

## Corrosion resistance of epoxy composite coatings for the transport industry in aggressive environments

A. V. Buketov\*, O. M. Bezbakh, N. M. Buketova, T. I. Ivchenko, D. V. Zhytnyk, K. M. Klevtsov

Kherson State Maritime Academy;  
20 Ushakov Prospect, Kherson, 73000, Ukraine

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### Abstract

Epoxy diene oligomer ED-20, 2,4-diaminoazobenzene-4'-carboxylic acid modifier, polyethylene polyamine hardener, microdispersed particles of synthesized powder charge and a mixture of discrete fibers were used to form composite materials and protective coatings for the transport industry. The influence of aggressive media: oil, gasoline, sea water, acetone, NaOH (50 %), HCl (10 %) and H<sub>2</sub>SO<sub>4</sub> (10 %) on the corrosion resistance of the developed composite materials with different content of ingredients was studied. The results of experimental studies suggest that the least swelling was observed for samples of composite containing components in the following ratio – modified binder: microdisperse filler in the form of a synthesized powder charge (Fe (70 %) + Ti (10 %) + TiC ) + Fe<sub>3</sub>C (5 %)) (d = 10–12 μm) : mixture of discrete fibers (modal (42 %), polyacrylic (38 %), polyamide (38 %)) – 100 : 0.05 : 0.10. The use of such a composite in the form of protective coatings of vehicles will ensure (if compared to the modified epoxy matrix) reduction of the permeability of aggressive media in: 1.5–1.7 times (when being used in oil and gasoline); 1.6–1.8 times (when being used in seawater, acetone and NaOH solution (50 %)); 3.0 and 2.5 times (when being used in solutions (10 %) of hydrochloric and sulfuric acids, respectively). Increased corrosion resistance compared to the matrix is caused by a decrease of the amount of polymer in the developed material and its increased cohesion strength, which increases the path of penetration of molecules of corrosive agents during their diffusion into the composite due to additives.

Keywords: *anti-corrosion properties; coating; discrete fibers; epoxy composite; filler.*

Nowadays, improvement of the performance of technological equipment, operating in various aggressive environments is a topical and important issue of modern industry. In this regard, it is important to improve the anti-corrosion properties of parts and mechanisms of the transport industry. The authors [1–3] demonstrate that it is possible to ensure the reliability of vehicles and increase their service life through the use of epoxy composites and protective coatings based on them. Such coatings are characterized by the stability of the properties over a sufficiently long period of time. At the same time their efficiency is proved at operation not only in various aggressive environments, but also at alternating temperatures and dynamic loads.

The authors [4–6] substantiate that the improvement of the cohesion characteristics of composite materials (CM) provides a simultaneous increase in their anti-corrosion properties. In this case, the synergy in improving the properties consists in the predicted and predetermined introduction of modifiers, disperse fillers and continuous and discrete fibers into the epoxy binder. The introduction of additives into the

oligomer only at the optimal content provides a significant improvement in the properties of the materials. It was considered that in order to improve the characteristics of polymeric protective coatings for transport parts, it is advisable to introduce microdispersed particles and discrete fibers with a critical homeopathic content into the binder apart from the modifier. In our opinion, only such an approach to the introduction of these components in the complex will ensure the production of materials with maximum cohesive strength. In this regard, it is advisable and effective to use active and relatively cheap microdisperse additives in the form of synthesized powder charge (SPC), as well as discrete fibers, which can intensify the crosslinking processes in the formation of epoxy composites.

The aim of the work is to study the influence of the content of SPC and discrete fibers on the anti-corrosion properties of epoxy composites for the transport industry.

### Materials and methods of research

The epoxy diene oligomer of ED-20 brand (GOST 10587–84) was chosen as the main component for the binder in the formation of epoxy CM. It is characterized by high adhesive and cohesive strength, low shrinkage and manufacturability while being applied to the surface of a complex profile. 2,4-diaminoazobenzene-4'-carboxylic acid modifier was introduced into epoxy oligomer in the amount of 0.5 weight parts per 100

\* Corresponding author:  
ksma@ksma.ks.ua

weight parts of ED-20 epoxy oligomer to improve the cohesive strength of CM.

