SELF-HEALING BIO-BASED CONCRETE PERFORMANCE AT LOW TEMPERATURES

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ABSTRAKT

Tento článek se zaměřuje na dvě hlavní úskalí samohojícího betonu na biologické bázi: ochrana bakteriálních spor v cementové matrici a chování materiálu při nízkých teplotách (mrazové cykly a 10 °C). Jako forma ochrany jsou použity superabsorpční polymery (SAP) a 16 % vodný roztok polyvinylalkoholu (PVA).

Po 28denním ponoření do vody při pokojové teplotě vykazovala série obsahující SAP a bakteriální spory (BAC_SAP) nejvýraznější zacelení thrliny – hodnota průměrné maximální šířky zacelené trhliny (Δw_{max}) dosáhla 219 µm. Při nízkých teplotách se zdálo, že pozitivní vliv SAP je potlačen. Ve všech použitých podmínkách nebylo u vzorků obsahujících PVA dostatečné zacelení trhlin pozorovatelné.

KLÍČOVÁ SLOVA

Samohojící • Bakterie • Beton • SAP • PVA

ABSTRACT

This paper is focused on two main issues of the bio-based self-healing concrete: protection of the bacterial spores embedded in the cementitious matrix and behavior of the material at low temperatures (freeze-cycles, 5 °C, and 10 °C). As a form of protection, superabsorbent polymers (SAP) powder and 16 % polyvinyl alcohol (PVA) water solution are applied.

After 28-day immersion in water at the room temperature, the series containing SAP and bacterial spores (BAC_SAP) showed the most pronounced healing – the value of the average maximum healed crack width (Δw_{max}) reached 219 µm. At low temperatures, the positive impact of SAP seemed to be inhibited. In all of the applied conditions, insufficient crack-sealing was detectable in the samples containing PVA.

KEYWORDS

Self-healing • Bacteria • Concrete • SAP • PVA

1. INTRODUCTION

The reduction in the durability of concrete structures is closely related to the presence of cracks in their cover layer. Cracks accelerate the transport processes in the porous structure of concrete, thus making the material more susceptible to degradation (such as chloride corrosion, carbonation, etc.).

In the 19th century, the ability of certain microorganisms, specifically bacteria, to produce calcium carbonate (the so-called biocalcification process) was discovered (Henry Lutz Ehrlich, Dianne K. Newman 2015). Based on this knowledge, in 2008, Jonkers introduced self-healing concrete with a biological agent (H. Jonkers and Schlangen 2008). In this novelty material, calcite-producing bacteria is in its inactive form of spores embedded together with necessary organic compounds into the concrete matrix. After a crack occurs, the spores close to the crack surfaces are activated by the penetrating moisture and organic compounds. The now active bacteria then metabolize and convert the mineral precursor compounds to calcium carbonate ($CaCO_3$), which gradually seals the crack.

Pilot studies proved the idea of self-healing biological concrete to be promising, but subsequent research highlighted several potential drawbacks. Although the applied bacteria is sporulated, experiments showed that the number of viable bacterial spores significantly decreases after approx. 7 days from casting (H. M. Jonkers et al. 2010). To overcome this limitation, researchers have been suggesting and investigating numerous methods of the bacteria protection: e.g. lightweight aggregates (LWA) (Alghamri, Kanellopoulos, and Al-Tabbaa 2016), silica gel and polyurethane (J. Wang et al. 2012), standard and pH-responsive hydrogels (J. Y. Wang, Snoeck, et al. 2014), melamine-based microcapsules (J. Y. Wang, Soens, et al. 2014), or the so called "Activated Compact Denitrifying Cores" (ACDC) particles (Ersan, Boon, and de Belie 2018).

Another problematic factor of the self-healing bio-based concrete is its potential dependence on temperature. The majority of studies was performed under optimal and stable conditions, i.e. at room temperature (around 22 ° C) with a sufficient water supply. However, the average monthly temperature in the Central European region, for example, exceeds 15 ° C only three times a year, while the average cultivation temperature for the most commonly used bacteria is up to 30 °C.

