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Water-soluble polymers in cementitious materials: A comprehensive review of roles, mechanisms and applications

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ABSTRACT

This review paper provides an extensive assessment of the diverse roles played by water-soluble polymers in cementitious materials. It commences with an introduction that provides a thorough overview of the background, objectives and limitations of the review. Subsequently, the various types of water-soluble polymers, encompassing natural, semi-synthetic and synthetic variants, are examined in detail, alongside an exploration of their working mechanisms within cementitious materials. Mechanisms discussed include entanglement and association, adsorption and complexation, as well as bridging. Furthermore, this review delves into the influence of water-soluble polymers on the microstructure, fresh properties, mechanical properties and durability of cementitious materials. A comprehensive analysis of the challenges and opportunities associated with the implementation of water-soluble polymers in cementitious materials is also presented, followed by a summary of the key findings and recommendations for both practical applications and future research endeavors. Overall, this review provides invaluable insights for researchers and practitioners, shedding light on the multifaceted functions of water-soluble polymers in cementitious materials.

1. Introduction

Water-soluble polymers have been widely used as an admixture in cement and concrete for several decades to enhance the properties of cement-based materials. The polymer is added to the mix to modify the properties of fresh and hardened concrete. Polymer-modified cement (PMC) is created by adding water-soluble polymers to cement mixes. These polymers enhance the performance of cement by improving its mechanical, physical and chemical properties. Various types of water-soluble polymers, including polyvinyl alcohol, polyacrylamide, polycarboxylates and styrene-butadiene rubber (SBR), have been used in cement and concrete [24,37,90].

Water-soluble polymers are used as superplasticisers or water reducers to reduce the water-cement ratio (W/C) in cement-based materials. The addition of these polymers increases the workability of fresh concrete, reduces segregation, improves pumpability and increases early strength development. Superplasticisers can be classified into three types: sulfonated melamine-formaldehyde (SMF), sulfonated naphthalene-formaldehyde (SNF) and polycarboxylate ether (PCE) [37]. PCE superplasticisers are a new generation of superplasticisers, which have been developed in recent years. They have excellent dispersing properties, high water-reducing capability, and are compatible with different types of cements. The mechanism of action of PCE is based on the steric repulsion of the

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polymer chains, which reduces the attractive forces between cement particles, leading to an increase in workability.

Polymers can also be added to cement mixes to improve the durability of concrete structures. The addition of polymers can improve the resistance of concrete to water, abrasion and chemical attack. Polyvinyl alcohol and SBR are commonly used to enhance the durability of concrete [24,39,50,90]. SBR is a water-soluble polymer that has been used extensively as an admixture in cement and concrete. It is a copolymer of styrene and butadiene, which has excellent mechanical properties and is resistant to oil and chemicals. The addition of SBR to cement mixes improves the workability of fresh concrete and enhances the mechanical properties of hardened concrete. SBR-modified cement exhibits improved strength, toughness and crack resistance. The mechanism of action of SBR is based on the formation of a polymer matrix, which enhances the bond between cement and aggregates, resulting in improved mechanical properties ([75], Barluenga & Hernández-Olivares, 2004; [76,68]). Polyacrylamide (PAM) is another water-soluble polymer that has been used in cement and concrete. PAM is a linear polymer with excellent water-absorbing and binding properties. The addition of PAM to cement mixes improves the workability of fresh concrete and enhances the rheological properties of cement paste. PAM modifies the rheology of fresh cement paste by reducing its viscosity, leading to improved pumpability. The addition of PAM to cement mixes also improves the strength and durability of concrete [5].

Water-soluble polymers have also been used in the repair and retrofitting of damaged concrete structures. Epoxy resins are commonly used to repair concrete structures due to their excellent mechanical and adhesive properties. The addition of water-soluble polymers, such as PVA, to epoxy resins improves their mechanical properties and enhances their durability. The combination of epoxy resins and water-soluble polymers creates an interpenetrating polymer network (IPN), which enhances the mechanical properties of the repair material [1,53,59].

The motivation behind writing this paper is to explore and present a comprehensive evaluation of the roles of water-soluble polymers in cementitious materials. The use of water-soluble polymers in concrete has gained significant attention due to their potential to improve various properties and performance aspects of cementitious materials. However, there is a need to consolidate existing knowledge and provide a clear understanding of the functions, mechanisms, and influences of water-soluble polymers in cementitious systems. By conducting this review, the paper aims to fill the knowledge gap by outlining the background, objective, scope, and limitations of the research. It delves into the different types of water-soluble polymers, including natural, semi-synthetic, and synthetic, and thoroughly discusses their working mechanisms in cementitious materials. Additionally, the paper examines the influence of water-soluble polymers on microstructure, fresh properties, mechanical properties, and durability properties of cementitious materials.

The objective of this review paper is to critically examine and synthesise the existing literature on the functions of water-soluble polymers in cementitious materials. The review aims to provide an in-depth understanding of the different types of water-soluble polymers and their working mechanisms, as well as to investigate how they influence the microstructure, fresh properties, mechanical properties and durability of cementitious materials. The review also aims to identify the challenges and opportunities associated with the use of water-soluble polymers in cementitious materials and provide recommendations for future research. Overall, the review seeks to enhance our knowledge and inform best practices in the use of water-soluble polymers in cementitious materials.

The limitations of this paper are that it is based on the currently available literature and may not cover all the latest developments in the field. Additionally, the review may have a bias towards the studies that were conducted in specific regions or countries. The review is focused on the functions of water-soluble polymers in cementitious materials and does not consider the impacts of other additives or admixtures. Finally, the findings of the review are based on the laboratory experiments and may not necessarily reflect the performance of these materials in real-world conditions.

2. Types of water-soluble polymers

Water-soluble polymers can be categorized into four main groups according to their chemical composition: synthetic polymers, natural polymers, semi-synthetic polymers, and protein-based polymers. Synthetic polymers are chemically synthesized and designed to have specific properties. Natural polymers are derived from natural sources, such as plants or animals. Semi-synthetic polymers are produced by modifying natural polymers through chemical reactions. Protein-based polymers are composed of amino acids and exhibit unique properties. Understanding the different categories of water-soluble polymers is essential for comprehending their behaviour and functionality in cementitious materials.

2.1. Synthetic polymers

Synthetic water-soluble polymers have found widespread applications due to their unique properties, such as high water solubility, biocompatibility and biodegradability. These polymers can be synthesised using various methods, including radical polymerisation, anionic polymerisation and cationic polymerisation. One important class of synthetic water-soluble polymers is polyvinyl alcohol (PVA), which is commonly used in adhesives, films and coatings. PVA is a biocompatible and biodegradable polymer that can be synthesized by the hydrolysis of polyvinyl acetate. Another example of a water-soluble polymer is polyethylene glycol (PEG), which is widely used in pharmaceuticals and cosmetics due to its biocompatibility and low toxicity. Other water-soluble polymers include polyacrylamide (PAM), which is used as a flocculant in water treatment processes, and polyethylene oxide (PEO), which is used as a thickener and binder in various applications. These polymers have unique properties such as high molecular weight, high viscosity, and good solubility in water.

Synthetic water-soluble polymers have garnered significant attention in various fields due to their unique properties and wide range of applications. The synthesis and characterization of these polymers have been the focus of extensive research efforts. One approach to synthesising water-soluble polymers is through controlled radical polymerisation. Nomura et al. [49] investigated the controlled radical polymerisation of acrylamide using a water-soluble ruthenium complex as a catalyst. The study explored the polymerization kinetics, molecular weight control, and the resulting properties of the synthesised polymers. The research demonstrated the potential of controlled radical polymerisation for producing water-soluble polymers with tailored properties.

The adsorption of proteins onto materials is a crucial consideration for biocompatibility. Andrade and Gilman [2] conducted a comprehensive review on protein adsorption and its impact on material biocompatibility. Although not directly focused on synthetic water-soluble polymers, the review provided insights into the factors influencing protein adsorption and the strategies to mitigate it. This information is relevant to the design and development of water-soluble polymers for biomedical applications where protein interactions play a vital role. Inoue et al. [25] investigated the formation of polyion complex vesicles using mixes of di-block copolymers of ethylene oxide and propylene oxide and anionic surfactants. The study explored the self-assembly behaviour and properties of these vesicles, which have potential applications in drug delivery and encapsulation. While the study did not specifically focus on water-soluble polymers, it contributes to the understanding of the self-assembly phenomena and the design of functional water-soluble polymer-based systems.

2.2. Natural polymers

Natural water-soluble polymers have gained significant attention in various applications due to their unique properties. One such polymer is xanthan gum, which is extensively used in the food industry. Xanthan gum, derived from the Xanthomonas campestris bacterium, exhibits excellent thickening, stabilizing, and emulsifying properties, making it a versatile additive in food products [29,61]. It enhances the texture, mouthfeel, and shelf life of food products while providing viscosity and stability to suspensions and emulsions.

Another important natural water-soluble polymer is pectin, which is primarily extracted from fruits and vegetables. Pectin finds applications in the food and pharmaceutical industries due to its gel-forming and stabilizing properties. It is widely used as a gelling agent, thickener, and stabilizer in jams, jellies, and confectionery products [46,54]. In the pharmaceutical field, pectin is utilised for drug delivery systems, particularly in controlled release formulations [66].

Chitosan, derived from chitin, is another natural water-soluble polymer with versatile properties. It is obtained from the shells of crustaceans such as shrimp and crab. Chitosan exhibits biocompatibility, biodegradability, and antimicrobial properties, making it suitable for various applications, including drug delivery systems, wound healing, and water treatment [30,42,71]. The modification of chitosan, such as carboxymethylation, enhances its water solubility and expands its application potential [14,16,18].

Dextran, a polysaccharide composed of glucose units, is also a natural water-soluble polymer. It is widely used in the pharmaceutical and biomedical fields due to its biocompatibility and biodegradability [73]. Dextran-based hydrogels have been explored for drug delivery systems and tissue engineering applications. In summary, natural water-soluble polymers such as xanthan gum, pectin, chitosan and dextran offer a wide range of applications in various industries. Their unique properties, biocompatibility, and biodegradability make them valuable materials for food, pharmaceutical and biomedical application.

Natural polymers offer promising prospects due to their biocompatibility, biodegradability and renewable nature. They find applications in diverse fields such as medicine, food science and materials engineering. However, limitations exist, including variability in composition and properties, mechanical and thermal limitations, and processing challenges. The inherent variability hinders consistent material properties, and the inferior mechanical properties and thermal stability restrict their use in certain applications. Despite these limitations, ongoing research and development efforts aim to overcome these challenges and optimise the use of natural polymers, making them a viable and sustainable alternative to synthetic polymers in various industries.

2.3. Semi-synthetic polymers

Semi-synthetic water-soluble polymers are a class of biopolymers that have gained significant attention in recent years due to their unique properties and potential applications in various fields. They are synthesized by modifying natural polysaccharides using chemical or enzymatic methods. These modifications improve their properties such as solubility, stability and biocompatibility, making them ideal candidates for drug delivery systems.

In the article by Sithole et al. [64], the authors review the use of semi-synthetic biopolymer complexes as modified polysaccharide nano-carriers for enhancing oral drug bioavailability. They discuss the various methods of synthesizing these polymers, their physicochemical properties, and their applications in drug delivery systems. In another study by Balaga and Kulkarni [3], the authors review the use of synthetic polymers as filtration control additives for water-based drilling fluids for high-temperature applications. They discuss the importance of filtration control in drilling operations and the use of synthetic polymers such as polyacrylamides and xanthan gum as additives to improve filtration control.

In a review by Mignon et al. [44], the authors discuss the characteristics and applications of superabsorbent polymers (SAPs), which include synthetic, polysaccharide-based, semi-synthetic, and 'smart' derivatives. They discuss the various methods of synthesizing SAPs, their physicochemical properties, and their applications in areas such as agriculture, hygiene products, and drug delivery systems. Overall, semi-synthetic water-soluble polymers have numerous potential applications in various fields, including drug delivery systems, filtration control in drilling operations, and superabsorbent materials. The use of these polymers can improve properties such as solubility, stability, and biocompatibility, making them ideal candidates for a wide range of applications. The molecular structures of these polymers are presented in Figs. 1(d)-1(f) [80].

