The Use of Complex Additives for the Formation of Corrosion- and Wear-Resistant Epoxy Composites

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Abstract

The corrosion resistance and hydroabrasive resistance of the developed epoxy composite coatings are investigated in this paper. The analysis of the penetration index change after \( t = 50–150 \) days of immersion in a water medium and 10% sulfuric acid solution is carried out. The optimal ratio of the modifier and nanodispersed (Si\(_3\)N\(_4\), Al\(_2\)O\(_3\), AlN, and TiN) and fibrous (viscose, polyamide, matka silk, rong, and cashmere) fillers in the epoxy binder is determined. It was allowed to slow down the process of electrochemical reaction on the metal surface. The penetration of aggressive media in such a coating during the time \( t = 150 \) days is 0.8–2.8%. It is 1.5–2 times lower than the similar indexes of the initial epoxy matrix. The rational combination of the fibrous filler (wool, acrylic PAN, and cashmere), modifier, and nanodispersed (Si\(_3\)N\(_4\), Al\(_2\)F\(_3\), IH, and ZrH) filler in the epoxy binder is found, which allows to provide optimum indexes of wear rate. The wear rate under the action of a hydroabrasive of such a coating is \( I = 0.20\% \), which is 4 times lower than the similar indexes of the initial epoxy matrix. The wear mechanism of such coatings is caused by the physical and mechanical processes of microcutting and plastic deformation of the surface layer of the material.

1. Introduction

Improvement in operational characteristics of technological equipment, which is used in various branches of industries, is possible by applying plasma, eutectic, and epoxy coatings [1–8]. At the same time, the introduction of additives in the epoxy binder improves the technological properties of polymers and also significantly affects the physical and mechanical properties, anticorrosion properties, and wear resistance of the equipment. Therefore, a rational combination of components in the epoxy binder will provide the necessary complex of the protective coatings properties in specific operational conditions [6–11].

The analysis of works [6–18] allows to state that epoxy composites are characterized by chemical stability and wear resistance in different operational conditions, wherein the adhesive strength of the polymers to the base and the cohesive strength of the material are main criteria that provide protective properties for a long time of operation. As it is known, acid solutions are the most aggressive medium for epoxy composites. Therefore, it is important from a scientific and practical point of view to develop new materials that can maintain their properties in different operating conditions.

The aim of the work is to investigate the corrosion resistance and wear resistance of the developed epoxy composites.

2. Materials and Methods

For the formation of epoxy composite materials (CM), as the main component of the binder, the epoxy diane oligomer ED-20 was used, which is characterized by high adhesion
and cohesive resistance, slight shrinkage capacity, and processability when applied on the surface of a complex profile.

2,4-Diaminotoluene (DAT) is used as a modifier. According to the results of previous studies, the modifier is added into a binder at the content of 1.00 pts. wt. per 100 pts. wt. of epoxy oligomer ED-20. The molecular formula of the modifier is \( \text{C}_5\text{H}_{10}\text{N}_2 \). The molecular weight of DAT is 122.17 g/mol. The melting point is 98°C. The modifier is soluble in polar organic solvents (methanol, ethanol, acetone, and ethyl acetate) and is insoluble in water.

Powders that are a mixture of nanodispersed compounds (MNDC) are used as nanodispersed fillers for experimental studies. They are as follows: \( \text{Si}_3\text{N}_4 \), \( \text{Al}_2\text{O}_3 \), \( \text{AlN} \), and \( \text{TiN} \) (MNDC 1) with the dispersion \( d = 20–80 \) nm and \( \text{Si}_3\text{N}_4 \), \( \text{AlF}_3 \), \( \text{IH} \), and \( \text{ZrH} \) (MNDC 2) with the dispersion \( d = 30–40 \) nm.

In addition, a mixture of discrete fibers (MDF) is used: MDF 1 (viscose, 37%; polyamide, 23%; matka silk, 18%; rong, 18%; cashmere, 4%) with parameters \( l = 0.5–1.0 \) mm and \( d = 18–25 \) μm and MDF 2 (wool, 60%; polycrylonitrile (PAN), 30%; cashmere, 10%) with parameters \( l = 0.5–1.0 \) mm and \( d = 18–25 \) μm.

Polyethylene polyamine (PEPA) curing agent, which allows to solidify the materials at room temperature, was used for cross-linking of epoxy compositions. PEPA is a low-molecular-weight substance, which consists of the following interconnected components: [-CH\(_2\)-CH\(_2\)-NH-]m. To cross-link CM, the curing agent was added to the composition at the stoichiometric ratio of components (parts by weight): ED-20: PEPA = 100:10.

