result of experimental studies, it was established (Fig. 3.1) that for epoxy composites filled with iron powder PZR-3 and carbonyl iron P-20 for the contents of the filler 6–10 parts by weight. the decrease in adhesion strength was 1.6–1.7 times compared to the incomplete system due to the formation of an insufficient number of chemical bonds between the macromolecules of the epoxy polymer matrix and the highly dispersed particles. This is due to the fact that in this case a structure characterized by a low content of gel fraction ($G = 91\%$) and a large number of defects: pores, cavities ($d = 50\text{--}150\ \mu\text{m}$) and agglomerates ($d = 10\text{--}40\ \mu\text{m}$) (Fig. 3.2, a, b). At higher levels of filling systems with Powder brands PZR-3 and P-20 in the amount of 10–40 parts by weight. an increase in adhesion strength of epoxycomposites is observed in 1.4–2.4 times in comparison with the low-filling system (6–10 wt. h), which is associated with a decrease in the residual stresses in the material (Fig. 3.8).

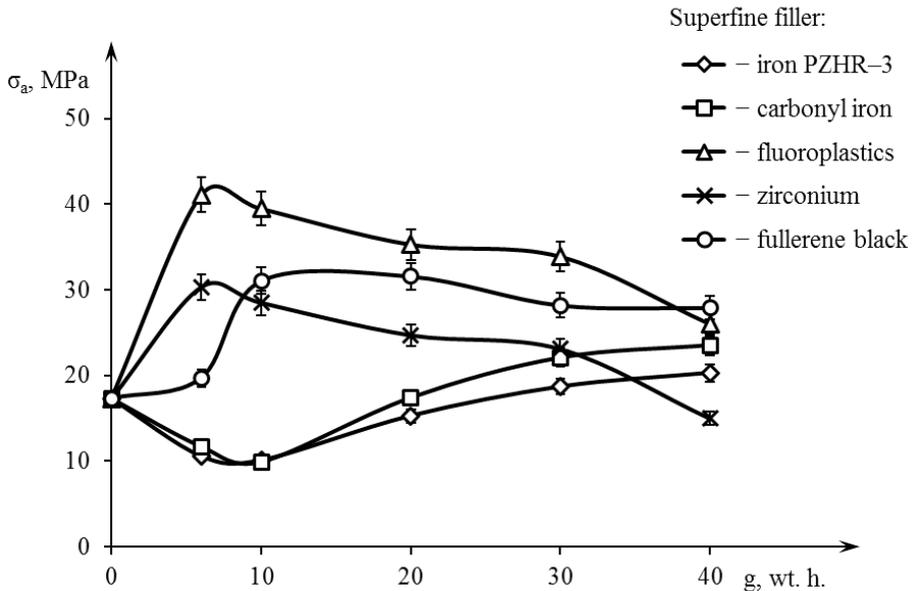


Figure 3.1. Dependence of the adhesive strength of epoxy composites on the content and type of highly dispersed filler

The introduction of fluoroplastic powder in an amount of 6 parts by weight in the epoxy polymer matrix leads to an increase in adhesion strength 2.5 times compared to the imperfect system ($\sigma_a = 17.3$ MPa). The fluoroplastic powder contributes to the formation of the structure of epoxy composites with low residual stresses ($\sigma_{rs} = 1.96$ MPa) due to the ability of the system to relax in the structuring process due to the high plasticity of the fluoroplastic particles and the formation of a structure with low air content inclusions ($d = 50\text{--}100$ μm) (Fig. 3.2, c). It was established that the range of optimal content of fine particles of fluoroplastic in the matrix is 6–10 wt. h., in which the adhesive strength of the epoxy composites reaches the maximum values. Increase the powder content in the composite to 10–30 wt. h. leads to a smooth reduction of adhesion strength on 3–15%, and within 30–40 wt. h. there is a sharp decrease in the studied characteristics by 20–30%, which is due to the presence of agglomerates ($d = 100\text{--}200$ μm) and other defects in the structure (pores in diameter 200–300 μm) (Fig. 3.2, g), which were formed due to the uneven distribution of the filler particles in the

volume of the matrix, resulting in incomplete wetting of the polymer of highly dispersed particles.

It has been established that the introduction of zirconium powder into the epoxy matrix results in an increase in adhesion strength by 75% ($\sigma_a = 30.3$ MPa) in the content of the filler 6 parts by mass. compared to the incomplete system. The zirconium powder contributes to the formation of a strong bond between the surface of the filler particles and the polymer matrix with minimum residual stresses ($\sigma_{rz} = 1.48$ MPa) in the epoxy-composite coatings without processing due to the high ability of the surface of zirconium particles to wetting with the polymer and the formation of homogeneous compositions. Increase in the content of zirconium powder to 40 parts by weight. leads to a decrease in adhesion strength by 50% ($\sigma_a = 15.7$ MPa), which is mainly due to the appearance of various defects in the form of cavities, pores ($d = 150\text{--}200$ microns) on the surface of the coatings (Fig. 3.2, d). Low levels of adhesion strength under conditions of a high content of the filler can also be explained by the increased viscosity of the composition, resulting in complexes of macromolecules not completely fill the micron- iveness of the substrate.

It has been experimentally established that the introduction into the epoxy composite of a highly dispersed fullerene black powder results in an increase in adhesion strength by 1.5 times from 17.3 MPa (for epoxy polymers) to 31.7 MPa (for epoxy composites with a powder content of 4 to 8 parts by mass).

The presence of highly dispersed particles in the system leads to an increase in the cohesive strength of composites due to the ability of the particles to intensively interact with the oligomer macromolecules, which leads to an increase in the content of the gel fraction ($G = 95\%$) due to the increase in the number of chemical bonds.

It has been established that the epoxy composition (Fig. 3.3) is sensitive to the influence of the electromagnetic field since the growth of the adhesive strength of the epoxy polymer is 13% compared to the epoxy polymer, the composition of which has not been processed in the physical field. Epoxy composite materials, filled with powder of fullerene black, with the treatment of compositions in the electromagnetic field ($\sigma_a = 70.6$ MPa), is the maximal adhesive strength compared to similarly treated epoxy polymers.

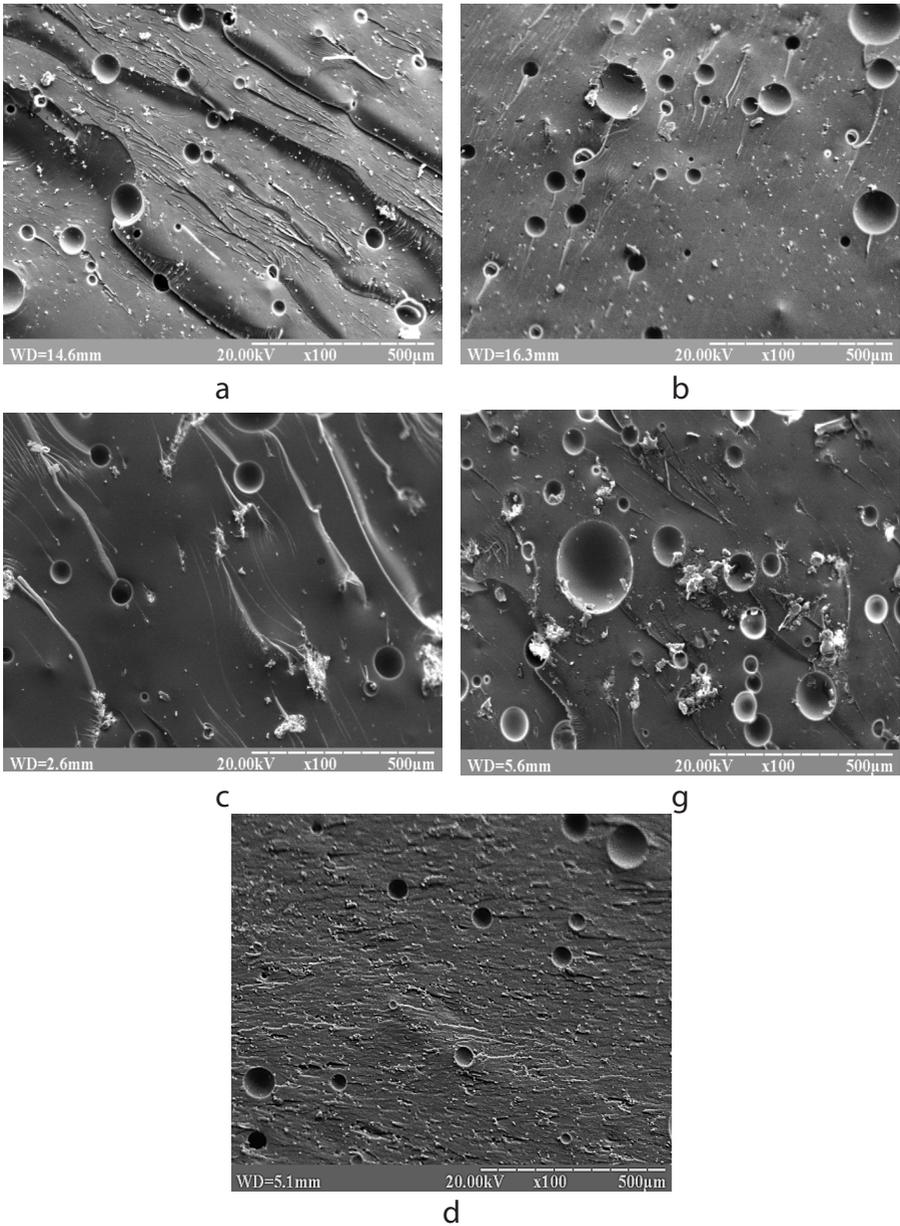


Figure 3.2. Fractograms of the fracture of epoxy composites filled with fine particles: a – iron of the brand PZR-3; b – carbonyl iron; c – fluoroplastics (6 parts by weight); g – fluoroplastics (30 parts by weight); d – zirconium, $\times 100$

The treatment carried out results in the localization of macromolecules and supramolecular oligomer structures on the surface of the disperse particles, which leads to an increase in the degree of crosslinking ($G = 97\%$) of the matrix in the surface layers [124].

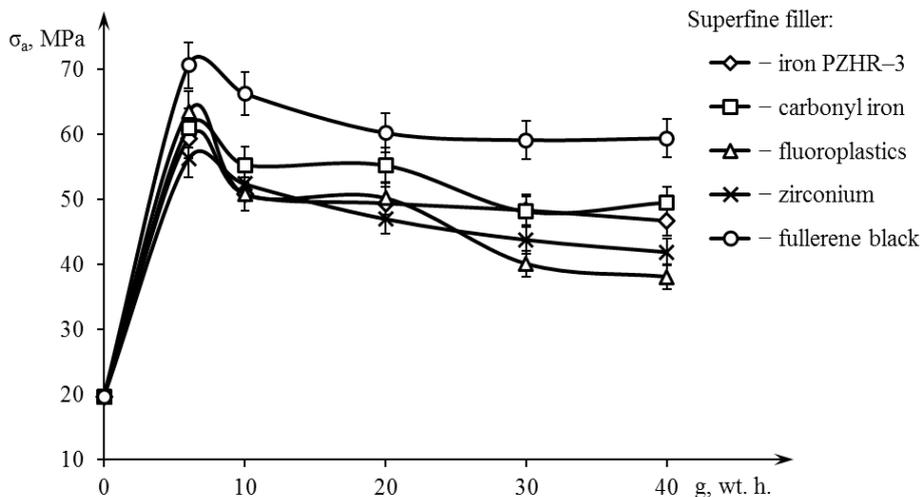


Figure 3.3. Dependence of the adhesive strength of epoxy composites, the compositions of which are processed in the electromagnetic field, on the content of the filler

It has been experimentally established that the treatment in the electromagnetic field of epoxy constituents results in a sharp increase in the adhesive strength of epoxy composites with a low content of highly dispersed powders (6–10 wt. h.). In the 3.1–4.2 times, compared with the treated epoxy polymer. For epoxy-composite materials filled with iron powders of the grades PZR-3 and P-20, there is a maximum increase in adhesion strength in 5.2–5.6 times compared with epoxy composites whose compositions have not been processed in physical fields. For composites filled with fine particles of fluoroplastics and zirconium, the growth of adhesion strength in 1.5–1.8 times ($\sigma_a = 63.5$ MPa – epoxy composite with fluoroplastic powder, $\sigma_a = 56.25$ MPa – epoxy composite with zirconium powder), compared to similar composite systems without processing. Treatment in the electromagnetic field of compositions containing fine particles contributes

to increasing the adhesive capacity of the filler, since on the surface of fine particles, reactive centers are activated due to the action of the external field, which, in the process of forming the epoxy composites, provide additional structure formation by increasing the number of bonds between the binders and the surface of particles, which determines the overall improvement of the mechanical properties of epoxy composites [125].

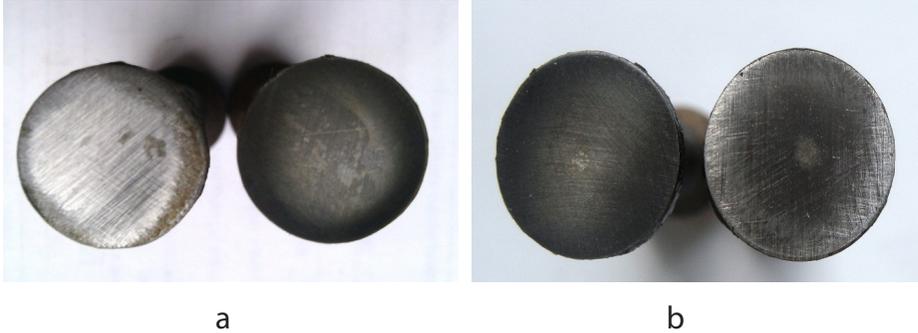


Figure 3.4. General view of the surface of adhesive bonding of epoxy composite coatings filled with fine particles: a – without treatment; b – treatment of compositions in the electromagnetic field

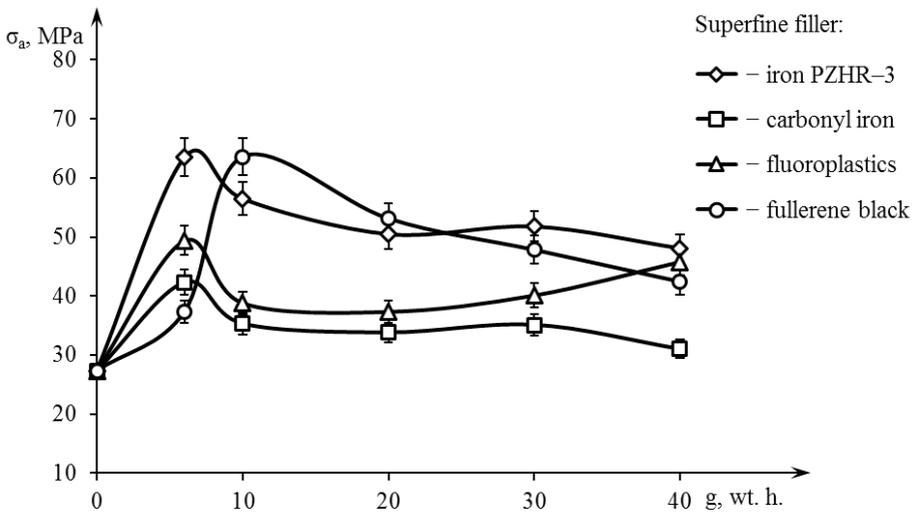


Figure 3.5. Dependence of the adhesive strength of epoxy composites, the compositions of which are processed by ultrasound, on the content of the filler

The adhesive strength of epoxy polymers by processing the composition with an ultrasound (Fig. 3.5) increases 1.7 times in comparison with the untreated compositions (Fig. 3.1) and 1.5 times in comparison with epoxypolymers whose compositions are processed in the electromagnetic field (Fig. 3.3).

Ultrasonic treatment contributes to a 1.2 times increase in the adhesion strength of epoxy composites for a low degree of filling of the system (6–10 parts by weight) with powder of fluoroplastics, 3 times by powder of carbonyl iron, 12.6 times by iron powder of grade PZHR-3 and in 3.6 times – a powder of fullerene black compared to epoxy polymers. The increase of the adhesive strength of epoxy composites, the composition of which is processed by ultrasound, is associated with improved wetting of the surface of the particles with viscous oligomer [127]. An increase in the content of the filler is accompanied by a decline in adhesion strength due to the presence of agglomerates ($d = 30\text{--}70\ \mu\text{m}$) (Figure 3.7 a, b), which remained in the system and limit the wetting of the surface of individual particles by the polymer, as well as the increased stressed state due to the low segmental capacity macromolecules to micro-displacements in the outer surface layers of the filler particles.

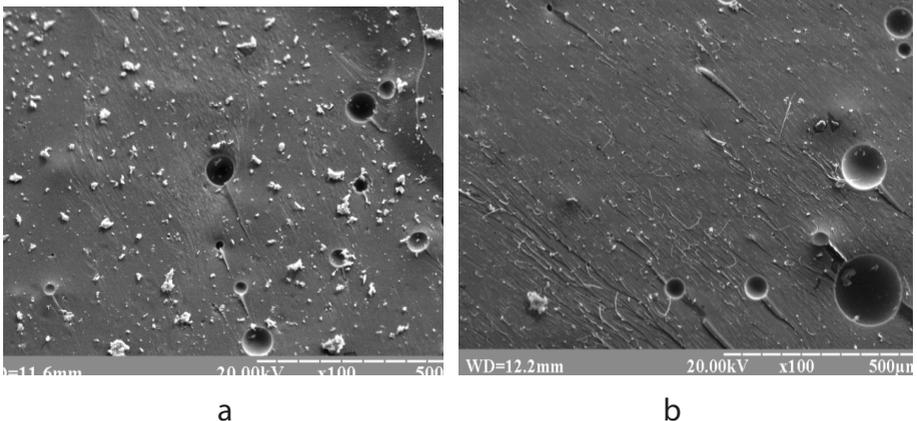


Figure 3.7. The fractograms of the fracture of epoxy composites, the compositions of which were modified by ultrasound and filled with fine particles: a – iron of the mark PZR-3; b – carbonyl iron, $\times 100$

3.2 Investigation of the stressed state of epoxy composite coatings modified by fine particle

It has been experimentally established that the introduction of highly dispersed powders (10 parts by weight) leads to an increase of 2.2 times the residual stresses (Figure 3.8) for epoxy composites filled with PZR-3 grade iron powder and 1.4 times for epoxy composites filled the fluoroplastic powder in comparison with epoxy polymers ($\sigma_{zal} = 1.46$ MPa), since the introduction of highly dispersed particles into the polymeric system leads to a significant increase in the viscosity of the composition due to the preservation of the agglomerates of the particles (Figure 3.9, a, b) and the reduction of the thermodynamic equilibrium with them [128].

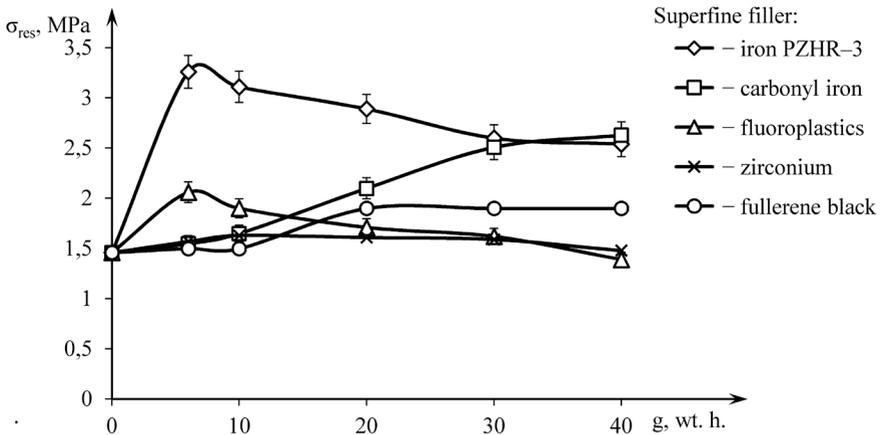


Figure 3.8. Dependence of residual stresses in epoxy composites on the content of the filler

The increase in the content of PZR-3 iron powder (10–40 parts by weight) leads to a decrease in the investigated characteristic by 4.6–22% and by 7.7% to 32.5% in the case of the introduction of fluoroplastic powder. The introduction into the epoxy polymeric composition of carbonyl iron powder (6–40 parts by weight) leads to an increase in residual stresses up to 80% compared to the incomplete system, which can be explained by the presence of structural defects (pores, agglomerations of

particles) and a large number of lines of shaving, indicating high tense state of the system (Figure 3.9, c).

