Nanosilica-Modified Hydrogels Encapsulating Bacterial Spores for Self-healing Concrete

J. Feng and S. Qian

Abstract Microbially induced calcium carbonate precipitation is effective in achieving self-healing of concrete cracks when the bacteria are well protected in concrete with a high pH and dense microstructure. Calcium alginate hydrogels are appropriate for encapsulating bacteria in concrete due to the mild environment with rich moisture in the hydrogels. Nevertheless, the low alkaline tolerance and breakage ratios of the hydrogels after concrete cracking restrict their applications in concrete. To address these problems, nanosilica was doped into calcium alginate hydrogels with encapsulated bacterial spores to react with the $Ca(OH)_2$ surrounding hydrogels in concrete. Due to the modification by nanosilica, the bond of the hydrogels with cement matrix was enhanced as needle-like C–S–H was generated at the interface after hydration for 7 days. Moreover, the urease activity of the encapsulated spores in the modified hydrogels was higher than that in plain hydrogels after submersion in saturated $Ca(OH)_2$ solution or simulated concrete solution for 7 days. Therefore, it can be concluded that nanosilica holds promise for modifying hydrogels to improve the effectiveness of encapsulated bacterial spores for self-healing of concrete.

Keywords Bacterial spores · Hydrogels · Nanosilica · Self-healing concrete

1 Introduction

Concrete is widely used in construction engineering due to its good durability, adjustable strength, and low cost. However, cracking can occur in concrete due to overloading and volume instability [1], which will reduce both the mechanical performance and durability of concrete structures. Hence, to prolong the service life of concrete structures, timely repair of concrete is critical.

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Currently, concrete repair is achieved manually using epoxy resin [2] or some cementitious material [3]. Nevertheless, manual repairing cannot be timely because the detection of cracks takes time and is not feasible for inaccessible cracks. Therefore, developing concrete with a self-healing capacity that can effectively heal cracks without human intervention is desired.

Concrete itself has a certain self-healing ability resulting from further hydration of cementitious materials and carbonation [4, 5], but only for cracks of limited sizes. The self-healing capacity can be further improved by incorporating some components specific for self-healing into the concrete. For example, minerals [6, 7], superabsorbent polymers [8, 9], and shape memory alloy [10, 11] have been added to concrete to enhance self-healing. In addition to these materials, bacteria-based self-healing agents for self-healing concrete has been investigated in recent years and promising results have been obtained [12]. For bacterial self-healing agents, carriers to encapsulate or immobilize the bacteria are required as the concrete environment with high pH [13] and dense microstructure is incompatible [14].

Among the carriers to encapsulate bacteria in concrete, hydrogels with moderate pH environment and rich moisture content have high potential for protecting bacteria [14]. Specifically, calcium alginate, which has good biocompatibility [15, 16], can be used to encapsulate bacteria, but its susceptibility to environmental factors [17] and poor bonding with concrete matrix could lead to the ingress of alkalis and low efficiency of releasing bacteria after cracking.

To address these issues, nanosilica was doped into calcium alginate hydrogels to react with the surrounding calcium hydroxide, simultaneously lowering the local pH and generating C–S–H at the interface between the hydrogel and cement matrix, which can enhance the bonding of hydrogels with concrete. A previous report [18] revealed that hydration product could be generated around or within hydrogels that contain silica, indicating the feasibility of the approach in this research. Herein, the microstructure of cement paste with hydrogels was observed and the alkali tolerance of hydrogels encapsulating bacterial spores was evaluated to analyze the effects of nanosilica modification on calcium alginate hydrogels.

2 Methods

2.1 Preparation of Bacterial Spores

One ureolytic bacteria *Lysinibacillus sphaericus LMG 22,257* from Belgian Co-ordinated Collection of Micro-organisms were used to prepare bacterial spores. The preparation methods were in accordance with the steps in [19].

