Study of micromycete destructive power in gypsum and polymeric binding composite construction materials

L Matveeva, V Pakhtinov, Yu Tikhonov

Building materials technology and metrology department, St. Petersburg University of Architecture and Construction, 4, Vtoraya Krasnoarmeiskaya, St. Petersburg 190005, Russia

E-mail: lar.ma2011@yandex.ru

Abstract. Analyzing fungus resistance of gypsum and organic composites is extremely important since fungi may both lead to deterioration in mechanical and operational properties of construction materials and adversely affect people’s health, including development of chronic diseases. We study fungus resistance and fungicidity characteristics of popular finishing gypsum and organic (epoxy- and polyester-based) composites. Plaster materials get exposed to micromycete biocorrosion faster than the ones based on a polymeric binding. Micromycetes adapt on plaster samples quicker than on epoxy and polyester samples. During their metabolism, micromycetes intensively allocate acid products on plaster samples, their high enzymatic activity is also noticed on polymeric materials.

1. Introduction

Construction materials are designed to withstand the impact of aggressive environment factors resisting corrosion which ultimately leads to loss of useful properties and destruction. Environmental factors can be diverse including not just atmospheric conditions, such as temperature drops or humidity, but also the results of microorganism vital activity [1, 2]. Bacteria and mold fungi belong to the most widespread microorganisms causing biological corrosion. Mold fungi, micromycetes, are natural biodestructors playing the leading role in biodamage processes of construction materials operated under conditions of usual temperatures and increased [3-7]. The microdestruction mechanism is based on chemical reactions of splitting the substrate material using the metabolism products – acids and enzymes. These substances participate in nutrition, development, and growth of micromycete colonies. Fast destruction of material is caused by rapid cell growth of mold fungi mycelium, the power and lability of enzymatic device. When micromycetes appear on the surfaces of construction materials, mechanical and operational characteristics of a material deteriorate, sanitary conditions get worse, esthetic properties are lost. Massive development of mold fungi in living quarters is often the reason of serious diseases dangerous to humans.

Nowadays, in apartment finishing a number of construction materials is used based on plaster, polymeric and mixed binders [8-12]. All of them consist of two main structural components – binders and fillers [13-19]. Therefore, it is important to study fungus resistance properties of popular plaster and organic polymeric binder construction composite materials.
2. Research methods and materials

The fungus resistance and fungicidity of materials is defined according to GOST 9.048-89 “Unified system of corrosion and aging protection. Technical items. Methods of laboratory tests for mold resistance”, GOST 9.049-91 "Unified system of corrosion and aging protection. Polymeric materials and their components. Methods of laboratory tests for mold resistance”.

Materials samples 3×3 cm are infected with blend sporous suspension of the most widespread mold fungi of the species Aspergillus, Alternaria, Paecilomyces, Penicillium, Chaetomium, Trichoderma. The temperature is maintained at 28±2ºC. Assessment of a mold resistance and a fungicidity of samples was carried out on the 28th day.

Table 1 shows the compositions of the materials studied. The epoxy binding composite contains the mix consisting of epoxy oligomer pitch EP-20 and a polyethylene polyamine (PEPA) in a 10:1 proportion. The polyester binding composite has a mix of polyester oligomer pitch PN-1, cyclohexanone peroxide (PPC) polymerization initiator, and the naphthenate of cobalt (UNC-2) accelerator in the ratio of 100:1.5:1.5.

| Material       | Composition components, mass. p. | Binder    | Filler       | Water |
|----------------|----------------------------------|-----------|--------------|-------|
| Plaster stone  | Gypsum plaster (G-7 B II) – 100  | –         | –            | 0.6   |
| Gypsum concrete| Gypsum plaster (G-7 B II) – 100  | Sawdust (pine) 150 | 0.65 |
| Wood concrete  | Portland cement M400 Д-20 (CEM II A-S 32.5) | Sawdust (pine) 95 | 0.55 |
| Cement concrete| Portland cement M400 Д-20 (CEM II A-S 32.5) | Quartz sand 95 | 0.45 |
| Epoxy composite| EP-20 + PEPA                     | Quartz sand 82 | – |
| Polyester composite | PN-1 + PPC + UNC-2 | Quartz sand 90 | – |

3. Discussion

The results of fungus resistance analysis of samples are presented in table 2 and table 3. Materials based on plaster and polymeric composites have lowers fungus resistance comparing to construction materials based on cement. Further research is needed to develop measures to improve their fungus resistance.