On the positive side, semi-synthetic polymers inherit the beneficial properties of natural polymers, such as biocompatibility and biodegradability, while offering enhanced control over their composition and properties through chemical modifications. This versatility opens up a wide range of applications in fields like biomedicine, drug delivery, and tissue engineering. Additionally, blending natural and synthetic polymers can lead to improved mechanical strength, thermal stability, and processing characteristics. However, there are certain limitations to consider. The modification process introduces complexity and can result in inconsistent material properties. Achieving optimal modification levels and maintaining batch-to-batch consistency can be challenging. Furthermore, the introduction of synthetic components may compromise the eco-friendly nature of the material and raise concerns regarding long-term environmental impact.

2.4. Protein-based polymers

Protein-based water-soluble polymers have gained significant attention in various fields due to their unique properties and versatile applications. These polymers, derived from proteins, exhibit excellent water solubility, biocompatibility and biodegradability. They can be tailored to possess specific functionalities and molecular structures, making them suitable for drug delivery systems, tissue engineering and biomaterial applications. Protein-based water-soluble polymers offer advantages such as controlled release of bioactive compounds, enhanced stability, and improved biocompatibility. Their ability to interact with proteins and other biomolecules makes them promising candidates for targeted delivery and regenerative medicine. Ongoing research in this area continues to explore novel synthesis methods and functional modifications to optimise their performance and expand their applications.

The study by Matsudo et al. [43] investigates the complex formation between proteins and different water-soluble synthetic polymers. While the study provides valuable insights into protein-polymer interactions, there are certain limitations to consider. Firstly, the research primarily focuses on understanding the binding affinity and stability of protein-polymer complexes, without delving into the specific applications or functional properties of these complexes. Therefore, the practical implications of the findings remain unclear. Additionally, the study lacks a comprehensive analysis of the structure and conformational changes induced by the protein-polymer interactions, limiting our understanding of the underlying mechanisms.

The review article by Das et al. [15] offers a broader perspective on the preparation, physicochemical characterization, and bioengineering applications of biopolymers. Although the reference does not explicitly focus on protein-based water-soluble polymers, it provides a comprehensive overview of biopolymers in general. However, the review lacks a critical analysis of the recent advances and fails to highlight potential challenges or limitations in the field. Furthermore, the review appears to cover a wide range of topics related to biopolymers, potentially sacrificing depth and specificity regarding protein-based water-soluble polymers.

Protein-based polymers offer excellent biological interactions and can mimic the extracellular matrix, making them suitable for tissue engineering, drug delivery and regenerative medicine applications. Their unique structures also allow for modification and functionalization, enabling precise control over their properties. Additionally, protein-based polymers possess inherent bioactivity, promoting cell adhesion, proliferation, and differentiation. However, there are challenges associated with protein-based polymers. The variability in source materials, extraction methods and purification processes can result in inconsistent material properties. Moreover, their susceptibility to enzymatic degradation and limited mechanical strength pose limitations in certain applications. Achieving sufficient stability, controlling degradation rates and addressing immunogenicity concerns are ongoing research areas.

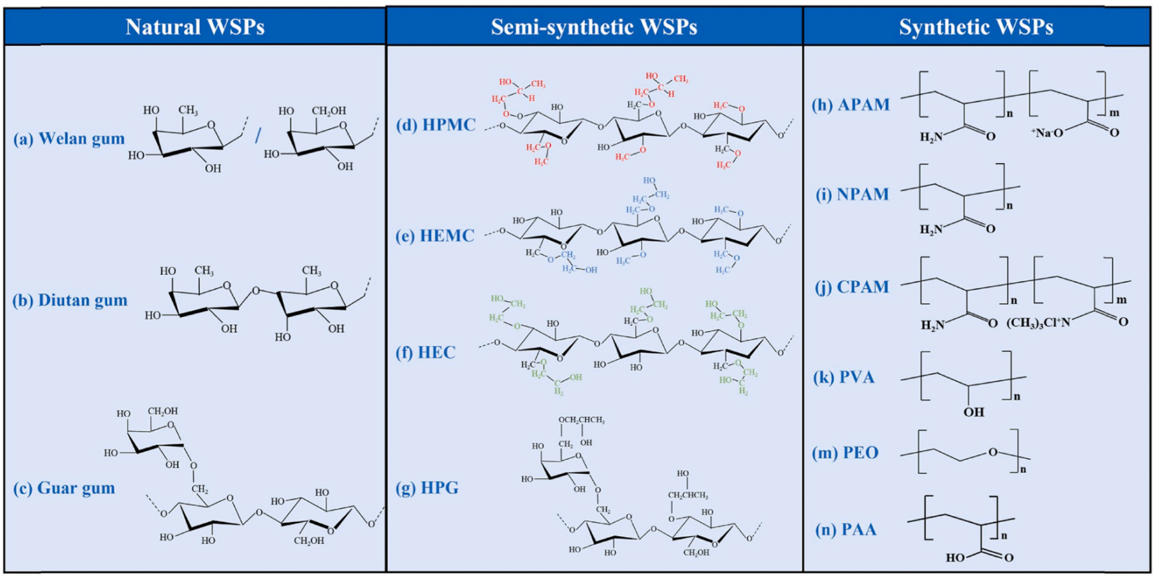

Fig. 1. Molecular structures of commonly used Water-soluble polymers [80].

3. Working mechanisms of water-soluble polymers

Water-soluble polymers have various working mechanisms in concrete. One mechanism is entanglement and association, where the polymers form a network that improves the cohesiveness and stability of the concrete mix. Another mechanism is adsorption and complexation, where the polymers bond with the cement particles and improve the workability and strength of the concrete. Bridging is also a mechanism where polymers form a physical bridge between cement particles, reducing the chances of particle aggregation and improving the flow properties of the concrete. These working mechanisms are crucial in improving the performance of cementitious materials and achieving the desired properties in concrete mixes.

3.1. Entanglement and association

To better understand the effectiveness of water-soluble polymers in retaining water, numerous studies have investigated their entanglement and association with the cement matrix. Brumaud et al. [10] found that higher molecular weight and degree of substitution in cellulose ethers lead to better water retention capacity due to their increased entanglement and association with the cement matrix. Additionally, they found that the type of cellulose ether used can affect water retention capacity, with hydroxypropyl methylcellulose (HPMC) showing the highest retention capacity. Bülichen et al. [11] examined the working mechanism of methyl hydroxyethyl cellulose (MHEC) as a water retention agent and found that MHEC adsorbs on the surface of cement particles to create a

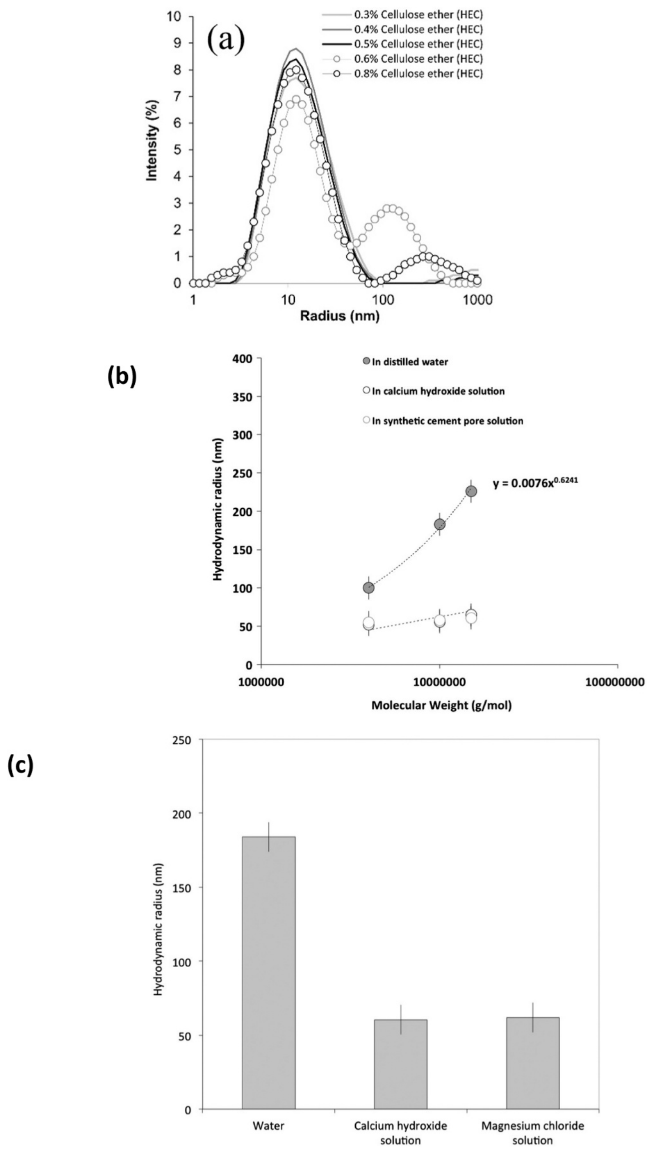

Fig. 2. Hydrodynamic sizes for HEC and PAM in cement pore solution [5].

physical barrier that prevents water from leaving the cement paste. The water retention capacity of MHEC is influenced by its degree of substitution, which affects its solubility and ability to interact with the cement particles.

Marliere et al. [41] investigated the water retention capacity of cellulose ethers in porous media and found that the polymers form a gel-like network that fills the pores and prevents water from escaping. The degree of substitution and molecular weight of the cellulose ether affect the polymer's water retention capacity and gel-forming ability. Bülichen and Plank (2012) studied the use of carboxymethyl hydroxyethyl cellulose (CMHEC) as a fluid loss control additive in oil well cement and found that CMHEC forms a highly entangled network in the cement paste that acts as a filter cake, preventing the loss of fluid to the formation. The researchers also observed that the degree of substitution and concentration of CMHEC affect its fluid loss control ability.

Poinot et al. [56] evaluated the effectiveness of hydroxypropylguars (HPG) as water retention agents in cement-based mortars and found that HPG with longer and more branched chains had higher water retention capacity due to increased coil-overlapping, which leads to better entanglement and association with the cement matrix. Bessaies-Bey et al. [5] examined the effect of polyacrylamide on the rheology of fresh cement pastes and found that it increases the viscosity and yield stress of the cement paste due to its association with the cement particles. They also monitored the effects of PAMs with different molecular weights on fresh cement pastes. As shown in Fig. 2b and c, the hydrodynamic sizes of water-soluble polymers increased with rising molecular weight. Besides, metal ions such as Mg^{2+} and Ca^{2+} reduced this value.

These studies suggest that the water retention capacity of water-soluble polymers in cement-based materials depends on their entanglement and association with the cement matrix. Higher molecular weight and degree of substitution, longer and more branched chains, and higher concentration of the polymer lead to better water retention capacity due to increased entanglement and association. The type of polymer used and its degree of substitution also affect its solubility and ability to interact with the cement particles. These findings have implications for developing more effective water retention agents for use in cement-based materials.

The entanglement and association mechanisms of water-soluble polymers provide valuable insights into their behaviour and applications. Entanglement enhances viscosity and mechanical strength, while association mechanisms enable supramolecular structures and complexation. These properties find applications in diverse fields such as materials science, drug delivery and nanotechnology. However, challenges exist in controlling and predicting these mechanisms due to factors like polymer concentration, molecular weight, and solution conditions. The reversible nature of these interactions can also impact stability and functionality. Further research is necessary to advance our understanding, optimise control and expand the applications of water-soluble polymers in a range of industries.