2.2 Preparation of Hydrogels Encapsulating Bacterial Spores

7.5 g/L nanosilica powder (10–20 nm) was dispersed in sodium alginate solution (15 g/L) by sonication for 15–20 min before 2.0wt% bacterial spores were added to the mixture. Next, the mixture was dropped into calcium nitration solution (0.1 M) using a peristaltic pump with a rotary speed of 3 rpm. The prepared hydrogels were collected by gravity sedimentation then hardened in a fresh 0.1 M calcium nitrate solution for 24 h at 5 °C. Finally, the hydrogels were separated and washed three times with distilled water before being freeze-dried and stored at 4 °C. The plain hydrogels were synthesized using the same procedures except for the incorporation of nanosilica powder.

2.3 Observation of Interface Between Hydrogel and Cement Matrix

Cement paste with hydrogels was prepared by using Portland Cement I 52.5, tap water and hydrogels at a mass ratio of 1:0.5:0.0055. After moist curing (23±1°C, 75±5%°C relative humidity) for 7 and 28 days, the specimens were broken into pieces before being immersed in isopropanol for 24 h to stop hydration. The samples were impregnated in epoxy, then cut with a precision saw to expose the cement paste with hydrogels; the exposed surface was further ground, polished and washed with ethanol. Afterwards, the samples were vacuum dried and coated with gold before being observed under a scanning electron microscope (FESEM, JEOL JSM-7600F) at backscattered electron (BSE) mode at an accelerating voltage of 15 keV.

2.4 Revival of Bacterial Spores Encapsulated in Hydrogels After Exposure to Alkali Environments

The hydrogels with encapsulated endospores were immersed in saturated $Ca(OH)_2$ solution and simulated concrete pore solution containing 0.001 M $Ca(OH)_2$, 0.2 M NaOH and 0.6 M KOH [20] for 7 days respectively. After that, 1 g hydrogels were removed from the solution and washed three times with distilled water before being incubated in 100 mL sterile UYE medium (20 g/L urea and 20 g/L yeast extract). The optical density at a wavelength of 600 nm and the urease activities of the medium were measured by using a UV/Vis spectrometer (UV mini-1240, Shimadzu) and conductivity meter (DDS-11A, Lightning), respectively, after the inoculated mediums were cultivated for 1, 2, and 3 days.

3 Results and Discussion

The morphology of cement paste with modified hydrogels is shown in Fig. 1. After hydration for 7 days, nanosized calcium silicate hydrate (C–S–H) with needle-like morphology was observed on the outer surface of modified hydrogel, as shown in Fig. 1a, b. The generations of C–S–H were due to the reaction of the incorporated nanosilica on the hydrogel surface with calcium hydroxide in the cement paste, suggesting the effect of nanosilica modification on interface enhancement between the hydrogels and cement matrix. After hydration for 28 days, the BSE image shown in Fig. 1c revealed no obvious gaps or cracking at the interface, indicating the modified hydrogels bonded well with the cement matrix. The improved bonding of the hydrogels with cement matrix could facilitate the release of encapsulated bacterial spores after concrete cracking, as the cracks might propagate through the hydrogels rather than the interfaces, leading to breakage of the hydrogels and exposure of bacterial spores to the cracks. After the release of bacterial spores, the endospores can conduct germination and outgrowth with leaching of nutrients from the concrete matrix, contributing to the generation of calcium carbonate within cracks by producing urease to catalyze hydrolysis of urea.

The alkaline tolerance of the hydrogels encapsulating bacterial spores is shown in Fig. 2. After immersion in the alkaline solution for 7 days, the growth of the encapsulated bacteria in the modified hydrogels during incubation was more rapid than in the plain hydrogels, as illustrated in Fig. 2a. The optical densities of the medium with the modified hydrogels reached approximately 2 and 2.5 approximately after cultivation for 2 days respectively, while the optical densities of the medium with bacteria in plain hydrogels were close to 2 after cultivating for around 3 days. With the growth of bacteria, the medium with bacteria encapsulated bacteria in modified hydrogels presented higher urease activities than that with bacteria in plain hydrogels, as shown in Fig. 2b. After incubation for 1 day, the urease activities of medium were 3.7 U/mL and 6.6 U/mL approximately for hydrogels undergoing 7-day submersion in simulated concrete or saturated $Ca(OH)_2$ solution respectively, while those in medium with plain hydrogels was < 1 U/mL. Although the urease activities of medium with plain hydrogels further increased with incubation duration,

