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Biodegradation of Mineral and Silicone Plasters and Its Comparison

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Abstract. The article focuses on the determination of a fungal growth range on plaster depending on external conditions. The experiments compare three types of plaster which are the most widely used in Europe. The selected plaster is two mineral and one silicone. These types of plaster are standard mixtures developed and donated by manufacturing company from Czech Republic.

The article contains comparison of germination and growth of mould on the surface of samples with the type of used degradation process before inoculation of mould. The types of used degradation were carbonation, freeze-thaw cycle, degradation by soil microorganism and high moisture. The microbial resistance was made based on modified Norm ČSN EN ISO 846. The samples were placed on mineral agar and in the 100 % humidity. The resistance of samples was evaluated by microscopy analyses.

1. Introduction

The aging of building materials is complex process. The main degrading processes are rain, sunlight and cycles of freeze-thaw and by action of microorganism. At first it is assumed that the biodegradation begins soon after complete of building [1]. At the first period it is only aesthetic problem which changes colour of external surface. This colour spots consist from biogenic pigment which are made by chlorophyll, carotene and melatonin and so on [2]. The next effect is creation extracellular polymeric substance (EPS), which load mechanically materials by cyclic shrinkage and swelling [3]. The results of these processes are change of pore distribution and change of water and heat transport [1]. The last thing is accumulation of pollutant which enrich building materials by organic substance and other nutrient [4]. Microbial colonisation of building materials and intensity their due to biodegradation is connect with water amount, concentration of needed nutrient, optimal pH and temperature [4].

The biodegradation of external plasters is serious problem too. The first visible fungal colonies are occurred in first or second year after application. The common opinion, which occurs very often, is that moulds grow between pH 6 to 8 and the necessary moisture content is higher than 60%. [5]. Our newest study shown that this limitation is not quite correct. The necessary conditions for growth fungi on building materials are more complicated. The most important condition is water occurrence; the minimum concentration is up to 80%. The second important one is nutrient. Some plasters have organic supplement which serves as a source of carbon and nitrogen. This research should show the degrading of plasters in the first period after application and their dependent of fungal occurrence on the used degrading processes.



2. Materials and methods

The chosen mixtures are typically and commonly used commercial plaster which are very often applied as a final coat to building in the Czech Republic. We were focused on three mixtures, first one was silicone plaster (**labelled Si**) and two mineral plaster: mineral scraped brick-plaster (**labelled Br**) and lime-cement plaster (**labelled LC**).

The samples had prepared as a cylinder with a diameter of 3 cm and a height of 2 cm. The mixtures were taken out from forms after 48 hours and placed at room temperature and humidity. The samples were prepared for begin of experiments after 28 curing day.

The fungi do not occur on the plasters in early life stages, they need nutrient and suitable conditions for their life as a water content and optimal temperature. The nutrients come from environment as pollutant, debris of organism from air and so on. These fresh samples of plasters have not any nutrient as an organic component in themselves mixtures and therefore samples were adjusted for microbiological assays by degradation. We used four basic degradations and their combination, see table 1. They were freeze-thaw (**labelled F**), burial in the soil (**labelled S**), carbonation (**labelled C**) and action of water (**labelled W**). The degradation processes and their influence were monitored by measuring of pH.

Table 1. The label of degradation processes

Label	Degradation 1	Degradation 2
N	None	None
F	Freeze thaw	None
S	Burial in the soil	None
C	Carbonation	None
W	Water	None
FC	Freeze thaw	Carbonation
CW	Carbonation	Water
CS	Carbonation	Burial in the soil

The freeze-thaw (F) were made by norm ČSN 72 2452 [6], the number of cycles were 10 for microbiological assay.

The degradation by burial in the soil (S) was made by using standard soil from garden localized in Prague 5. The soil was wetted by drinking water, tempered in the room temperature (25°C) for 24 hours. The samples were placed into so prepared soil and the humidity was kept by additional vessel with water. The closed container with soil and samples was placed in room temperature for 28 days. After it the samples was picked out and it served for next experiments.

The carbonation process (C) made in chamber with concentration CO₂ around 20% and 50% relative humidity for 5 days. The last type of degradation was done by water (W). The samples were soaked in distilled water for 10 days and water was changed every day. The samples labels are Si, Br and LC, the sample labelled N is a control which wasn't degraded. The control samples (N) were saved in dry at room temperature during degradation processes on other samples.