3.2. Adsorption and complexation

One of the main mechanisms involved in the interaction between water-soluble polymers and cement is adsorption. The adsorption of non-ionic cellulose ethers on cement particles has been revisited by Hurnaus and Plank [23], who found that the adsorption behaviour is influenced by the polymer concentration, molecular weight, and substitution degree. The authors suggest that a model based on the Langmuir adsorption isotherm could be used to describe the adsorption process. Similarly, Sugama et al. [67] investigated the interactions at water-soluble polymer/$Ca(OH)_2$ or gibbsite interfaces and concluded that adsorption is the primary mechanism for polymer-cement interaction. In addition to adsorption, complexation is another mechanism involved in the interaction between water-soluble polymers and cement. Mohamed et al. [45] used molecular modelling to study the interactions between chemical admixtures and cement, and found that the complexation between polycarboxylate superplasticisers and calcium ions plays a critical role

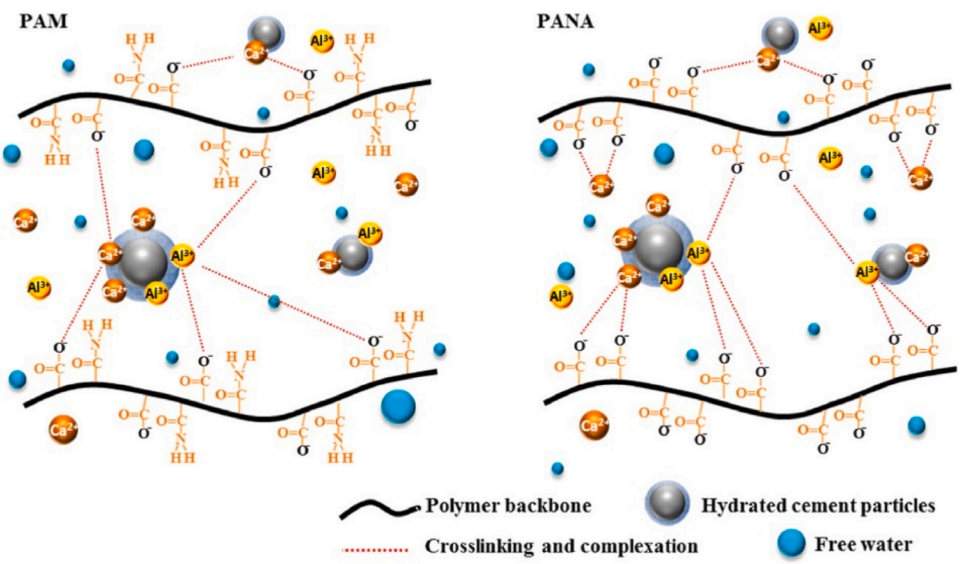

Fig. 3. Complexation of PAM and PANA by metal ions [21].

in controlling the dispersion of cement particles.

Several studies have investigated the effect of different types of water-soluble polymers on the properties of cement-based materials. For example, Bessaies-Bey et al. [6] studied the use of viscosity modifying agents as key components for advanced cement-based materials with adapted rheology. They found that the rheological behaviour of the materials can be tailored by selecting the appropriate polymer type, molecular weight and concentration. Similarly, Gu et al. [21] compared the effect of polyacrylamide (PAM) and polyacrylonitrile (PANA) on the properties of fresh cement paste and concluded that PAM is more effective in improving the fluidity and stability of the paste as shown in Fig. 3.

Other studies investigated the use of water-soluble polymers in combination with other admixtures to enhance the properties of cement-based materials. For example, Xie et al. [79] studied the effect of polyvinyl alcohol powder on the bonding mechanism of a new magnesium phosphate cement mortar and found that the addition of the powder improved the bonding strength and reduced the water absorption of the mortar.

The adsorption and complexation mechanisms of water-soluble polymers play a crucial role in various applications, including wastewater treatment, drug delivery, and surface coating. This critical analysis aims to assess the advantages and limitations of these mechanisms. Adsorption of water-soluble polymers onto surfaces occurs through a combination of electrostatic, hydrophobic, and hydrogen bonding interactions. This process can improve colloidal stability, enhance flocculation, and control surface properties. Similarly, complexation with small molecules or metal ions offers opportunities for controlled release, drug encapsulation, and metal ion removal. However, there are limitations to consider. The adsorption and complexation behaviour of water-soluble polymers can be influenced by factors like polymer structure, molecular weight, and solution conditions, making optimisation challenging. Furthermore, the reversibility of these interactions and their long-term stability can be a concern in practical applications.

3.3. Bridging

The bridging mechanism involves the formation of a network structure that fills the voids in the cement matrix and prevents water from escaping, while the adsorption mechanism involves the physical adsorption of the polymer onto the surface of cement particles, creating a barrier that impedes water flow. The research studies by Bessaies-Bey et al. [5] and Roussel et al. [58] provide insights into the bridging mechanisms of water-soluble polymers in cement-based materials. Bessaies-Bey et al. [5] investigated the effect of polyacrylamide on the rheology of fresh cement pastes and found that the polymer increases the viscosity and yield stress of the cement paste due to its association with the cement particles. They observed that the molecular weight and concentration of polyacrylamide affect its rheological properties. Polyacrylamide functions through a bridging mechanism, forming a network structure that fills the voids in the cement matrix and prevents water from escaping. Roussel et al. [58] investigated the origins of thixotropy of fresh cement pastes and found that the addition of water-soluble polymers such as hydroxyethyl cellulose (HEC) and xanthan gum increases the thixotropy of the paste, leading to improved stability and workability. They observed that the polymers function through a bridging mechanism, forming a gel-like structure that fills the voids in the cement matrix and prevents water from escaping. The researchers also found that the degree of substitution and molecular weight of the polymer affect its bridging ability.

Fig. 4 shows the evolution of cement particle interactions during the dormant period [58]. In Fig. 4(a) At the end of the mixing phase, cement particles are dispersed. (b) Within a couple of seconds after mixing, colloidal attractive forces cause cement particles to flocculate, forming an interconnected network. Darker particles represent a percolation path, where nucleation of calcium-silicate-hydrate (CSH) immediately initiates at the pseudo contact points between particles. This leads to the transformation of soft colloidal interactions into rigid interactions. (c) Cement particles within the percolation path become linked by CSH bridges, forming a rigid and continuous network throughout the material. (d) The elastic modulus of the mix continues to increase as the size of CSH bridges expands. Due to colloidal attractive forces, cement particles flocculate within seconds, creating a network capable of withstanding stress and exhibiting an elastic modulus (Fig. 4(b)). Simultaneously, nucleation of CSH occurs at the pseudo contact points between particles within the network during the dormant period. This local nucleation transforms the soft colloidal interactions into CSH bridges. As a result, the elastic modulus increases at the macroscopic scale. After several tens of seconds, a percolation path forms, consisting of particles solely interacting through CSH bridges (Fig. 4(c)). The macroscopic elastic modulus continues to rise due to the growth in size or number of CSH bridges between the percolated cement particles (Fig. 4(d)).

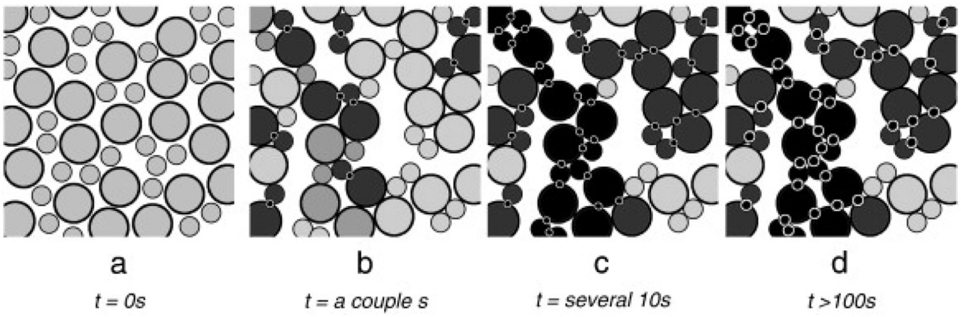

Fig. 4. Network(s) of interacting cement particles in the dormant period [58].

These studies provide evidence for the bridging mechanisms of water-soluble polymers in cement-based materials. The polymers form a network structure that fills the voids in the cement matrix, preventing water from escaping and leading to improved properties such as stability and workability. The molecular weight, degree of substitution, and concentration of the polymer all play a role in its bridging ability, highlighting the importance of careful selection and optimisation of water-soluble polymers for use in cement-based materials.

The bridging mechanisms of water-soluble polymers play a crucial role in various applications, particularly in the field of flocculation and stabilisation. Bridging occurs when water-soluble polymers adsorb onto particle surfaces and form physical links between them, leading to the formation of aggregates or flocs. This process enhances the flocculation and sedimentation of suspended particles, making it beneficial for wastewater treatment and clarification processes. Moreover, the bridging mechanisms can provide colloidal stability by preventing particle aggregation and maintaining dispersion. However, there are limitations to consider. The effectiveness of bridging mechanisms is influenced by factors such as polymer concentration, molecular weight, and the nature of the particle surface. Controlling and optimising these factors can be challenging and excessive bridging can lead to the formation of rigid and compact flocs, limiting the efficiency of separation processes.

4. Influence of water-soluble polymers on the fresh properties of cementitious materials

Water-soluble polymers have a significant impact on the fresh properties of cementitious materials. These polymers can enhance the water retention, thickening, and air entraining properties of cementitious materials. Water retention is crucial for maintaining adequate hydration levels in the fresh cementitious materials, while thickening helps to prevent segregation and bleeding during mixing and placing. Air entraining properties are also essential for durability and freeze-thaw resistance of the concrete. Additionally, water-soluble polymers can also improve the workability and reduce the rate of setting, allowing for more extended workability time during placement.

4.1. Water retention

The water retention effect of water-soluble polymers in concrete has been a topic of interest in various research studies. Patural et al. [55] employed nuclear magnetic relaxation dispersion investigations to explore the water retention mechanism of cellulose ethers in mortars. Their study aimed to understand how cellulose ethers interact with water and influence the water retention capacity of mortar mixes. The findings shed light on the ability of cellulose ethers to retain water in concrete, which can contribute to improved

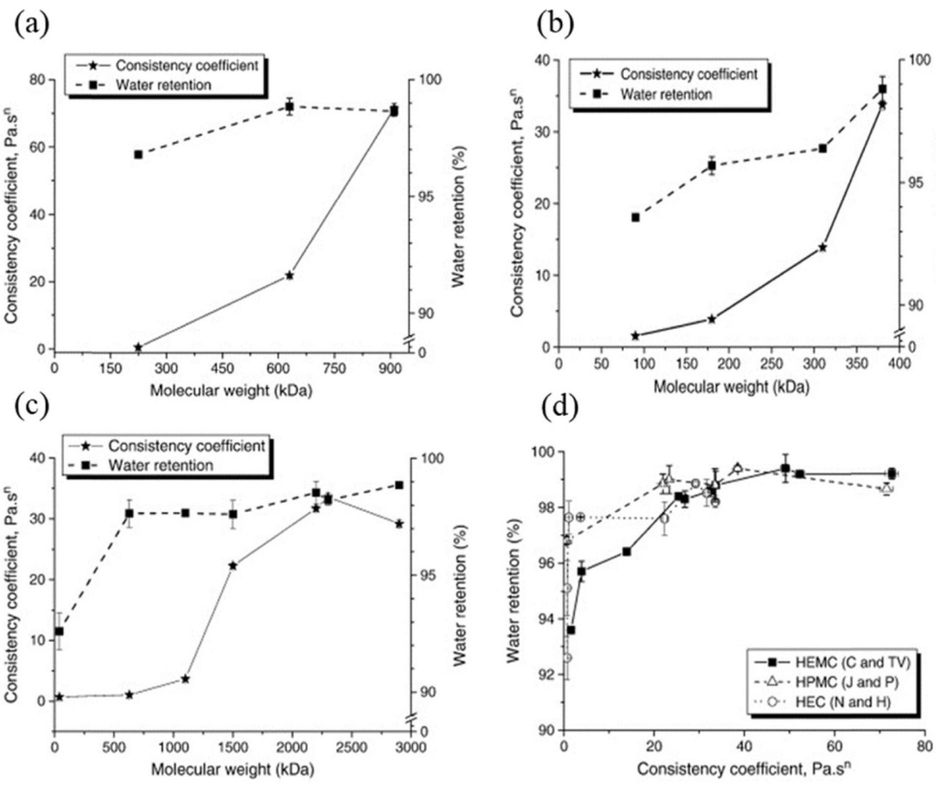

Fig. 5. Consistency coefficient and water retention rate of cementitious materials modified by (a) HEMC, (b) HPMC, (c) HEC, (d) Relationship between water retention and consistency coefficient.

workability, hydration, and overall performance. The results are shown in Fig. 5. Wan et al. [74] specifically focused on the water retention mechanism of cellulose ethers in calcium sulfoaluminate cement-based materials. By investigating the interaction between cellulose ethers and the specific cement matrix, the authors aimed to elucidate the role of cellulose ethers in enhancing the water retention capacity of calcium sulfoaluminate cement-based materials. Understanding this mechanism is crucial for optimizing the formulation of cementitious materials and improving their durability and mechanical properties.