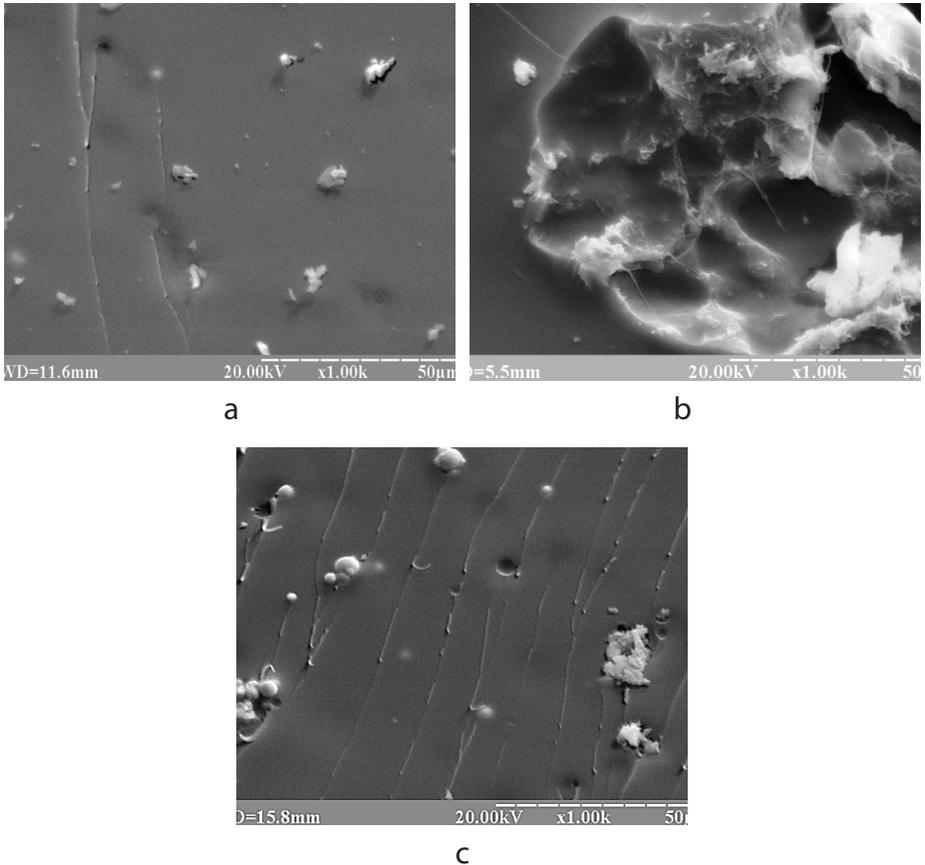


Figure 3.9. Fractograms of the fracture of epoxy composites, filled with fine particles: a – iron grades PZHR-3; b – fluoroplastic; c – carbonyl iron, $\times 1000$

The processing of compositions in the electromagnetic field (Fig. 3.10) resulted in a reduction of 3.6 times the residual stresses in epoxy composites containing ferromagnetic fillers (6–10 wt. h.) ($\sigma_{rz} = 0.902$ MPa) using iron powder of the grade PZHR-3 and 2 times ($\sigma_{rz} = 0.762$ MPa) using carbonyl iron powder in comparison with epoxy polymers ($\sigma_{rz} = 1.68$ MPa).

Treatment of compositions in an electromagnetic field at low content (6–10 wt. h) of ferromagnetic highly dispersed iron particles helps

to structure epoxy composites with the formation of additional physical and chemical bonds between active groups on the surface of the filler and functional groups of the epoxy matrix, since the content of the gel fraction is at a high level ($G = 96 \dots 97\%$). The action of the magnetic field contributes to the uniform distribution of ferromagnetic particles in the epoxy composite at the formation stage and reduces the number of agglomerates ($d = 5\text{--}7 \mu\text{m}$) (Figure 3.11, a, b).

Treatment in the electromagnetic field of compositions containing highly pure fluoroplastic powder does not affect the residual stresses in epoxy composites in the amount of 6–20 parts by weight, which can be explained by the diamagnetic nature of the filler. In the case of the formation of a medium-filled system (30–40 wt. h.), the growth of the investigated characteristic is observed at 22–48%, as agglomerates remain in the structure acting as stress concentrators (Figure 3.11, c).

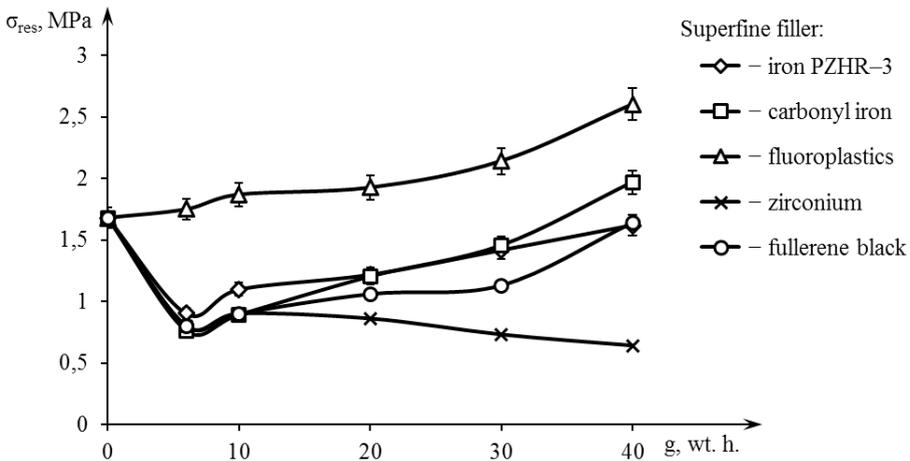


Figure 3.10. Dependence of residual stresses in epoxy composites, the compositions of which are processed in the electromagnetic field, on the content of the filler

It was established that the treatment of compositions filled with zirconium powder in the electromagnetic field contributes to reducing the residual stresses in epoxy composites by 60... 80 compared with epoxy composites of a similar composition without pre-treatment of compositions

($\sigma_{rz} = 1.8$ MPa), because degassing and reduction of macroscopic defects occurs systems (Fig. 3.12, a, b). It has been experimentally established that electromagnetic treatment of compositions contributes to reducing residual stresses by 27% in epoxy composites filled with powder of fullerene black, which provides high values of adhesion strength ($\sigma_a = 70.6$ MPa).

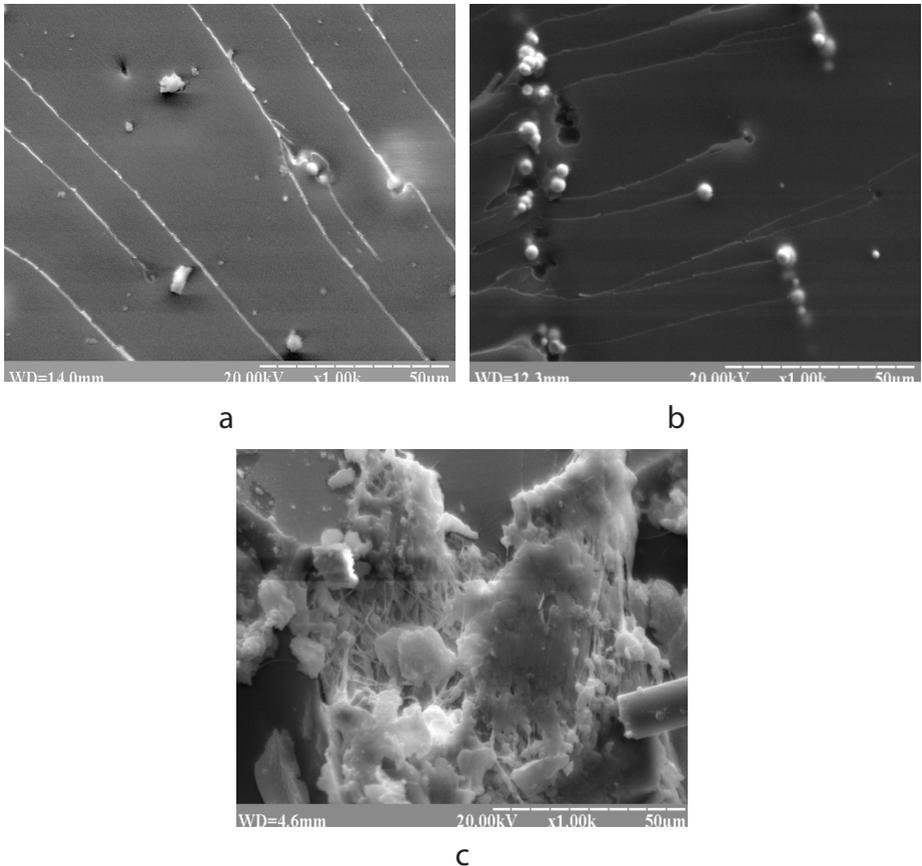


Figure 3.11. The fractograms of the fracture of epoxy composites, the compositions of which are digested in an electromagnetic field with a fine particle: a – iron; marks PZR-3; b – carbonyl iron; c – fluoroplastic, $\times 1000$

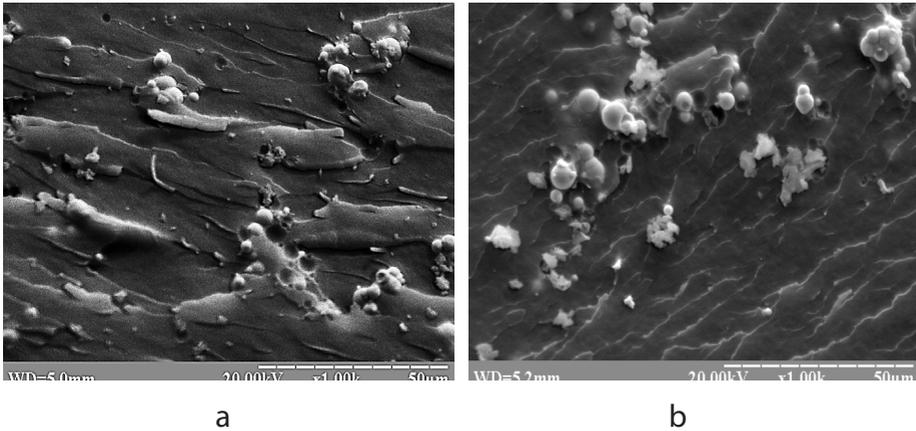


Figure 3.12. Fractograms of the fracture of epoxy composites filled with fine particle zirconium: a – without processing; b – processing in an electromagnetic field, $\times 1000$

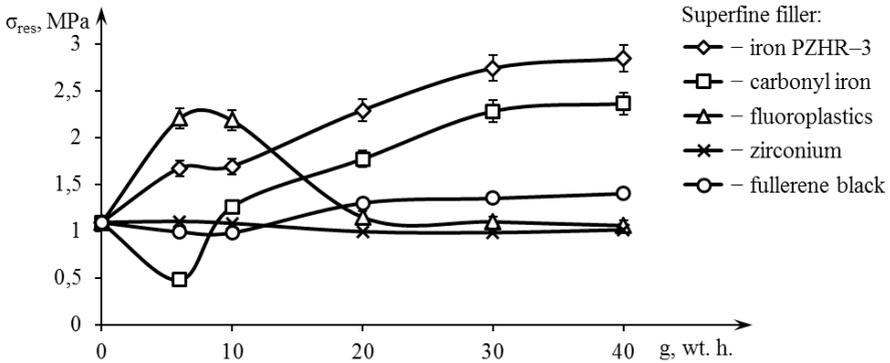


Figure 3.13. Dependence of residual stresses in epoxy composites, the compositions of which are processed by ultrasound, on the content of the filler

In the epoxy composites, the compositions of which were processed by ultrasound (Fig. 3.13), the minimum value of the residual stresses ($\sigma_{rz} = 0.48$ MPa) was recorded for a low degree of filling of the system (6 parts by mass) with a fine powder of carbonyl iron. In the epoxy composites filled with PZR-3 grade iron powder, with the preliminary processing of compositions by ultrasound, the growth of the

investigated characteristic is increased by 1.5–2.6 times in comparison with epoxy polymers ($\sigma_{tz} = 1.09$ MPa). Ultrasonic waves increase the uniformity of the arrangement of ferromagnetic particles in the epoxy polymeric matrix (Fig. 3.14 a, b) and ensure the adsorption of the segments of the macromolecules of the matrix in the outer surface layers of the particles [129]. An increase in the content of carbonyl iron powder (10–40 parts by weight) leads to an increase in residual stresses in the system in 1.1–2.6 times.

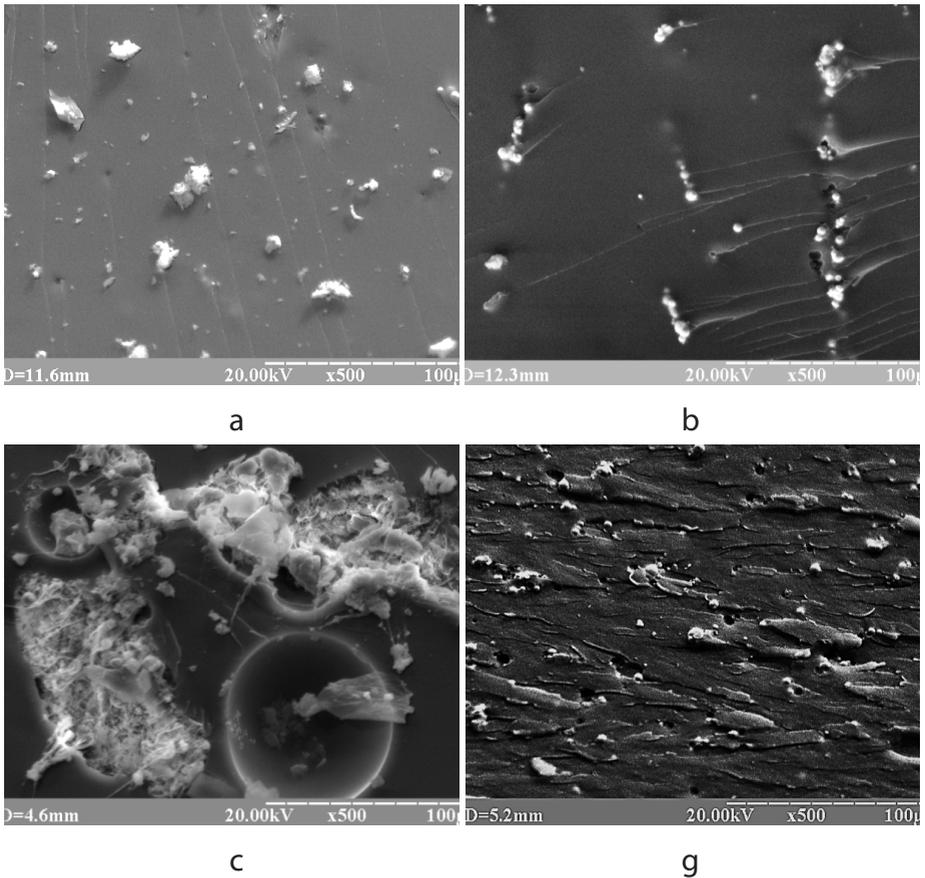


Figure 3.14. The fractograms of the fracture of epoxy composites, the compositions of which are processed by ultrasound, containing ultrafine particles: a – iron of the brand PZR-3; b – carbonyl iron; c – fluoroplastics, g – zirconium, $\times 500$

The introduction of a fluoroplastic powder (6–10 wh. h.) into the structure of the epoxy polymer matrix results in a sharp increase in residual stresses 2 times compared to the incomplete system due to the formation of a defective structure (Fig. 3.14, c). Further increase of the content of the filler leads to a reduction of this characteristic in 2.1 times due to an insufficient level of structure of the epoxy composite and high ability of the system to relax.

Treatment of compositions by ultrasound helps to reduce the residual stresses of epoxy composites filled with zirconium powder by 60 ... 80% ($\sigma_{rz} = 0.8$ MPa) compared to epoxy composites without pre-treatment of compositions ($\sigma_{rz} = 1.8$ MPa). The effect of ultrasound on compositions containing the fullerene ink provides a reduction of 18% of residual stresses in epoxy composites compared to composite materials whose compositions have not been previously treated in physical fields, since this treatment facilitates the ordering of components of the system during polymerization and causes a change in the conformational set of macromolecules matrix [130].

3.3 Investigation of mechanical and thermophysical characteristics of epoxy composites modified by fine particle

It has been experimentally established that the highest compressive strength (Fig. 3.15) has epoxy composites filled with iron powder. The grades of PZR-3 ($\sigma_{st} = 113.17$ MPa), zirconium ($\sigma_{st} = 111.76$ MPa) and fluoroplastics ($\sigma_{st} = 111.46$ MPa) in the amount of 6 parts by weight. A further increase in the content of the fluoroplastic powder results in a gradual reduction of the investigated characteristic of the epoxy composites, which can be explained by an increase in the content of the filler, the hardness of which is lower than the hardness of the epoxy polymer matrix. It has been experimentally established that the introduction into the epoxy polymer system of a fullerene black powder results in a reduction of the compressive strength by 33%.

For epoxy composites (Fig. 3.16), filled with dispersed iron powders of grade PZHR-3 and grades P-20 in the amount of 6–10 parts by mass, the compositions of which were processed in an electromagnetic field, the increase of compressive strength increased by 75% compared with

epoxy polymers, the compositions of which have also been processed in the electromagnetic field, and the growth of this characteristic by 20–50% compared with epoxy composites of the same composition without pre-processing of the compositions. This treatment improves the interaction between the components of the system and provides a uniform distribution of ferromagnetic particles in the epoxy matrix (Fig. 3.11, a, b).

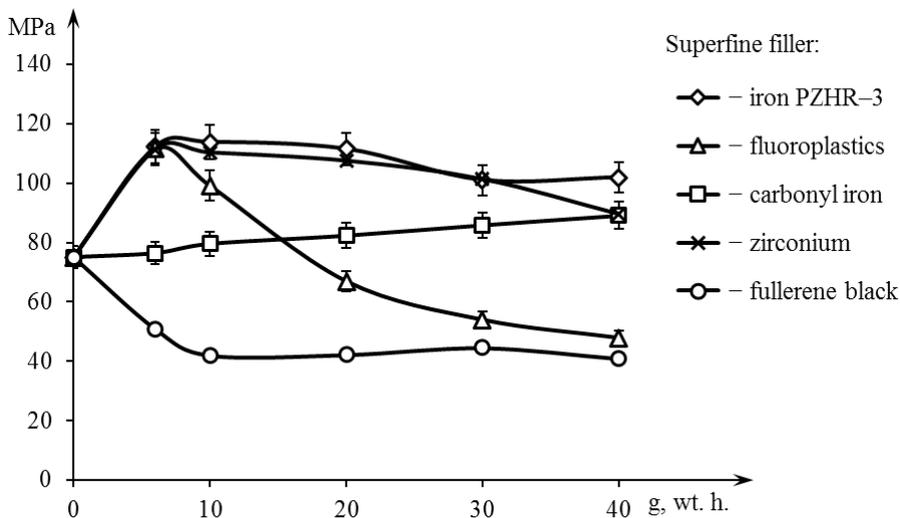


Figure 3.15. Dependence of the strength of the compression of epoxy composites on the content of the filler

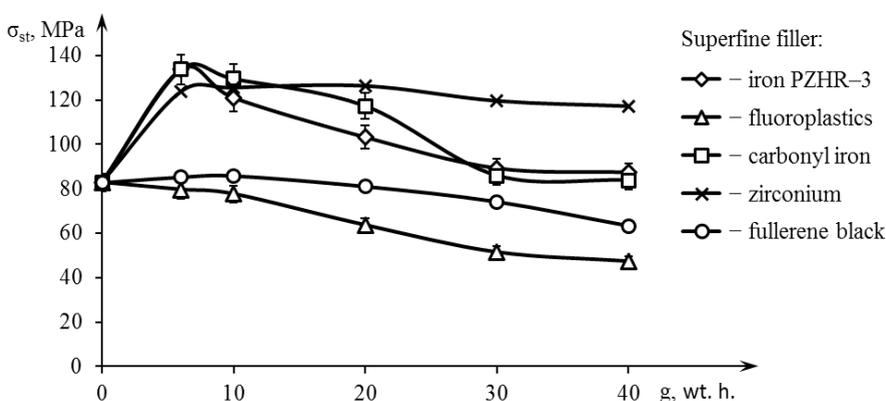


Figure 3.16. Dependence of the strength of the compression of epoxy composites, the composition of which is modified in the electromagnetic field, on the content of the filler

Treatment in the electromagnetic field of compositions filled with powder of fullerene black increases the strength of the compression of epoxycomposites by 1.7 times compared with epoxy composites whose compositions have not been treated, which confirms the ability of this treatment to intensify physicochemical processes that are associated with the formation of the structure epoxy composites (Fig. 3.17, a, b, c).

