INCREASING THE RELIABILITY OF WATER TRANSPORT VIA THE USAGE OF MODIFIED EPOXY COATINGS

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Resume

In solving the problem of energy and resource conservation in transport, polymer composites are of paramount importance. Polymer composite using makes it possible to significantly improve the mechanical properties of the materials and simultaneously to increase the durability of the parts of transport machines. The authors of this article focus on the substantiation of introducing the modifier 4.4'-methylenebis(2-methoxyaniline) with low concentrations into the epoxy resin. Such materials are characterized by increased mechanical strength and the ability to withstand static, dynamic stresses, as well as impact loads, since the values of the properties are: bending stresses at bending - σ = 51.2 to 54.4 MPa, modulus of elasticity at bending - E = 3.0 to 3.2 GPa, impact toughness is W = 8.8 to 9.0 kJ/m^2. The obtained results of experimental studies of the composite materials properties are in good agreement with the results of testing samples by optical microscopy, which indicates their reliability.

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1 Introduction

The problem of energy and resources conservation, based on a great development of scientific and technological progress, especially in the recent decades has exceedingly drawn our attention. Polymer composite materials (CMs) and protective coatings based on CMs are the important things in this problem solving. Polymer coatings, especially epoxy-based ones, are used in various industries, including transport, for protecting metal parts from corrosion, which significantly increases their durability [1-5]. Moreover, protective coatings should be characterized in a complex manner, by the increased indicators of physical and mechanical properties. Only the latter determine the anti-corrosion characteristics of adhesive, which, in turn, provide the resource conservation of the process equipment [6-9].

It is well-known [10-11], that the protective coatings should be multifunctional. On the one hand, they should be characterized by increased adhesion and cohesion strength, and on the other hand, the shrinkage and residual stresses should be minimal in the protective coatings. Hence, the authors of [12-14] claim that for improving the properties of the polymeric materials in a complex manner, it is necessary to introduce the modifiers with low content into the epoxy binder. Moreover, the additives must be active before the physical and chemical interfacial interaction with the epoxy oligomer at crosslinking of compositions. Only such an approach will allow to obtain the materials

with a high content of gel fraction, and, in its turn, will provide the maximum increase of cohesive strength of the protective coatings.

Taking into account everything that has been mentioned above, the modifier 4.4'-methylenebis (2-methoxyaniline) at the homeopathic content is proposed to introduce into the epoxy binder. This additive contains active groups, which, in our opinion, activates the physical and chemical processes of crosslinking and will improve the increase of the physical and mechanical characteristics of the testing materials.

2 Materials and methods

The objective of the research is to investigate the effect of the modifier 4.4'-methylenebis (2-methoxyaniline) content on the physical and mechanical properties of epoxy composite materials.

The epoxy diane oligomer ED-20 (GOST 10587-84) was chosen as the main component for the binder in the formation of epoxy CMs. In this work, the structural formula of the epoxy diane oligomer ED-20 fragment is represented according to reference [12] and shown in Figure 1. The 4.4'-methylenebis (2-methoxyaniline) (MDMA) was used as a modifier [15]. As explained in [15], the modifier content 0.1 to 2.0 pts. wt. by 100 pts. wt. of epoxy oligomer ED-20 was introduced into the binder (hereinafter mass parts are given by 100 parts by mass of epoxy oligomer ED-20). The molecular weight of 4.4'-methylenebis (2-methoxyaniline) is 258.3 [15]. Chemical formula is $C_{15}H_{18}N_2O_2$. The modifier is soluble in benzene, ethanol, acetone, however, it is marginally soluble in water. The structural formula of the modifier is shown in Figure 2.

Polyethylene polyamine hardener PEPA (TS 6-05-241-202-78) was used for crosslinking of epoxy compositions that allow to harden the materials at normal and elevated temperatures [5, 10]. It is known [10] that PEPA is a low molecular weight substance that consists of the following interconnected components $[-CH_2-CH_2-NH-]_n$. The structural formula of the PEPA hardener fragment is shown in Figure 3. The hardener was introduced into the composition with a content of 10 pts. wt. on 100 pts. wt. of epoxy oligomer ED-20. The main characteristics of the epoxy diane oligomer are