Cappellari et al. [13] explored the influence of organic thickening admixtures on the rheological properties of mortars and their relationship with water retention. Their study aimed to establish the correlation between the rheological behaviour of mortar mixes and their water retention characteristics. By examining the impact of organic thickening admixtures on the flow properties and water retention capacity of mortars, the researchers provided insights into the role of these additives in improving the workability and stability of concrete mixes. Govin et al. [20] investigated the modification of water retention and rheological properties of fresh state cement-based mortars using guar gum derivatives. Their research focused on evaluating the potential of guar gum derivatives as additives for enhancing the water retention capacity and rheological properties of cement-based materials. By modifying the formulation of mortars, the authors aimed to optimise the workability and performance of fresh concrete mixes. Kim et al. [35] studied the structure and properties of poly(vinyl alcohol)-modified mortar and concrete. Their research aimed to understand the effects of incorporating poly(vinyl alcohol) (PVA) as a water-soluble polymer on the structure and properties of hardened mortar and concrete.

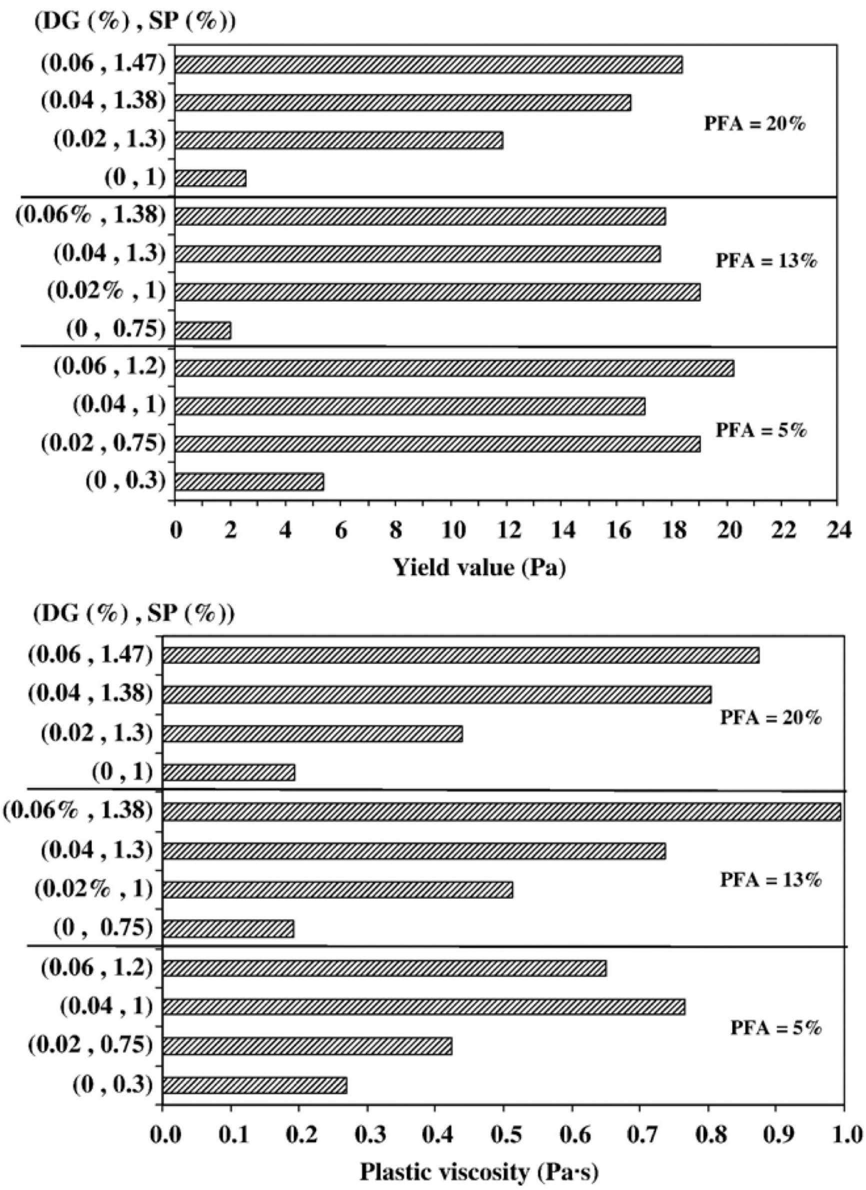

Fig. 6. Variations of yield value and plastic viscosity with dosages of PFA, SP and diutan gum [65].

By examining the mechanical properties, durability and microstructure of PVA-modified cementitious materials, the study provided insights into the potential benefits and limitations of using PVA as a water-retaining additive in concrete.

While these studies collectively contribute to our understanding of the water retention effect of water-soluble polymers in concrete, further research is necessary. Future investigations should focus on the long-term effects, durability and practical applications of these water-soluble polymers in real-world concrete construction scenarios. Additionally, optimising the dosage, compatibility, and interactions between water-soluble polymers and cementitious materials is crucial for maximising the benefits of these additives in concrete production.

Water-soluble polymers, when added to cementitious materials, can enhance water retention by forming a network that reduces water evaporation and enhances hydration. This property is particularly beneficial in hot and dry climates or during extended curing periods. By maintaining adequate water content, these polymers can improve workability, reduce cracking, and enhance overall durability of concrete or mortar. However, there are limitations to consider. The effectiveness of water-soluble polymers depends on various factors, including polymer type, dosage, and compatibility with cementitious materials. Improper selection or dosage can lead to undesirable effects such as decreased strength, increased air content, or compromised setting time. Additionally, the cost of these polymers and their potential environmental impact should be evaluated.

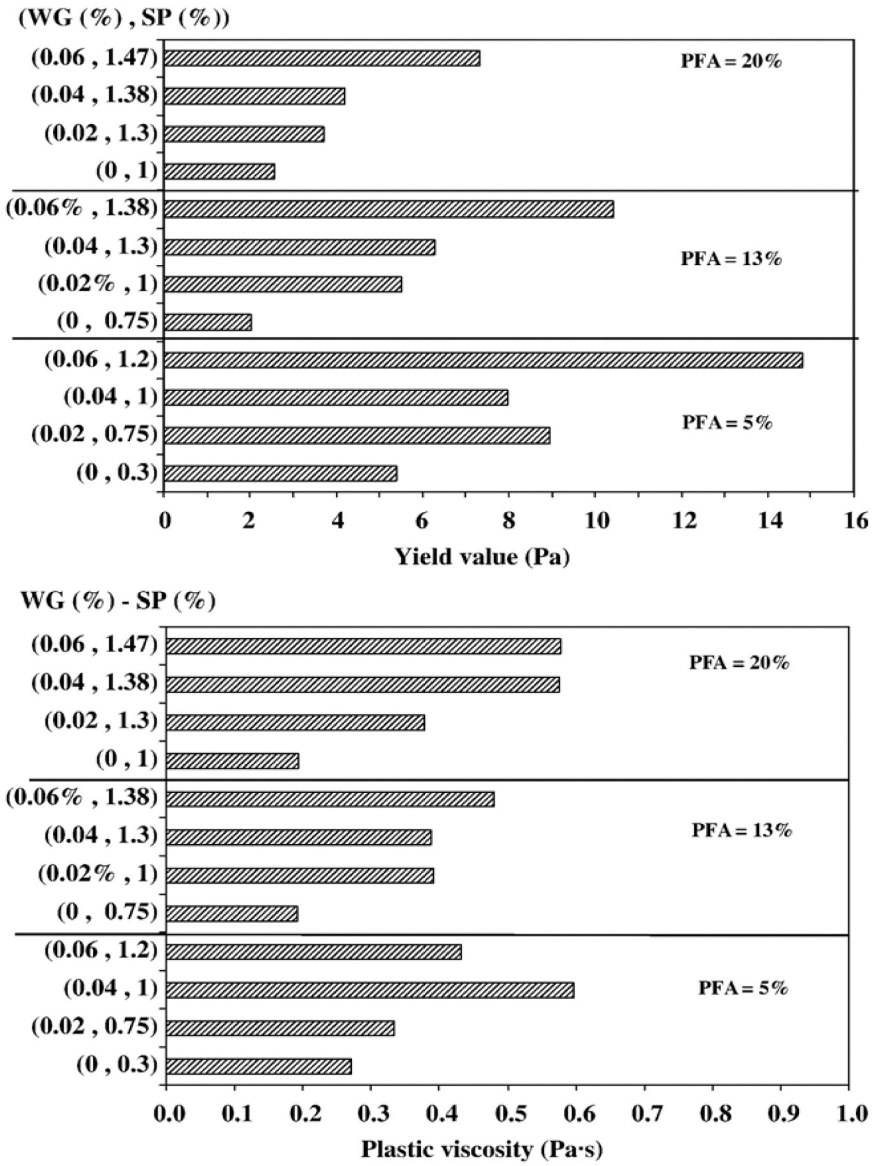

Fig. 7. Variations of yield value and plastic viscosity with dosages of PFA, SP and welan gum [65].

4.2. Thickening

Water-soluble polymers are widely used in concrete as thickening agents, and their effectiveness in improving concrete performance has been the subject of numerous studies. Several studies have been conducted to investigate the effects of hydroxypropylmethyl cellulose ether (HPMC) on the rheology of cement paste plasticised by polycarboxylate superplasticiser (PCE). The study by Govin et al. [19] investigated the combination of superplasticisers with hydroxypropyl guar and found that the addition of HPMC led to an increase in workability and improved mechanical properties of the cement-based mortars. Similarly, Brumaud et al. [9] reported that HPMC improved the yield stress of cement pastes by inducing a thicker microstructure.

Other studies have investigated the rheological properties of other types of water-soluble polymers. Xu et al. [81] studied the rheological properties and thickening mechanism of aqueous diutan gum solutions and found that the viscosity of the solutions increased with increasing temperature and ionic strength. Similarly, the study by Sonebi [65] investigated the rheological properties of grouts with viscosity modifying agents such as diutan gum and welan gum and found that these agents improved the stability and workability of the grouts. According to the results presented in Fig. 6 and Fig. 7 [65], the addition of 5%, 13%, and 20% PFA resulted in a slight increase in the plastic viscosity when compared to grout mixes made solely with 100% C, for any given combination of VMA-SP. For instance, when 5% PFA was added to a grout mix containing 0.04% diutan gum and 1% SP, the plastic viscosity increased from 0.60 Pa·s to 0.77 Pa·s. Similarly, the incorporation of welan gum and 5% PFA resulted in an increase of plastic viscosity from 0.45 Pa·s to 0.60 Pa·s.

Polyvinyl alcohol (PVA) is another water-soluble polymer that has been widely investigated for its use in concrete. Thong et al. [70] reviewed the engineering properties and microstructure behaviour of PVA in cement-based composite materials and reported that PVA enhanced the mechanical properties and durability of concrete. Kim et al. [35] investigated the structure and properties of PVA-modified mortar and concrete and found that PVA improved the compressive strength and durability of concrete. Some studies have investigated the use of water-soluble polymers in 3D printing of cementitious materials. For example, the study by Yuan et al. [87] compared the early properties of cement modified with different ionic polyacrylamides and found that the addition of polyacrylamide improved the workability and interlayer interface properties of 3D printed cementitious materials. Similarly, the study by Xu et al. [82] correlated the interlayer properties and rheological behaviours of 3D printed concrete with various printing time intervals.

Water-soluble polymers, such as hydroxyethyl cellulose (HEC) and methyl cellulose (MC), can significantly enhance the viscosity and thixotropic behaviour of cementitious materials. They form a three-dimensional network that traps water and slows down its movement, resulting in improved workability, reduced sagging, and enhanced verticality in applications like tile adhesives or renderings. The influence of water-soluble polymers on thickening depends on various factors, including polymer type, dosage, and compatibility with cementitious materials. Excessive dosage can lead to excessive thickening, compromising the flowability and workability of the material. Moreover, the cost of these polymers and their impact on setting time should be carefully evaluated.

In summary, water-soluble polymers have been found to improve the rheological properties and performance of cement-based materials. Different types of polymers have different effects on concrete, and their effectiveness depends on various factors such as temperature, ionic strength, and printing time intervals. Further research is needed to optimise the use of water-soluble polymers in concrete and to develop new types of polymers that can further enhance the properties of cement-based materials.

4.3. Retardation

Water-soluble polymers, such as polycarboxylates or lignosulfonates, can effectively delay the setting and hardening of cementitious materials. By adsorbing onto cement particles, these polymers create a barrier that slows down the diffusion of water and ions, thereby retarding the hydration process. This property is particularly valuable in hot weather or when extended workability time is required. However, the effectiveness of water-soluble polymers as retarders depends on factors such as polymer type, dosage, and compatibility with specific cement compositions. Improper selection or excessive dosage can lead to inadequate retardation or undesired effects such as reduced early strength or increased setting time. Furthermore, the cost and potential impact on long-term durability should be evaluated.

