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REGULAR ARTICLE

Promising Technologies in Water Transport: Development and Implementation of Fungus-Resistant and Ecologically Clean Epoxy Nanocomposites

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This study investigates the fungal resistance and fungicidal properties of epoxy nanocomposites designed to improve waterborne transport systems' operational and repair characteristics. It has been shown that curing epoxy nanocomposites with the addition of nano- and micro-resins and discrete fibers is essential for significantly extending the service life of water transport systems. These modifications do not reduce the mechanical strength or corrosion resistance of the dry coatings. The research employs testing methods based on ISO 846:2019 to evaluate two key properties: fungal resistance and fungicidal activity. The fungal growth test revealed that modified epoxy composites with dispersed fillers and discrete fibres exhibit significant resistance to fungal growth. Specifically, composites with added modifiers and fibres show clear fungicidal effects, completely inhibiting fungal growth. In contrast, basic epoxy matrices and composites with fewer modifications show increased fungal proliferation. The importance of using eco-friendly materials in waterborne transport is emphasized. The study demonstrates the resistance of modified materials to the growth of aquatic fungi. An analysis of the fungicidal properties of the composites confirms their effectiveness in preventing fungal growth. Additionally, the study presents the development of an eco-friendly, corrosion-resistant epoxy composite. The material formulation includes epoxy resin (ED-20), polyethene polyamine (PEPA) hardener, ascorbic acid modifier, and specialized fillers. This composite, tested for both fungal resistance and mechanical properties, aims to enhance the durability and repairability of water transport structures. The preparation process and composition of this composite are detailed, providing a guide for potential applications in marine transport components.

Keywords: Epoxy nanocomposites, Transport technologies, Coatings, Service life, Reliability, Molding technology, Environmental sustainability.

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1. INTRODUCTION

Polymer epoxy nanocomposites are increasingly used in water transport systems to enhance the operational lifespan of equipment [1-4]. The adoption of new advancements in transport technologies, which involve the use of innovative materials for the repair and restoration of machinery and mechanisms, has become essential. In this regard, epoxy nanocomposites have proven to be highly efficient. However, studies [5-9] have shown that in order to further extend the service life of water transport equipment, it is crucial to incorporate not only nano-fillers but also micro-fillers and discrete fibers into the epoxy resin. These modifications [10-17], as well as high-entropy film materials [18-20], not only improve the mechanical properties of protective coatings, but also significantly increase their corrosion resistance.

An important aspect of the development of these materials is their environmental impact, especially given the increasing demands for eco-friendly solutions in water transport [13]. This has led to a growing focus on researching and analyzing the resistance of these materials to fungi commonly found in aquatic environments. Additionally, evaluating the fungicidal properties of these composites is of paramount importance. Research has demonstrated that some epoxy composites exhibit significant fungicidal activity, effectively inhibiting fungal growth and preventing damage to the coatings, which is crucial for maintaining the integrity of water transport systems.

Given the growing concerns about sustainability and environmental impact, further testing of these materials' resistance to common aquatic fungi is particularly timely and relevant. Conducting such tests will provide valuable insights into the durability and eco-friendliness of these materials, making them crucial components for enhancing the reliability, operational lifespan, and repairability of water transport systems.

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References to the relevant studies and standards further support the significance of these findings and underline the importance of continued research in this area. These efforts not only contribute to advancing transport technologies but also ensure the development of more sustainable and long-lasting materials for marine infrastructure.

2. MATERIALS AND METHODS

2.1 Research Materials

The widely used epoxy resin of the ED-20 brand (ISO 18280:2010) was employed to form the polymer matrix. Polyethylene polyamine (PEPA) (TU 6-05-241-202-78) was used as the hardener for the epoxy binder.

