




REGULAR ARTICLE

The Method of Increasing the Mechanical Characteristics of Sea Transport Vehicles due to Environmentally Friendly Nanomodification of Epoxy Composites

A.V. Buketov<sup>1\*</sup> , K. Dyadyura<sup>2</sup>, Yu.M. Shulga<sup>3</sup>, V.V. Sotsenko<sup>1</sup>, L. Hrebenyk<sup>4</sup>,  
O.A. Pastukh<sup>5</sup>, D.V. Zhytnyk<sup>1</sup>

<sup>1</sup> Kherson State Maritime Academy, 73000 Kherson, Ukraine

<sup>2</sup> Odesa Polytechnic National University, 65044 Odesa, Ukraine

<sup>3</sup> Danube Institute of the National University "Odesa Maritime Academy", 68607 Izmail, Ukraine

<sup>4</sup> Sumy State University, Medical Institute, 40022 Sumy, Ukraine

<sup>5</sup> Ternopil Ivan Puluj National Technical University, 46001 Ternopil, Ukraine

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Protective polymer composite coatings are widely used in marine transport owing to their improved adhesion and cohesion properties. Modifiers are introduced to enhance the performance characteristics of polymer coatings based on epoxy binders. This study investigates the impact of the eco-friendly nano modifying additive *d*-ascorbic acid on the structure and properties of an epoxy matrix. Based on the test results, a modified epoxy matrix with improved adhesion and physicomechanical properties was developed. The nature of the chemical bonds in the structure of the synthesized modifier and its molar mass were investigated by gas chromatography. A significant number of hydroxyl groups in the structure of the *d*-ascorbic acid molecule is one of the main criteria that determine the activity of this nano modifying additive in terms of homogeneous interactions during the cross-linking of the epoxy binder-based compound. It has been established that modifying epoxy compositions with *d*-ascorbic acid in the amount of 0.75 to 1 mass % per 100 mass % of ED-20 epoxy resin ensures an increase in adhesion strength while reducing residual stresses. The positive impact of the modifier on improving the adhesive properties of the modified epoxy matrix to the metal substrate is due to the chemical structure of the nano modifying additive, which determines the intermolecular interaction in the homogeneous polymer system. It has been proven that the epoxy composite's cohesive property indicators (elastic modulus, destructive stresses, impact toughness) significantly increase at the optimal *d*-ascorbic acid content. This is due to the additional formation of physical and chemical bonds in the structural network of the compound during its cross-linking in the presence of the modifying additive, which affects the indicators of the material's cohesive strength and impact resistance.

**Keywords:** ED-20 Epoxy resin, Eco-friendly nano modifying additives, D-ascorbic acid, PEPA hardener, Epoxy composites, Epoxy marine coatings, Cohesive properties, Adhesive strength

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1. INTRODUCTION

The reliability of marine and river transport equipment is primarily determined by the characteristics of structural materials, such as corrosion resistance and wear resistance, while the physical and mechanical properties of products rely on their mechanical strength indicators [1-4]. Simultaneously, the environmental efficiency of marine and river transport receives considerable attention in a global strategy to reduce the anthropogenic impact on the environment. Consequently, high demands are placed on the structure and properties of materials used in modernizing and repairing machinery and mechanisms used in marine and river transport.

In this context, the effectiveness of polymer composite materials (CM), which can be used as products or protective coatings, is particularly noteworthy. It is well-known [5-8] that protective polymer composite coatings are widely used across various industrial sectors because of their enhanced adhesive, cohesive, and

thermophysical properties. These properties are primarily influenced by the characteristics of polymer matrices, which are often formed using epoxy oligomers to protect transport assets. In addition, catalysts, additional layers, plasticizers and modifiers, including nanomodifying additives, are used to improve the operational characteristics of protective materials [9-17] in the form of polymer coatings based on epoxy binders, as well as multi-layer films.

Incorporating such additives in small quantities activates the course of physicochemical interactions, thereby increasing the gel fraction in CM and consequently improving the durability of new materials. In this regard, it was expedient to enhance the properties of the epoxy matrix by incorporating the chemically active and environmentally friendly nano modifying additive *d*-ascorbic acid (DAA).

The positive impact of chemically active nano modifying additives on epoxy matrix properties has been

\* Correspondence e-mail: [tt.scaet@gmail.com](mailto:tt.scaet@gmail.com)



demonstrated by researchers [18-22]. Specifically, it has been found that modifying the epoxy binder with additives such as 4,4-sulfonylbis, 4,4-sulfonylbis (4,1-phenylene) bis (N,N-diethylthiocarbamate), 3,31-(1,4-phenylene) bis (2-chloropropionitrile), 2-methyl-2-thiocyanate-3-(4-thiocyanate phenyl) propionamide, phthalimide, and others significantly enhances the adhesive, physicochemical, and thermophysical properties of epoxy composites, depending on the chemical nature of the activator.

It should be noted that the introduction of nano modifying additives in small quantities (0.1...3 mass % per 100 mass % of epoxy binder) activates matrix structuring processes, leading to an increase in the gel fraction by increasing the material density through the formation of additional chemical and physical bonds between the macromolecules of the epoxy oligomer and the additive per unit volume of the compound.

The study of DAA as a modifier, even in small quantities, has been of significant interest from both scientific and practical viewpoints, particularly concerning its impact on the structure and properties of epoxy matrices. This nano modifying additive contains hydroxyl and carbonyl groups that interact during curing with nitrogen-containing groups of the hardener, forming additional chemical bonds with both the primary amine-epoxy adduct (PEPA) and similar side groups in the ED-20 epoxy oligomer's main chain. As noted previously, this interaction can effectively increase matrix cross-linking, thereby enhancing its adhesive and cohesive properties.

At the same time, using d-ascorbic acid allows for environmentally safe nanomodification of epoxy polymers. This modifier is one of the stereoisomers of ascorbic acid, a natural, non-toxic compound. The *D*-stereoisomer of ascorbic acid does not occur in nature but has similar physicochemical properties. Therefore, the use of synthesized DAA as a nano modifying additive should be considered an environmentally safe approach to forming epoxy polymers, which will be in constant contact with the environment when used as coatings for marine transport.

## 2. MATERIALS AND METHODS

Epoxy resin grade ED-20 (ISO 18280:2010) was used to form the polymer matrix, a widely adopted choice in global applications. The epoxy resin has a molecular weight of 390...430 with an epoxy group content of 20.0...22.5 %, a hydroxyl group content of 1.25%, and an average functionality of 2.0 based on the epoxy groups.

This indicates the enhanced activity of the side groups and segments in the main chain of epoxy resin macromolecules for homogeneous and heterogeneous interphase interactions with nano modifying additives or plasticizers in compositions and with active centers on the surface of dispersed or fibrous fillers.