The microbiological assay is made based on norm ČSN ISO 846 [7]. The assay was made with usage complete nutrient medium (Czapek Dox) and in high humidity (100 % RH moderated by water). The model organism was used the fungal inoculum with following combination of fungi: *Cladosporium cladosporioides*, *Alternaria alternata*, *Penicillium brevicompactum*, and *Penicillium purpurogenum* in ratio 1:0:5:1:1. The fungal culture stock had concentration 4.2×10^6 to 5.7×10^6 CFU/ ml as a spore in saline solution.

The agar plates were inoculated by 100 μ l fungal spores and they were pre-incubated in 25 °C for 3 days. After pre-incubation, the samples were placed on agar and the samples are inoculated by spraying with same mixture as before. The complementary experiment was assembled as above except fungal inoculation. This experiment was used for determination natural occurring of microorganism and microorganism gained during degrading in the samples. The samples were incubated in 25°C for next 28 days. The results were evaluated every week as rate of fungal coverage on samples by scale mentioned at table 2.

Table 2. The scale of intensity of coverage

Intensity of growth	Evaluation
0	There is no growth under the microscope
[1]	The visible a few hyphae under microscope
1	The growth with the naked eye invisible, clearly visible under the microscope
2	The visible growth coverage up to 25 % of sample surface
3	The visible growth coverage up to 50 % of sample surface
4	The visible growth coverage more than 50 % of sample surface
5	Rich growth covering the entire test surface

The experiment without nutrient was made in desiccator with humidity close 100%. The samples were placed on board in it and they were inoculated by spraying same fungal mixture as above. The evaluation of fungal occurring was amounted every week by scale mentioned in table 2.

3. Results

3.1. The degradation part

The samples were prepared and cured 28 days in room temperature. After this waiting time the samples were degraded by freeze-thaw cycles, carbonation, water soaking, burial in soil and their combinations. The degradation processes were evaluated by pH measuring; the results are shown in table 3. The initial pH of mineral plasters is around 13.3 for control non-degraded samples. The most effective degradation is combination of burial in soil and carbonation, then followed combination of freeze-thaw and carbonation, and after it combination of bicarbonate and water soak. The most efficiency simple degradation process was burial in soil and the similar effects had carbonation and freeze-thaw. There was existed one exception and it is for freeze-thaw silicone plaster. The silicone plaster should be most prone for microbial attack from the view pH.

Table 3. The pH of samples by the usage of degradation

Sample	Br	CL	Si
N	13.49	13.26	8.093
C	12.71	12.34	8.449
F	12.93	12.87	7.944
FC	10.43	9.44	8.253
W	13.13	12.8	8.5
CW	11.98	11.93	8.3
S	12.5	9.4	7.914
CS	9.08	9.27	7.866

The change pH in time is shown at table 4 for sample Br, Br-C, CL and its carbonated equivalent. The decreasing is only in rate 0,5. The leaching of alkali ion as a sodium, calcium and potassium is gradual and therefor the soaking of samples decrease pH only very slow.

Table 4. The time dependence of change pH by water soak, the label of sample are follow: the first part is sample name and the second one is degrading process

Time [day]	Br	Br-C	CL	CL-C	Si	Si-C
1	13,49	12,71	13,26	12,34	7,90	8,70
2	13,38	12,56	13,13	12,22	8,59	8,92
3	13,21	12,19	13,01	12,15	/	/
4	13,34	12,44	/	/	/	/
5	/	/	/	/	/	/
6	/	/	/	/	8,69	8,94
7	13,40	12,58	/	/	8,91	8,92
8	13,26	12,31	13,28	12,29	/	/
9	13,22	12,09	12,80	12,01	8,67	8,85
10	13,13	11,98	12,80	11,93	8,50	8,30

3.2. The microbial assay

In the part experiment where the samples were placed into desiccator with 100% humidity, the mould grew up only at mineral scraped brick-plaster and lime cement plaster. The fungal growth was less visible for lime cement plaster then for mineral scraped brick-plaster. The fungal hyphae were seen only under microscope. The silicone plaster was clear, there were not observed any hyphae. The mineral scraped brick-plaster samples degraded by burial in soil and carbonation had some visible colonies.

The samples Br-CW was covered only a little number hypha from third week. The sample Br-S showed coverage to few percent which was visible to the naked eye from third week and at fourth week the coverage was reached up to 25 %, see figure 2. The results for lime cement plaster is similar as for mineral scraped brick-plaster with the different that the fungi were visible is only under microscope. The sample which were made from silicone plaster have shown any fungal hyphae during whole experiment.