To enhance the properties of the polymer matrix, the following components were added to the epoxy binder:

1. Nanomodifier in the form of D-ascorbic acid (DAA) with a content of 0.1-2.0 wt. % relative to 100 wt. % of the ED-20 epoxy resin. Molecular formula of the modifier: $C_6H_8O_6$.
2. Microdispersed filler in the form of a synthesized aluminum-copper compound (SAMC). This powder is obtained through high-frequency processing and has the following composition: Al + Cu + $CuAl_2$ + Al_4C_3. The high-modulus compounds have an average particle size of $d_{avg} = 13 \pm 1$ μm.

Multifunctional discrete fibrous filler (BDVN) consisting of the following components, by percentage: polyester – 52 %, viscose – 40 %, elastane – 8 %.

Dimensions of the discrete fibers: length (l) = 0.8-1.2 mm, diameter (d) = 22-26 μm.

2.2 Research Methods for Epoxy Composites

The effect of microorganisms on polymer composites was evaluated according to ISO 846:2019, "Assessment of the action of microorganisms on plastics" [21]. This standard describes test methods for detecting the degradation of plastics caused by fungi, bacteria, and soil microorganisms.

The testing method requires inoculating samples with a spore suspension, incubating the inoculated samples, assessing any physical effects on the samples, and analyzing the fungal growth dynamics. The scope of the tests and the type of test strains depend on the intended application of the plastic. Under specific climatic and environmental conditions, microorganisms settle on the surface of plastic products and spread rapidly. However, their presence and metabolic products not only damage the polymer composite but also negatively affect the metal parts and mechanisms they are meant to protect.

The standard defines methods for assessing the degradation of plastics under the action of fungi and bacteria. Its goal is to determine the biodegradability of plastics and to establish the type and extent of the degradation of their properties [21]. Within the framework of this standard, the type and extent of degradation are determined by the following methods:

- visual inspection;
- mass change;
- change in physical properties.

The tests conducted according to the standard are applicable to all plastic materials with a flat surface that can be easily cleaned.

According to the standard, the following testing methods were used: Method A (fungal growth test) and Method B (determination of fungistatic effects). In Method A, the experiment was carried out as follows. Samples were formed into square shapes with dimensions of 50 ± 1 mm, with a recommended thickness of 0.5-2 mm. The samples were placed on the surface of a non-carbonated agar medium. The agar surface, as well as the test tubes, were inoculated with a spore suspension. Each test tube (petri dish) contained one sample, with all variants tested on five samples. Incubation was carried out at 28 ± 1 °C for 28 days. During this time, the tested microorganisms used the polymer as a food source for their growth. This test includes the impact of test fungal and bacterial strains on the material under specified temperature conditions over an agreed period.

In Method B, samples were placed in Petri dishes with nutrient media and loaded into special chambers operating at a temperature of 28 ± 1 °C and humidity above 90 %. According to ISO 846:2019, the following fungal strains were used for testing: *Aspergillus niger* (ATCC 6275), *Penicillium funiculosum* (ATCC 36839), *Chaetomium globosum* (ATCC 6205), *Trichoderma virens* (ATCC 9645), *Paecilomyces varioti* (ATCC 18502).

The samples were kept for 3 months. One sample was placed in each Petri dish, and all variants were tested on five samples. The criteria for evaluation were the change in mass and the biological resistance coefficient after 1, 2, and 3 months of exposure.

The tests and testing conditions described in the ISO 846:2019 standard are experimental and cover predefined potential programs. Procedures reflecting performance under real-world conditions should be applied for specific applications and long-term testing.

Primarily, the impact of microorganisms on the materials under investigation occurs through two distinct processes:

– direct action: degradation of the polymer, which serves as a nutrient for microorganism growth;

– indirect action: the effect of microbial metabolic products, such as discoloration, leading to further deterioration of properties.

3. DISCUSSION OF RESEARCH RESULTS

3.1 Study of Fungal Resistance and Fungicidal Properties of Composites

The ISO 846:2019 standard offers various options for evaluating fungal and bacterial proliferation independently and in combination. The following testing methods were selected for this study:

- Method A: Fungal Growth Test.
- Method B: Determination of Fungistatic Effect.