Additionally, the viscosities of the epoxy resin ranged from 13 to 20 Pa s, and its density was 1.16 g/cm<sup>3</sup>. It should be noted that epoxy resins are reactive plastics that cure even at room temperature [17]. Considering this and the technology for forming composites and protective coatings under industrial conditions, it was deemed appropriate to use polyethylene polyamine (PEPA, TU 6-05-241-202-78)

as the hardener for the epoxy binder. PEPA has a molecular weight of 230...250, a hardener viscosity of 0.9 Pa s, and a density of 1.05 g/cm<sup>3</sup>. The general chemical formula of PEPA is represented as [-CH<sub>2</sub>-CH<sub>2</sub>-NH-]<sub>n</sub>.

To enhance the properties of the polymer matrix, a nano modifying additive in the form of d-ascorbic acid was added to the epoxy binder at a content of 0.1-2.0 mass % per 100 mass % of epoxy resin ED-20. The molecular formula of the modifier is C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>. The molar mass of d-ascorbic acid is 176.032088 g/mol. It has a density of 1.69 g/cm<sup>3</sup>. Its thermal properties include a melting point of 190 °C and boiling point of 553 °C. *D*-Ascorbic acid dissolves in water and breaks down upon prolonged boiling. It actively participates in oxidation-reduction reactions by transferring hydrogen protons. It exhibits antioxidant properties, ensuring stability in homogeneous systems. Additionally, it influences iron metabolism. Under conditions of physicochemical interaction with active sites on the surface of additives, trivalent iron can be reduced to its divalent state.

### Technology of Forming Polymer Composites.

The technology used to fabricate polymer composites is described below. Before composite formation from the independent ingredients, preparatory work is necessary because the gelation period of the resulting mixtures after component alignment is 40...60 min. Components are manually mixed for 4...6 min using a drill with a special mixer at a rotor rotation speed of  $n = 600...800$  rpm. Additionally, in certain cases, if possible, hydrodynamic mixing of ingredients is conducted at a temperature of 25...30 °C for  $\tau = 10 \pm 0.1$  min. After cooling the mixture to room temperature ( $\tau = 60 \pm 5$  min), the hardener is added, and the compositions are stirred for a period of  $\tau = 5 \pm 0.1$  min.

The mold should be filled slowly and continuously to allow for the removal of air residues from the composites and to avoid "capturing" new air inclusions. The pouring should continue uninterrupted until the mold is completely filled, after which the material is cured at room temperature ( $T = 295 \pm 2$  K) for  $\tau = 12.0 \pm 0.1$  h. The next step involves heating the composition to a temperature of  $T = 393 \pm 2$  K, holding it at this temperature for a period of  $\tau = 2.0 \pm 0.05$  hours, and then cooling it to a temperature of  $T = 293 \pm 2$  K.

### Research Methods for Epoxy Composites

During the development of composites with enhanced characteristics, standard methods were employed to investigate adhesive and physicochemical properties (destructive stresses and modulus of elasticity in bending, impact toughness), residual stresses in materials, and their structures [19-22].

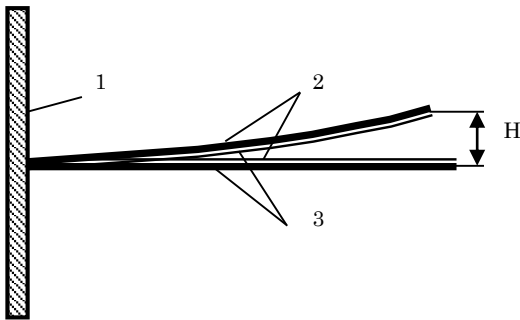
In studying the adhesive strength of polymer composite materials (CM), destructive stresses were determined during uniform separation of samples in accordance with ISO 8510-2:1990. The diameter of the working part of the steel samples was  $d = 25 \pm 0.2$  mm.

To analyze the indicators of residual stresses that arise during the curing of polymer composites in the presence of a metal base, a methodology was used to analyze the behavior of a cantilever under load [19].

The thickness of the adhesive was maintained within  $\delta = 0.1...0.2$  mm. The parameters of the base were: total length  $l = 100$  mm; working length  $l_0 = 80$  mm; thickness  $\delta = 0.18$  mm.

It should be noted that during the curing process of the polymer coating, adhesive interaction occurs at the phase boundary "polymer-base." As a result, deviations of the cantilever from its initial position were observed. This characteristic, along with the parameters of the substrate and coating, is important for calculating the magnitude of residual stresses in cured adhesives after their polymerization. The experimental setup is shown in Figure 1 [19].

The investigated stresses were destructive stresses, the modulus of elasticity under bending, and the impact toughness of materials.



**Fig. 1** – Scheme of analysis of residual stresses in adhesives polymerized on the selected substrate: 1 – pillar; 2 – adhesive; 3 – lining

Destructive stress indicators were determined following ISO 178:2001(E) using the following formula

$$\sigma_p = \frac{3 \cdot F_{max} \cdot L}{2 \cdot b \cdot h^2}, \quad (1)$$

where  $F_{max}$  – maximum load at failure of the specimen, measured in newtons (N);  $L$  – distance between pillars of the specimen, measured in millimeters (mm);  $b$  – width of the specimen, measured in millimeters (mm);  $h$  – thickness of the specimen, measured in millimeters (mm).

The modulus of elasticity was determined using a four-point bending scheme ISO 178:2001(E) according to the following equation

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

where  $L_v$  – distance between s pillars of the specimen, measured in millimeters (mm);  $\Delta F$  – load applied, measured in newtons (N);  $b$  – width of the specimen, measured in millimeters (mm);  $h$  – thickness of the specimen, measured in millimeters (mm);  $\Delta z$  – deflection of the specimen, measured in millimeters (mm).

The impact toughness CM was investigated using the Charpy method without a notch (ISO 179-1) on the MK-30 pendulum hammer at a temperature of  $T = 298 \pm 2$  K and relative humidity of  $\varphi = 50 \pm 5\%$ . Sample dimensions were  $(65 \times 12 \times 12) \pm 0.5$  mm. The distance between the pillars was  $40 \pm 0.5$  mm. The impact toughness CM was determined using the following formula:

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

where  $A_n$  – energy absorbed by the specimens during fracture without notches, measured in joules;  $b$  – width of the specimen, measured in millimeters (mm);  $s$  – thickness of the specimen, measured in millimeters (mm).

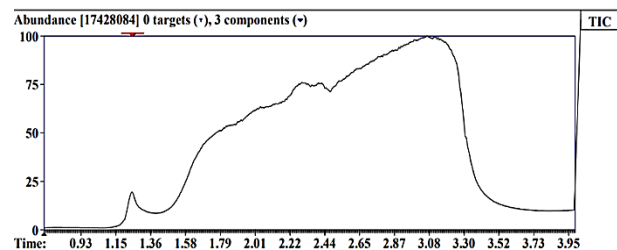
Additionally, the fracture surfaces of the developed materials were analyzed by optical microscopy. For this purpose, a metallographic microscope model XJL-17AT with a 130 UMD camera (1.3 Mega Pixels) was used. The images were processed using the "Image Analyse" software.