Yao et al. [84] investigated the retardation and bridging effects of anionic polyacrylamide (PAM) on cement paste and its relationship with early properties. The study revealed that the addition of PAM delayed the setting time of cement paste and improved its workability. However, the retardation effect was more significant when the PAM dosage was increased, leading to a decrease in the compressive strength of the hardened paste. The authors attributed the retardation effect to the adsorption of PAM molecules on the cement particles, which inhibited their hydration and resulted in the formation of a PAM-cement bridging network that restricted the movement of water molecules.

Pourchez et al. [57] investigated the changes in C_3S hydration in the presence of cellulose ethers. The study showed that the addition of cellulose ethers delayed the initial rate of C_3S hydration but had little effect on the overall degree of hydration. The authors suggested that cellulose ethers acted as a physical barrier, hindering the diffusion of water and ions to the surface of the C_3S particles, thereby delaying their reaction. Yuan et al. [87] conducted a comparative study on the hydration, mechanical properties, and microstructural characteristics of cement pastes with different ionic polyacrylamides (IPAMs). The study showed that the addition of IPAMs delayed the setting time of cement pastes and improved their workability. However, the retardation effect was more significant when the IPAM dosage was increased, leading to a decrease in the compressive strength of the hardened paste. The authors suggested that the retardation effect was due to the adsorption of IPAM molecules on the cement particles, which hindered their hydration and resulted in the formation of an IPAM-cement bridging network that restricted the movement of water molecules.

Mohamed et al. [45] employed molecular modelling to investigate the behaviour of chemical admixtures in cement hydration. The study revealed that the interaction between chemical admixtures and cement was complex and depended on several factors, such as the chemical structure of the admixture and its concentration. The authors suggested that molecular modelling could provide valuable insights into the mechanism of action of chemical admixtures in cement hydration. Wang et al. [77] studied the properties and microstructure of cement mortars containing hydroxyethyl methyl cellulose (HEMC) after controlling the air content. The study showed that the addition of HEMC improved the workability of the mortar but had little effect on its compressive strength. The authors attributed the improvement in workability to the formation of a HEMC-water network that reduced the viscosity of the mortar. According to the findings of Wang et al. [77], as the concentration of HEMC increased from 0 to 1 wt% (M0 to M10), the heat flow and cumulative heat release of cement-based materials exhibited a decrease, as depicted in Fig. 7. [89,91] investigated the early hydration of calcium sulfoaluminate cement in the presence of HEMC. The study revealed that the addition of HEMC delayed the initial rate of cement hydration but had little effect on the overall degree of hydration. The authors suggested that HEMC acted as a physical barrier, hindering the diffusion of water and ions to the surface of the cement particles, thereby delaying their reaction. Betioli et al. [7] studied the effect of HEMC on the consolidation of cement pastes using isothermal calorimetry and oscillatory rheometry. The study showed that the addition of HEMC increased the yield stress and storage modulus of the paste, indicating an improvement in its strength.

The reviewed studies provide valuable insights into the effects of various additives on cement hydration and properties. The findings consistently demonstrate that the addition of polymers, such as polyacrylamide and cellulose ethers, can delay the setting time and improve workability of cement pastes. However, there is a trade-off as higher dosages lead to a more significant retardation effect and decreased compressive strength. Molecular modelling approaches, as employed by Mohamed et al. [45], offer promising avenues for understanding the complex interactions between chemical admixtures and cement hydration. Overall, these studies contribute to our understanding of cement chemistry, but further research is needed to optimise the dosage and application of additives to achieve desirable mechanical properties without compromising strength.

4.4. Air entraining

The influence of water-soluble polymers on various properties of cementitious materials is a topic of significant interest in the construction industry. While water-soluble polymers offer valuable benefits such as improved water retention, thickening, retardation, and air entrainment, careful consideration is necessary to optimise their use. Factors like polymer type, dosage, compatibility, and long-term effects on durability must be thoroughly evaluated. Furthermore, striking a balance between achieving desired properties and avoiding adverse effects is crucial. Ongoing research efforts are needed to enhance understanding, develop more efficient and sustainable polymers, and expand the application potential of water-soluble polymers in cementitious materials.

The use of water-soluble polymers as air-entraining admixtures in concrete has gained significant attention in recent years. The review by Shah et al. [60] provides a comprehensive overview of air entrainment in fresh and hardened concrete. The study emphasizes the importance of air entrainment in improving concrete durability and frost resistance. It discusses various methods for air entrainment and their effects on concrete properties. However, the review lacks specific focus on the effects of water-soluble polymers.

Kim and Robertson [33] investigated the prevention of air void formation in polymer-modified cement mortar by pre-wetting. The study suggests that pre-wetting the polymer particles reduces air void formation, thereby improving the performance of polymer-modified mortar. Although the study focuses on polymer-modified mortar, it provides insights into the mechanisms of air void formation and potential strategies for controlling it.

Zhao et al. (2021) explored the use of viscosity modifying admixtures (VMAs) to reduce diffusion in cement-based materials. The study examines the effect of molecular mass on the performance of VMAs. While it does not specifically address air entrainment, it offers valuable insights into the modification of cement-based materials using water-soluble polymers. Hisseine et al. [22] investigated the feasibility of using cellulose filaments as a viscosity modifying agent in self-consolidating concrete. Although the study primarily focuses on self-consolidating concrete, it sheds light on the potential of water-soluble polymers as viscosity modifiers and their impact on concrete properties. The studies by Jenni et al. [27,28] discuss the influence of polymers on the microstructure, adhesive strength, and physical properties of polymer-modified mortars. While these studies do not directly address air entrainment, they provide valuable insights into the effects of polymers on concrete performance and durability.

Tunstall et al. [72] conducted a comprehensive investigation on air-entraining admixtures, including their mechanisms, evaluations and interactions. While the study does not specifically focus on water-soluble polymers, it offers a broader understanding of air entrainment in concrete and the potential role of admixtures. Overall, the reviewed literature provides limited direct evidence on the air-entraining effects of water-soluble polymers in concrete. Further research specifically targeting the air entrainment properties and mechanisms of water-soluble polymers is needed to fully understand their potential in enhancing the performance and durability of air-entrained concrete.

5. Influence of water-soluble polymers on the mechanical properties of cementitious materials

Water-soluble polymers can enhance the mechanical properties of cementitious materials by improving the adhesion between the cement paste and aggregates, increasing the workability of fresh concrete, and reducing the porosity and cracking of hardened concrete. The addition of water-soluble polymers has been found to increase the compressive, tensile, flexural, and bond strength of cementitious materials, which makes them suitable for a wide range of applications. The type, dosage, and mixing method of water-soluble polymers can affect the mechanical properties of cementitious materials, and further research is needed to optimise the performance of these materials.

5.1. Compressive strength

Water-soluble polymers can impact the compressive strength of cementitious materials positively or negatively, depending on various factors like polymer type, dosage, and interaction with cement hydration. Proper selection and dosage of polymers can enhance compressive strength by improving the workability, reducing water content, and controlling the pore structure. However, excessive dosage or incompatibility with cement can result in reduced strength or compromised hydration reactions. Understanding the interactions between water-soluble polymers and cementitious systems is crucial to optimise their use and achieve the desired compressive strength.

The study by [89,91] investigated the effect of welan gum on the hydration and hardening of Portland cement. Welan gum is a water-soluble polysaccharide that was added to cement to enhance its workability and strength. The results showed that the addition of welan gum increased the compressive strength of cement pastes and reduced their porosity.

In a recent study, Zhao et al. (2021) examined the effect of viscosity modifying admixtures (VMAs) on reducing diffusion in cement-based materials. The study showed that the molecular mass of the VMA significantly affected the compressive strength of concrete. The compressive strength of concrete decreased with an increase in the molecular mass of the VMA. Yuan et al. [87] conducted a comparative study on the effect of different ionic polyacrylamides on the hydration, mechanical properties, and microstructural characteristics of cement pastes. The study found that the compressive strength of cement pastes increased with an increase in the concentration of ionic polyacrylamide.

Wang et al. [77] investigated the evolution of properties and microstructure of cement mortars containing hydroxyethyl methyl cellulose (HEMC) after controlling the air content. The study found that the compressive strength of cement mortars decreased with an increase in the content of HEMC. However, the addition of HEMC improved the workability of the mortar.

Li et al. [38] studied the influence of cellulose ethers structure on the mechanical strength of calcium sulphoaluminate cement mortar. The study found that the compressive strength of mortar decreased with an increase in the substitution rate of cellulose ether. The substitution rate is the proportion of cement replaced by the admixture. Knapen and Van Gemert [36] investigated the effect of underwater storage on bridge formation by water-soluble polymers in cement mortars. The study found that the compressive strength of cement mortars increased with the addition of water-soluble polymers, but this effect was reduced when the mortars were stored underwater.

Pourchez et al. [57] examined the influence of cellulose ethers on water transport and porous structure of cement-based materials. The study found that the addition of cellulose ethers reduced the permeability of cement-based materials, but this effect varied depending on the type of cellulose ether used. Silva et al. [62] investigated the pore size distribution of hydrated cement pastes modified with polymers. The study found that the addition of polymers increased the proportion of small pores in the cement pastes. Small pores are considered desirable as they improve the compressive strength of the concrete.

The influence of water-soluble polymers on the compressive strength of concrete is contingent upon several factors, including the type of polymer, its concentration, and the molecular mass. The effect observed in compressive strength can vary, as reported by different studies. Some investigations have indicated an enhancement in compressive strength with the incorporation of water-soluble polymers, while others have observed a decrease. The varying outcomes can be attributed to the specific properties and characteristics of the water-soluble polymer being used, as well as its intended purpose and dosage in the concrete mix. Different polymers exhibit distinct interactions with cementitious materials, affecting the hydration process, pore structure, and interfacial bonding. Consequently, the resulting impact on the compressive strength of the concrete can vary. Therefore, it is imperative to exercise caution and careful consideration when selecting and utilizing water-soluble polymers as admixtures in concrete. The properties of the polymer, such as its chemical composition, solubility, and compatibility with the cement matrix, must align with the desired objectives of the concrete application. Additionally, the appropriate concentration and dosage need to be determined based on comprehensive testing and evaluation. By taking into account the specific properties and intended use of water-soluble polymers, engineers and practitioners can make informed decisions regarding their incorporation as concrete admixtures, aiming to optimise the overall performance and desired compressive strength of the concrete.

5.2. Flexural, tensile and bond strength

Water-soluble polymers can have a positive impact on flexural, tensile, and bond strength by improving the overall cohesiveness and adhesion of cementitious materials. These polymers can enhance the bonding between the cement matrix and aggregates, resulting in increased bond strength. Additionally, they can improve the flexural and tensile properties by enhancing the cohesion and ductility of the material. However, the effectiveness of water-soluble polymers on these properties depends on factors such as polymer type, dosage, and compatibility with cementitious systems. Excessive dosage or improper selection can lead to reduced strength or compromised properties. It is crucial to carefully select and optimise the use of water-soluble polymers to achieve the desired flexural, tensile, and bond strength in cementitious materials.

The effects of water-soluble polymers on the flexural, tensile, and bond strength of concrete have been investigated in several studies. Kim and Robertson [34] studied the effects of polyvinyl alcohol (PVA) on aggregate-paste bond strength and the interfacial transition zone. The study revealed that PVA improved the bond strength between aggregates and paste, leading to enhanced flexural and tensile strength of concrete. The improved interfacial transition zone contributed to better stress transfer between the aggregates and the paste matrix.

Negro et al. [47] examined the influence of flocculant molecular weight and anionic charge on the manufacture of fibre cement composites. Although this study did not directly focus on the flexural, tensile, or bond strength, it highlighted the importance of molecular weight and charge characteristics in the overall behaviour of cement composites. These factors can affect the dispersion of fibres and their bonding with the matrix, which can subsequently influence the flexural and bond strength properties. Thong et al. [70] provided a comprehensive review of the application of polyvinyl alcohol (PVA) in cement-based composite materials. The review indicated that PVA can enhance the flexural and tensile strength of concrete due to its ability to improve the microstructure and reduce the formation of cracks. PVA also exhibited good bonding properties, leading to improved bond strength between the substrate and the applied material.