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Only a few studies addressed this issue. Palin et al. (Palin 2017) reported that cracks in cementitious composite containing a bacterial self-healing agent reduced their permeability by 95 % in the case of 0.4 mm wide cracks and by 93 % in the case of 0.6 mm wide cracks, when immersed in artificial seawater at 8 °C for 56 days. In contrast, a field study carried out by Paine et al. (Paine et al. 2018) with reinforced concrete wall panels placed on a highway did not report such optimistic results.

In the study presented in this paper, both of the aforementioned issues – the protection of bacterial spores in concrete matrix and application of the material under non-ideal conditions – are addressed. As the protective agents, two types of polymers are applied - superabsorbent polymer (SAP) powder and polyvinyl alcohol (PVA) in the form of a water solution.

SAP has already been successfully applied to a similar purpose by Gupta et al. (Gupta, Kua, and Pang 2018), where the combination of SAP, biochar and bacteria led to closure of cracks up to 800 μm and higher recovery of mechanical properties compared to non-bacterial samples. There is no mention in the existing literature of the application of PVA water solution in self-healing bio-based concrete.

MATERIALS AND METHODS

1.1. Mix design, mixing, specimens, cracking

The composition of the mixture is provided in Table 1. The mixing procedure was kept identical in all cases. Yeast extract (bacterial metabolic activator) was homogenized with cement prior to mixing and calcium lactate (a calcium source for the $CaCO_3$ precipitation) was dissolved in mixing water (containing dispersed bacterial spores if applied – B, B_S, B_P). In the case of SAP (C_S, B_S) and PVA series (C_P, B_P), both polymers were applied alongside cement and mixed prior to the aggregate and water addition.

From the prepared mixes, two types of specimens were prepared - specimens for mechanical testing and specimens for crack-sealing investigations. All the specimens were prepared in triplicates for each mix design and testing method. Both types were casted in 40x40x160 mm^3 steel molds, thoroughly vibrated using a vibrating table. In the case of the specimens intended for the crack-sealing, around 20 profiled steel wires were placed in the middle of the span, approx. 1 cm from the mold top.

The molds were then left at room temperature covered with plastic foil for 24 hours to harden. Thereafter, all the specimens were unmolded and placed in a climate chamber with temperature 24 °C and relative humidity up to 95% for 28 days. After the end of the curing period, dimensions of the specimens were thoroughly measured, and the samples were weighed.

To estimate the healing capacity of the proposed combinations of bacteria and protective methods, the prepared reinforced samples were cracked after the end of the curing period. The cracks were introduced through three-point bending using a calibrated electric loading machine. The loading rate was controlled manually and operatively altered to avoid complete destruction of the sample.

Table 1: *Compositions of the mixtures containing bacteria (B) and/or SAP (S) or PVA (P).*

Compound	C [kg/m^3]	C_S [kg/m^3]	C_P [kg/m^3]	B [kg/m^3]	B_S [kg/m^3]	B_P [kg/m^3]
Portland cem.	586	586	586	586	586	586
Distilled water	293	337	262	293	337	262
Medium agg.	440	440	440	440	440	440
Fine agg.	1319	1319	1319	1319	1319	1319
SAP	no	2.93	no	no	2.93	no
16 % PVA	no	no	36,63	no	no	36.63
Calcium lactate	17.58	17.58	17.58	17.58	17.58	17.58
Yeast extract	2.64	2.64	2.64	2.64	2.64	2.64
Bacillus Pseudofirmus [CFU/ml]	no	no	no	8x10^8	8x10^8	8x10^8

1.2. Methodology

The cracked samples were subjected to three different healing conditions: optimal, low temperature and temperatures below the freezing point. The optimal environment (25 ± 2 °C) served as the reference. This value also more or less corresponds to the highest reachable average month temperatures in the place of our research - the Central Europe region. To inspect the healing potential in the ideal conditions, the cracked samples were placed into separate plastic containers filled with tap water and left at temperature for 28 days. All the series were exhibited to the ideal conditions in order to obtain a complete overview of each material's healing capacity. Thus, the contribution of bacteria and each protective method to the healing process could be determined.

