The study of species composition of the mycoflora, selected surface samples poliferation composites in humid maritime climate

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Abstract. The results of the study to establish the species composition of microorganisms settled on samples of polyether-acrylate composites after they are kept in sea water and in climatic conditions of the black sea coast are presented. The composition of the curing system in the composite and the conditions of holding the samples have a significant effect on the species composition of microorganisms.

Introduction

Building materials and products in some buildings and structures, as well as in the air in open areas, along with physical and chemical effects are damaged by microbiological media [6,7,8,9]. Living organisms settle on the surface of samples of concrete and other building materials, if there are organic substances on this surface or in contact with the surface there is a medium (air, water, liquids) containing substances that serve as food for microorganisms (organic substances, sulfur and its compounds, hydrocarbons, etc.) [5,10,11]. Such conditions are more typical for buildings of food production, livestock buildings, enterprises of microbiological industry, etc. [3,4,5,9]. For building materials and products of microorganisms have an impact not only with internal but also with external parties. The causes of biological fouling of structures of buildings and structures from the outside are usually dustiness of facades, high content of ammonia, sulfur, carbon and other compounds in the air, as well as violations of drainage elements and waterproofing [1,2,9].

Microorganisms settled on the structures (bacteria, mycelial fungi, etc.) lead to destruction, discoloration of materials. Microorganisms, in the process of life settled on the surface or at some depth in the body of the material of construction, secrete metabolic products. As a rule, metabolic products (________, enzymes) cause damage to concrete and other materials of inorganic nature. Materials on the basis of wood, as well as some types of plastics, paints and other organic building materials, along with damage from metabolites can be used by microorganisms in the life cycle as a source of energy – food.

Prevention of corrosion due to biological factors is possible by giving biocidal structure of the material, as well as by applying to its surface corrosion protective coatings, which are usually performed on the basis of polymeric materials.

Currently, polymer composite materials based on various synthetic resins are increasingly used in construction. They are more effective in comparison with traditional materials (cement, lime, gypsum and other concrete) during operation under the influence of aggressive factors: physical, chemical, biological [4,12]. Polymer materials are used both for the manufacture of structural materials and for
coating on building structures and technological equipment [4]. In the first case, polymer concrete, glass and carbon fiber are used, in the second – paint materials. The main component of these materials – synthetic binders, which after curing form a thin solid film or solid binds to a common monolith filler of various types (granules, fibers, etc.). Epoxy, furan, polyester and other resins are used as synthetic binders. These binders are cured by heating, but most often under the action of various hardeners. The composition also includes plasticizers and fillers.

An important element in the search for the causes of biodegradation is to identify resistance to microscopic fungi polymer compositions obtained using different compositions of the curing system of the polymer binder and components of the polymer-mineral mixture.

Mushroom resistance of polymeric materials and their components in the laboratory is evaluated according to GOST 9.049-91 and GOST 9.050-89. However, laboratory studies do not allow to take into account the impact of climatic factors on polymer building materials, i.e. to determine the degree of relationship between the intensity of the processes of biological damage and climatic aging. It is known that the action of climatic factors causes a change in the composition and structure of polymeric materials and, as a result, changes the species composition of microorganisms involved in destructive processes [5].

Materials and methods
The aim of this work was to study the changes in species richness of mycoflora isolated from polyethyracrylate polymer composites depending on their composition and test conditions (humid Maritime climate, solar radiation, sea water). Compositions on the basis of polyester-acrylate resin of MGF-9 brand, cured by a system consisting of a hardening initiator of cyclohexanone peroxide (PCON-2) and a hardening accelerator of cobalt octoate (OK-1) were considered. Also, samples filled with sand fractions of 0.16-0.315 mm and 0.315-0.63 mm were tested, the composition of the curing system in them did not change. Compositions with different content of the curing system obtained by the planning matrix (Kono plan) are shown in table. One

| №   | Planning matrix | Working matrix |
|-----|-----------------|----------------|
|     | X₁  | X₂  | content OK-1, mass / h per 100 mass / h resin | the content of PCON-2, mass / h per 100 mass / h resin |
| 1   | -1  | -1  | 3.2                          | 1.6                           |
| 2   | 0   | -1  | 4.4                          | 1.6                           |
| 3   | +1  | -1  | 5.6                          | 1.6                           |
| 4   | -1  | 0   | 3.2                          | 2.8                           |
| 5   | 0   | 0   | 4.4                          | 2.8                           |
| 6   | +1  | 0   | 5.6                          | 2.8                           |
| 7   | -1  | +1  | 3.2                          | 4                             |
| 8   | 0   | +1  | 4.4                          | 4                             |
| 9   | +1  | +1  | 5.6                          | 4                             |