| Material       | Extent of fouling, a score according to GOST 9.048–91 | Qualification according to GOST 9.048–91 |
|----------------|-------------------------------------------------------|----------------------------------------|
| Plaster stone  | 1                                                     | Not fungus resistant                    |
| Gypsum concrete| 2                                                     | Not fungus resistant                    |
| Wood concrete  | 0                                                     | Fungus resistant                        |
| Cement concrete| 0                                                     | Fungus resistant                        |
| Epoxy composite| 3                                                     | Not fungus resistant                    |
| Polyester composite | 3                                                         | Not fungus resistant                   |

The fungus resistance and fungicidity of polymeric composites differs from those of their unfilled binders (table 3).
Table 3. Fungus resistance and fungicidity of polymeric composites and binders.

| Material              | Fouling by mold fungus, a score according to GOST 9.048–91 | Qualification according to GOST 9.048–91, score |
|-----------------------|-------------------------------------------------------------|-------------------------------------------------|
|                       | Method A  Method B                                          |                                                 |
| Epoxy composite       | 3 5                                                         | Not fungus resistant, 5 No fungicidity, 4       |
| Polyester composite   | 3 5                                                         | Not fungus resistant, 4 No fungicidity, 4       |
| Binder EP-20 + PEPA   | 2 4                                                         | Not fungus resistant, 3 No fungicidity, 3       |
| PE binder PN-1+ PPC + UNC-2 | 2 4                | Fungus resistant, 1 No fungicidity, 3          |

Besides the standard definition of a fungus resistance and a fungicidity, we also analyze the mold fungus colony growth dynamics and the biomass accumulation speed. Materials samples are infected with water sporous suspension of mold fungus mix maintained for 3 months (90 days) in the Capek-Doksa agar circle at 28±2ºС and relative air humidity of more than 90%. Radial growth rate was measured weekly using a eyepiece micrometer diameter of micromycete colonies. Biomass accumulation was determined using a weight method. Figure 1 and figure 2 present radial growth rates and biomass accumulation rates versus the number of days the samples were exposed based on pilot studies.

As can be seen figure 1, mold fungi colony radial growth rates change non-linearly. During the initial period (1–7 days), the growth rate of micromycete colonies on the surface of samples is low. Apparently, during this period the micromycetes adapt to the existing conditions and mobilize the corresponding organic acids and enzymes production.

![Figure 1](image_url)

**Figure 1.** Mold fungi colony radial growth rates on the surfaces of construction materials samples.

The micromycetes adaptation period on the polymer composite samples is much longer, averaging to 14 days. After 7–14 days from the beginning of the experiment, a significant increase in colonies growth rate on the surfaces of plaster stone and gypsum concrete is noticed. Probably, it is related to the mycelium exponential growth phase and corresponding micromycete biomass accumulation (figure 1...
and figure 2). During the days 14–21, there is a noticeable growth of micromycete colonies on the surface of polymer composites samples. Days 10–14 correspond to the phase of stabilization of micromycete colonies growth rates on the samples of gypsum concrete and plaster stone, while on samples of polymeric composites it occurs after 21–23 days. Days 22–30 days – the stationary phase, increase in the growth rates of colonies is not observed but the intensive sporogenesis is noticeable. On days 30–58, the growth processes slow down sharply, intensive spore formation and subsequent dying of a part of mycelium follows.

![Figure 2. Dynamics of mold fungi biomass accumulation on the surfaces of construction materials.](image)

The analysis of biomass accumulation dynamics (figure 2) shows that most actively mold fungi biomass increases during the days 14–42, then the growth happens weakly. Active biomass growth is accompanied by significant accumulation of metabolism products – organic acids and enzymes. Acid concentration is investigated Capek-Doksa on nutrient agar medium and is estimated using electrometric method with bromophenol blue. The enzymatic activity was estimated by the titrimetric method using hydrogen peroxide, which decayed under the influence of enzyme.

Results of micromycete acid and enzymatic activity studies (figure 3 and figure 4) show that the mold fungi produce the largest amount of metabolites during the colony exponential growth phase. The analysis of acid products (figure 3) allowed to establish that micromycetes developing on the surface of plaster materials have the highest concentration of organic acids. The enzymatic activity analysis (figure 4) showed that the enzyme synthesis is strongest for the micromycetes developing on the surfaces of polymeric composites with the highest rate being on the surface of polyester composite (figure 4).

4. Conclusion
Micromycetes develop faster and more intensively on gypsum concrete and on unfilled plaster stone, most likely, due to wood filler and bigger porosity, both much quicker and more intensively than on epoxy and polyester composites.

Growth of mold fungi colonies on samples happens non-uniformly. During the initial period (1–7 days for plaster and 1–14 days for epoxy and polyester composites), the growth rate of micromycete colonies on the surface of materials is low.

