Research Article
ISSN 2658-5553
Received: December 10, 2022 Accepted: December 20, 2022 Published: December 29, 2022

The effect of solvents on the biostability of epoxy composites in the marine climate

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Keywords:

Bio-damage, Climate resistance, Mycelial fungi, Epoxy resin, Polyethylenepolyamine, Solvent

Abstract:

The object of research is epoxy composite materials with various solvents. Acetone, gasoline, solvent grade P647 and butanol were considered as solvents. The aim of the work is to establish the biological resistance of epoxy materials in marine climate conditions with the prospect of their use as impregnating compositions. **Method.** The biological resistance of epoxy composites was assessed by the species composition of microorganisms on the surface of the samples after they were kept for 21 months in an open area under natural and climatic conditions in Gelendzhik (Russia). The fingerprint method was used to identify microorganisms from the surface of the samples. **Results.** The species composition of microorganisms inhabiting epoxy composites was experimentally determined, depending on the type of solvent and the quantitative content of the hardener. Samples with solvents in their composition (gasoline and butanol) turned out to be the most resistant of the studied (30 mass parts of the solvent) to the aggressive effects of microorganisms. Compositions containing 12 mass parts of the hardener in their composition have the lowest biological resistance of the studied ones.

1 Introduction

The solving problems related to the biological destruction of materials and structures reduces the danger and intensity of biological contamination. Experiments to study the behavior of materials under the influence of microorganisms indicate a decrease in strength indicators, destruction of concrete and stone structures, peeling of plaster coatings, discoloration or the formation of pigment spots on paint coatings [1], [2], [3]. In many buildings and structures, contamination of premises by microorganisms exceeds the maximum allowable rate by several tens and even hundreds of times. At the same time, biodegradation processes are progressing every year.

An effective way to increase the durability and efficiency of concrete and reinforced concrete structures is their surface and zonal treatment with special compositions based on polymeric materials [2], [4], [5], [6]. Synthetic materials used in construction are generally more resistant to biological damage from microorganisms than materials based on natural products due to their specific structure and the insolubility of the components in water [7]. But in practice, there are significant cases of biological degradation of synthetic materials [8].

The biological resistance of protective polymer coatings largely depends on the composition of the composite material, the chemical nature of film-forming substances, hardeners, solvents, plasticizers and fillers [9], [10], [11]. The inclusion of additives such as stabilizers, plasticizers, fillers in them often makes materials vulnerable to microorganisms that change the properties and color of plastics, causing a loss of resistance and elasticity. In this case, bio-damage is associated with low bio-resistance of lowmolecular weight additives. In general, the development and creation of biostable compositions is reduced to optimizing the composition of the material for all its components.

During operation in natural and climatic conditions, building materials and structures based on polymer binders are subjected to the complex effects of the following negative effects that have a destructive effect on composites: UV radiation, salt mist, temperature drop and increased humidity. Also, the processes of operation of building materials and products in various climatic conditions are associated with the risk of exposure to composite building materials of various microorganisms that have a destructive effect [12], [13], [14], [15]. Among the biodestructors affecting materials and structures, mycelial fungi, bacteria and other microorganisms are isolated [2], [16], [17]. Building materials interact with these biodestructors in different ways [14], [18], [19], [20]. The process of bio-damage is triggered by the impact of their metabolic products (acids, alkalis, redox and hydrolytic enzymes and other aggressive substances) on the components of building materials, destroying binders, solutions, concrete, metal products, protective coatings and other structural elements [21]. The vital activity of microscopic organisms is most active under favorable conditions of their development. Biodegradation is most intense at high humidity, relatively high temperatures, an abundance of dust and organic pollution, and the quality of the surface of the structure. Ecological features of the development of microorganisms are associated with the habitat in the region where the exposure of the studied samples takes place [22], [23], [24]. Biodegradation directly depends on the aging of materials, products and structures. Atmospheric aging of polymers leads to a chemical change in the structure and composition of the initial composite, which can contribute to the use of available degradation products as a food source for mycelial fungi and the penetration of their hyphae into the structure [4], [25].

