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MODERN STRATEGIES FOR REPAIRING TRANSPORT SYSTEMS AND FACILITIES USING MODIFIED EPOXY PLASTICS

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Summary. The important feature of the ship transportation systems and facilities operation is the possibility of using methods of current and capital repair of machines and mechanisms. The durability of machine parts and elements operation significantly depends on the state of the mechanisms at the current moment, the critical conditions of their thermal and power load. This applies especially to engine room components of modern vessels. Based on the above-mentioned problem, the solution of the issue of current repair of transport systems and facilities is important today, since the occurrence of emergency condition while the systems are in operation requires their immediate leveling during the vessels voyage. In this context, the application of modern strategies for the repairing of transport systems and facilities, which involve the use of modified polymer epoxy plastics, is promising. The development of new materials with improved properties is impossible without scientific research of their cohesive characteristics. The latter can be improved by introducing chemically active modifiers into epoxy oligomer. The optimal content of the modifier in the epoxy oligomer was determined in this paper according to the cohesive strength criteria, such as destructive stresses and flexural elastic modulus, impact strength of composites. Epoxy oligomer ED-20 was chosen as the basis for binder formation. Compositions were polymerized with PEPA hardener. 2,4-diaminoazobenzene-4'-carboxylic acid was used as a modifier. It is proved that for the formation of materials with improved cohesive properties, it is necessary to use the composition of the following content: epoxy oligomer ED-20 (100 wt. parts), hardener PEPA (10 wt. parts), modifier 2,4-diaminoazobenzene-4'-carbonate acid (0.5... 1.0 wt. parts). The formation of such material ensures significant increase in the mechanical properties of composites compared to the original epoxy matrix. An important scientific and technical problem regarding the improvement of modern strategies for transport systems and facilities repairing by means of new modified epoxy plastics is solved in this paper. This is achieved by selecting the structural component materials based on the results of the investigations of interphase interaction processes during the formation of heterogeneous systems and their cohesive properties.

Key words: material, composite, oligomer, modifier, properties.

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Statement of the problem. An important feature of the operation of ship transport systems and facilities is the possibility of using methods of current and capital repairing of machines and mechanisms. The durability of machine parts and elements operation significantly depends on the state of mechanisms at the current moment, critical conditions of their thermal and power load. This applies especially to the engine room units of modern vessels, such as sealing between the nasal end, propeller hub and stern lining, the shaft cone on the aft side, deadwood seals, and the deadwood complex as a whole.

As the result, the parts of engine room mechanisms of transport systems and facilities are exposed to corrosive and cavitation effects of aggressive environments. For example, when water gets on the surface of the propeller shaft (as the result of its waterproofing violation), the fatigue strength of the shaft decreases sharply. In this case, cracks occur and intensively develop on the surface with their propagation in depth. In the area between the lining and the propeller hub, the shaft destruction is electrochemical in nature (due to the ingress of seawater into this area) with the occurrence of corrosion-fatigue cracks.

Analysis of available researches and publications. Based on the above-mentioned problem, the solution of the problem of current repairing of transport systems and facilities is of great importance today, since the occurrence of emergency condition while the systems are

in operation requires their immediate leveling during the vessels voyage. In this context, the application of modern strategies for the repairing of transport systems and facilities, which involve the use of modified polymer epoxy plastics, is promising [1–7]. The development of new materials with improved properties is impossible without scientific research of their cohesive characteristics. The latter can be improved by introducing chemically active modifiers into epoxy oligomer. Such strategies cover the following areas of activity in critical conditions of the of transport systems functioning:

- to carry out instant qualitative analysis of the structure, characteristic faults using the latest diagnostic technologies of modern deadwood complexes;
- to develop (or apply known) technology for the formation and repair of deadwood seals, elements or pump casings;
- to carry out mathematical calculation of the ingredients and modes of formation of new polymer materials to eliminate breakdowns;
- to take into account the economic feasibility of using the developed composites for the restoration of elements of transport systems and facilities, including seals, bearings, pump impellers, etc.
- take into account labor and environmental protection measures.