The epoxy composite, filled with particles of disperse filler, was formed using the following technique: preliminary dosage of ED-20 epoxy diane resin, heating the resin to a temperature of \( T = 80 \pm 2 \) °C, and its exposition at a temperature over time \( \tau = 20 \pm 0.1 \) min; dosage of disperse filler and its subsequent introduction into an epoxy binder; hydrodynamic combination of the oligomer ED-20 + DAT + MNDC during the time \( \tau = 10 \pm 0.1 \) min; introduction of MDF; ultrasonic processing (USP) of the composition (epoxy binder, modifier, nanoparticles, and fibers) during the time \( \tau_{U} = 1.5 \pm 0.1 \) min; cooling the composition to room temperature during the time \( \tau = 60 \pm 5 \) min; introduction of PEPA curing agent; and mixing of the composition over time \( \tau = 5 \pm 0.1 \) min. Subsequently, the CMs were solidified according to the following conditions: the formulation of specimens and their exposition over time \( t = 120 \pm 0.1 \) h at a temperature \( T = 20 \pm 2 \) °C, heating at a speed of \( v = 3 \) °C/min to a temperature \( T = 120 \pm 2 \) °C, exposition of the specimens at a given temperature during the time \( t = 2.0 \pm 0.05 \) h, and slowly cooling to a temperature \( T = 20 \pm 2 \) °C. In order to stabilize the structural processes in the matrix, the specimens were kept during time \( t = 24 \) h in air at a temperature \( T = 20 \pm 2 \) °C, followed by conducting experimental tests.

The following properties of CM were studied: adhesion strength at break, elastic modulus and fracture stresses during the flexion, impact strength, corrosion resistance, and hydroabrasive wear resistance.

The adhesion strength of the matrix to the metal base was investigated by measuring the destructive tension (“fungal method”) with a uniform separation of the pair of glued specimens in accordance with work [6]. The force of detachment of adhesive compounds of steel specimens was measured on an automated breaking machine UMM-5 at a loading rate of \( v = 10 \) N/s. The diameter of the working part of the steel specimens at break was \( d = 25 \) mm.

The fracture stresses and elastic modulus during the flexion were determined according to [15]. Parameters of the specimens are as follows: length \( l = 120 \pm 2 \) mm, width \( b = 15 \pm 0.5 \) mm, and height \( h = 10 \pm 0.5 \) mm.

The impact strength was determined by the Charpy method according to ASTM D6110 on the pendulum copper MK-30 at a temperature of \( T = 25 \pm 2 \) °C and relative humidity \( \varphi = 50 \pm 5 \)%. Specimens with the following parameters were used: \( (63.5 \times 12.7 \times 12.7) \pm 0.5 \) mm. The distance between the supports is \( 40 \pm 0.5 \) mm.

Corrosive resistance of the protective coatings is determined by immersion of specimens in water and 10% sulfuric acid solution. The duration of exposition specimens with a size of \( 60 \times 10 \times 10 \) mm in aggressive media is 150 days at the temperature \( T = 20 \pm 2 \) °C. Specimens with a mass \( 10.0–12.0 \) g prior to study and after exposition in aggressive media are weighed on electronic scales DRS-8000 “Shimadzu” with an accuracy of \( 0.02 \pm 0.001 \) g.

The calculation of the penetration of aggressive media is carried out according to the following formula:

\[
\chi = \frac{b-a}{a} \cdot 100\%,
\]

where \( \chi \) is the corrosion resistance, %; \( a \) is the mass of the specimens before tests, \( g \); and \( b \) is the mass of the specimens after tests, \( g \).

The relative resistance of the CM to the action of hydroabrasive was found by the method of materials and coatings testing on the gas-abrasive wear with a centrifugal accelerator. This method enables one to model the real process of wear of mechanisms parts under the hydroabrasive action. The rotor rate of the centrifugal accelerator was equal to 3000 rpm. A mixture of technical water and abrasive particles of quartz sand (with volume ratio 5:1) was chosen as a hydroabrasive suspension. Specimens \( 30 \times 20 \times 4 \) mm in size for an attack angle of the hydroabrasive mixture equal to 45° were tested. The mass of quartz sand consumed in the investigation was \( 9 \pm 0.1 \) kg.

The relative intensity of wear is given by the following formula:

\[
I = \frac{m_0 - m_{end}}{m_0} \cdot 100\%,
\]

where \( m_0 \) and \( m_{end} \), kg, are the masses of the specimen at the beginning and at the end of the tests, respectively.

