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Submitted date: 13/12/2019 • Posted date: 19/12/2019
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Citation information: Qu, Zhengyao; Guo, Shuaiqi; Sproncken, Christian C. M.; Surís-Valls, Romà; yu, qingliang; Voets, Ilja (2019): Enhancing the Freeze-Thaw Durability of Concrete Through Ice Recrystallization Inhibition by Poly(vinyl Alcohol). ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.11363843.v1

Frost weathering of porous materials caused by seasonal temperature changes is a major source of damage to the world’s infrastructure and cultural heritage. Here we investigate poly(vinyl alcohol) (PVA) addition as a means to enhance the freeze-thaw durability of concrete without compromising its structural or mechanical integrity. We evaluate the ice recrystallization inhibition activity of PVA in a cementitious environment and the impact of PVA on key structural and mechanical properties, such as cement hydration (products), microstructure, strength, as well as freeze-thaw resistance. We find that a low amount of PVA significantly reduces the surface scaling of concrete and displays excellent ice recrystallization inhibition in the saturated Ca(OH)$_2$ solution which has a similar pH value as cement pore solution, while it does not affect cement hydration, microstructure, nor its mechanical properties. These findings contribute to new insights on freeze-thaw damage mechanism and more importantly we disclose a new direction for the design of concrete with excellent freeze-thaw resistance.
Enhancing The Freeze-thaw Durability of Concrete through Ice Recrystallization Inhibition by Poly(vinyl alcohol)

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**Abstract:** Frost weathering of porous materials caused by seasonal temperature changes is a major source of damage to the world’s infrastructure and cultural heritage. Here we investigate poly(vinyl alcohol) (PVA) addition as a means to enhance the freeze-thaw durability of concrete without compromising its structural or mechanical integrity. We evaluate the ice recrystallization inhibition activity of PVA in a cementitious environment and the impact of PVA on key structural and mechanical properties, such as cement hydration (products), microstructure, strength, as well as freeze-thaw resistance. We find that a low amount of PVA significantly reduces the surface scaling of concrete and displays excellent ice recrystallization inhibition in the saturated Ca(OH)$_2$ solution which has a similar pH value as cement pore solution, while it does not affect cement hydration, microstructure, nor its mechanical properties. These findings contribute to new insights on freeze-thaw damage mechanism and more importantly we disclose a new direction for the design of concrete with excellent freeze-thaw resistance.

**Keywords:** Concrete; cement; freeze-thaw durability; ice recrystallization inhibition; poly(vinyl alcohol); pore structure
1 Introduction

Ice is one of the few substances on Earth that expands upon solidification. This expansion can be destructive to porous materials that take up water such as cement and concrete exposed to freeze-thaw cycles (1). Cement and concrete are the most used man-made materials with a global annual consumption of 4 billion and 25 billion tonnes, respectively (2). Seasonal temperature changes induce freezing-thawing cycles in many landscapes across the globe and are responsible for visible deterioration of concrete structures, costing $18-21 billion annually on repairs in the U.S. alone (3). This has spurred great interest in effective strategies applicable on industrially relevant scales to reduce frost damage.

The first studies conducted on the mechanism of frost damage in concrete hypothesized that the hydraulic pressure generated by the volume expansion of freezing water is the driving force for the damage (4,5). This hydraulic pressure theory argues that ice formation inside the concrete matrix forces unfrozen water to flow away from the ice growth site, which generates a pressure gradient resulting in microcracks and spalling once the local tensile strength of the concrete (capillaries) is exceeded. Decades later, several researchers reported experimental evidence for the importance of crystallization pressure (6,7). This pressure is exerted by a growing ice crystal on its constraining concrete matrix if there is a thin supercooled water film in between the growing ice crystal and the pore wall (8). More recent studies by Scherer and co-workers show that both the hydraulic and crystallization pressures damage the concrete in freeze-thaw cycles and one may dominate the other under different conditions (9).