Figure 1. Sample Br after 28 days in 100% humidity

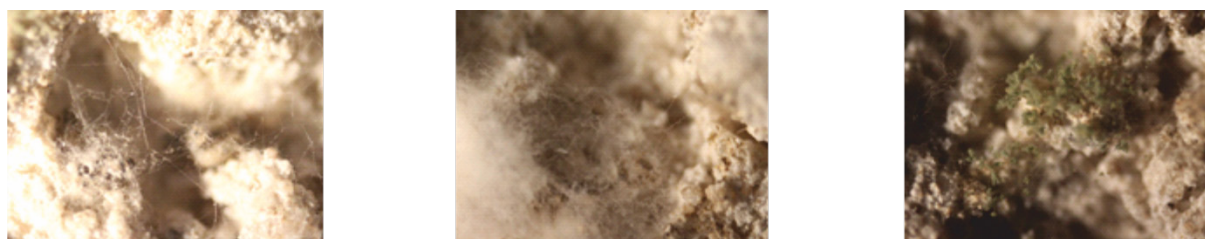


Figure 2. The microscope picture of samples after 4 week in 100 % humidity, the label samples are in row: Br-C; BR-S, BR-CW

The results of part experiment with nutrient agar is shown at table 5 and figure 3. The results are divided to evaluation of sample side and top. The non-degraded samples had coverage of side up to 30% with that the row is lime cement > silicone > mineral scraped brick-plaster (the last is worst). The top of silicone had without fungal growth but the lime cement had visible a few hyphae under microscopy.

Table 5. The results after 28 day inoculation

	Sample	Part	N	C	F	FC	W	CW	S	CS
Inoculated	Br	Top	1,66	0,66	2	2	[0,33]	2	3,33	1,66
		Side	2,66	4	4	3	2	4	3,33	2,66
	LC	Top	0,33	2,33	[1]	1,33	1	2,33	2,33	4
		Side	0,66	4	2	3	1,33	4,33	3	4,66
	Si	Top	0,00	0,00	0,00	0,00	1,33	2,00	2,00	2,00
		Side	1,33	0,67	0,67	0,00	2,00	2,33	2,00	2,67
Non-inoculated	Br	Top	2	0	3	0	0	2	2	2
		Side	2	0	4	2	2	4	4	4
	LC	Top	2	4	2	3	2	3	2	4
		Side	2	5	2	5	0	5	4	5
	Si	Top	0	0	0	0	2	2	2	0
		Side	0	0	0	0	2	5	3	2

The influence of particular degradation processes on occurrence fungus grow is dependent on type of plaster. The degradation of mineral scraped brick-plaster by carbonation and soaking in water had a little effect on rate of fungal occurrence on the top of samples. The sides of the samples shown similar results with that the biggest coverage was reached on samples degraded by carbonation, freeze-thaw cycles, burial in the soil or combination of carbonation and soaking in water. The coverage was up to 50 % for this mentioned samples. The results for experiment without inoculation were similar but slightly lower than with inoculation. The samples which was degraded by carbonation were clear.

The all types of used degradation had high effect on fungal occurrence on lime cement plaster. The highest effect had combination of carbonation and burial in soil. The coverage of samples was more 50% on the top and the sides were covered nearly whole. The other experiment without inoculation showed that the lime cement samples probably contain spores as a germ of microorganism, because the coverage of this samples were lower than in previous experiment but it was still high. The coverage had reached from 25 to 100 %, with except of soaking samples, where fungi were not visible nor under a microscope.

The silicone plasters showed the best results. The coverage came up to 35%. The tops were without fungi for follow degradation: control, carbonation, freeze- thaw cycles, and combination of freeze- thaw cycles and carbonation. The samples which were degraded others processes, had covered up to 25%. The silicone samples, which was degraded by combination of freeze- thaw and carbonation, were not covered at all by hyphae.