### 3. DISCUSSION OF RESEARCH RESULTS

Prior to this, the nature of the chemical bonds in the structure of the synthesized nano modifying additive DAA and its molecular mass was investigated. Gas chromatography (GC) with mass-selective detection was employed for this purpose. According to our methodology, a 0.01-g sample of the material was dissolved in methanol. The experiments were conducted using gas chromatography-mass spectrometry (GC-MS; Agilent Technologies 6890 N instrument) with an HP 19091S-433 column (HP-5MS). The capillary column was 30 m in diameter and 0.25 mm thick, and its phase thickness of 0.25  $\mu$ m. The experiments were conducted using helium as the carrier gas at a constant flow rate of 1.5 ml/min. Additionally, an autoinjector 7683, Split 20:1, and a mass-selective detector with an interface temperature of 280  $^{\circ}$ C were used during the experiment.

The chromatographic analysis of the samples was conducted at an evaporator temperature of 255  $^{\circ}$ C under the following heating protocol: initial and final experiment temperatures were  $T_{start} = 100$   $^{\circ}$ C and  $T_{end} = 285$   $^{\circ}$ C, respectively. The samples were held for 2 min at a rate of 15  $^{\circ}$ C/min. Electron impact ionization at 70 eV was applied at an ion source temperature of 230  $^{\circ}$ C and a quadrupole temperature of 150  $^{\circ}$ C.

At the initial stage, testing was conducted by chromatographing samples, resulting in the establishment of the dependency of signal intensity ( $I$ , %) on the retention time ( $t$ , minutes) of nano modifying additive. The results of this study are presented in Fig. 2. As a result, the first peak on the curve of "signal intensity-retention time of the sample" was identified, allowing for the evaluation of the structure and characteristics of the investigated substance. Experimentally, the maximum signal intensity parameter was determined to fall within the retention time range of  $t = 1.14-1.31$  min (Fig. 2).



**Fig. 2** – Dependency of signal intensity ( $I$ , %) on exposure time ( $t$ , min) of the nano modifying additive (DAA)

In the next stage, based on the experimentally determined exposure range (within the time interval  $t = 1.14...1.31$  min), additional investigations were conducted regarding the dependency of signal intensity ( $I$ , %) on the

duration ( $t$ , minutes) of the sample exposure. The experimental exposure time of the signal was established as  $t = 1.246$  minutes, according to which the characteristics of the synthesized modifier were further investigated (see Fig. 3).

The dependence of the intensity of characteristic signals on the ratio of the pre-specified mass of the investigated sample of the modifier to the charge size at the signal exposure duration ( $t = 1.246$  minutes) is presented in Fig. 4. Relative intensity indicators of characteristic signals (Fig. 4, a) have been determined by us, as well as similar intensity parameters in expanded coordinates, aiming to provide additional confirmation of the reliability of the obtained results of the conducted experiment.

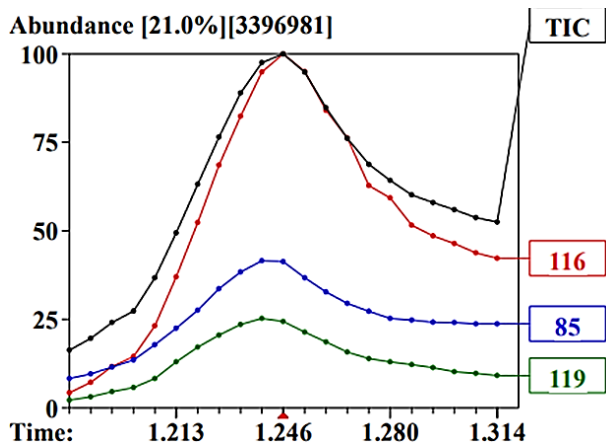
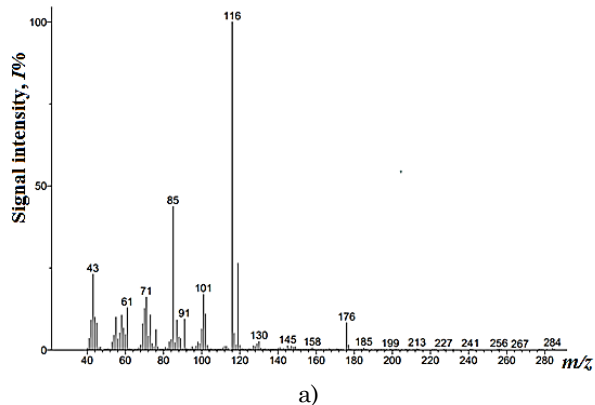


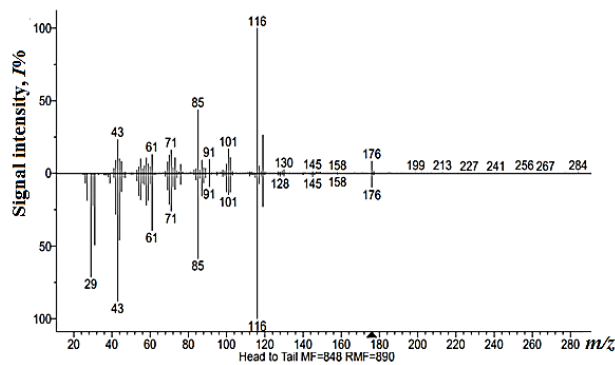
Fig. 3 – Dependency of signal intensity ( $I$ , %) on exposure time ( $t$ , min) of the sample (within the time interval  $t = 1.14...1.31$  min)

Analytical calculations of the dependency of signal intensity ( $I$ , %) on the  $m/z$  ratio, obtained based on experimental curves, are presented in Table 1. As a result of the analysis of the obtained data (Table 1), the highest peaks of the characteristic signal intensities ( $I$ , %) and their corresponding  $m/z$  ratio values were identified (Table 2).

