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A comprehensive review on the performance, mechanisms and design of polyvinyl alcohol (PVA)-enabled self-healing concrete

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ABSTRACT

This review critically examines the roles, mechanisms, and future potential of polyvinyl alcohol (PVA) in self-healing concrete, with particular emphasis on the effects of polymer form, degree of polymerization (DP), and degree of alcoholysis (DA). Most of existing studies focus predominantly on PVA fibers for crack control. This review provides a comprehensive comparison between fiber-based and soluble PVA systems and evaluates their distinct influences on fresh properties, mechanical performance, durability, permeability, and self-healing efficiency. Recent experimental and simulation studies indicate that while PVA fibers mainly enhance autogenous self-healing by refining crack widths and providing nucleation sites, soluble PVA—especially low-DP variants—shows potential to actively promote autonomous healing through calcium-ion complexation and accelerated carbonate precipitation. Based on these comparisons and discussions, this review proposes a conceptual extension of the complexation–precipitation theory as a potential unifying framework to interpret PVA-enabled self-healing behavior. Key challenges related to workability, strength trade-offs, long-term durability, and cost are critically assessed. Finally, emerging perspectives are discussed, including synergistic use of multiscale PVA systems, integration with biomineralization agents, and broader extension of complexation-based healing strategies. This review aims to bridge material engineering performance with underlying chemical mechanisms, providing guidance for the rational design of next-generation self-healing concrete systems incorporating PVA.

1. Introduction

1.1. PVA and DP/DA influence

Polyvinyl alcohol (PVA) is a polyhydroxy organic polymer characterized by excellent hydrophilicity, and its molecular structure is shown in Fig. 1(a). The monomer unit of the polymer is vinyl alcohol; however, since the enol structure is intrinsically unstable, it

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predominantly exists in the form of its keto or aldehyde tautomer, as illustrated in Fig. 1(b). Owing to the instability of its monomer, PVA cannot be synthesized through direct polymerization of vinyl alcohol, as is typical for most polymers. In 1924, German chemists Hermann and Haehnel first successfully prepared PVA in the laboratory by introducing a potassium hydroxide solution into an alcohol solution of polyvinyl acetate (PVAc) to induce alcoholysis [1–4]. Since the 1950s, PVA has been produced on an industrial scale. Its main commercial products, classified according to different degrees of polymerization, degrees of alcoholysis, and physical forms, have been widely applied in various fields, including construction, textiles, papermaking, agriculture, pharmaceuticals, cosmetics, and the dyeing industry.

The chemical properties of PVA primarily depend on its degree of polymerization (DP) and degree of alcoholysis (DA). The degree of polymerization refers to the number of monomeric units contained in a PVA molecule, represented by the value n in Fig. 1(a). In practice, since it is impossible to synthesize PVA with an exact n value—whether through industrial production or laboratory preparation—the reported DP of industrially produced PVA typically represents a characteristic value corresponding to a range of polymerization degrees within the product. Industrial-scale PVA is generally produced via solution polymerization, through which the achievable DP typically ranges from 300 to 2600. For PVA with a DP below 300 or above 2600, alternative synthesis methods are required, and the production costs for such materials are usually significantly higher than those of PVA produced on an industrial scale [1]. Strictly speaking, there is no clear boundary for classifying PVA according to its DP. However, by convention, PVA with a DP higher than 2400 is generally referred to as “high-polymerized PVA”, that with a DP of around 1700 is classified as “medium--polymerized PVA”, and that with a DP below 600 is known as “low-polymerized PVA”. Furthermore, PVA with a DP lower than 300 is typically categorized as “ultra-low-polymerized PVA” [5].

The current global development trend of PVA products is characterized by a bifurcation toward both extremely high and extremely low DP. On one hand, research and production focus on high-DP (HDP) PVA, while on the other, efforts are directed toward developing low-DP (LDP) PVA. HDP PVA products have now achieved a DP of approximately 5000 (The highest DP mentioned in research article is 20,000) [6,7]. Due to their high DP and DA, these materials exhibit outstanding mechanical properties, making them widely and successfully used in applications such as high-strength and high-modulus fibers, high-grade adhesives, and cement reinforcement agents. Their industrial applications are well established and technically mature. In contrast, LDP PVA used in engineering materials typically has a DP below 1000—most commonly around 600. PVA with even lower DP, particularly ultra-low-DP (ULDP) PVA (DP $<$ 300), is scarcely applied. This is partly because the industrial production of ULDP PVA was developed significantly later than that of

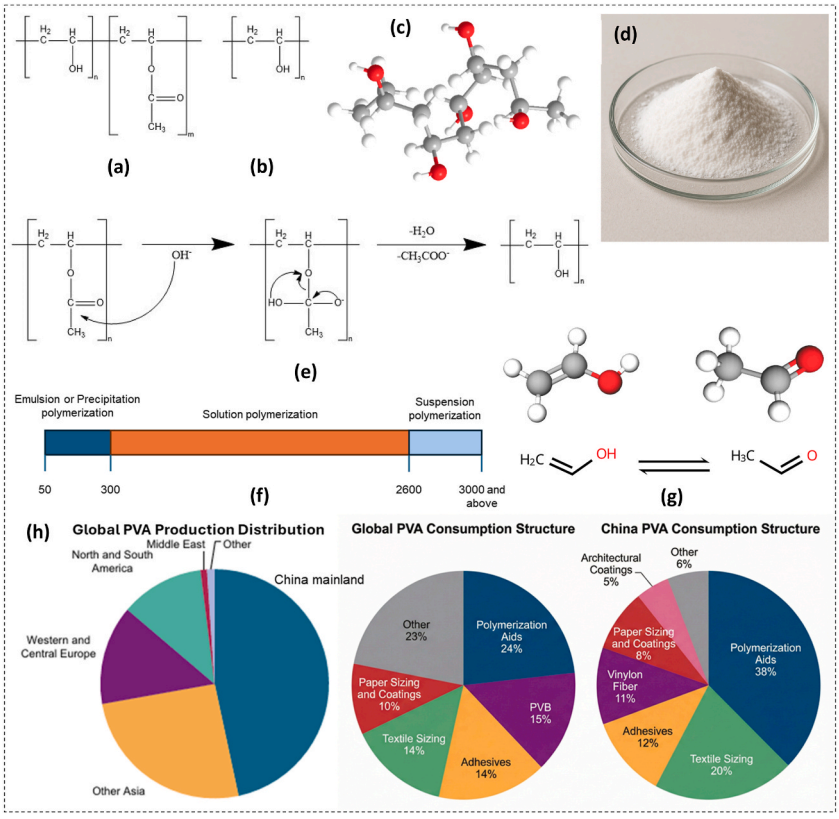


Fig. 1. Chemical properties of PVA: (a) Structure of partially hydrolyzed PVA; (b) Structure of fully hydrolyzed PVA. (c) Fragment structure on PVA molecular chain; (d) PVA powder; (e) Mechanism of PVA hydrolysis in alkaline aqueous solution; (f) Production methods of PVA with different degrees of polymerization; (g) Vinyl alcohol monomer and its tautomeric forms; (h) Global PVA production distribution, global PVA consumption structure and China consumption structure. (Data sourced from S&P and SSE).

ultra-high-DP (UHDP) PVA, and the mainstream synthesis methods remain proprietary to commercial manufacturers. Additionally, conventional LDP PVA already demonstrates sufficient performance in applications such as surface modification of recycled concrete aggregates. Overall, research on low-DP, and especially ultra-low-DP PVA in the field of engineering materials, remains relatively limited [5].

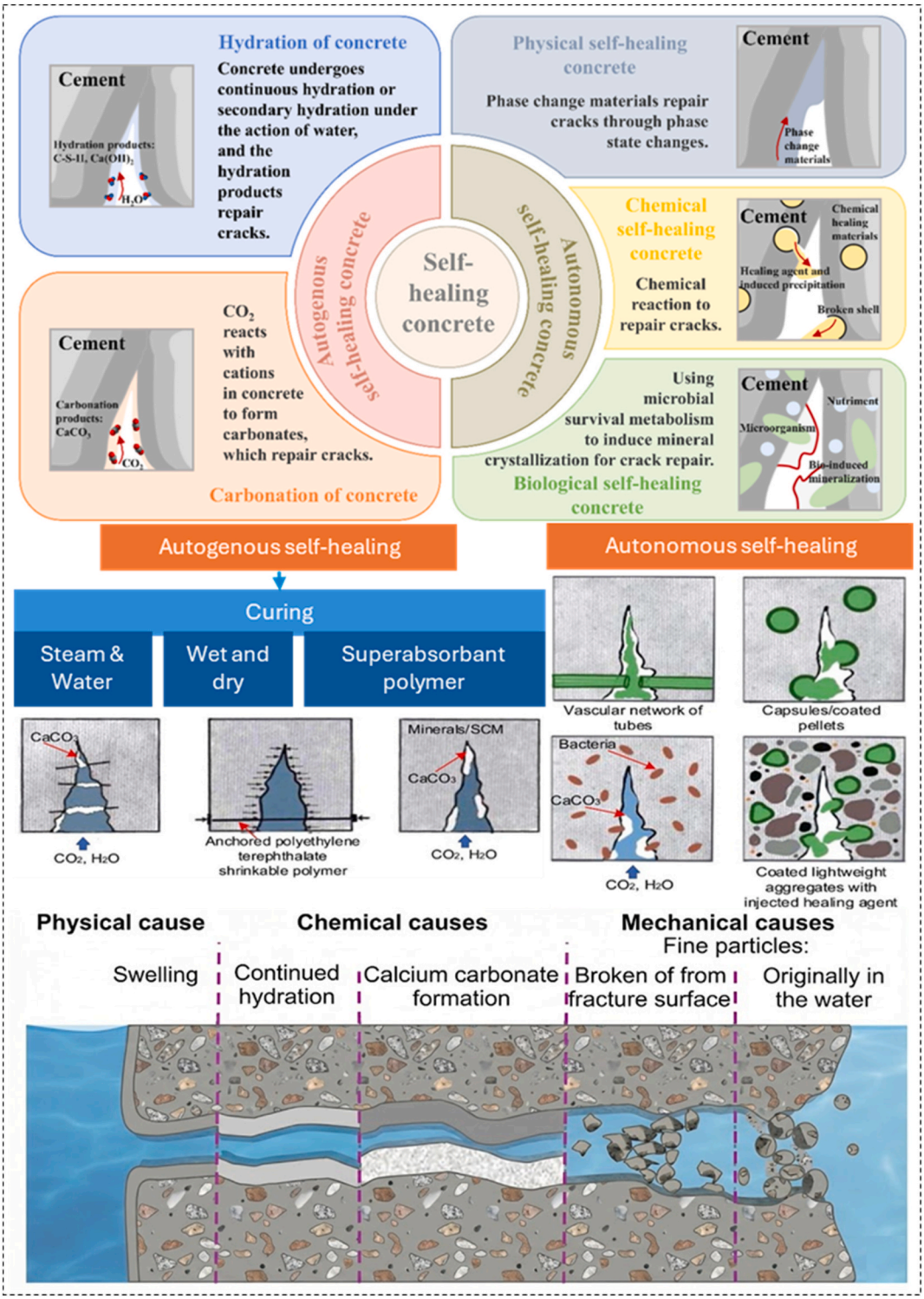


Fig. 2. Schematic illustrations of the mechanisms underlying two types of self-healing [13,14,15].

1.2. Self-healing concrete

Concrete is the most widely used construction material in the world today. Since the invention of Portland cement in the 1820s, it has become the primary binder in concrete, greatly promoting the widespread adoption and application of this material. The mechanical behavior of concrete is characterized by quasi-brittleness; it performs well under compression but exhibits very weak tensile resistance, making it highly susceptible to cracking. Therefore, in modern engineering practice, concrete is commonly used in combination with steel reinforcement to form reinforced concrete, which effectively enhances its tensile performance.

Numerous microscopic studies have shown that when concrete is subjected to load, numerous microcracks form both on its surface and within its interior. The widths of these microcracks typically range from a few micrometers to several tens of micrometers [8]. Typically, the formation of cracks in concrete is not considered a direct criterion for structural failure, it is mainly considered for serviceability issues. In practical engineering design, concrete is deemed to have failed only when crack widths reach a certain critical value. Both the latest Chinese standard "Code for Design of Concrete Structures" GB/T 50,010-2010, "Code for Durability Design of Concrete Structures" GB/T 50,476-2019, and the Australian standard AS 3600-2018 "Concrete Structures" specify that, depending on the class of the concrete structure, the permissible crack width ranges from 0.2 to 0.4 mm.

For cracks in buildings that exceed the permissible width after service, regular maintenance and repair are typically required. Conventional crack-repair methods primarily include surface sealing, groove filling, dowel stitching, pressure grouting, chemical injection, and carbon-fiber reinforcement, all of which have been widely applied in practical engineering over the years. However, these methods mainly target surface cracks and are difficult to implement for internal cracks within concrete. Moreover, some techniques primarily serve as a sealing function and provide limited restoration of structural strength. If both the loss of strength and the reduction in impermeability caused by cracks need to be addressed, a combination of these methods is generally required [9]. However, traditional repair methods often prove ineffective for micro-cracks that are too fine to be readily detected by the naked eye ($<$100 μm), as well as for cracks located in inaccessible regions, such as beam-column joints, the soffits of long-span structures, and deep-water caissons.

Self-healing concrete is a recently emerging research direction in the field of advanced concrete materials; however, its origins predate even the history of PVA. In 1836, the French Academy of Sciences first observed the phenomenon of concrete's self-healing [9]. In 1925, Abrams observed that outdoor-exposed, previously crushed concrete specimens exhibited significantly higher compressive strength compared to their initial measurements. He attributed this self-healing behavior of concrete to the continued hydration of unhydrated cement particles [10]. Furthermore, later studies have indicated that autogenous healing cannot be ascribed exclusively to the rehydration of unreacted cement; it is equally contingent upon the carbonation of cementitious products, whereby calcium carbonate preferentially forms at the crack mouths to seal the fractured surfaces. This self-healing phenomenon does not result from the addition of external components; rather, it arises entirely from the inherent characteristic of concrete that not all cement particles hydrate completely. This form of self-healing is referred to as autogenous self-healing. In ordinary concrete, the capacity for autogenous self-healing is generally limited. Significant self-healing effects typically require favorable conditions, including a moist environment, relatively narrow crack widths, removal of applied loads after crack formation to allow healing, and sufficient time for the healing process to occur [11,12]. Due to these limitations, autogenous self-healing is generally regarded merely as an inherent property of concrete and is rarely leveraged for practical engineering applications.

However, given the significant potential value of self-healing concrete, and recognizing the limitations of autogenous self-healing, considerable research has focused on enhancing concrete's self-healing capacity by incorporating additional components. This approach allows cracks to heal more rapidly through the action of additives and is referred to as autonomous self-healing. Autonomous self-healing involves the incorporation of various healing agents into the concrete matrix, enabling cracks to repair themselves after formation. In this method, the healing agents are pre-added to the concrete mixture and can automatically repair cracks as they develop, thereby potentially reducing costs compared to conventional repair techniques [9]. Fig. 2 shows the schematic illustrations of the mechanisms underlying two types of self-healing.

At present, both academia and industry have investigated and utilized a wide variety of autonomous self-healing additives, including but not limited to fibers, bacteria, microcapsules, crystalline admixtures, nano silica, and shape-memory alloys [16–19]. Broadly, these additives can be divided into three main categories. One category consists of physically active additives that exploit their inherent physical properties to alter the formation and propagation of cracks, thereby enhancing autogenous self-healing, with fibers and shape-memory alloys being typical representatives. Another category comprises microbial additives, in which alkali-resistant endospore-forming bacteria are incorporated into the concrete matrix to actively precipitate carbonate minerals and repair cracks. The third category includes chemical additives, which involve the targeted addition—either dispersed or encapsulated—of chemical agents that promote concrete self-healing, allowing the additives to be released and fill cracks when they occur, with expansive agents, microcapsules, and crystalline admixtures being the main representatives [9,13–15,20–23].

Among these three main types of additives, the first category primarily functions by reducing crack widths from 150 to 200 μm to less than 100 μm (sometimes less than 50 μm) under the same loading, and the repair mechanism after crack formation is essentially the same as that of autogenous self-healing. Consequently, repair efficiency remains highly sensitive to factors such as humidity and loading conditions. Although microbial additives, the second category, can achieve significant repair effects during the early stages of concrete setting, their functional lifespan within the concrete matrix is considerably shorter than the intended service life of the structure. It can heal the cracks about 300 μm in certain situations for 28 days. Bacterial spores can generally survive for about 10 years in the highly alkaline environment of concrete, and some studies have shown that under specially sealed conditions, spore viability can be extended to as long as 50 years [24]. Although the design life of ordinary concrete structures is also around 50 years, the intended service life of concrete structures in large-scale infrastructures such as bridges, dams, ports, and tunnels—generally exceeds 50 years.

As a result, microbial additives are often insufficient to meet these long-term requirements. The third category, chemical self-healing additives, has been extensively studied. Most of them could heal the 200-250 μm width cracks for 28 days. Among them, microcapsules represent a particularly active research direction in the field of self-healing concrete, with a substantial body of work already established [25–30]. Crystalline admixtures currently have matured commercial products that are applied in practical engineering. In addition to enhancing the self-healing performance of concrete, they also offer other benefits, such as reducing porosity and mitigating alkali–aggregate reactions [31,32]. However, since the compositions of these products are considered commercial secrets, their underlying self-healing mechanisms and constituent components remain subjects for further investigation.