Deviations of corrosion resistance and hydroabrasive wear resistance indexes of the developed CMs are 4–6% of the nominal.
3. Results and Discussion

At the first stage, the study of the CM properties at the different contents of the modifier was carried out. It is found that its optimum content is \( q = 1.00 \) pts. wt. per 100 pts. wt. of ED-20 oligomer. At this content of modifier, the adhesion strength at break is \( \sigma_a = 39.1 \text{ MPa} \), the elastic modulus during the flexion is \( E = 3.4 \text{ GPa} \), the fracture stress during the flexion is \( \sigma_f = 57.2 \text{ MPa} \), and the impact strength is \( W = 7.9 \text{ kJ/m}^2 \). Similarly, the optimum content of discrete fibers in the epoxy matrix was determined, which is \( q = 0.02 \) pts. wt. per 100 pts. wt. of ED-20. At this content, the fracture stresses during the flexion are \( \sigma_f = 35.6–57.4 \text{ MPa} \), the elastic modulus at bending is \( E = 3.0–3.1 \text{ GPa} \), and the impact strength is \( W = 7.9–8.2 \text{ kJ/m}^2 \). The optimal content of nanoadditives in the epoxy binder is \( q = 1.00 \) pts. wt. The adhesion strength at break is \( \sigma_a = 47.5–59.2 \text{ MPa} \), the fracture stresses during the flexion are \( \sigma_f = 63.7–65.2 \text{ MPa} \), the elastic modulus at bending is \( E = 3.8–3.9 \text{ GPa} \), and the impact strength is \( W = 7.9–8.1 \text{ kJ/m}^2 \) at this content of nanoadditives.

Furthermore, the optimization of the ingredient content in the polymer matrix was carried out to develop coatings with increased corrosion resistance and hydroabrasive wear resistance. Based on the mathematical planning of the experiment, four types of protective coatings (with different contents of the ingredients), which are characterized by maximum cohesive strength, were selected [16]. The corrosion resistance and hydroabrasive wear resistance of these materials were investigated.

Five compositions of composite materials were tested (the ratios are given in wt. parts):

(i) Control specimen (the matrix is formed at the following components ratio: ED-20 : PEPA = 100 : 10)

(ii) CM 1 (the composite is formed at the following ratio of components: binder : 2,4-diaminotoluene modifier (DAT) : a mixture of nanodispersed compounds MNDC 1 (20–80 nm) : mixture of discrete fibers (viscose, polyamide, matka silk, rong, and cashmere) (MDF 1) (\( \ell = 0.5–1.0 \text{ mm and } d = 18–25 \text{ } \mu \text{m} ) = 100 : 1.00 : 0.75 : 0.02)

(iii) CM 2 (binder : DAT modifier : MNDC 1 : MDF 1 = 100 : 1.00 : 1.00 : 0.02)

(iv) CM 3 (binder : DAT modifier : a mixture of nanodispersed compounds MNDC 2 (30–40 nm) : a mixture of discrete fibers (wool, acrylic PAN, and cashmere) (MDF 2) (\( \ell = 0.5–1.0 \text{ mm and } d = 18–25 \text{ } \mu \text{m} ) = 100 : 1.00 : 1.25 : 0.01)

(v) CM 4 (binder : DAT modifier : MNDC 2 : MDF 2 = 100 : 1.00 : 1.00 : 0.02)

It is experimentally found that epoxy matrix (in the time range \( r = 50–150 \text{ days} \)) is characterized by the highest value of the penetration index in water media (\( \chi_{1.5–1.6\%} \) (Figure 1) and 10% sulfuric acid solution (\( \chi_{2.9–3.6\%} \) (Figure 2). It is believed that this indicates low values of the cohesive strength of the polymer, due to the formation of microdefects in the structure (during the study time—150 days), and leads to the swelling of the coating due to the sorption of aggressive media, as a result of the electrochemical oxidation reactions in the interface metal base-epoxy coating. Therefore, the adhesive strength of the protective coating is also significantly reduced.

At the same time, the analysis of studies [17–21] allows to state that the controlled introduction of components of various dispersion and physical and chemical natures provides a significant increase in the performance characteristics of protective coatings, including corrosion resistance. Obviously, this can explain a decrease in the water penetration index to \( \chi = 0.8–1.2\% \) during the study of developed protective coatings (Figure 1). In this case, CM 1 is the most resistant to aggressive environment, since the value of penetration index is \( \chi = 0.8–0.9\% \), indicating the maximum packing of the spatial network and the absence of stress condition in the volume of the polymer. At the same time, one can put forward the hypothesis that, as a result, strong adhesive bonds are created that prevent the formation of microcracks in the volume of the polymer, which in turn...
prevents the penetration of aggressive media and the subsequent disintegration and spreading of the crack network.