Thus, there is an important problem of joint research of the processes of climatic and biological resistance of polymer materials of building materials and identification of the influence of system components on the distribution of the main biodestructors of these composites.

The purpose of the work is to establish the effect of solvents on the biological resistance of polymer materials with the prospect of their use as impregnation compositions.

Research objectives:

1. Consider the climatic factors of the Black Sea coast as environmental conditions.
2. Conduct studies to determine the species composition of microorganisms that populate on samples of epoxy composites with various solvents when kept on an open site in a marine climate.
3. Evaluate the effect of the quantitative content of the hardener and the type of solvent on the biological stability of epoxy composites.

2 Materials and Methods

Epoxy-diane resin of ED-20 grade was used as binder in the test compositions. The hardener was polyethylene polyamine. The amount of solvent was 30% by weight of the binder, which corresponds to the preparation of low viscosity impregnation compositions. As a binder in the studied compositions, epoxy-diane resin of the ED-20 brand was used. The hardener was polyethylenepolyamine. The amount of solvent was 30% by weight of the binder, which corresponds to the preparation of impregnating compositions of low viscosity. The following were considered as solvents: 1) AI-92 gasoline; 2) acetone; 3) solvent brand P647; 4) butanol. Epoxy resin grade ED-20 is a liquid reactive oligomeric product based on diphenylolpropane diglycidyl ether. Polyethylene polyamine is a universal amine-type hardener used for cold curing of epoxy resins, which is a viscous liquid from light yellow to dark brown without inclusions with a density of 950-1100 kg/m^3.

As solvents were considered:

1) gasoline of the AI-92 grade;
2) acetone;
3) solvent grade R647;
4) butanol.

Unleaded gasoline of the AI-92 brand is a high-octane fuel, an aliphatic hydrocarbon, an organic compound with linear and branched chains of atoms.

Acetone $(CH_3)_2CO$ is a colorless, highly volatile and flammable liquid with a characteristic pungent odor, containing from 99.5% acetone. The density of organic matter is from 78.9 to 79.1 g/cm^3.

The solvent of the R647 brand is a transparent colorless or yellowish liquid without suspension, which does not delaminate, does not produce a precipitate. Its composition includes the following elements: acetone 7%, ethyl cellosolve 8%, butyl acetate 10%, ethyl alcohol 10%, butanol 15%, toluene 50%. Flammable composition, maximum water content 0.6%, density 0.87 g/ cm^3.

Butanol (C_4H_9OH) is a colorless, flammable, viscous liquid with a characteristic smell of fusel oil. Density at 20 °C 0.809-0.810 g/cm^3.

The quantitative content of the components in the compositions is shown in Table 1.

Table 1. The quantitative content of the components in the compositions

Composition No.	Component content, mass part			Type of solvent
	Epoxy-diane resin	Hardener	Solvent	
1	100	8	30	gasoline grade AI-92
2		10		
3		12		
4		8		acetone
5		10		
6		12		
7		8		solvent grade R647
8		10		
9		12		
10		8		butanol (C_4H_9OH)
11		10		
12		12		

The biological stability of epoxy composites was evaluated by the species composition of microorganisms on the surface of the samples after they were kept for 21 months in an open area under natural and climatic conditions in Gelendzhik (Krasnodar Krai, Russia). After the expiration of the experiment in laboratory conditions, the identification of the type of micromycetes was carried out. The imprint method was used to identify microorganisms from the surface of the samples. This method provides for direct contact of a dense nutrient medium with the object under study with further keeping the obtained samples under optimal conditions for the development of microorganisms and their subsequent species identification.