Polyethylene polyamine PEPA hardener (TU 6-05-241-202-78) was used for cross-linking of epoxy compositions, which allows to harden materials at room temperatures. PEPA is a low molecular weight substance consisting of the following interconnected components:  $[-CH_2-CH_2-NH-]_n$ . CM was crosslinked by introducing the hardener into the composition at a stoichiometric ratio of components by content (weight parts) – ED-20 : PEPA – 100 : 10  $[-CH_2-CH_2-NH-]_n$ .

SPC was used as a microdisperse filler for experimental studies. The filler was formed by high-voltage electric discharge synthesis. SPC contains the following ingredients, %: Fe – 70, Ti – 10, TiC – 15, Fe<sub>3</sub>C – 5. Powder grain size  $d_{av} = 11.5 \mu\text{m}$ .

In the form of a filler, a mixture of discrete fibers (DF) is additionally used, which contain the following ingredients in the complex, %: modal – 42; polyacrylic – 38; polyamide – 20. Dimensions of discrete fibers:  $l = 1.5\text{--}2.0 \text{ mm}$ ,  $d = 30\text{--}35 \mu\text{m}$ .

Epoxy composites were formed by the following technology: heating the resin to a temperature  $T = 353 \pm 2 \text{ K}$  and holding at a given temperature for a time  $\tau = 20 \pm 0.1 \text{ min}$ ; hydrodynamic combination of oligomer and filler particles during time  $\tau = 10 \pm 0.1 \text{ min}$ ; ultrasonic treatment of the composition during time  $\tau = 1.5 \pm 0.1 \text{ min}$ ; cooling the composition to room temperature over time  $\tau = 60 \pm 5 \text{ min}$ ; the introduction of the hardener and stirring the composition for a time  $\tau = 5 \pm 0.1 \text{ min}$ . CM was hardened according to the mode: formation of samples and their aging over time  $\tau = 12.0 \pm 0.1 \text{ h}$  at a temperature  $T = 293 \pm 2 \text{ K}$ , heating at a rate of  $v = 3 \text{ K/min}$  to a temperature  $T = 393 \pm 2 \text{ K}$ , holding over time  $\tau = 2.0 \pm 0.05 \text{ h}$ , slow cooling to a temperature of  $T = 293 \pm 2 \text{ K}$ . In order to stabilize the structural processes in the composite, the samples were kept for a time  $\tau = 24 \text{ h}$  in air at a temperature of  $T = 293 \pm 2 \text{ K}$ , followed by experimental tests.

The corrosion resistance of CM was determined by immersing the samples in the following aggressive media: oil, gasoline, sea water, acetone, NaOH (50 %), HCl (10 %) and H<sub>2</sub>SO<sub>4</sub> (10 %) [7,8]. Samples of size  $60 \times 10 \times 10 \text{ mm}$  were kept in aggressive media for a time  $t = 720 \text{ h}$  at a temperature  $T = 293 \pm 2 \text{ K}$ . Samples before and after exposure to aggressive media were weighed on analytical balances brand VLR-200 with an accuracy of  $\pm 0.0001 \text{ g}$ .

When increasing (decreasing) the mass of the samples, the calculation of durability was performed according to the formula

$$\chi = 100 \frac{|b-a|}{a},$$

where  $\chi$  is corrosion resistance, %,  $a$  is the mass of the sample before test,  $b$  is the mass of the sample after test, g.

#### Discussion of the results of the experiment

For corrosion protection of technological equipment operated in aggressive environments, we researches the anticorrosive properties of the developed

polymer CM based on a modified epoxy binder with a dispersed filler and discrete fibers, the content of which was previously determined [9, 10].

We tested five compositions of anti-corrosion composites:

matrix (control sample) the matrix was formed by the following ratio of components – epoxy oligomer (ED-20): modifier 4,4'-methylenebis (2-methoxyaniline) (MBMA): polyethylene polyamine (PEPA) – 100: 0,25: 10);

CM 1 (composite was formed by the following ratio of components – modified binder: microdisperse filler in the form of a synthesized powder charge (SPC: Fe (70 %) + Ti (10 %) + TiC (15 %) + Fe<sub>3</sub>C (5 %)) ( $d = 10\text{--}12 \mu\text{m}$ ): a mixture of discrete fibers (DV 1: modal (42 %), polyacrylic (38 %), polyamide (38 %)) ( $l = 1.5\text{--}2.0 \text{ mm}$ ,  $d = 30\text{--}35 \mu\text{m}$ ) – 100 : 0.05 : 0.10);