Samples of 5-fold repetition were kept on the black sea coast of Krasnodar region in an open area, under a canopy, as well as in sea water. After 6 months in the laboratory, identification to the type of micromycetes contaminating the above samples was carried out. Identification of micromycetes was carried out on the basis of their morphological and cultural characteristics using the identification keys: Raper K. B., S. A. (Raper, Thorn, 1949); K. B. Raper, D. I. fennel (Raper, Fennell, 1965); N. M. PI-duplica (1971); M. A. Litvinov (1967); A. A. mil’ko (1974); T. S. Kirilenko (1977); K. Dons, V. Gamay (Donch, Gams, 1980); A. Yu. Lugauskas, A. N. Mikul-Skene, D. J. Laurene (1987); V. I. Bilai, E. Z. Koval (1988).
Results

The results of studies of the species composition of micromycetes, contaminating various formulations of polymer composites, which are for a long time in the climatic conditions of the black sea coast, are presented in table. 2-4.

Table. 2. Test result

| Composition number of composites | Species composition of microorganisms on the samples aged for 3 months on the open area of the Black Sea coast |
|---------------------------------|---------------------------------------------------------------------------------------------------------|
| 1.                              | Aspergillus oryzae, Aspergillus candidus, Aspergillus niger, Aspergillus sydowi, Penicillium tardum, Cladosporium elatum, Cladosporium macrocarpum |
| 2.                              | Aspergillus ustus, Aspergillus oryzae, Aspergillus candidus, Aspergillus niger, Aspergillus sydowi, Aspergillus clavatus, Cladosporium elatum, Cladosporium macrocarpum, Gliocladium roseum, Gliocladium catenulatum |
| 3.                              | Aspergillus oryzae, Aspergillus candidus, Penicillium canescens, Gliocladium catenulatum |
| 4.                              | Aspergillus oryzae, Aspergillus clavatus, Penicillium canescens, Gliocladium catenulatum, Gliocladium roseum, Cladosporium macrocarpum |
| 5.                              | Aspergillus ustus, Aspergillus terreus, Gliocladium roseum, Cladosporium macrocarpum |
| 6.                              | Aspergillus oryzae, Aspergillus candidus, Aspergillus niger, Aspergillus ustus, Aspergillus clavatus, Penicillium urticae, Cladosporium macrocarpum, Gliocladium catenulatum, Gliocladium roseum |
| 7.                              | Aspergillus candidus, Aspergillus niger, Aspergillus oryzae, Penicillium tardum, Cladosporium elatum, Cladosporium macrocarpum, Gliocladium catenulatum, Gliocladium roseum |
| 8.                              | Aspergillus oryzae, Penicillium urticae, Gliocladium catenulatum, Cladosporium macrocarpum, Chaetomium dolichortrichum |
| 9.                              | Aspergillus oryzae, Penicillium urticae, Gliocladium catenulatum, Cladosporium macrocarpum, Chaetomium dolichortrichum |

Table. 2 shows the composition of the microflora isolated from samples aged in an open area near the Black sea. In this case, the polymer samples are destroyed by solar radiation, salt fog and high humidity. As a result of tests, 17 types of micromycetes belonging to the class of hypomycetes (SEM. Moniliaceae (p.p. Aspergillus - 7; Penicillium – 3, Gliocladium – 2):, Dematiaceae (p.p. Cladosporium - 2 species) and 1 species to the class Ascomycetes (p. Chaetomium). The results showed the predominant contaminants of the composition R. fungi Aspergillus, Penicillium and R. R. Gliocladium.

In table. 3 and 4 shows the composition of microflora isolated from samples under a canopy on the coast and after aging in seawater, respectively.

Table. 3. Test result

| Composition number of composites | Species composition of microorganisms on the samples aged for 3 months under a canopy on the Black Sea coast |
|---------------------------------|---------------------------------------------------------------------------------------------------------|
| 1.                              | Aspergillus oryzae, Alternaria brassicae, Chaetomium dolichortrichum, Cladosporium elatum |
| 2.                              | Aspergillus terreus, Aspergillus clavatus, Aspergillus oryzae, Cladosporium elatum, Gliocladium roseum, Gliocladium catenulatum |
3. *Aspergillus oryzae*, Aspergillus ustus, Penicillium claviforme, Botryosporium longibrachiatum

4. *Aspergillus niger*, Aspergillus clavatus, *Aspergillus ustus*, Alternaria brassicae, *Gliocladium catenulatum*, Cladosporium macrocarpum

5. *Gliocladium catenulatum*, Cladosporium macrocarpum

6. *Aspergillus ustus*, Aspergillus candidus, *Gliocladium catenulatum*, Gliocladium roseum