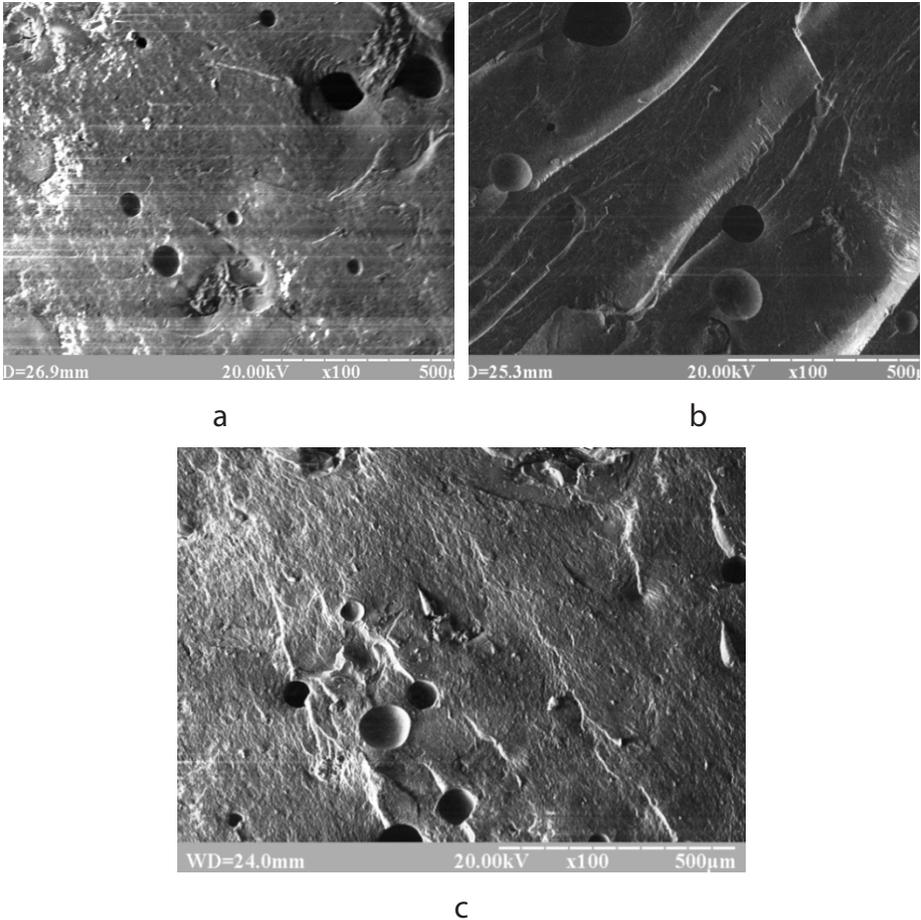


Figure 3.17. Fractograms of the fracture of epoxy components containing powder of fullerene black:
a – without processing; b – treatment in the electromagnetic field, c – ultrasound treatment, $\times 100$

It has been experimentally established that the processing of compositions by ultrasound increases the strength of the compression of epoxy composites (Fig. 3.18) for a small content (6–10 wt. h.) of iron PZR-3, carbonyl iron, and zirconium by increasing the mobility of the macromolecules of the epoxy matrix, which provides the formation of a more equilibrium structure epoxy composites (Fig. 3.14, a, b, g).

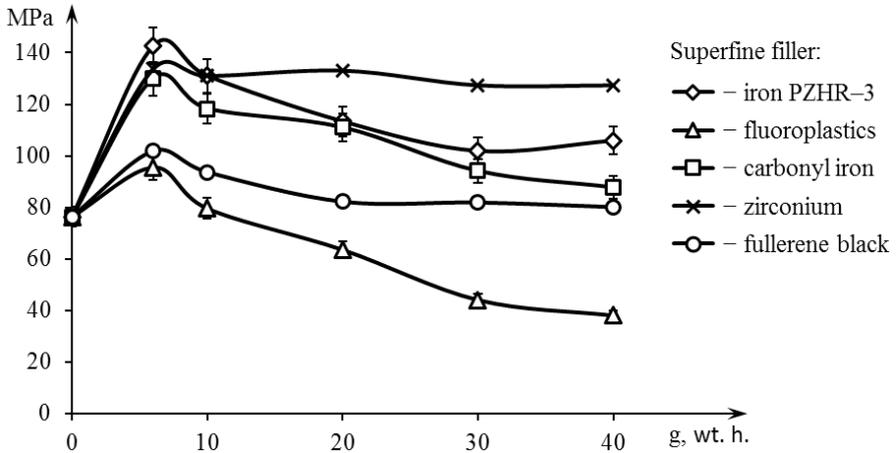


Figure 3.18. Dependence of strength when compressing epoxy composites, the compositions of which are processed by ultrasound, from the content of the filler

The maximum hardness values were recorded in epoxy composites filled with carbonyl iron (Fig. 3.19), the compositions of which were processed by ultrasound or in an electromagnetic field. It is established that the highest hardness is epoxy composites, the compositions of which are processed in an electromagnetic field ($HB = 297.3$ MPa). In epoxy composites, the compositions of which are processed by ultrasound, this characteristic is reduced by 5% ($HB = 276.3$ MPa). High values of hardness can be explained by the presence of a solid in the system of the form of a filler that prevents the placement of segments of macromolecules during deformation.

High-hardness values ($HB = 246.3$ MPa) were also recorded in epoxy composites filled with carbonyl iron, whose compositions were not processed in the physical field, due to the high reactivity and hardness of the fine particles of the filler. Minimum values of hardness are obtained

for epoxy composites filled with fluoroplastics, which is due to the presence of agglomerates, which were formed due to the high specific energy of the filler particles. After processing the composition with ultrasound, the hardness of the epoxy composites increases 2.3 times ($HB = 188.3$ MPa), compared with the hardness of the epoxy composites without processing the compositions ($HB = 78.8$ MPa). For epoxy composites, the compositions of which were exposed to pre-treatment in an electromagnetic field, higher values of the investigated characteristic ($HB = 197.8$ MPa) were recorded compared to epoxy composites, the compositions of which were processed by the ultrasound ($HB = 188.3$ MPa).

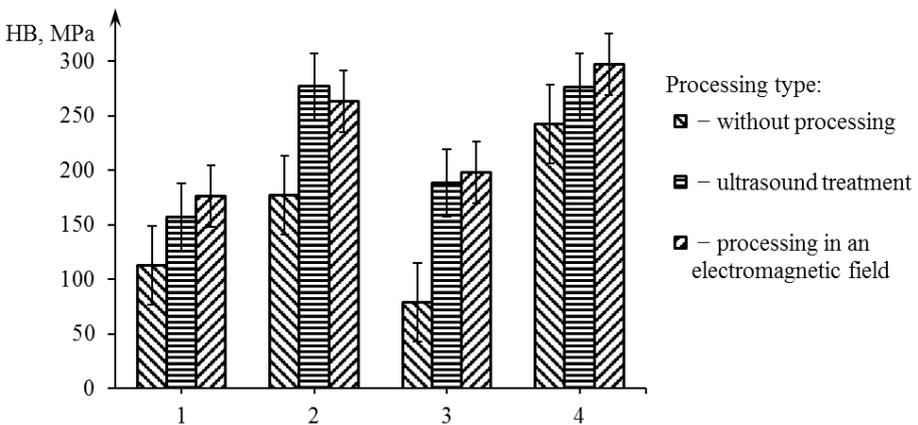


Figure 3.19. Dependence of the hardness of epoxy composites, the compositions of which are processed in the physical field and contain powders: 1 – without filler; 2 – iron grades PZR-3; 3 – fluoroplastic; 4 – carbonyl iron

In epoxy composites filled with PZR-3 grade iron, the maximum hardness value was recorded in the case of processing of compositions by ultrasound ($HB = 276.9$ MPa). As a result of the processing of compositions in the electromagnetic field, this value is reduced by 24% ($HB = 263.1$ MPa). In epoxy composites, without hardening of the compositions, the hardness is also reduced by 42% ($HB = 176.8$ MPa) compared to epoxy composites, the compositions of which are processed by ultrasound. The maximum hardness value was recorded for epoxy polymers whose compositions are processed in an electromagnetic field

(HB = 176.3 MPa), and the hardness of epoxy polymers with a preliminary treatment of the composition by ultrasound is reduced by 20% (HB = 157.8 MPa).

In epoxy polymers without pre-treatment of compositions, hardness is reduced by 55% compared to epoxy polymers whose compositions are processed in physical fields, due to the presence of high residual stresses in the system.

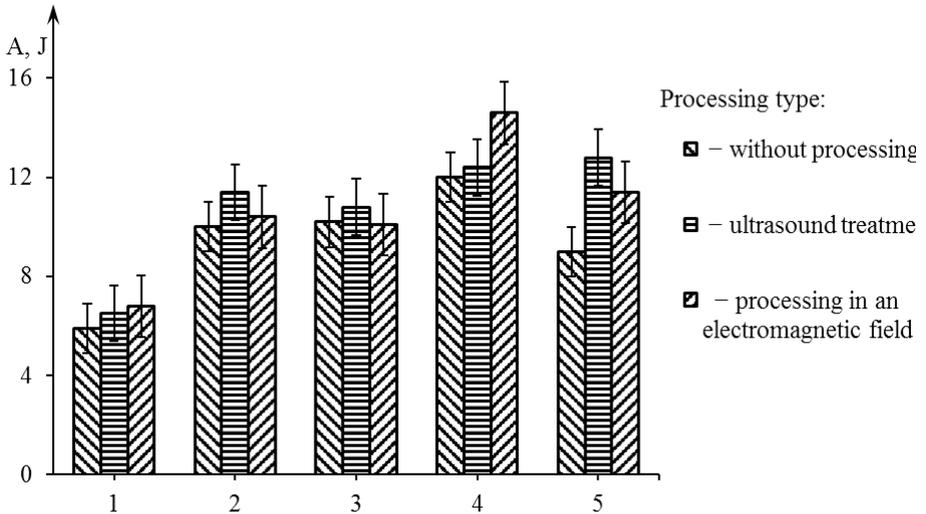


Figure 3.20. Dependence of impact strength of epoxy composite coatings filled with powders: 1 – without filler; 2 – iron grades PZR-3; 3 – fluoroplastic; 4 – carbonyl iron; 5 – zirconium

Strength tests have shown (Fig. 3.20) that the maximum impact strength values are characteristic of epoxy composites filled with carbonyl iron with pre-treatment of compositions in an electromagnetic field ($A = 14.6$ J), which is confirmed by the formation of a through-the-line destruction of the coating in the form of a hole without the presence of areas of detachment and the spread of cracks (Fig. 3.21, g).

The impact strength of epoxy composites increases with the prior processing of the composition by ultrasound, which provides a higher degree of homogeneity of the component placement in the volume of the composite due to the intensification of the process of distribution of the components of the system and reduction of defect in the composite

as a whole, compared with epoxy composites, the compositions of which have not been processed in physical fields.

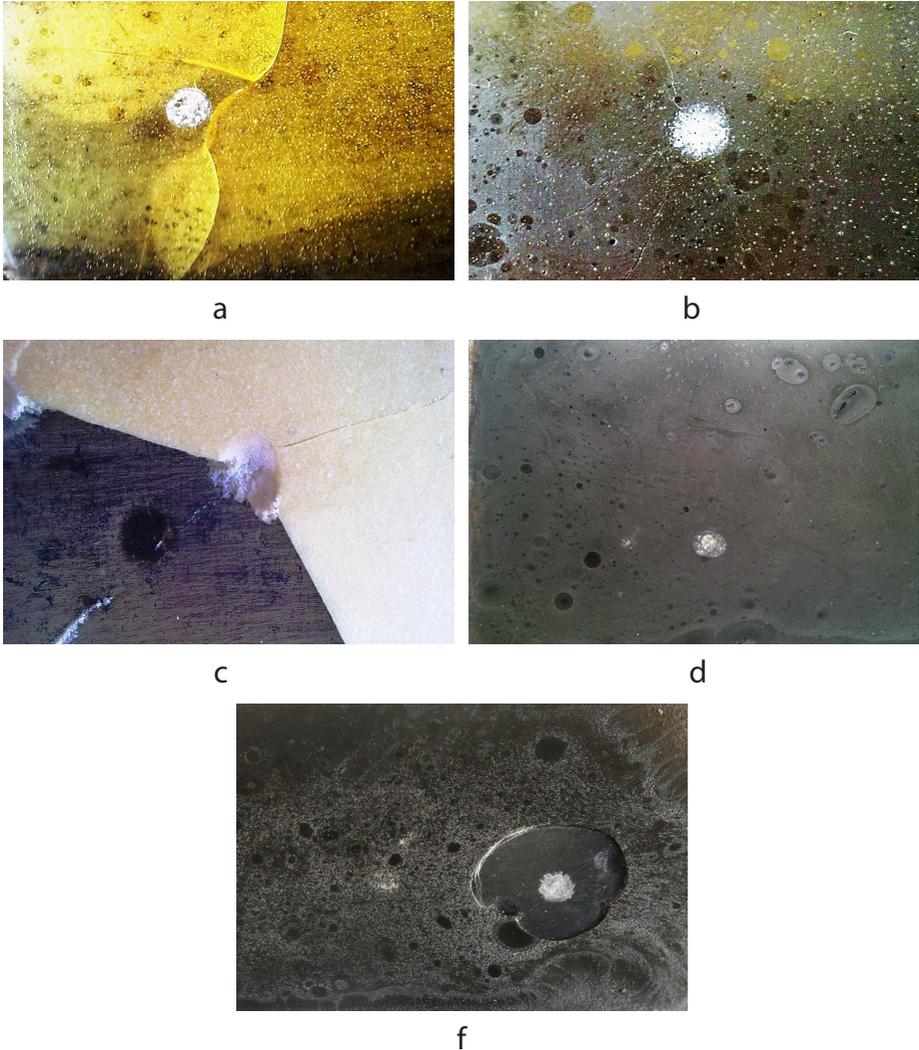


Figure 3.21. General view of the surface of epoxy composite coatings, the compositions of which are processed in physical fields after studies on impact strength: a – epoxy polymer; b – epoxy composite with powder of iron of grade PZR-3; c – epoxy composite with powder of fluoroplastic; g – epoxy composite with powder of carbonyl iron; e – epoxy composite with zirconium powder

The application of the treatment of compositions in the physical field does not provide high values of the impact strength of epoxy polymers ($A = 6.5 \text{ J}$), which is confirmed by the formation of the areas of detachment and the propagation of trunk cracks (Fig. 3.21, a). The area of destruction of the epoxy-polymeric coating without preliminary processing of the composition practically does not change and the results are almost the same. Epoxy compounds filled with iron powder PZR-3, have lower by 25% the value of the impact strength in the case of processing compositions in the electromagnetic field in comparison with epoxy composites filled with carbonyl iron. This is due to the complexity of the particle orientation in the epoxy polymer matrix under the influence of the electromagnetic field since the size of these particles is ten times higher than that of carbonyl iron powder particles. The analysis of the surface of the coating after the destruction confirms the experimental results since there is a presence of cracks around the zone of direct dynamic load (Fig. 3.21, b).

Ultrasound treatment of compositions filled with fluoroplastic powder causes the decrease of this characteristic for epoxy composites ($A = 5.2 \text{ J}$) since the particles remain in the agglomerated state, which reduces the adhesion strength and leads to catastrophic destruction with the excruciation of large areas of the coating (Fig. 3.21, b)

A similar situation is observed in epoxy composites, the composition of which was not subjected to the effect of pre-processing in the physical field ($A = 4.1 \text{ J}$). For epoxy composites, the compositions of which were processed in an electromagnetic field, a decrease in impact strength of 5% were established ($A = 1.5 \text{ J}$).

The highest values of the impact strength was recorded for epoxy composite coatings filled with zirconium powder, the compositions of which were processed in an electromagnetic field, which is 45% higher than the value of the impact strength of the non-filled epoxy polymers. In the case of processing of compositions by ultrasound filled with zirconia, the lower values of this characteristic ($A = 12.8 \text{ J}$) were obtained compared with the treatment of compositions in the electromagnetic field, since this field has a dominant influence. The analysis of the surface after the dynamic load confirms these results since the destruction zone represents a significant area of the layered coating (Fig. 3.21, d). Similar

results were obtained for epoxy composite coatings, the composition of which was not subject to preliminary processing in physical fields ($A = 9 \text{ J}$). Accordingly, this leads to the formation of a zone of through-all damage to the coating and areas of detachment around the zone.

The use of composite materials and protective coatings on an epoxy basis requires prediction of their behavior at elevated temperatures, since the thermal stability of composites materials [131]. The paper studies the thermal stability of epoxy composite materials filled with highly dispersed powder of carbonyl iron by thermogravimetric (TGA) analysis (Fig. 3.22).

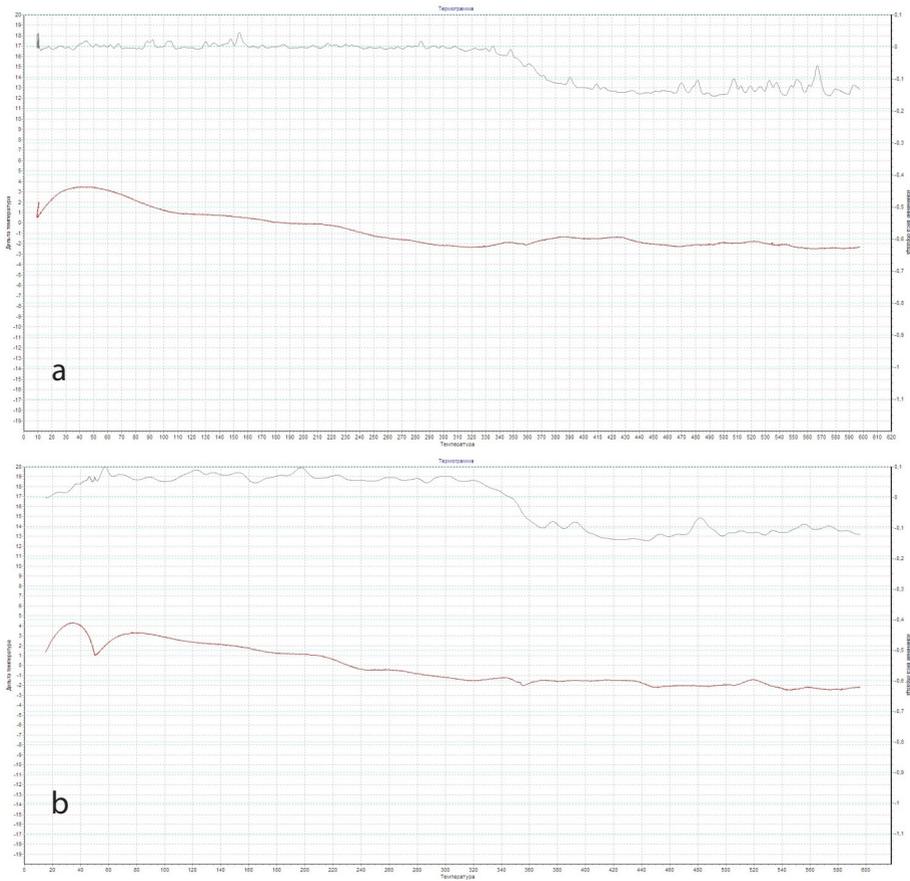


Figure 3.22. Thermogravimetric and differential-thermal analysis of epoxy composites filled with powder of carbonyl iron: a – treatment in an electromagnetic field; b – ultrasound treatment

The analysis of the TGA curve of epoxy composites, whose compositions are processed in an electromagnetic field (Fig. 3.22, a), showed that in the temperature range $T = 283\text{--}585\text{ K}$ These materials are heat-resistant because there is no mass loss. This indicates the lack of non-reactive components of the binder during polymerization and the high degree of structure of the epoxy-composite system under the influence of the physical field.

