Influence of environmental factors on the processes of biodegradation of vinylester composites

E N Kablov\(^1\), V T Erofeev\(^2\), A V Dergunova\(^2\)*, E V Deraev\(^2\) and D A Svetlov\(^2\)

\(^1\)The Russian Research Institute of Aviation Materials, 17 Radio str., Moscow, Russian Federation
\(^2\)National Research Mordovia State University, 68 Bolshevistskaya str., Saransk, Russian Federation

* anna19811981@mail.ru

Abstract. Polymer composite materials based on various binders are widely used in the construction industry. Polymer composites are characterized by high performance. Of great interest is the study of more economical compared to other polymers vinylester composites. They are successfully used in the US and European countries. In Russia, the use of polyester resin as a binder is not as common as abroad. At the same time, the influence of environmental factors on the biodegradation of vinyl ester polymer composites has not been sufficiently studied to date. This study is devoted to the study of the biostability of vinyl-ether composites under the influence of environmental factors. The most significant are the processes of atmospheric aging of materials, which include a complex effect of climatic and environmental factors. The study of changes in the species composition of microflora and indicators of resistance of composites, depending on their composition and operating conditions in the conditions of the seacoast.

Keywords: polymer composites, vinylester resin, bio-damages, microbiological impact, climate factors

1. Introduction

An important direction of modern industrial and construction production is the creation of composite materials, among which polymer plays a leading role due to the highest values of specific indicators of strength, stiffness and other properties [1-10]. Their development is associated with the development of new binders, which, in addition to high mechanical performance, must have heat and heat resistance, chemical resistance, etc., and, of course, manufacturability, since there is a relationship between the properties of the binder and the composite material. Among polymer binders, reactive oligomers and monomers predominate (phenolic, polyethyl, acrylate, furan, and primarily epoxy), whose chemical curing results in solid thick-mesh polymers with a high level of intermolecular physical interaction (for example, in epoxy polymers, the density of the van der Waals and hydrogen bonds is 2-4 times higher than the mesh of chemical crosslinking).

Polymer composite materials based on an epoxy binder have high physical and mechanical properties, impermeability, chemical resistance, etc., but at the same time have a high cost [1-10]. This makes their use not always economically justified. From this point of view, it is interesting to study the properties and effectiveness of other polymer composites.

It is advisable to use new types of synthetic resins developed with the latest scientific achievements in mind. In this regard, it is promising to obtain composite construction materials based on vinyl ester resin.
The use of vinyl ester resin as a binder for the production of polymer concrete in the Russian Federation is still at the level of experimental work. However, its foreign analogues have found wide distribution and production application in the US and European markets [11]. Foreign specialists have developed a large number of modified vinylester resins and the search for new types of them is expanding intensively [3]. Vinylester resins are used for the production of: fiberglass, laminate, pipelines, tanks, etc. These resins are characterized by tensile elasticity, and due to the high mechanical properties of vinyl ester resins, they can be used in the aerospace industry. Their high chemical resistance is used in the manufacture of fiberglass containers and in various industries. Pipelines, tanks, scrubbers and other products made of complex high-quality vinyl-ester resins demonstrate good durability and resistance characteristics in the chemical industry, the oil and gas sector, and the pulp and paper industry.

As you can see, vinylester resins are quite popular abroad.

At the same time, the influence of environmental factors on the biodegradation of vinyl-ether polymer composites has not been sufficiently studied to date.

The destruction of polymer and other materials occurs as a result of their interaction with the environment or external factors. These include: temperature and humidity of the surrounding air, light and penetrating radiation, oxygen, aggressive gaseous impurities contained in the air, mechanical loads from wind, dynamic energy of water droplets, sand, and dust [13-14].

The most significant are the processes of atmospheric aging of materials, including the complex action of climatic and environmental factors (light, moisture, temperature, chemical state of the atmosphere, ionizing radiation, etc.). These factors influence not only the vital activity of microorganisms, but under their influence changes in the chemical composition and structure of polymer materials begin [15-18]. Depending on the type, intensity and duration of exposure to these aging factors of polymer materials, they undergo chemical changes, and after some time may become compounds that differ in chemical composition and structure from the original ones. Thus, at a certain point, these materials begin to undergo destruction and are used as a source of nutrition by certain types of fungi that have a corresponding complex of metabolites. Chemical "aging" of materials under the influence of environmental factors can affect such parameters of the process of bio-damage as the start time of biodegradation, destruction mechanisms and the species composition of destructors.