7. Aspergillus sydowi, *Aspergillus oryzae*, *Fusarium sambucinum*, *Gliocladium catenulatum*, Gliocladium roseum

8. *Aspergillus niger*, *Fusarium sambucinum*, *Gliocladium catenulatum*, Gliocladium roseum

9. *Aspergillus niger*, *Fusarium sambucinum*, *Gliocladium catenulatum*, Gliocladium roseum

| Composition number of composites | The species composition of microorganisms on the samples, after aging for 3 months in sea water |
|---------------------------------|-------------------------------------------------------------------------------------------|
| 1.                              | *Aspergillus oryzae*, Alternaria brassicae, *Chaetomium dolichortrichum*, Cladosporium elatum |
| 2.                              | Aspergillus terreus, Aspergillus clavatus, *Aspergillus oryzae*, Cladosporium elatum, *Gliocladium roseum*, *Gliocladium catenulatum* |
| 3.                              | *Aspergillus oryzae*, Aspergillus ustus, Penicillium claviforme, Botryosporium longibrachiatum |
| 4.                              | *Aspergillus niger*, Aspergillus clavatus, *Aspergillus ustus*, Alternaria brassicae, *Gliocladium catenulatum*, Cladosporium macrocarpum |
| 5.                              | *Gliocladium catenulatum*, Cladosporium macrocarpum |
| 6.                              | *Aspergillus ustus*, Aspergillus candidus, *Gliocladium catenulatum*, Gliocladium roseum |
| 7.                              | Aspergillus sydowi, *Aspergillus oryzae*, *Fusarium sambucinum*, *Gliocladium catenulatum*, Gliocladium roseum |
| 8.                              | *Aspergillus niger*, *Fusarium sambucinum*, *Gliocladium catenulatum*, Gliocladium roseum |
| 9.                              | *Aspergillus oryzae*, Penicillium urticae, *Gliocladium catenulatum*, Cladosporium macrocarpum, *Chaetomium dolichortrichum* |

From table 3 and 4 it can be seen that the composition of the mycoflora isolated from the samples subjected to these climatic influences is almost identical. This can be explained by the similarity of the test conditions characterized by high humidity. Mushrooms retain vital activity both in the absence of air and in the air, in both cases, almost no exposure to solar radiation. With samples of polymeric composites has been allocated 21 hyphomycetes in this respect. Moniliaceae (p.p. Aspergillus - 7; Penicillium – 1, Gliocladium – 2), Dematiaceae (p.p. Cladosporium – 2 types; Alternaria - 1), Tuberculariaceae (p. 11). Fusarium - 1 species) and 1 species of Ascomycetes (p. Chaetomium). The results of the studies showed the predominance among the contaminants of this composition of fungi R. Aspergillus and R. Gliocladium. This, apparently, can be explained by the fact that micromycetes
of R. Aspergillus, having a powerful metabolic apparatus, can actively destroy a wide range of polymeric materials of different chemical composition, including hydrocarbons.

On the surface of the samples disappeared such species of fungi as Penicilium tardum and Penicillium canescens, but compared with samples aged in the open area, there are new species such as Alternia brassae, Chaetomium dolichortrichum, Botryosporium longibranchiatum, Fusarium sambucinum. There is a tendency to a smaller number of species of microorganisms on the composition №5. Movement patterns preferability compositions of sea water under a canopy no effect on the species richness of the microflora isolated from the samples with different content of the hardening system.

A different picture of the species composition of micromycetes is observed on the above composites placed on an open area (table.2). The appearance of R. R. Penicilium tardum and Penicillium canescens was noted.

Analyzing the distribution of the species composition of the microflora on the composition of preferability composites, we note that the lowest diversity of mycoflora from selected samples of the composition No. 5. At the same time it is completely absent the most common R. Aspergillus. This can be explained by the fact that at this ratio of components there is a more complete reaction and there are no components of the original curing system in its pure form, which serve as a nutrient medium for p. Aspergillus. This is confirmed by studies of strength parameters of these compositions [14]. Composition №5 showed maximum compressive strength.

Non-filled compositions of polymeric materials are used as a basis for the creation of paints and varnishes, and filled - in the production of anti-corrosion thickened coatings. The latter are manufactured using various fillers, which reduces the consumption of the polymer binder and increases the wear resistance of the composite material.