CM 2 (composite was formed by the following ratio of components – modified binder: SPC: DV 1 – 100 : 0.05 : 0.15);

CM 3 (composite was formed by the following ratio of components – modified binder: SPC: a mixture of discrete fibers (DV 2: polyacrylic (40 %), natural wool (40 %), bamboo (20 %)) ( $l = 1.5\text{--}2.0 \text{ mm}$ ,  $d = 30\text{--}35 \mu\text{m}$  – 100 : 0.05 : 0.05);

CM 4 (composite was formed by the following ratio of components – modified binder: SPC: DV 2 – 100 : 0.05 : 0.10).

The research results confirm the high chemical stability of the developed materials based on the modified epoxy resin ED-20 in various aggressive environments. This is primarily due to the slowing down of the permeability of aggressive media in the volume of epoxy composites due to the increase of their cohesive strength [11, 12]. The latter, in turn, depends on the degree of crosslinking of the epoxy matrix, which is determined by the kinetics of physicochemical processes in the structure of materials. The introduction into the binder of active fillers, in our case – microdispersed particles and discrete fibers at a critical content, provides maximum conversion of the polymer matrix into the state of the outer surface layers, which provides a synergistic effect in improving the physical and mechanical properties of the developed composites.

Analysis of the results shown in Table 1 shows that the least aggressive media for the developed epoxy composites are oil and gasoline. It is proved (Table 1) that the exposure of samples based on a modified polymer matrix in aggressive media of oil and gasoline for a time  $t = 720 \text{ h}$  leads to swelling of the polymer, resulting in its weight increases by 2.9 and 2.8 %, respectively. Additionally, it was found that exposure to samples from the polymer matrix in seawater, acetone and NaOH (50 %) under similar temperature and time modes leads to more significant swelling, as a result of which the material weight increases by 3.0–3.2 %. In addition, it was found that the most aggressive media to the polymer matrix are solutions of hydrochloric and sulfuric acids. It is shown (Table 1) that as a result of holding the samples in these media for a time  $t = 720 \text{ h}$ , a decrease in their mass by 0.3 and 0.5 %, respectively,

**Table 1 – Corrosion resistance of CM after exposure to aggressive environments during time  $t = 720$  h at temperature  $T = 293 \pm 2$  K**

Aggressive environment	Change of the mass of the samples, %				
	Modified polymer matrix	CM 1	CM 2	CM 3	CM 4
Oil	2.9	1.9	2.4	2.2	2.6
Gasoline	2.8	1.8	2.5	2.2	2.7
Seawater	3.2	1.8	2.6	2.0	2.9
Acetone	3.0	1.9	2.8	2.4	2.7
NaOH (50 %)	3.1	1.7	2.2	2.1	2.9
HCl (10 %)	- 0.3	-0.1	-0.2	-0.2	-0.3
H <sub>2</sub> SO <sub>4</sub> (10 %)	- 0.5	-0.2	-0.3	-0.3	-0.4

was observed. In our opinion, the destruction of the polymer in acid solutions is explained by the ability of the matrix to oxidation processes, sorption during the experiment of components of aggressive media, resulting in changes in the structure of the matrix and the destruction of unstable physical bonds in the material volume and phase separation «matrix – filler».

The results of experimental studies (Table 1) suggest that the introduction of a modified epoxy binder of microdispersed particles and discrete fibers helps to increase the chemical resistance of the developed CM due to increased cohesion characteristics of epoxy composites. In particular, it is shown that the exposure of samples to aggressive media of oil and gasoline during the time  $t = 720$  h leads to swelling of the polymer and, accordingly, to an increase in their mass by 1.8–2.7 %. Note that the least swelling was observed for samples of CM 1 containing components in the following ratio – modified binder: microdisperse filler in the form of SPC: Fe (70 %) + Ti (10 %) + TiC (15 %) + Fe<sub>3</sub>C (5 %) ( $d = 10$ – $12$   $\mu\text{m}$ ): mixture of discrete fibers (DV 1: modal (42 %), polyacrylic (38 %), polyamide (38 %)) – 100 : 0.05 : 0.10). The use of such a composite in the form of protective coatings, which are used in oil and gasoline, will provide a 1.5–1.7 times reduction in the permeability of aggressive media compared to the modified epoxy matrix. The increase in the chemical resistance of CM is due to a decrease in the amount of polymer in the volume of composites and increased cohesion strength of materials. In addition, one of the reasons for the decrease in the permeability of polymer composites is the increase in the path of molecules of corrosive agents during their diffusion in the volume of CM.