Conventional methods used to counter freeze-thaw deterioration in cementitious materials include entrainment of 5-10% air in the cement mixture and application of de-icing salts and/or coatings on the concrete surface. Introducing air voids protects the concrete matrix from frost damage as these offer space for the expansion of ice inside the material (5). Air entrainment is effective up to a certain extent, but disadvantageously facilitates the penetration of aggressive fluids into the concrete and reduces its mechanical properties (10,11). De-icing salts lower the freezing point of water on concrete surfaces and in the porous structure, but result in chloride-induced leaching of calcium hydroxide and other hydration products, leading to corrosion of the steel reinforcements and scaling. More importantly, saturation by de-icing salts will induce more damage (12–14). Surface treatment with suitable coatings can decrease water transport into the
concrete matrix, but current strategies usually suffer from an increased probability of crack propagation and elevated costs (15). For lack of a better alternative, the above methods to mitigate frost damage to concrete have been used for over 70 years, despite their disadvantages.

We set out to develop a simple method to improve the freeze-thaw durability of cementitious materials, using small quantities of a suitable additive that reduces ice formation and growth without sacrificing the mechanical properties of the final material. For this purpose we selected poly(vinyl alcohol) (PVA), which is a commodity polymer known for its ability to drastically slow ice crystal growth by recrystallization processes (16). PVA is not only the most potent synthetic ice recrystallization inhibitor by far, it is also relatively easy and inexpensive to synthesize, and abundantly available (17–21). Its ice recrystallization inhibition ability has been related to the good match between the conformation of atactic PVA and the ice lattice on the primary and secondary prism planes (22,23). In the present study we investigate whether PVA improves the freeze-thaw durability of Portland cement concrete. We further evaluate the ice recrystallization inhibition (IRI) activity of PVA in a cementitious alkaline environment and the impact of PVA on key structural and mechanical properties of cement mortar. Gratifyingly, we find that <0.1wt% of PVA displays excellent ice recrystallization inhibition in the saturated Ca(OH)\textsubscript{2} solution (pH = 12.5, similar to the pore solution of concrete) and significantly reduces the surface scaling of concrete, while it does not affect cement hydration, microstructure, nor its mechanical properties. These findings disclose a new direction for the design of concrete with excellent freeze-thaw resistance with great potential for large-scale industrial application.
2 Experimental Section

Materials. Saturated Ca(OH)$_2$ solution was prepared by dissolving calcium hydroxide (Aldrich, ≥95%) in ultrapure water (18.2 MΩ). The pH of the solution is 12.5 which is close to the value of pore solution of concrete. Atactic poly(vinyl alcohol) (Aldrich), with a weight-average molar mass of $M_w = 146,000$-$186,000$ g mol$^{-1}$ and a degree of hydrolysis of >99%, was added at $4\times10^{-3}$ M monomer concentration ($\approx 0.18$ g L$^{-1}$) to the saturated Ca(OH)$_2$ solution as well as to the mortar specimens. This concentration was previously shown to be sufficiently high to inhibit ice recrystallization (20), however, it has not been proven to be active in a saturated Ca(OH)$_2$ solution. Sucrose (BioUltra, ≥99.5%) was added in 30 wt% to the pore solutions to perform sucrose sandwich IRI assays (23,24). Cover slides (24x24 mm Menzel glasses, ThermoScientific) were purchased from VWR and cleaned by sonication in ultrapure water and technical grade acetone (Aldrich) for 10 min, followed by drying with N$_2$ flow. For mortar specimen preparation, the PVA was added to tap water (hardness $\sim 1.1$ mmol L$^{-1}$, pH$\sim 7.7$) and dissolved by stirring the mixture at 90 °C for 2 hours. Mortar specimens were prepared with a water/cement ratio of 0.5 applying CEM III/A 52.5 N and standard sand, with and without the addition of 0.018 wt% ($4\times10^{-3}$ M monomer concentration) PVA to the water (Table 1).

Table 1. Recipe of the mixture for mortar specimen preparation [kg m$^{-3}$].

| Sample            | Cement | Sand | Water | PVA |
|-------------------|--------|------|-------|-----|
| Reference         | 450    | 1350 | 225   | 0   |
| PVA-modified      | 450    | 1350 | 225   | 0.04|

Methods. Ice recrystallization inhibition assays were performed using a Nikon ECLIPSE Ci-Pol optical microscope controlling the temperature with a Linkam LTS 420 stage, following the sucrose sandwich assay as described elsewhere (25). A home-built analysis script in ImageJ was used to determine the area of each ice crystal, and an equivalent ice crystal radius is calculated. To quantify the ice recrystallization driven by Ostwald ripening, rate of ice recrystallization ($k_0$) was calculated by plotting the cubic number-average radius ($<r^3>$) versus time as described previously (26).