The appearance of an endeavor on the DTA curve at a temperature $T = 313\text{ K}$ indicates an additional process of structuring the epoxy composites during the temperature rise. Destruction of epoxy composites whose compositions are processed in an electromagnetic field begins at a temperature $T = 613\text{ K}$ and ends $T = 853\text{ K}$.

It has been established that epoxy composites whose compositions are processed by ultrasound (Fig. 3.22, b), In the temperature range $\Delta T = 293\text{--}573\text{ K}$, are characterized by the unstable mass loss. A number of endo- and exothermic processes have been found on the DTA curve in the region of low temperatures, indicating the course of additional structuring processes in the materials during the temperature rise. The endeavor is observed at a temperature $T = 303\text{ K}$, followed by an exo effect at a temperature $T = 323\text{ K}$. The destruction processes in epoxy composites begin at a temperature $T = 593\text{ K}$, which are characterized by an unstable mass loss and above the temperature $T = 673\text{ K}$ at temperatures $T = 593\text{ K}$ – stable.

Thus, it has been established that the treatment of compositions in an electromagnetic field at the formation stage results in the displacement of the temperature degradation interval for epoxy composites to higher temperatures, indicating inhibition of destructive processes and, consequently, an increase in the thermal stability of the investigated composite materials.

3.4 Investigation of the structuring processes and morphological parameters of the structure of epoxy composites

Experimentally found that the content of gel-fraction is reduced on 5–8% in epoxy composites, the compositions of which have not been previously treated in physical fields, compared to composites whose compositions are modified by ultrasound or in an electromagnetic field

(Fig. 3.23), indicating the incompleteness of the polycondensation reactions of the epoxy matrix, in which the particles of the filler adsorb macromolecules epoxy resin without bond formation.

Conducting ultrasound treatment of compositions filled with iron powder of grade PZR-3 (6 parts by weight), resulted in a significant increase in the degree of structuring ($G = 98.2\%$). This is due to the mixing of the system components at the micro level, which increased the likelihood of more physicochemical bonds in the system.

An increase in the content of the gel fraction was recorded for epoxy composites filled with zirconium powder after preliminary processing of compositions by ultrasound, which ensured the destruction of fine particles of agglomerates and promoted the absorption of macromolecules of the epoxy matrix on the surface of the filler particles.

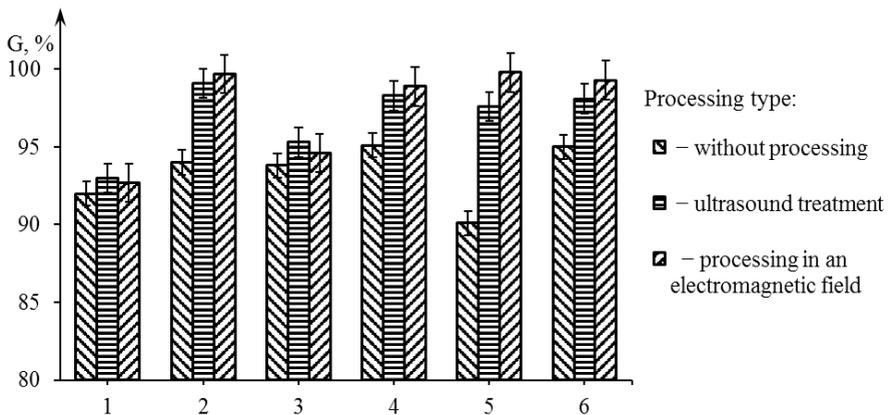


Figure 3.23. Dependence of the content of gel fraction in epoxy composite coatings, filled with powders (6 parts by weight):
 1 – without filler; 2 – iron br and PZR-3; 3 – fluoroplastic;
 4 – carbonyl iron; 5 – zirconium; 6 – black fullerene

Carrying out treatment in the electromagnetic field of compositions filled with fluoroplastic powder (6 parts by mass), provided a slight increase in the degree of structuring of epoxy composites ($G = 94.7\%$). In this case, higher values of the gel fraction content were obtained for epoxy composites, the compositions of which were processed by ultrasound ($G = 96\%$). An increase in the content of the gel fraction was recorded for epoxy composites filled with powder of carbonyl iron (6 parts

by mass), after processing the compositions at the stage of formation by ultrasound ($G = 99.2\%$), which contributed to the separation of agglomerated particles (Fig. 3.26, b), which increased the specific energy of the firmly-phase system and ensured the intensive interaction of the components of the system with each other.

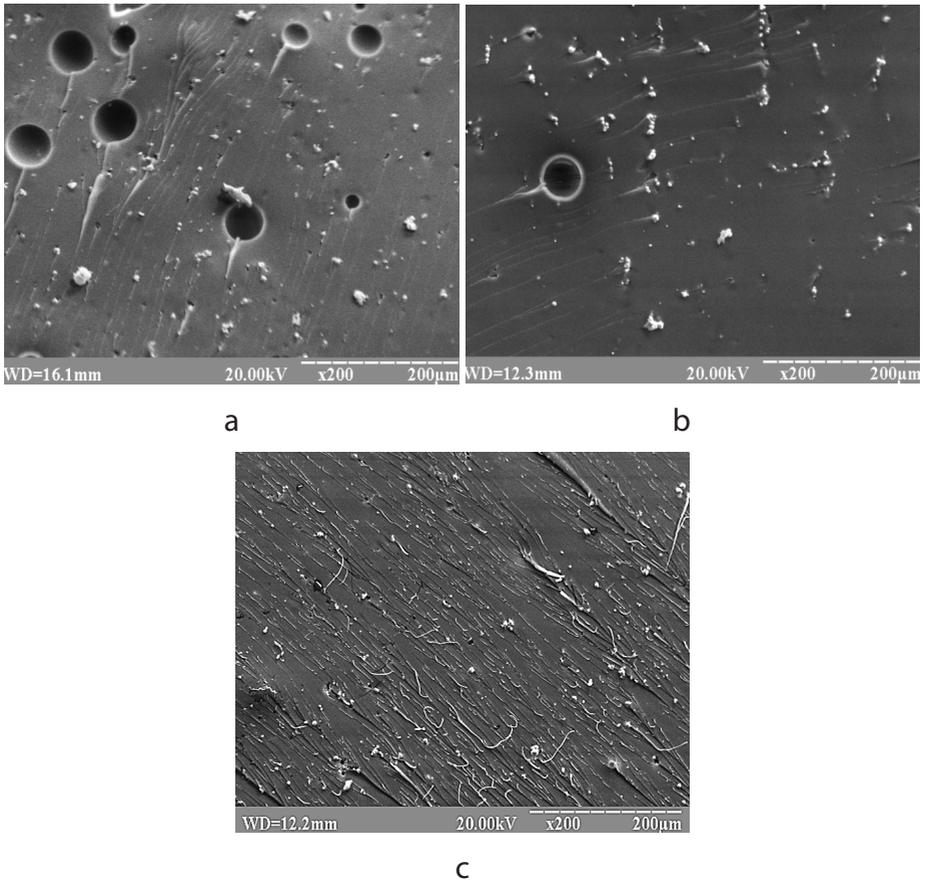


Figure 3.24. Fractograms of the fracture of epoxy composites, filled with iron particles of grade PZHR-3: a – without processing; b – processing of compositions in an electromagnetic field; c – processing of compositions by ultrasound, $\times 200$

Carrying out treatment in the electromagnetic field for compositions filled with zirconium powder (6 parts by weight) showed a significant increase in the degree of structuring of epoxy composites ($G = 99.8\%$).

This is due to the activation of the polar groups of the epoxy component and the formation of a system with a significant number of physicochemical bonds formed due to the presence of high specific energy of the surface of the solid-phase component.

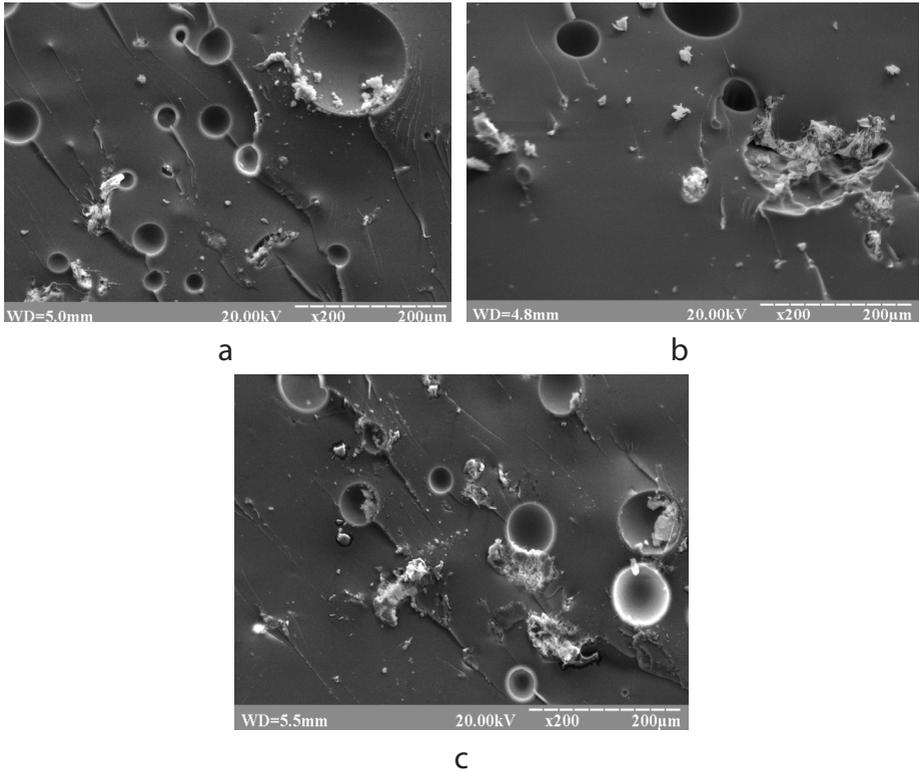


Figure 3.25. Fractograms of the fracture of epoxy composites filled with fluoroplastic particles: a – without processing; b – processing of compositions in an electromagnetic field; c – processing of compositions by ultrasound, $\times 200$

On the fractogram of the fracture of an epoxy composite filled with fine particles of iron of the grade PZH-3, whose composition was not processed in the external physical fields (Fig. 3.24, a), pores of different diameters (10–50 μm) were detected, which is associated with high in Elasticity of the epoxy composition through the use of solid-phase components with high specific energy. Also, agglomerates (5–10 microns in size) were formed which were formed prior to the introduction of

the composition and complicated the wetting of the particles by a liquid polymer, which leads to an uneven distribution of the filler particles in the volume of the epoxy polymer matrix.

It was established that the treatment of epoxy compositions in the electromagnetic field (Fig. 3.24, b) contributes to a significant degassing of the system, but a reduction of the size and number of iron powder agglomerates of grade PZHR-3 (6 parts by weight) was not fixed. On the surface, there are almost no lines of material shredding and the agglomeration ordering is found in one of the directions, indicating the ability of electromagnetic treatment to change the structure of epoxy composites containing ferromagnetic particles, resulting in the formation of an anisotropic system with a slight stress state and an increased degree of structuring.

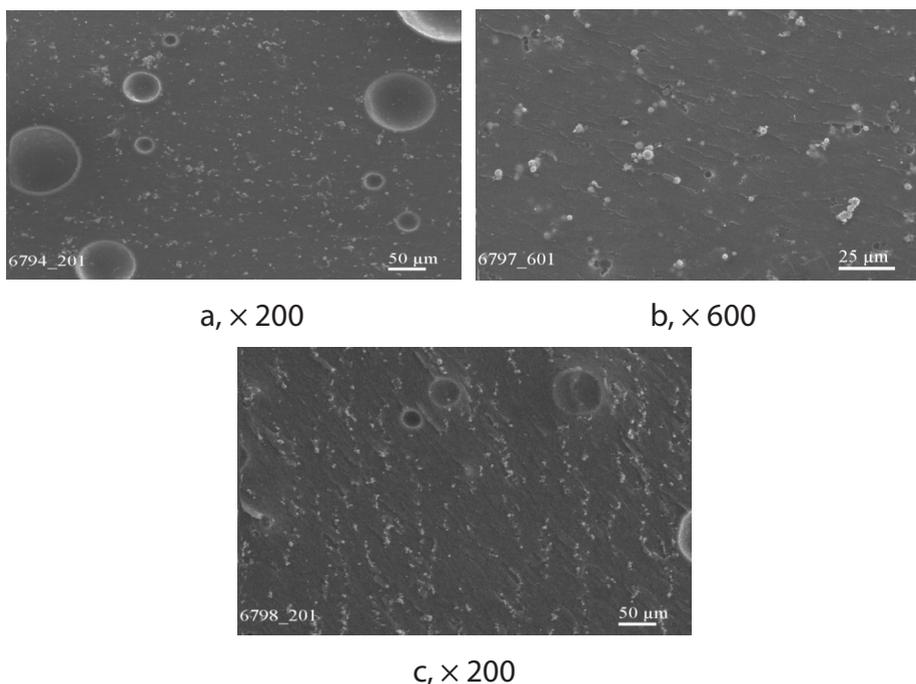


Figure 3.26. The microstructure of epoxy composites, filled with particles of carbonyl iron: a – without processing; b – processing of compositions by ultrasound; c – treatment of compositions in the electromagnetic field

The surface of the fracture of the epoxy composites after the treatment of the compositions at the stage of ultrasound formation (Fig. 3.24, c) is characterized by the presence of a large number of pronounced microscopic lines of shaving, which have significant branching, indicating the structuration of the epoxy composite system with a high tensile state.

It has been experimentally established that a large number of pores ($d = 50\text{--}500\ \mu\text{m}$) and agglomerates of particles are present on the surface of the fracture of epoxy composites filled with dispersed particles of fluoroplastics (6 parts by mass) (Fig. 3.25, a, b, c) ($d = 50\text{--}100\ \mu\text{m}$), which greatly reduces the overall physical and mechanical characteristics of epoxy composites. According to the results of the fractographic analysis, it has been established that the microstructure of the epoxy composite filled with high-disperse powder of carbonyl iron (6 parts by mass) without processing the composition in the physical field (Fig. 3.26, a) is represented by fine particles of round shape and unevenly distributed in volume of epoxy matrix. On the surface of the fracture of the epoxy composite there is a large number of pores, the sizes of which make up 30–100 microns. These structure defects testify to the uneven distribution of air inclusions, which is due to the high viscosity of the polymer composition.

The ultrasound treatment (Fig. 3.26, b) contributes to the degassing of compositions, which leads to an increase in the physicochemical characteristics of epoxy composites, especially in the case of the formation of highly-filled systems. However, the processing of polymeric compositions by ultrasound does not ensure the destruction of agglomerates of particles of carbonyl iron 5–15 microns, which leads to the emergence of residual stresses and the formation of a thermodynamical nonequilibrium system.

The processing of compositions in the electromagnetic field at the formation stage provided a uniform and orderly distribution of iron particles in the volume of the epoxy matrix (Fig. 3.26, c), which provides a significant increase in the physical and mechanical properties of epoxy composites. During the electromagnetic treatment of compositions, there is a torque that returns the particle, which results in better wetting and the formation of additional physicochemical bonds.

On the surface of the fracture, an epoxy composite filled with a highly dispersed zirconium powder (6 parts by mass), whose composition

was not processed in physical fields (Fig. 3.27, a), recorded a large number of pores, the size of which is 30–100 microns. These structure defects indicate a high viscosity of the system and the presence of air inclusions. Ultrasonic processing provides degassing of compositions, which increases the physical and mechanical characteristics of composites (Fig. 3.27, c). An analysis of fracture fractograms of a fracture of an epoxy composite, the composition of which is processed in an electromagnetic field (Fig. 3.27, b), indicates a partial orientation in the distribution of zirconium particles in the volume of the epoxy matrix.

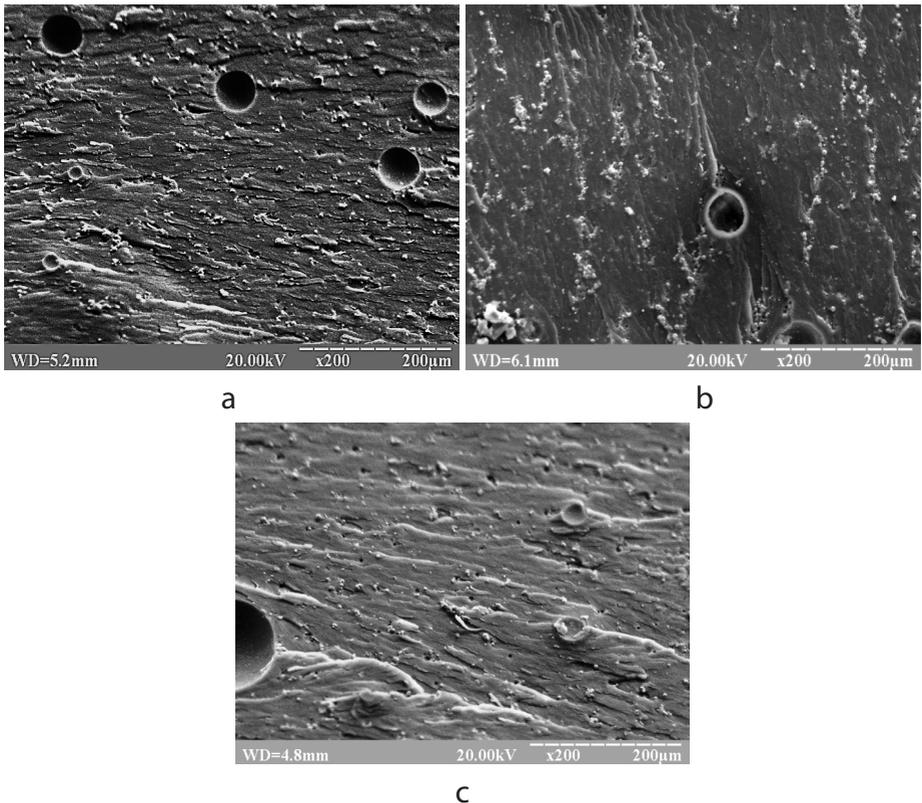


Figure 3.27. Fractograms of the fracture of epoxy composites filled with dispersed particles of zirconium: a – without processing; b – processing of compositions in an electromagnetic field; c – treatment of compositions by ultrasound, $\times 200$

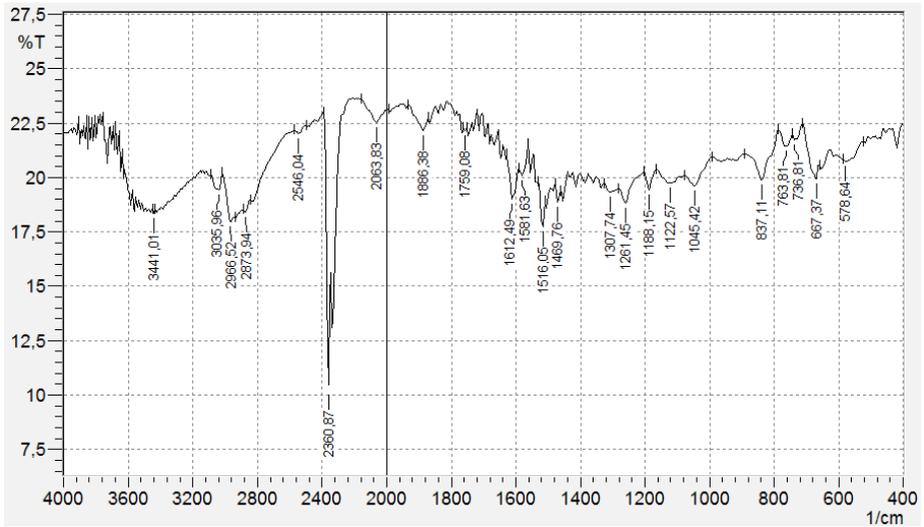
Thus, the results of experimental studies confirm the positive effect of highly dispersed fillers on the formation of the structure of epoxy composites provided that the compositions are pretreated in an alternating electromagnetic field or ultrasound, which leads to a significant increase in the adhesion and cohesive characteristics of the materials. It has been experimentally proved that the improvement of the performance of epoxy composites is due to the increase of adhesion strength and reduction of residual stresses as a result of adsorption and orientation effects at the boundary between the phases of the “polymer-filler” systems under the influence of physical fields during the structuring of the system.