This period corresponds to adaptation of micromycetes to dwelling conditions. During that time, the development by micromycete organic acids and enzymes amplifies further.
Figure 3. Acid concentration on the surfaces of construction materials.

Figure 4. Micromycete enzymatic activity on the surfaces of construction materials.

Intensive growth and development of mold fungi colonies is accompanied by significant production of metabolites. The higher concentration of acid products occurs on the surfaces of gypsum concrete and plaster stone, while enzymatic activity of mold fungi prevail on the surface of polymeric samples. Active growth of mold fungi on the surfaces of polymeric composite construction materials results in enzymatic metabolites accumulation that stimulate destructive processes in polymeric materials and cause changes in their chemical properties.

A reasonable avenue for further research would be the assessment of metabolites depth of penetration into the structure of materials, analysis of specific structural changes that a micromycete colony growth causes, and development of protective measures to increase fungus resistance of plaster and polymeric composites.
References

[1] Gorlenko M 1979 Microbial damage of industrial materials *Microorganisms and lower plants – destroyers of materials and products* (Moscow: Nauka) pp 10–16

[2] Gorlenko M 1984 Some biological aspects of biodegradation of materials and products *Biological damage in construction* (Moscow: Stroizdat) pp 9–17

[3] Irassar E, Bonavetti V and Gonzalez M 2003 Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature *Cement and Concrete Research* **33**(1) 31–41

[4] Andreyuk E, Bilai E, Koval E and Kozlova I 1980 *Microbe Corrosion and Its Pathogens* (Kiev: Naukova Dumka) p 287

[5] Andreyuk E, Kozlova I and Rozhanskaya A 1984 Microbiological corrosion of construction steels and concretes *Biological damage in construction* (Moscow: Stroizdat) pp 209–18

[6] Anisimov A and Smirnov V 1980 *Biodamage in Industry and Protection from It* (Gorkiy: Gorkiy State University)

[7] Volzhenskiy A, Rogovoy M and Stambulko V 1960 *Gypsum Cement and Gypsum Slag Binding Materials and Products* (Moscow: Gosstoyizdat) p 162

[8] Bazhenov Y, Korovyakov V and Denisov G 2003 *The Technology of Dry Building Mixtures* (Moscow: ASV Publishing House)

[9] Ferronskaja A 2004 *Gypsum Materials and Products (Production and Application). Ref. book* (Moscow: ASV Publishing House)

[10] Arikam M and Sobolev K 2002 The optimization of gypsum-based composite material *Cement and Concrete Research* **32**(11) 1725–8

[11] Rakhimov R, Khaliullin M and Gayfullin A 2012 Composition and structure of the stone composite gypsum binder with additives of lime and the ground haydite dust *Stroitelnuye Materialy* **7** 13–16

[12] Babkov V, Latypov V, Lomakina L, Asyanova V and Shigapov R 2012 Modified gypsum binders of high water resistance and gypsum-claydite-concrete wall blocks for low-rise housing construction on their basis *Stroitelnuye Materialy* **7** 4–8

[13] Wang Y, Urbonas L and Heinz D 2012 Einfluss von verschiedenen Puzzolanen auf die Eigenschaften von Gips-Zement-Puzzolan-Bindemitteln. In 18. *Internationale Baustofftagung* F.A. Figner – Institut fur Baustoffkunde, Bauhaus – Universität Weimar, Weimar, B. 1, pp. 1-0424-31

[14] Kim S 2009 Incombustibility, physico-mechanical properties and TVOC emission behavior of the gypsum-rice husk boards for wall and ceiling materials for construction *Industrial Crops and Products* **29**(2-3) 381-7

[15] Bijen J and van der Plas C 1992 Polymer-modified glass fiber reinforced gypsum *Mater. Struct.* **25**(2) 107–14

[16] Colak A 2001 Characteristics of acrylic latex-modified and partially epoxy-impregnated gypsum *Cement Concrete Res.* **31**(11) 1539–47

[17] Eve S, Gomina M, Hamel J and Orange G 2006 Investigation of the setting of polyamide fibre/latex-filled plaster composites *J. Eur. Ceramic Soc.* **26**(13) 2541–6

[18] Rubio-Avalos J, Manzano-Ramirez A, Luna-Barcenas J, Perez-Robles J, Alonso-Guzman E, Contreras-Garcia M and Gonzalez-Hernandez J 2005 Flexural behavior and microstructure analysis of gypsum-SBR composite material *Mater. Lett.* **59**(2-3) 230–3

[19] Dalmay P, Smith A, Chotard T, Sahay-Turner P, Gloaguen V and Krausz P 2010 Properties of cellulosic fiber reinforced plaster: influence of hemp or flax fibers on the properties of set gypsum *J. Mater. Sci.* **45**(3) 793–803