Mortar was prepared by mixing cement, sand and water in a laboratory mixer at a low speed for 30 s, rested for 30 s before another 120 s of mixing at a medium speed. Here PVA was first mixed with water prior to the mortar preparation. The fresh mortar was cast into moulds with
dimensions of 40 mm × 40 mm × 160 mm. The prisms were demoulded 24 h after casting and cured at 100% RH at about 21 °C. After curing for 7 and 28 days, the flexural and compressive strengths of the specimens were tested according to EN 196-1 (27). At least three specimens for the flexural strength and six for the compressive strength were tested at each age to compute the average strength and standard deviation.

The pore size distribution was measured using mercury intrusion porosimetry (MIP, Autopore IV, Micromeretics), with a maximum applied mercury pressure of 228 MPa, contact angle of 130° and equilibration time of 20 s. The pore size range was set to 0.0063-900 μm. X-ray diffraction (XRD) was performed on diffractometry equipped with a Cu tube (40 kV, 30 mA) with a scanning range from 5° to 65° 2θ, applying a step 0.02° and 5 s/step measuring time. The qualitative analysis was carried out using the Diffracplus Software (Bruker AXS) and the PDF database of ICDD. Isothermal calorimetry tests were conducted at 20 °C in a TAM AIR Calorimeter following CEM III/A 52.5 N.

![Temperature profile for the 24 hour-long freeze-thaw cycle, following the CEN standard.](image)

The surface scaling freeze-thaw test was performed following CEN/TS 12390-9 (28). The mortar specimens were cast in PVC tubes with a diameter of 100 mm and height of 60 mm. After one day, the mortar was demoulded and cured at 100% RH for 27 days. Three specimens were tested for each mix, resulting in a total exposed surface area of 0.024 m². After saturation, the freeze-thaw test was carried out with a 3-mm layer of demineralized water poured on the top surface. The temperature profile in the climate chamber followed the standard recommendations.
(Fig. 1) (28). The water level on the surface of the samples was adjusted regularly. In total, 56 freeze–thaw cycles were applied, during which the surface scaling was measured weekly.
3 Results and discussion

Ice-recrystallization of a saturated Ca(OH)$_2$ (artificial cement pore solution) solution. To probe whether PVA hampers ice recrystallization in a saturated Ca(OH)$_2$ solution, we monitor the process with and without 0.018 wt% PVA in the presence of 30 wt% sucrose to warrant a low ice volume fraction. As expected (26), large ice crystals grow at the expense of small ones in both samples during 60 min annealing at -7.0 °C (Fig. 2). Over time, the mean ice crystal size increases, while the total ice crystal number density decreases. Noticeable differences in mean crystal size and shape become more pronounced over time. The ice crystals in the PVA-containing solution remain small and are shaped into rectangular morphologies with sharper edges compared to the larger crystals formed in the solutions without PVA, which have relatively round shape.

Fig. 2. Microphotographs of samples annealed at -7.0 °C in a saturated Ca(OH)$_2$ solution without (a,b) and with 0.018 wt% PVA (c, d), at t = 0 min for a) and c); t = 60 min for b) and d). The scale bars represent 50 µm.
We use the Lifshitz, Slyozov and Wagner (LSW) theory of Ostwald ripening to quantify the observed differences in ice crystal growth kinetics caused predominantly by differential migratory recrystallization rates (26). It states that the temporal increase in cubic mean radius at constant volume fraction, temperature and pressure can be expressed as:

$$\dot{\langle r^3 \rangle} = \dot{\langle r^3 \rangle}_0 + k_d \cdot t$$

Here, $\langle r \rangle_0$ ($\mu$m) is the initial mean radius at time $t = 0$ min and $k_d$ ($\mu$m$^3$ min$^{-1}$) is the observed rate constant of recrystallization. This rate constant is thus extracted from the slope of the cubed number-average mean radius versus time (Fig. 3). In the pore solution (Fig. 2a and b), small ice crystals of around one micrometer in radius grow into larger crystals of tens of micrometers within 60 min. Addition of PVA hampers this process (Fig. 2c and 2d), lowering the ice growth rate constant by more than 99% from $k_d = 15$ $\mu$m$^3$ min$^{-1}$ to $k_d < 0.1$ $\mu$m$^3$ min$^{-1}$ upon addition of just 0.18 g L$^{-1}$ of the polymer (Fig. 3). PVA is thus highly IRI-active in the alkaline cement pore solution.