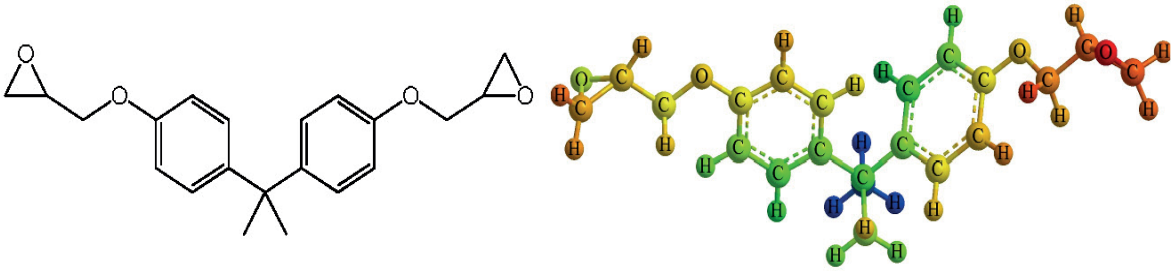


Figure 1 *Structural formula of the fragment of epoxy diane oligomer ED-20 [12]*

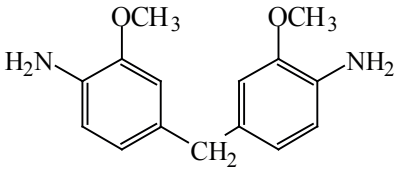


Figure 2 *General view of the chemical bonds of modifier 4.4'-methylenebis (2-methoxyaniline) (MDMA) [15]*

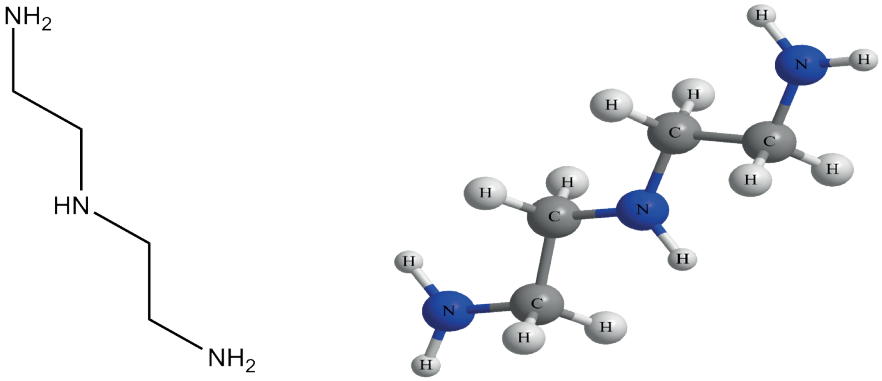


Figure 3 *Structural formula of the fragment of hardener PEPA [12]*

Table 1 *Characteristics of epoxy binder components [15]*

Characteristics	Epoxy oligomer ED-20	Modifier MDMA	Hardener PEPA
Molecular weight	390-430	258.3	230-250
The content of epoxy groups, [%]	20.0-22.5	-	-
The content of hydroxyl groups, [%]	1.25	-	-
Average functionality by epoxy groups, *fn*	2.0	-	-
Nitrogen content, [%]	-	10.84	19.5-22.0
Carbon content, [%]	-	69.74	-
Hydrogen content, [%]	-	7.02	-
Oxygen content, [%]	-	12.39	-
Toughness, η, [Pa s]	13-20	-	0.9
Density, ρ, [g/cm^3]	1.16	-	1.05

pointed in [15]. The characteristics of the epoxy diane oligomer, modifier and hardener are given in Table 1.

In the works [5, 12, 15], the main stages of the technology of forming and hardening of materials are given. Based on those studies, we were focused on the following. Epoxy composites were formed by the following technology: 1) heating of the resin up to the temperature T = 353 ± 2 K and exposure at this temperature during τ = 20 ± 0.1 min; 2) hydrodynamic combining of the oligomer and filler during τ = 1 ± 0.1 min; 3) ultrasonic processing (RCD) of the compositions during τ = 1.5 ± 0.1 min; 4) cooling the compositions to room temperature during τ = 60 ± 5 min; 5) introducing of the hardener and mixing of compositions during τ = 5 ± 0.1 min. Then the CM hardening was conducted under the experimentally determined mode: 1) formation of samples and their testing during τ = 12.0 ± 0.1 h at the temperature T = 293 ± 2 K; 2) heating with a rate of υ = 3 K/min up to the temperature T = 393 ± 2 K; 3) strengthening during τ = 2.0 ± 0.05 h; 4) slow cooling down to the temperature T = 293 ± 2 K. To stabilize the structural processes in the matrix, the samples were tested (strengthened) during τ = 24 h in the open air at the temperature T = 293 ± 2 K with further experimental testing.