Method A – Fungal Growth Test

The treated plastic samples are exposed to a mixed spore suspension of fungi containing sufficient nutrients (without carbon) to allow fungi to utilize the polymer as a nutrient source. When fungi grow on the sample, it can be concluded that the polymer has low resistance to fungal growth, and indicating that the fungi utilize the sample material as a nutrient source.

After the predetermined incubation period, it is established whether the treated sample contains any nutrients or if the fungus has grown on the material, causing a decline in properties. At the end of the experiment, the samples are evaluated through visual inspection before and after cleaning, and the change in mass or other physical properties is determined.

If the samples do not contain any nutrients, the fungi cannot form mycelium, and the polymer does not undergo degradation.

Evaluation Criteria

The microbial growth on the sample surface is assessed visually. The rating scale varies from 0 (no growth) to 5 (significant growth):

0 – No visible growth of mold fungi was observed (under a microscope), indicating excellent resistance to fungal growth.

1 – Germinated spores and slightly developed mycelium observed (under a microscope).

2 – Branched mycelium observed (under a microscope).

3 – Slight growth visible to the naked eye but clearly observable under a microscope.

4 – Fungi observed on the sample surface, covering up to 25% of the area.

5 – Fungi observed on the sample surface, covering more than 25 % of the area.

If the evaluation test results show a score between 0 and 2, the material is considered resistant to fungi. A score of 0 or 1 indicates that the material has fungicidal properties.

Material Selection for Fungal Resistance Testing

Based on the mechanical properties of the materials, as described in previous works [13, 14], the following materials were selected for fungal resistance testing:

- base epoxy matrix (epoxy resin ED-20: hardener (PEPA) – 100: 10);
- MEK 1 (epoxy resin : DAA modifier : hardener – 100 : 1.5 : 10);
- MEK 2 (epoxy resin : SAMC filler : hardener – 100 : 2 : 10);
- MEK 3 (epoxy resin : DAA modifier : SAMC filler: hardener – 100 : 1.5 : 2 : 10);
- MEK 4 (epoxy resin : DAA modifier : SAMC filler: BDVN filler : hardener – 100 : 1.5 : 2 : 0.02 : 10).

The results of the fungal resistance study for the developed epoxy composites according to Method A are shown in Table 1.

Table 1 – Results of the evaluation of fungal growth on the surface of polymer composites

Material	The scale rating is suitable for method A	Assessment test results
Base epoxy matrix	3	Susceptible to fungi
MEK 1	3	Susceptible to fungi
MEK 2	2	Resistant to fungi
MEK 3	1	Fungicidal properties
MEK 4	0	Fungicidal properties

It can be asserted that the materials made from the base epoxy matrix and modified polymer, which received a rating of 3, contain an adequate amount of nutrients that promote fungal growth. A slight fungal growth was observed. As a result, they were classified as susceptible to fungi.

The material containing the dispersive filler (MEK 2) demonstrated minimal fungal growth, visible only under high magnification. This suggests that the material contains nutrients in very small amounts, making it resistant to fungal growth.

Composites incorporating both the modifier and filler (MEK 3) and those further enhanced with discrete fibers (MEK 4) exhibited significantly better performance, with ratings of 1 and 0, respectively. Based on these evaluations, it can be stated that these materials do not serve as nutrients for fungi. MEK 3 can be classified as fungistatic, with minor spore growth observed in isolated areas, while MEK 4 demonstrates fungicidal properties, completely preventing fungal growth.

Therefore, MEK 3 and MEK 4 composites are recommended for protecting components and products used in biologically active and aggressive environments. Their fungistatic and fungicidal properties ensure durability and reliability in conditions such as high humidity, contaminated soil, or marine environments.

Method B – Determination of Fungistatic Effects.