The temperature of 10 °C was chosen for the investigation at low temperatures. In the place of our research, Czech Republic, the long-term air temperature normal (1981-2010) reaches and exceeds this value from May to August, i.e., in 5 months of the year, according to the data from the Czech Hydrometeorological Institute. In the case of sufficient crack sealing at this temperature, the self-healing could potentially take place for a large part of the year, thus the material could be declared applicable in the Central European region. In order to inspect this hypothesis, identically as in the ideal conditions, the cracked samples were submerged in water in plastic containers. The containers were then placed in a climate chamber with a controlled temperature of 10 °C for 28 days. In this case, only specimens with protective polymers (i.e., B_S and B_P) and control (C) were used.

An investigation of the impact of temperatures below the freezing point on the self-healing ability is a unique extension of the current state of the art. Although the crack sealing due to the metabolic activity of bacteria at freezing temperatures is not expected, it is crucial to answer the question, whether the bacteria immobilized in the cementitious material/protective polymer can withstand these conditions and restore its activity

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once the temperature raises. To simulate the freezing conditions, the cracked samples, prior to any water submersion, were placed into a freeze-thaw chamber. Through air flow, the temperature was precisely and gradually varied from 0 °C to -5 °C. The time of one cycle was 24 hours. The samples were left at the chamber for 14 days (i.e., 14 cycles).

Although such conditions do not necessarily correspond completely to reality, they are sufficiently testing a range of frequently occurring values in a relatively short test time. After the below-zero temperature cycles in the chamber, the samples were taken out and placed into water-filled containers in ideal conditions (as described above) for 28 days. As in the previous case, only specimens with protective polymers (i.e., B_S and B_P) and control (C) were used.

1.3. Test methods

Mechanical tests

To determine the suitability of the mixture design, three-point bending and compressive strength test were carried out. Both measurements were performed only on non-bacterial samples as no noticeable influence of bacteria on the strengths was expected.

Visual inspections of the crack-healing

The maximum sealed crack width was selected as the basic indicator of the self-healing potential. Through this value, the extent of the crack sealing can be easily compared through the individual series without the need for uniformed damages. The average maximum healed crack width (Δw_{max}) was determined as:

$$\Delta w_{max} = \frac{\sum w_{max}}{n}, \tag{1}$$

where w_{max} is the maximum crack width that was sealed in each specimen and n is the number of specimens in each series.

In order to document the development of the crack sealing, all cracked reinforced specimens were subjected to high-resolution photography at the beginning of the healing period, and after 28 days in the respective environment. To obtain further information about the crack-closure, selected specimens were also additionally scanned with a 3D scanning optical microscope.

Dynamic Young's modulus recovery

The crack-sealing in the bio-based concrete primarily aims to the extension of the structure's durability, thus improvement of the material's watertightness through reduction of the crack area. However, recovery of mechanical properties would surely be a welcome side effect. Furthermore, the information about the changed properties may appropriately supplement the information obtained from the visual assessments.

In this paper, the dynamic modulus was measured on all the reinforced specimens before cracking, after the cracking and after the healing period. For the quantity evaluation, the Resonance Frequency dynamic methodology was applied.

The Resonance Frequency dynamic method is a non-destructive test for determination of dynamic modulus (E_d) based on the responses obtained from a vibrating signal induced in the specimen. The resonance frequency of the specimen, which produces the maximum amplitude of vibration, is then used to calculate the corresponding E_d value (Marques et al. 2020). For the evaluation, the Brüel & Kjaer assembly (measurement station type 3560-B-120, type 4519-003 acceleration transducers, an 8206 impact hammer type, and a computer) was used.

The dynamic Young's modulus was evaluated based on the longitudinal natural frequency of the samples as

$$E_{d,l} = \frac{4lmf_l^2}{bt}, \tag{2}$$

where $E_{d,l}$ is the dynamic Young's modulus [Pa], l is the sample length [m], m is the sample mass [kg], f_l is the basic longitudinal natural frequency of the sample [Hz], b is the sample thickness [m], and t is the sample height [m].