In the studies [12, 15], the main methods of studying the mechanical properties of the materials are given. Those methods were taken as a principle in our work for the study of the following properties of CM: breaking stress and modulus of elasticity during bending, impact toughness.

Breaking stresses and modulus of elasticity in bending were determined in accordance with State standards GOST 4648-71 and GOST 9550-81 [16]. Sample parameters are the following: length l = 120 ± 2 mm, width b = 15 ± 0.5 mm, height h = 10 ± 0.5 mm [15].

According to State standard "GOST 4648-71" (ASTM D 790-03) the breaking stresses were determined as:

$$\sigma_3 = \frac{3F_{\max}L}{2bh^2}, \quad (1)$$

where ΔF_{max} - is the maximum load before breaking of the sample, N; L - is the distance between the props, mm; b - is a width, mm; h - is a thickness, mm.

According to the four-point bending loading scheme (GOST 9550-81) (ASTM D 790-03), the modulus elasticity was determined as:

$$E = \frac{0.185 \cdot L_v^3 \cdot \Delta F}{bh^3 \cdot \Delta z}, \quad (2)$$

where L_v - is the distance between props, mm; ΔF - is a load, N; b - is a width, mm; h - is a thickness, mm; Δz - is a deflection of the sample, mm [15].

Based on the method of research of impact viscosity of materials [5, 12, 15], in this study, the impact strength of CMs was measured by Charpy impact test without a notch (GOST 4647-80) [16] (ISO 179-1) by using a pendulum dill MK-30 at the temperature T = 298 ± 2 K and a relative humidity φ = 50 ± 5 %. The sizes of the samples are (65 × 12× 12) ± 0.5 mm. The distance between the props is 40 ± 0.5 mm. The impact strength of CMs was determined as:

$$W = \frac{A_n}{bs} \cdot 10^3, \quad (3)$$

where A_n - is the impact energy consumed for the fracture of the samples without notches; b - is a width, mm; s - is a thickness, mm.

Our study is based on the method of studying the strength of adhesive joints of materials to a metal substrate with uniform detachment and shear [12]. The scheme of sample formation for studying of the adhesive strength of composites in tearing and shearing is, respectively, shown in Figure 4 and Figure 5.

It should be noted, the diameter of the working part of the steel samples (St 3 grade) [17] during the tear-off and shearing was 25 ± 0.1 mm [12].

The study of adhesive strength in shear (Figure 5) was carried out similarly, measuring the tear-off force of adhesive joints of steel samples on the UM-5 automated tearing machine at the loading rate υ = 10 m/s.

Based on the method of studying materials by the method of optical microscopy [5, 12, 15], in this study,

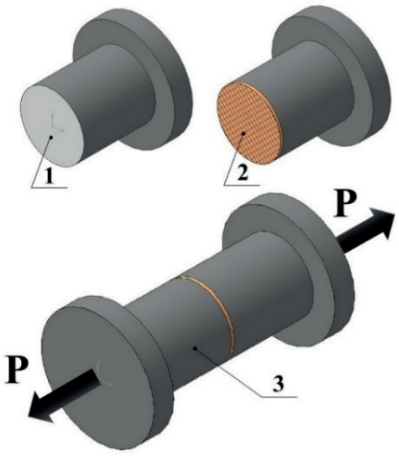


Figure 4. *The scheme of the sample formation for studying the adhesive strength of composites during the separation: 1 - the sample surface after cleaning (with the purpose of removing the oxide film) and degreasing; 2 - the sample surface after applying a uniform adhesive layer; 3 - adhesive samples that are subjected to the destructive load applied perpendicular to the plane of the contact surface contact*

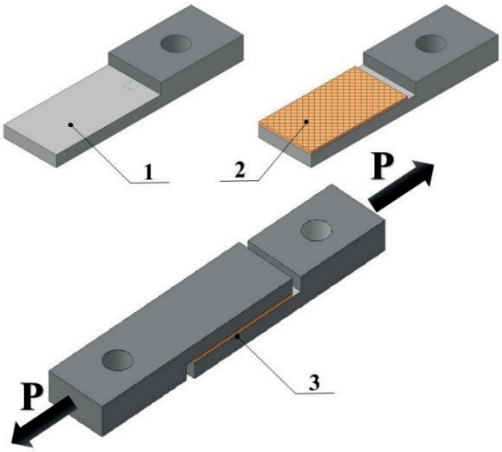


Figure 5. *The scheme of the sample formation for studying the adhesive strength of composites in shearing: 1 - the sample surface after cleaning (with the purpose of removing the oxide film) and degreasing; 2 - the sample surface after applying a uniform adhesive layer; 3 -adhesive samples subjected to a critical loading in the direction parallel to the plane of the contact surface*

the research of CM structure was also performed on XJL-17AT metallographic microscope, which is equipped with 130 UMD (1.3 Mega Pixels) camera. "Image Analyse" software was used for image processing.