In addition, it can be stated that CM 2 and CM 4 should be used as anticorrosive materials, since the values of the penetration index during the study differ insignificantly ($\chi = 0.8\%–1.0\%$) (Figure 1).

At the next stage, the dependence of the sorption of H$_2$SO$_4$ solution onto the surface of developed protective coatings on the duration of exposition was analyzed. An increase in the sorption process rate of the aggressive medium of sulfuric acid, in comparison with water, is experimentally determined. Thus, the initial period, which, characterized by the polymer swelling, is $\tau = 1–50$ days (H$_2$SO$_4$ solution), which is lower than in water environment: $\tau = 1–75$ days. Additionally, a double increase in sorption by protective coatings is observed (Figure 2).

It is believed that the high chemical activity of H$_2$SO$_4$ and the ability to oxidation processes are the reasons, which provide a change in the polymer structure, due to the destruction of unstable bonds. In this case, CM 1 is the most resistant to the aggressive H$_2$SO$_4$ solution, since the value of the penetration index is $\chi = 1.8–2.0\%$ (Figure 2). This material is characterized by the maximum cross-linking degree (which is agreed with the results of physical and mechanical research studies), which provides a slowing down of the electrochemical reaction process on the metal surface, while fulfilling the role of the diffusion barrier.

Analysis of the study results of corrosion resistance of the developed materials suggests that CM 1 is characterized by maximum resistance $\tau$ to the penetration of aggressive media to the metal base.

Additionally, wear resistance under the influence of hydroabrasive of developed materials is studied. In the work, the intensity of wear of the developed materials during the indirect impact is investigated, namely, at the attack angle $a = 45^\circ$. Since the shear stresses dominated that cause micro- and macrocutting of the material, and normal stresses, which lead to plastic deformations of the CM surface layer.

It is ascertained that the epoxy matrix is characterized by the maximum indexes of wear intensity ($I = 0.8\%$) among the developed materials. After testing, the surface of the epoxy matrix is characterized by chaotic microcavities. In addition, the traces of the cracking of the material are revealed, which indicates the plastic deformation due to low values of cohesion strength (which is agreed with the results of physical and mechanical studies).

It is experimentally established that CM 4 is characterized by the lowest wear intensity ($I = 0.20\%$). It is ascertained that the surface of such materials is characterized by minor microcuttings, which is typical for the wear of solid and rigid heterogeneous CMs. It is agreed with the study results shown in the works [17, 22, 23].

It is additionally revealed that CM 3 surface has the similar nature of the destruction under the influence of a hydroabrasive mixture (Figure 3). Accordingly, the wear intensity of such materials is $I = 0.26\%$. The analysis of the destruction surface of CM 1 and CM 2 under the influence of the hydroabrasive mixture is allowed to found the presence of indentation traces, that is, the formation of insignificant pitting, which is the result of fatigue destruction of the material. Therefore, the wear intensity of such materials is higher (among developed composite materials) ($I = 0.30–0.40\%$).

It was believed that the content of nanoadditives influences the growth of hydroabrasive wear resistance of CM 3 and CM 4. It is higher by $q = 0.25$ pts. wt. and $q = 0.50$ pts. wt., respectively (compared to CM 1).

Within this framework, it can be stated that the composite materials CM 3 and CM 4 should be used for operation under the conditions of the hydroabrasive medium.

4. Conclusion

On the basis of conducted overall studies, the following conclusions are established:

1. The material (CM 1) at the following composition: epoxy binder: the modifier 2,4-diaminotoluene: nanopolymers (Si$_3$N$_4$, Al$_2$O$_3$, AlN, and TiN) (20–80 nm): mixture of discrete fibers (viscose, polyamide, matka silk, rong, and cashmere) ($I = 0.5–1.0$ mm and $d = 18–25$ $\mu$m) = 100 : 1.00 : 0.75 : 0.02, is characterized by the improved corrosion resistance indexes, during the $r = 150$ days of exposition of the developed coatings in various aggressive environments. The developed material has a high chemical resistance due to the high adhesion and cohesive strength at the boundary of the phases “polymer base” and “polymer filler,” which provide a reduction of sorption of aggressive environment and, consequently, an increase in the duration of operation of the functional purpose equipment.
The wear intensity of the developed composite materials ($I = 0.20–0.40\%$) is smaller by 50% compared to the epoxy matrix ($I = 0.80\%$). The wear mechanism of composite materials is determined by the physical and mechanical processes of microcutting of the surface layer of materials under the action of abrasive particles at a certain angle of attack of the hydroabrasive mixture ($a = 45\%$).

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest regarding the publication of this paper.

References