Analysis of infrared spectra of epoxy composites filled with iron powder P-20 in an amount of 6 parts by mass. (Figure 3.28), it was found that absorption bands in the range of the wave number $V = 489.92\text{--}578.64\text{ cm}^{-1}$, which arise from the valence oscillations of the $-\text{CH}_2-$ groups and the deformation oscillations of parabensol, which directly indicates the presence of particles of high-iron iron [132]. The absorption bands for the wave number $V = 667.37\text{ cm}^{-1}$ are characteristic of the valence vibrations $\text{CH} = \text{CH}$. The absorption bands in the field of wave numbers $V = 730.81\text{--}837.11\text{ cm}^{-1}$ show deformation oscillations of the $\text{C}\text{--}\text{C}$ bond in the benzene ring and the valence fluctuations of the $-\text{CH}-, -\text{CH}_2-$ groups.

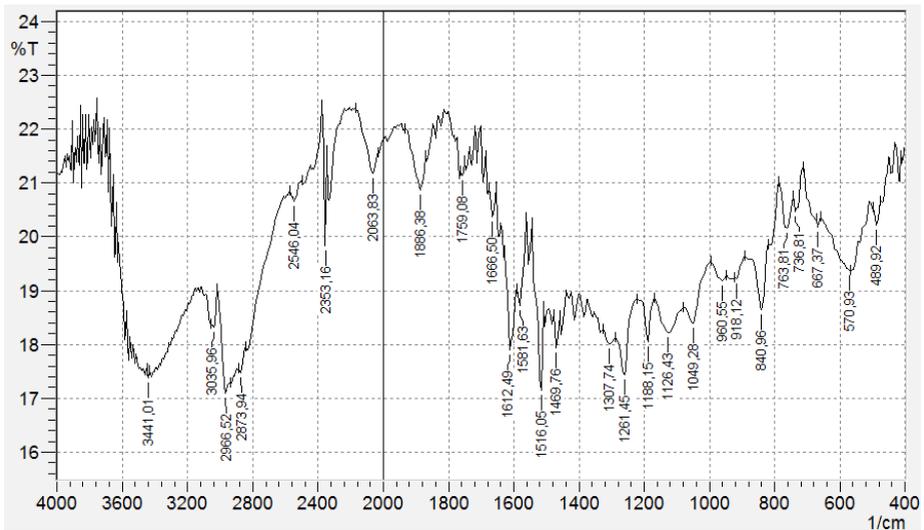
For epoxy composites whose compositions have been processed in the electromagnetic field (Fig. 3.28, a), there is a decrease in the intensity of absorption bands in the region of $578.64\text{--}837.11\text{ cm}^{-1}$ compared to compositions treated with ultrasound (Fig. 3.28, b). This indicates an increase in the degree of structuring of the epoxy composite material as a result of the influence of the electromagnetic field [133].

The presence of absorption bands in the range of wave numbers $V = 1045.42\text{--}1188.15\text{ cm}^{-1}$ indicates the valence fluctuations of $-\text{C}\text{--}\text{O}-$ in the material. The detected absorption bands in the region for the frequency $V = 1261.45\text{--}1307.74\text{ cm}^{-1}$ indicate deformation oscillations of $-\text{OH}$ groups, valence fluctuations $-\text{CO}-, -\text{CN}$ and the presence of epoxy groups and secondary $-\text{NH}\text{--}\text{R}$ amino groups in epoxy composite materials.

The absorption band for the wave number $V = 1469.76\text{ cm}^{-1}$ shows the deformation fluctuations of the $-\text{CH}-$, methylene $-\text{CH}_2-$, flame-group $\text{CH}_3\text{--}\text{C}$ groups and the presence of epoxy groups that increase the adhesion strength of the system [134].



a



b

Figure 3.28. Infrared spectra of epoxy composites filled with highly dispersed iron powder: a – the composition is processed in an electromagnetic field; b – the composition is processed by the ultrasound

Absorption bands in the $V = 1516.05\text{--}1612.49\text{ cm}^{-1}$ range indicate the deformation vibrations of the -NH- groups, the secondary amino group and the vibration of the benzene ring. This indicates the involvement of the group -NH- and the amino group in the polymerization reaction, which contributes to the improvement of the physical and mechanical properties of epoxy components [135].

The range of wave numbers $V = 1045.42\text{--}1612.49\text{ cm}^{-1}$ is characterized by a lower absorption intensity for epoxy composites, with the prior processing of compositions in the electromagnetic field. This indicates the intensive interaction of macromolecules of the binder with the centers on the surface of the filler, resulting in the formation of primary and secondary amines in the polymer, which leads to the formation of a structure with a small molecular weight. As a result, the physical and mechanical properties of the composite are improved materials [136].

The absorption bands at a frequency of $2759.08\text{--}2546.04\text{ cm}^{-1}$ indicate oscillations -C = N- , -C = C- and -C = O- groups. Reducing the spectrum of these groups' oscillations in the case of processing in the electromagnetic field of compositions compared with ultrasound processing provides an increase in the degree of crosslinking of epoxy composite materials [131].

The region $2873.94\text{--}3035.96\text{ cm}^{-1}$ and the frequency 1469.76 cm^{-1} characterize the fluctuations of NH_2 , NH_3 , the radical $\text{-CH}_2\text{-}$ and =C-H groups in this radical. For epoxy composites whose compositions are processed in an electromagnetic field, a significant decrease in the intensity of the absorption band is characteristic compared with epoxy composites, the compositions of which are processed by ultrasound. This is due to the decrease of -SO- and hydrogen -OH- groups, which leads to an increase in the degree of structuring and increasing the physical and mechanical characteristics of epoxy-composite materials. In the IR spectrum, there are absorption bands for the wave number $V = 3444.01\text{ cm}^{-1}$, due to valence fluctuations of the OH- groups of the binder, which are associated with the formation of intramolecular hydrogen bonds [135].

The structuring process begins as a result of the introduction of a polyethylene polyamine cementitious containing the terminal groups -NH_2 ,

In the process of structuring the final epoxy ring and the radical $=\text{CH}-\text{OH}$ with the $\text{NH}-$ group, the more stable bonds $\equiv\text{C}-\text{C}\equiv$, $\equiv\text{C}-\text{N}=\text{C}=\text{O}$ are formed, the weight and length of the linear polymer chains grow due to the influence of the electromagnetic fields. Due to the prior processing of compositions in the physical field, the molecule of the epoxy oligomer has a sufficient number of polar hydroxyl groups that are capable of forming strong physical and chemical bonds with a metal filler to form hydrogen $\text{C}-\text{OH}$, $\text{OH}-\text{Me}$ or covalent $\text{C}-\text{O}-\text{Me}$ bonds. Due to the presence of hydroxyl, amino, and epoxy groups in the composition, it is possible to form hydrogen bonds between the surface oxygen groups on the surface of the filler and the functional groups of the binding agent [133]. Thus, it has been found that among the investigated materials the best properties are characterized by epoxy composites, the compositions of which have been pre-modified in an electromagnetic field. The confirmation of this is a significant decrease in the absorption band intensity in the range of wave numbers $\nu = 2546.04-3444.01 \text{ cm}^{-1}$, characteristic for oscillations of the $-\text{N}-\text{H}-$ and $-\text{C}-\text{H}-$ groups. In addition, it has been confirmed that in the case of the introduction of carbonyl iron particles, the disclosure of epoxy cycles followed by the formation of primary and secondary amines. This indicates an intensive interaction of macromolecules of the binder with active centers on the surface of the filler, which improves the adhesion properties of the material [130].

CHAPTER 4.

INFLUENCE OF FORMATION TECHNOLOGIES FOR STRUCTURING EPOXY COMPOSITES PROCESSING IN PHYSICAL FIELDS

4.1 Influence of the method of introduction of a hardener on the physical and mechanical properties of epoxy composites

The management of the structure formation process in the inter-phase interaction zones during the formation of epoxy composite materials can improve the main performance characteristics of the coatings, therefore an important stage is the development of technology for the formation of multicomponent polymer composite coatings for the purpose of its implementation in industrial production [137].

The initial stage of the formation of composite materials was to obtain a homogeneous composition, which included the necessary components. Polymer compositions were formed in one of two ways: I – to the epoxy resin, PEPA (12 parts by weight per 100 parts by weight of ED-20) and a filler (6 parts by weight) were introduced into the epoxy resin with the mechanical displacement of the components at each stage and the following ultrasound or electromagnetic field; II – the filler was added to the epoxy resin (6 parts by weight), the components were mechanically mixed and sonicated or in the electromagnetic field, after which a PEPA cement was introduced in an amount of 12% by weight. Determination of the optimal method for the formation of polymer composites was carried out, assessing its effect on the mechanical characteristics of composite materials.

Taking into account the technology of formation of epoxy composites, namely the sequence of introduction of a hardener into a composition, the study of adhesion strength was carried out (Fig. 4.1). It has been experimentally established that the introduction of a hardener into the composition after treatment in the physical field leads to an increase of 75% of the adhesive strength of epoxy polymers, as the result of the action of ultrasound or the influence of the electromagnetic field is an increase in

the temperature of the composition and a decrease in its viscosity, which increases the likelihood of a larger amount chemical bonds between functional groups of solids macromolecules and epoxy resin [138].

It has been experimentally established that the value of adhesion strength for epoxy polymers whose compositions have not been treated in physical fields is ($\sigma_a = 16.9$ MPa). As a result of preliminary processing of compositions in physical fields, an increase in adhesion strength of epoxy composites was observed at 58–75%: $\sigma_a = 28.3$ MPa in the case of ultrasonic composition processing and $\sigma_a = 34.5$ MPa in the case of processing in an electromagnetic field, since processing in physical fields Provides a higher degree of homogeneity of the structure of the material due to the even distribution of component systems [139].

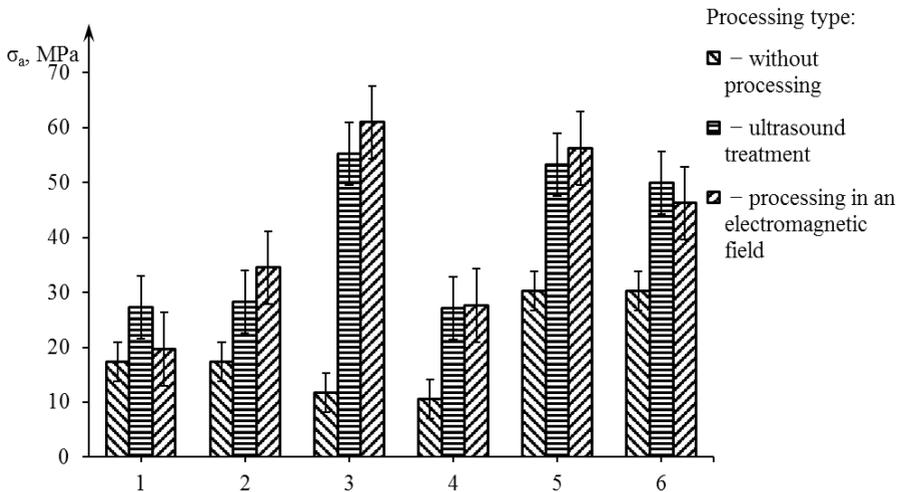


Figure 4.1. The dependence of adhesion strength on the method of introducing a hardener for epoxy polymers (1, 2), epoxy components, filled with powder iron grades P-20 (3, 4) and zirconium (5, 6): 1, 3, 5 – I method; 2, 4, 6 – II method

In the case of the introduction of the elastomeric epoxy resin before treatment in the physical field, the maximum values of the adhesion strength of the epoxy composites filled with iron particles of the P-20 grade ($\sigma_a = 61.1$ MPa in the case of processing of compositions in the electromagnetic field, $\sigma_a = 55.3$ MPa in the case of processing of compositions by ultrasound) due to better wetting of the particle surface with an

epoxy resin (Fig. 4.2, a). The introduction of a hardener after treatment with an epoxy resin leads to a decrease in adhesion strength of epoxy composites by 50–54% ($\sigma_a = 27.6$ MPa in the case of processing compositions in an electromagnetic field, $\sigma_a = 27.1$ MPa in the case of ultrasonic compositions), since the treatment of compositions in a physical field without a hardener leads to the formation of primary bonds between the end groups of the epoxy component and the hydroxyl groups on the surface of the filler particles, which, upon the subsequent introduction of PEPA, are destroyed due to the mechanical mixing of the compositions. In the case of the introduction of a hedge to processing in the physical field, the formation of primary physicochemical bonds, which are stored during the subsequent structuring of the composition occurs. In the case of structuring epoxy composites without processing of compositions, the adhesive strength is reduced by 5–6 times ($\sigma_a = 11.6$ MPa), which is obviously due to the formation of an insufficient number of chemical bonds between the components and incomplete wetting of the dispersed phase polymer (Figure 4.2, b).

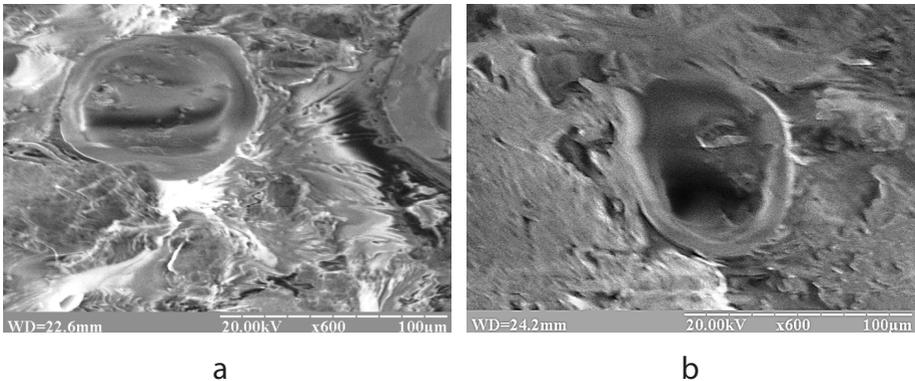


Figure 4.2. Fractograms of fracture of epoxy composites, filled with fine particles of iron grade P-20: a – I method; b – II method, $\times 600$

The maximum value of the adhesive strength is fixed for epoxy composites in the case of pretreatment in the electromagnetic field of solidified compositions containing highly dispersed zirconium powder ($\sigma_a = 56.2$ MPa), since this field contributes to the temperature increase of the composition and reduces its viscosity (Fig. 4.3, a) due to the orientation of the segments of the macromolecules, which increases the likeli-

hood of the formation of a greater number of chemical bonds between the filler and the astringent. The introduction of the hardener into the composition after treatment results in a 24.2% reduction in adhesion strength ($\sigma_a = 46.25$ MPa), since the treatment of non-curable compositions contributes to the formation of bonds between the filler and the epoxy resin, which is partially destroyed during the next introduction of the cement and Re-structuring of the system is less effective without the influence of physical fields, resulting in the formation of epoxy composite material with a significant number of structural defects (pores, cavities) (Fig. 4.3, b).

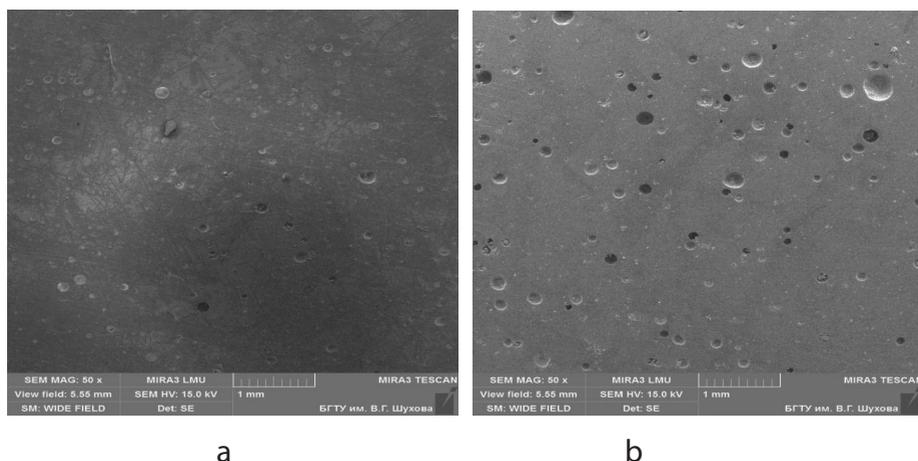


Figure 4.3. Microstructures of epoxy composites filled with fine particle zirconium: a – I method; b – II method, $\times 50$

It has been experimentally established that the maximum values of the compression strength were fixed (Fig. 4.4) for epoxy polymers, the compositions of which were treated with an ultrasound ($\sigma_{st} = 82.9$ MPa) or in an electromagnetic field ($\sigma_{st} = 76.4$ MPa) under the condition of maintaining the cement before processing.

The maximum value of the compression strength limit is fixed for epoxy composites, the compositions of which contain P-20 iron powder with ultrasound ($\sigma_{st} = 129.9$ MPa) or in the electromagnetic field ($\sigma_{st} = 133.8$ MPa), in which PEPA was introduced to the treatment (Method I). The minimum value ($\sigma_{st} = 76.4$ MPa) has epoxy composites in the case of adding a hardener after treatment in an electromagnetic field

(method II). Epoxy composites filled with highly dispersed zirconium powder have maximum values of compression strength ($\sigma_{st} = 137.8$ MPa), provided the fortress is introduced before the compositions are processed by ultrasound.

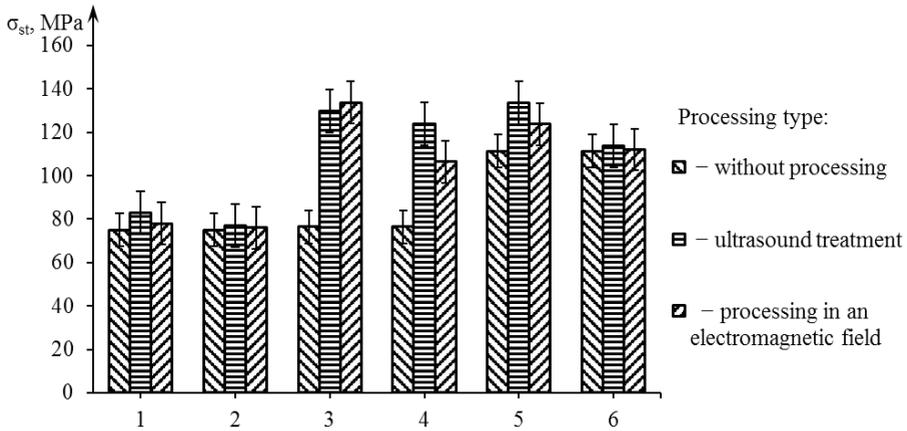


Figure 4.4. The dependence of the compressive strength limit on the method of introducing a forcement for epoxy polymers (1, 2) and epoxycomposites filled with iron P-20 (3, 4) and zirconium (5, 6) iron: 1, 3, 5 – I method; 2, 4, 6 – II method

It was established that the introduction of a hardener into compositions with processing in the physical field leads to an increase in the mechanical characteristics of epoxy composites filled with iron powder or zirconium, since this treatment promotes the formation of a strong adhesion bond between the surface of the filler and the macromolecules of the epoxy matrix and the formation of the structure with minimal residual by stresses [140], due to improved wetting of the polymer and increased homogeneity of the mixture (Fig. 4.5, a, b).

It has been experimentally established that the residual stresses for epoxy polymers whose compositions were not exposed to pre-treatment were $\sigma_{rz} = 1.46$ MPa (Fig. 4.6). Conducting processing of compositions in an electromagnetic field, provided that the hardener is introduced before processing, leads to a reduction of residual stresses by 12% ($\sigma_{rz} = 1.28$ MPa). The maximum value of residual stresses is epoxy composites filled with powder P-20 grade iron without processing the compositions in the

physical field ($\sigma_{rz} = 1.5$ MPa), and the minimum in case of adding the hardener to the treatment ($\sigma_{rz} = 0.7$ MPa). The high residual stresses ($\sigma_{rz} = 1.46$ MPa) were also recorded in epoxy composites without processing of compositions in physical fields filled with zirconium powder. Preliminary treatment of compositions contributes to the reduction of residual stresses in the case of the introduction of a hardener before processing since the macromolecules of epoxy resin and hardener in the electromagnetic field have increased mobility, which contributes to the uniform structure of epoxy composites [141].