Wang et al. [77] investigated the properties and microstructure of cement mortars containing hydroxyethyl methyl cellulose (HEMC) after controlling the air content. The study reported that the addition of HEMC reduced the flexural and compressive strength of cement mortars. However, the improved workability and reduced segregation of the mortar were observed, indicating a trade-off between workability and strength. Jenni et al. [27] studied the influence of polymers on the microstructure and adhesive strength of cementitious tile adhesive mortars. The results showed that the addition of polymers, such as re-dispersible powders, enhanced the adhesive strength of the mortar. The improved bond strength between the adhesive mortar and tiles contributed to better performance in terms of flexural and tensile strength.

Liu et al. [40] focused on the development of ultra-lightweight cement composites with excellent flexural strength. Although not directly related to water-soluble polymers, the study emphasized the establishment of an interpenetrating network within the composite, which contributed to enhanced flexural strength. This highlights the significance of the overall material design and reinforcement strategies in improving the flexural properties of concrete. Cannon and Groves [12] investigated the time-dependent mechanical properties of high-strength cements. While this study did not specifically focus on water-soluble polymers, it provided insights into the long-term behaviour of cementitious materials. Time-dependent phenomena such as creep and relaxation can affect the flexural and tensile properties of concrete over time. Wang et al. [78] evaluated the long-term performance and hydration of cement mortars with hydroxyethyl methyl cellulose (HEMC) cured at low temperatures. The study indicated that the addition of HEMC improved the early-age and long-term strength development of cement mortars. This implies that the presence of water-soluble polymers can positively affect the flexural, tensile, and bond strength properties of concrete, especially under low-temperature curing conditions.

Various studies have examined the effects of water-soluble polymers on the flexural, tensile, and bond strength of concrete. Polyvinyl alcohol (PVA) was found to enhance the bond strength between aggregates and paste, leading to improved flexural and tensile strength. Molecular weight and charge characteristics of flocculants were identified as important factors in the behaviour of fibre cement composites. Polyvinyl alcohol (PVA) was also shown to enhance the microstructure, reduce crack formation, and improve bonding properties, resulting in increased flexural and tensile strength. However, the addition of hydroxyethyl methyl cellulose (HEMC) decreased the flexural and compressive strength of cement mortars, although it improved workability and reduced segregation. The incorporation of polymers, such as re-dispersible powders, improved adhesive strength and subsequently enhanced flexural and tensile strength. Other studies emphasized the significance of interpenetrating networks and material design strategies in achieving superior flexural strength. While the long-term behaviour of cementitious materials was explored in terms of time-dependent properties, the addition of HEMC was found to enhance early-age and long-term strength development, especially under low-temperature curing conditions. Overall, water-soluble polymers can have a positive impact on the flexural, tensile, and bond strength properties of concrete, although the specific effects may vary depending on the type of polymer and its characteristics.

6. Influence of water-soluble polymers on the durability properties of cementitious materials

Water-soluble polymers can significantly enhance the durability properties of cementitious materials by providing protection against environmental factors such as carbonation, chloride attack, shrinkage, and frost resistance. The incorporation of these polymers can improve the durability of cementitious materials by enhancing their resistance to the harsh environment and increasing their service life. For instance, the use of water-soluble polymers in concrete can increase its resistance to carbonation, which is a common cause of concrete degradation. Moreover, the addition of these polymers can also improve the chloride ion penetration resistance of

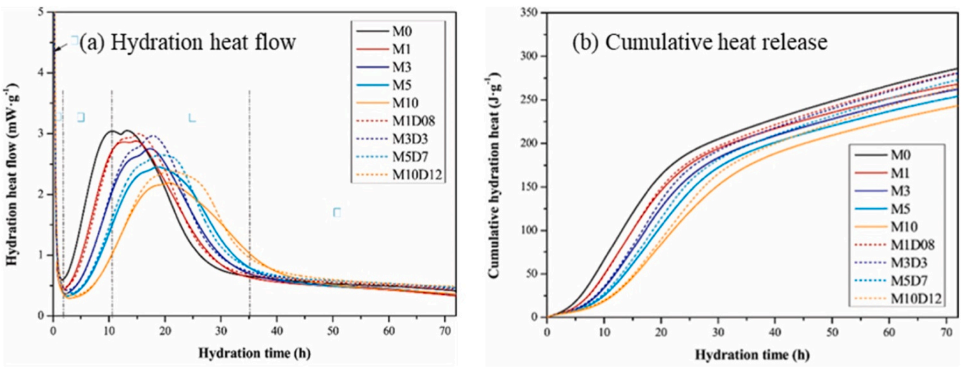

Fig. 8. Calorimetric characteristics of HEMC-modified cement pastes: (a) heat flow and (b) cumulative heat.

concrete, thereby increasing its durability in marine and coastal environments.

6.1. Carbonation

The carbonation of concrete is a critical process that affects its durability and service life. Water-soluble polymers are known to improve the mechanical properties of concrete, but their influence on the carbonation behaviour of concrete remains unclear. Zhi et al. [94] investigated the effect of polyacrylamide (PAM) on the carbonation behaviour of cement paste Fig. 8. The study found that PAM can delay the carbonation of cement paste by reducing its permeability and pore structure. The results indicated that PAM could improve the durability of concrete under carbonation conditions.

Omikrine Metalssi et al. [52] and [51] investigated the influence of cellulose ether on the carbonation kinetics of mortars. The studies revealed that cellulose ether can delay the carbonation of mortar by reducing its permeability and increasing its porosity. However, the influence of cellulose ether on the carbonation behaviour of mortar was dependent on its dosage and the curing conditions. The studies suggest that water-soluble polymers can influence the carbonation behaviour of concrete by reducing its permeability and porosity. The reduction in permeability and porosity can delay the carbonation of concrete and improve its durability. However, the influence of water-soluble polymers on the carbonation behaviour of concrete is dependent on the type and dosage of the polymer and the curing conditions.

In summary, research findings suggest that water-soluble polymers have an impact on the carbonation behavior of concrete. The incorporation of these polymers has shown potential to enhance the durability of concrete in carbonation conditions. However, it is crucial to conduct additional studies to explore the long-term effects of water-soluble polymers on concrete carbonation behavior and their influence on other aspects of durability. Further investigations will contribute to a better understanding of the role of water-soluble polymers in mitigating carbonation and improving the overall performance of concrete structures in the face of carbonation-related challenges.

6.2. Chloride attack resistance

The durability of concrete structures can be affected by various factors, including chloride attack, which can lead to corrosion of the reinforcing steel. The addition of water-soluble polymers to concrete has been explored as a potential method to improve the chloride attack resistance of concrete. Zhao et al. [92] investigated the effect of polyethylene glycol (PEG) on chloride binding in mortar (Fig. 9). The study found that the addition of PEG increased the chloride binding capacity of the mortar, which was attributed to the formation of hydrogen bonds between the PEG and the chloride ions. The authors suggested that PEG could be used as an effective

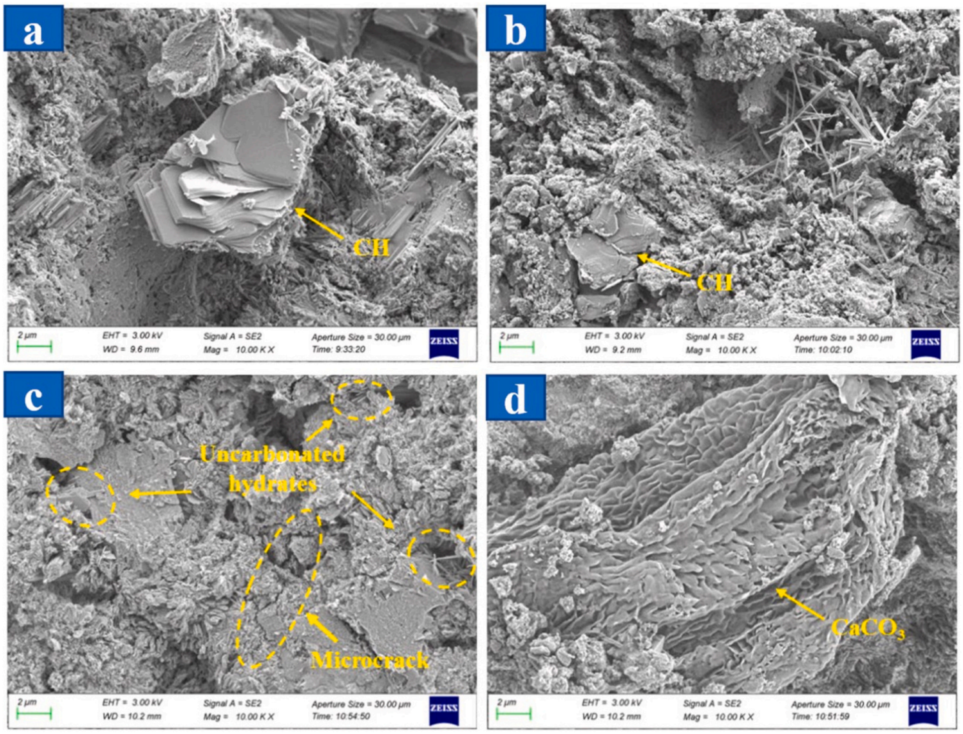

Fig. 9. Micromorphology of cement samples; (a) without PAM, (b) with 0.1 wt% PAM before carbonation; (c) without PAM, (d) with 0.1 wt% PAM after 28 d carbonation [94].

admixture to enhance the chloride resistance of concrete. In a related study, Zhao et al. [93] investigated the use of viscosity modifying admixture (VMA) to reduce diffusion in cement-based materials. The study found that the molecular mass of the VMA had a significant effect on the diffusion coefficient of chloride ions in the cement-based materials. The authors suggested that the use of VMA could be an effective method to reduce the chloride penetration in concrete and improve its durability.

Bentz et al. [4] explored the use of nanoscale viscosity modifiers to reduce ion mobility and improve the durability of concrete structures. The study found that the addition of nanoscale viscosity modifiers could effectively reduce the mobility of ions in the concrete, leading to improved chloride attack resistance. The authors suggested that the use of nanoscale viscosity modifiers could potentially double the service life of concrete structures.

Zhang et al. [90] proposed a novel method of self-healing cement paste using gel microparticles encapsulating phosphate. The study found that the addition of the gel microparticles could significantly improve the chloride resistance of the cement paste, attributed to the formation of a protective layer on the surface of the cement particles. The authors suggested that the use of gel microparticles could be a promising method to improve the durability of concrete structures.

Singh et al. [63] investigated the effects of hydroxyethyl cellulose and oxalic acid on the properties of cement. The study found that the addition of hydroxyethyl cellulose and oxalic acid could significantly reduce the chloride permeability of cement. However, the authors noted that the addition of these admixtures could also reduce the compressive strength of the cement. Khayat [32] studied the effects of anti-washout admixtures on the properties of hardened concrete. The study found that the addition of anti- washout admixtures could improve the workability and reduce the segregation of concrete. However, the authors noted that the effect of anti-washout admixtures on the durability of concrete was limited.

In summary, numerous studies have demonstrated that incorporating water-soluble polymers in concrete has the potential to enhance its resistance to chloride attack, a critical aspect of durability in concrete structures. Various types of water-soluble polymers, including polyethylene glycol (PEG), viscosity-modifying agents (VMA), and nanoscale viscosity modifiers, have shown effectiveness in reducing chloride penetration and improving the durability of concrete. However, it is important to note that the addition of these admixtures may have an impact on other concrete properties, such as compressive strength. Further research is necessary to optimise the utilisation of water-soluble polymers in concrete, striking the ideal balance between enhanced durability and maintaining the desired mechanical properties. This entails investigating the dosage, compatibility with different cementitious systems, and long-term performance of concrete with water-soluble polymer admixtures. By conducting in-depth studies, researchers can determine the most suitable types and concentrations of water-soluble polymers to achieve optimal chloride attack resistance without compromising other vital concrete characteristics.

6.3. Shrinkage

The addition of water-soluble polymers in concrete mixes is known to influence the shrinkage behaviour of concrete, which can ultimately affect its durability and performance. Wang et al. [77] investigated the effect of hydroxyethyl methyl cellulose (HEMC) on the properties and microstructure of cement mortars after controlling the air content. The results showed that the addition of HEMC led to a reduction in drying shrinkage due to its water retention properties, which allowed for more complete hydration of the cement. This finding was consistent with the work of Izaguirre et al. [26], who found that the addition of water-retaining agents, including HEMC, led to reduced shrinkage in lime-based mortars.