Considering the above mentioned, it is effective to use polymer composites that can be used in the form of elements, including for deadwood seals, in the current repair of transport systems. This makes it possible to improve significantly the physical-mechanical, anti-corrosion and other operational characteristics of deadwood complexes and mechanisms under the influence of static and dynamic loads. The use of polymer composite materials (CM) based on epoxy binders is important. Such materials are characterized by good manufacturability when applied to the parts with complex surface profile and increased operational characteristics under critical operating conditions. The development of new materials with improved properties is impossible without scientific investigation of their cohesive characteristics. The latter can be improved by introducing chemically active modifiers into the epoxy oligomer. This results in the formation of materials with increased operational characteristics, which are regulated by technological modes of composites formation.

The objective of the paper is to substantiate the need for the use of modified epoxy plastics in the restoration of machine parts in the context of the development of modern strategies for transport systems and facilities repairing.

Materials and methods of investigation. Epoxy dian oligomer brand ED-20 (ISO 18280:2010) was chosen as the basis for the binder formation. Epoxy compositions were polymerized with PEPA hardener (TU 6-05-241-202-78). 2,4-diaminoazobenzene-4'-carboxylic acid (DAABCA) was used as modifier during the formation of coatings.

Indicators of destructive stresses and modulus of elasticity were determined according to ASTM D 790–03. During the investigation, samples of the following dimensions were used: length $l = 120 \pm 2$ mm, width $b = 15 \pm 0.5$ mm, height $h = 10 \pm 0.5$ mm.

The impact viscosity of CM was determined by Charpy method (ISO 179-1) on the MK-30 pendulum probe. Sample dimensions: $(65 \times 12 \times 12) \pm 0,5$ mm.

Presentation of the main investigation material. As it was mentioned above, materials with improved cohesive properties should be used during current repairing on the ship. Therefore, it is necessary to use new materials with predetermined amount of active modifier. In this regard, the optimal content of the additive in the epoxy oligomer was determined according to the cohesive strength criteria, such as destructive stress and modulus of elasticity in bending, impact toughness of CM.

Physical and mechanical properties of the initial epoxy matrix modified by ultrasonic treatment were experimentally investigated. It was proved (Fig. 1) that the indicators of its characteristics are as follows: the modulus of elasticity at bending is 2.8 GPa, the destructive stresses at bending are 48.0 MPa, and the impact toughness is 7.4 kJ/ m².

It is proved (Fig. 1) that the introduction of DAABCA modifier at small content (0.25 wt. parts) results in slight decrease in the modulus of elasticity of the modified matrix (from 2.8 GPa (for the original epoxy matrix) to 2.7 GPa). Subsequently, the increase in the content of the additive provides monotonous increase in the modulus of elasticity of CM, and the maximum on «E – q» dependence curve was observed at the concentration of the modifier in the amount of 1.00 wt. parts. Such developed CM is characterized by modulus of elasticity of 3.8 GPa. The introduction of the modifier in the amount more than 1.00 wt. parts results in the deterioration in the investigated properties of CM, since the modulus of elasticity decreases to 3.6 GPa (with the content of DAABCA in the amount of 2.00 wt. parts).

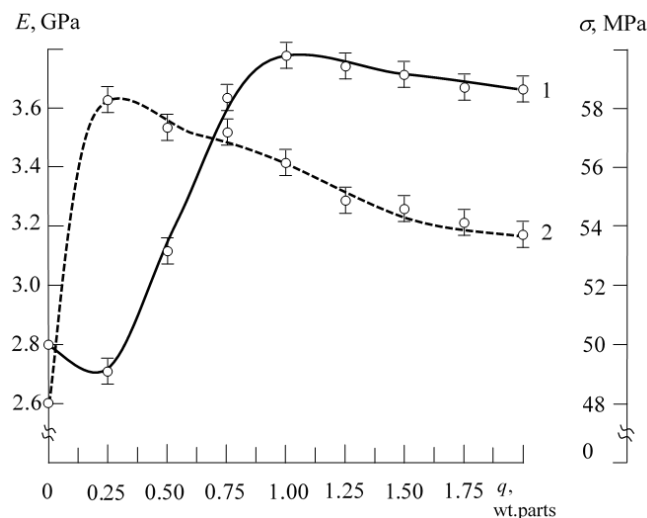


Figure 1. Dependence of physical and mechanical properties of epoxy matrix on the content of DAABCA modifier: 1) modulus of elasticity in bending (E); 2) destructive stresses during bending (σ)