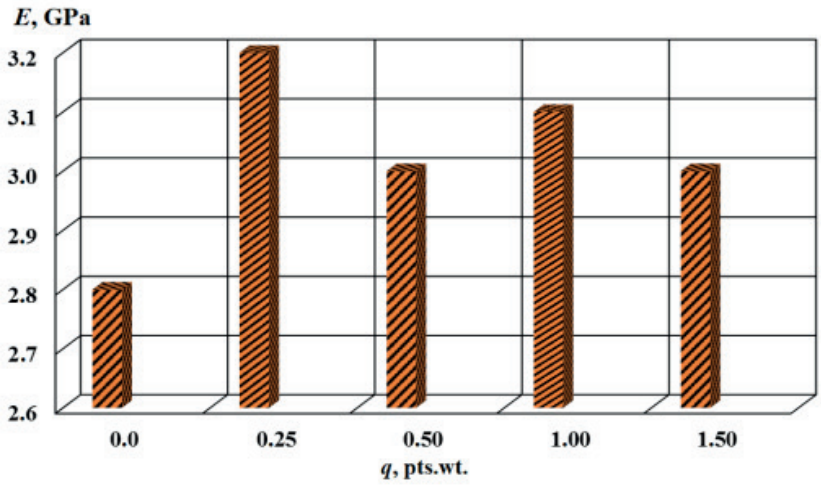
3 Discussion of the experimental results

To analyse the modifier impact on the cohesion properties of the matrix, the indicators of its physical and mechanical characteristics at different additive contents were investigated.

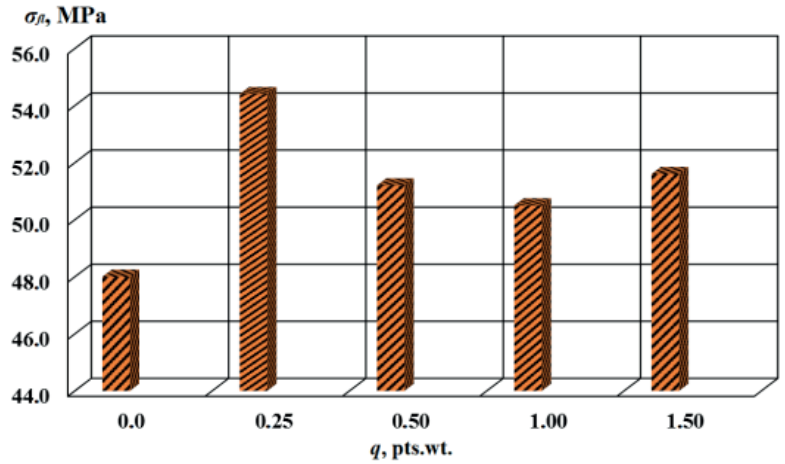
The physical and mechanical properties of the original epoxy matrix, modified by ultrasonic treatment, were previously experimentally established and represented in references [5, 15]. It is proved (Figure 6) that their characteristics are the following: modulus of elasticity in bending is E = 2.8 GPa; breaking stresses in bending is σ_{bn} = 48.0 MPa; impact strength is W = 7.4 kJ/m^2 [5, 15].

It is experimentally established (Figure 6a) that the introduction of the modifier at a low content (q = 0.25 pts. wt.) provides increasing of the CM modulus of elasticity from E = 2.8 GPa (for the original but ultrasonically modified epoxy matrix) to E = 3.2 GPa. These results of the study can be explained as follows [15].