In contrast, Bílek et al. [8] found that the molecular weight of polyethylene glycol (PEG), another water-soluble polymer, can significantly affect the drying shrinkage and hydration of alkali-activated slag mortars and pastes. Specifically, they found that increasing the molecular weight of PEG led to an increase in drying shrinkage due to its higher viscosity and reduced water mobility. Similarly, Ye et al. [85] found that adding polypropylene glycol (PPG) with different molecular weights to alkali-activated slag led to different shrinkage behaviours, with lower molecular weight PPG leading to greater reduction in shrinkage.

Cannon and Groves [12] also investigated the time-dependent mechanical properties of high-strength cements, which are often used in structural applications. They found that shrinkage in these cements is mainly due to autogenous shrinkage, which occurs as a result of the chemical reaction between cement and water. This suggests that the use of water-soluble polymers that can influence the water-cement ratio and the hydration rate of the cement can have a significant impact on the shrinkage behaviour of high-strength cements.

The utilisation of water-soluble polymers in concrete mixes can exert both beneficial and adverse effects on the shrinkage behaviour of the resulting concrete. The impact largely depends on the specific properties and characteristics of the water-soluble polymers employed. Certain water-soluble polymers, such as hydroxyethyl methyl cellulose (HEMC), possess water retention capabilities. These polymers promote improved hydration of the cement, thereby reducing shrinkage by ensuring a more complete and uniform distribution of water throughout the mix. This enhanced hydration helps mitigate the loss of moisture, which is a key contributor to shrinkage in concrete. On the other hand, other water-soluble polymers, such as polyethylene glycol (PEG) and polypropylene glycol (PPG), can affect the mobility of water within the concrete matrix due to their viscosity and molecular weight. This altered water mobility can potentially lead to increased shrinkage in the hardened concrete. To effectively control and manage shrinkage in concrete, it is essential to have a thorough understanding of the specific properties and behaviours of different water-soluble polymers. By selecting the appropriate polymer type and considering its impact on water retention, hydration, and water mobility, engineers and practitioners can optimise the use of water-soluble polymers to achieve the desired balance between shrinkage control, durability, and overall performance of the concrete structures.

6.4. Frost resistance

Water-soluble polymers are known to affect the frost resistance of concrete by influencing its pore structure and water transport properties. Izaguirre et al. [26] investigated the use of water-retaining agents, including hydroxyethyl methyl cellulose (HEMC) and polyvinyl alcohol (PVA), in aerial lime-based mortars. They found that the addition of HEMC and PVA improved the frost resistance of the mortars by reducing their porosity and increasing their pore size distribution, which allowed for better drainage of water during freezing and thawing cycles. This finding was consistent with their earlier work on the ageing of lime mortars with admixtures, where they found that HEMC and PVA improved the durability of the mortars by reducing their water absorption and capillary suction.

Khayat [31] investigated the effect of viscosity-modifying admixtures, including hydroxypropyl methyl cellulose (HPMC) and modified starch, on the frost durability of concrete. He found that the addition of these admixtures led to a reduction in the rate of water absorption and diffusion in concrete, which improved its frost resistance. However, he also noted that the effect of these admixtures on frost durability was influenced by their dosage, the water-cement ratio, and the air-void system in the concrete. Yamato et al. [83] studied the freezing and thawing resistance of anti-washout concrete, which is designed to resist washing out of the cement paste due to the flow of water. They found that the addition of water-reducing admixtures, including polycarboxylate-based admixtures, improved the frost resistance of the concrete by reducing its water-cement ratio and improving its workability. However, they also noted that the frost resistance of the concrete was reduced at high dosages of these admixtures due to the formation of air voids. Yu et al. [86] investigated the effect of compounding an antifoaming agent and a viscosity-modifying agent on the frost resistance of mould bag concrete. They found that the addition of these agents improved the frost resistance of the concrete by reducing its porosity and water absorption, which was attributed to the formation of a more compact and uniform structure. However, they also noted that the optimal dosage of these agents depended on the water-cement ratio and the curing temperature of the concrete.

The incorporation of water-soluble polymers in concrete can have a significant impact on its frost resistance, which is vital for structures exposed to freeze-thaw cycles. The effects are contingent upon various factors, including the type and dosage of the polymer, as well as other considerations such as the water-cement ratio and the air-void system. Water-retaining agents and viscosity-modifying admixtures are examples of water-soluble polymers that can enhance the frost resistance of concrete. These polymers work by reducing the porosity of the concrete and inhibiting water transport through the capillary network. By restricting the ingress of water, they help minimise the potential for freeze-thaw damage. Additionally, water-reducing admixtures can improve the frost resistance of concrete by reducing the water-cement ratio. This not only enhances the workability of the mix but also reduces the overall moisture content, mitigating the risk of excessive ice formation during freezing conditions. However, it is crucial to strike a careful balance in the dosage of these admixtures to avoid adverse effects. Excessive dosages can lead to the formation of air voids, which can compromise the durability and strength of the concrete. It is therefore necessary to determine the optimal dosage of water-soluble polymers through careful testing and consideration of the specific project requirements. Furthermore, the frost resistance of concrete is influenced by several other factors, such as the quality and distribution of air voids. Proper design and control of the air-void system, along with the judicious use of water-soluble polymers, are essential for achieving optimal frost resistance.

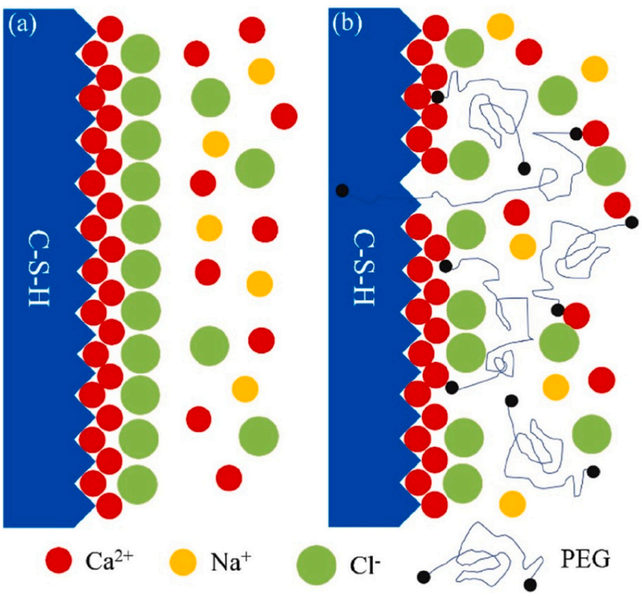

Fig. 10. The competitive adsorption on C–S–H gels between PEG and chloride ion, (a) without PEG; (b) with PEG [92].

7. Influence of water-soluble polymers on the microstructure of cementitious materials

Water-soluble polymers exert a notable impact on the microstructure of cementitious materials. These polymers serve as nucleating agents, facilitating the formation of hydration products and contributing to the densification of the microstructure. Moreover, they have the ability to modify the distribution of pore sizes, enhance the packing density of particles, and improve interparticle bonding. These effects collectively lead to a reduction in porosity and an increase in the strength and durability of the cementitious materials. By optimizing the microstructure through the use of water-soluble polymers, researchers and practitioners can effectively enhance the overall performance and longevity of cement-based structures.

The study by Knapen and Van Gemert [36] investigated the effect of water-soluble polymers on cement hydration and microstructure formation. They found that the presence of polymers can modify the microstructure of concrete by enhancing pore refinement and delaying the nucleation of hydrates. The study suggests that polymers can improve the durability and strength of concrete by reducing the pore volume. Sun and Xu [69] conducted a micromechanical analysis of polyacrylamide-modified concrete. Their study showed that polyacrylamide can enhance the mechanical properties of concrete by improving the interfacial bonding between aggregates and cement paste. Moreover, they found that polyacrylamide can improve the microstructure of concrete by reducing the porosity and enhancing the densification of cement paste.

Yuan et al. [87] compared the effect of different ionic polyacrylamides on cement hydration, mechanical properties, and microstructural characteristics of cement pastes. Their study showed that the addition of ionic polyacrylamides can enhance the early-age strength and microstructure of cement paste. Fig. 10 illustrates the impact of different types of PAMs on the porosity and pore size of cement. The addition of APAM resulted in a reduction in cement porosity to a certain extent. Conversely, the inclusion of CPAM and NPAM increased the porosity of cement. Regardless of the PAM type, all three PAMs played a role in refining the pore size of the mortar. Notably, this refining effect became more pronounced with increasing PAM content. Moreover, they found that the type of ionic group in the polymer affects the mechanism of polymer-cement interaction and the microstructural characteristics of cement paste. Kim and Robertson [33] studied the prevention of air void formation in polymer-modified cement mortar by pre-wetting. Their study showed that pre-wetting can prevent the formation of air voids in polymer-modified cement mortar and improve its microstructure.

The addition of methylcellulose in small amounts leads to the formation of undistorted $Ca(OH)_2$ crystals arranged in layered stacks at the surfaces of air voids as can be seen Fig. 11 [36]. Furthermore, at higher magnifications, the presence of polymer bridges between the $Ca(OH)_2$ layers is observed, providing additional bonding that binds the layers together. In MC modified mortars, polymer bridges can be found between all $Ca(OH)_2$ crystals, stretching across the crystal layers. However, in PVAA and HEC modified mortars, the different orientation of the $Ca(OH)_2$ crystals makes it impossible to inspect the interlayer spaces and detect potential polymer bridges. Bentz et al. [4] conducted X-ray absorption studies of drying of cementitious tile adhesive mortars. Their study showed that the presence of polymers can delay the drying of cementitious tile adhesive mortars and improve their microstructure by reducing the cracking and enhancing the hydration rate. Nguyen et al. [48] investigated the impact of water-soluble cellulose ethers on polymer-modified mortars. Their study showed that the addition of cellulose ethers can improve the microstructure and mechanical properties of polymer-modified mortars by reducing the porosity and enhancing the interfacial bonding between polymer and cement paste.

The formation of a polymer film is observed in hardened cement-based materials containing water-soluble polymers (WSPs). For instance, Sun and Xu [69] demonstrated that concrete without WSPs exhibited distinct edges and corners, as depicted in Fig. 12(a). Conversely, upon the inclusion of polyacrylamide (PAM), the concrete exhibited a gel-based composite appearance, with the polymer film intertwining with the cement phase (Fig. 12b). Moreover, the interfacial transition zone became more compact as the slender calcium hydroxide (CH) crystals exhibited reduced orientations and lower crystallinity. Similarly, the addition of other natural or semi-synthetic WSPs to hardened cement mortar resulted in the noticeable presence of a polymer film (Fig. 12c and d) [48]. Furthermore, the utilisation of certain WSPs, such as polyethylene glycol (PEG), which act as self-curing agents, led to microstructures

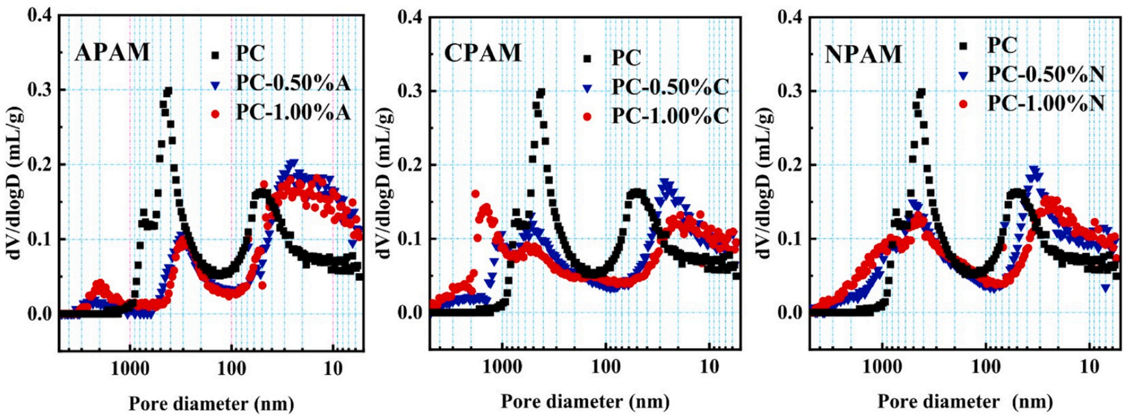

Fig. 11. Pore size characterisation of mortar with different types and contents of PAM [88].