The purpose of this work was to study the changes in the species composition of microflora isolated from vinylester composites depending on their composition and operating conditions (seacoast).

2. Materials and methods
Vinyl ester resin of the RP-14C brand was used as a binder for vinylester composites. The Composites were cured by an initiating system consisting of cyclohexanone peroxide (PCON-2), dimethylaniline (DMA), and cobalt octoate (OK-1). The fillers kaolin, lithopone and white soot were introduced into individual mixtures. The compositions are shown in table 1.

| Components                        | The content of components in the compositions, % |
|-----------------------------------|-------------------------------------------------|
|                                  | 1     | 2     | 3     | 4     | 5     | 6     |
| Vinyl ester resin                 | 100   | 100   | 100   | 100   | 100   | 100   |
| Cyclohexanone peroxide            | 0.5   | 1.5   | 0.5   | 1.5   | 0.5   | 1.5   |
| Cobalt octoate                    | 1     | 3     | 5     | 1     | 5     | 1     |
| A 10% solution of dimethylaniline in styrene | 1     | 1     | 1     | 1     | 1     | 1     |
| Kaolin                            | -     | -     | 100   | -     | 25    | -     |
| Lithopone                         | -     | -     | -     | 100   | -     | -     |
| Silica white                      | -     | -     | -     | -     | -     | 10    |

Table 1. The studied compounds
After exposure for 3 and 10 months in natural conditions of the seacoast (Gelendzhik), identification of the type of micromycetes that contaminate the above samples was carried out.

3. Results and discussion
The species composition of microorganisms on the surface of composites based on vinylester binders in conditions of variable humidity is shown in table 2.

Table 2. Species composition of mycelial fungi on the surface of composites based on vinyl ester resin RP-14C in conditions of variable humidity of the seacoast (Gelendzhik)