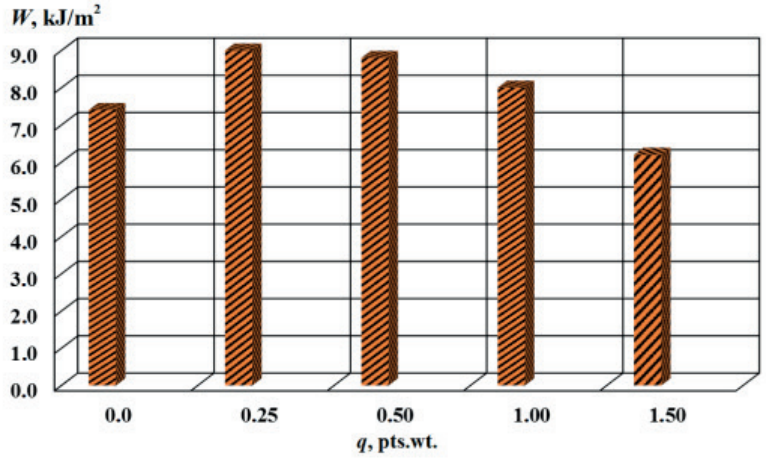
Firstly, it should be noted that the ultrasonic processing (US) of the compound was performed at the preliminary stage of the composition preparations (epoxy oligomer + modifier) after mixing of the ingredients. First of all, it provides uniform mixing of the components and degassing of the compositions. On the other hand, the formation of free radicals [14] was observed as a result of ultrasonic processing (US). In this case, free hydrogen ions and NH-, NH_2- or -CH-groups (in the modifier) and hydrogen ions and OH-groups (in the



a)



b)



c)

Figure 6 *Dependence of physico-mechanical properties and impact strength of epoxy matrix on the content of the modifier 4.4'-methylenebis (2-methoxyaniline): a - modulus of elasticity in bending (E); b - breaking stresses in bending (σ_{bn}); c -impact strength (W, kJ/m²)*

epoxy oligomer) are separated from both the modifier and the epoxy resin. Such ions and radicals are quite active in chemical interaction in crosslinking of epoxy compositions, which provides increasing of the modified matrix crosslinking degree.

Secondly, after ultrasonic processing (US), a significant percentage of macromolecules either of epoxy macromolecules or molecules of the modifier remain in the initial state. However, the presence of methyl CH_3-C, methylene - CH_2- groups and, especially, primary amines

- NH_2 in the structure of the additive provides the formation of additional chemical bonds with hydroxyl and epoxy side groups of the resin macromolecules.

Taking into account everything that has been already mentioned, including additional physical interaction of epoxy resin macromolecules either with each other or with the modifier, the authors considered that such a mechanism of structure formation of modified epoxy compositions is the most apprehended, and therefore it provides the improve of CM cohesive characteristics [18-22].

Increasing of the modifier content does not lead to the increase of the elastic modulus of epoxy matrix, which is confirmed by the study results given in Figure 6a. On the contrary, the introduction of additive in the range of 0.5 to 1.5 pts. wt. into the binder causes a decrease of the elastic modulus in the range of 2.9 to 3.1 pts. wt. in the whole investigated range of concentrations which indicates that the concentration of the modifier 0.25 pts. wt. for this investigated characteristic is critical, and its further increasing in the binder causes the incomplete crosslinking of the matrix during the polymerization. In our opinion, it is caused by the excessive number of molecules of the modifier in the compositions, so such materials are characterized by a high content of sol fraction that provides the decrease of physical and mechanical characteristics of the developed matrices.

The next stage of our research was focused on the study of the breaking stresses in CM bending dependence on the modifier content of MDMA. It was experimentally established (Figure 6b) that the introduction of additive with a low content (0.25 pts. wt.) into the binder provides the increase of the breaking stresses in bending of the modified matrix compared to the original one from σ_{bn} = 48.0 MPa to 54.4 MPa. Further MDMA introduction in the amount of 0.5 to 1.5 pts. wt. causes the deterioration of the composite cohesive properties, since the values of the breaking stresses are in the range of 50.5 to 51.6 MPa. According to the results of the study, the obtained properties are practically similar and are within the limits of the experiment deviation, and therefore further testing to improve the characteristics of the materials by increasing the content of the additive is not advisable. At the same time, it should be noted that the obtained data correlate with a similar dependence of the modulus of elasticity in bending on the modifier content (Figure 4), and the maximum values of E, at the same amount of introduced additive, were similarly revealed. Based on this, we can confirm the critical content of the modifier in the epoxy binder, which is 0.25 pts. wt. by 100 pts. wt. of epoxy oligomer ED-20.