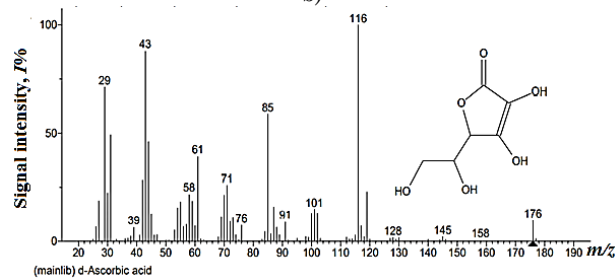
The obtained experimental results were further correlated with library data, resulting in the determination of the structural formula (Fig. 4, c) and the molecular mass of the synthesized modifier. Thus, it was established that the molecular formula of the modifier is  $C_6H_8O_6$ . Additionally, calculations determined the molar mass of  $d$ -ascorbic acid, which is 176.032088.



a)



b)



c)

Fig. 4 – Dependence of the intensity of characteristic signals on  $m/z$  at a signal duration of  $t = 1.246$  min;  $m$  – mass of the substance;  $z$  – charge: a) relative indicators of the intensity of characteristic signals; b) relative indicators of intensity in expanded coordinates; c) chemical formula of the modifier molecule, determined according to the signal intensity indicators and library data

Table 1 – Dependence of the signal intensity ( $I$ , %) on the value of  $m/z$

$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %
25	0.8	26	6.7	27	18.6	29	71.3	30	22.3
31	49.1	33	0.8	36	1.2	37	1.4	38	2.3
39	6.7	41	2.8	42	28.2	43	87.9	44	45.9
45	12.5	46	2.8	47	3.0	50	0.5	51	0.5
53	5.2	54	15.3	55	18.1	56	6.8	57	7.8
58	21.8	59	18.5	60	7.2	61	39.2	62	1.1
63	0.5	68	2.0	69	11.3	70	21.3	71	25.9
72	9.2	73	11.0	74	3.0	75	0.6	76	7.5
83	0.9	84	4.5	85	58.7	86	3.4	87	15.6
88	6.5	89	3.0	91	9.1	92	0.5	95	1.3
98	2.1	99	1.8	100	12.7	101	14.6	102	12.8
103	1.3	112	1.8	113	1.0	114	1.1	115	2.8
116	99.9	117	7.2	118	2.1	119	22.8	120	1.0
127	1.3	128	1.9	129	0.9	130	1.9	140	0.8
144	0.6	145	2.2	146	0.8	158	0.6	176	9.6

Based on the conducted tests, the following conclusion can be drawn: The structure of the  $d$ -ascorbic acid modifier molecule contains a significant number of hydroxyl groups. This is one of the main criteria that determine the activity of the additive in terms of homogeneous interactions during the crosslinking of the epoxy-based compound. Chemical bonds were expected to form with the active groups of the PEPA hardener and similar side hydroxyl groups of the ED-20 epoxy oligomer.

Additionally, it should be noted that the structure of the modifier contains carbonyl  $C=O$  groups, which can also participate in the structuring of materials. This can increase the degree of gel fraction and, consequently, the cohesive

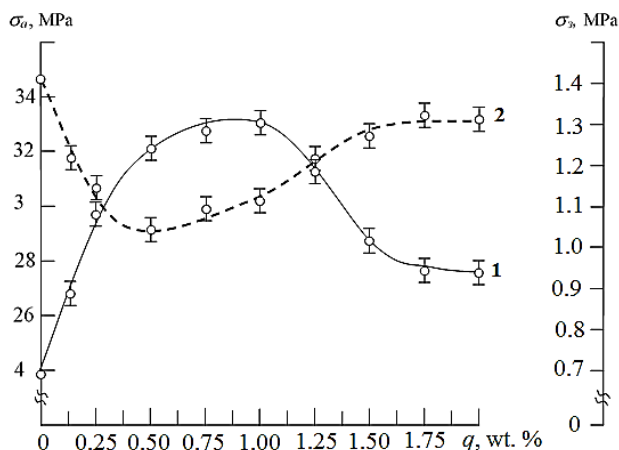


properties of the nanomodified matrix. To confirm these assumptions, studies were conducted on the adhesive and physicomachanical properties of the original and modified matrix with varying contents of d-ascorbic acid in the binder, the results of which are presented below.

**Table 2** – The highest peaks of signal intensity ( $I$ , %) and  $m/z$  charge values for them

$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$	$I$ , %	$m/z$
22.8	119	25.9	71	28.2	42	39.2	61	45.9	44
49.1	31	58.7	85	71.3	29	87.9	43	99.9	116

Initially, the adhesive and cohesive properties of the original epoxy matrix (control sample) were investigated. It was observed (Fig. 5) that the adhesive strength of the original epoxy matrix, formed according to the polymerization scheme described in the "Research Methodology" section, is  $\sigma_a = 24.8$  MPa. Introducing the nano modifying additive DAA modifier into the epoxide oligomer at low concentrations ensures an increase in the adhesive characteristics of the developed composites. In particular, it can be stated that modifying epoxy composites by adding 0.25 wt.% DAA ensures an increase in the adhesive strength from 24.8 MPa to 29.5-32.1 MPa (Fig. 5, dependence 1). The maximum adhesion values in the entire range of the studied composites were noted for modified materials containing DAA in 0.75...1.00 wt.%.



**Fig. 5** – Dynamics of adhesive strength to a steel substrate (steel St 3) and residual stresses in the composite material (CM) depending on the concentration of the nano modifying additive DAA: 1 – adhesive strength ( $\sigma_a$ ); 2 – residual stresses ( $\sigma_r$ )

Such developed materials are characterized by an adhesive strength of 32.6...33.1 MPa. Further increasing the amount of modifier in homogeneous systems is not advisable in terms of improving material adhesion because the strength indicators of adhesive bonding to the metal substrate decrease. In particular, it was found that filling systems with the addition of DAA in the amount of 1.25...2.00 wt.% results in materials for the matrix with an adhesive strength of 27.4...31.7 MPa. The obtained adhesion values are somewhat lower than the quantitative adhesion values characteristic of composites with the optimal additive content.

Thus, it has been experimentally proven that the modifier positively affects the improvement of the adhesive

properties of the epoxy matrix. The obtained research results can be explained as follows.

The authors [18, 19] reported that the intermolecular interaction in a homogeneous polymer system depends on the chemical structure of the modifier. The possibility of forming van der Waals, hydrogen, or acceptor bonds between the macromolecules of the modifier and the main oligomer or polymer is of significant importance. These bonds significantly influence the main properties of polymer compounds, such as adhesive and mechanical strength, modulus of elasticity, intermolecular distribution, and molecular packing density.

In the case of filling the epoxy oligomer with the nano modifying additive DAA, it can be stated that the presence of hydroxyl and carbonyl groups in the additive allows for the catalysis or inhibition of polymerization reactions. The IR spectroscopy method was used to study the interaction mechanism of the ED-20 epoxy resin with DAA. It was experimentally established that the IR spectra of the original epoxy composite based on ED-20 showed an absorption band at a wavenumber of 821...828  $\text{cm}^{-1}$ , indicating the  $\delta$ -deformation vibrations of C-H bonds in the aromatic ring. In composites with the modifier, the absolute value of this band decreased. This effect was particularly noticeable in the IR spectra of composites containing the additive at amounts of 0.75...1.25 wt.%. This indicates additional interactions between these groups in the presence of the nano modifying additive, leading to the formation of new bonds.