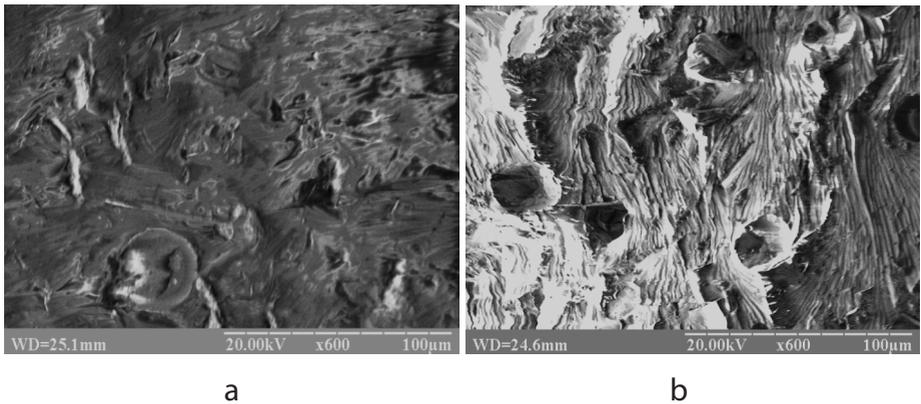


Figure 4.5. Fractograms of the fracture of epoxy composites filled with fine particles of zirconium: a – I method; b – II method, $\times 600$

In epoxy polymers, without preliminary processing of compositions, the minimum hardness values ($HB = 113.1$ MPa) (Fig. 4.7) were recorded in comparison with epoxy polymers, the compositions of which were subjected to processing in physical fields, which is associated with the formation of additional physical-chemical bonds. An increase of 38% in the hardness of epoxy polymers is observed in the case of pretreatment of the compositions with the cure by ultrasound and by 55% in the case of processing in an electromagnetic field. Since the cohesive strength of composites is determined largely by the amount of adhesion between the components of the system, therefore, it is necessary that the number of primary bonds is retained in the process of structuring epoxy composites. The application of physical fields increases the number of chemical bonds, which provides an increase in the hardness of epoxy polymers. In

the case of the structuring of epoxy composites with a cementitious in the physical field, primary bonds between the functional groups of the epoxy resin macromolecules and the active centers on the surface of the particles are formed and destroyed upon introduction of the curative after processing of the compositions in the physical field [141]. Therefore, the structure of epoxy composites has a decisive influence, which is the formation of bonds in the presence of a hardener, the number of which increases significantly after processing in the physical field.

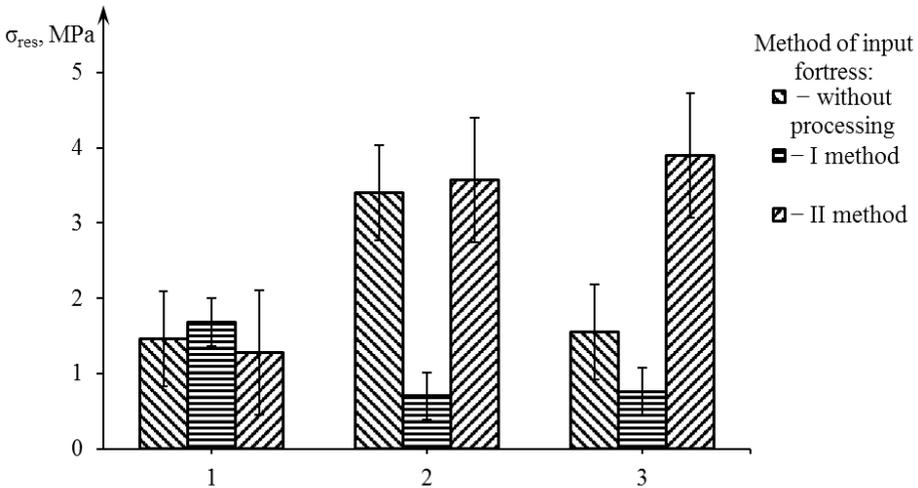


Figure 4.6. Dependence of residual stresses on the method of introduction of a cement in epoxy composites, modified in an electromagnetic field and filled with fine particles:
1 – without filler; 2 – iron grades P-20; 3 – zirconium

Low hardness values have epoxy composites, the compositions of which have not been processed in physical fields since there are agglomerates of particles formed prior to the introduction into the composition of the epoxy composition due to the significant specific energy of the highly dispersed filler. The increase of the investigated characteristic by 56% ($HB = 276.9 \text{ MPa}$) was fixed for epoxy composites compared to epoxy polymers in the case of introduction of a hardener before processing of compositions by ultrasound. The increase in hardness is due, firstly, to the presence of iron powder particles in the solid phase system,

and secondly to the positive influence of ultrasound, which facilitates the mixing of the system components and the reduction of the number of air bubbles, resulting in an increase in the homogeneity of the epoxy-composite system (Fig. 4.8, a, b), as well as the processes of structuring begin to intensify [142].

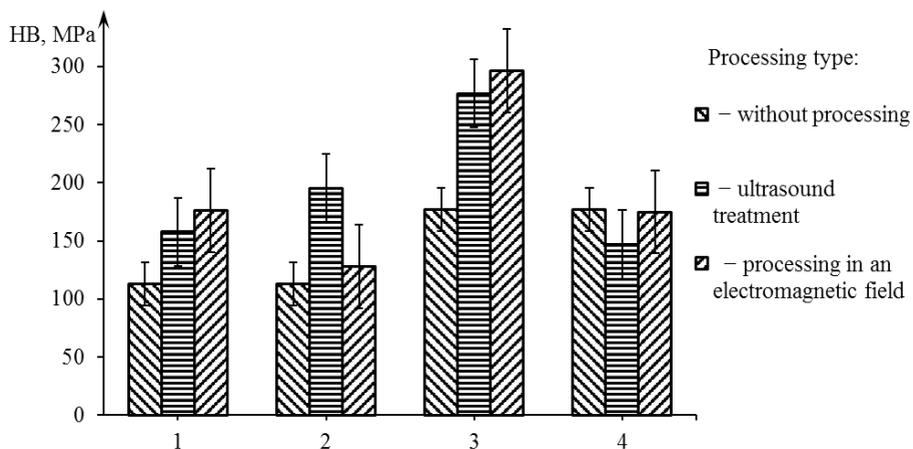


Figure 4.7. Dependence of hardness on the method of introducing a hardener for epoxy polymers (1, 2) and epoxy components filled with powder iron grades P-20 (3, 4): 1, 3 – I method; 2, 4 – II method

The hardness of epoxy composites structured under the influence of an electromagnetic field with the introduction of a hardener after treatment is lower by 60% in comparison with the treatment of solidified compositions due to processes of partial destruction of bonds between system components in the transition zones at the interface with the surface of the filler during the introduction of the cement. The treatment of the composition in the electromagnetic field provides a significant increase in the hardness of the epoxy systems with the hardener compared to the untreated compositions, since this treatment provides mechanical micron mixing of the components and the approach of the end groups of macromolecules without intensifying the structuring processes and contributes to the formation of a system with low residual stress [143].

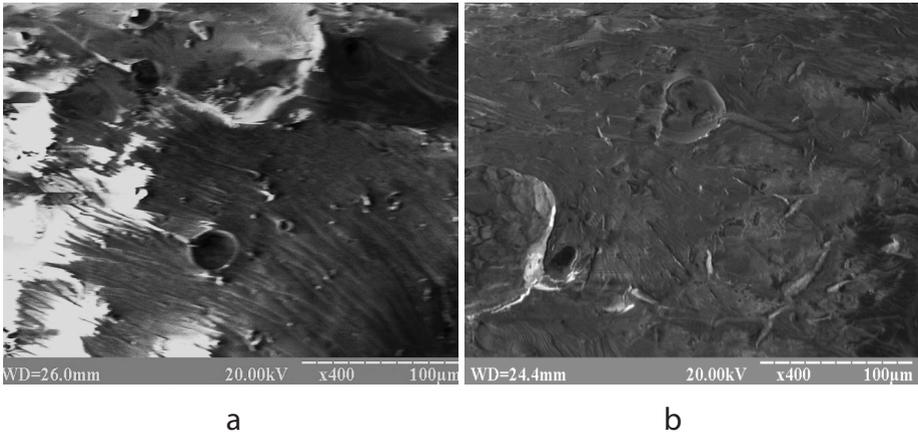


Figure 4.8. Fractograms of fracture of epoxy composites, filled with fine particles of iron of grade P-20: a – I method; B – II method, $\times 400$

The introduction of a hardener into compositions filled with iron powder after ultrasound treatment results in a reduction of 2.2 times the hardness compared with composites, the treatment of which compositions at the stage of formation was carried out in the presence of a hardener in the system, due to the complexity of the surface of particles saturated macromolecules of the epoxy resin, adsorb the macromolecule of the hardener in the case of mechanical application only without the effect of processing in the physical field. Similar results are obtained for epoxy composites whose compositions are processed in an electromagnetic field with the subsequent introduction of a cement, indicating the dominant influence of physical fields on the formation of physical and chemical bonds between all components of epoxy composites at the stage of polymerization of the epoxy matrix.

Determination of the content of the gel fraction in epoxy-polymeric and epoxy-composite materials allowed to develop a hypothesis of the assertion about increasing the degree of system structuring (Figure 4.9), due to the pre-processing of compositions in physical fields. The lowest content of the gel fraction ($G = 92.8\%$) was recorded for epoxy polymers, the composition of which was not processed. This indicates that low values of the hardness of epoxy polymers are caused not only by the presence of air inclusions but also by the low degree of system structuring.

Conducting pre-treatment of the non-filled solids containing compositions allows obtaining a material with a lower content of gel-fraction compared to epoxy polymers, the compositions of which do not contain a hardener during processing in the physical field. It is obvious that physical fields cause local structure formation, which leads to a decrease in the number of chemical bonds. The effect of physical fields on an epoxy resin without a hardener is to reduce the viscosity of the oligomer, which improves the subsequent mechanical mixing of the components and increases the number of physico-chemical ties [144].

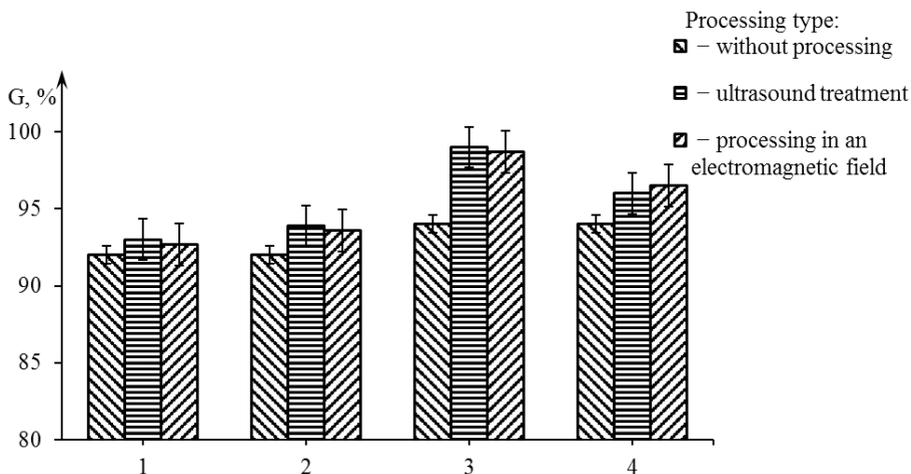


Figure 4.9. Dependence of the content of gel fraction on the method of introducing a cement in epoxy polymers (1, 2) and epoxy composites filled with powder Iron grades P-20 (3, 4): 1, 3 – I method; 2, 4 – II method

Introduction to the composition of the epoxy matrix of highly dispersed iron powder without processing in physical fields leads to an increase in the content of gel fraction by 17%. This is due to the growing degree of structuring of the epoxy polymer matrix in the outer surface layers of the filler particles, which improves the mechanical and operational properties of epoxy composite systems. Experimentally found that the highest content of gel fraction ($G = 99.2\%$) have epoxy composites filled with iron powder in the case of introducing the hardener

to ultrasonic treatment. Ultrasonic treatment initiates the formation of chemical bonds and intensifies the processes of structuring in the outer surface layers as the penetration of macromolecule complexes into nanosized pores on the surface layers of particles of a highly dispersed filler is complicated [145]. As a result, higher values of the content of the gel fraction in epoxy composites, the compositions of which contained a hardener, were obtained and processed in physical fields in comparison with epoxy composites, the composition of which the cinder was taken after treatment.

In epoxy polymers, without preliminary processing of compositions, the minimum values of impact strength ($A = 5.9\text{J}$) were recorded in comparison with epoxy polymers, the compositions of which were subjected to processing, which is related to the formation of a porous defect system in the absence of the influence of the external physical field (Fig. 4.10). An increase of 10% of the impact strength of epoxy polymers occurs in the case of pre-treatment of the composition with the cure with ultrasound and by 15% in the case of treatment in the electromagnetic field, since the viscosity of the system decreases and there are favorable conditions for the uniform formation of physicochemical bonds.

Dynamic tests have shown that the maximum values of impact strength ($A = 14.6\text{J}$) have epoxy composite coatings, filled with the fine particle of iron, the compositions of which were exposed to ultrasound, provided that the hardener was introduced before processing by the external physical field.

The impact strength of epoxy composite coatings increases in the case of processing of compositions by ultrasound, which provides a higher degree of homogeneity of the structure of epoxy composites due to the uniform distribution of components and reduction of the defect in the system as a whole. The general appearance of the surface at the site of destruction is confirmed by the experimental results of determining the impact strength since the zone of destruction of the coating is a local damage in the form of a well without cracks and detachments (Fig. 4.11, a). It has been experimentally established that the impact strength of epoxy composite coatings filled with highly dispersed iron powder with the treatment of the composition in the electromagnetic field is

commensurate with the values of the impact strength of epoxy composites, the composition of which has not been processed in physical fields, indicating the ineffectiveness of this treatment for the ferromagnetic filler.

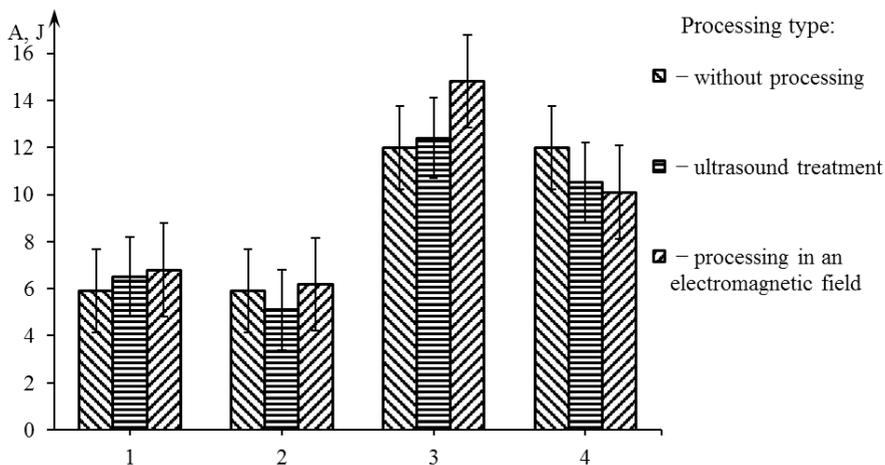


Figure 4.10. Dependence of impact strength on the method of introducing a hardener for epoxy polymers (1, 2) and epoxy composites filled with powder iron grades P-20 (3, 4): 1, 3 – I method; 2, 4 – II method

The introduction of a cement into a composition after ultrasonication results in a 20% reduction in impact strength ($A = 12.4$ J), since the treatment of a non-solidifying composition leads to the formation of primary bonds between the end groups of the epoxy component and the hydroxyl groups on the surface of the filler particles, which during the introduction of PEPA are destroyed through the subsequent mechanical mixing of the components of the composition. The strength of the formed bonds is lower compared to the bonds formed in the presence of a hardener, therefore, the efficiency of processing a composition without a hardener also decreases. This is confirmed by the general appearance of the destruction zone, which is a local transient damage to the epoxy composite coating at the site of impact, which is accompanied by the formation of areas of detachment and the spread of cracks with the extinction of large areas (Fig. 4.11, b).



Figure 4.11. General view of epoxy composite coatings filled with iron powder of grade P-20 with the treatment of compositions by ultrasound after studies on impact strength: a – helium was introduced into the composition prior to treatment; b – the fortress is introduced into the composition after treatment

4.2 Impact of processing time on the physical and mechanical characteristics of epoxy composites

For optimization of the structure of epoxy-composite systems filled with highly dispersed P-20 carbonyl iron powder, the influence of the processing time in the physical field on the adhesion strength of the coatings and the strength of the compression have been investigated. It has been experimentally established that the value of the adhesive strength (Fig. 4.12) of epoxy composite coatings filled with carbonyl iron without processing the compositions in the physical field is $\sigma_a = 25.43$ MPa.

In epoxy composites, the compositions of which were subjected to processing in an external physical field of 30 minutes duration, the growth of adhesion strength was 1.7 times ($\sigma_a = 43.34$ MPa in the case of processing of compositions by ultrasound, $\sigma_a = 43.56$ MPa in the case of treatment of compositions in electromagnetic field) compared to epoxy composites whose compositions have not been processed. Reducing the processing time of compositions in the physical field to 15 minutes does not lead to significant changes in the characteristics studied.

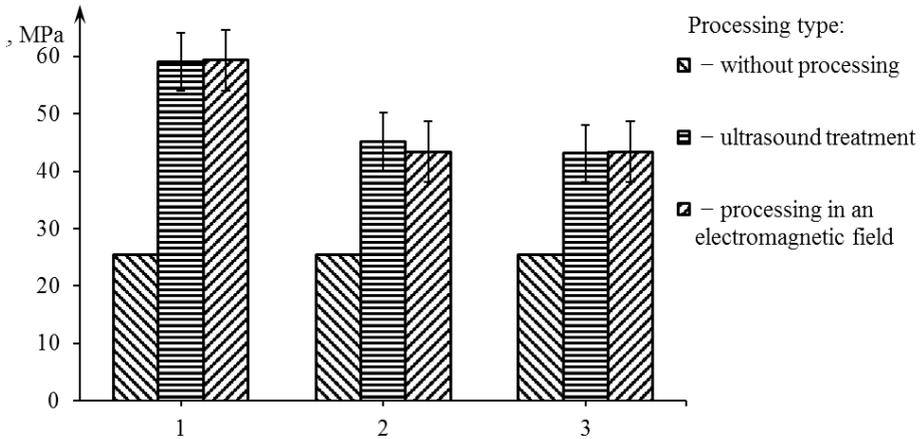


Figure 4.12. Dependence of adhesion strength of epoxy composites filled with fine particle powder P-20 on the length of treatment: 1–5 min; 2–15 minutes; 3–30 min

The maximum values of the adhesion strength of the epoxy composites were obtained in the case of ultrasound processing of the compositions ($\sigma_a = 59.14$ MPa) and in the electromagnetic field ($\sigma_a = 59.3$ MPa) for a duration of 5 minutes. Reducing the processing time to 5 minutes leads to an increase in the adhesion strength of the studied system by 30–35% compared with the length of the processing of compositions 15 min or 30 min.

An increase in the length of the treatment leads to a decrease in adhesion strength characteristics, which is explained by the intensive structuring of the epoxy composite material during processing, which in turn causes an increase in the stress state of the system.

Experimentally established (Fig. 4.13) that the maximum values of compression strength are epoxy composites, the compositions of which were exposed to physical fields for 5 minutes ($\sigma_{st} = 135.2$ MPa in the case of ultrasound compositions, $\sigma_{st} = 130.1$ MPa in the case of processing of compositions in an electromagnetic field).

An increase in the processing time to 15 minutes reduces compressive strength (by 28% in the case of processing of compositions by ultrasound, and 41% in the case of processing of compositions in an electromagnetic field). Treatment with a duration of 30 minutes leads to similar

results, as in the case of processing for 15 minutes, because the continued treatment leads to a rise in the temperature of the composition, as a result, the viscosity of the composition decreases and surface layers with dislocations are formed that lead to an increase in residual stresses [146].