3 Results and Discussion

As a result of experimental studies of samples of epoxy composites exposed in the natural and climatic conditions of the marine climate, various microorganisms were detected on the surface of the samples. The results of the corresponding microbiological study c are shown in Tables 2-5.

Table 2. Species and quantitative composition of microorganisms on the surface of composites with gasoline grade AI-92

Composition No.	Species composition of microorganisms on samples	Quantity of fungi		Presence of bacteria
		types	genus	
1	Aspergillus niger, Aspergillus oryzae, Chaetomium dolichotrichum, Alternaria brassicicola, Mucor corticola	5	4	-
2	Aspergillus oryzae, Chaetomium dolichotrichum, Alternaria brassicicola, Cladosporium elatum, Fusarium moniliforme, Mucor corticola	6	6	-
3	Aspergillus niger, Aspergillus oryzae, Chaetomium dolichotrichum, Alternaria brassicicola, Cladosporium elatum, Mucor corticola	6	5	-

Analyzing the composition of the microflora (Table 2), isolated from the surface of epoxy materials with the addition of AI-92 gasoline after testing in atmospheric conditions of a humid maritime climate, the following genera of fungi related to asconomycete fungi were established: Aspergillus, Chaetomium, Alternaria, Cladosporium and Fusarium, as well as the genus of lower mold fungi of the Zygomycete class Mucor. When adding gasoline in the amount of 30 mass parts per 100 mass parts resins, Aspergillus oryzae, Chaetomium dolichotrichum, Alternaria brassicicola, Mucor corticola were found on samples after climatic exposure. Aspergillus niger is present only on the surface of compositions 1 and 3. The composition with a minimum amount of hardener (in the amount of 8 mass parts) was not subject to colonization by filamentous fungi of the genera Cladosporium and Fusarium. These compositions of composites are characterized by the absence of bacteria on the surface of the samples.

Table 3. Species and quantitative composition of microorganisms on the surface of composites with acetone

Composition No.	Species composition of microorganisms on samples	Quantity of fungi		Presence of bacteria
		types	genus	
4	Aspergillus oryzae, Aspergillus terreus, Aspergillus ustus, Alternaria brassicicola, Cladosporium elatum, Cladosporium macrocarpum, Fusarium avenaceum, Fusarium moniliforme, Mucor corticola	9	5	-
5	Aspergillus niger, Aspergillus ustus, Alternaria brassicicola, Alternaria tenuissima, Cladosporium elatum, Cladosporium macrocarpum, Fusarium avenaceum, Fusarium moniliforme, Mucor corticola	9	5	-
6	Aspergillus ustus, Chaetomium dolichotrichum, Chaetomium globosum, Alternaria brassicicola, Alternaria alternata, Cladosporium elatum, Cladosporium macrocarpum, Fusarium moniliforme, Penicillium chrysogenum	9	6	+

Analyzing the data obtained for a group of samples with acetone, 15 species of micromycetes belonging to the genus Aspergillus (4 species), Chaetomium (2 species), Alternaria (3 species), Cladosporium (2 species), Fusarium (2 species), Penicillium (1 species), Mucor (1 species). According to the studies, it was found that the filamentous fungi Alternaria brassicicola, Cladosporium elatum and Fusarium moniliforme were found on all formulations that contain acetone. The genera of micromycetes Chaetomium and Penicillium, as well as bacteria, are found only on the surface of composites of composition No. 6, which includes 12 mass parts hardeners per 100 mass parts astringent.

Analyzing the data in Table 4, epoxy composites with the specified solvent at 10 mass parts of the hardener were exposed to the least aggressive action from microorganisms. The samples containing 12 mass parts of the hardener received the maximum volume of colonization by microorganisms, and only on them were fungi of the genus Penicillium found. According to the results obtained, indicated in Table 4, we come to the following conclusions: 1) on composites containing 30 wt. including P647 solvent, from 5 to 11 species of fungi of the following genera were isolated: Aspergillus (4 species), Chaetomium (2 species), Alternaria (3 species), Cladosporium (2 species), Fusarium (2 species), Penicillium (1 species) , Mucor (1 species), while bacteria were not found on the samples; 2) fungi Cladosporium elatum, Alternaria brassicicola are present on the surface of all studied composites; 3) a smaller number of species of filamentous fungi is established for composition 8 containing 10 parts of hardener; 4) samples containing 12 mass parts of the hardener received the maximum volume of colonization by microorganisms.