2. Material engineering properties of PVA-added concrete

Since the self-healing of concrete inherently requires the presence of cracks, and crack formation is closely related to the fundamental properties of concrete—such as its mechanical behavior, durability, and porosity—it is necessary to first provide a brief overview of these basic properties in PVA-modified concrete before discussing its self-healing performance. Moreover, because different forms of PVA addition have distinct effects on these properties, the following discussion presents each property separately for PVA fibers and soluble PVA to ensure clarity and accuracy. PVA fibers can be produced via wet or dry–wet spinning processes, in which a spinning solution containing a substantial amount of surfactant is injected into an alkaline coagulation bath. The spinning solution can be prepared by dissolving medium to high molecular weight PVA with a degree of polymerization of at least 1500, to which 1–20% surfactant by polymer weight is added. Since surfactants can induce phase separation structures, nonionic organic surfactants, such as polyethylene glycol–type compounds, are particularly suitable for incorporation into the PVA spinning solution as surfactants [1]. In most research and practical applications, PVA fibers are generally not differentiated by their degree of polymerization (DP) and degree of hydrolysis (DA), although the industry predominantly utilizes fully hydrolyzed PVA with a medium-to-high DP for fiber production. However, because PVA fibers do not participate in the chemical reactions within the concrete matrix (except at the surface interface) variations in DP and DA have a negligible impact on concrete performance. Consequently, subsequent discussions regarding the properties of PVA fibers will not distinguish between specific DP and DA values [33–36].

2.1. Workability

Similar to most other fibers, PVA fibers tend to reduce the workability of concrete. This effect arises from two main factors. First, the

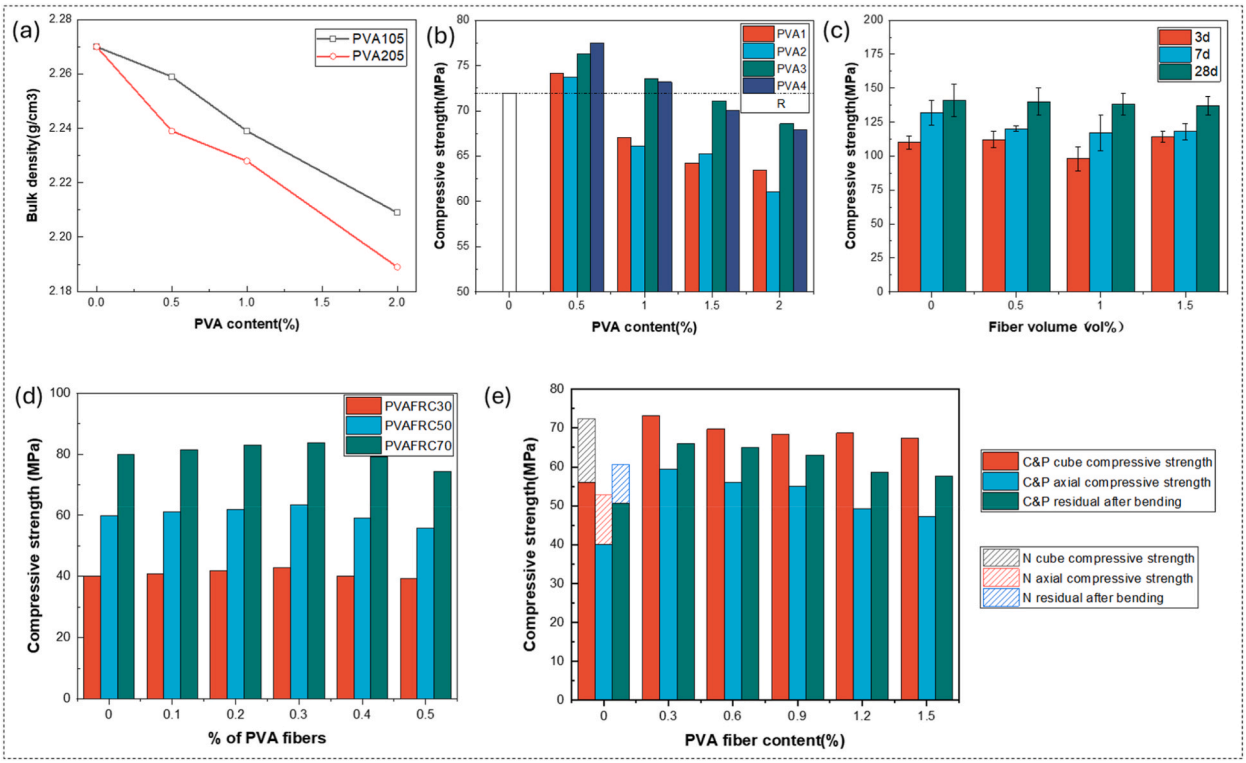


Fig. 3. Effect of PVA fibers on compressive strength: (a) Reduction in density caused by the addition of soluble PVA, where PVA105 is fully hydrolyzed and PVA205 is partially hydrolyzed [39]; (b) Effect of various PVA addition on the compressive strength of concrete(PVA1 is fully hydrolyzed, PVA2,3,4 is partially hydrolyzed; PVA1,2 is low DP, PVA3,4 is high DP) [42]; (c)(d)(e) Variation in compressive strength of concrete with PVA fiber addition across different studies [46–48].

fibers themselves possess a certain stiffness, and when dispersed within the concrete matrix, they form a three-dimensional network that inevitably affects the plasticity of the overall mixture [37]. The second factor is the inherent water-absorbing property of PVA fibers, which reduces the effective water content in fresh mortar and consequently decreases its workability [38]. The addition of soluble PVA, on the other hand, improves the workability of concrete, and this effect is strongly influenced by the DA and DP of the PVA [39]. The general trend indicates that partially hydrolyzed PVA enhances the workability of concrete more effectively than fully hydrolyzed PVA, and that low–molecular-weight PVA has a greater positive effect compared to high–molecular-weight PVA. In summary, a progressive decrease in DA allows soluble PVA to more effectively enhance the workability of fresh concrete, and a corresponding trend is observed with a reduction in the DP.

2.2. Compressive strength

PVA added in the form of a solution, hydrogel, or surface impregnation can all be classified as soluble PVA. Overall, the effect of soluble PVA on the compressive strength of concrete remains a subject of debate, with conflicting findings reported in the literature [40–42]. It is generally believed that in cement mortar, the early-age strength may decrease with the addition of PVA, whereas the later-age strength tends to increase [42,43]. The reduction in early-age strength is primarily attributed to the increase in the liquid-phase viscosity of fresh cement mortar caused by the addition of soluble PVA, which facilitates the formation of stable small air bubbles in the mixture, potentially leading to higher porosity and decreased compressive strength. In contrast, the increase in later-age strength is mainly due to the water-retention effect of PVA under drying conditions, which prolongs the hydration period of the cement mortar specimens [44]. This behavior is also influenced by the DP and DA of PVA. Specifically, higher DP increases the viscosity of the concrete's liquid phase, stabilizing the entrained air bubbles and thus causing a more pronounced reduction in compressive strength. Conversely, higher DA makes it more difficult to introduce air into the concrete, so fully hydrolyzed PVA has a smaller negative impact on compressive strength compared to partially hydrolyzed PVA [39]. Moreover, this effect is also related to the dosage of PVA. It is generally recognized that increasing the amount of PVA does not necessarily enhance performance; instead, there exists an optimal dosage that maximizes compressive strength. Some studies suggest that this optimal content is approximately 0.5% of the total concrete mass [42].

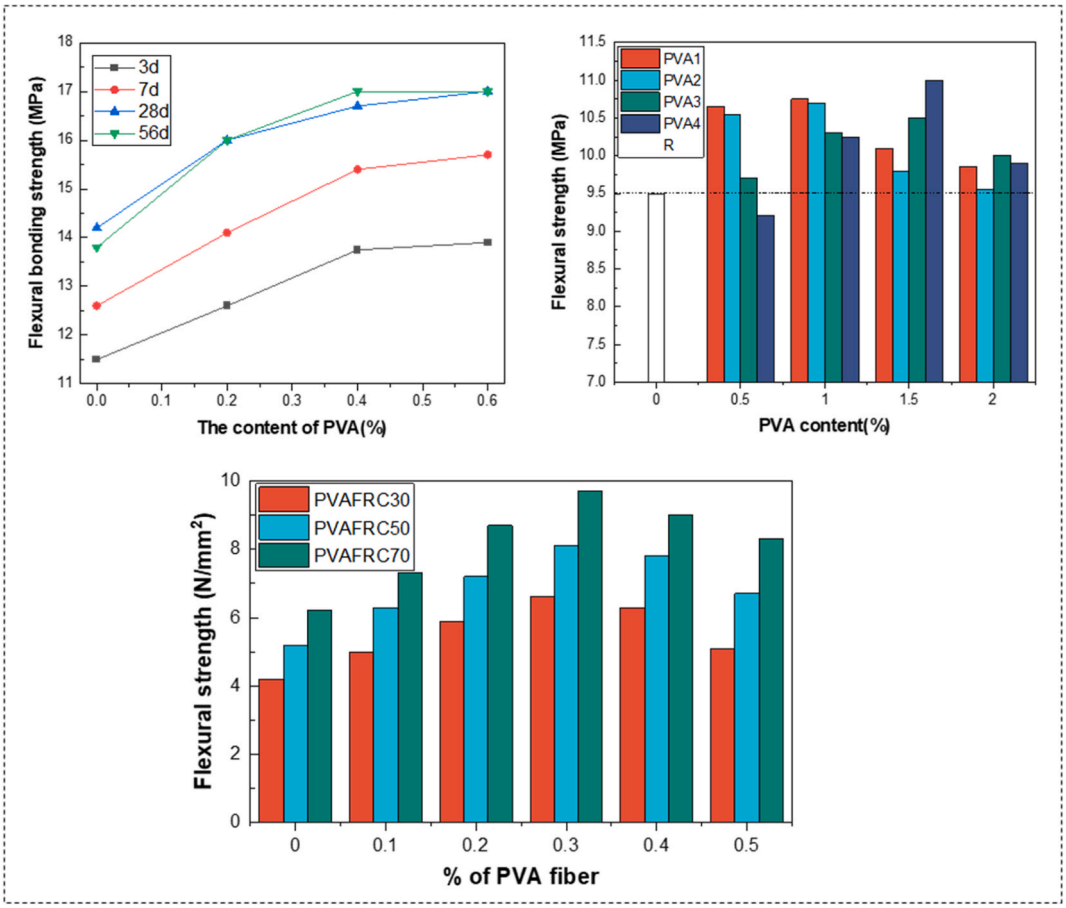


Fig. 4. Variation in flexural strength of concrete with the addition of soluble PVA and PVA fibers across different studies [39,47,48].

Fig. 3 shows the effects of incorporating PVA fibers and soluble PVA on the apparent density and compressive strength of concrete. Soluble PVA alters the viscosity of the mortar, thereby affecting its porosity; this aspect will be discussed separately in a later section. In terms of compressive strength, PVA fibers exhibit a slightly strengthening effect for about 2% to 5%, which probably because they can restrain the propagation of internal microcracks in concrete. However, excessively high dosages (more than 0.3%wt) may lead to a diminished strength enhancement. By contrast, soluble PVA modifies multiple properties of the mortar and therefore, at most dosage levels, results in compressive strength values that are comparable to or slightly lower than those of the control group from +3% to −5%. Some research declares the addition of PVA fibers to concrete results in a considerable improvement in compressive strength, but several other experimental studies have shown that the effect of PVA fibers on compressive strength largely depends on other influencing factors, such as curing age, fiber content, and porosity. Overall, compressive strength may slightly increase or decrease under different conditions, but the overall variation remains limited [45–48].

2.3. Flexural strength

In terms of flexural strength, PVA in any form can effectively enhance the bending resistance of concrete, although increasing the dosage does not necessarily lead to better performance as Fig. 4. Adding the soluble PVA into concrete could increase flexural strength by about 10% through improving the dispersion of concrete particles and forming strong bonding with the main hydration products. It also reduces the thickness of the interfacial transition zone (ITZ) which is mainly consist of calcium hydroxide (CH), thereby inhibiting the formation and propagation of microcracks and enhancing the tensile and flexural strength of concrete in many types of cementitious mixtures [39,41,42,44,49–56].

PVA fibers, on the other hand, are dispersed throughout the concrete matrix and can bridge the faces of cracks as they form, thereby providing additional tensile resistance and enhancing the flexural strength of concrete, which proved by experiment that it could increase the flexural strength by from 10% to 50%. Moreover, due to the surface characteristics of PVA fibers being similar to those of soluble PVA, they can form a combined mechanical and adhesive bond with the concrete matrix and influence the distribution of calcium ions within the cement hydration products [44,45,57,58].

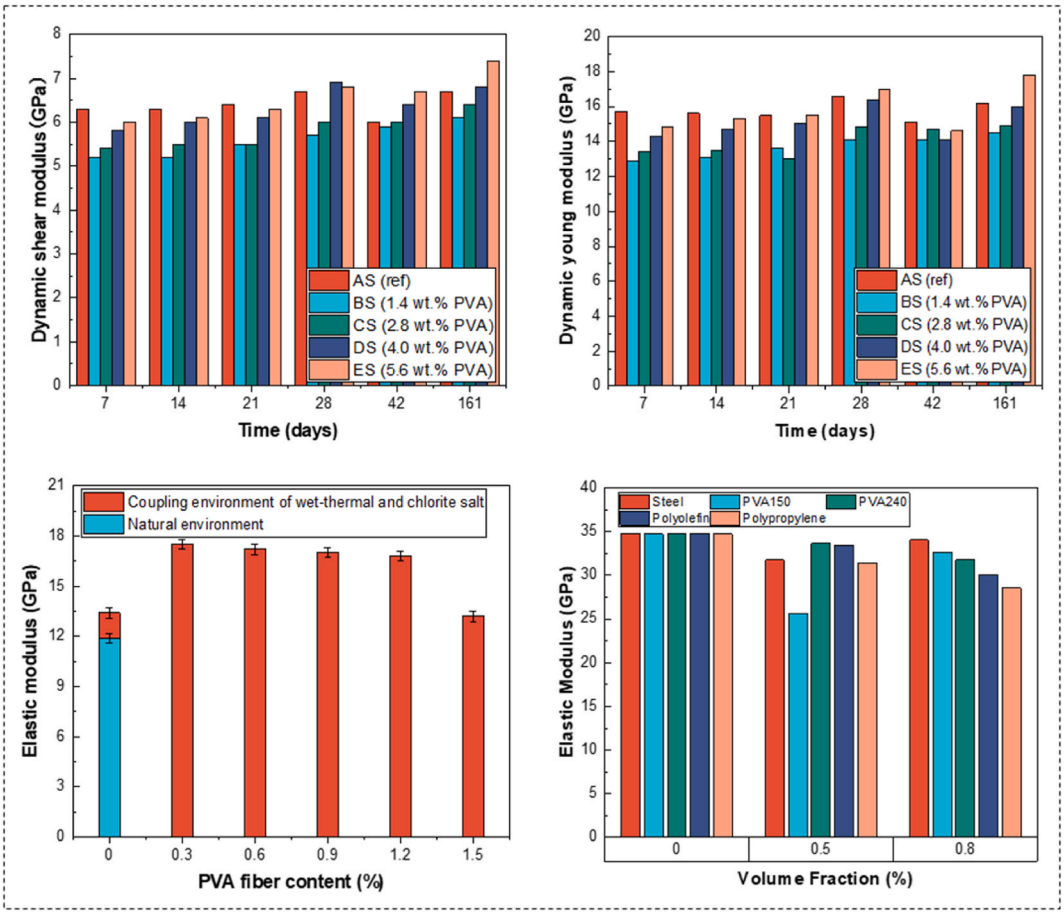


Fig. 5. Variation in elastic modulus of concrete with the addition of soluble PVA and PVA fibers across different studies [44,48,60].

2.4. Elastic modulus

Research on the elastic modules and dynamic modules of concrete is relatively limited compared to studies on strength. Overall, its behavior is like that of compressive strength concluded from Fig. 5. Numerous factors influence all the modules, including but not limited to concrete type, external environment, curing age, whether fibers are coated with oil, and fiber length. Some experimental results from different studies are even conflicting. The general trend remains ambiguous: under varying conditions, the elastic modulus may slightly increase or decrease, but the overall variation is relatively small [44,48,59,60]. In practical engineering applications, the effect of PVA addition on the elastic modulus and dynamic modulus is generally considered limited, and it is often either neglected or determined through on-site measurements.

2.5. Durability

The durability of concrete encompasses multiple aspects, including but not limited to resistance to freeze–thaw cycles, chloride ion penetration, carbonation, sulfate attack, abrasion, and vibration fatigue. Among these, resistance to chloride and sulfate ingress is closely related to the permeability discussed earlier and therefore exhibits similar trends in performance [61]. As shown in Table 1, the crack pattern and pore distribution in concrete also influence its carbonation process, and a key pathway for concrete self-healing involves limited carbonation within the crack regions. This aspect will be discussed in detail in the subsequent section on self-healing. Regarding the durability of PVA-modified concrete, this section focuses primarily on freeze–thaw resistance and mechanical performance, including wear resistance and fatigue durability.

For concrete incorporating PVA fibers, numerous studies have evaluated its performance under various conditions, including freeze–thaw cycling as well as wear and fatigue resistance in Fig. 6 [63,64]. Adding PVA fibers could reduce from 70% to over 90% mass loss compared to PP fibers and steel fibers in certain freeze–thaw situations. The overall trend indicates that the addition of PVA fibers can effectively enhance the durability of concrete; however, the effects on individual aspects vary. Their primary contribution lies in durability parameters related to cracks and porosity, while improvements in concrete properties associated with ions and electrical charge are relatively limited [61,65,66].

Studies on the durability of concrete containing soluble PVA are relatively limited. The available studies suggest that the addition of soluble PVA can clearly improve the freeze–thaw resistance of concrete; however, its effectiveness is influenced by DP and DA of the PVA. Experimental results indicate that careful selection of the PVA type is crucial to ensure that concrete retains its performance after multiple freeze–thaw cycles. A higher DA provides PVA with a greater number of hydroxyl groups, resulting in more active functional groups available during freeze-thaw cycles; thus, high-DA PVA is more advantageous. Conversely, a higher DP is likely associated with enhanced bonding properties, which can mitigate the microstructural damage inflicted on the concrete by thermal expansion and contraction. So, the general guideline is to avoid using PVA with low hydrolysis and low molecular weight. Similar findings have been reported in studies on soil modification using soluble PVA, and this enhanced resistance to freeze–thaw cycles may be attributed to the formation of a three-dimensional polymer network between PVA and calcium silicate hydrates [67].