2. MECHANICAL TEST RESULTS

The mechanical tests revealed several important aspects of the cementitious composite with polymer additions applied in this study. The mean values of the measured quantities are shown in Figure 3. Firstly, the proposed dosage of the nutritive compounds (3 % wt. of cement of calcium lactate and 0.45 % wt. of cement of yeast extract) proved to be suitable as the compressive and tensile strength reached sufficiently high values (mean values 39.4 MPa and 6.4 MPa, respectively).

The series C_S evinced satisfactory behaviour in tension. Its tensile strength reached slightly higher values compared to the control mix (the mean value about 7% greater). On the other hand, the applied alterations of the mix caused rather significant drop in the compressive strength. The mean value of the compressive strength was about 30% lower compared to the control.

The addition of 1 % wt. of cement of PVA (in the form of 16% water solution) in the series C_P resulted in a drastically weaker material in both cases. The tensile strength reached only 44% of the control mix strength, the compressive strength as low as 21%. This finding contradicts with the results presented elsewhere as generally, the compressive strength decreased similarly as in our case, but the tensile strengths tended to be improved (Pique and Vazquez 2013).

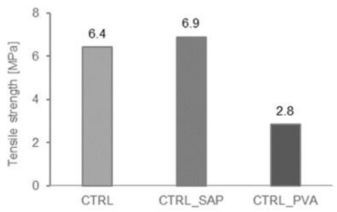

Figure 1: *The mean values of tensile strength of the non-bacterial mixes obtained through the mechanical tests.*

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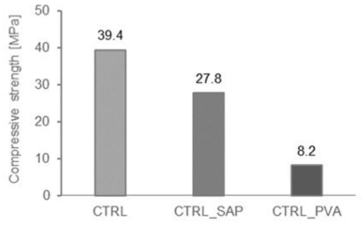

Figure 2: *The mean values of compressive strength of the non-bacterial mixes obtained through the mechanical tests.*

3. VISUAL INSPECTIONS OF THE CRACK HEALING EFFICIENCY

In this work, we sought to establish the applicability of the proposed bio-based self-healing concrete in other than ideal in-vitro conditions, thus extending the scope of the majority of earlier studies. In Figure 3, for the sake of completeness, all values of the average maximum sealed crack width (Δw_{max}) that could be identified in each series are summarized.

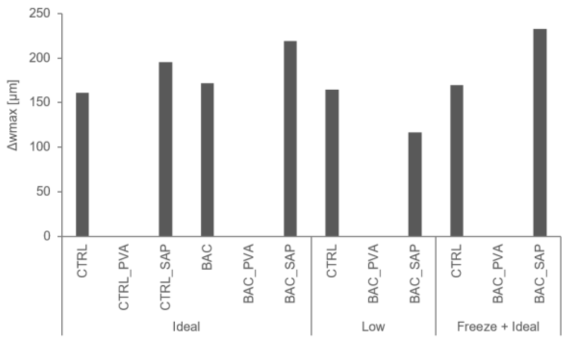

Figure 3. *An overview of the average maximum healed crack widths (Δw_{max}) in each series.*

3.1. Optimal temperature

In general, the data suggest that detectable crack-sealing took place in all of the prepared series except the ones containing liquid PVA. In the reference series (CTRL), the value of Δw_{max} reached 161 µm. As in the CTRL series no enhancement of the self-healing capacity was applied, this value can be considered achievable through the natural autogenous crack-sealing ability of the cementitious material in this study.

A slightly higher value (172 µm) was recorded when bacterial spores without any protection (BAC) were incorporated into the cementitious composite. This would indicate that in this study, the natural autogenous crack-sealing potential could be increased by the bacteria-driven CaCO3 precipitation by around 7 %.

In the ideal conditions, the widest crack parts were sealed in the case of the SAP addition. In the composite with SAP alone (CTRL_SAP), the Δw_{max} increased to 195 µm. When a combination of SAP and bacterial spores was applied (BAC_SAP), the Δw_{max} reached as high as 219 µm.