The authors of [4, 12] defined that, from a practical point of view, the resistance of protective coatings to the impact is important during the operation of equipment under the dynamic loads. Based on this, the impact strength of the developed materials, depending on the content of MDMA modifier, was studied. As shown in Figure 6, c the maximum on the curve of dependence "impact strength - modifier content" was observed for the CM that contains MDMA in the amount of 0.25 pts. wt. For such a material, the impact strength increases from W = 7.4 kJ / m^2 to 9.0 kJ / m^2 in comparison with the original matrix. Further increasing of the modifier content from 0.5 pts. wt. to 1.5 pts. wt. causes a monotonic decreasing of the impact of the developed CM. The obtained data are correlated and coordinated well with the investigation results of the elastic modulus dependence and breaking stresses in bending that indicate the reliability of the obtained indicators based on the test results of the complex of physical and mechanical properties of the materials.

In addition, to confirm the abovementioned results of the physical and mechanical CM properties, the analysis of the surface of their fraction after testing on the pendulum dill by optical microscopy method was carried out. As shown in Figure 5a, the fracture surface of the sample based on the original epoxy matrix is heterogeneous. The crack propagation front is displaced during the impact loads that points out the presence of a stress state in the polymerized material.

The analysis of the image of the fracture of CM filled with the modifier in the amount of 0.25 pts. wt. (as shown in the Figure 7b) indicates the following: the trajectory of crack propagation during the impact is in a zigzag form. The formation of a high residual stress material can be established, on the one hand, as well as its increased cohesive properties on the other hand. That is, the sufficient number of physical and, especially, chemical bonds in the material resists the cracks propagation. As a result, the front of their distribution changes in the direction of the least resistance. Hence, it can be stated that the formation of a three-dimensional polymer net in the polymerization process with a high intermolecular distribution by volume implies a high degree of this CM crosslinking.

As shown in Figures 7c and 7d, the character of the fractures of the samples with CM filled with a modifier in the amount of 0.5 pts. wt. and 1.0 pts. wt. is approximately the same. The trajectory of the crack propagation is straight, but the area of CM destruction is slightly offset from the point of the impact at the final stage. That confirms the presence of the net with a sufficiently high degree of crosslinking and the density of physical and chemical bonds in CM, although it is not in the same amount as in the material of the modifier content of 0.25 pts. wt. It can be confirmed that such CMs have slightly lower cohesion strength. The obtained data are correlated well with the testing results of physical and mechanical properties of the materials. It is proved that the matrix with the modifier 0.25 pts. wt. is characterised by maximum values of the elastic modulus, breaking stresses in bending and impact strength.

Macroanalysis of the samples containing the modifier at the amount of 1.5 pts. wt. allows to state the following: the trajectory of crack propagation that