Fig. 7 indicates the fully hydrolyzed high Mw PVA achieves higher results in mass loss compared to the unmodified group and maintains a stable microstructure after 25 freeze-thaw cycles. The enhancement is primarily attributed to improved ice nucleation inhibition capacity, which positively correlates with DH and Mw. In addition, PVA alters the permeable porosity of concrete, and the mass loss of specimens after freeze–thaw cycling is approximately positively correlated with permeable porosity. Therefore, the type of PVA that more effectively reduces the permeable porosity of concrete is also likely to make a greater contribution to its freeze–thaw

Table 1
The crack patterns between the gauge length (80-mm length) when specimens were tensioned to peak load at 28 d [62].

	Air curing	Water curing
PVA		
PE		
Hybrid		

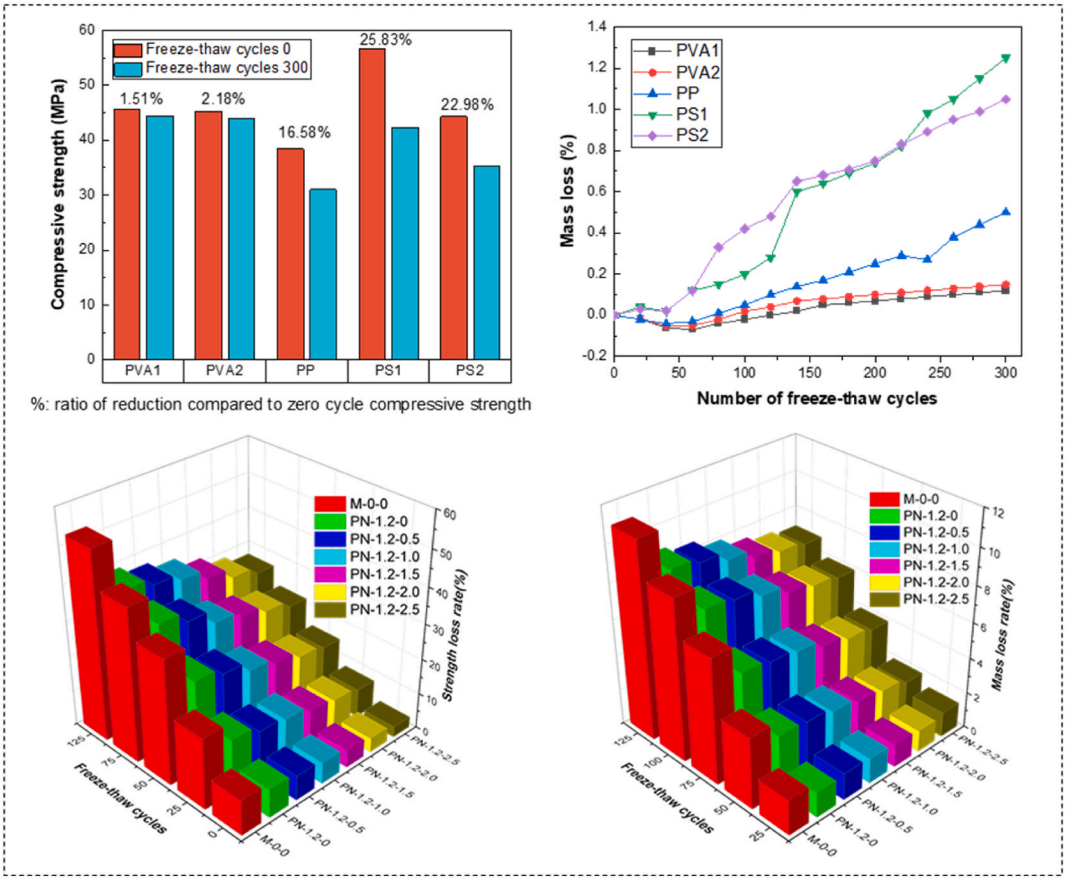


Fig. 6. Freeze–thaw resistance of concrete with PVA fiber addition; in the lower two subfigures, the last two digits of the labels indicate the amounts of PVA fibers and nano silica added, respectively [63,66].

resistance.

With respect to abrasion resistance and mechanical fatigue performance, the majority of studies reported in the literature focus on PVA fibers, whereas investigations into the effects of soluble PVA on the abrasion and fatigue behavior remain very limited as Fig. 8. The enhancement of abrasion resistance and fatigue performance by PVA fibers follows a consistent toughening crack control mechanism [69–74]. Under water–sand erosion or abrasive wear conditions, PVA fibers increase the tensile and shear (frictional) resistance of the material and suppress the propagation of microcracks in the surface mortar layer, thereby reducing mass loss due to abrasion. Several studies have shown that increasing the volume fraction of PVA fibers in ECC can significantly decrease abrasion loss and improve abrasion resistance; however, the incremental benefit tends to plateau at higher fiber contents. In addition, some investigations have demonstrated that the combined incorporation of PVA fibers and silica fume can achieve superior abrasion resistance through the synergistic effects of enhanced matrix densification and improved fiber dispersion and interfacial bonding. In such hybrid systems, abrasion resistance can be improved by approximately 10% relative to control specimens, with additional gains compared to mixes containing only silica fumes or only fibers [74]. From a macroscopic perspective, the key controlling factors governing abrasion and erosion are strongly correlated with compressive strength and overall mechanical characteristics, which explains why the coupled strategy of strength enhancement and improved toughness/crack resistance can reliably reduce erosion rates.

In terms of fatigue behavior, the crack-bridging effect of PVA fibers results in slower damage evolution and improved residual load-bearing capacity under cyclic loading. After cyclic loading at relatively low stress levels, PVA-ECC specimens retain favorable residual flexural strength, deformation capacity, and energy absorption under subsequent static loading. For a given fatigue life, the allowable flexural stress range of PVA-ECC is also significantly higher than that of ordinary concrete [69,74]. Furthermore, under coupled freeze–thaw and fatigue actions, PVA fibers mitigate freeze–thaw damage while synergistically enhancing fatigue resistance. Compared with plain concrete, PVA fiber-reinforced concrete exhibits higher retention of relative dynamic modulus and strength and demonstrates superior flexural fatigue strength during subsequent wheel-loading fatigue tests, reflecting a combined resistance to freeze–thaw degradation and fatigue damage. At the mesoscopic level, cyclic loading drives the development of interfacial fatigue debonding between PVA fibers and the matrix in the form of “tunnel cracks,” with the debonded length increasing with the number of cycles and loading intensity [73]. Meanwhile, interfacial frictional bonding parameters tend to increase or harden under fatigue loading, whereas surface oil treatment of fibers can significantly attenuate or alleviate such fatigue-induced hardening and interfacial

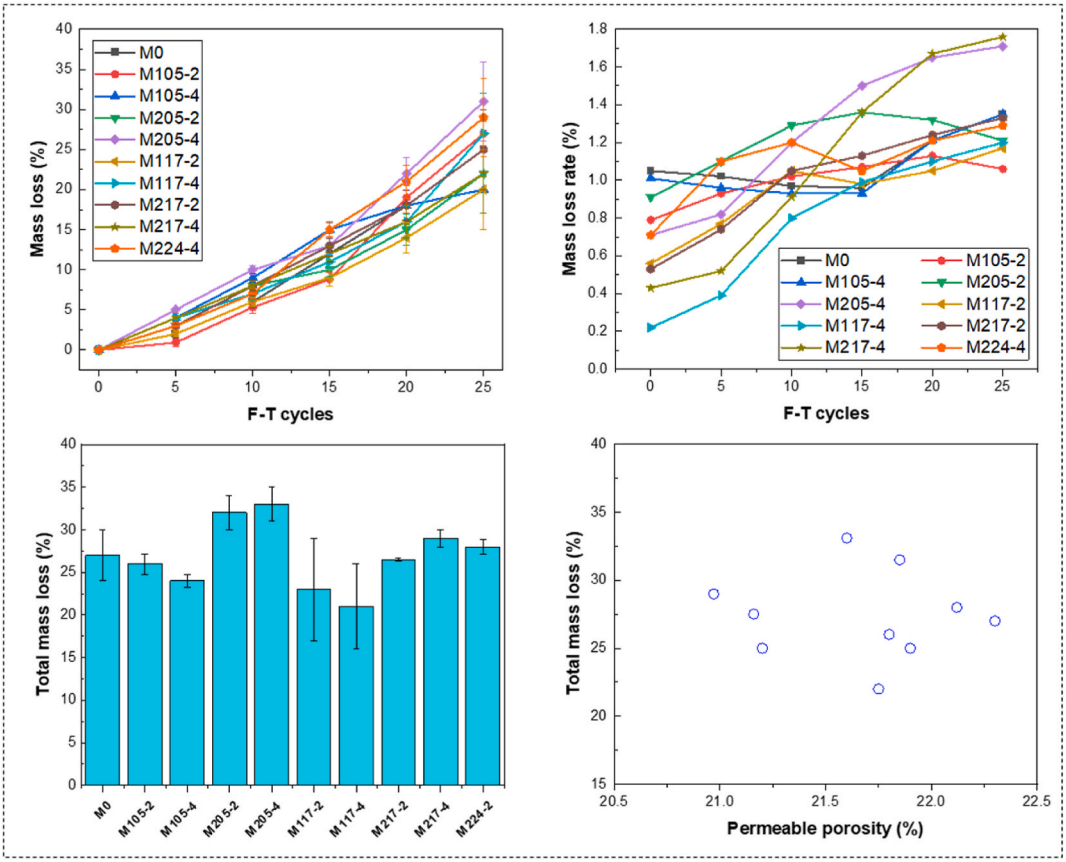


Fig. 7. Effect of different types of soluble PVA on the freeze–thaw resistance of concrete; the numeric suffix in the labels indicates the dosage of PVA added [68].

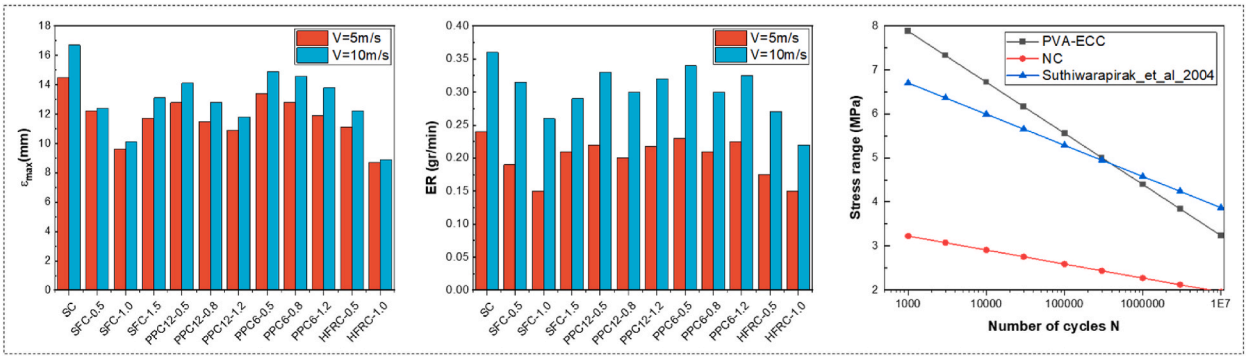


Fig. 8. Effect of different types of PVA on the abrasion resistance and mechanical fatigue performance of concrete (ER is erosion rate) [71,72].

degradation.

Overall, PVA fibers enhance matrix toughness and crack stability and optimize interfacial load transfer and energy dissipation mechanisms, thereby reducing material spalling and mass loss under abrasive environments and delaying damage accumulation while improving service life and residual performance under fatigue loading. The synergistic incorporation of mineral admixtures such as silica fume can further amplify these beneficial effects.

2.6. Porosity and permeability

In terms of permeability, concrete containing PVA fibers is generally considered to exhibit a slight reduction in permeability,

although this effect is strongly influenced by the content of other concrete components. This limited impact arises because PVA fibers are added in an insoluble form and primarily function mechanically, making it difficult for them to affect the hydration process of the concrete. In contrast, soluble PVA has a much more pronounced effect on improving concrete permeability. Numerous simulations and experimental studies have shown that the addition of soluble PVA can significantly reduce concrete's permeability. This improvement is attributed to the enhanced uniformity of particle distribution and improved adhesion between particles, which collectively lower the permeability and enhance the water-resistant properties of concrete [41,75,76].

Fig. 9 illustrates the effect of soluble PVA on the pore structure of concrete. PVA has the most pronounced influence on pore size distribution: compared with the control group, concrete containing PVA exhibits a greater proportion of fine pores and a reduced proportion of large pores. Moreover, changes in water absorption suggest that the altered pore size distribution also affects pore connectivity, thereby reducing the surface water absorption rate.

Changes in permeability are often associated with variations in porosity. The weak correlation between PVA fibers and permeability arises from their limited influence on the concrete's porosity [38,77]. Most experimental studies indicate that the addition of a small amount of PVA fibers slightly reduces concrete porosity, whereas excessive fiber content can have the opposite effect [78,79]. Other studies have suggested that the effect of PVA fibers on porosity also depends on the presence of other additives in the concrete [80]. For concrete incorporating soluble PVA, the impact on porosity appears to be influenced by multiple factors. Early literature reported that directly adding PVA in solution form often increased porosity because of higher velocity of liquid paste [81,82]. However, more recent approaches—such as adding PVA powder directly to the mix or coating concrete aggregates with PVA—have been shown to reduce porosity [76,78]. Some studies have also indicated that the addition of soluble PVA decreases the average pore size within the concrete.

3. Self-healing performance of PVA-added concrete

3.1. Recent research directions and achievements

As a well-established material that has already been widely applied in practical engineering, PVA has received relatively limited research attention in the field of self-healing concrete in recent years. Even in studies where PVA is involved, it is often not the primary

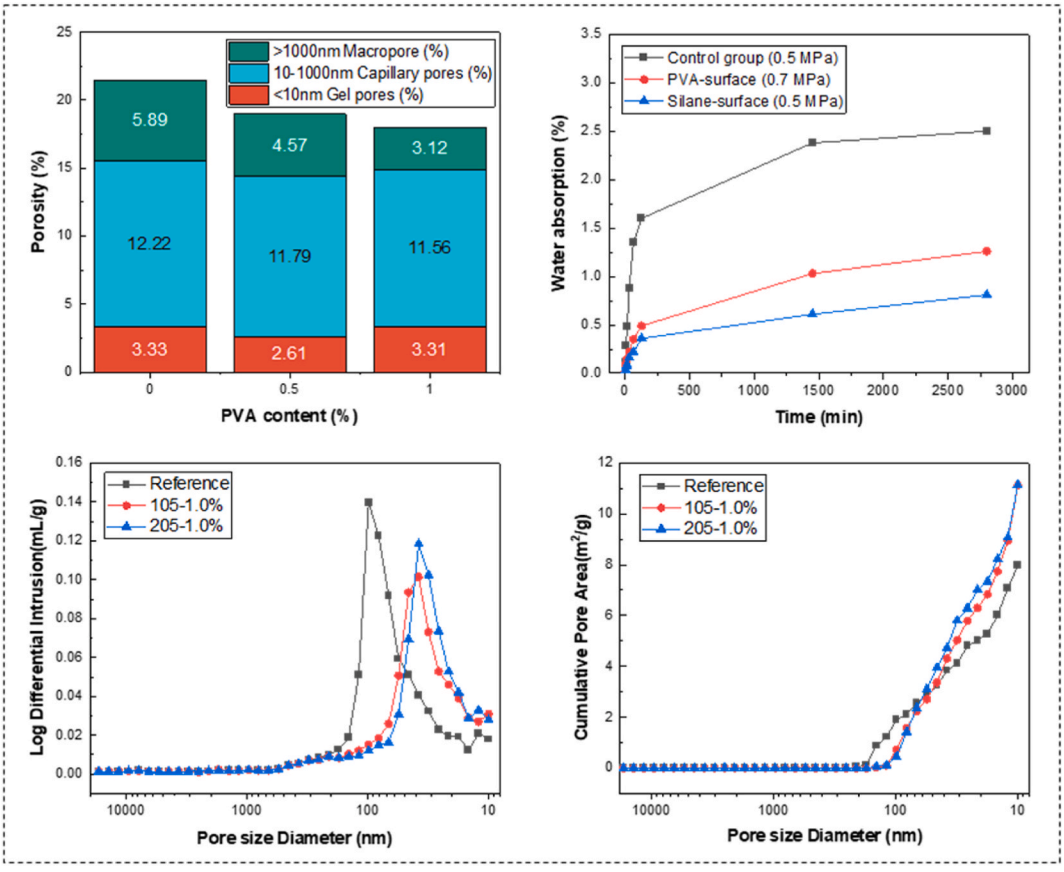


Fig. 9. Changes in permeability and porosity of concrete with the addition of soluble PVA across different studies [39,75,76].

focus of investigation. It should be noted that the studies summarized in Table 2 exhibit significant heterogeneity in research objectives, material systems, and experimental methodologies. In many cases, PVA is not the primary variable under investigation but rather serves as a supplementary component within broader self-healing systems. As a result, a strict classification of these studies based on a single criterion is not always feasible. Instead, Table 2 is intended to provide a comprehensive overview of representative research directions and to highlight the diverse roles of PVA in self-healing concrete over the past decade. Table 2 summarizes significant publications over the past decade that address PVA-related topics within the context of self-healing concrete. It also indicates the types of PVA and cementitious binders used in each study.

Although the primary form of PVA addition remains fibers, studies have also been conducted using soluble forms such as powders or films. Additionally, some research has employed computational simulations to analyze the interactions between PVA and various concrete components to elucidate the mechanisms by which it promotes self-healing. Overall, however, research on non-fiber forms of PVA in self-healing concrete remains relatively limited. The following sections will discuss the performance of PVA in self-healing concrete according to its different forms.

Therefore, based on the publication trends in top-tier journals in this field over the last ten years, the self-healing properties of PVA no longer appear to be a primary focus of academic research. Its main application remains as fibers incorporated into concrete, often compared with other novel materials in terms of various performance metrics, while studies on other forms of PVA addition remain scarce. On a more optimistic note, research published in non–top-tier journals are relatively abundant, and the scope of investigation is no longer limited to PVA fibers.