| No. | Species composition of microorganisms on samples exposed at the sea in an open area | Species composition of microorganisms on samples exposed near the sea under a canopy |
|-----|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| 1.  | Penicillium nigricans, Cladosporium clatum, Aspergillus ustus, Aspergillus terreus, Cladosporium macrocarpum, Chaetomium dolichorchrichum, Chaetomium bostrychodes, Alternaria tenuissima, Alternaria brassicae, Alternaria pluriseptata, Penicillium urticae, Aspergillus oryzae, Penicillium lanosum | Paecilomyces variotii, Alternaria brassicae, Alternaria pluriseptata, Aspergillus niger, Aspergillus terreus, Aspergillus nigricans, Chaetomium dolichorchrichum, Chaetomium bostrychodes, Alternaria brassicae, Alternaria tenuissima, Penicillium variabile |
|     | 3 months | 10 months | 3 months | 10 months |
| 2.  | Aspergillus niger, Alternaria tenuissima, Aspergillus ustus, Chaetomium bostrychodes, Penicillium lanosum, Alternaria brassicae, Alternaria pluriseptata, Cladosporium macrocarpum, Botrytichrichum piluliferum, Cladosporium clatum, Penicillium nigricans, Chaetomium dolichorchrichum | Aspergillus oryzae, Chaetomium bostrychodes, Penicillium canescens, Alternaria brassicae, Alternaria tenuissima, Aspergillus ustus, Penicillium variabile | Aspergillus oryzae, Chaetomium bostrychodes, Penicillium canescens, Alternaria brassicae, Alternaria tenuissima, Aspergillus ustus, Penicillium variabile | Aspergillus niger, Alternaria tenuissima, Aspergillus ustus, Chaetomium bostrychodes, Penicillium canescens, Alternaria brassicae, Alternaria tenuissima, Aspergillus ustus, Penicillium variabile |
| No. | Species composition of microorganisms on samples exposed at the sea in an open area | Species composition of microorganisms on samples exposed near the sea under a canopy |
|-----|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
|     | 3 months | 10 months | 3 months | 10 months |
| 3   | Aspergillus terreus, Aspergillus clavatus, Aspergillus ustus, Penicillium urticae, Alternaria brassicae, Aspergillus niger, Chaetomium dolichortrichum, Alternaria pluriseptata, Alternaria alternate, Cladosporium herbarum, Penicillium canescens, Scopulariopsis brevicaulis, Penicillium lanosum, Cladosporium macrocarpum, Cladosporium clatum | Aspergillus terreus, Aspergillus clavatus, Aspergillus ustus, Penicillium urticae, Alternaria brassicae, Aspergillus niger, Chaetomium dolichortrichum, Alternaria pluriseptata, Alternaria alternate, Cladosporium herbarum, Penicillium canescens, Scopulariopsis brevicaulis, Penicillium lanosum, Cladosporium macrocarpum, Cladosporium clatum | Chaetomium bostrychodes, Chaetomium dolichortrichum, Aspergillus ustus, Alternaria brassicae, Penicillium chrysogenum, Alternaria pluriseptata, Alternaria alternate, Cladosporium herbarum, Penicillium canescens, Scopulariopsis brevicaulis, Penicillium lanosum, Cladosporium macrocarpum, Cladosporium clatum | Chaetomium bostrychodes, Chaetomium dolichortrichum, Aspergillus ustus, Alternaria brassicae, Penicillium chrysogenum, Alternaria pluriseptata, Alternaria alternate, Cladosporium herbarum, Penicillium canescens, Scopulariopsis brevicaulis, Penicillium lanosum, Cladosporium macrocarpum, Cladosporium clatum |
| 4   | Penicillium chrysogenum, Penicillium claviforme, Aspergillus terreus, Aspergillus ustus, Penicillium lanosum, Penicillium nigricans, Aspergillus niger, Penicillium urticae, Aureobasidium pullulans, Penicillium canescens, Aspergillus versicolor, Penicillium aurantio candidus, Penicillium oxalicum, Alternaria pluriseptata | Penicillium chrysogenum, Penicillium claviforme, Aspergillus terreus, Aspergillus ustus, Penicillium lanosum, Penicillium nigricans, Aspergillus niger, Penicillium urticae, Aureobasidium pullulans, Penicillium canescens, Aspergillus versicolor, Penicillium aurantio candidus, Penicillium oxalicum, Alternaria pluriseptata | Aspergillus oryzae, Paecilomyces variotii, Chaetomium dolichortrichum, Alternaria brassicae, Aspergillus fumigatus, Penicillium chrysogenum, Penicillium godlewskii | Aspergillus oryzae, Paecilomyces variotii, Chaetomium dolichortrichum, Alternaria brassicae, Aspergillus fumigatus, Penicillium chrysogenum, Penicillium godlewskii |
| 5   | Aspergillus niger, Aspergillus ustus, Aspergillus clavatus, Penicillium oxalicum, Penicillium lanosum, Cladosporium macrocarpum, Penicillium clavigerum, Penicillium godlewskii | Aspergillus niger, Aspergillus ustus, Aspergillus clavatus, Penicillium oxalicum, Penicillium lanosum, Cladosporium macrocarpum, Penicillium clavigerum, Penicillium godlewskii | Aspergillus oryzae, Fusarium sambucinum, Penicillium variabile, Paecilomyces variotii, Aspergillus clavatus, Aspergillus ustus, Penicillium nigricans, Alternaria pluriseptata, Alternaria brassicae, Aspergillus versicolor, Chaetomium globosum, Penicillium chrysogenum | Aspergillus oryzae, Fusarium sambucinum, Penicillium variabile, Paecilomyces variotii, Aspergillus clavatus, Aspergillus ustus, Penicillium nigricans, Alternaria pluriseptata, Alternaria brassicae, Aspergillus versicolor, Chaetomium globosum, Penicillium chrysogenum |
The results of changes in the mass and strength characteristics of composites on vinyl-ether binders in the process of holding them in conditions of variable humidity of the seacoast in an open area and under a canopy near the sea are shown in table 3.

**Table 3.** Changes in the mass content and durability of composites, aged for 10 months in variable humidity conditions seacoast (Gelendzhik)

| composite number | Under a canopy | Open area |
|------------------|----------------|-----------|
|                  | Change in mass content, % | The coefficient of resistance | Change in mass content, % | The coefficient of resistance |
| 1                | 0.38            | 1.08      | 0.273         | 1.13         |
| 2                | 0.17            | 0.76      | 0.195         | 0.82         |
| 3                | 0.42            | 1.02      | 0.73          | 1.00         |
| 4                | 0.13            | 0.96      | 0.21          | 1.01         |
| 5                | 0.36            | 0.89      | 0.48          | 0.92         |
| 6                | 0.64            | 0.85      | 1.28          | 0.86         |

Climate stability of composites based on vinyl-ether binders in conditions of variable humidity of the seacoast (Gelendzhik) has its own characteristics (see table 3). After ten months of exposure of samples of vinyl-ether composites under a canopy, the strength of the samples decreases (from 4% to 24%), however, compositions #1 and #3 show a slight increase in strength (from 2% to 8%). In the case of composites filled with kaolin in the ratio of 100 wt. hours per 100 wt. for example, the increase in strength is associated with the strength set of this composition under atmospheric influence.