The test results of the samples filled with quartz powder are shown in table. 5.

| Composition No. | Test conditions | Species composition of microflora |
|----------------|----------------|----------------------------------|
| The fractions filled with sand 0,16-0,315 | In the open area | Aspergillus oryzae, Penicillus urticae, Gliocladium roseum, Cladosporium macrocarpum, |
| | Under the canopy | Aspergillus oryzae, Penicillus urticae, Gliocladium catenulatum, Cladosporium elatum, Fusarium solani |
| | In sea water | Aspergillus oryzae, Penicillus urticae, Gliocladium catenulatum, Cladosporium elatum, Fusarium solani |
| The fractions filled with sand 0,316-0,63 | In the open area | Aspergillus oryzae, Aspergillus candidus, Aspergillus sydowi, Aspergillus niger, Penicillum canescens, Gliocladium catenulatum |
| | Under the canopy | Aspergillus ustus, Chaetomium dolichortrichum, Penicillum canescens, Gliocladium catenulatum |
| | In sea water | Aspergillus ustus, Chaetomium dolichortrichum, Penicillum canescens, Gliocladium catenulatum |

According to the results of the tests of composites filled with quartz powder, it can be noted that in the filled composites the number of species of microorganisms isolated from the surface of the tested samples increases with an increase in the size of the filler (replacing the sand fraction of 0.16-0.315 mm. by a fraction of 0.315-0.63 mm.) This pattern is observed both in tests in sea water and in the open air and under a canopy near the Black sea.
Summary
1. With a species composition of microorganisms staying on preferability composites while maintaining the samples in wet conditions the black sea coast under the open sky, under a canopy, and also after ageing in sea water.
2. It is established that the surface of the samples while maintaining the under the open sky experiencing the effects of solar radiation, is inhabited by a large number of species of mycoflora than the samples aged under the canopy and in sea water.
3. It was found that the samples aged on the coast under a canopy have the same species diversity of fungi on the surface as the samples aged in sea water.
4. The optimal content of curing systems is established, in which the smallest number of species of microorganisms is characteristic.
5. The identified increase in species composition of microorganisms in preferability composites under the change of dispersion and the amount of filler.

References
[1] Erofeev V T, Dergunova A V 2008 Economic efficiency dolgovechnost stroitelnih structures (Building materials) 2 88-89.
[2] Erofeev V T, Bogatov A D, Bogatova S N, Kaznacheev S V, Smirnov V F 2012 The influence of the operating environment on the biostability of slinging composites (civil Engineering journal) 7 (33) 23-31.
[3] Erofeev V T, Lazarev A V, Bogatov A D, Kaznacheev S V, Smirnov V F, Khudyakov V A 2013 Optimization of the composition of biostatic epoxy composites, utverjdaet aminophenolic hardener (proceedings of Kazan state University of architecture and construction) 4 (26) 218-227.
[4] Bobryshev A N, Erofeev V T, Kolemasov V N 2013 Kompozicionnye polymeric materials (Publishing house DIA, Moscow).
[5] Erofeev V T, Lazarev A V, Bogatov A D, Smirnov V F, Smirnova O N, Zakharova E A 2013 Species composition of microflora isolated polymer composites based on polymer resins in humid marine climate (proceedings of the Kazan GUS) 2 (24) 233-237.
[6] Alekseev S N, Ivanov F M, Modry S, Shlisel P 1990 Durability of reinforced concrete in aggressive environments (sovm, Stroizdat, Moscow).
[7] Komokhov P G, Komokhov A P 2004 Biodegradation of structural materials and the scientific basis of their protection, biological Damage and biocorrosion in construction: materials mezhdunarod (Science-tech. Conf., Saransk, Publishing house of Muzzles. UN-TA) 12-14.
[8] Elders S A, Startsev S A 2004 Methods of elimination of consequences of the biodeterioration of building structures, Biodeterioration and corrosion in construction: proceedings of the international (Science-tech. Conf. – Saransk: Publishing house of Muzzles. UN-TA) 15-20.
[9] Solomatov V I, Erofeev V T, Smirnov V F 2001 Biological mechanics of materials (Publishing house of Muzzles. UN-TA, Saransk).
[10] Erofeev V T, Yerofeyev V T, Bogatov A D, Bogatova S N, Smirnov V F 2010 The effect of binder aging on abiological durability (proceedings of the Kazan state architectural-construction University) 2 (14) 213-217.
[11] Gusev B V, Erofeev V T, Smirnov V F, Dergunova A V, Bogatov A D 2012 Influence of aging binders on their biological stability (Industrial and civil engineering) 4 52-58.
[12] Gusev B V, Kondrashenko V I, Maslov B P, Pisupati A S 2006 Formation of structure of composite materials and their properties (Scientific world, Moscow).
[13] Kablov E N 2012 Corrosion or life (Science and life) 11 16-21.
[14] Erofeev V T, Myshkin V A, Kablov E N etc. 2014 Durability of polymeric composites based on preferability resin in the humid marine climate (Regional architecture and construction) 3 5-12.