Table 4. Species and quantitative composition of microorganisms on the surface of composites with solvent P647

Composition No.	Species composition of microorganisms on samples	Quantity of fungi		Presence of bacteria
		types	genus	
7	Aspergillus ustus, Chaetomium dolichotrichum, Alternaria brassicicola, Alternaria tenuissima, Cladosporium elatum, Cladosporium macrocarpum, Fusarium avenaceum, Fusarium moniliforme, Mucor corticola	9	6	-
8	Chaetomium dolichotrichum, Alternaria brassicicola, Cladosporium elatum, Fusarium moniliforme, Mucor corticola	5	5	-
9	Aspergillus niger, Aspergillus oryzae, Aspergillus terreus, Chaetomium globosum, Alternaria brassicicola, Alternaria tenuissima, Alternaria alternata, Cladosporium elatum, Cladosporium macrocarpum, Penicillium cyclopium, Mucor corticola	11	6	-

Table 5. Species and quantitative composition of microorganisms on the surface of composites with butanol

Composition No.	Species composition of microorganisms on samples	Quantity of fungi		Presence of bacteria
		types	genus	
10	Aspergillus niger, Aspergillus oryzae, Aspergillus ustus, Alternaria brassicicola, Cladosporium elatum, Penicillium nigricans, Paecilomyces variotii	7	5	-
11	Aspergillus niger, Alternaria alternata, Cladosporium elatum, Cladosporium macrocarpum, Penicillium cyclopium	5	4	-
12	Aspergillus niger, Aspergillus oryzae, Aspergillus ustus, Alternaria brassicicola, Alternaria tenuissima, Cladosporium elatum, Cladosporium macrocarpum, Fusarium moniliforme	8	4	-

Table 5 shows the results of studies of polymer fouling by micromycetes using butanol (C_4H_9OH) as a solvent. Found from 5 to 7 species of fungi: Aspergillus (3 species), Alternaria (3 species), Cladosporium (2 species), Penicillium (2 species), Paecilomyces (1 species), Fusarium (1 species), no bacteria were found. Micromycetes of the species Aspergillus niger and Cladosporium elatum were found on the surface of samples of all studied compositions. Separate types of filamentous fungi are identified on certain formulations: Penicillium nigricans (composition No. 10); Penicillium cyclopium and Alternaria alternata (composition No. 11). Samples of composition No. 11 with a content of 10 mass parts of the hardener were subjected to a minimum colonization by microorganisms.

4 Conclusions

1. The total number of fungal genera identified on samples that are kept in an open area under conditions of variable temperatures, UV radiation, salt fog and high humidity on the Black Sea coast is 8, species - 19. As can be seen from the analysis, the most common on the surface of epoxy composites in the specified air conditions are the following genera of microscopic fungi - Aspergillus, Alternaria, Cladosporium, Mucor.

2. The most resistant of the studied samples (30 mass parts of the solvent) to the aggressive action of microorganisms were samples containing solvents: AI-92 gasoline and butanol.

3. The compositions of composites containing 8 and 10 mass parts of the hardener are the least susceptible to colonization by various microorganisms in a humid maritime climate, both in quantitative and qualitative terms.

4. Compositions containing 12 mass parts of the hardener in their composition have the lowest biological resistance among those studied.

5. The conducted studies make it possible to establish the formulation of impregnating and other materials based on epoxy binders, which makes it possible to prevent or minimize the likelihood of microscopic organisms populating the surface of polymer concrete.

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