In addition, the vibration band at 922  $\text{cm}^{-1}$ , which illustrates the presence of epoxy groups, was absent in the composites with the optimal content of DAA. This indicates the opening of epoxy rings during crosslinking with polyethylene polyamine in the presence of the modifying additive.

In the IR spectrum of the modifier, absorption bands were observed at 1716...1732  $\text{cm}^{-1}$ , which correspond to the stretching vibrations of the C=O bond in aldehydes, ketones, and complex ethers. In the compounds, these bands shifted toward lower wavenumbers, along with a decrease in peak intensity. This is also evidence of the interaction of the carbonyl group with the hardener and possibly with active radicals of the epoxy oligomer. The results indicate that the additive activates crosslinking in epoxy polymers, enhancing the degree of structural formation in epoxy composites.

It is crucial to note separately the presence of hydroxyl groups both in the epoxy oligomer (3441  $\text{cm}^{-1}$  – stretching vibrations of OH groups) and in the modifier (3206  $\text{cm}^{-1}$  – stretching vibrations of OH groups). In materials with the nano modifying additive, significant broadening of the absorption band and a reduction in peak height were observed compared with the original epoxy matrix. This clearly indicates the overlap of two or more peaks in the spectra of the modified composites. Moreover, the decreased peak intensity suggests that both the hydroxyl groups of the epoxy oligomer and the nano modifying additive are involved in the crosslinking process.

It should also be noted that in the modified composites, new absorption bands appeared in the wavenumber range of 2965...2976  $\text{cm}^{-1}$  compared to the epoxy matrix. These bands indicate stretching vibrations of C-H bonds in epoxy and methyl groups. Therefore, new peaks appear on the IR spectra of the composites with the modifier. This directly

demonstrates the formation of additional chemical bonds in the developed materials, indicating an increase in their cross-linking degree.

Based on the above, it can be concluded that the influence of the nano modifying additive DAA on the structure and properties of the crosslinked polymer in the composite manifests itself in a kinetic aspect, as the modifier increases the rate and degree of crosslinking reactions. Additionally, compared with the original epoxy matrix, the formed polymer is characterized by a narrower intermolecular distribution and thus limited molecular mobility, which results from the action of energetic and entropic factors. It can be asserted that such activation of the physico-chemical processes during composite crosslinking in the presence of the nano modifying additive significantly enhances the properties of the materials, including their adhesive strength.

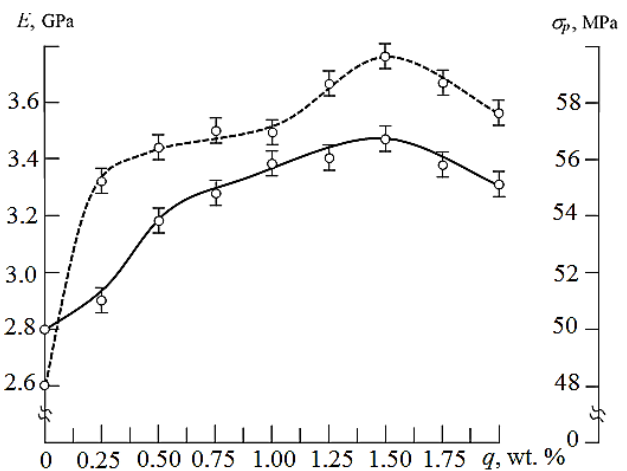
To confirm the above-mentioned mechanism of interaction between DAA and the ED-20 epoxy oligomer in the formation of compounds, an analysis of residual stress dynamics in the composites was conducted depending on the additive content. The magnitude of residual stress was determined for the original epoxy matrix as  $\sigma_z = 1.4$  MPa (Fig. 5, curve 2). Upon introduction of the nano modifying additive in amounts ranging from 0.25 % to 0.50 % by weight, materials with residual stress values within 1.0-1.2 MPa were formed. It is important to note that this reduction in residual stress values indirectly indicates a deterioration in the cohesive strength of the newly formed systems. This could be explained by the decrease in gel fraction content in the composites due to an ineffective interaction between the additive and the hardener. It is evident that, in this case, the modifier does not fully act as a catalyst for the molecular interaction.

Conversely, when the additive is introduced at concentrations ranging from 0.75 % to 2.00 % by weight, materials with elevated residual stress levels are formed compared to those previously mentioned. For such composites, residual stresses fall within the range of 1.1 to 1.3 MPa. This indicates the formation of a structural network within the compound, characterized by a substantial number of physical and chemical bonds per unit volume in the material. This further underscores the activation of interaction within the homogeneous system in the presence of the nano modifying additive.

Therefore, based on the above-mentioned research results, it can be stated the following. To achieve an epoxy matrix with enhanced adhesive characteristics to a metal substrate, a d-ascorbic acid modifier should be incorporated into the epoxy oligomer (100 % by weight) at concentrations of 0.75 % to 1.0 % by weight. In this case, the modified epoxy matrix exhibits the following properties: adhesive strength upon detachment 32.6-33.1 MPa, residual stress 1.1 MPa.

In the next stage, the physical and mechanical properties of the modified materials were investigated. It was shown that the elastic modulus of the original epoxy oligomer matrix was  $E = 2.8$  GPa, and the flexural strength at rupture was  $\sigma_p = 48.0$  MPa (Figure 6). According to the results of the conducted tests, introducing a modifier into the epoxy oligomer enhanced the mechanical properties of the epoxy resin. Specifically, incorporating d-ascorbic acid into the epoxy oligomer ED-20 significantly improved both the elastic modulus

and the flexural strength at rupture. It is important to note that such improvement dynamics in material properties are observed only under conditions in which compounds are modified up to the optimal concentration of the modifier, which is 1.5 wt.% based on 100 wt.% of the investigated epoxy oligomer (Figure 6). These materials exhibit enhanced physical and mechanical properties. Experimentally, it was established that the parameters for these composites increased from 2.8 to 3.5 GPa (elastic modulus) and from 48.0 to 59.4 MPa (flexural strength at rupture) compared with the epoxy matrix. Furthermore, increasing the additive concentration leads to further deterioration of the mechanical properties of the materials. Specifically, compared to composites with optimal additive content, the properties decrease to 3.3 GPa (elastic modulus) and to 57.3 MPa (flexural strength at rupture).



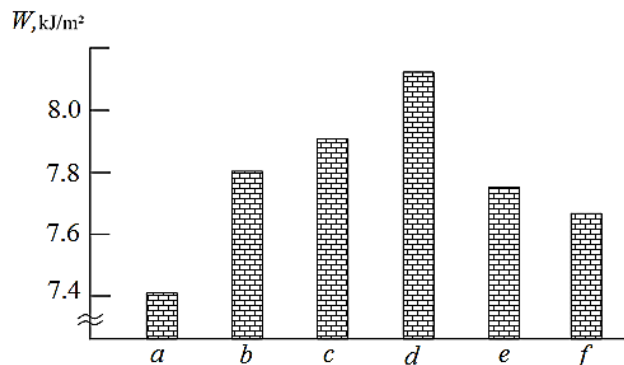
**Fig. 6** – Dynamics of the physico-mechanical properties of epoxy matrix as a function of DAA concentration: 1. Young's modulus ( $E$ ); 2. Flexural strength ( $\sigma_p$ )

Note that one of the objectives of this work was to develop an epoxy matrix to form polymer composites designed to withstand impact loads. Therefore, it is essential to conduct tests to determine the impact resistance of the modified materials.