3.2. PVA fibers

The incorporation of PVA into concrete as a self-healing additive is a relatively well-established research area compared with soluble PVA. Hereafter, the relevant literature will be discussed according to three principal research domains: comparative performance evaluations against traditional fibers, surface modification strategies for PVA fibers, and the synergistic interactions between PVA fibers and other concrete admixtures. In terms of engineering performance as conventional fibers, several researchers have compared the differences between PVA fibers and other fiber types. Notably, the literature focusing on crack width control indirectly demonstrates the advantages of PVA fibers for self-healing applications. Conventionally, PVA fibers are primarily used to enhance the

Table 2
Publications closely related to PVA-Based self-healing concrete, 2015–2025.

PVA type	Research field object	Study outcomes	Refs.
Fiber	Portland cement	Synergistic self-healing effect of Biochar-immobilized bacteria, SAP and PVA fiber.	Wei et al. [83]
Fiber	Portland cement	Synergistic effect with nano-silica makes the performance after healing higher than before cracking.	Bo et al. [84]
Fiber	Portland cement	Comparison of developed SAP with PP and PVA fibers, illustrating the carbon emission advantages of SAP over PVA.	Heede et al. [85]
Fiber	Portland cement	X-ray CT computer quantitative analysis of the self-healing process of concrete with urea-formaldehyde microcapsules and PVA fibers.	He et al. [26]
Fiber	3D printing concrete	Recovery of the mixture with the crystallized admixture was higher than that of the mixture with only fiber.	Zahabizadeh et al. [86]
Fiber	Cement-based composite material	Superfine water-absorbent fibers were prepared by surface modification of PVA fibers.	Ma et al. [87]
Fiber	Portland cement	Coupling effect of PP fibers, PVA fibers, and bacteria on the self-healing concrete achieve better performance.	Feng et al. [88]
Fiber	Portland cement	Strengthening mechanism of KH560 and PVA synergistically on concrete.	Feng et al. [89]
Fiber	Portland cement/fly ash/ground granulated blast furnace slag	Tensile ductility of the PE fiber group was higher than that of the PVA fiber group.	Wang et al. [29]
Fiber	Portland cement/sulfoaluminate cement/GGB furnace slag	Simultaneous incorporation of PVA fibers and CA attenuated the negative influence on the compressive strength.	Niu et al. [90]
Fiber	Portland cement	Using MD to study the PVA-modified C-S-H and polybutadiene rubber interface, showing the performance was improved after inserting PVA.	Yu et al. [91]
Fiber	Ground granulated blast replaced Portland cement	GGB furnace slag and PVA fiber in terms of flexural strength recovery and crack sealing behavior.	Sun et al. [92]
Solution	Portland cement	PVA effectively promoted the healing of mortar specimens. PVA and bacteria group showed the most efficient.	Prosek et al. [93]
Low DP molecular	Computer simulation/Typical Portland cement hydration product	Introducing PVA directly into cracks lets its chains form multiple bonds with the host matrix.	Jia et al. [94]
High DP Powder/ film	Portland cement	Different types of pellets agg. showed higher porosity and lower crushing strength compared to normal sand.	Alghamri et al. [95]
High DP Powder/ film	Portland cement	Samples with PVA coated particles showed considerable recovery of flexural strength and stiffness.	Alghamri et al. [96]
High DP Powder/ film	Magnesium phosphate cement	PVA powder has good film forming properties and will encapsulate reactants and hydration products by forming structure with Mg^{2+}.	Xie et al. [49]

tensile strength of concrete; however, some studies indicate that this may come at the expense of compressive strength and can result in a slightly lower elastic modulus. Due to their polar affinity for cement components and aggregates, PVA fibers bond more effectively with the concrete matrix than traditional hydrophobic polypropylene (PP) fibers. This enables them to act as bridges across cracks under tensile stress, thereby improving the tensile strength of concrete. Nevertheless, some studies have also noted that under higher load conditions, the tensile strength of PVA fibers is lower than that of PP fibers, which may lead to comparatively reduced performance under such conditions [58,88].

Although PVA fibers inherently exhibit good bonding with concrete, some studies have investigated the properties of surface-modified PVA fibers. For example in Fig. 10, treating PVA fibers with silane coupling agents such as KH560 can enhance their affinity for C–S–H and other concrete components, thereby improving the tensile strength of concrete reinforced with these fibers [89]. Other researchers have explored introducing additional hydroxyl groups onto the fiber surface to enhance bonding with the concrete matrix, while some have incorporated sodium ions onto the fiber surface to produce highly water-absorbent PVA fibers [47,85].

In the context of using PVA fibers as a self-healing additive, some straightforward studies have compared the self-healing capabilities of concrete specimens incorporating PVA fibers with those containing fly ash or crystalline admixtures. The inclusion of PVA fibers has been shown to significantly enhance the self-healing performance of concrete [97]. Other studies have incorporated PVA fibers together with silica fume, copper slag, crystalline admixtures (CAs) etc. into concrete and investigated the effects of self-healing under different loading conditions, comparing scenarios with and without external loads. These studies also examined the long-term strength behavior of the specimens [11,55,98,99]. Overall, however, as shown in Table 3, the effect of adding PVA fibers alone is less pronounced than that of mainstream additives such as crystalline admixtures. The primary role of PVA fibers is to control crack formation during concrete cracking, preventing the development of long and wide cracks, which could otherwise adversely affect the conditions for self-healing [100,101].

3.3. HDP PVA made PVA-coated granules and PVA hydrogel

It should be noted that although the main component of PVA fibers is also high degree polymerized (HDP) PVA, they primarily function in an undissolved state, contributing through both their intrinsic mechanical properties and surface activity. In addition to HDP PVA added in fiber form, it can also be dissolved in hot water (mainly existing as PVA hydrogel) to form a solution, which can then be incorporated into concrete. Due to the relatively high viscosity of the PVA solution, the addition of PVA increases the viscosity of the cement mortar or concrete, causing more air bubbles to be entrained during mixing. These bubbles are difficult to remove through vibration, resulting in a significant increase in the porosity of the final concrete [1,42,49,50,52]. To address this issue, a relatively straightforward approach is to reduce the air content introduced during mixing by pre-wetting the PVA and using lower mixing speeds. However, even with this method, the resulting concrete still exhibits a noticeably higher porosity compared to concrete without the addition of PVA hydrogel [81]. Therefore, the addition of HDP PVA hydrogel inevitably reduces the compressive strength of cement

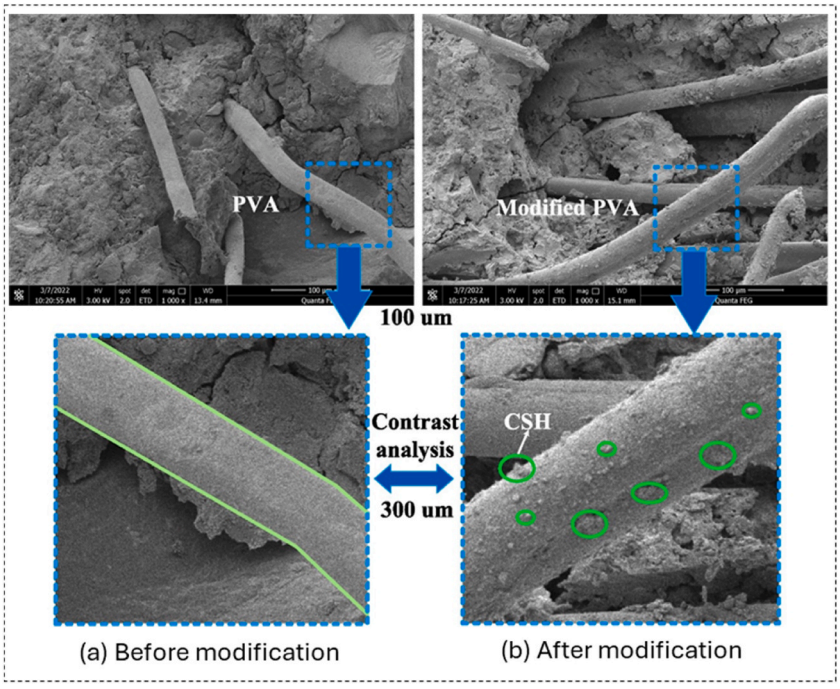
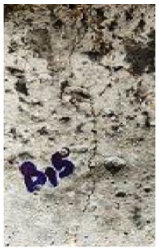
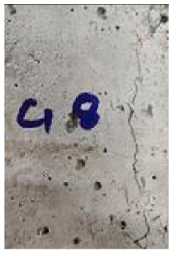


Fig. 10. 1000X and 4000X microstructures showing the change in affinity of untreated PVA fibers and KH560-treated PVA fibers for C–S–H in concrete [89].

Table 3
Comparison of self-healing performance among the control group (M1), PVA fiber group (M2), fly ash group (M3), and crystalline admixture (CA) group (M4) [100].

Mixes		M1	M2	M3	M4
Early age crack	3days before healing				
	42days after healing				

mortar specimens. However, some tests on concrete specimens have shown that although incorporating HDP PVA hydrogel increases the porosity, the compressive strength of the concrete is not significantly reduced [54]. The underlying reason is speculated to be that the addition of PVA alters the microstructure of the concrete's interfacial transition zone, enhancing the bonding between the cementitious matrix and the aggregates, thereby compensating for the strength reduction caused by the increased porosity [1,50].

The effects of PVA hydrogel on concrete self-healing remain a relatively underexplored research area. A more recent method for incorporating PVA hydrogel involves immersing the surfaces of certain additive particles (e.g., expansive agents, cementitious materials) into the PVA hydrogel and then drying them, forming a PVA coating on the particle surfaces to introduce PVA into the concrete [102]. This method allows PVA to be incorporated without adversely affecting the workability or strength of the concrete, thereby avoiding the air-entrainment issues associated with directly adding PVA hydrogel. In addition to being directly incorporated into concrete for solidification, several relatively niche studies have attempted to utilize modified high-molecular-weight PVA coatings to achieve protective and self-healing functions in steel and concrete structures. However, the underlying mechanisms differ substantially from those of PVA when blended into concrete. In some cases, the self-healing capability and resistance to physical damage and chemical attack (e.g., acid rain) originate primarily from microcapsules embedded within the coating matrix, which enable the coating to autonomously repair microcracks [103]. In other approaches, PVA is employed as a sacrificial template to construct a vascular network; after concrete hardening, the PVA is dissolved and removed, leaving behind interconnected channels that facilitate self-healing processes [104,105].

In addition to studies on chemical agents as catalysts for concrete self-healing, some research has shown that the incorporation of

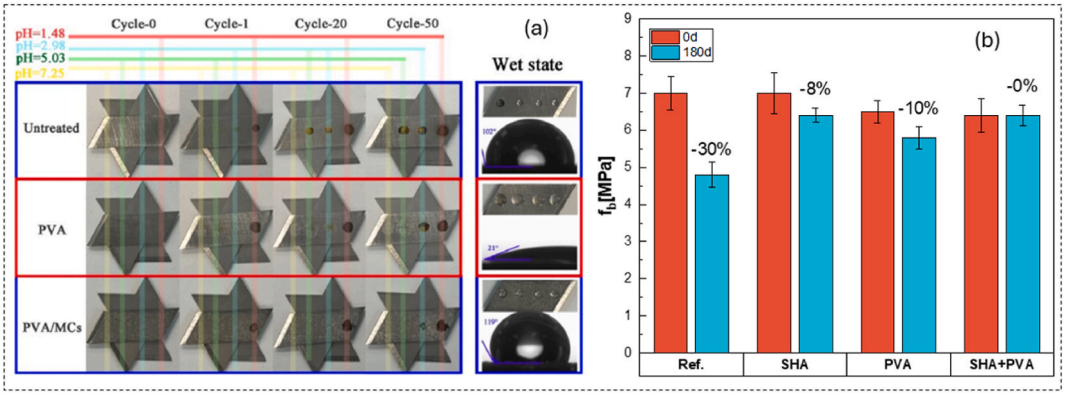


Fig. 11. Contribution to intrinsic mechanical properties and surface activity: (a) Corrosion process and water contact angle of untreated, PVA, and PVA-MC coatings on carbon steel for acid rains of different pH values [103]; (b) Comparison of flexural strength recovery of cement specimens incorporating PVA and those incorporating bacterial SHA [93].

PVA hydrogel can enhance the self-healing efficiency of bacterial cement mortars [93]. Experimental studies have shown that both specimens containing only PVA and those with bacteria encapsulated by PVA can promote concrete self-healing. In Fig. 11 (b), experiment results indicate that the self-healing performance of specimens containing only PVA is slightly lower than that of the PVA + bacterial SHA combination [93]. While the bacterial-containing group exhibits better crack sealing, the improvement in flexural strength is comparable between the two groups. Similar synergistic effects have also been observed in other simulation and experiments involving the addition of PVA fibers together with bacteria [88,106–108]. Which specific approach yields the greatest improvement in overall concrete performance remains to be further investigated. Interestingly, the film-forming capability of PVA hydrogels remains effective on metal surfaces; however, it provides essentially no enhancement in corrosion resistance at the chemical level. Fig. 11 (a) presents a study on the acid-corrosion resistance of metals coated with PVA and related film-forming materials. The experimental results once again demonstrate the excellent film-forming properties and acid inertness of PVA hydrogels [103].

3.4. *Low degree polymerized PVA*

The incorporation of low degree polymerized (LDP) PVA into conventional concrete is relatively rare. Currently, LDP PVA is primarily applied for surface modification through impregnation of materials, including recycled concrete aggregates, and most studies do not specifically report the polymerization degree of the PVA used [1,30,109,110]. Compared with natural aggregate concrete, the mechanical properties of recycled aggregate concrete, such as compressive and flexural strength, are generally found to decrease significantly. This is typically attributed to the rougher surface texture and higher water absorption of recycled aggregates, which reduces the bond strength between cement and aggregates. By modifying the surfaces of recycled aggregates with PVA, low degree polymerized (LDP) PVA can partially replace the water adsorbed on the aggregate surfaces. Moreover, because PVA also exhibits good affinity for cement hydration products, it can substantially reduce the thickness of the interfacial transition zone (ITZ) and alter its morphology, thereby markedly improving the mechanical performance of recycled aggregates.

Overall, cases of using LDP PVA as a concrete additive are relatively scarce. Furthermore, because some studies provide only vague descriptions of the materials used, certain research that ostensibly involves LDP PVA cannot be fully adopted or verified as it is often inferred from the viscosity of aqueous solutions, which is not always reliable.

4. Self-healing mechanism and conceptual extension framework

Fig. 12 shows the principles for PVA on the enhancement of self-healing efficiency of concrete. As discussed previously, PVA fibers primarily function by controlling crack width, and the dominant healing mechanism remains autogenous self-healing. In contrast, soluble PVA operated predominantly through an autonomous self-healing mechanism. The discussion from Section 4.1 to Section 4.3 will introduce the verified and wide-accepted mechanisms of autogenous and autonomous self-healing. And it should be noted that, while the mechanisms of autogenous and autonomous self-healing in concrete have been extensively studied, the role of soluble PVA in promoting self-healing has not yet been fully established within a unified theoretical framework. Although the complexation–precipitation mechanism has been widely applied to explain the behavior of certain active chemical additives such as TEA and

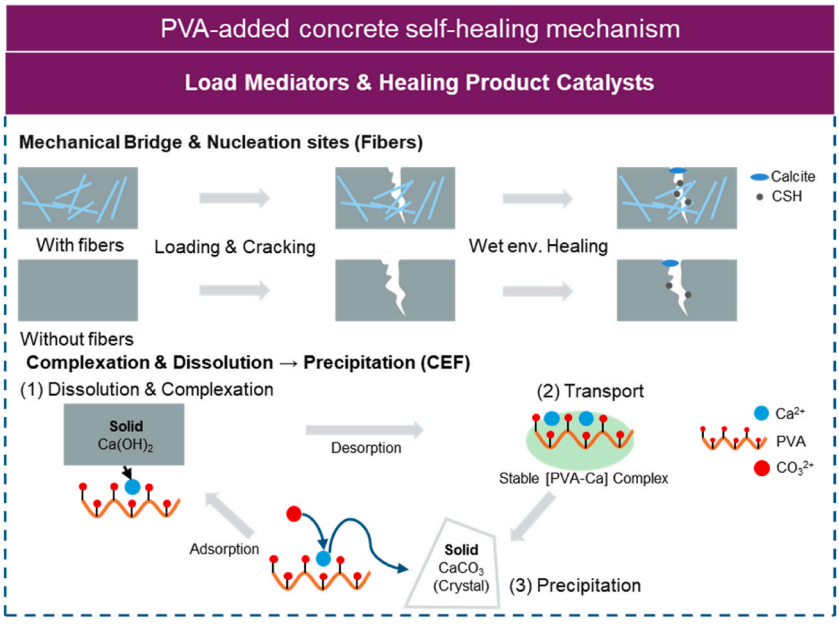


Fig. 12. schematic figure of the principles for PVA on the enhancement of self-healing efficiency of concrete.

glycine, there is currently no direct experimental evidence explicitly confirming its applicability to PVA systems. Therefore, the discussion in Section 4.4 will introduce the mechanism as a conceptual extension framework (CEF) to interpret the potential role of PVA in self-healing processes, rather than as a verified or established theory.

4.1. Mechanism of autogenous self-healing process in concrete

In academic research, the self-healing of concrete is generally categorized into autogenous and autonomous types. The primary distinction between these two lies in whether additional healing agents are incorporated into the concrete to facilitate the healing process. Autogenous self-healing refers to self-healing that occurs without any externally added components; the healing products are formed solely through reactions between the intrinsic constituents of concrete and external water or carbon dioxide [111–113]. In contrast, autonomous self-healing involves the intentional incorporation of additives that promote the healing process, either by accelerating existing autogenous mechanisms or by generating new healing products within the cracks to achieve improved self-healing performance. Except for autonomous self-healing systems based on expansive agents, the fundamental mechanisms of autogenous and autonomous self-healing are similar. The following section will focus on these underlying mechanisms.

In the preceding introduction, the self-healing properties of concrete were briefly outlined. Before discussing the mechanisms by which PVA promotes self-healing in concrete, it is necessary to clarify the primary mechanisms underlying concrete's intrinsic self-healing. The self-healing capacity of concrete originates from its chemical characteristics, which comprise a mixture of crystalline and amorphous phases and a combination of unreacted reactants and hydration products. This feature is directly observable in any cracked concrete cross-section, where unhydrated cement particles coexist alongside the products formed from cement hydration [15, 28].