The treated samples are exposed to a mixed spore suspension of fungi, which includes a nutrient medium (with a carbon source). Even if the polymer does not contain nutrients, fungi can grow on the samples, and the products of their metabolism may attack the material, particularly the metabolized nutrient-agarized medium.

The surface of the samples was initially inoculated with a water suspension of test fungi (*Aspergillus niger, Penicillium funiculosum, Chaetomium globosum, Trichoderma virens, Paecilomyces varioti*) by evenly spraying the suspension using a sprayer. The samples were placed in Petri dishes with nutrient medium (seawater) and incubated for 3 months. Any inhibition of growth, both on the polymer composite and in the nutrient-agarized medium (area of inhibition), indicates their fungistatic activity (fungal death) or the presence of a fungicidal effect (fungal growth and reproduction cease).

Analysis of the fungal species formed on the sample surfaces revealed the following. The sample made from the base epoxy matrix showed a wide range of fungi that proliferated both in the volume and on the surface of the polymer. Specifically, all of the tested fungal species were identified: *Aspergillus niger, Penicillium funiculosum, Chaetomium globosum, Trichoderma virens, and Paecilomyces varioti*. The sample with the modifier (MEK 1) also contained all of these species except *Chaetomium globosum*. The MEK 2 material contained fungi of the species *Aspergillus niger, Penicillium funiculosum*, and *Trichoderma virens*.

Special attention should be given to the MEK 3 and MEK 4 samples. Specifically, the MEK 3 sample contained Trichoderma virens and Paecilomyces varioti, while MEK 4 contained only Trichoderma virens. However, their concentration was not sufficiently high. It can be concluded that the MEK 3 material, due to the presence of the modifier and dispersive filler, exhibits fungicidal effects. These ingredients prevent the growth and reproduction of almost all the tested fungi. In contrast, MEK 4, which also contains discrete fibers, produces a fungistatic effect. This fungistatic activity is demonstrated by the death of the fungi, as confirmed experimentally by two methods.

3.2 Technological Basis for the Formation of the Developed Protective Coating

Based on a series of experimental tests on mechanical properties and fungal resistance, a modified eco-friendly epoxy composite has been developed to improve water transport vehicles' operational and repair characteristics.

The primary purpose is to enhance the operational and repair properties of water transport vehicles by applying an eco-friendly, corrosion-resistant composite. The developed material can be used as a molded object (mechanism casing, bearing, foundation substrate), a protective anticorrosion coating, or as a high-performance adhesive.

Composition of the modified eco-friendly anti-corrosion composite (wt.%):

- epoxy dian resin ED-20 – 100;
- polyethylene polyamine hardener (PEPA) – 10;
- modifier: D-ascorbic acid – 1.5...2.5;
- fillers:
- synthesized aluminum-copper charge (Al (81 %) + Cu (9 %) + $CuAl_2$ (6 %) + Al_4C_3 (4 %)) (d_{ser} = 13 ± 1 μm) – 2...3;
- multifunctional discrete fibrous filler (polyester (52 %), viscose (40 %), elastane (8 %)) (l = 0.8...1.2 mm, d = 22...26 μm) – 0.02...0.03;

Technology for Forming the Material for Molding (for Three-Dimensional Objects) or Protective Coating.

Before forming the composition from individual ingredients, preparatory steps should be carried out, as the gelation period of the mixture, once the components are combined, ranges from 40 to 60 minutes. The dispersive powder is sieved to the required size at the preliminary stage, and fibers are crushed from waste using a crushing machine (Figure 1). The components are then manually mixed for 4 to 6 minutes using a drill with a special mixer at a rotor speed ranging from 600 to 800 rpm. Additionally, in some cases, the ingredients are mixed hydrodynamically at 25 to 30 °C for 10 ± 0.1 minutes, followed by ultrasonic treatment (UST) of the composition for 1.5 ± 0.1 minutes. After cooling the mixture to room temperature (within 60 ± 5 minutes), the hardener is added, and the composition is mixed for 5 ± 0.1 minutes.