The results of the study of anticorrosive properties of CM in aggressive environments of sea water, acetone and NaOH (50 %) confirm the above mentioned assumptions. In particular, it was proved (Table 1) that the introduction of additives in the epoxy binder reduces the weight of the samples during the study by 1.7–2.9 %. In this case, the formation of the composite CM 1 contributes to the maximum (among the whole range of investigated materials) improvement of anti-corrosion properties compared to the matrix. It is shown (Table 1) that the formation of protective coatings based on such composites reduces the permeability of materials in these aggressive environments compared to the matrix by 1.6–1.8 times. This is due to the fact that

the molecules of aggressive media according to the second Rehbinder effect [13], penetrating the material provide the formation of a wedging effect, especially at the interface "matrix – filler". This, in its turn, leads to the accumulation of moisture at the hydrophilic centers of the solid phase and the emergence of osmotic pressure sufficient for swelling and subsequent stratification of the composite. Diffusion forces increase the intensity of moisture permeability in the materials, which destroys the adhesive bonds of the matrix with the filler, which reduces the cohesive strength of the systems.

At the final stage, the change in the mass of the samples after their exposure in aggressive media of hydrochloric and sulfuric acids was analyzed. It is shown (Table 1) that as a result of the study of predetermined temperature and time parameters, the mass of composites decreases by 0.1–0.4 %. It is proved that CM 1 is characterized by minimal weight loss, which is in good agreement with the results of the above studies. Compared to the epoxy matrix, after exposure to hydrochloric and sulfuric acids for this material, the permeability decreases by 3.0 and 2.5 times, respectively. In our opinion, the destruction of epoxy composites occurs due to the destruction of the polymer or due to the chemical interaction of the filler and the molecules of aggressive media. In addition, as a result of research, it was found that the destruction of composites in acid solutions is preceded by swelling of the samples due to sorption and diffusion of aggressive media into the polymer matrix. This is due to defects in the structural network of the polymer due to the high speed of the crosslinking processes in the presence of filler, as well as the nature of the aggressive environment.

To confirm the above mentioned test results, the change of physical and mechanical properties of CM 1 samples previously aged in selected aggressive media for a time  $t = 720$  h at a temperature  $T = 293 \pm 2$  K were additionally investigated. It was experimentally established (Table 2) that the destructive stresses in tension and bending, as well as the hardness of samples of CM 1, aged in aggressive media of sea water, acetone, oil, gasoline and NaOH (50 %), do not change (indicators at the beginning and at the end of the study are within the error of the experiment). At the same time, it should be noted that after holding similar samples in hydrochloric and sulfuric acid media, the indicators of physical and mechanical properties of CM 1

**Table 2 – Influence of aggressive environments (during time  $t = 720$  h at temperature  $T = 293 \pm 2$  K) on physical and mechanical properties of CM**

Aggressive environment	Indicators of properties of CM 1		
	Destructive tensile stresses, MPa	Destructive bending stresses, MPa	Hardness, HRB
Initial conditions	66.1	78.6	56
Seawater	64.2	74.2	54
Acetone	62.8	75.0	53
Oil	61.2	76.9	53
Gasoline	63.4	75.0	52
NaOH (50 %)	62.0	74.8	52
HCl (10 %)	44.2	61.6	46
H <sub>2</sub> SO <sub>4</sub> (10 %)	41.3	60.8	45

decrease by 1.3–1.6 times. After the tests, the appearance of the samples did not change, but in the samples tested in acid solutions, a change in color and, accordingly, a decrease in mass were observed. Based on this, it can be stated that the stability of the properties of CM 1 in the studied aggressive media can be explained by the plasticizing effect of sorbed ingredients, and a significant decrease in physical and mechanical properties after exposure to acid solutions due to the penetration of aggressive media molecules.

### Conclusions

It was found out that polymer composite materials based on modified epoxy resin, microdisperse filler and discrete fibers are characterised by improved anti-corrosion properties due to increased cohesive strength.