Furthermore, the difference between the series with only SAP and SAP-bacteria combination was higher (around 12%) compared to the difference between the reference series (CTRL) and series containing the unprotected bacteria (BAC). Thus, these results may suggest the possible SAP protective potential as it seems to improve the biocalcification process itself.

In this study, as mentioned previously, the self-healing potential of PVA-based cement composite series (CTRL_PVA and BAC_PVA) showed to be completely disappointing as no crack-sealing was detectable in the case of the liquid PVA addition.

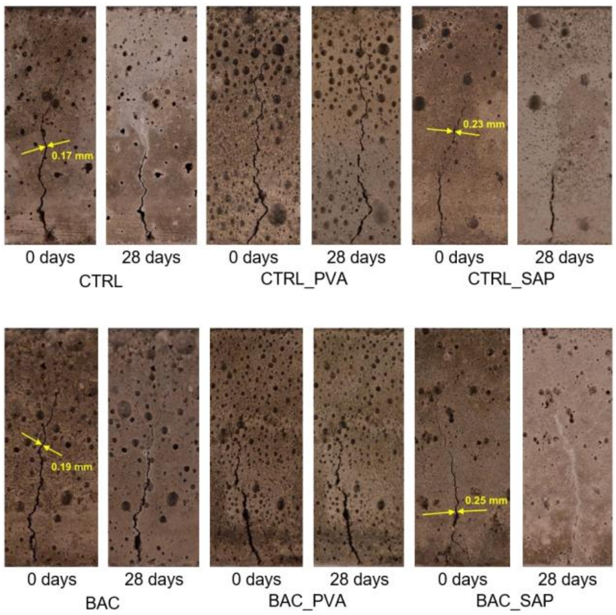

Figure 4: *High-resolution photography before (0 days) and after the healing period (28 days) in ideal conditions of the samples. The maximum healed crack width on the individual samples is marked.*

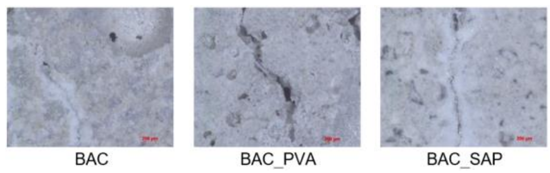

Figure 5*: Images obtained using a 3D scanning microscope.*

3.2. Low temperatures

As previously outlined, the problematic functionality of the bio-based self-healing concrete at lower temperatures was frequently mentioned in earlier studies. In our case, the findings are in line with the pessimistic presumptions (see Figure 4 for complete overview and Figure 6 for selected cracks).

In the 10 °C environment, the autogenous crack-sealing detected in the case of CTRL did not noticeably differ from the values achieved in the ideal conditions (Δw_{max} = 165 µm). Interestingly,

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in the BAC_SAP series, the Δw_{max} dropped to 117 μm. Thus, it seems that not only the bacteria-driven biocalcification was limited at low temperatures as expected, but also the results indicate that the positive impact of SAP to the self-healing may be inhibited by the temperature as well. Further, it seems that the SAP at low temperatures possibly even limits the natural autogenous crack-sealing capacity as the Δw_{max} was even lower by 30 % compared to the control series.

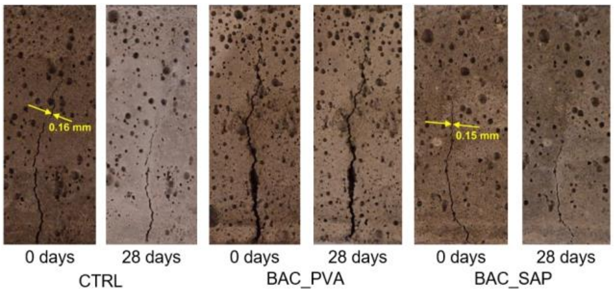

Figure 6: *High-resolution photography before (0 days) and after the healing period (28 days at low temperature) of the samples. The maximum healed crack width on the individual samples is marked.*

3.3. Freeze-thaw cycles

From Figure 4 it can be seen that, interestingly, the Δw_{max} reached in both CTRL and BAC_SAP even slightly higher values compared to the series without the freeze treatment (170 and 233 μm, respectively). However, the difference between the two mentioned series remained almost identical in both environments i.e., around 35% increase in the case of BAC_SAP. Thus, the bacteria viability was not negatively affected by the freezing cycles, possibly thanks to the SAP that served as a sufficient protective method. Consistently with the previous results, even after the freeze treatment, no crack-sealing could be observed in the series containing liquid PVA as illustrated in Figure 3 and Figure 7.

