

Research review of water-based epoxy resin modified cement based materials

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Traditional cement-based materials commonly experience issues such as cracking, flaking, and holes, which reduce their lifespan. However, by adding epoxy resin, these problems can be effectively addressed. This modification enhances the mechanical strength, resistance to folding, fluidity, resistance to infiltration, corrosion resistance, and reduces shrinkage rate of the cement-based materials. This text presents an overview of the current research on water-based epoxy emulsion, modified cement-based materials, and their use in road construction and cementing engineering. It analyzes the characteristics of these materials and summarizes the modification mechanism of water-based epoxy resin-modified cement-based materials. Lastly, it proposes future research directions for these modified cement-based repair materials.

Keywords: Water-based epoxy resin, Cement based material, Repair material, Concrete.

Introduction

Cement is an inorganic adhesive material that hardens when mixed with water. It is derived from various raw materials and is produced through a straightforward process. Cement has numerous applications and is extensively utilized due to its high compressive strength and resistance to deformation. It finds wide usage in water conservancy projects, construction industry, road and bridge construction, as well as marine engineering and other significant fields [1]. Nevertheless, cement-based materials are not flawless due to their non-homogeneous and porous nature. When exposed to external factors like load, freeze-thaw cycles, erosion, and internal factors, such materials develop defects such as cracks, corrosion, and peeling, ultimately leading to reduced durability. Concrete materials have exhibited deficiencies in recent years, leading to deterioration that causes a decrease in the lifespan of structures, financial losses, and significant risks to human well-being. Oil and gas exploitation in China has caused a number of safety catastrophes, including oil and gas seepage and other gas fluxes, in recent years [2-4]. During the 1980s, Japan's transportation system conducted inspections on more than one hundred reinforced concrete piers across the country. According to the findings, piers that had been in use for over 20 years showed signs of degradation and needed urgent repairs [5]. A significant proportion of concrete buildings in the United States have not yet fulfilled their projected lifespan and are also experiencing widespread deterioration. Furthermore, the frequency

of such disasters has been on the rise [6]. Repairing slightly damaged concrete structures in a timely manner using suitable materials can increase the lifespan of the structures, restore their functionality, and save economic expenses, as opposed to completely reconstructing them [7, 8]. Thus, to address the limitations of cement-based materials, such as their high brittleness, low toughness, poor durability, and low tensile strength, a new material with enhanced qualities has been developed [9, 10].

To address the aforementioned drawbacks of cement-based materials, researchers from both local and international backgrounds have started employing various polymer resins to alter their physical and chemical characteristics. Epoxy resins, which are part of the group, exhibit resistance to both acidic and alkaline substances. They are frequently employed in the production of modified concrete-based materials. Waterborne epoxy resin, when added to cement paste, undergoes a process of slow dehydration and curing, forming a film as the cement's hydration reaction eats a portion of the water. The outcome of this procedure is the creation of a three-dimensional polymer network that permeates and strengthens the cement-based material, hence improving its bonding strength, toughness, durability, and impact resistance. Moreover, the application is uncomplicated, and it has the capability to heal in submerged or humid conditions.

Epoxy resin-modified cement based materials provide exceptional mechanical qualities, chemical stability, and bonding capabilities, together with the capacity to perform underwater coagulation repairs. Consequently, they hold a significant place in the use of polymer-modified cement based materials. Currently, there is a scarcity of review publications on aqueous epoxy resin-modified cement based repair products. This

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study presents a thorough examination of the current research progress, both domestically and internationally, regarding the utilization of aqueous epoxy resin for the modification of cement-based products. The text examines the mechanics, benefits, and drawbacks, and provides logical recommendations for future study paths.

Methods: Preparation of water-based epoxy resin

Since the 1970s, researchers have been studying aqueous epoxy resins. Initially, these resins were utilized in the coating business. Over time, as polymers advanced, they began to be applied in other disciplines, primarily for modifying inorganic materials. Due to their lack of water solubility and only being soluble in organic diluents, epoxy resins cannot be mixed directly with water. Therefore, it is necessary to explore the use of an emulsifier to achieve homogenization [11]. The objective is to incorporate hydrophilic interaction molecular chains or hydrophilic molecular organization into macromolecular chains in order to enhance their solubility in water. Epoxy resin molecules consist of two or more epoxy groups. When exposed to a curing agent, these groups undergo addition polymerization or catalytic polymerization, resulting in the formation of a three-dimensional crosslinked network structure. Epoxy resins can be categorized as either liquid or solid based on their physical state at ambient temperature. Based on their chemical composition, these substances can be categorized as glycidyl amines, glycidyl esters, aliphatic epoxy resins, and new epoxy resins.

There are four primary techniques used to prepare epoxy resins: mechanical method, reverse rotation method, curing agent emulsification method, and chemical modification method [12]. The initial three preparation procedures are primarily delineated.