The obtained results can be explained in the following way. The introduction of the modifier in relatively small amount (0.25 wt. parts) ensures the formation of CM, which is characterized by low degree of crosslinking. Insufficient amount of the modifier in epoxy binder results in the formation of material with significant content of sol fraction. Under the above mentioned modes of matrix crosslinking, in our opinion, free uncrosslinked radicals are formed in homogeneous polymerized system, ensuring material plasticity, but cohesive properties deterioration. On the contrary, when DAABCA content is increased to 1.0...1.5 wt. parts the matrix with maximum values of the modulus of elasticity is formed. It was considered that in this case, the maximum number of side hydroxyl and epoxy groups of the epoxy oligomer, as well as hydroxyl and primary amines of 2,4-diaminoazobenzene-4'-carboxylic acid, were involved in the process of crosslinking of the composition. In this case, the indicators of gel fraction of the developed materials increase as much as possible, which, accordingly, ensures the increase in their modulus of elasticity during bending.

Analysis of the investigation results regarding the effect of modifier content on the destructive stresses during bending makes it possible to state the following. It has been proven (Fig. 1) that the introduction of the modifier provides the increase in destructive stress indicators of CM, and the maximum values (56.7...58.3 MPa) are characterized by materials with the content of DAABCA in the amount of 0.25...1.00 wt. parts. Further, the increase in modifier content results in the deterioration of matrix properties within the range of the investigated additive concentrations. It is shown (Fig. 1) that the introduction of DAABCA in the amount of 2.00 wt. parts ensures the formation of CM with indicators of destructive stresses, which do not differ significantly from similar values for the original epoxy matrix (54.3 MPa). At the same time, it should be noted that the maxima on the curves of the dependence of modulus of

elasticity and destructive stress during CM bending on the modifier concentration, slightly differ (by additive content). In particular, on the «E – q» curve, the highest values of the modulus of elasticity are characteristic of CM containing DAABCA in the amount of $q = 1.00...1.50$ wt. parts, and analysis of « $\sigma - q$ » curve made it possible to determine the following optimal concentration range modifier – $0.25...1.00$ wt.parts. Based on this and in order to confirm the results of the above mentioned tests, the impact toughness of the original and modified epoxy matrices was investigated at the next stage,.

It is determined experimentally (Fig. 2) that the initial epoxy matrix is characterized by $7,4 \text{ kJ/m}^2$ impact viscosity index.. Introduction of the modifier in the amount of $0.25...1.00$ wt. parts makes it possible to increase the impact viscosity of CM up to $8.0...8.2 \text{ kJ/ m}^2$, moreover maximum (8.2 kJ/ m^2) is observed for the material with DAABCA content – 0.5 wt. parts. Introduction of additive in the amount of 1.50 wt. parts results in the decrease of matrix resistance to impact loads, since its impact viscosity (7.5 kJ/ m^2) practically does not differ from similar values characteristic for the initial matrix. Therefore, it can be argued that optimal range of modifier concentrations for the formation of matrices with maximum impact viscosity is $0.25...1.00$ wt. parts, which completely coincides with the similar content of DAABCA in CM with the highest values of destructive stresses during bending.