During prolonged storage of liquid compositions, fillers tend to settle, especially at elevated temperatures. Therefore, it is recommended to pre-mix the mixtures (resin + modifier + fillers) in the containers before combining them with the hardener. After the hardener is added and thoroughly mixed with the composition, the mixture should be allowed to rest for 5 to 10 minutes before pouring (for three-dimensional object formation) or applying (for protective coatings) to remove air from the mixture, depending on ambient temperature.

The mold should be filled slowly with continuous pouring to allow for air removal from the compositions and to avoid "trapping" new air inclusions. Pouring should be continuous until the mold is completely filled, after which the material is kept at room temperature (295 ± 2 K) for 12.0 ± 0.1 hours. The next step is heating the composition to a temperature of 393 ± 2 K, maintaining this temperature for 2.0 ± 0.05 hours, and then cooling to 293 ± 2 K. The technological scheme for the formation and polymerization of the poured material in a mold or as a protective coating is shown in Figure 1. It should be noted that the molded object or coating can be polymerized at room temperature. In this case, the full curing time is 72 ± 1 hours.

The service life of the developed eco-friendly anticorrosive composite, depending on the operating conditions of the equipment and the implementation object, is 6 to 8 years. It is worth noting that the developed anticorrosive material demonstrates superior adhesion, mechanical, thermophysical, and anticorrosive properties compared to known global analogs (Table 2).

Table 2 – Properties of the developed modified composite

Property	MEK
Adhesion strength, MPa	43.1
Tensile stress, MPa	92.2
Impact toughness, kJ/m^2	15.3
Thermal stability, K	361
Chemical resistance – weight loss of samples after exposure (90 days) in acid solutions (HCl (12 %), H2SO4 (12 %)), %	0.1

The scope of application of polymer materials and protective coatings.

Polymeric materials and protective coatings, similar to those described in this article, are widely used in key industrial sectors, providing protection against corrosion and other aggressive impacts, significantly increasing the durability of equipment and infrastructure. The authors of this study believe that the developed materials can be effectively applied in areas such as transport, shipbuilding, and automotive industries to protect the hulls of ships and cars from external damage and corrosion. In marine ports, as well as in gas and oil refining industries, such materials could be used to protect equipment operating in aggressive environments. Additionally, the authors suggest that these coatings could enhance the reliability and longevity of critical components in the aerospace and military industries. Furthermore, it is anticipated that these materials may also be utilized in construction, offering corrosion protection in environments with high humidity or aggressive chemical conditions.

Promising areas for implementing protective coatings in waterborne transport and various industries to prevent equipment corrosion.

The epoxy nanocomposites developed, as discussed in this article, demonstrate significant potential for use across various industrial sectors and in waterborne transport, offering robust corrosion protection and enhancing the longevity of equipment. These composites, designed to improve the operational and repair characteristics of water transport systems, can be applied to protect the hulls of marine vessels of any tonnage, as well as both surface and underwater unmanned marine vehicles (drones). Additionally, they show promise in wind energy, where they can protect the bodies and blades of wind turbines. The composites are also applicable in automotive manufacturing, providing durable corrosion-resistant coatings. Furthermore, they are suitable for protecting pressure-resistant containers and any other industrial equipment exposed to harsh environments, such as seawater, gasoline, oil, alkalis, and acid solutions.

The authors believe that the versatility of these epoxy nanocomposites presents significant opportunities for enhancing the durability and functionality of equipment across various industries while maintaining eco-friendliness and corrosion resistance.