According to the results of the conducted studies, it was found that the impact strength of the original epoxy matrix was found to be  $W = 7.4$  kJ/m<sup>2</sup> (Fig. 7). Modification of the compound increased the impact strength of the composites due to the improvement of their cohesive strength. It has been proven that adding DAA as a modifier at an optimal content (1.5 wt. %) results in a material whose impact strength increases from 7.4 to 8.6 kJ/m<sup>2</sup> compared to the original epoxy matrix. As described above, this is due to the additional formation of physical and chemical bonds in the compound's structural network during cross-linking in the presence of the modifying additive. This undoubtedly affects the cohesive strength of the materials and, consequently, their impact resistance.

To validate the earlier findings on the physicomechanical properties of the developed epoxy composites, their structure was further analyzed using optical microscopy. Experimental observations (Fig. 8, a-g) revealed that epoxy composites modified with 0.5...0.75 wt.% of DAA exhibited branched fracture lines on their surfaces, indicating uneven fracture patterns and the presence of crater formations suggestive of material tearing upon impact.

These surface characteristics highlight the heterogeneous nature of the composites' cohesive properties within their volume.



**Fig. 7** – Impact strength (W) dynamics as a function of DAA concentration: a) original epoxy matrix; b) 0.75 wt. %; c) 1.25 wt. %; d) 1.50 wt. %; e) 1.75 wt. %; f) 2.00 wt. %

The composites modified with 1.25 wt.% of DAA showed directional crack propagation on the fracture surfaces (Fig. 8, d, e). Notably, these major cracks exhibited complex relief, indicating significant residual stresses within the heterogeneous system. This phenomenon can be attributed to intensified structural formation processes during composite bonding. Consequently, the resulting materials lack equilibrium from a kinetic standpoint, potentially compromising their cohesive properties during operational use.

In contrast, analysis of the fracture surface of the composites containing 1.5 wt.% DAA reveals the formation of a uniformly distributed structure (Fig. 8, f, g). The images show smooth surfaces devoid of craters or air inclusions. This surface homogeneity indicates the material's kinetic and thermodynamic equilibrium, which serves as the foundation for achieving enhanced cohesive properties. Therefore, the findings from the image analysis corroborate the results of the mechanical tests.

As demonstrated earlier (Fig. 6, 7), the composite with 1.5 wt.% additive content exhibits the highest mechanical properties.

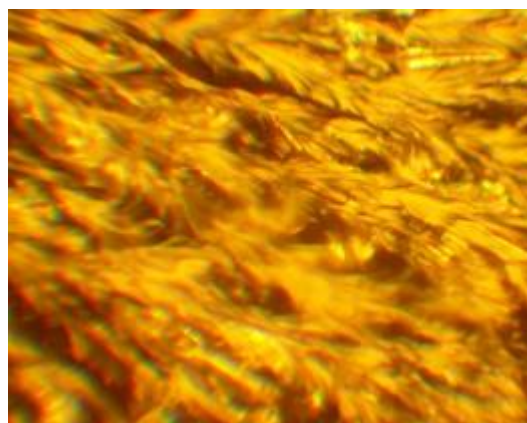
Analysis of the images of composites containing 1.75 and 2.0 wt.% DAA reveals uneven surface characteristics, marked by deep fracture lines and irregular cracks. This unevenness is attributed to an excessive amount of the nano modifying additive in the systems, resulting in a decline in their cohesive properties.

Therefore, based on the results discussed above, it is confirmed that optical microscopy validates the research outcomes on the physico-mechanical properties of the modified materials. It has been demonstrated that adding 1.5 wt.% of the nano modifying additive modifier to the epoxy matrix is optimal to enhance both the mechanical properties and impact resistance of the materials. As shown earlier through IR spectroscopy, this specific concentration allows maximum involvement of side groups and segments from both the epoxy oligomer and the modifier in the composite bonding processes. This contributes significantly to the improved cohesive strength of the modified composite, thereby positively influencing its mechanical properties.

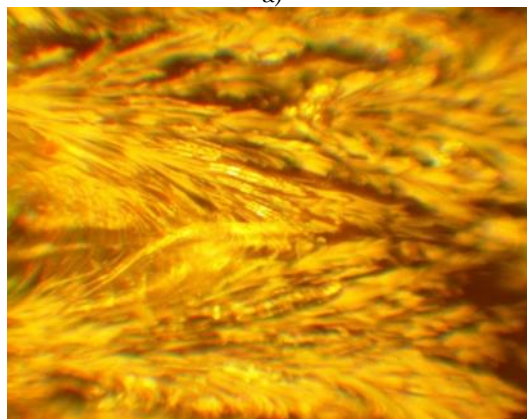
#### 4. CONCLUSIONS

This study investigated the influence of eco-friendly nano modifying additive d-ascorbic acid (DAA) on the structure and properties of epoxy matrix. Based on the test results, a modified epoxy matrix with improved adhesive and physico-mechanical properties was developed. In this regard, the following conclusions can be drawn:

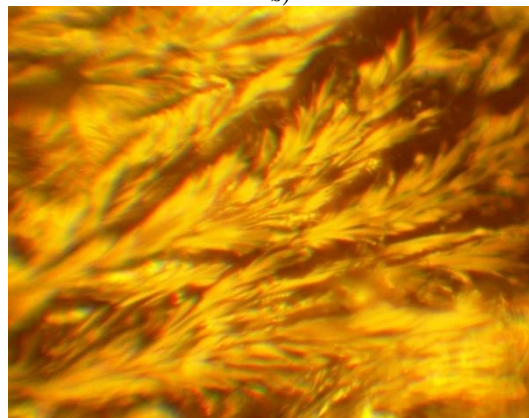
Using gas chromatography, the nature of chemical bonds in the structure of the synthesized d-ascorbic acid for nanostructural modification and its molar mass were studied. It was determined that the molecular formula of the modifier is  $C_6H_8O_6$ . According to calculations, the molar mass of DAA was found to be 176.032088.



a)