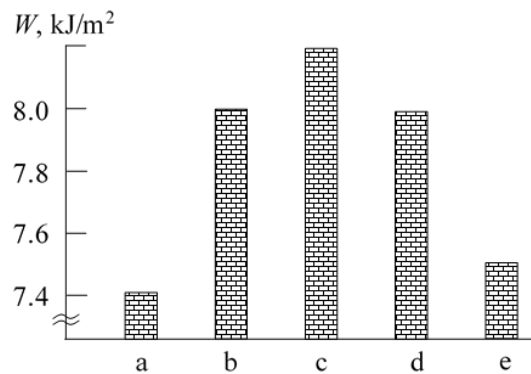


Figure 2. Dependence of the impact viscosity (W) on the content (q) of the modifier in matrix: a) initial matrix; b) $q = 0.25$ wt. parts; c) $q = 0.50$ wt. part; d) $q = 1.00$ wt. parts; e) $q = 1.50$ wt. parts

In addition, in order to confirm the above mentioned results of the investigation of CM physical and mechanical properties, we analyzed the surface of their fracture after testing on pendulum copra by optical microscopy. It is shown (Fig. 3, a) that the fracture surface of samples of the original epoxy matrix has wavy character. At the same time, branched chipping lines are visible on the samples (Fig. 3, b – the upper part of the photo), and the presence of craters is also noted, which can be caused by air inclusions in the material due to the technological process of its formation. Such heterogeneity in volume indicates the formation of the system with kinetically unbalanced state. And this, in turn, makes it possible to confirm high rates of residual stresses that occur during matrix polymerization of the. The latter results in the increased material brittleness and premature aging.

Flat fracture surface was observed while analyzing samples of the modified matrix with additive content of 0.25 wt. parts At the same time, it should be noted that the crack propagation front at such material fracture under impact is almost perpendicular to the sample horizontal axis (Fig. 3, c). This indicates low cohesive properties of CM, which implies insignificant resistance to external impact loads. It should be noted that the fracture surface is characterized by uniformly distributed structure, without available air inclusions (Fig. 3, d). It is definitely in comparison with the initial epoxy matrix, provides the improvement of cohesive properties of the developed material.

Branched front of crack propagation was observed during the analysis of the fracture surface of epoxy composite samples with modifier content of $0.5...1.0$ wt. parts. (Fig. 3, d, e).

Curvilinear trajectory of the fracture surfaces indicates increased cohesive strength of CM, and three-dimensional network of chemical bonds of macromolecules of epoxy oligomer and modifier reduces the crack propagation time and increases the path of their propagation (Fig. 3, e, g). Accordingly, such materials are characterized by increased indicators not only of impact viscosity, but also of destructive stresses during bending (Fig. 1, Fig. 2).

Surface analysis of the fracture photograph of CM modified with 1.50 wt. parts DAABCA also indicates linear and perpendicular to the horizontal axis of the sample character of crack propagation (Fig. 3, h, i). During the impact, the fracture of the samples is observed with the formation of significant number of small volume fragments (Fig. 3, h), the fracture surface is characterized by deep cracks (Fig. 3, i). The above mentioned analysis results make it possible to assert the formation of brittle material during its polymerization, which increases its elastic modulus, but the values of fracture stresses and impact viscosity are not high enough (Fig. 1, Fig. 2).