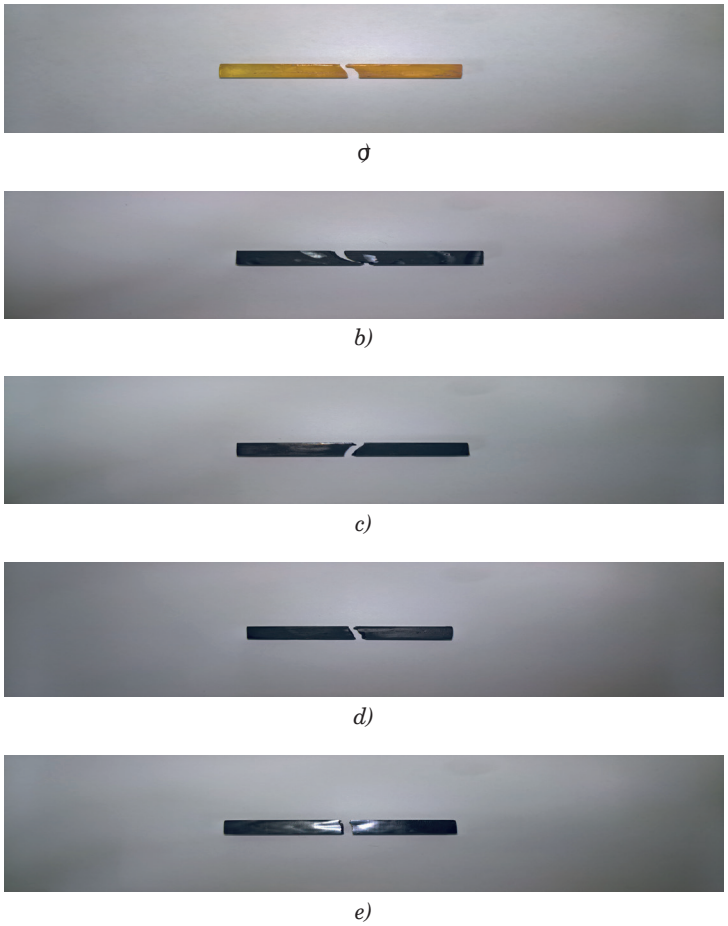


***Figure** 7 Micrographs of fracture of the original and modified 4.4'-methylene-bis (2-methoxyaniline) epoxy matrices (Range 1:2): a) the original epoxy matrix (control sample); b) q = 0.25 pts. wt. modifier; c) q = 0.50 pts. wt. modifier; d) q = 1.0 pts. wt. modifier; e) q = 1.50 pts. wt. modifier*

was perpendicular to the longitudinal axis of the sample (Figure 7e) was observed. We can state that there is a small intermolecular distribution of physical and chemical bonds in the volume of modified matrix on the one hand, and there is a significant content of sol fraction in the CM due to the excessive amount of the additive on the other hand. It is obvious that a net structure with an even distribution of the chemical bonds but with a low density in volume of the material is formed in these CMs that does not allow to provide sufficient resistance to fracture under shock loads.

Thus, it has been established that for the formation of materials with improved cohesion properties, it is necessary to use a binder of the following content: epoxy oligomer ED-20 (100 pts. wt.), hardener polyethylene polyamine PEPA (10 pts. wt.), 4.4'-methylenebis (2-methoxyaniline) modifier (0.25 pts. wt.). Formation of such a material provides a significant improvement of physical and mechanical properties in comparison to the original ultrasonically modified epoxy matrix.

Furthermore, the adhesive properties of the developed materials were investigated in this study. As shown in Figure 8, the strength of the adhesive joints is 24.8 MPa (the matrix is peeled), and it is 8.5 MPa (the matrix is sheared). Introduction of additives into the epoxy resin increases the strength of the adhesive joints of the samples (Figure 8). That is, the introduction of additives into the epoxy resin at a concentration of 0.1 to 0.2 pts. wt. provides an improvement in the strength of adhesive joints at the separation of CM from 24 MPa to 26.8 to 31.4 MPa. The subsequent increase in the concentration of the additive (up to 0.4 pts. wt.) ensures the deterioration of the strength of the adhesive joints of CM to 28.9 MPa. Further increasing in the amount of additive active to interphase interaction from 0.7 wt. h. up to 2 wt. h. causes decreasing in the adhesion of the protective coatings to the metal substrate. The value of the strength of the adhesive joints materials was observed to be 26.5 to 28.5 MPa.

Hence, it was pointed out that the maximum on the curve of dependence of adhesion on the concentration of the modifier (28.7 to 31.4 MPa) is in the range of additive concentrations of 0.2 to 0.6 wt. (Figure 8). At this concentration of additives, the physico-chemical processes of interphase interaction are improved. As a result, additional bonds are formed in the structural network of the polymer.