![Fig. 3. The ice growth rate constant ($k_d$) is determined from the slope of the cubic mean crystal radius ($\langle r^3 \rangle$) versus time for saturated Ca(OH)$_2$ solution without (○) and with 0.018 wt% PVA (△) containing 30 wt% sucrose.](image)

**Hydration kinetics and reaction products:** Adding extra compounds to the concrete mixture can affect its curing process, therefore it is important to evaluate the impact of PVA addition on the hydration rate and products of the cement mixture. Isothermal calorimetry gives insight into
the reaction kinetics by monitoring the heat release per solid mass over 40 hours (Fig. 4a,b). The calorimetric peaks of the initial dissolution stage with significant higher heat flow during the first few minutes is shown in the inset of Fig. 4a, corresponding to wetting and dissolution of raw materials. It can be seen that the addition of PVA has little influence on this process as the two curves present very similar shapes. Both the reference and PVA-modified mixtures display four typical reaction stages (Fig. 4a): initial dissolution (I), induction (II), acceleration (III) and a deceleration period (IV), in accordance with a previous study (29,30). These stages correspond to the initial wetting and dissolution of the raw materials (I), the formation of a protective phase inhibiting dissolution or delayed nucleation and growth (II), the massive formation of reaction products (III), and reaction was slowed down by forming a diffusion barrier at the surface of reaction products and water deficiency (IV). Evidently, PVA addition does not significantly impact the hydration kinetics as the calorimetric profiles of the PVA-modified and reference samples are virtually identical within the experimental error. An acceleration peak at the same time point of equal magnitude indicates that reaction products appear in similar quantities in stage III after approximately 10 h in both samples. X-ray diffraction profiles further reveal that the composition and phase state of the hydrated cement is also unaltered by PVA addition (Fig. 4c). The XRD results of the paste samples show typical reaction products of hydrated cement paste. The peaks of at 2θ = 18° and 34° are portlandite and the peaks at 2θ = 29° are silicate hydrate (CSH).
Fig. 4. a) Heat evolution (initial profile shown in the inset), b) cumulative heat evolution and c) XRD patterns of the reference (dashed black lines) and PVA-modified (red solid lines) cement mixtures. Peaks correspond to Ettringite, Calcium aluminate hydrate, portlandite (CH), Melilite, Quartz, calcium silicate hydrate (C-S-H), dicalcium silicate (C₂S) and tricalcium silicate (C₃S).

**Structural integrity:** To critically assess whether it is advantageous to add PVA to enhance the freeze-thaw resistance of cementitious materials, we next evaluated by mercury intrusion porosimetry and mechanical testing if the required PVA dosage does not deteriorate the structural integrity and mechanical properties of the concrete. The differential intrusion curves of reference and PVA modified samples demonstrate a pore size distribution with two main peaks belonging to the capillary pores (Fig. 5a). The first and second peaks are located around 10-40 nm and 0.05-0.1 µm, respectively, which all are remnants of the original water-filled space between the cement particles. The striking similarity in the pore size distribution curves implies a preservation in total porosity and rules out differences in effective volume upon the addition of low dosages of PVA.

It is equally important that PVA addition does not weaken the mechanical properties of concrete. Gratifyingly, measurements of the flexural and compressive strength of reference and PVA-modified samples show the same trend of increasing resistance to flexural and compressive stresses upon aging (Fig. 5b). No significant differences were observed between samples. We ascribe this to the almost identical porosity of the samples, since the amount of air entrainment in cement is one of the key determinants of its mechanical properties of cement. Our findings contrast with previous studies which reported that the addition of PVA to concrete mixtures
decreased their mechanical properties, due to generation of more pores after hydration of the cement (31). We do not observe such an adverse effect, due to the much lower amount of PVA used in this study (0.018 wt%) compared to the dosage of 2 wt% in the previous study (31). Our findings thus confirm that PVA can be applied at sufficiently low concentrations to strongly inhibit ice recrystallization without any decline in mechanical strength, which is of high importance for cementitious materials.