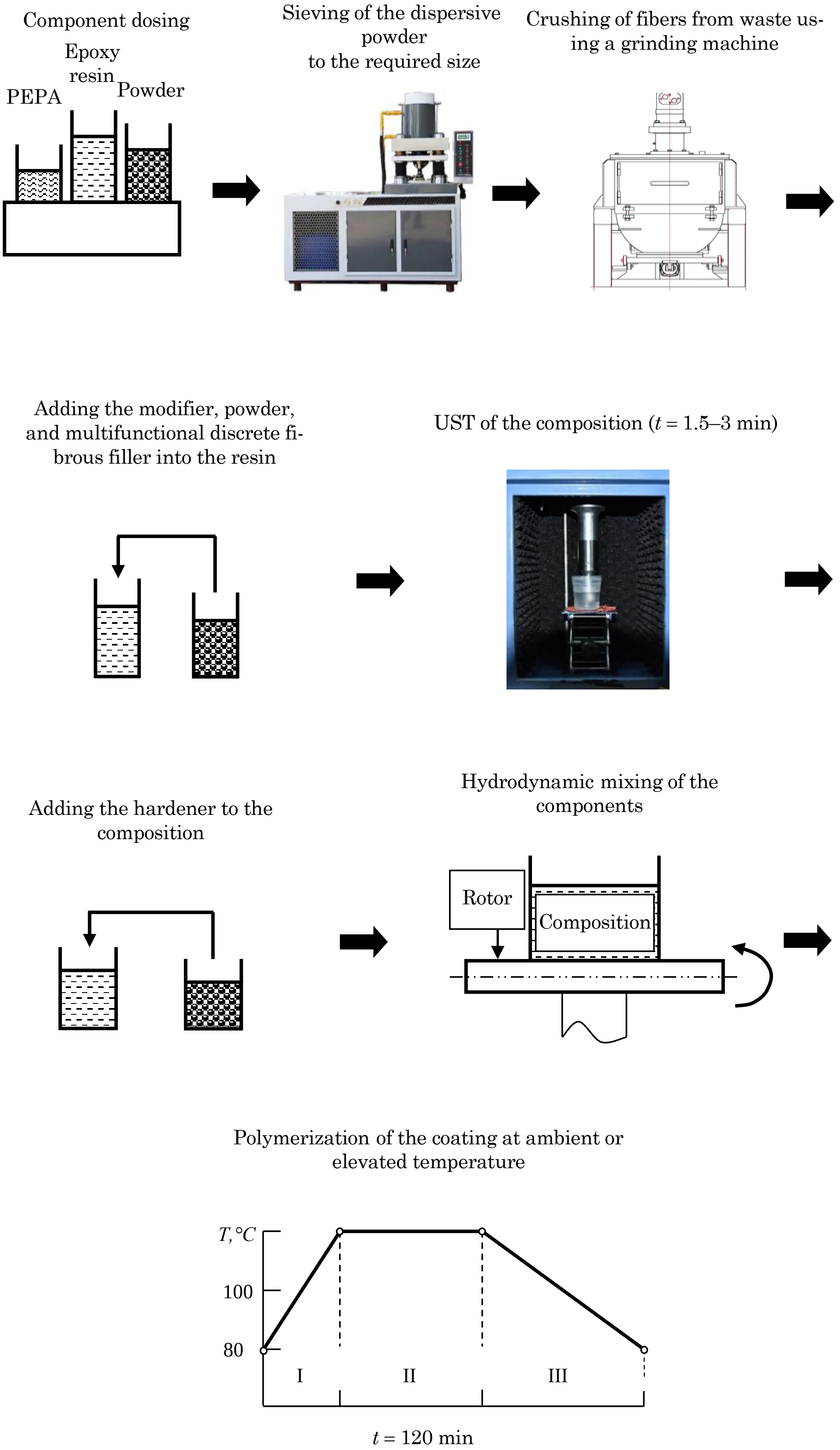

Fig. 1 – Technological scheme for coating formation and polymerization

The advantages of the developed material, compared to traditional options.