This characteristic means that even without considering reactions beyond cement hydration, the mere presence of unreacted cement particles in the clinker endows concrete with self-healing potential. Accordingly, the earliest proposed mechanism for concrete self-healing is as follows: after cracking, previously unhydrated cement particles become exposed and react with water that penetrates the cracks, forming new hydration products. Because this reaction involves an increase in solid volume, it can fill the voids within the cracks, thereby endowing the concrete with self-healing capability [114–116].

The self-healing products generated through this mechanism are highly like the original components of concrete, consisting primarily of C–S–H–based cementitious material. Since this process is essentially a delayed cement hydration reaction, it shares both the advantages and disadvantages of cement hydration. On the positive side, because the products are mainly calcium silicate hydrates, they possess a structure and strength characteristics like those of the cementitious matrix. As a result, these products can bond closely with the existing solid phase at the cracked interface and contribute significantly to the restoration of the concrete's strength during self-healing [21,31]. However, it also retains the inherent limitations of cement hydration. During hydration, the formation of hydration products on the outer layers of cement particles can hinder water penetration into the particle interiors. Consequently, for cement particles newly exposed by cracking, complete reaction during self-healing remains difficult, and the volume expansion available to fill the crack voids is relatively limited. Furthermore, since unhydrated cement particles are distributed relatively sparsely across the crack surfaces, the secondary hydration products form a discrete, point-like network that is insufficient to cover the entire

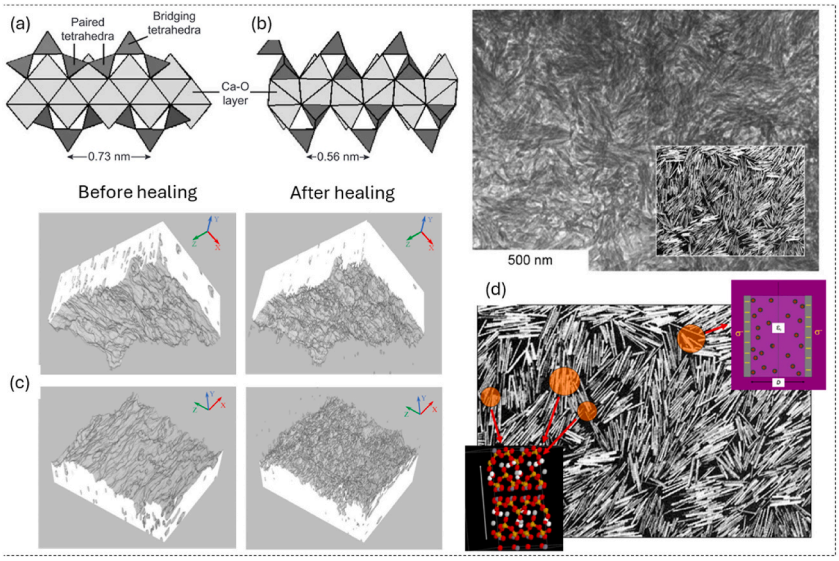


Fig. 13. Single layer of 1.4-nm tobermorite seen along (a) [210] and (b) [010] illustrating the Ca – O main layer (light gray) with attached dreierketten (dark gray). Water molecules and Ca atoms present in the interlayer spaces are omitted [118]; (c) Micro-CT scan models of concrete cracks before and after self-healing [117]; (d) Schematic illustration of the structural decomposition of tobermorite microcrystals within dense C–S–H products [119].

crack cross-section [117]. Due to the amorphous nature of calcium silicate hydrates, the microstructure of the self-healing products is not uniform. Overall, it resembles the normal cement hydration process, exhibiting dense inner regions and loose, disordered outer layers. Microscopically, this manifests as irregular, unevenly shaped aggregates on the surfaces [118]. From a crystallographic perspective, both the dense inner products and the loose outer products consist of amorphous or poorly crystalline C–S–H. However, due to spatial constraints, the inner products are more likely to form short-range ordered microcrystalline structures resembling tobermorite as shown in Fig. 13 [119–121].

In practical engineering, the tensile strength of concrete is generally not considered in structural design because most concrete structures are reinforced with steel. However, cracks allow the ingress of harmful substances from the external environment, which can cause significant damage to concrete structures. Therefore, sealing cracks is often a more urgent requirement than restoring strength. The continued hydration of unhydrated cement within cracks provides only limited crack-sealing capacity. This necessitates consideration of another self-healing mechanism: the partial dissolution of calcium hydroxide (CH) in portlandite form as Fig. 14(c)–(e), a product of cement hydration, within cracks. The dissolved CH reacts with CO_2 dissolved in the infiltrating water, forming solid $CaCO_3$, which fills the cracks and contributes to self-healing [10,20,14,115–117,120]. The reaction to domination is as follows:

$$CO_2 + 2OH^- \rightarrow H_2O + CO_3^{2-} \quad (1)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$

This reaction mechanism is similar to the carbonation process of concrete. Typically, it does not occur in situ but is transport driven. Although CH is present throughout various regions within the concrete, it dissolves and is transported through the pore solution, subsequently reacting with CO_2 and precipitating at the crack openings [10,15,27,122]. Although concrete carbonation is generally considered detrimental to its strength and durability [123]. However, because carbonation primarily occurs within the cracks, which constitute only a small fraction of the concrete volume, and the reaction products can cover the reactants and fill the cracks, the process is self-limiting. Once the cracks are completely sealed, CO_2 can no longer penetrate, and the reaction ceases [124]. Some further studies have indicated that the rate of the healing process primarily depends on the available CH content and the microstructural changes resulting from the formation of $CaCO_3$ [125]. Therefore, the effect on concrete strength and durability is generally positive.

The $CaCO_3$ formed by this reaction is primarily in the calcite crystal structure as Fig. 14(a) and (b), with minor amounts possibly present as vaterite [126]. Calcite belongs to the trigonal crystal system and exhibits perfect rhombohedral cleavage. This means that its crystals have specific weak planes along which they can easily split into rhombohedral fragments under mechanical stress. At the macroscopic level, calcite has a Mohs hardness of 3, indicating a relatively soft texture, consistent with its microscopic crystal properties. Consequently, calcite formed within cracks does not contribute significantly to the restoration of concrete strength. It is generally considered that the primary role of calcite formation is to seal cracks, thereby preventing the ingress of harmful substances from the external environment into the concrete.

4.2. *Mechanism of autonomous self-healing process in concrete*

For most current concrete self-healing processes, the two reaction mechanisms described above are generally applicable. For instance, the recently prominent microbial-assisted concrete self-healing technology still relies fundamentally on the formation of $CaCO_3$ (calcite) to fill cracks. The difference lies in the source of CO_2: non-biological methods require CO_2 from the air to dissolve into the cracks and react, whereas the microbial approach generates CO_2 directly through the biochemical activity of microorganisms present on the crack surfaces, making the process more efficient than passive CO_2 absorption. Nevertheless, the core reaction mechanism remains the same. Some studies have also noted that the presence of microorganisms can alter the crystal morphology of calcium carbonate; compared to the predominantly calcite formed in aqueous solutions, microbial addition can result in vaterite becoming the dominant phase [127].

Additionally, research on concrete self-healing using expansive agents focuses on incorporating such agents into the concrete so that, after crack formation, they react to generate additional solid phases, thereby filling the cracks. Representative expansive agents include calcium sulfoaluminate (CSA), calcium oxide (CaO), and magnesium oxide (MgO) [75,96,128]. However, the healing products of these expansive agents generally have lower strength compared to C–S–H, and the amount produced is insufficient to fill larger cracks relative to calcite. This limitation arises because the dosage of expansive agents is restricted, typically not exceeding 10% of the cement mass, whereas calcium hydroxide (CH), the precursor for calcite formation, accounts for approximately 20% of the hardened cement matrix. Consequently, concrete self-healing driven by expansive agents often struggles to address cracks of larger width.

Numerous studies have concluded that the two primary factors influencing concrete self-healing are crack width and the ability of concrete's own components to generate healing products that fill the cracks [129]. Crack width directly determines the amount of reaction required, thereby defining the reaction's target and endpoint, while the properties of the healing products dictate the reaction pathway and the progress of the healing process. Among these factors, Ca^{2+}, as the most important metal ion in cement, plays a crucial role in concrete self-healing, profoundly affecting both of these key factors [8].

Regarding crack width, numerous studies have confirmed that most microcracks formed under load in concrete occur within the interfacial transition zone (ITZ) between the aggregates and the cement paste [10,20]. The main component of the ITZ is calcium hydroxide (CH), formed from cement hydration, which typically contains the highest calcium content among all cement hydration products. In ordinary Portland cement, CH generally accounts for about 20% of the hydration products. Its early content mainly depends on the C_3S content of the cement, while the total amount accumulates progressively as hydration proceeds. The natural

mineral form of CH, portlandite, is a trigonal, platy crystal with a Mohs hardness of approximately 2. Due to its relatively low hardness compared to other major hydration products such as C–S–H, CH contributes only minimally to the strength of concrete [130]. It is generally believed that the ITZ region has a very high porosity, and its thickness directly influences the ease of microcrack formation in concrete. The thicker the ITZ, the more susceptible the concrete is to microcracking, and vice versa [131,132]. It is generally considered that, because CH exists as stacked platy crystals, it is less capable of bearing loads compared to the main cement hydration product, C–S–H, which forms an interlaced, chain-like network. Therefore, the CH content plays a crucial role in the formation of microcracks [9,21,14].

Some studies on novel cementitious materials have shown that in concrete where part of the hydration reactions are replaced by pozzolanic reactions, the CH content is significantly lower than in traditional Portland cement [59,63,77,80]. These materials exhibit significantly narrower cracks under the same loading conditions, although the number of cracks increases. Therefore, compared with traditional Portland cement, concrete made with novel cementitious materials capable of pozzolanic reactions is generally more prone to self-healing. This is because the pozzolanic reaction consumes part of the CH produced during hydration, reducing the CH content in the hardened concrete and, correspondingly, decreasing the thickness of the ITZ, which in turn limits the regions prone to microcrack formation as shown in Fig. 15. Some studies have also indicated that the ITZ can locally promote concrete carbonation [133]. However, reducing the CH content in concrete may limit the formation of $CaCO_3$ during carbonation. In cases where CO_2 is abundant but the concrete lacks other components capable of providing sufficient soluble calcium, this could lead to the decalcification of the primary cement hydration product, C–S–H [134,135].

Regarding the healing products, after cement hydration is largely complete, the main and abundant product, C–S–H, has very low solubility. In saturated aqueous solution at room temperature, the calcium ion concentration is typically 1–20 mmol/L ($pK_{sp} \approx 5$–7), and kinetically, dissolution is slow, with complete equilibrium requiring approximately five days [118,137]. The content of more soluble calcium sulfoaluminate (CSA) is quite limited. Therefore, for hardened concrete blocks, the most readily available and sufficient calcium source for dissolving within cracks is CH. In saturated solution at room temperature, the calcium ion concentration of CH typically exceeds 20 mmol/L, with a pK_{sp} of 5.24 [138]. Although rigorous experimental studies in chemistry indicate that the application of solubility products in complex multi-solute solutions requires consideration of ion activity, in the small-volume solutions present within cracks, such ion activity data are difficult to obtain. Moreover, in qualitative analyses, these effects are generally not decisive. Therefore, they are commonly neglected in concrete research [139]. Furthermore, the dissolution products of CH readily react with CO_2 dissolved in air to form $CaCO_3$ and water, whereas the dissolution of C–S–H, CSA, and other crystalline phases releases anions such as silicates and sulfates, which limit further dissolution of calcium-containing compounds. Consequently, CH effectively becomes the primary source of Ca^{2+} in cement clinker, and $CaCO_3$ emerges as the main product responsible for filling cracks in concrete [14].

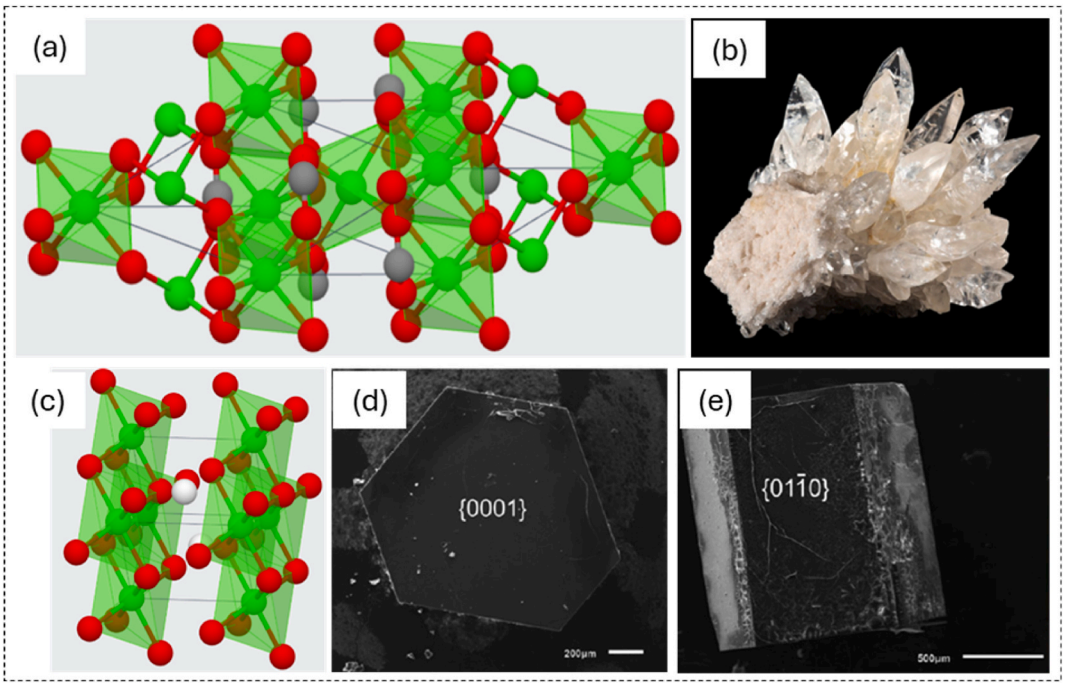


Fig. 14. Mechanism of autogenous self-healing: (a) Rhombohedral crystal structure of calcite; (b) Natural pure crystal of calcite; (c) Single crystal of portlandite and its trigonal unit cell structure; (d) Single crystal of portlandite in surface {0001}; (e) Single crystal of portlandite in one of the surface {0110} [136].

4.3. Complexing and dissolution properties of calcium ions in CH

However, although CH is somewhat more soluble than C–S–H, its solubility remains low from a macroscopic perspective. The relatively low Ca^{2+} concentration in saturated solution reacts too slowly with CO_2, which is present in the air at less than 0.1%. Therefore, many researchers have sought methods to accelerate this reaction, the most typical being the incorporation of microorganisms into concrete to increase the CO_2 concentration within cracks [24,83,88,93,128,140]. Another feasible approach is to accelerate the dissolution of Ca^{2+} from CH, which would promote earlier and faster formation of calcite under unchanged external conditions, thereby speeding up the self-healing process. Although some studies have shown that Ca^{2+} solubility can be influenced by added calcium sources or specific anions such as sulfate and nitrate, such effects are uncommon in typical concrete or remain controversial, and thus will not be considered further in this discussion [141,142].

As an ionic salt crystal, the dissolution of CH can be generally considered to occur in the following two steps: Lattice dissociation: Ions detach from the crystal surface by overcoming the lattice energy, breaking free from the crystal lattice and transitioning toward the free ionic state. Solvation: In pure water, no other free ions exist apart from OH^- and H_3O^+. Therefore, the ions detached from the lattice must undergo hydration, forming solvated ions as shown in Fig. 16.

Additionally, the aqueous coordination behavior of Ca^{2+} has been extensively studied. Numerous experimental studies and molecular orbital simulations have confirmed that the coordination number of calcium ions with oxygen atoms can start from 4, with numbers above 10 being relatively rare. As shown in Fig. 16 (c), the most common coordination numbers are 6–8 [144,145]. In aqueous solution, calcium ions typically adopt a two-shell coordination structure. The inner first coordination shell exhibits an irregular geometry and is strongly influenced by the outer second coordination shell. Numerous DFT calculations indicate that, when the second coordination shell is not considered, an isolated six-coordinated hydrated calcium ion is slightly more stable than seven- or eight-coordinated species. However, because DFT calculations are performed at 0 K, the additional molecular thermal motion present at room temperature stabilizes higher coordination structures in actual solutions [146]. Therefore, it is generally considered that the coordination number of calcium ions in bulk aqueous solution is not a fixed value but exists as a macroscopically quasi-stable distribution resulting from rapid fluctuations among many individual ions. The distribution typically exhibits a main peak between 6 and 8 [147].

Since CH in concrete generally exists as fine powder particles, its lattice energy cannot be significantly altered, and thus the first step of dissolution allows little additional intervention. However, the solvation step can be influenced by introducing nucleophilic agents, other than water molecules, into the solvent, which can interact with Ca^{2+} via complexation or ion–dipole interactions. As long as these added nucleophiles bind more favorably to Ca^{2+} than water molecules, they can promote the dissolution of CH. This promotion can occur via two pathways: a kinetic pathway and a thermodynamic pathway.

The thermodynamic pathway promotes CH dissolution by forming ions with Ca^{2+} that are more stable and have lower free energy than hydrated calcium ions, thereby reducing the concentration of hydrated Ca^{2+} in the solvent and accelerating CH dissolution. A representative additive for this pathway is EDTA, which forms stable Ca–EDTA complexes and, according to Le Chatelier's principle, shifts the dissolution–precipitation equilibrium of CH toward increased solubility. While this approach can significantly dissolve CH in concrete, it is detrimental to the subsequent reaction of Ca^{2+} with CO_2 to form calcite. This is because the complex formation constant of EDTA with Ca^{2+} ($pK_f \approx 10.7$) slightly exceeds the solubility product of calcite ($pK_{sp} \approx 8.5$), so Ca^{2+} released from CH preferentially forms stable Ca–EDTA complexes rather than precipitating as calcite. At the macroscopic level, this delays the complete healing of cracks and reduces the maximum recoverable crack width [148].