In addition, the effect of the modifier on the shear

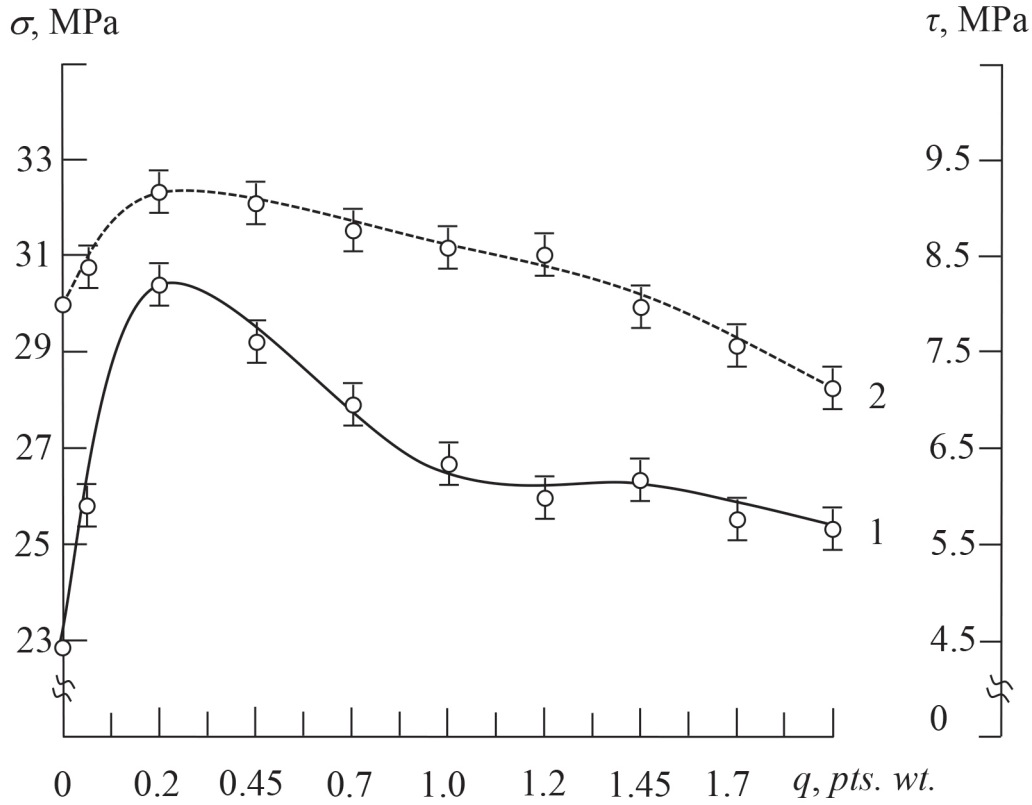


Figure 8 *The change of the strength of the CM adhesive joints depending on the additive concentration: 1 - peel strength of the adhesive joints (σ); 2 - shear strength of adhesive joints (τ)*

strength of adhesive joints was analyzed by authors.

It was established (Figure 8) that the presence of the additive concentration of 0.1 to 0.3 wt. provides increasing in the strength of adhesive joints from 8 MPa to 9 to 9.5 MPa. It shoud be noted that increasing of the additive concentration significantly worsens the strength of the adhesive joints at the materials shearing. Adhesion decreases from 9 MPa to 8 MPa (the amount of the additive is 2 pts. wt.). So, it must be admited that the highest strength of adhesive joints (9.2 to 9.5 MPa) was obtained for materials with an additive amount of 0.2 to 0.6 wt.

4 Conclusions

Based on the experimental analyses presented in this work, the following conclusions are drawn:

1. For formation of the materials with improved cohesion properties, it is necessary to use the composition with the following content: epoxy oligomer ED-20 (100 pts. wt.), PEPA hardener polyethylene polyamine (10 pts. wt.), and 4.4'-methylenebis (2-methoxyaniline) modifier (0.25 pts. wt.). Formation of such a material, in comparison to the original ultrasonically modified epoxy matrix, provides the increase of the following physical and mechanical properties:
   - ❑ modulus of elasticity in bending in the range of 2.8 GPa to 3.2 GPa;
   - ❑ breaking stresses in bending in the range of 48.0 MPa to 54.4 MPa;
   - ❑ impact strength in the range of 7.4 kJ/m^2 to 9.0 kJ/m^2.
2. The fracture surface of the original matrix is heterogeneous that is proved by optical microscopy technique. The crack propagation front is displaced during the shock loads that indicates the presence of a stress state in the polymerized material. After analysing the fracture image of the composite, filled with the modifier in the amount of 0.25 pts. wt., we point out that the crack propagation trajectory during the impact is of the zigzag form. We can confirm the formation of a material with high residual stresses, on the one hand, as well as increased cohesive properties on the other hand. That is, a sufficient number of physical and, especially, chemical bonds in the material resist the spread of cracks. As for the samples from the composites filled with the modifier in the amount of 0.5 pts. wt. and 1.0 pts. wt., it should be noted that the crack propagation trajectory is straight, but the area of materials destruction at the final stage is slightly shifted from the point of impact. That confirms the presence of net with a sufficiently high degree of crosslinking and the density of

physicochemical bonds in composites, although it is not in the same amount in comparison to the material of modifier content of 0.25 pts. wt.

3. In addition, the adhesive joints strength of the developed composites dependence on the amount of the additive has been investigated in the work. The required content of the modifier, the introduction of which provides the maximum strength iof the adhesive joints among all the studied materials, has been revealed. It has been substantiated that the additive concentration (0.2 to 0.6 pts. wt.) must be introduced into epoxy resin for formation of the materials with maximum adhesion. These materials have the following properties: peel strength of the adhesive joints 28 to 32 MPa, and shear strength of the adhesive joints - 9.1 to 9.7 MPa.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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