The results of experimental studies suggest that the least swelling was observed for samples of composite containing components in the following ratio – modified binder: microdisperse filler in the form of a synthesized powder charge (Fe (70 %) + Ti (10 %) + TiC (15 %) + Fe<sub>3</sub>C (5 %)) (d = 10–12 μm) : mixture of discrete fibers (modal (42 %), polyacrylic (38 %), polyamide (38 %)) – 100 : 0.05 : 0.10).

The use of such a composite in the form of protective coatings will provide (if compared to the modified epoxy matrix) reduction of the permeability of aggressive media in: 1.5–1.7 times (when being used in oil and gasoline); 1.6–1.8 times (when being used in seawater, acetone and NaOH solution (50 %)); 3.0 and 2.5 times (when being used in solutions (10 %) of hydrochloric and sulfuric acids), respectively. The increase in chemical resistance compared to the matrix is caused by a decrease in the amount of polymer in the developed material and its increased cohesion strength, which increases the path of penetration of molecules of corrosive agents during their diffusion into the composite due to additives.

It was found that the destructive tensile and bending stresses, as well as the hardness of the epoxy composite with SPC and discrete fibers aged in aggressive environments of sea water, acetone, oil, gasoline and NaOH (50 %) for a time  $t = 720$  h at a temperature  $T = 293 \pm 2$  K practically do not change (indicators at the beginning and at the end of test are within an error of experiment). At the same time, it

should be noted that after exposure to similar samples in hydrochloric and sulfuric acid media, the indicators of physical and mechanical properties of the composite decrease by 1.3–1.6 times. It can be stated that the stability of the properties of the composite in the studied aggressive media can be explained by the plasticizing effect of sorbed ingredients, and the significant deterioration of physical and mechanical properties after exposure to acid solutions is due to the penetration of aggressive media molecules into the polymer and partial destruction of epoxy matrix.

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## Корозійна тривкість епоксикомпозитних покриттів для транспортної галузі в агресивних середовищах

*А. В. Букетов, О. М. Безбах, Н. М. Букетова, Т. І. Івченко, Д. В. Житник, К. М. Клевцов*

*Херсонська державна морська академія;  
проспект Ушакова, 20, м. Херсон, 73003, Україна*

Для формування композитних матеріалів і захисних покриттів для транспортної галузі використано епоксидний діановий олігомер ЕД-20, модифікатор 2,4-діаміноазобензол-4'-карбонова кислота, твердник поліетиленполіамін, мікродисперсні частки синтезованої високовольтним електророзрядом порошкової шихти і суміш дискретних волокон. Досліджено вплив агресивних середовищ (нафта, бензин, морська вода, ацетон, NaOH (50 %), HCl (10 %) і H<sub>2</sub>SO<sub>4</sub> (10 %)) на корозійну тривкість розроблених композитних матеріалів із різним вмістом інгредієнтів. Результати експериментальних досліджень дозволяють стверджувати, що найменше набухання спостерігається для зразків композиту, що містить компоненти за такого співвідношення – модифікований зв'язувач : мікродисперсний наповнювач у вигляді синтезованої порошкової шихти (Fe (70 %) + Ti (10 %) + TiC (15 %) + Fe<sub>3</sub>C (5 %)) ( $d = 10\text{--}12$  мкм) : суміш дискретних волокон (модал (42 %), поліакрил (38 %), поліамід (38 %)) – 100 : 0.05 : 0.10. Використання такого композиту у вигляді захисних покриттів засобів транспорту забезпечить порівняно з модифікованою епоксидною матрицею зменшення проникності агресивних середовищ у: 1.5–1.7 раз при експлуатації у нафті і бензині; 1.6–1.8 раз при експлуатації у морській воді, ацетоні і розчині NaOH (50 %); 3.0 та 2.5 раз при експлуатації у розчинах (10 %) соляної і сірчаної кислот відповідно. Підвищення корозійної тривкості порівняно з матрицею зумовлено зменшенням кількості полімеру в розробленому матеріалі та підвищеною його когезійною міцністю, що передбачає збільшення проникнення молекул корозійно-активних агентів під час їхньої дифузії в об'єм композиту за рахунок наявності добавок.

Ключові слова: *антикорозійні властивості; дискретні волокна; епоксидний композит; наповнювач; покриття.*