The kinetic pathway promotes CH dissolution by lowering the activation energy of the intermediate transition state for the formation of hydrated Ca^{2+}, thereby enhancing the transfer efficiency of calcium ions. As an alkaline earth metal ion, Ca^{2+} has an outer electron configuration of 3 d^0, resulting in a crystal field stabilization energy (CFSE) of zero. These ions exchange water molecules on extremely short timescales, making the process kinetically very fast. Molecular dynamics studies on the dissolution of calcium hydroxide crystals are relatively scarce. Compared with the dissolution process of the structurally similar belite, the anions of calcium hydroxide can directly dissolve into the liquid phase without requiring complete hydration of calcium ions at the crystal surface [149,

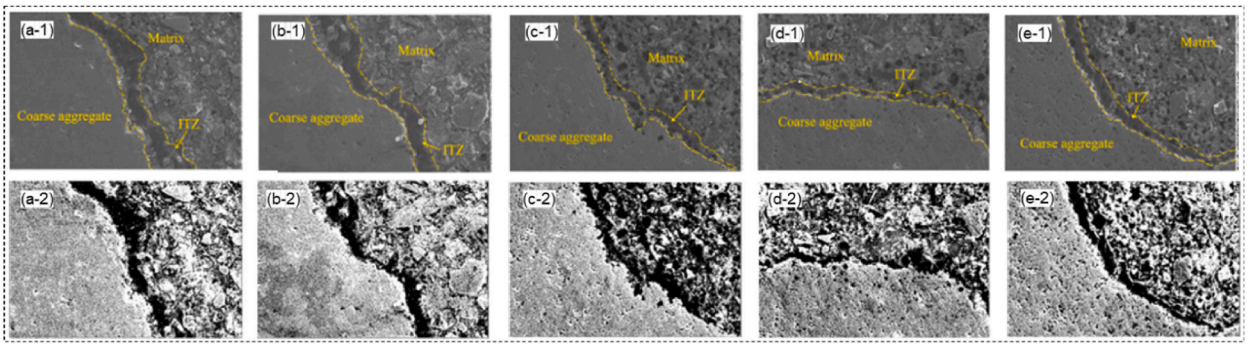


Fig. 15. Microstructure of the ITZ in samples with different coarse aggregate sizes: (a) 4.75–9.5; (b) 9.5–16.0; (c) 16.0–19.0; (d) 19.0–26.5; (e) 26.5–37.5 at a water-to-cement ratio of 0.4, 500X [143].

150]. Some studies on the microstructure of Portlandite single crystals have shown that the dissolution of calcium hydroxide predominantly occurs parallel to the Ca–OH planes, with the surface (010) exhibiting much higher reactivity than the surface (001) [151,152]. The calcium ions in this plane are situated within octahedral units coordinated by six hydroxide ions. Since the dissolution of the Ca–OH octahedra involves extensive ligand exchange, the process is relatively complex, with numerous possible pathways. A representative pathway involves the direct detachment of $Ca(OH)_6^{4-}$ octahedra at the crystal edges into the solution, which subsequently undergo ligand exchange in the solvent to form hydrated calcium ions. The adjacent octahedra left on the crystal surface, lacking full coordination, must adsorb electrophilic molecules from the solution to re-establish the six-coordinated structure. This pathway requires the formation of an ion carrying four negative charges, thus overcoming a relatively high electrostatic lattice energy. Another representative pathway proceeds via ligand exchange at the crystal surface, where three OH^- ions on one side of the surface octahedral layer are replaced by water molecules. The resulting $Ca(H_2O)_3(OH)_3^-$ octahedron carries a lower net charge, making it easier to dissociate into the solution [153,154]. Both mechanisms apply to the calcium ions that detach first from the plane. AFM deflection images of dissolving Portlandite surfaces show that once a calcium ion detaches from the lattice within a layer, the remaining calcium ions continue to interact with the solvent through the defect site, further propagating surface defects. This process results in crystal surface morphologies that resemble concentric hexagons and helical patterns [136]. Therefore, some thermodynamically fewer stable ligands that can form 2–3 coordination bonds with calcium ions can accelerate this process. These ligands can replace solvent water molecules by directly complexing with calcium ions on the crystal surface, reducing the activation energy through chelation and forming relatively more stable dissolution intermediates. Well-established chelating ligands of this type include glycine and triethanolamine (TEA), and their specific mechanisms will be discussed in detail later in the context of the complexation–precipitation theory.

4.4. Conceptual chemical extension framework: complexation-precipitation theory

Nevertheless, research investigating the enhancement of concrete self-healing by PVA at the molecular chemistry level is conspicuously scarce. Therefore, a comparative analysis of the self-healing mechanisms associated with alternative hydroxyl-bearing organic substances is provided to propose a potentially viable theory. The complexation–precipitation mechanism is a well-established concept in cement chemistry and has been widely used to explain the behavior of certain reactive chemical additives. However, its direct applicability to PVA systems has not been explicitly demonstrated in existing literature. Based on the structural characteristics of PVA and its known interactions with calcium ions, this study proposes that a similar mechanism may operate in PVA-containing systems. In this conceptual framework, the polyhydroxyl structure of PVA could enable weak complexation with Ca^{2+}, potentially influencing both the dissolution kinetics of calcium hydroxide and the nucleation and precipitation behavior of calcium carbonate. It should be emphasized that this interpretation is proposed based on analogy with known chemical systems and indirect evidence from experimental and simulation studies and therefore requires further validation through targeted experimental investigations.

The complexation–precipitation process is a common chemical reaction, frequently applied in fields such as mineral separation and chemical synthesis [155–157]. In the field of concrete chemistry, it is commonly used to explain the formation of self-healing products catalyzed by reactive chemical agents. Traditionally, this theory has been applied to concrete specimens containing active chemical additives such as glycine, triethanolamine (TEA), EDTA, and ethylenediamine (EDA) [158–160]. The main content of the complexation–precipitation theory posits that the self-healing reactions in concrete occur in two stages. In the early stage following crack formation, the initial products formed on the crack surfaces primarily consist of ettringite and some monosulfate phases containing aluminum and iron. Upon dissolution and given that the newly formed crack environment remains alkaline—but less so than during concrete hardening—some iron- and aluminum-based hydroxide floccules are generated. These serve as the first batch of self-healing products to fill the cracks. After the cracks are exposed to air or a humid environment for a period, these iron–aluminum hydroxides generally transform into iron–aluminum oxides upon absorption of CO_2 from the atmosphere or dissolved in water, due to the further reduction of alkalinity. Simultaneously, as the alkalinity within the crack environment gradually decreases, calcium ions released from the dissolution of CH and ettringite react with CO_2 to form calcium carbonate crystals, further filling the cracks and further reducing the alkalinity of the crack environment [13]. Therefore, the reaction continues until the cracks are completely sealed, at which point external CO_2 can no longer enter the cracks to produce further products. Chemical analyses of crack-healing products from numerous experiments indicate that calcium carbonate constitutes a substantial proportion of the self-healing products and serves as the primary material responsible for sealing the cracks [9,10,14,20,21,24,100,102].

Therefore, the complexation–precipitation theory posits that if certain reactive chemical agents are added—agents capable of forming complexes with calcium ions to accelerate the dissolution of concrete components such as CH and ettringite—and if these complexes in solution can subsequently react with carbonate ions derived from atmospheric CO_2 to form solid calcium carbonate, then these agents participate in the reaction without being consumed, functioning effectively as catalysts [161,162]. As previously described, calcium ions dissolve from CH into the solution, and the precipitation aspect of the complexation–precipitation theory is equally important. The precipitation process can be divided into two steps: the first step is nucleation, and the second step is the growth of large crystals around the nuclei. For calcium carbonate, the typical nucleation process in pure aqueous solution involves Ca^{2+}(aq) and CO_3^{2-}(aq) ions reaching supersaturation and colliding via thermal motion to form electrically neutral clusters. Numerous crystallographic experiments have confirmed that the precipitation of calcium carbonate possesses a relatively high activation enthalpy ΔH, indicating that substantial energy is required in the activation step to break the interactions between ions and the water molecules in their coordination shells. In the presence of impurities, the activation enthalpy for precipitation is much lower, and specific components in the solution can significantly influence the nucleation rate of calcium carbonate. Some studies have also noted that although vaterite exhibits a lower activation enthalpy ΔH for precipitation, its free energy ΔG is higher, leading it to spontaneously dissolve in aqueous solution and subsequently reprecipitate as calcite [127,163].

Relevant studies indicate that most of these ligands coordinate with calcium ions primarily through oxygen atoms, while nitrogen atoms exhibit relatively weaker coordination with calcium. This aligns with the principal characteristics of PVA as a ligand. Additional studies on polyhydroxy organic compounds have also corroborated this observation [161,162,164,165]. Meanwhile, the introduction of PVA produces effects on CH similar to those of the mentioned active chemical additives. The originally well-ordered, plate-like CH crystals become more disordered and finer, disrupting the original sliding planes of the layered crystals. Fig. 17 illustrate the effects of adding PVA and TEA, respectively, on the morphology of CH crystals formed in concrete. These effects can be summarized as the formation of products with smaller particle sizes and more isotropic macroscopic structures [166]. Overall, PVA exhibits effects analogous to those of these chemically active additives in all respects as shown in Figs. 18 and 19 [167]. Therefore, the complexation–precipitation theory can also be applied to explain the promoting effect of PVA on self-healing.

The polyhydroxyl chemical structure of PVA renders it a hydrophilic and polar additive. The hydroxyl groups along its molecular chains function similarly to water molecules, enabling PVA to participate in the formation of hydration products during the concrete hardening process [51,168]. Meanwhile, because the hydroxyl groups along the PVA carbon chain are spaced apart, its spatial structure can potentially form ring-shaped bidentate or polydentate ligands with favorable geometry, as illustrated in Fig. 19(c) and (d). The coordination form shown in (c) has been reported in multiple studies, whereas (d) depicts a possible coordination structure in which two looped PVA chains coordinate with a calcium ion. Although the structure in (d) is difficult to form in practice due to the steric hindrance of the PVA molecular conformation, there remains a considerable possibility for PVA to form polydentate complexes with Ca^{2+} because not all calcium–oxygen complexes are limited to the predominant 6–8 coordination; 4-coordination cases also exist, and free water molecules in solution can supplement vacant coordination sites [49,51,91,144,145,168–171]. Moreover, some similar organic polymers have exhibited comparable calcium-ion complexation abilities, further supporting this hypothesis [140,172–176].

Some studies in the fields of medicine, nanomaterials, and computational chemistry have also confirmed that PVA polymer chains exhibit a certain binding affinity toward free calcium ions and the main cement hydration product, CSH chains [169–171,177,178].

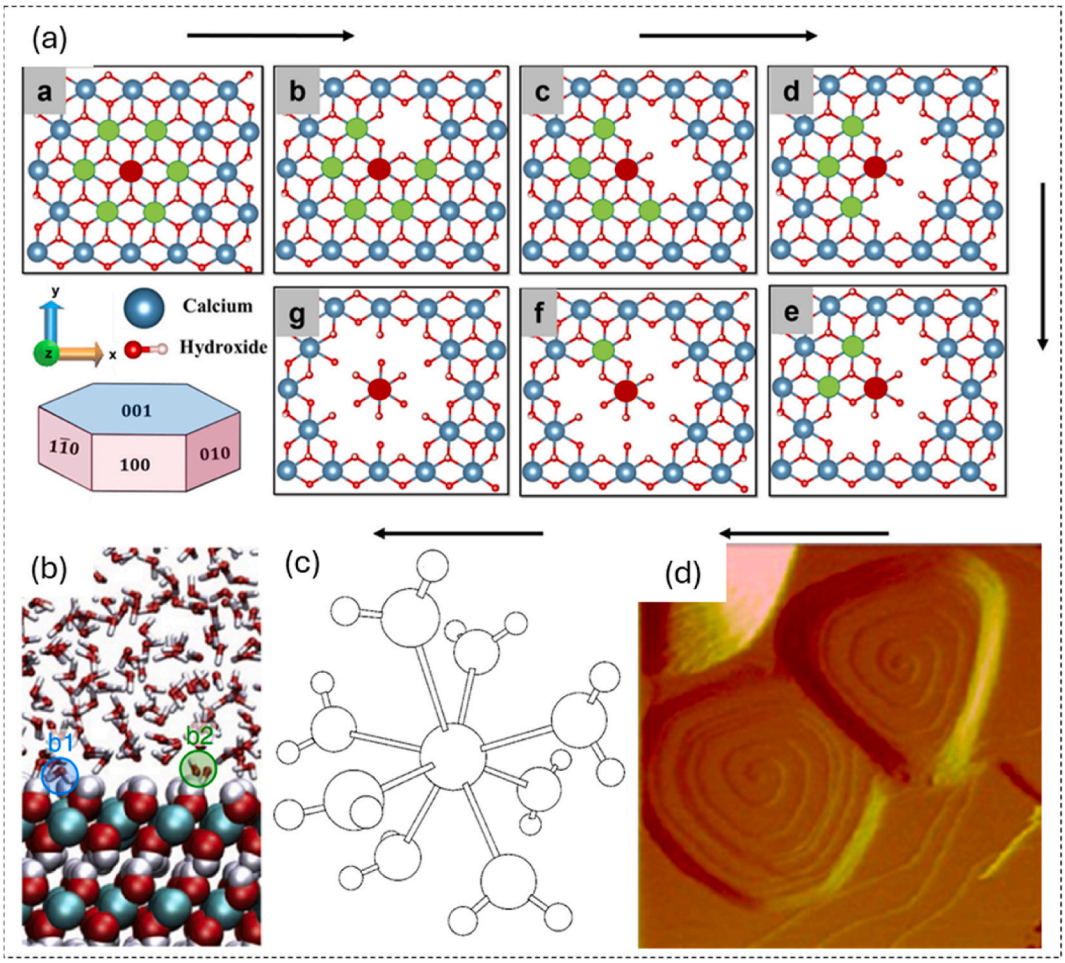


Fig. 16. Complexing and dissolution properties of calcium ions: (a) Dissolution mechanism of Calcium Hydroxide in (001) surface; (b) Interface structure between water and Portlandite; (c) Typical distorted cubic configuration of the hydrated ion $Ca(OH_2)_8^{2+}$ [146]; (d) AFM deflection images of the (001) Portlandite surface during dissolution in deionized water, image size 5 × 5 μm [136,149,151].

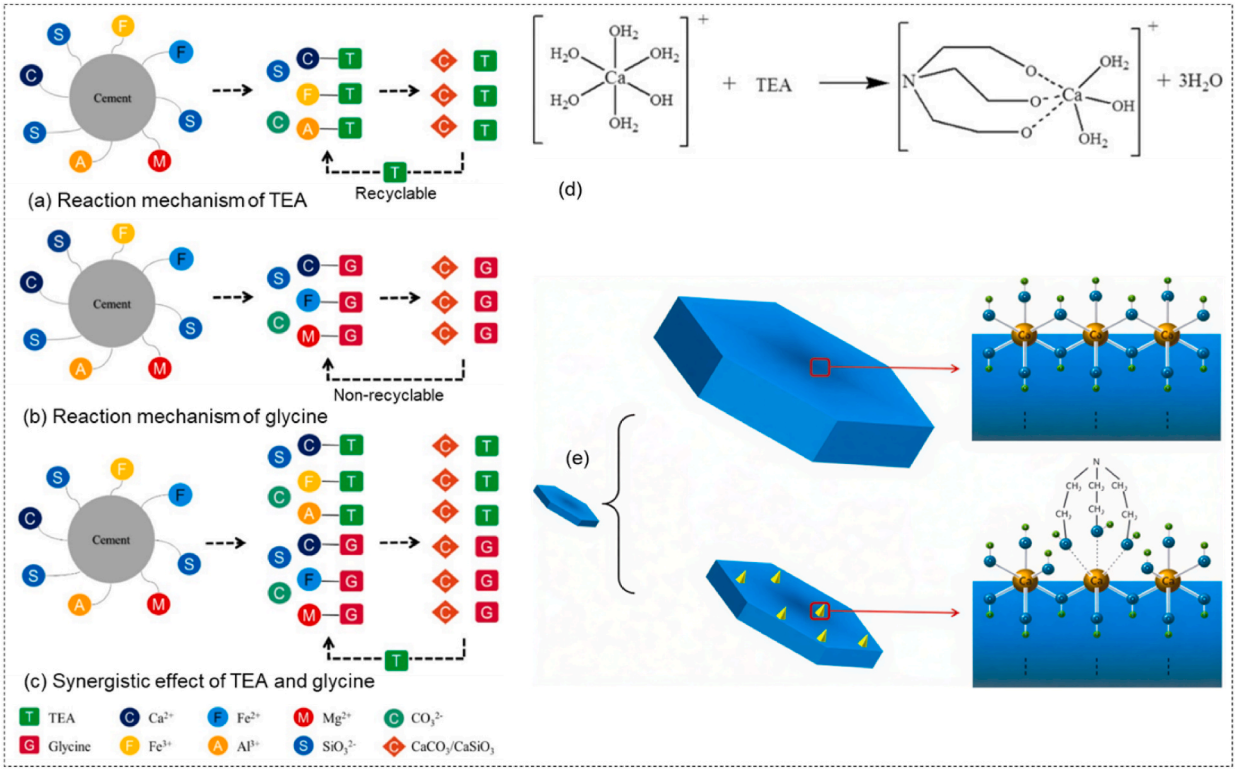


Fig. 17. Complexation-precipitation theory: (a) to (c) Complexation reaction mechanism of the TEA-glycine composite chemical additive [164]; (d) Formation of a complex between TEA and calcium ions; (e) Schematic of TEA acting on the CH crystal surface to accelerate CH dissolution [161].

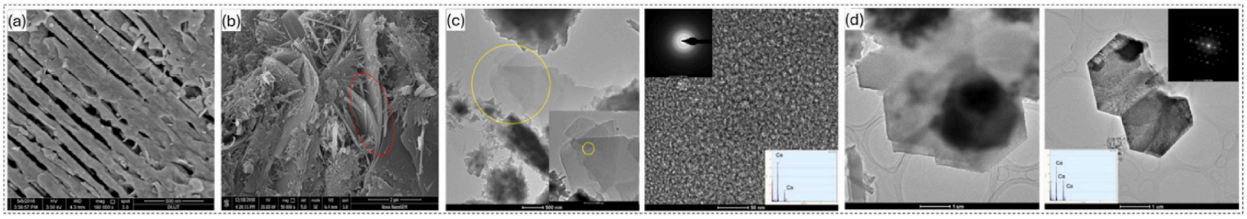


Fig. 18. Microstructure and morphology of CH crystals: (a) CH crystals in concrete without PVA under SEM; (b) CH crystals in concrete containing PVA [39]; (c) TEM image of CH crystals in concrete without TEA; (d) TEM image of CH crystals in concrete with TEA [161].