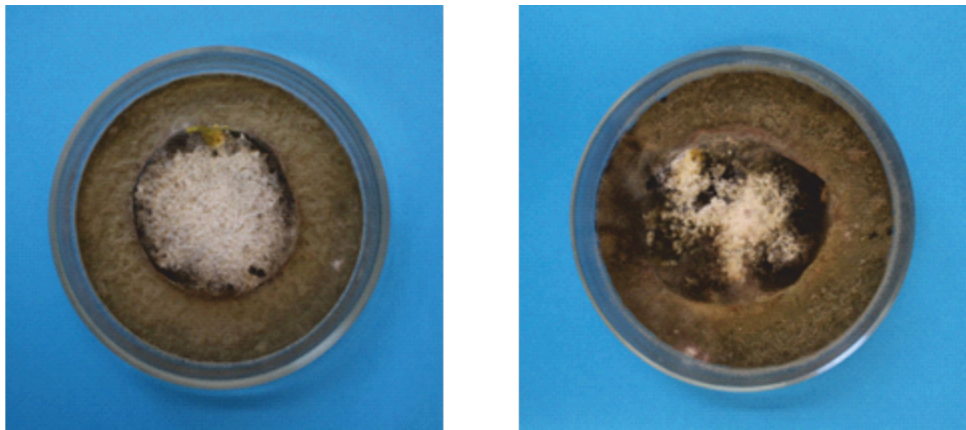


Figure 3. The picture of samples after 4 week on Czapek dox agar with inoculation, the label samples are left Br CW, right LM CS

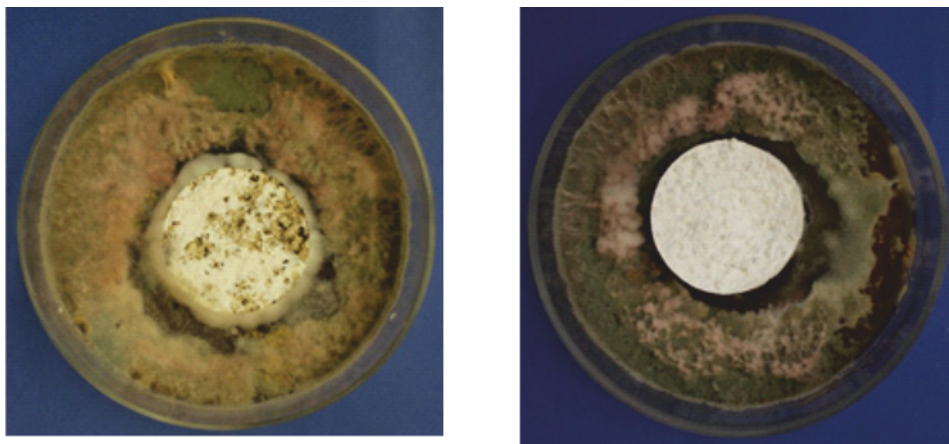


Figure 4. The silicone plaster after 4 weeks on Czapek Dox agar, left Si-CW, right Si-W

4. Discussion and conclusion

The results show that the silicone had the pH value around 8 and this value is decreased by all used degrading processes very slow. This value is very stable and it is shown that pH of the plaster had not obstacle for fungi growth, because this value is optimal. This silicone plaster is very resistant for fungi growth, it is protected by additional biocidal supplement in cane, which is used for protection of the material during storage before application. The silicone plaster has a tendency to get rid of chemical supplement during the first half year to the year and the plaster loses biocidal protection.

The pH value of mineral plaster is more dependent on used degrading processes. The un-degraded samples had pH around 13.3 and the value is decreased to 9.08 after degrading processes, exactly for sample BR -CS. The degrading by burial in soil and soaking in the water were the most nutritional enrichment process for plaster. The samples of plaster were in situation or state which corresponds approximately degradation of plaster in situ in one or two years after application. This premise is agreeing with the results where the samples were exposed only at high humidity.

The experiment with agar plate shown that the most vulnerable plaster is follow: Br, LC and Si (from the worst to the best). The most covered samples were lime cement plaster degraded by carbonation and combination of carbonation and burial in the soil, the coverage were more than 50%. The coverage around 50% had the samples from lime cement plaster degraded by carbonation in combination with soaking and

mineral scraped brick plaster degraded by carbonation, freeze-thaw cycles and carbonation in combination with soaking. The silicone plasters degraded by carbonation and have freeze cycles were almost clear, the total clear were silicone plaster degraded by freeze-thaw cycles combination with soaking.

This research shown how prepare samples for study of biodegradation processes in plaster for in vitro experiment. The fresh plaster hold "sterile" environment without necessary nutrients. This nutrient come into plaster from natural degrading processes from the surrounding environment. The artificial sample preparation in laboratory, which is common used, changes the sample in the structural level. The "best" degrading process is combination of freeze-thaw cycle, carbonation and burial in soil for laboratory experiment. The best results were achieved by silicone plasters which is not corresponded situation in real building. This results are distorted by additional of biocidal supplement for protection during storage time.

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