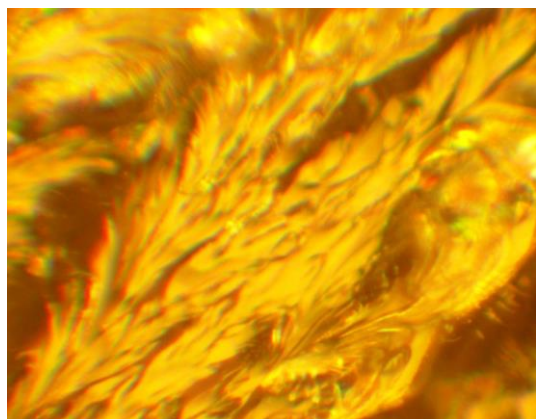


b)

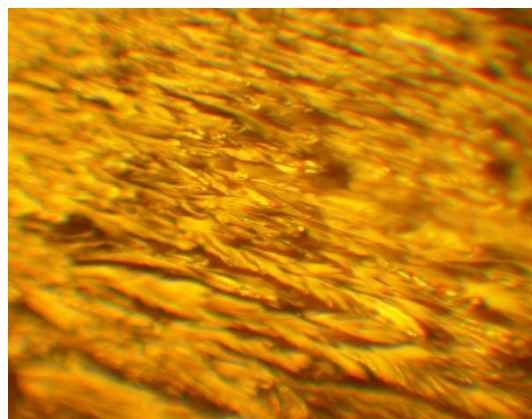


c)

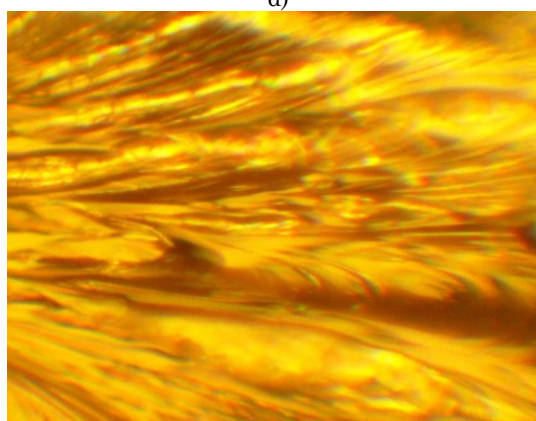




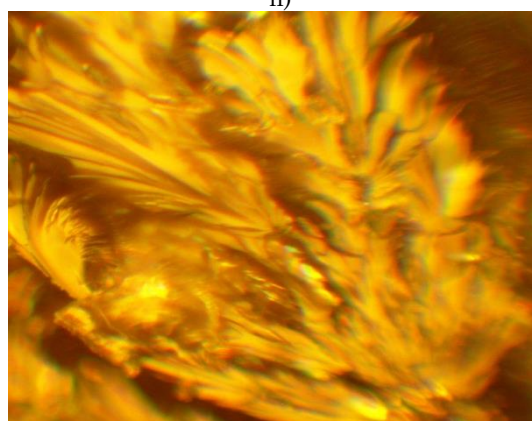
d)



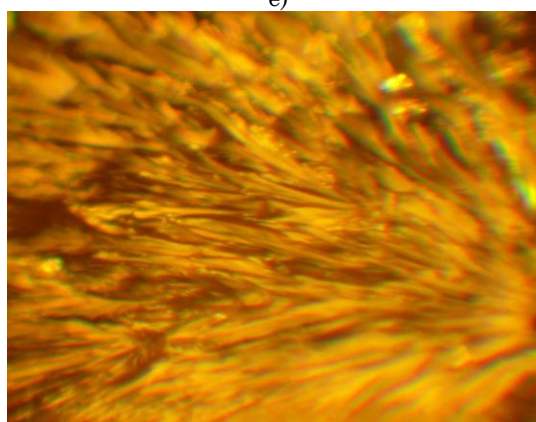
h)



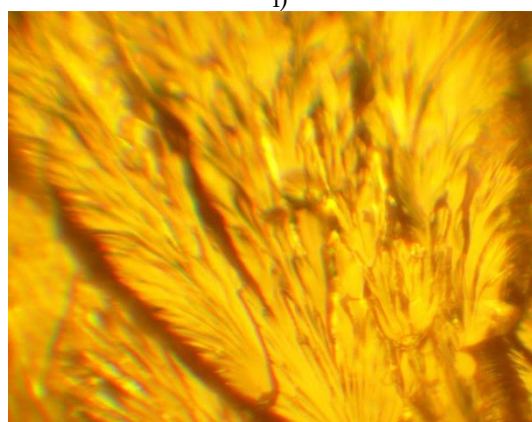
e)



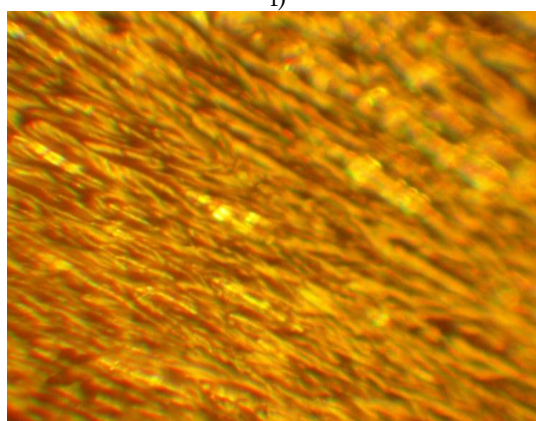
i)



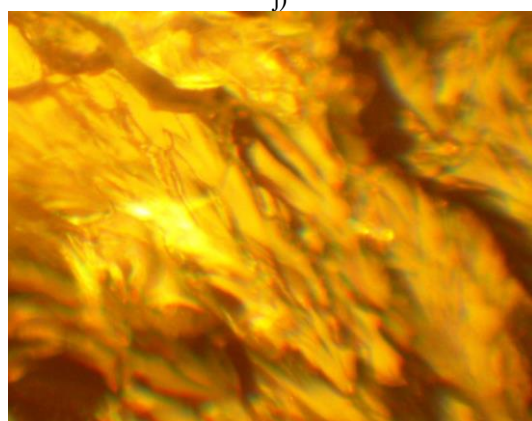
f)



j)

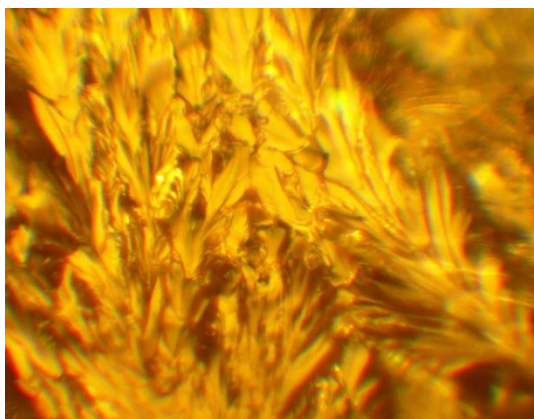


g)



k)





l)

**Fig. 8** – Micrographs of fracture surfaces of epoxy composites at different DAA concentrations,  $q$ , wt.% (calculated relative to 100 wt.% ED-20) ( $\times 50$ ): a, b) 0.50; c, d) 0.75; e, f) 1.25; g, h) 1.50; i, j) 1.75; k, l) 2.00.