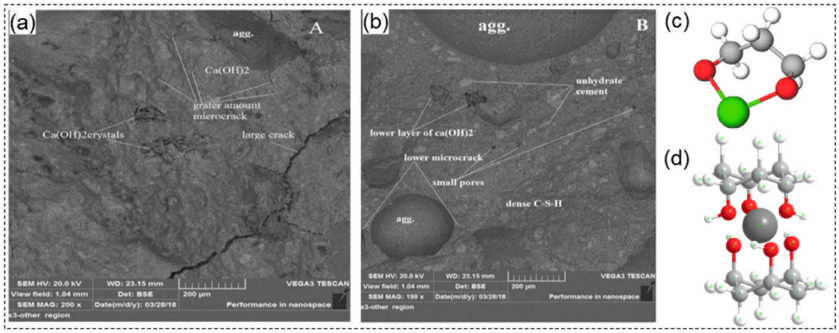


Fig. 19. Explanation for PVA-enhanced concrete self-healing: (a) Crack healing in concrete without PVA; (b) Crack healing in concrete with PVA [52]; (c) Schematic of a six-membered ring complex formed by two adjacent hydroxyl groups in PVA coordinating with Ca^{2+} (white spheres: hydrogen atoms; gray spheres: carbon atoms; red spheres: oxygen atoms; green sphere: calcium ion); (d) Schematic of a potential hexadentate chelate formed by two extended PVA chains enveloping a Ca^{2+} ion.

These properties enable PVA molecules to bind effectively with cement and aggregates in concrete as shown in Fig. 20 without forming agglomerated clusters that could lead to localized mechanical heterogeneity, thereby ensuring the uniformity of the concrete matrix. The interaction between PVA and CSH primarily occurs between the PVA polymer chains and the CSH crystal chains, forming O–Si, O–Ca, and hydrogen bonds, which allow the PVA molecules to stably intercalate between two or more CSH chains. Although molecular dynamics models indicate that the incorporation of PVA can reduce the stiffness of CSH perpendicular to the chain direction, the total amount of PVA typically added to concrete is much lower than the number of CSH chains produced by cement hydration. Additionally, considering the effect of PVA on reducing the ITZ thickness, numerous experimental results have shown that the stiffness of PVA-modified concrete generally remains largely unchanged or exhibits only a slight decrease [169,179]. Moreover, some molecular dynamics simulations suggest that PVA chains may not stably adsorb onto the surfaces of CSH chains. Therefore, the effects of PVA addition on primary cement hydration products, such as CSH, still require further validation through experimental studies [53].

As previously mentioned, PVA possesses a certain ability to complex calcium ions, and the self-healing products in PVA-containing concrete are also primarily calcium carbonate. Therefore, the overall framework of the complexation–precipitation theory can, in principle, be applied to explain the self-healing behavior of concrete with added PVA. However, current studies discussing the complexation–precipitation theory generally do not consider PVA as an active chemical substance. At present, there is no literature explicitly using this theory as a framework to explain the promotion of concrete self-healing by soluble PVA. Consequently, this paper only presents an introduction to the existing findings and theoretical framework, without treating this theory as a definitive explanation for PVA-enhanced concrete self-healing.

5. Comparison with some related fields and further consideration

5.1. Complexation-precipitation theory: more applicable object

The complexation–precipitation mechanism, although widely recognized as a fundamental chemical process, has seen extensive application in other industrial fields but remains relatively uncommon as a mechanistic pathway for admixtures in concrete self-healing [156]. As discussed in Sections 4.2 and 4.3, the applicability of this mechanism is by no means limited to the few compounds mentioned earlier; in principle, any molecule capable of calcium complexation—particularly organic compounds bearing multiple hydroxyl groups—may operate through this pathway. Similar observations have been reported in studies involving sugars, sugar alcohols, and other polyols in cementitious materials [140,172,180,181].

Monosaccharides share structural similarity with PVA in that both possess hydroxyl-substituted carbon chains. The distinction lies in the spatial arrangement: hydroxyl groups in PVA are distributed with spacing along the chain, whereas those in sugars are positioned adjacently. Consequently, despite structural resemblance, sugar molecules impose stricter conformational requirements for

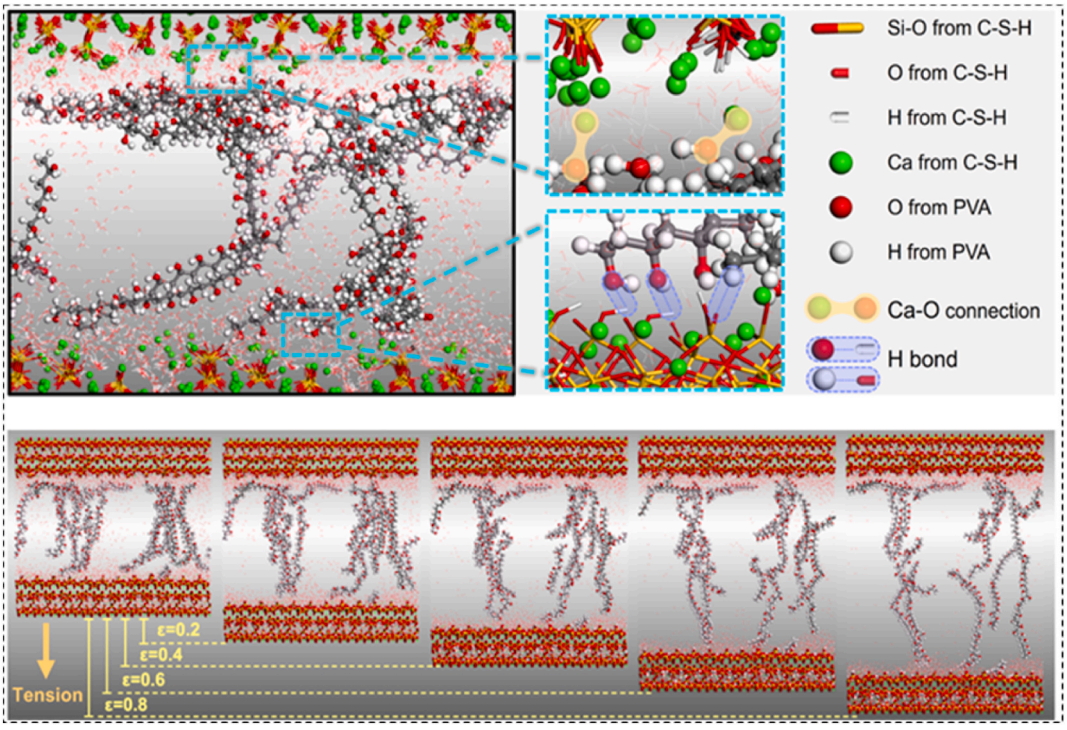


Fig. 20. Molecular models of Ca–O bonds and hydrogen bonding at the CSH/PVA interface; molecular models of CSH/PVA composites under 0, 0.2, 0.4, 0.6, and 0.8 strain applied perpendicular to the CSH layer direction [179].

complexation. As shown in Fig. 21, adjacent hydroxyls in sugars rarely coordinate a single Ca^{2+} ion simultaneously, as monosaccharides typically exist in cyclic conformations wherein neighboring hydroxyls frequently occupy opposite sides of the ring plane [182]. Only when hydroxyls incidentally align on the same side—which is further influenced by optical isomerism—can effective bidentate complexation occur [180].

Given that common sugars and polyols are more readily available and industrially scalable than PVA, they offer potential advantages in cost and accessibility; however, they are also more prone to degradation under service conditions.

Regarding conventional material properties, these hydroxyl-only organic additives have consistently demonstrated delayed initial setting, increased fresh-mix fluidity, and postponed hydration-heat peaks—trends strikingly similar to those observed in concrete containing soluble PVA [140,172,180–182]. This supports the notion that functional groups, rather than polymer identity alone, dominate the governing behavior. Nonetheless, contradictory results have also been reported; for example, some studies showed that glycerol significantly accelerated cement setting, indicating that the phenomenon requires further investigation [183].

The prevailing explanation within current literature attributes these effects to complexation between the additive molecules and Ca^{2+} ions in the cement pore solution. Complexation reduces free calcium concentration, slowing the attainment of supersaturation and thereby inhibiting nucleation and growth of hydration products. This mechanistic interpretation closely parallels the complexation–precipitation framework discussed earlier. Studies on sugar alcohols further suggest that when hydroxyl groups align on the same side of the carbon chain, hydration promotion on C_3S is markedly stronger—again analogous to monosaccharides [184]. For PVA, most backbone carbons carrying hydroxyl substituents are chiral; however, industrial PVA is typically produced as a racemic mixture, making conformational effects on calcium binding difficult to quantify.

In summary, given that calcium carbonate precipitation is a dominant pathway in concrete self-healing, accelerating calcium dissolution through weak complexing agents expands the scope of viable admixtures to virtually all oxygen-containing ligands. This substantially broadens the palette of potential catalytic additives capable of enhancing autonomous healing in cementitious systems.

5.2. *Cooperation with bio agents as carbon nutrition source or substrate*

Although the long-term self-healing performance of bacteria-based self-healing concrete remains challenging, its ability to repair cracks formed shortly after hardening is highly effective. Consequently, it is widely regarded in academia as a highly promising research direction for concrete self-healing. The contribution of microorganisms to concrete self-healing can be summarized in two main aspects. First, upon crack formation and subsequent water ingress, microbial cells become activated and generate carbon dioxide through metabolic respiration, thereby enhancing the precipitation efficiency of calcite within cracks. Second, certain microorganisms can induce the formation of calcium carbonate crystals through specific proteins, reducing the nucleation energy barrier by generating liquid precursors [185,186]. This pathway typically involves the initial formation of vaterite-type calcium carbonate, which subsequently dissolves and recrystallizes into thermodynamically stable calcite. In addition to their well-recognized role in crack width control, PVA fibers may also contribute to self-healing by acting as preferential nucleation and attachment sites for mineral precipitation. Due to their hydrophilic surface and abundant hydroxyl functional groups, PVA fibers can interact with calcium ions and hydration products, creating localized environments favorable for the nucleation of calcium carbonate. These surfaces may facilitate the initial formation of mineral phases and enhance the adhesion of precipitated products to the crack interface. This effect is particularly relevant for relatively wide cracks or under flowing water conditions, where healing products formed in the bulk solution may otherwise be washed away before effective deposition. In such cases, the presence of PVA fibers provides stable anchoring sites for mineral growth, improving the retention and accumulation of healing products within the crack region. Furthermore, in systems involving microbial or enzyme-induced mineralization, PVA fibers can also serve as substrates for bacterial colonization or enzyme immobilization, thereby enhancing localized biomineralization efficiency. The former mechanism has been reported in the majority of microbial self-healing concrete studies, whereas the latter can be broadly divided into two major routes: microbial-induced calcium carbonate precipitation (MICP), which involves the direct incorporation of microbial cells or spores, and enzyme-induced calcium carbonate precipitation (EICP), in which active enzymes are introduced using non-cellular carriers [187–190].

Due to its polyhydroxyl structure, PVA is structurally analogous to sugars and can serve as an exogenous carbon source for microorganisms. Moreover, PVA-based hydrogels can act as carriers for enzymes, enabling their incorporation into concrete while mitigating enzyme deactivation under highly alkaline conditions. Compared with conventional soluble sugar-based carbon sources, such ‘polymeric carbon sources are more likely to minimize interference with early cement hydration and can provide localized, on-demand supply through crack-driven water ingress and microbial metabolism, thereby improving the spatiotemporal matching of biomineralization processes. In addition, PVA exhibits excellent film-forming and immobilization capabilities in the form of hydrogels, fibers, films, and porous coatings, making it a suitable carrier and protective matrix for mineralization-related enzymes such as carbonic anhydrase (CA) [191–193]. Through physical entrapment, covalent crosslinking, or hybridization with inorganic porous phases, PVA can provide microenvironmental shielding and diffusion regulation for enzymes in highly alkaline pore solutions, extending the effective catalytic time window. Furthermore, enzyme-triggered carbonate deposition can be activated when crack water ingress and CO_2 diffusion induce localized pH reduction, enabling practical enzymatic functionality even under highly alkaline conditions.

The polymer-induced liquid precursor (PILP) concept, a core principle in biomineralization, was first proposed in the late twentieth century. PILP theory posits that during biologically induced carbonate precipitation—initially studied in protein-mediated systems and later extended to polysaccharides and non-biological polymers—macromolecular organic polymers regulate crystal morphology through specific oxygen-containing functional motifs. By forming ordered liquid-like amorphous microdroplets and integrating these precursors into crystalline structures, PILP effectively reduces the nucleation energy barrier [194,195]. Figs. 22, 23 and 24 show the similar effect of adding PVA and CAs. From a PILP perspective, the high-density hydroxyl segments of PVA can serve as favorable

substrates for the wetting and retention of liquid precursors. Within crack surfaces or pore networks, PVA promotes enrichment, infiltration, and subsequent phase transformation of precursor phases in confined spaces through hydrogen bonding and ion association. This facilitates the formation of continuous, dense calcium carbonate deposits with enhanced interfacial bonding to the cement matrix, thereby improving the stability and erosion resistance of crack sealing. Overall, if material design enables synergistic regulation of PVA structural parameters with microbial metabolism or enzyme stabilization, as well as coordinated transport and phase transformation of PILP precursors, PVA may emerge as a critical bridge linking biological activity and biomimetic mineralization [196, 197]. By simultaneously serving as a carbon source or enzyme carrier within cementitious systems and as a nucleation and deposition interface for mineralization, PVA holds the potential to advance biologically enhanced self-healing concrete from single-use repair toward a new paradigm of repeatable, targeted, and controllable healing processes.

To further verify the proposed conceptual framework of PVA-assisted self-healing, future studies should focus on direct experimental and multi-scale validation of the underlying mechanisms. For experimental aspect, at the microscale, in situ spectroscopic techniques, such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray absorption spectroscopy (XAS), could be employed to identify potential complexation interactions between PVA hydroxyl groups and Ca^{2+} ions within crack environments. These techniques may provide direct evidence of coordination structures and chemical bonding evolution during the healing process. At the mesoscale, advanced imaging methods such as environmental scanning electron microscopy (ESEM), micro-computed tomography (micro-CT), and atomic force microscopy (AFM) can be used to monitor the nucleation, growth, and spatial distribution of healing products in real time. In particular, time-resolved observations under controlled humidity and CO_2 conditions could help distinguish between purely autogenous healing and PVA-assisted processes.

For simulation aspect, molecular dynamics (MD) simulations and density functional theory (DFT) calculations are promising tools to investigate the coordination behavior between PVA chains and calcium ions, as well as their influence on dissolution kinetics and nucleation pathways. Such simulations can provide insights into the stability of PVA–Ca^{2+} complexes, the role of hydroxyl group distribution, and the potential formation of multi-dentate coordination structures. In addition, isotope tracing techniques could be

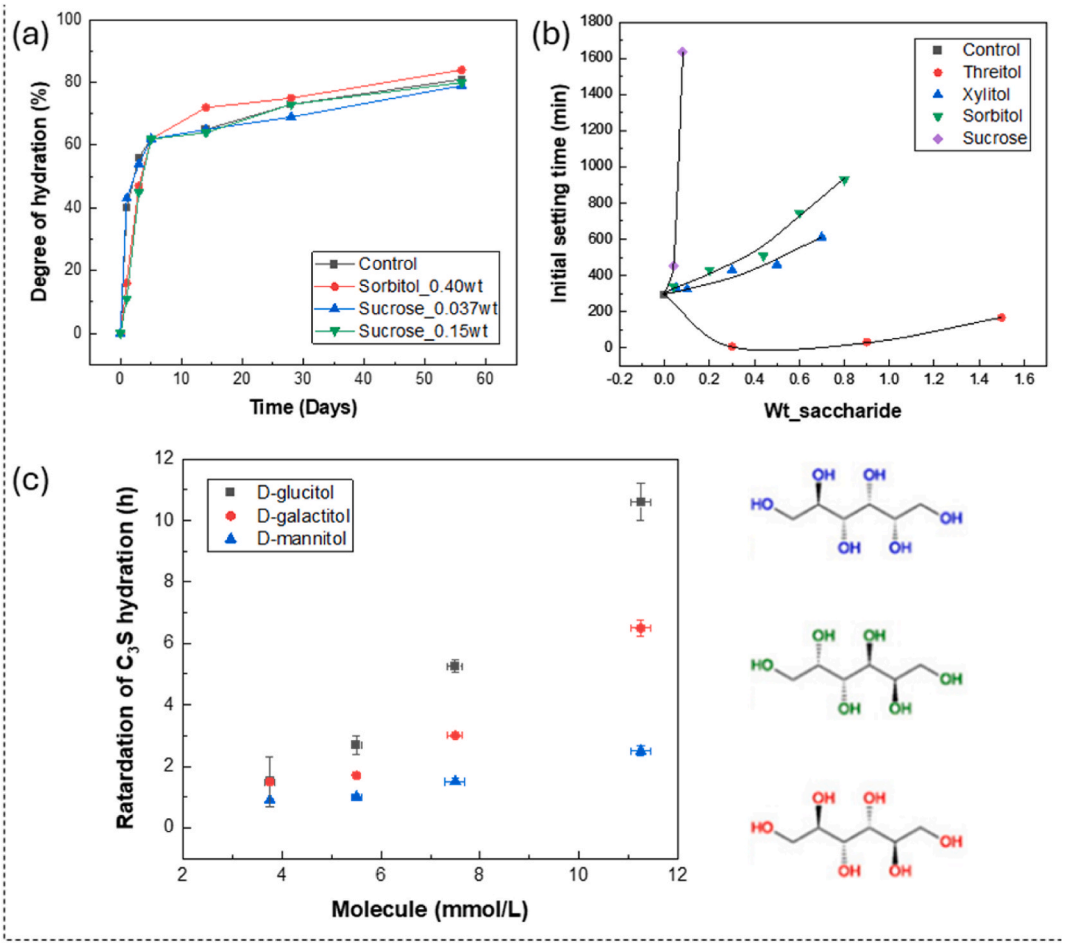


Fig. 21. Cooperation with bio agents as carbon nutrition source or substrate: (a) Effects of different organic compounds on cement hydration properties; (b) Effects of different organic compounds on initial setting time of cement; (c) Effects of sugar alcohols with different conformations on cement hydration [180,184].