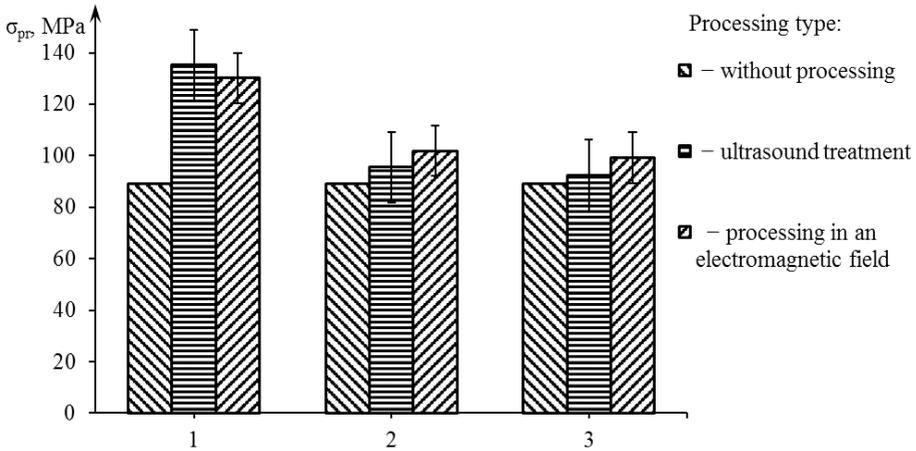


Figure 4.13. Dependence of the strength of the compression of epoxy composites, filled with fine particle powder of iron P-20 from the length of processing: 1–5 min; 2–15 minutes; 3–30 min

4.3 Influence of induction of electromagnetic field on the physical and mechanical characteristics of epoxy composites

It was established that the growth of the induction of the electromagnetic field (Fig. 4.14) leads to an increase of 2.5–4.0 times the adhesion strength of epoxy composite materials compared to epoxy composites without pre-treatment of compositions in the physical field ($\sigma_a = 18.43$ MPa). The maximum values of the characters were obtained in the range 0.3–0.5 T ($\sigma_a = 49.4$ – 56.4 MPa), which is associated with the formation of the maximum number of chemical bonds in the epoxy-composite system.

The introduction of paramagnetic particles into the epoxy polymer system changes the conditions for the structure of epoxy components. Processing of compositions in a variable magnetic field in the process

of structuring activates the interaction between the macromolecules of the matrix and the surface of the dispersed particles. The growth of the induction of the electromagnetic field amplifies the orientation effect of paramagnetic filler particles and promotes the uniform distribution of highly dispersed reinforcing elements [147], which leads to an improvement of the physical and mechanical properties of epoxy composites.

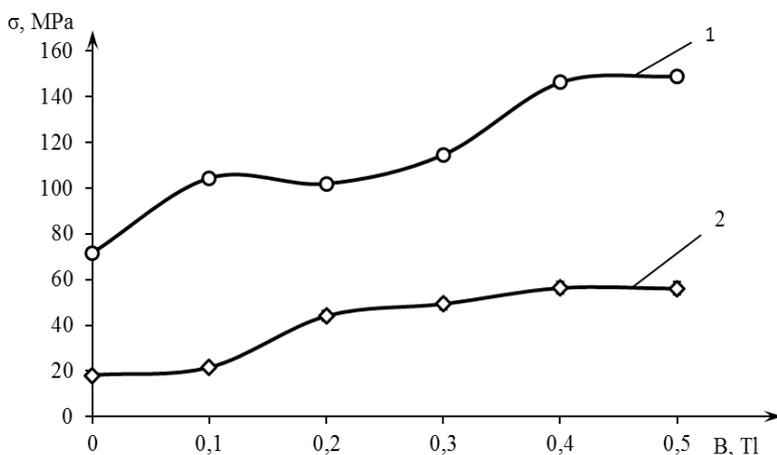


Figure 4.14. Dependence of the compressive strength (1) and adhesion strength (2) of epoxy composite materials filled with zirconium powder from the change in the induction of the electromagnetic field

It has been experimentally established that with the growth of magnetic induction an increase in the strength of the compression of epoxy composites is observed (Fig. 4.14) due to the fact that the induction is the main strength characteristic of the electromagnetic field and with the increase of its absolute magnitude the spatial orientation is intensified. This ensures the ordering of the macromolecules of polymers and the highly paramagnetic filler particles along the magnetic field strength lines. The maximum value of the studied characteristic ($\sigma_{st} = 149.6$ MPa) was obtained for the magnitude of the magnetic induction in the range of 0.4–0.5 T.

An increase in the magnetic induction (Fig. 4.15) to 0.5 T leads to an increase in residual stresses in epoxy composites ($\sigma_{rz} = 2.3$ MPa). This

is due to the fact that, along with the positive influence on the structure during the orientation of macromolecules, high values of magnetic induction cause the appearance of induction vortex currents, which determine the allocation of heat. Significant additional heating by induction currents is undesirable since it leads to a local structuring of the epoxy-composite system [149; 150].

It has been experimentally determined that the optimal values of magnetic field induction are within the range 0.2–0.4 T, in which the minimum values of residual stresses in epoxy composites were obtained.

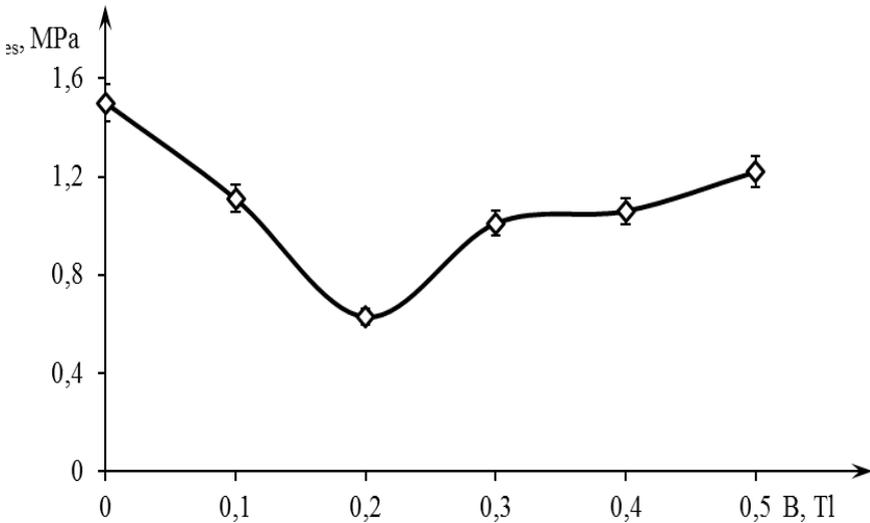


Figure 4.15. Dependence of the residual stresses of epoxy composite coatings filled with zirconium powder on the change in the induction of an electromagnetic field

CHAPTER 5.

INVESTIGATION OF OPERATIONAL CHARACTERISTICS AND TECHNOLOGICAL PROCESSES OF FORMATION OF EPOXY COMPOSITES MODIFIED BY HIGH-DYSPER PARTICLES

Epoxy composite materials modified with fine particles are used to create products with controllable electrophysical properties, with high corrosion resistance and wear resistance [144; 145]. On their basis, coatings that effectively interact with electromagnetic radiation over a wide range of frequencies can be created and are stable under the influence of aggressive environments. High resistance to the influence of the operating factors of polymer-composite coatings is mainly determined by such criteria as nature, content and distribution of fine particles, methods of modifications of compositions and the number of functional layers in coatings [146].

5.1 Investigation of the Corrosion Resistance of Epoxy Composites Modified by Fine Particles

The resilience of epoxy composite coatings to the effects of aggressive media is determined by the ability of the material to resist penetration of the aggressive medium to the surface protected by the coating during operation [147]. In order to introduce developed materials as coatings for anti-corrosion protection of parts, assemblies and mechanisms operating in aggressive environments, epoxy composites modified with highly dispersed fillers (fluoroplastic powders, iron PZR-3, carbonyl iron, zirconium), optimum content (6 wt. ch.) which are predefined by their physical and mechanical characteristics.

The results of experimental studies confirm the high chemical resistance of the developed materials on the basis of epoxy resins (Table 5.1) in various aggressive environments, since the epoxy polymer matrix slows down the electrochemical reactions on the metal surface and

affects the kinetics of the process, forming a diffusion barrier [144]. It has been established that nitric and sulfuric acids cause the maximum loss of mass of epoxy polymeric samples. The destruction of the polymer in the solutions of these acids is due to their ability to oxidize the substance and polymer sorption of molecules of aggressive media, resulting in a change in the structure of the material and collapse of unstable [144].

Table 5.1 – Corrosion resistance of epoxy composite materials

Aggressive environment	Change in the mass of samples of epoxy composite materials filled with fine particles, %				
	Polymer matrix	Fluoroplastic	Ironmarks PZHR-3	Carboniferous iron	Zirconium
H ₂ SO ₄	- 1.18	- 1.01	- 3.00	+ 2.08	+1.44
HNO ₃	- 1.94	+ 0.00	- 2.2	- 0.60	+ 0.88
HCl	- 1.12	+ 0.13	+ 0.46	+ 0.57	+ 0.00
NaCl	- 1.01	+ 0.23	+0.66	+ 0.33	- 0.6
NaOH	- 0.97	+ 0.49	+0.76	- 0.59	+ 0.65

Introduction to the composition of the epoxy polymer matrix of highly dispersed fillers contributes to increased chemical stability by reducing the volume of the polymer matrix of the composite and increasing the number of physicochemical bonds [147]. After immersion of epoxy composites in solutions of acids H₂SO₄ and HNO₃, a decrease in the mass of samples filled with powders of carbonyl iron and iron of grade PZR-3, which is associated with the dissolution and removal of corrosion products. The increase in the mass of samples occurs after the endurance of epoxy composites filled with fluoroplastic powders, iron PZR-3 or carbonyl iron, in the medium of HCl acids or aqueous NaCl salt solution. For samples of a similar composition, the exposure in acids H₂SO₄ and HNO₃ also leads to an increase in mass. The surface of the epoxy composites is covered by-products of corrosion (Fig. 5.1), which leads to an increase in the mass of samples.

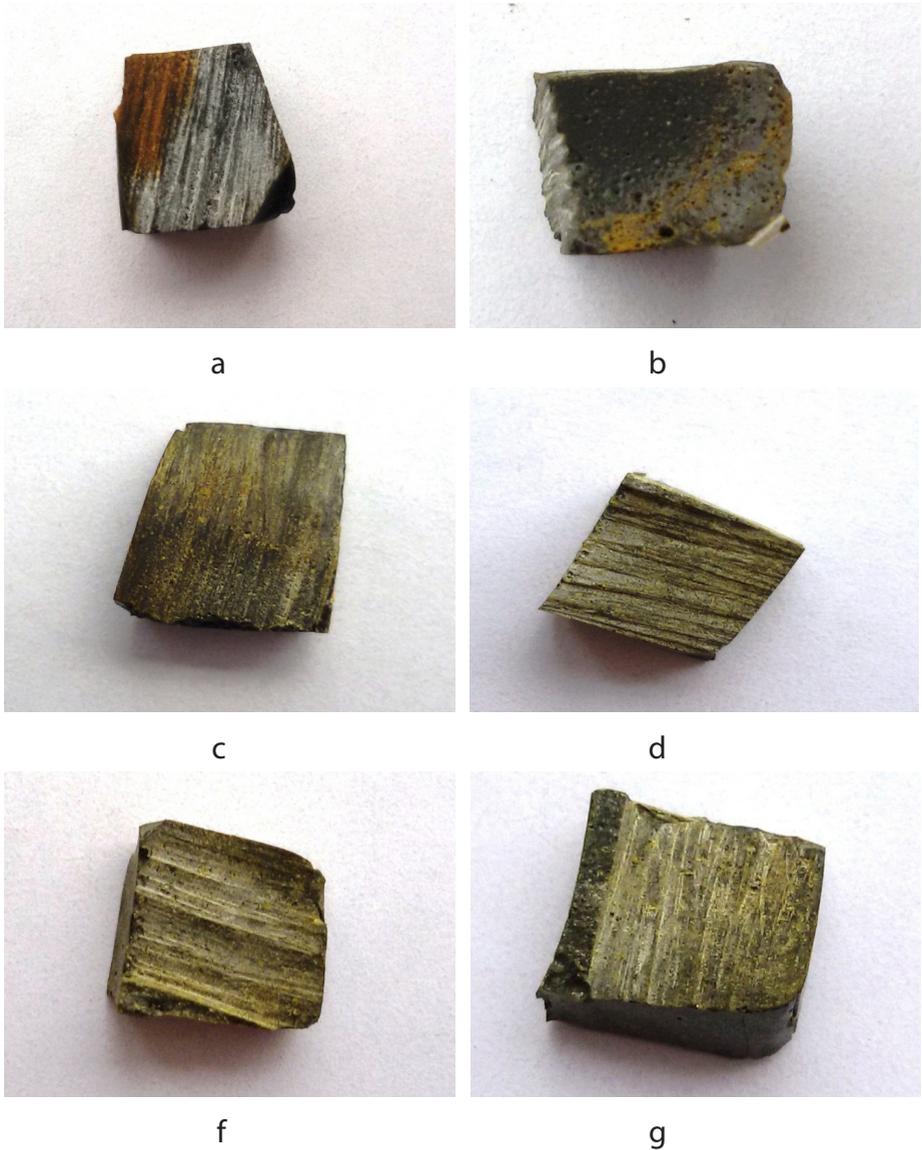


Figure 5.1. General view of epoxy composite samples after research on corrosion resistance: a, b – epoxy composite with zirconium powder; c, d – epoxy composite with powder of carbonyl iron; f, g – epoxy composite with powder of iron of grade PZR-3; a, c, f – H_2SO_4 ; b, d, g – HNO_3

It was established that for epoxy composites filled with zirconium powder, changes in the mass of investigated samples after exposure in an aggressive environment of HCl were not observed due to the presence of corrosion-resistant filler particles that prevent the penetration of corrosion-active substance molecules into the volume of the epoxy polymer matrix [148]. Similar results were obtained for epoxy composites filled with fine particles of fluoroplastics immersed in HNO_3 acid.

5.2 Determination of the stability of epoxy composite coatings, modified by physical fields, to the influence of alternating temperatures

One of the main drawbacks of polymer composites is the partial or total loss of operational properties at low temperatures, that is, limited frost resistance. According to the results of experimental studies, [137], mechanical, dielectric, relaxation and other properties of polymers are significantly changed with temperature.

The tendency of polymers to crack formation during deformation at a temperature lower than the temperature of fragility, due to the increase in stress in the composite due to the slowing of relaxation processes in macromolecules. The highest deformations are observed in polymers of the linear and polar structures since at low temperatures external stresses cause the appearance of elastic and plastic deformations in them [140].

For technology operated in cold climates, the temperature range in which the mechanical properties of structural materials should provide the required reliability and durability are usually taken from (-40) to (40) . A large number of scientific works [135–139] are devoted to the reliability of machinery in conditions of negative temperatures, but they do not address the problem of the development of stable polymer composite coatings under the influence of alternating temperatures and methods of improving the criterion of resistance to abrupt changes in climatic conditions.

It has been experimentally determined that the index of frost resistance of polymeric composites depends on the size of the filler particles and on the modification of the epoxy composition (Table 5.2).

Table 5.2 – Criterion of resistance of epoxy composite coatings to the influence of alternating temperatures

The composition of epoxy composite coating	Processing in physical fields	Degree of cracking
Coating with powder of carbonyl iron	No processing	0.55
	Ultrasound treatment	0.33
	Treatment in the electromagnetic field	1
Coating with powder of fullerene black	No processing	0.1
	Ultrasound treatment	1
	Treatment in the electromagnetic field	1
Coating with zirconium powder	No processing	0.88
	Ultrasound treatment	1
	Treatment in the electromagnetic field	1

It has been experimentally established that epoxy composite coatings filled with highly dispersed powder of carbonyl iron without preliminary processing of compositions in physical fields and, in the case of ultrasonic compositions, are characterized by low values of cracking coefficient ($P = 0.33\text{--}0.55$). This is due to the fact that the effect of the alternating temperatures leads to an increase in the residual stresses in the coatings, which results in the destruction of the adhesive bond between the matrix and the cracker with the filler (Fig. 5.2, a, d).

The introduction of fullerene black into a polymer matrix without pre-treatment of compositions reduces the cracking resistance of epoxy composites ($P = 0.1$), which is confirmed by significant bundle banding (Fig. 5.2, b) and is associated with the formation of a high-voltage state of the system [144]. In epoxy composite coatings filled with a fine particle of fullerene black, the compositions of which were exposed to the physical fields, defects of the surface layer were not detected after investigations under conditions of alternating temperatures (Fig. 5.2, f, k), which is evidence of an increase in the crack resistance of epoxy composite coatings. Similar results were obtained for epoxy composite coatings filled with carbonyl iron in the case of pre-treatment of compositions in an electromagnetic field (Fig. 5.2, g).

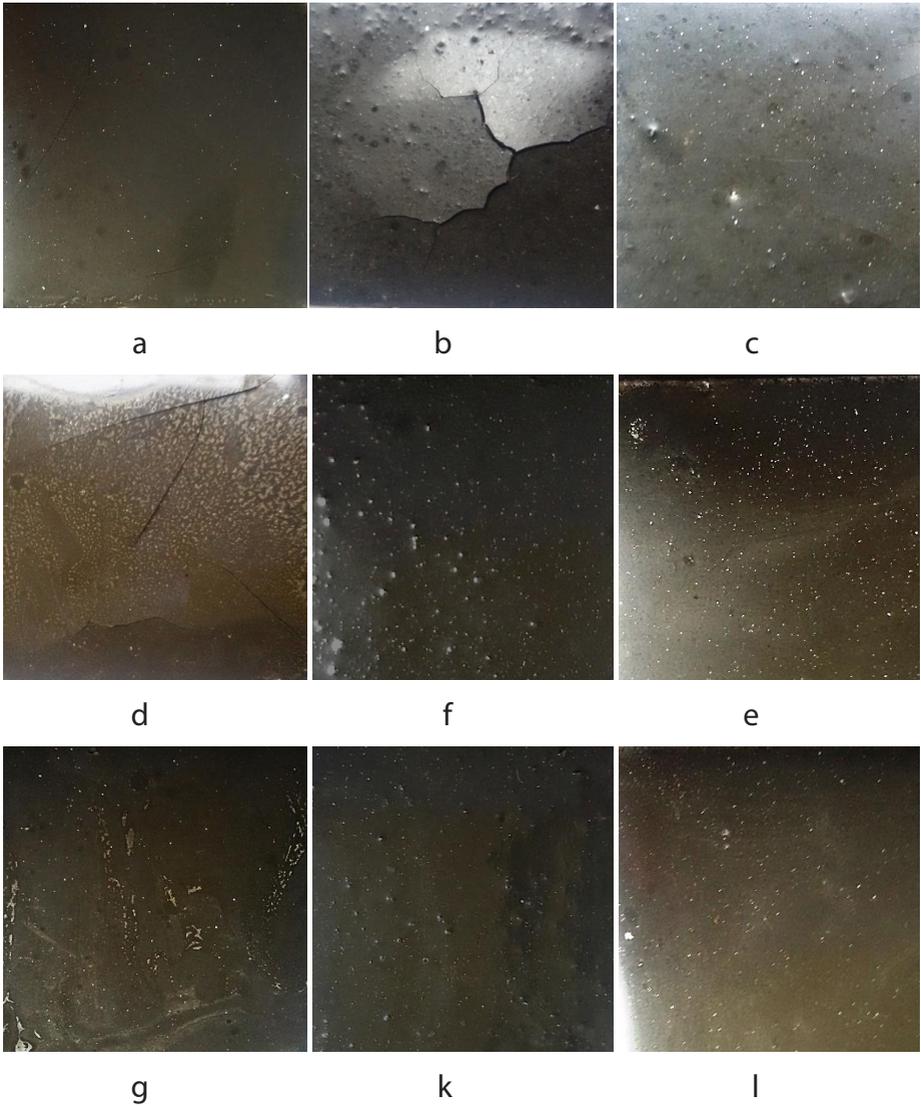


Figure 5.2. General view of the surface after the influence of temperature changes of epoxy composite coatings, filled with:
 a, d, g – carbonyl iron; b, f, k – black fullerene; c, e, l – zirconium;
 with pre-processing of the composition: a, b, c – without processing;
 g, f, e – ultrasound treatment; g, k, l – processing
 in the electromagnetic field

Epoxy composite coatings filled with zirconium powder, without processing the compositions in the physical field, are characterized by the presence of small cracks in the surface (Fig. 5.1, c), which arise due to insufficient wetting of the surface of the particles, which leads to the formation of micro-defects. Increased frost resistance has coatings, filled with fine particle zirconium powder ($P = 1$) with the preliminary processing of compositions by ultrasound or in an electromagnetic field. Visually it is found that the coating remains integral, no external defects are detected (Fig. 5.1, e, l), since the effect of external fields provides high adhesion strength at the interface between phases in the matrix-filler system and improves the resistance to the influence of alternating temperatures.