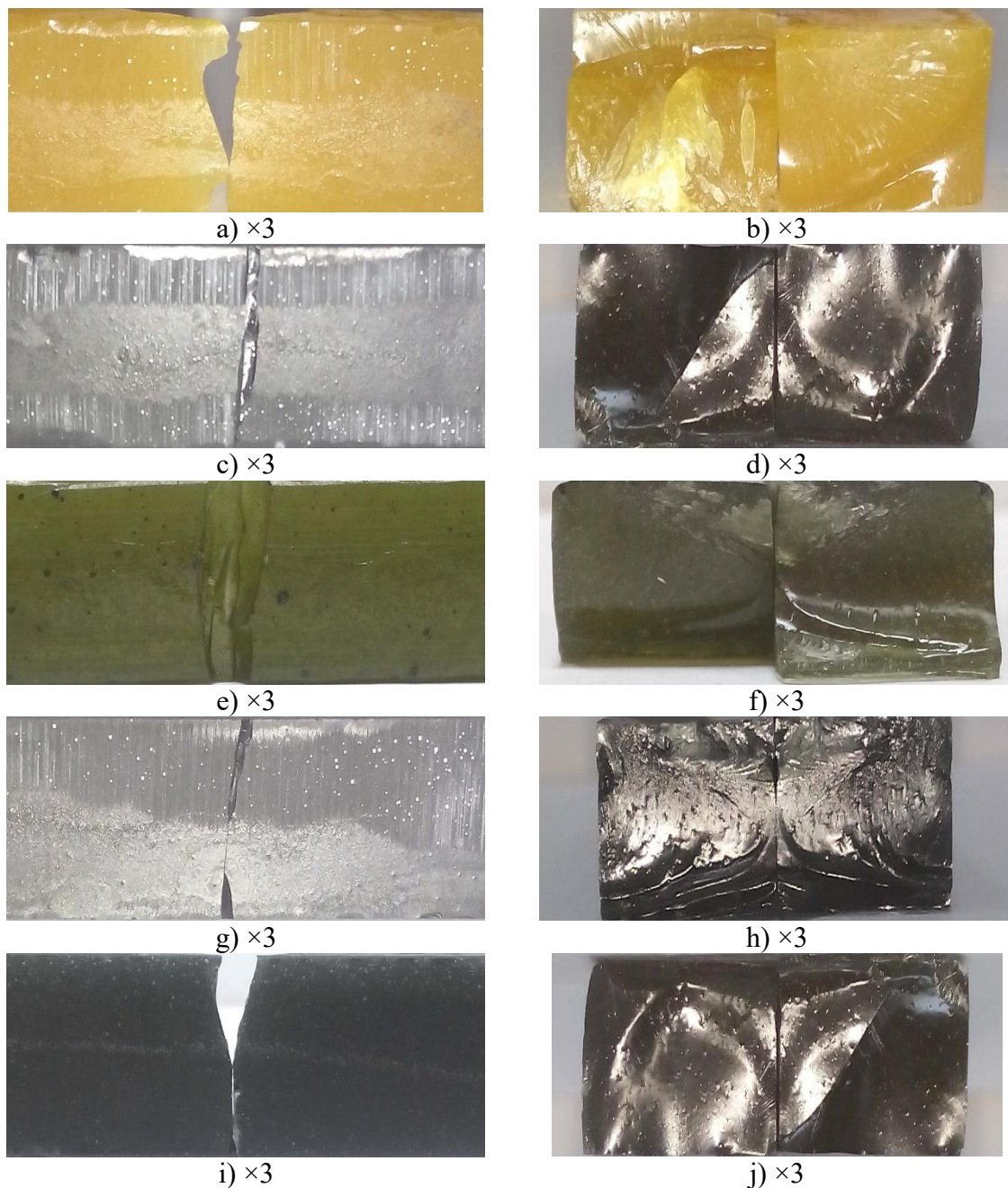


Figure 3. Photomicrographs of the fracture of the initial and modified epoxy matrices: a, b) initial epoxy matrix (control sample); c, d) 0.25 wt. parts; d, f) 0.5 wt. parts; g, h) 1.0 wt. parts; i, j) 1.5 wt.h.

Conclusions. An important scientific and technical problem regarding the improvement of modern strategies for the repair of transport systems and facilities using new modified epoxy plastics is solved in this paper. This is achieved by selecting the structural component materials based on the results of the investigations of the processes of interphase interaction during the formation of heterogeneous systems and their cohesive properties. At the same time, we have determined the following.

1. It is substantiated that in order to obtain materials with improved cohesive properties, it is necessary to use the composition with the following content: epoxy oligomer brand ED-20 (100 wt. parts), polyethylene polyamine hardener PEPA (10 wt. parts), modifier 2,4-diaminoazobenzene-4' – carboxylic acid (0.5...1.0 wt. parts). The formation of such material provides, in comparison with the initial ultrasonically modified epoxy matrix, the increase in the following indicators of composites physical and mechanical properties:

- modulus of elasticity – from 2.8 GPa to 3.2...3.8 GPa;
- destructive stresses – from 48.0 MPa to 56.7...57.0 MPa;
- impact viscosity – from 7.4 kJ/m² to 8.0...8.2 kJ/m².