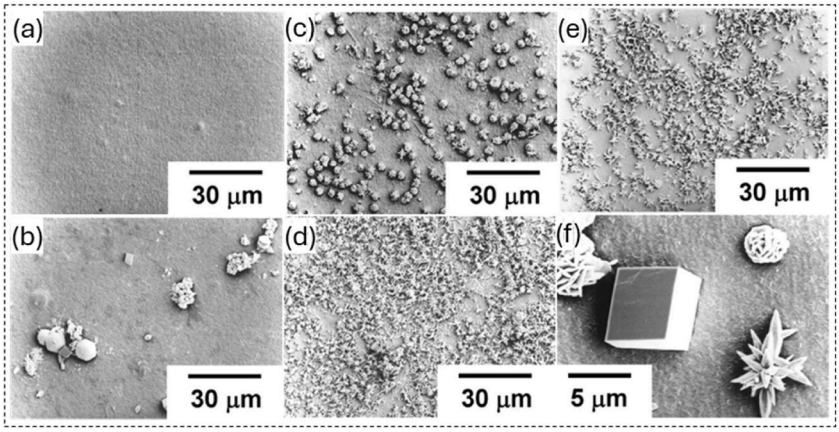


Fig. 22. SEM images of the surfaces of (a) a 10-step PVA-coated PE film, CaCO3-deposited (30 cycles) films coated with; (b) non; (c) 1-step; (d) 5-step; and (e) 10-step coating of PVA [198].

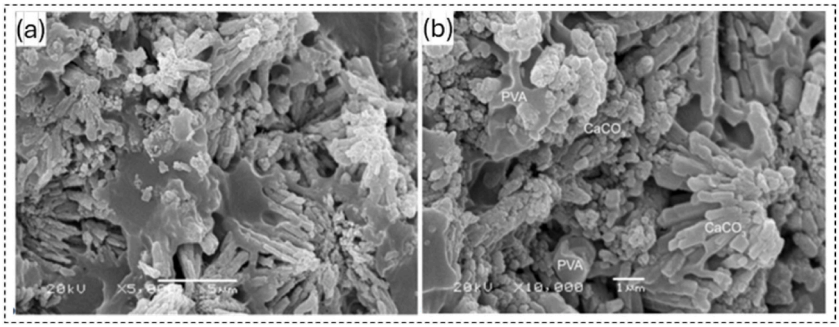


Fig. 23. Cross-sectional microstructures of PVA–$CaCO_3$ composite COM-2 containing PVA with magnification of (a) ×5000; (b) X10 000 to reveal microstructural organization of PVA and CaCO3 polymorphs [199].

applied to track the origin and transport pathways of carbonate species during crack healing, enabling a more precise understanding of reaction kinetics and product formation.

By integrating these experimental and computational approaches, it would be possible to establish a systematic validation framework for the proposed mechanism and to bridge the gap between macroscopic self-healing performance and underlying chemical processes.

6. Challenge and perspective

6.1. Challenge

As a well-established concrete additive, PVA has been widely incorporated into both laboratory formulations and practical engineering applications. With respect to conventional material properties, current studies on PVA-modified self-healing concrete consistently report that the introduction of PVA, whether in fiber form or as a soluble additive, inevitably alters the engineering properties of the concrete, and such effects are not always beneficial.

For PVA fibers, workability represents a major challenge. As the fiber volume fraction increases, both slump and flowability decrease markedly; the mixture becomes more viscous and difficult to handle, often requiring additional mixing of water or high dosages of superplasticizers to restore acceptable workability. During mixing, as Fig. 25 shows, fibers tend to agglomerate or "ball," resulting in regions with excessively high or insufficient fiber content, which means it still requires additional treatment to get acceptable dispersion [200,201]. This nonuniform distribution undermines the intended crack-bridging and crack-refinement benefits and is detrimental to both mechanical and durability performance. Like other polymer-modified systems, PVA modification is commonly associated with certain losses in workability, which must be carefully controlled during engineering implementation. With respect to mechanical behavior, as noted in Chapter 2, the addition of PVA fibers yields limited improvements—and in some cases slight reductions—in compressive strength. Changes in elastic modulus are generally small but highly sensitive to curing age, fiber dosage, and mix proportions, and results across different studies are sometimes contradictory. Such inconsistencies impose limitations on the widespread engineering application of PVA fibers. Regarding self-healing performance, PVA fibers primarily promote healing

by refining crack widths and providing favorable sites for the precipitation of healing products. However, the self-healing effect is typically confined to microcracks smaller than approximately 200 μm, and the efficiency of healing is strongly dependent on environmental moisture and curing duration. In essence, PVA fibers improve the conditions for autogenous self-healing rather than functioning as an effective autonomous self-healing agent. Consequently, their use in self-healing systems often requires combination with other additives or further surface modification, and their standalone effectiveness as healing promoters remains limited (see Fig. 25).

For soluble PVA, challenges also arise in multiple aspects. In terms of workability, PVA solutions exert pronounced effects on rheology, air-entrainment, interfacial bonding, and the degree of cement hydration. As a polyhydroxy polymer, PVA can prolong hydration and improve fluidity in a manner similar to other polyols; however, strong intramolecular hydrogen bonding prevents excessive fluidization that could impair structural integrity. Even so, the dosage and degree of alcoholysis must be carefully controlled to avoid excessive retardation of initial setting and potential detrimental effects on early-age strength. In terms of mechanical performance, small dosages may slightly improve or maintain compressive strength, but higher dosages tend to increase liquid-phase viscosity and introduce other experimental studies air voids, altering the pore structure and leading to noticeable reductions in compressive strength. The elastic modulus exhibits only minor changes and no clearly established pattern. Regarding self-healing, most existing studies focus on mortars or small specimens; little is known about performance under complex stress states, large structural members, or long-term field conditions.

Moreover, as an organic polyhydroxy compound, PVA may be subject to environmental degradation over extended service periods, effects that have not been adequately investigated. From a life cycle assessment (LCA) perspective, the environmental implications of incorporating PVA into concrete systems should be evaluated not only in terms of production-related carbon emissions but also with respect to its potential environmental fate during service and after disposal. Available studies on water-soluble PVA indicate that it is susceptible to microbial degradation under biologically active aqueous environments. For example, measurable biodegradation has been reported in wastewater systems, where approximately 30% degradation can occur within 30 days, while standardized aerobic biodegradation tests (OECD protocols) have demonstrated substantial mineralization to CO_2 for certain PVA grades [204–207]. These findings suggest that PVA may ultimately contribute to carbon release through biodegradation pathways. However, it should be emphasized that these data are primarily derived from wastewater or controlled laboratory testing systems with active microbial populations and favorable degradation conditions. Such environments differ fundamentally from the highly alkaline, low-permeability, and microbially limited pore solution conditions in cementitious materials. Therefore, the biodegradation rates and mineralization behavior of PVA observed in these studies cannot be directly extrapolated to real concrete service environments. Consequently, the potential contribution of PVA degradation to carbon emissions over the service life of concrete remains uncertain and should be treated with caution in LCA evaluations. A comprehensive assessment should consider both the possible long-term degradation of PVA, and the potential environmental benefits associated with extended service life and reduced maintenance due to self-healing functionality. Thus, the reproducibility and reliability of self-healing performance in real structures remain uncertain.

Beyond the performance-related challenges described above, additional concerns arise in terms of cost and durability. Compared with steel or polypropylene fibers, PVA fibers are significantly more expensive. Compared with conventional fibers used in cementitious composites, PVA fibers are substantially more expensive. Recent market quotations suggest that concrete-grade PVA fibers are typically around US$2800–3100 per ton, whereas polypropylene fibers and common concrete steel fibers are generally in the range of about US$700–1100 per ton and US$600–1100 per ton, respectively. In other words, PVA fibers may cost roughly three to four times as much as PP or steel fibers on a mass basis. Classical PVA-ECC mixtures typically rely on high binder content and relatively high PVA fiber dosages, resulting in material costs substantially exceeding those of ordinary concrete or conventional fiber-reinforced concrete. Furthermore, high-strength concrete exhibits considerably higher heat of hydration than normal-strength concrete, leading to elevated internal temperatures during curing in practical construction. Such thermal conditions may degrade the mechanical performance of PVA fibers or induce hydroxyl condensation into ether linkages, thereby diminishing fiber–matrix affinity [67,167,208].

6.2. *Research perspective*

Although PVA is already a well-established concrete additive, it is most used in a single form—either as PVA fibers alone or as PVA with a fixed DP and DA. Consequently, its functionality is often confined to a single performance scale. Inspired by the workability analysis in Chapter 2, PVA fibers are known to reduce the fluidity of cementitious slurry, whereas soluble PVA enhances flowability and delays initial setting. How these opposite effects interact when PVA fibers and soluble PVA are incorporated simultaneously, and which form exerts dominant influence on rheology and workability, remains largely unexplored in current literature.

Beyond workability, similar synergy could potentially be achieved in other property domains. The contribution of PVA fibers to self-healing primarily arises from crack width refinement induced by fiber bridging and from their role as crystallization nucleation sites; thus, they mainly enhance autogenous self-healing. In contrast, soluble PVA—particularly low-DP PVA—possesses the potential to serve as an autonomous healing catalyst by promoting crystal precipitation within crack zones. Therefore, a combined system of PVA fibers + low-DP soluble PVA may exhibit cooperative self-healing behavior. Moreover, soluble PVA chains can form hydrogen bonds with the long-chain PVA molecules on the fibre surface, potentially amplifying the nucleation-inducing capability of fibres. However, research in this direction remains extremely limited [42,200].

This synergistic concept also suggests the possibility of innovation in PVA incorporation strategies. Studies on PVA degradation indicate that long-chain PVA can be microbially cleaved into shorter oligomers and can also undergo oxidative scission to generate low-DP fragments [5,209]. If the oxidation products do not negatively impact concrete, it may be feasible to synchronize oxidative cleavage with cement hydration. In this scenario, adding an oxidizing agent together with high-DP PVA (primarily in fibre form) could

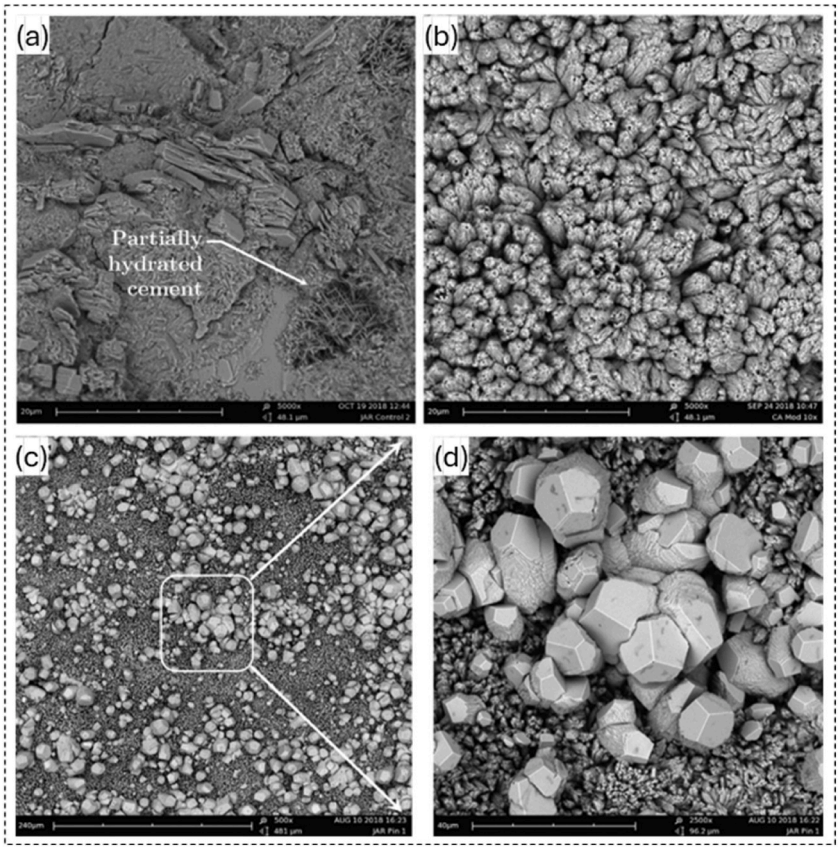


Fig. 24. Microstructures with scale bars of (a) Partially hydrated cement needle-like particles are present in the control sample, 5000X; (b) The cured surface of a CA-Mod-5x sample shows regular and even crystal formation, 5000X; (c) Crystals develop on the surface of a CA-Mod-5x sample after soaking in DI water, 500×; (d) A magnified view of the surface crystals on a CA-Mod-5× sample show evidence of cubic shapes and clustered formation, 2500X [202].

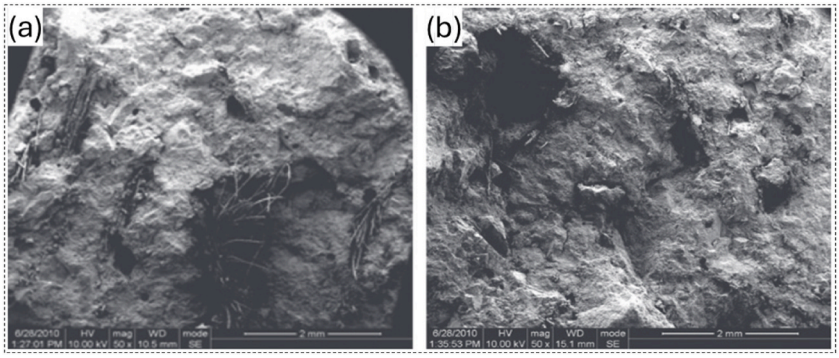


Fig. 25. Microstructures of the dispersion of PVA fibers in cement mortar: (a) untreated fibers; (b) treated fibers [203].

generate low-DP oligomers in situ as crystallization catalysts, enabling targeted deposition at healing-active interfaces. Such an approach may yield more favorable spatial distribution of solid-phase catalytic species and improved local self-healing efficacy under the same material dosage.

Complex service conditions should be considered more explicitly in future research on PVA-based self-healing systems. In flowing-water environments, recent work on crack healing under dynamic water conditions shows that continuous water movement can substantially affect the healing process, making the retention of reactive species and newly formed products a key issue [98]. Under such conditions, the interfacial role of fibres becomes more important because they can provide physical anchoring and preferential deposition sites for healing products. This interpretation is also consistent with studies reporting that PVA fibres provide attachment

points for self-healing products and can cooperate with additional healing agents to improve crack repair, especially for wider cracks. For saline environments, the currently available evidence suggests that the influence of salts is not uniformly negative. A recent review on marine crack healing reported that seawater can promote surface crack healing because Ca^{2+} and Mg^{2+} in seawater may participate in the formation of additional healing products [90]. Likewise, recent work on modified repair mortars found simulated seawater to be more conducive to self-healing than clean water in some cases. In PVA-fibre-reinforced cementitious composites, self-healing has also been shown to markedly reduce chloride penetration after cracking. However, other ECC studies under sulfate–chloride exposure has simultaneously emphasized the need for longer-term and field-condition validation.

7. Conclusions

In summary, this paper provides a relatively detailed overview of the applications of PVA in concrete self-healing and the associated mechanisms. By discussing the application methods of PVA with different DP and the widely recognized self-healing processes of concrete—mechanisms that closely resemble the action of PVA—the following conclusions can be drawn.

(1) The effects of PVA on self-healing concrete depend on its form of incorporation. PVA fibers mainly act at the structural scale by bridging cracks, refining crack widths, and providing favorable sites for the deposition of healing products, thereby enhancing autogenous self-healing under moist conditions. In contrast, soluble PVA—particularly low-degree-polymerized variants—can directly influence chemical processes within cracks and shows greater potential to participate in autonomous self-healing.
(2) The incorporation of PVA inevitably alters fresh and hardened properties of concrete. PVA fibers tend to reduce workability and require careful dispersion control, while soluble PVA affects rheology, air entrainment, and early-age hydration. Although moderate dosages can maintain or slightly improve later-age strength and durability, excessive PVA content may introduce porosity or retard hydration, highlighting the need for optimized mix design.
(3) This conceptual framework provides a basis for future experimental validation and may contribute to the development of mechanism-driven self-healing design strategies. The polyhydroxyl molecular structure of PVA enables weak complexation with Ca^{2+}, influencing both the dissolution kinetics of calcium hydroxide and the nucleation behavior of calcium carbonate. These effects align well with the complexation–precipitation theory, which provides a chemically consistent framework to interpret PVA-assisted self-healing. However, direct experimental evidence remains limited, and further validation through targeted chemical characterization and in situ studies is required.
(4) Promising research directions include the synergistic combination of PVA fibers with low-DP soluble PVA, coupling PVA systems with biomineralization or enzyme-based healing agents, and extending the complexation–precipitation concept to other hydroxyl-rich organic additives. Such multi-scale and mechanism-driven strategies may enable PVA to evolve from a passive modifier into a key component of efficient, durable, and economically viable self-healing concrete systems.

CRediT authorship contribution statement

Yijian Miao: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Wenkui Dong:** Writing – review & editing, Writing – original draft, Validation, Supervision. **Fulin Qu:** Writing – review & editing, Writing – original draft, Validation, Supervision. **Yucheng Fan:** Writing – review & editing, Writing – original draft, Validation. **Hailong Ye:** Writing – review & editing, Writing – original draft, Validation. **Zushi Tian:** Writing – review & editing, Writing – original draft, Validation. **Doo-Yeol Yoo:** Writing – review & editing, Writing – original draft, Validation. **Daniel C.W. Tsang:** Writing – review & editing, Writing – original draft, Validation. **Wengui Li:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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