Fig. 5. a) Differential (with symbols) and cumulative (lines) pore volume distribution curves for the reference (dashed black line) and PVA modified (solid red line) mortar specimens; b) Flexural and compressive strengths of mortar specimens at three different ages show no significant influence of 0.018 wt% PVA addition (red triangle) compared to the reference (black circle). Dashed line and displaced data points for visual aid. Error bars indicate standard deviation between specimens.

Freeze-thaw resistance: Having confirmed the IRI efficacy of a low PVA dosage in pore solutions without compromising the hydration process (Fig. 4), porosity, mechanical properties of the cement (Fig. 5), we study its effect on the stability of concrete in freezing environments. Freeze-thaw tests were performed for 56 cycles of 24 hours, during which the surface scaling of concrete was measured every 7 days. The total surface scaling measured for the reference specimen after 56 cycles is 241 g m$^{-2}$, while that for the PVA-modified sample is only 99 g m$^{-2}$ (Fig. 6). A small amount of PVA is thus sufficient to reduce surface scaling by nearly 60%, which is below the 100 g m$^{-1}$ and thus classified as ‘very good’ in terms of freeze-thaw stable concrete using the Borås method (32,33). A close relationship between the pore structure and the
freeze-thaw durability of concrete was proposed previously (34). However, in this study, we find no such relation. The pore structure is unaffected by the low PVA dosage, while the freeze-thaw durability is enhanced more than twofold. This means that the reduced surface scaling must originate from another characteristic of PVA. We attribute its impact on freeze-thaw resistance to the observed ice recrystallization inhibition activity of PVA in the pore solution (Fig. 2).

Fig. 6. a) Cumulative surface scaling ($S_n$ in g m$^{-2}$) measured weekly for the duration of 56 freeze-thaw cycles for reference (○) and 0.04 kg m$^{-3}$ PVA-modified (△) mortar specimens. The low dosage of PVA reduced the total surface scaling by more than twofold. b) Reference and PVA-modified specimen surface showing distinct difference in surface scaling after 56 days.
4 Conclusions

Ice recrystallization in concrete pore solution is hypothesized to cause deterioration to cementitious materials upon exposure to freeze-thaw cycles. This study shows the effect of PVA addition on the freeze-thaw resistance of concrete. The ice recrystallization process of saturated Ca(OH)$_2$ solution is assessed and the poly(vinyl alcohol) (PVA) is shown to reduce the ice crystal growth rate by over 99% at a monomer concentration of only $4 \times 10^{-3}$ M ($\approx 0.18$ g L$^{-1}$). The structural and mechanical integrity of PVA-modified specimens were investigated to rule out that this advantage is offset by an adverse impact of polymer addition on e.g. the porosity, flexural and compressive strengths of the concrete. Our results show that neither the cement hydration kinetics and products, nor the pore structure of the cement matrix are affected by PVA addition, because of the low dosage. Furthermore, the mechanical strength of the modified concrete remains unaltered, indicating a high engineering application potential. Most notably, PVA addition (0.04 kg m$^{-3}$) significantly improved the freeze-thaw resistance of concrete, as the surface scaling of the prepared concrete after 56 freeze-thaw cycles decreased dramatically from 241 g m$^{-2}$ to 99 g m$^{-2}$ compared to the reference sample. This is attributed to the ability of PVA to inhibit ice recrystallization in the pore solution. We hypothesize that when water enters the pores and starts to crystallize upon cooling, the added PVA will adsorb to embryonic crystals, blocking their growth and helping to keep the pore structure intact. Our results thus disclose great potential for PVA as additive to improve the freeze-thaw stability of cementitious materials.
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**Acknowledgements**
ZYQ is grateful to the China Scholarship Council (20160695006) for its financial support; IKV is grateful to the European Union (ERC-2014-StG Contract No.635928), the Dutch Science Foundation (NWO ECHO Grant No. 712.016.0002), and the Dutch Ministry of Education, Culture and Science (Gravity Program 024.001.035) for their financial support.

**Author Contributions**
ZYQ and SQG conceived and initiated the project. ZYQ, SQG, CMS, RVS and IKV designed the experimental work. ZYQ, SQG, CMS, and RVS performed the experimental work. SQG and IVK supervised the research tasks. All authors analysed experimental results. ZYQ and SQG wrote the initial draft of the manuscript. CMS, RVS, QLY and IVK co-edited the manuscript. All authors reviewed the manuscript before submission.

**Additional Information**
**Competing Interests:** The authors declare no competing interests.
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