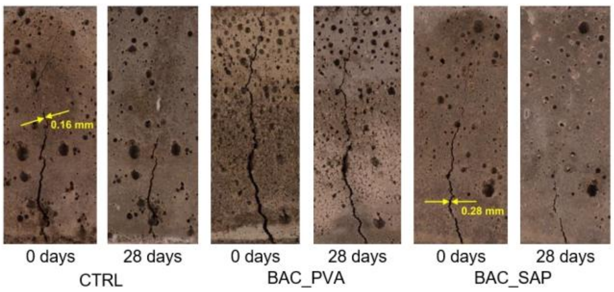

Figure 7: *High-resolution photography before (0 days) and after the healing period (28 days at optimal temperature after freeze-thaw cycles) of the samples. The maximum healed crack width on the individual samples is marked.*

4. DYNAMIC YOUNG'S MODULUS RECOVERY RESULTS

In Figure 8, the mean values of $E_{d,l}$ evaluated from longitudinal vibration measured on the specimens before cracking can be seen. These values more or less correspond to the tendencies noticeable from the mechanical tests – the addition of PVA generally caused drop of the monitored quantity, whereas the SAP series values were around the control values. After the controlled cracking, the value of $E_{d,l}$ in all of the series was zero as expected.

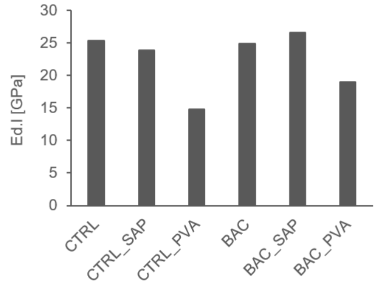

Figure 8: *The mean values of the dynamic modulus of elasticity E_d measured on the uncracked specimens.*

Measurements after the end of the healing period were far from complete as it was possible to detect the longitudinal frequency only for a fraction of the samples; for the rest $E_{d,l}$ remained zero. Provided that the measurement of the longitudinal frequency could be accomplished only if the filling of the crack was sufficiently rigid and solid, the data would suggest that the combination of bacteria and SAP leads to the most reliable crack-sealing as the majority of measurable samples was from the BAC_SAP series in all of the temperature conditions. Further, the recovery rate (healed/uncracked specimen) seemed to be consistently the highest in the case of BAC_SAP series (as much as 51%).

5. CONCLUSIONS

In the current study, the combination of bacteria *Bacillus pseudofirmus*, nutritional compounds, and SAP or PVA was applied in cement composite in order to evaluate the biologically enhanced material's self-healing potential in various healing conditions. The following conclusions can be drawn based on the current experimental investigation:

- SAP in all probability has a positive impact on the natural autogenous crack-sealing.
- In this paper, the SAP addition seemed to improve the biocalcification process, thus the bacteria driven crack-sealing.
- The SAP functionality might be limited at lower temperatures; however, more research on the exact mechanism is needed.
- The efficiency of the proposed self-healing cement composite containing the combination of SAP and

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bacterial healing agent did not seem to be affected by the freeze cycles.

- The application of liquid PVA, given the mixing procedures, turned out to be unsuitable from the point of view of both material characteristics and self-healing efficiency. Other mixing procedure such as addition after mixing water should be examined in future research.

ACKNOWLEDGEMENTS

This paper was prepared thanks to the support of the project "Durability of concrete structure and assessment of its life cycle" (SGS19/149/OHK1/3T/11).

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