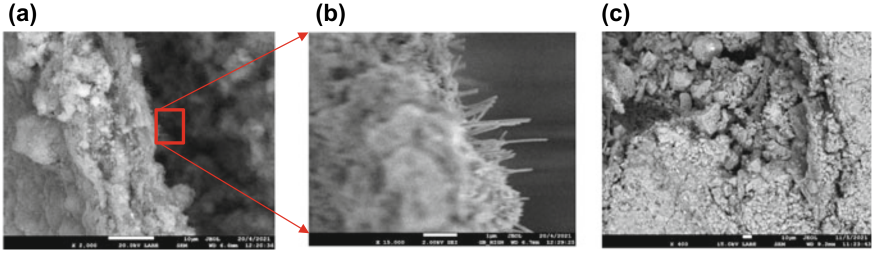

Fig. 1 Backscattered electron images of cement paste with nanosilica modified hydrogels. **a** After hydration for 7 days; **b** close-up view of the red box in (**a**); **c** after hydration for 28 days

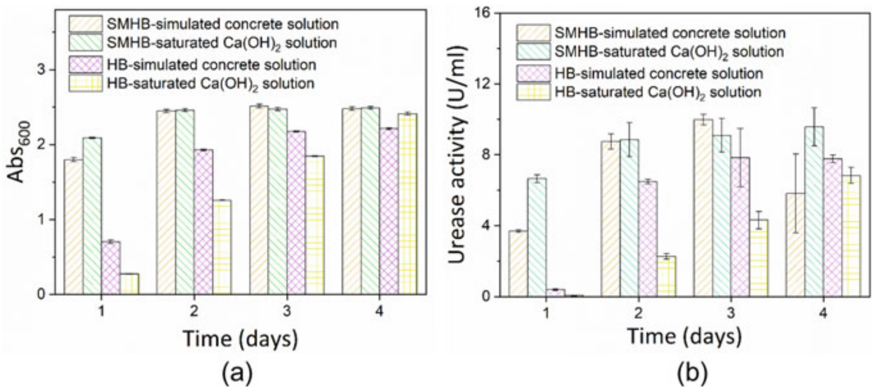

Fig. 2 **a** Optical densities of mediums with modified and plain hydrogels after being immersed in simulated concrete or saturated $Ca(OH)_2$ solution for 7 days; **b** urease activities of mediums with modified and plain hydrogels after being immersed in simulated concrete or saturated $Ca(OH)_2$ solution for 7 days. SMHB denotes the nanosilica modified hydrogels with encapsulated bacterial spores; HB denotes plain hydrogels with encapsulated bacterial spores

they were still lower than those with modified hydrogels after incubation for 2 and 3 days. Collectively, the bacteria in the modified hydrogels grew more rapidly and showed higher urease activities than those in plain hydrogels after exposure to an alkaline environment, which suggested the effectiveness of nanosilica modification on alkaline tolerance improvement of hydrogels for bacterial encapsulation.

4 Conclusions

This research investigated the feasibility of nanosilica modification of calcium alginate hydrogels for bacterial encapsulation in self-healing concrete. The results revealed that the nanosilica modification enhanced the bonding of the hydrogel with the cement matrix due to C–S–H generation at the interface. Moreover, the modified hydrogels with encapsulated endospores showed improved alkaline tolerance, because as the 7-day immersion in simulated concrete and saturated $Ca(OH)_2$ solution caused less inhibition on bacterial growth and urease activity in medium inoculated with modified hydrogels encapsulating endospores. Hence, it is feasible to modify calcium alginate hydrogels with nanosilica to increase the effectiveness of bacterial encapsulation in concrete. In the future, the effects of nanosilica-modified hydrogels encapsulating bacterial spores on self-healing performance (i.e. strength recovery, etc.) of concrete can be investigated.

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