2. By means of optical microscopy, it is determined that the fracture surface of samples of the original epoxy matrix has wave-like character. At the same time, branched chipping lines are visible on the samples, the presence of craters is noted, the cause of which may be caused by air inclusions in the material due to the technological process of its formation. Flat fracture surface is observed while analysing the samples of the modified matrix with additive content of 0.25 wt. parts. At the same time, it should be noted that the crack propagation front during the fracture of such material under impact is almost perpendicular to the horizontal axis of the sample. This indicates low cohesive properties of CM, which implies insignificant resistance to external impact loads. Branched front of crack propagation is observed while analysing the fracture surface photographs of epoxy composite samples with modifier content of 0.50...1.00 wt parts. The curvilinear trajectory of the fracture surfaces indicates the increased cohesive strength of CM, and three-dimensional network of chemical bonds of macromolecules of the epoxy oligomer and modifier reduces the time and increases the crack propagation path. Therefore, it can be stated that the results of the investigation by the method of optical microscopy are in good agreement and confirm the results of the tests of physical and mechanical properties of the developed materials.

In the future, it is planned to carry out investigations on determining the influence of the modifier content on thermophysical properties of protective coatings for repairing transport systems and facilities and improving their operational characteristics.

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**СУЧАСНІ СТРАТЕГІЇ РЕМОНТУ ТРАНСПОРТНИХ СИСТЕМ ТА
ЗАСОБІВ ІЗ ВИКОРИСТАННЯМ МОДИФІКОВАНИХ
ЕПОКСИПЛАСТІВ**

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***Резюме.** Важливою особливістю експлуатації судових транспортних систем та засобів є можливість використання методів поточного й капітального ремонту машин і механізмів. Довговічність роботи деталей та елементів машин суттєво залежить від стану механізмів у поточний момент, критичних умов їх теплового та силового навантаження. Це особливо стосується вузлів машинного відділення сучасних суден. Виходячи з наведеної вище проблеми, актуальним на сьогодні є вирішення питання поточного ремонту транспортних систем та засобів, позаяк виникнення аварійного стану при роботі систем потребує негайного їх нівелювання під час перебування суден у рейсі. В цьому контексті перспективним є застосування сучасних стратегій ремонту транспортних систем та засобів, які передбачають використання модифікованих полімерних епоксипластів. Розроблення нових матеріалів з поліпшеними властивостями не можливе без наукових досліджень їх когезійних характеристик. Останні можна покращувати за рахунок введення в епоксидний олігомер хімічно активних модифікаторів. У роботі визначали оптимальний вміст модифікатора в епоксидному олігомері за критеріями когезійної міцності, такими, як руйнівні напруження та модуль пружності при згинанні, ударна в'язкість композитів. У вигляді основи при формуванні зв'язувача обрано епоксидний олігомер ЕД-20. Полімеризували композиції твердником ПЕПА. Як модифікатор застосовували 2,4-діаміноазобензол-4'-карбонову кислоту. Доведено, що для формування матеріалів з поліпшеними когезійними властивостями необхідно використовувати композицію наступного складу: епоксидний олігомер ЕД-20 (100 мас.ч.), твердник ПЕПА (10 мас.ч.), модифікатор 2,4-діаміноазобензол-4'-карбонова кислота (0,5...1,0 мас.ч.). Формування такого матеріалу забезпечує порівняно з вихідною епоксидною матрицею суттєве підвищення показників механічних властивостей композитів. Таким чином, у статті вирішено актуальну науково-технічну задачу стосовно вдосконалення сучасних стратегій ремонту транспортних систем та засобів із використанням нових модифікованих епоксипластів. Цього досягали шляхом вибору структурних складових матеріалів на основі результатів дослідження процесів міжфазової взаємодії при формуванні гетерогенних систем та їх когезійних властивостей.*

***Ключові слова:** матеріал, композит, олігомер, модифікатор, властивості.*

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