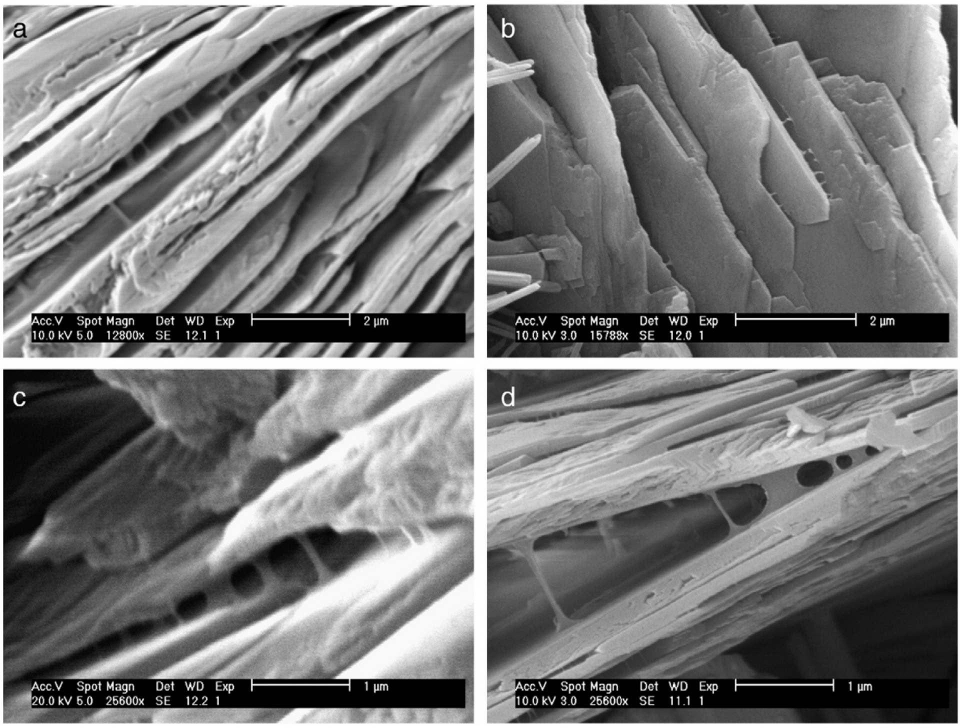

Fig. 12. Secondary electrons (SE) image of stacks of layered $Ca(OH)_2$ crystals in 1% MC modified mortars. Between the crystal layers, polymer bridges are detected [36].

with greater density and fewer thinner microcracks in the samples (Fig. 12e and f) [17].

Research findings indicate that incorporating water-soluble polymers in concrete can enhance its microstructure and mechanical properties through various mechanisms. These polymers effectively reduce porosity, promote the densification of cement paste, and

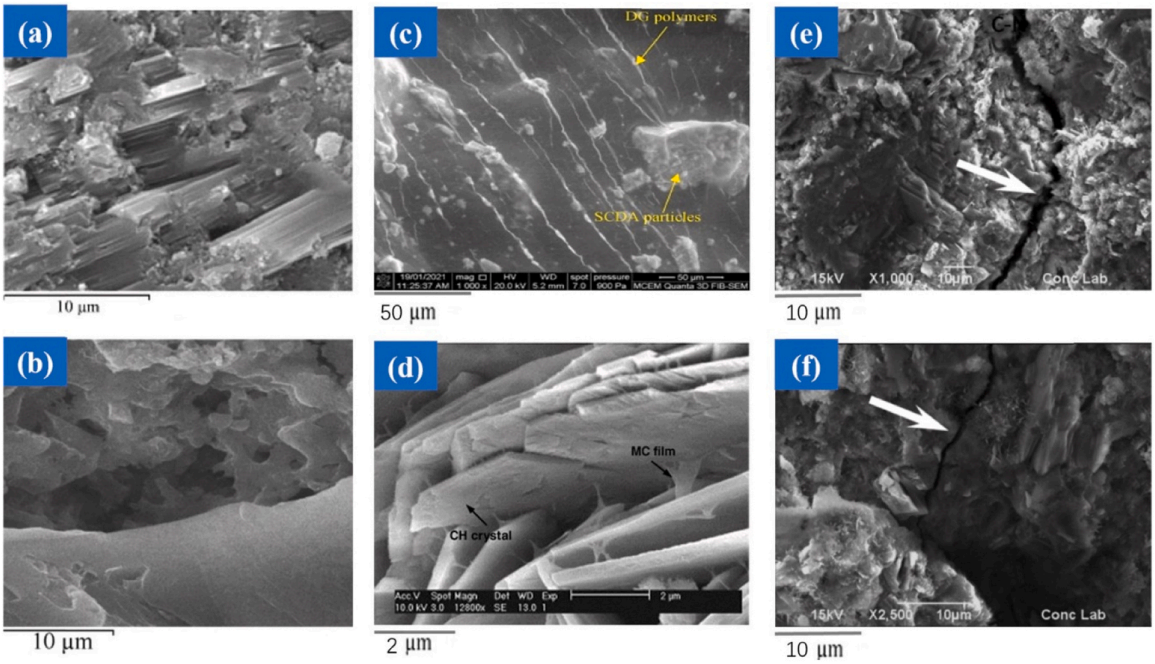

Fig. 13. Micromorphology of concrete samples (a) without PAM and (b) with 8 wt% PAM [69], Micromorphology of cement (c) without PEG (d) with PEG [17], Micromorphology of cement mortar with (e) diutan gum (f) CE [48].

improve the interfacial bonding between aggregates and cement paste. However, the specific type of polymer used and its concentration can influence the interaction mechanism between the polymer and cement, as well as the resulting microstructural characteristics of the concrete. Further research is necessary to optimise the utilisation of water-soluble polymers in concrete, aiming to enhance its microstructure and mechanical properties. Understanding the intricacies of polymer-cement interactions will facilitate the development of improved concrete formulations and construction practices..

8. Challenges and opportunities

The use of water-soluble polymers in cementitious materials has shown promising results in improving their properties and performance. However, there are several challenges that need to be addressed to fully exploit their potential and to develop efficient and sustainable applications. At the same time, there are also opportunities for further research and development that can enhance their performance and expand their applications. This section discusses some of the challenges and opportunities associated with the use of water-soluble polymers in cementitious materials.

One of the main challenges is related to the compatibility of the water-soluble polymers with cement and other admixtures. Cement-based materials are complex systems with different components that can interact with each other in various ways. The water-soluble polymers should not only be compatible with cement but also with other admixtures, such as superplasticizers, retarders, and air-entraining agents, that are commonly used to modify the properties of concrete. In addition, the water-soluble polymers should not affect the setting time and the early strength development of cementitious materials.

Another challenge is related to the cost and availability of water-soluble polymers. Some of the natural water-soluble polymers, such as cellulose ethers and xanthan gum, are expensive and their supply can be limited. On the other hand, some of the synthetic water-soluble polymers, such as polyethylene oxide and polyvinyl alcohol, are relatively cheap and can be easily produced. However, their properties and performance can vary depending on their molecular weight, degree of hydrolysis, and other factors.

The environmental impact of the water-soluble polymers is another challenge that needs to be addressed. Some of the natural water-soluble polymers, such as guar gum and locust bean gum, are obtained from plant sources and are biodegradable. However, their production can require significant amounts of water and energy, and their cultivation can compete with food production. Some of the synthetic water-soluble polymers, such as polyacrylamide and polyacrylic acid, are not biodegradable and can persist in the environment for a long time. Therefore, it is important to consider the environmental impact of the water-soluble polymers and to develop sustainable alternatives.

In addition to the challenges, there are also opportunities for further research and development that can enhance the performance and expand the applications of water-soluble polymers in cementitious materials. One of the opportunities is related to the use of functionalized water-soluble polymers that can provide additional benefits, such as self-healing, antimicrobial, and photocatalytic properties. For example, some researchers have reported the use of chitosan-based water-soluble polymers that can improve the durability and antimicrobial properties of cementitious materials. Another opportunity is related to the use of bio-based water-soluble polymers that are obtained from renewable sources and are biodegradable. Some of the bio-based water-soluble polymers that have been investigated include lignin, cellulose nanocrystals, and chitin. These polymers have shown promising results in improving the properties and performance of cementitious materials and can provide a sustainable alternative to synthetic water-soluble polymers.

Furthermore, the development of new techniques for the synthesis and modification of water-soluble polymers can also open up new opportunities for their use in cementitious materials. For example, some researchers have reported the use of electrospinning and spray drying techniques to produce water-soluble polymer fibres and particles that can improve the properties of cement-based materials. In addition, the modification of water-soluble polymers with nanoparticles and other additives can also enhance their performance and expand their applications.

9. Conclusions

9.1. Summary of key findings

- Water-soluble polymers have a significant impact on the properties and performance of cementitious materials.
- The addition of water-soluble polymers can improve the workability and rheological properties of cementitious mixes, allowing for better flow and reduced segregation.
- Water-soluble polymers can enhance the hydration process by promoting water retention and providing a continuous water supply for cement hydration, leading to improved strength development.
- The incorporation of water-soluble polymers can modify the microstructure of cementitious materials, resulting in reduced porosity, increased density and improved durability.
- Water-soluble polymers can enhance the resistance of cementitious materials to cracking, shrinkage and chemical attack, thereby improving their long-term performance.
- The specific type and dosage of water-soluble polymers influence the properties of cementitious materials, and careful selection is required to achieve the desired effects.
- The use of water-soluble polymers in cementitious materials presents both opportunities and challenges, requiring proper understanding, optimisation and compatibility with other additives or admixtures.

9.2. Implications and recommendations for practice and future research

Based on the reviewed literature on the effects of water-soluble polymers in cementitious materials, the following implications and recommendations for practice and future research can be made:

9.2.1. Implications for practice

1. Optimisation of polymer type and dosage: The choice of water-soluble polymer and its appropriate dosage is crucial for achieving desired effects in cementitious materials. It is important to consider factors such as workability, setting time, strength development and durability when selecting and dosing the polymer.
2. Compatibility with other admixtures: When using water-soluble polymers in combination with other admixtures, compatibility should be carefully evaluated to ensure their synergistic effects and avoid any undesirable interactions that may compromise the performance of the cementitious materials.
3. Quality control and testing: Adequate quality control measures should be implemented to ensure the proper dispersion and distribution of water-soluble polymers in cementitious mixes. Testing methods should be employed to assess the fresh and hardened properties of the materials, including workability, strength and durability, to verify the effectiveness of the polymer additives.
4. Consideration of environmental impact: The environmental impact of using water-soluble polymers should be taken into account. The selection of polymers with low environmental footprints and the optimisation of dosages to minimise waste and energy consumption are important considerations for sustainable construction practices.

9.2.2. Recommendations for future research

1. Mechanisms and interactions: Further research is needed to gain a deeper understanding of the mechanisms by which water-soluble polymers interact with cementitious materials. This includes investigating the adsorption, dispersion, and bonding mechanisms between polymers and cement particles, as well as their impact on hydration kinetics and microstructure development.
2. Performance under different conditions: The effects of water-soluble polymers in various environmental conditions, such as high temperatures, aggressive chemical environments, and freeze-thaw cycles, should be explored. This will help to assess the long-term performance and durability of polymer-modified cementitious materials.
3. Combined use with other additives: The synergistic effects of combining water-soluble polymers with other admixtures, such as superplasticisers, mineral additives, and fibres, should be investigated. This research can provide insights into optimising multi-component systems for enhanced properties and performance.
4. Standardisation and guidelines: The development of standardised testing methods, guidelines, and specifications for evaluating the performance of water-soluble polymers in cementitious materials is necessary. This will facilitate consistent assessment and comparison of different polymer products and their suitability for specific applications.
5. Life cycle assessment and sustainability: Further research should focus on conducting life cycle assessments to evaluate the environmental impacts associated with the production, use, and disposal of water-soluble polymers in cementitious materials. This will help identify opportunities for improving the sustainability of these materials and guide decision-making processes in construction practices.

By acknowledging and addressing the implications and recommendations outlined in this research, researchers and practitioners can significantly enhance their understanding and application of water-soluble polymers in cementitious materials. This, in turn, can pave the way for improved performance, enhanced durability, and increased sustainability in the field of construction. By incorporating the findings and recommendations into their practices, stakeholders can optimise the functions of water-soluble polymers, harnessing their potential to enhance various properties and performance aspects of cementitious materials. Ultimately, this will contribute to the development of more robust, long-lasting, and environmentally friendly construction materials and structures.

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.

Data availability

Data will be made available on request.

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