The decrease in the stability of samples, along with a decrease in their mass content, can be explained by the large impact of the black sea coast environment on the material (rain, sea water drops, etc.) and, as a consequence, an increase in the number of neoplasms in composites. However, it...
should be noted that the mass of samples after exposure does not increase as much as that of composites under a canopy. This is due to the leaching of soluble compounds from composites under the influence of atmospheric precipitation.

If we talk about the considered characteristics of composites that were located in the open area, we can observe an increase in the resistance of the same compositions as under the canopy. In General, the decrease in the strength of composites that were located in the open area is insignificant and did not exceed 18%, i.e. vinyl-ether composites resist the influence of the wet environment of the black sea coast, solar radiation, washing and weathering, as well as the impact of microflora.

4. Conclusion
This study considers the influence of environmental factors on the biodegradation of vinyl ester polymer composites.

The results show that vinylester composites have good resistance to aggressive environments and can be used in construction production in regions with a humid climate.

5. References
[1] Bobryshev A N, Erofeev V T and Kolomazov V N 2013 Polymer composite materials (Moscow: Publishing house of the Association of Civil Engineering)
[2] Perlin S M 1983 Chemical resistance of fiberglass (Moscow: Publishing house Hi-Miya)
[3] Erofeev V 2016 Frame Construction Composites for Buildings and Structures in Aggressive Environments Procedia Engineering 165 1444-1447
[4] Elshin I M 1980 Polymer Concrete in hydrotechnical construction (Moscow: Publishing house Stroiizdat)
[5] Patureau V V 1987 Polymer Concrete (Moscow: Publishing house Stroiizdat)
[6] Solomatov V I 1984 Technology of polymer concrete and arkapolimetal products (Moscow: Publishing house Stroiizdat)
[7] Sokolov Y A and Gottlieb E M 1990 Modified epoxy mixtures and coatings in construction (Moscow: Publishing house Stroiizdat)
[8] Chernin I Z, Laughtier F M, Zherdev Y V 1982 Epoxy polymers and compositions (Moscow: Publishing house Chemistry)
[9] Erofeev V, Rodin A, Rodina N, Kalashnikov V, Erofeeva I 2016 Biocidal Binders for the Concretes of Underground Constructions Procedia Engineering 165 1448-1454
[10] Khozin V G 2004 Strengthening of epoxy polymers (Kazan, Russia: House of Printing)
[11] Mechtcherine V and Reinhardt H W (Eds.) 2012 Application of Super Absorbent Polymers (SAP) in Concrete Construction (Springer)
[12] Seymour R B 1980 Adelantos en los concretos polimericos Hulemex. Y plast. 36(414) 20
[13] Erofeev V, Dergunova A, Pikaikina A, Bogatov A, Kablov E, Startsev O, Matvievskiy A 2016 The Effectiveness of Materials Different with Regard to Increasing the Durability MATEC Web of Conferences 73 04021
[14] Dergunova A, Pikaikina A, Bogatov A, Salman Aa D S D, Erofeev V 2019 The economic damage from biodeterioration in building sector IOP Conference Series: Materials Science and Engineering 698(7) 077020
[15] Erofeev V, Smirnov V, Dergunova A, Bogatov A, Letkina N 2020 Development and research of methods to improve the biosustainability of building materials Materials Science Forum 974 305-311
[16] De Belie N, Richardson M, Braam C R, Svennerstedt B, Lenehan J J and Sonck B 2000 Durability of building materials and components in the agricultural environment: Part 1, The agricultural environment and timber structures Journal of Agricultural Engineering Research 75 225-241
[17] Erofeev V T, Smirnov V F, Myshkin A V 2019 The study of species composition of the mycoflora, selected surface samples poliferation composites in humid maritime climate *IOP Conference Series: Materials Science and Engineering* **698**(2) 022082

[18] Erofeev V T, Rodin A I, Kravchuk A S, Kaznacheev S V, Zaharova E A 2018 Biostable silicic rock-based glass ceramic foams *Magazine of Civil Engineering* **84**(8) 48-56