The developed material offers several significant advantages over traditional alternatives. It exhibits outstanding corrosion resistance in various aggressive environments, ensuring its durability even under harsh conditions. Additionally, the material shows high adhesion and cohesion strength, providing a strong bond between the coating and the substrate. Its increased impact resistance makes it more durable against mechanical damage. The material can function effectively across a wide temperature range, from – 30 °C to 180–200 °C, making it versatile for different environmental conditions. Moreover, it is economically advantageous, as it uses inexpensive ingredients, providing cost efficiency. The material is environmentally friendly in its solid state, contributing to sustainable practices. Furthermore, it possesses fungicidal properties, effectively preventing fungal growth, thus ensuring the long-term reliability and functionality of the coating.

Advantages for the industry of Ukraine.

For Ukrainian industry, the use of these developed materials presents significant advantages. The development of new composite materials holds considerable potential for enhancing the efficiency and durability of technological equipment in aggressive environments. Compared to both foreign and domestic analogs, these materials take into account key factors of aggressive environments where equipment operates, especially in the case of waterborne transport. This enables high performance under both normal and elevated temperatures, as well as in conditions where traditional materials often fail to withstand prolonged use. It is also important to note that the developed composites exhibit increased resistance to fungal damage, which is particularly crucial for equipment used in high humidity conditions, such as marine transport.

The technological process used to form these materials adheres to the best global standards, developed in countries such as the USA, the UK, Japan, Germany, and the Baltic States, demonstrating a high level of scientific and technological expertise. All necessary ingredients for producing these epoxy composites, including resins, hardeners, modifiers, and fillers, are readily available on the Ukrainian market and are produced in large volumes, which helps reduce production costs and makes these materials more economically accessible for domestic manufacturers. Furthermore, the newly developed technology for manufacturing these composites is competitive on the global market and allows their use in producing anti-corrosion coatings for various industrial sectors.

4. CONCLUSIONS

1. The study shows that applying the developed corrosion-resistant and environmentally friendly composite is necessary and beneficial for enhancing the operational and maintenance characteristics of water transport vehicles and equipment in other industries. This solution addresses a significant challenge in transport technologies by improving equipment reliability and optimizing maintenance processes. It is also a globally relevant task and an important factor in strengthening Ukraine's defense capability.

2. Research indicates that the composite demonstrates high biological resistance to common natural fungi. Experimental results predict its behavior during chemical and biological corrosion and identify the metabolic byproducts formed in aggressive environments. These findings allowed for an accurate evaluation of its resistance to fungal exposure. The composite, made from epoxy resin, a diaminic acid modifier, dispersive fillers, and multibased viscose fillers, exhibits both fungistatic and fungicidal properties. It is recommended for protecting components and products used in biologically active and aggressive environments.

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Перспективні технології у водному транспорті: розроблення і впровадження грибостійких та екологічно чистих епоксидних нанокомпозитів

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Обґрунтовано необхідність застосування епоксидних нанокомпозитів для збільшення ресурсу роботи обладнання для водного транспорту. Показано, що для додаткового збільшення ресурсу роботи обладнання водного транспорту необхідно у епоксидну смолу вводити не лише нано-, але й мікронаповнювачі та дискретні волокна. Це дозволить поліпшити не лише механічні властивості захисних покриттів, але й їх корозійну тривкість. Доведено доцільність використання екологічно чистих захисних матеріалів у водному транспорті. У роботі досліджено стійкість розроблених матеріалів до дії поширених у водному середовищі грибків. Також проведено аналіз фунгіцидності епоксидних композитів. У роботі вирішено науково-технічну задачу у сфері транспортних технологій – розроблено екологічно чисті матеріали для підвищення надійності функціонування устаткування, експлуатації та ремонту морського транспорту, що є ключовою науковою проблемою світового рівня.

Ключові слова: Епоксидні нанокомпозити, Транспортні технології, Покриття, Термін служби, Надійність, Технологія формування, Екологічна стійкість.