Thus, an increase in the stability of epoxy composite coatings, the composition of which has been modified in physical fields to the influence of alternating temperatures from (-40) to (60) , has been experimentally recorded. Operation of parts or structures with polymer-composite protective coatings in a change-over temperature range is accompanied by a process of thermal deformation [145]. Due to different values of the coefficients of linear expansion of materials, there is a significant increase in residual stresses, causing the destruction of coatings. Treatment of compositions in an electromagnetic field or ultrasound leads to stress relaxation in the system during the structuring of epoxy composites, which greatly extends the temperature range of the use of protective polymer-composite coatings.

5.3 Formation of two-layered epoxy composite coatings

The development of the composition and technology of the formation of multilayer coatings and the application of methods for controlling their properties is an important task in the material science of polymer composites used to protect the surfaces of equipment, machines, and mechanisms. The drawbacks of the coatings include the technological limitations associated with the preparation and drawing of compositions, as well as the bundle of coatings caused by residual stresses, etc. [151]. In this section we present the results of experimental studies of the

formation of the structure and properties of two-layer epoxy-composite coatings, using additional processing of compositions in physical fields.

The peculiarity of epoxy composite coatings is the formation of an inhomogeneous structure in them as a result of the adsorption interaction of a polymer matrix with a filler and a surface of a metal base. Different speed of physical and chemical processes during the formation of materials is accompanied by the emergence of residual stresses, which in most cases determine the mechanical properties of epoxy composites. To obtain multilayer coatings with high physical and mechanical characteristics based on epoxy polymers in the process of their formation, the processing of compositions by ultrasound or in an electromagnetic field is used.

At the initial stage of the formation of epoxy composite coatings (Table 5.3), the treatment of the composition in the physical field was carried out, followed by application to the prepared surface of the substrate by the method of pneumatic spraying.

The resulting coating for 15 minutes was structured in a furnace at a temperature of 313 K. The outer operating layer was formed with an epoxy composition filled with fluoroplastic powder and applied over the primer (adhesion) layer (Fig. 5.1).

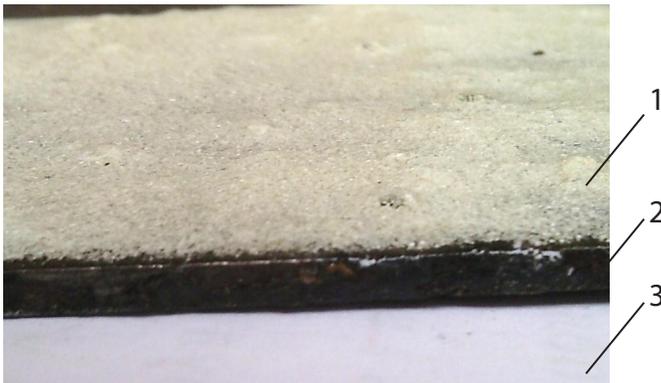


Figure 5.3. General view of the surface of a two-layer epoxy composite coating: 1 – operating layer; 2 – ground layer; 3 – metal base

It has been experimentally established that two-layer epoxy composite coatings, due to pre-treatment in the physical field of compositions for the primer layer, have a higher adhesion strength (Fig. 5.4).

The minimum values of the studied characteristic are recorded for epoxy polymers, which indicates the low efficiency of the use as a primer layer of the non-filled epoxy polymer. In the case of the introduction of carbonyl iron powder into the system, the adhesion strength increases 1.8 times due to the higher reactivity of the filler.

The treatment of the filled compositions in the electromagnetic field allowed us to achieve the extremum of adhesion strength of epoxy composites containing zirconium powder (6 parts by mass) ($\sigma_a = 56.5$ MPa). In epoxy composites filled with powder of carbonyl iron with the preliminary processing of compositions, high values of adhesion strength ($\sigma_a = 53.8$ MPa) were obtained in the electromagnetic field.

Table 5.2. – Formation of two-layer coatings

Experiment No.	1 layer	Type of processing	2 layer
1.	epoxy polymer	without processing	epoxy composite, filled with fluoroplastic powder (10 parts by weight)
2.	epoxy polymer	ultrasound	
3.	epoxy polymer	in the electromagnetic field	
4.	epoxy composite, filled with zirconium powder (6 parts by weight)	without processing	
5.	epoxy composite, filled with zirconium powder (6 parts by weight)	ultrasound	
6.	epoxy composite, filled with zirconium powder (6 parts by weight)	in the electromagnetic field	
7.	epoxy composite with carbonyl iron powder (6 parts by weight)	without processing	
8.	epoxy composite with carbonyl iron powder (6 parts by weight)	ultrasound	
9.	epoxy composite with carbonyl iron powder (6 parts by weight)	in the electromagnetic field	

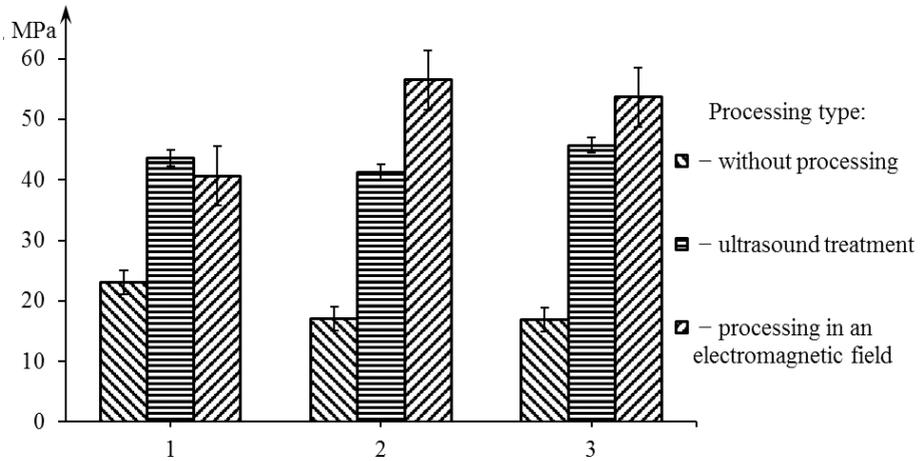


Figure 5.4. Dependence of adhesive strength of two-layer composite coatings on the type of treatment in case of use as a primer layer:
 1 – epoxy polymer; 2 – epoxy composite, filled with zirconium powder; 3 – epoxy composite, filled with powder of carbonyl iron

As a result of the analysis of the surface of the adhesive compound (Fig. 5.5), it was established that for a two-layer epoxy composite coating, in which the first layer is an epoxy composite, filled with carbonyl iron (Fig. 5.5, a, b), the inherent adhesion-cohesive nature of the deterioration due to the formation of insufficient number of physical and chemical connections between functional groups.

In the case of introduction into the composition of the epoxy matrix of zirconium powder, the cohesive nature of the destruction of the adhesive compound (Fig. 5.5, c) is characteristic, which is due to an increase in adhesion strength between the components of the epoxy composite.

The maximum value (Fig. 5.6) of impact strength ($A = 17.4J$) was obtained in the case of the introduction of a zirconium powder coating composition into the composition of the soil, with the preliminary treatment of compositions in the electromagnetic field. The lack of pre-treatment of compositions leads to a decrease in the impact strength of epoxy composites by 60% as a result of inadequate interaction between the components of the system in the boundary layers.

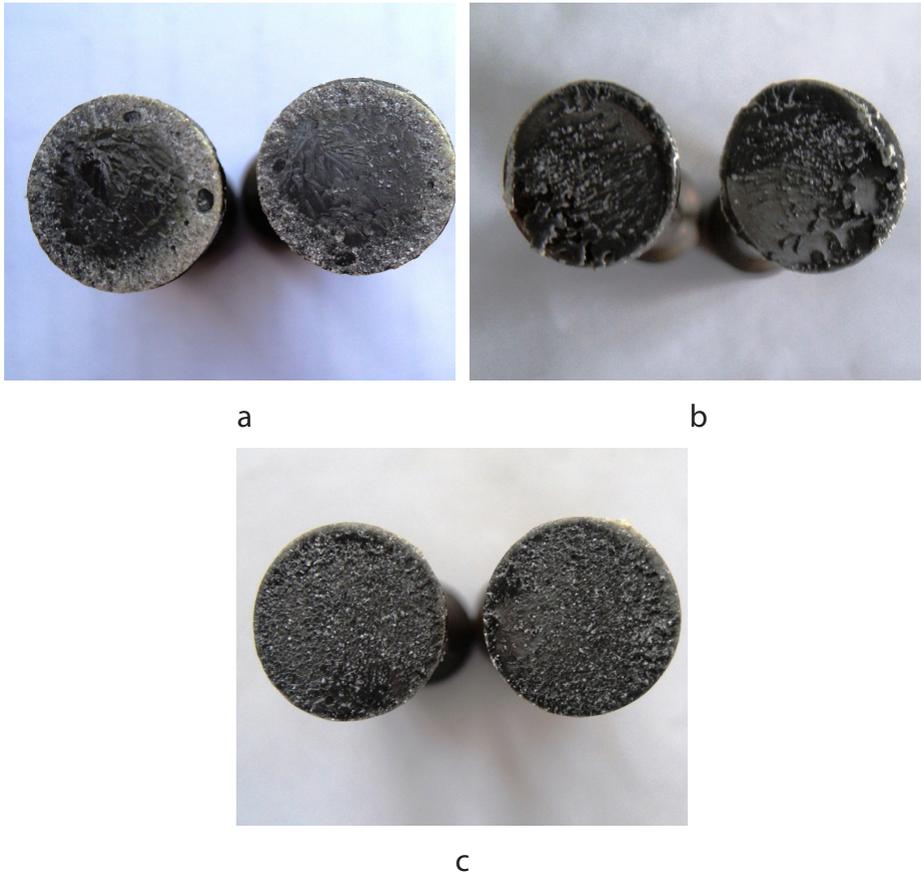


Figure 5.5 General view of the surface of the adhesive bonding of two-layer epoxy composite coatings with a treatment of compositions in an electromagnetic field in the case of use as a primer layer: a – epoxy polymer; b – epoxy composite, filled with powder of carbonyl iron; c – epoxy composite, filled with zirconium powder

High values of impact strength were fixed ($A = 15.5J$) for two-layer coatings, in which the epoxy composite was filled with powder of carbonyl iron with the treatment of compositions in the electromagnetic field as a primer layer. In the epoxy composites without processing the composition in the physical field, there is a decrease in this characteristic by 66%.

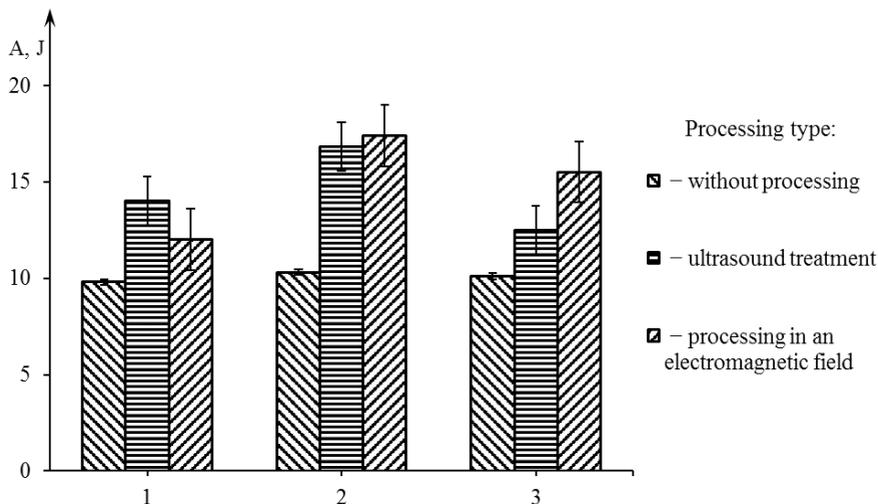


Figure 5.6. Dependence of impact strength of two-layer epoxy-composite coatings on the type of treatment in case of use as a primer layer: 1 – epoxy polymer; 2 – epoxy composite, filled with zirconium powder; 3 – epoxy composite, filled with carbonyl iron

Application as a soil layer of an epoxy polymer leads to a catastrophic destruction of the coating, which is accompanied by the extinction of large areas (Fig. 5.7, a) since the number of formed bonds with the surface of the substrate is small.

High values of the impact strength of epoxy composite coatings with pre-treatment of compositions in the electromagnetic field are confirmed by the presence of only the zone of plastic deformation of two-layer coatings without the formation of areas of detachment and the propagation of cracks after dynamic loading (Fig. 5.7, b) [152–154]. The lower values of the impact strength of two-layer epoxy-composite coatings filled with powder of carbonyl iron are confirmed by a small area of detachment of the coating (Fig. 5.7, c).

Experimental studies confirm the promising use of pre-treatment of compositions in physical fields during the formation of two-layer composite coatings. These kinds of processing of compositions allow to provide high-quality adhesive bonding between layers and to improve the physical and mechanical characteristics of the coatings.

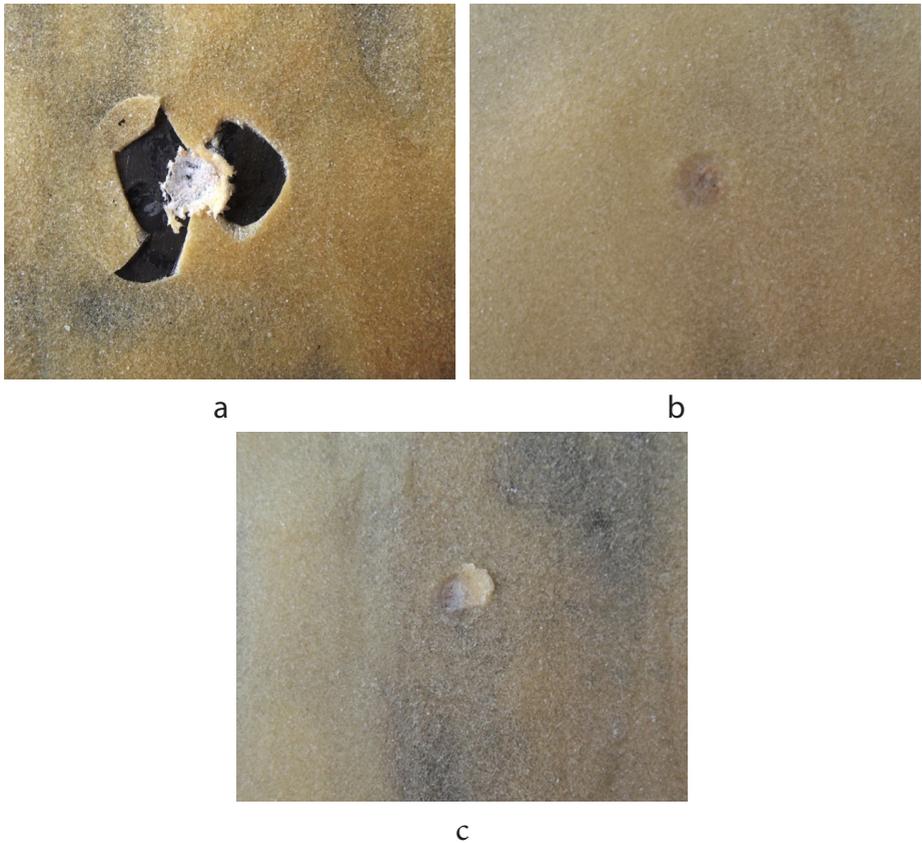


Figure 5.7. General view of the surface of two-layer coatings, the compositions of which are processed in an electromagnetic field, after studies on impact strength in the case of application as a primer layer: a – epoxy polymer; b – epoxy composite, filled with zirconium powder; c – epoxy composite, filled with powder of carbonyl iron

As the duration of coating operation is determined by a number of factors, the main of which is the high adhesion of the coating to the base and high physical and mechanical characteristics (strength, ductility, fragility, hardness), therefore the developed technology for the treatment of epoxy compositions in physical fields ensures achievement of the set goal.

The use of highly dispersed fillers for epoxy composites with the practical implementation of the developed technical solution for the

processing of compositions in physical fields offers wide opportunities in the development of new composite materials and provides the formation of multilayer protective coatings with high-performance characteristics on their basis [155–157].

The developed method of forming the soil layer will allow obtaining a two-layer structure of epoxy composite coating with high density and high adhesive strength between layers.

RESUME

It has been experimentally established that the preliminary treatment of compositions in an electromagnetic field causes an increase in adhesion strength of 3,1–5,6 times and up to 70% of the strength limits in compression of epoxy-containing highly dispersed powders in the amount of 4 to 8 mass. in comparison with the untreated system due to the compact placement of segments of macromolecules in the cavities of the solid phase and the formation of additional physicochemical bonds in the boundary layers due to the activation of free radicals of macromolecules, which intensively interact with hydroxyl groups on the surface of metal particles.

Treatment of compositions at low degree of filling of the system (6 parts by weight) in the physical field causes a reduction of 3.6 times the residual stresses in epoxy composites filled with iron powder of grade PZHR-3 after processing in the electromagnetic field and 4.8 times after ultrasound treatment for account of the increase in the mobility of particles and the local decrease in the viscosity of the matrix in the boundary layers as a result of the orientation of the dipole segments of the macromolecules, which allows the formation of the structure of the composite with a uniform distribution of chemical bonds.

It has been experimentally established that the treatment in the physical field of the compositions with the hardener leads to an increase of 50 to 54% of adhesion strength, 70 to 90% hardness and 20 to 40% of the impact strength of the epoxy composites compared to the composites whose compositions are treated without a hardener, since these fields increase adsorption the ability of a complex of macromolecules of epoxy resin with a hardener to enter difficult-to-reach areas on the surface of particles due to the local increase in the temperature of the composition and the reduction of its viscosity, I inclusions of air from the system and initiates the process of structure formation.

It has been established that optimal processing time in physical fields is 5 minutes, since the growth of adhesive strength is 30–35% and 30–40% of the strength limit during compression of epoxy composites in comparison with the treatment for 15–30 minutes, because the short-term treatment provides the formation of a homogeneous structure of

spatial epoxy polymer mesh and a sufficient number of physicochemical bonds in boundary layers with low residual stresses.

The electron microscopy method fixed the uniform distribution of ferro- and paramagnetic particles in epoxy composites whose compositions are processed in an electromagnetic field, while the fracture surface is characterized by smooth and shallow relief transitions compared to untreated materials, indicating an increase in cohesive strength and formation of a structure with low residual stresses ($\sigma_{rz} = 0.8$ MPa). It was recorded that in the case of processing of compositions by ultrasound filled with ferro- and paramagnetic particles, a significant decrease in the number of pores (up to 60–90%) occurs in epoxy composites filled with ferro- and paramagnetic particles, since ultrasound causes more powerful micro winning of high-density particles, which provides a significant reduction viscosity of the system compared with compositions filled with light filler (fluoroplastic).

On the basis of experimental researches, a technology for the formation of epoxy-composite two-layer coatings, which involves the processing of compositions in the electromagnetic field, was developed. The formation of the adhesive (primer) layer was carried out using zirconium powder, which allowed to increase the adhesive strength by 2.4 times and the impact strength of 74% of the protective coatings by reducing the viscosity and increasing the adsorption capacity of the system, which increases the solubility of the particles by activating the functional groups on the surface of the solid phase and free radicals of macromolecules of binder, as well as the appearance of favorable conditions for relaxation processes, resulting in the formation of a structure of epoxy-like structure with a high degree of low tensile condition. The formation of the operating layer was carried out using fluoroplastic powder since this filler is chemically inert and prevents the penetration of aggressive medium molecules in the case of high adhesion strength at the interface of the phases.

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