The molecule of this modifier contains a significant number of hydroxyl groups. This is a crucial criterion defining the activity of the additive in achieving homogeneous interaction during the bonding of compounds based on the epoxy binder. It was anticipated that chemical bonds would form with the active groups of the PEPA hardener and analogous side hydroxyl groups of the ED-20 epoxy oligomer. Additionally, the presence of carbonyl C=O groups in the structure of the modifier was noted. These groups can also participate in forming material structure, enhancing the degree of gel fraction and thereby improving the cohesive properties of the modified matrix.

1. It has been found that modifying epoxy compositions with d-ascorbic acid in the range of 0.75 % to 1 % by weight per 100 % of ED-20 epoxy resin increases the adhesive strength from 24.8 MPa to 32.6 to 33.1 MPa, while reducing residual stresses from 1.4 MPa to 1.2 MPa. The positive influence of the modifier on enhancing the adhesion of the modified epoxy matrix to the metal substrate is attributed to its chemical structure. This structure governs the intermolecular interactions within the homogeneous polymer system. In the presence of the additive, interactions are activated, allowing for additional bonding between the macromolecules of the modifier and the main oligomer through van der Waals, hydrogen, and acceptor bonds. These interactions significantly enhance the adhesive properties of the polymer compound to the metal substrate.

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2. IR spectroscopy has validated the interaction mechanism between the nano modifying additive DAA and ED-20 epoxy oligomer during compound formation. Specifically, this modifier impacts the structure and properties of the cross-linked polymer within the compound in two significant ways. Firstly, kinetically, the modifier accelerates the rate and extent of cross-linking reactions. Secondly, it results in a polymer with a narrower intermolecular distribution compared to the original epoxy matrix. Consequently, the polymer exhibits restricted molecular mobility influenced by energetic and entropic factors.

3. The evidence of this is the shift in absorption bands in the modified matrix at  $1716...1732\text{ cm}^{-1}$  (C=O groups) towards lower wavenumbers, along with a reduction in their peak intensity. This results from the interaction of the carbonyl group with the hardener and possibly with the active radicals of the epoxy oligomer. In filled materials, a significant broadening of the absorption band is observed at  $3200...344\text{ cm}^{-1}$  (OH groups) and a decrease in peak height compared to the original epoxy matrix. This indicates the overlapping of two or more peaks in the spectra of modified composites. Furthermore, the reduction in peak intensity suggests that both the hydroxyl groups of the epoxy oligomer and the modifying additive are involved in cross-linking. Additionally, new absorption bands appear in the modified composites in the wavenumber range of  $2965...2976\text{ cm}^{-1}$  compared to the epoxy matrix. This results from the valence vibrations of C-H bonds in epoxy and methyl groups. Thus, new peaks emerge in the IR spectra of the composites with the modifier, providing direct evidence of the formation of additional chemical bonds in the developed materials, thereby enhancing their degree of cross-linking.

4. It has been demonstrated that to form materials with improved cohesive properties in the form of a matrix, the following compound should be used: ED-20 epoxy oligomer (100 wt.%), polyethylene polyamine hardener (10 wt.%), and a nano-modifying additive d-ascorbic acid (1.5 wt.%). It has been established that the property indicators for such a composite, compared to the epoxy matrix, increase from 2.8 to 3.5 GPa (elastic modulus), from 48.0 to 59.4 MPa (ultimate tensile strength), and from 7.4 to 8.6 kJ/m<sup>2</sup> (impact toughness). The material's enhanced cohesive strength and impact resistance are attributed to the additional formation of physical and chemical bonds within the compound's structural network during cross-linking in the presence of the modifier.

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## Метод підвищення механічних характеристик засобів морського транспорту за рахунок екологічно чистої наномодифікації епоксидних композитів

А.В. Букетов<sup>1</sup>, К. Дядюра<sup>2</sup>, Ю.М. Шульга<sup>3</sup>, В.В. Соценко<sup>1</sup>, Л. Гребеник<sup>4</sup>, О.А. Пастух<sup>5</sup>, Д.В. Житник<sup>1</sup>

<sup>1</sup> Херсонська державна морська академія, 73000 Херсон, Україна

<sup>2</sup> Національний університет «Одеська політехніка», 65044 Одеса, Україна

<sup>3</sup> Дунайський інститут Національного університету "Одеська морська академія", 68600 Ізмаїл, Україна

<sup>4</sup> Сумський державний університет, Медичний інститут, 40022 Суми, Україна

<sup>5</sup> Тернопільський національний технічний університет імені Івана Пулюя, 46001 Тернопіль, Україна

Захисні полімерні композитні покриття широко використовуються на морському транспорті завдяки своїм покращеним адгезійним і когезійним властивостям. Модифікатори вводяться для підвищення експлуатаційних характеристик полімерних покриттів на основі епоксидних зв'язуючих. У цьому дослідженні досліджується вплив екологічно чистої наномодифікуючої добавки *D*-аскорбінової кислоти на структуру та властивості епоксидної матриці. За результатами випробувань була розроблена модифікована епоксидна матриця з покращеними адгезійними та фізико-механічними властивостями. Методом газової хроматографії досліджено природу хімічних зв'язків у структурі синтезованого модифікатора та його молярну масу. Значна кількість гідроксильних груп у структурі молекули *D*-аскорбінової кислоти є одним із основних критеріїв, що визначають активність даної наномодифікуючої добавки щодо гомогенних взаємодій при зшиванні компаунду на основі епоксидного зв'язуючого. Встановлено, що модифікування епоксидних композицій *D*-аскорбіновою кислотою у кількості від 0,75 до 1 мас.% на 100 мас.% епоксидної смоли ED-20 забезпечує підвищення адгезійної міцності при зменшенні залишкових напружень. Позитивний вплив модифікатора на поліпшення адгезійних властивостей модифікованої епоксидної матриці до металевої підкладки зумовлений хімічною структурою наномодифікуючої добавки, яка визначає міжмолекулярну взаємодію в однорідній полімерній системі. Доведено, що показники когезійних властивостей епоксидного композиту (модуль пружності, руйнівні напруження, ударна в'язкість) суттєво зростають при оптимальному вмісті *D*-аскорбінової кислоти. Це пов'язано з додатковим утворенням фізико-хімічних зв'язків у структурній сітці компаунду під час його зшивання в присутності модифікуючої добавки, що впливає на показники когезійної міцності та ударостійкості матеріалу.

**Ключові слова:** Епоксидна смола ED-20, Екологічно чисті наномодифікуючі добавки, *D*-аскорбінова кислота, Затверджувач РЕРА, Епоксидні композити, Епоксидні морські покриття, Когезійні властивості, Адгезійна міцність