Mechanical methods

The mechanical technique [13] entails dispersing epoxy resin in water by means of intense stirring or ultrasonic oscillation, and subsequently dissolving the fragmented and crushed epoxy resin particles using an emulsifier solution to acquire waterborne epoxy resin. This approach provides benefits such as an uncomplicated preparation process, direct procedure,

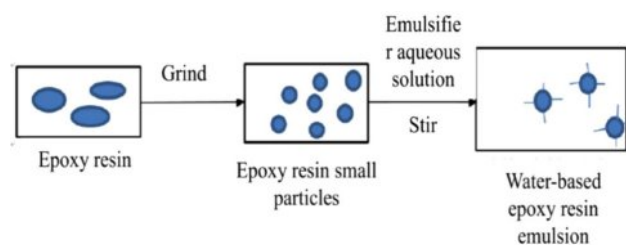


Fig. 1. Mechanical method technical route [14].

and economic savings. Fig. 1 illustrates the specific procedure for producing waterborne epoxy resin using the mechanical approach.

Reverse rotation

The phase inversion method [15] utilizes a straightforward preparation technique that does not necessitate chemical modification. The process entails the gradual addition of a tiny quantity of a mixture of emulsifier and water to the epoxy resin, while vigorously stirring, in order to create a high-viscosity water-in-oil (W/O) emulsion system. With an increase in water content, the viscosity of the system lowers, ultimately leading to the formation of a stable oil-in-water (O/W) emulsion system. Fig. 2 depicts the method of preparation. Conventional emulsifiers can cause problems with the production of a film during the curing process [16]. It is important to prepare a curing agent that can actively take part in the reaction. Wang and his colleagues employed surfactants to emulsify epoxy resin in order to create more stable aqueous emulsions of epoxy resin [17]. Yang [18] and his colleagues utilized BF₃-ether as a catalyst and combined epoxy resin, trimellitic anhydride, and PEG as raw materials to produce a multiblock epoxy resin emulsion. This emulsion contains carboxyl and hydroxyl groups. The particle size of the emulsion particles, prepared using the opposite method, was measured to be 312 nm. Furthermore, this waterborne epoxy emulsion demonstrated excellent storage stability, lasting for over 4 months. Additionally, the conversion rate of the emulsion was found to be above 90%, indicating a high level of efficiency. The reverse approach has several benefits, including easy operation, great efficiency in converting epoxy, the capacity to achieve nanometer-level particle size in aqueous epoxy emulsion production, and improved stability [19].

Curing agent emulsification method

The process of curing agent emulsification involves using a curing agent that has the ability to both emulsify and cure, in order to achieve the emulsification of epoxy resins [21]. The curing agent causes the epoxy resin to create an epoxy emulsion by emulsification, as seen in Fig. 3. During the curing process, the latex particles within the emulsion undergo first crosslinking on their

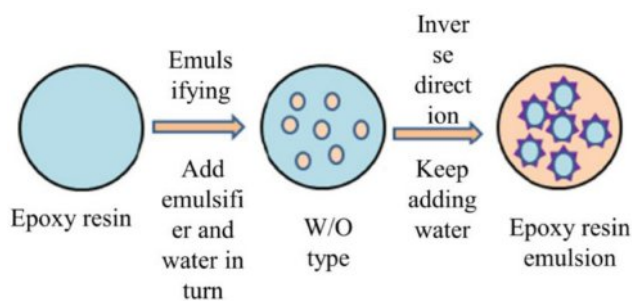


Fig. 2. Technical route of the opposite method [20].

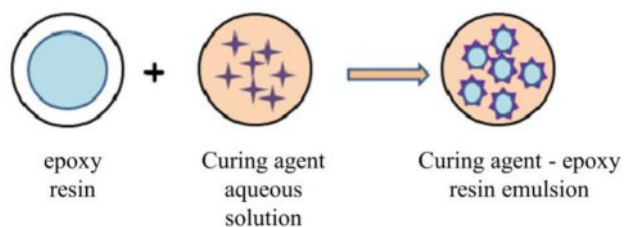


Fig. 3. Technical route of curing agent emulsification method [20].

surface. Afterwards, the curing agent permeates the epoxy resin dispersion system to undergo further reaction, finally resulting in the formation of a three-dimensional, evenly distributed coating [22, 23]. In their study, Wu et al. [24] developed a novel aqueous epoxy curing agent through the modification of epoxy resin E-51 using *m*-phenylenediamine. The curing agent has the ability to fully cure the epoxy resin emulsion, leading to a cured coating film that possesses high hardness, exceptional mechanical capabilities, and robust corrosion resistance. Bahraq et al. [25] utilized polyethylene glycol diglycidyl ether and epoxy resin E-51 as raw materials to modify the preparation of a self-emulsifying waterborne epoxy resin curing agent. The resulting coating film, prepared using this curing agent, exhibits excellent physical and mechanical properties, as well as strong resistance to acid and salt corrosion. The emulsification method of the curing agent offers the benefits of enhanced reactivity between epoxy resin and curing agent, as well as improved stability of the emulsion.

Chemical modification

The chemical modification method, sometimes referred to as the self-emulsifying method, is a chemical technique used to produce waterborne epoxy resin by polymerizing raw ingredients. This technique yields emulsions characterized by reduced and more consistent particle dimensions. Nevertheless, the procedure of preparation is comparatively intricate and expensive. Jo and her colleagues [26], along with other researchers, utilized bio-based materials as a starting point to chemically modify epoxy resin E-44. This modification process resulted in the production of epoxy coatings that possess exceptional resistance to corrosion. Afridi and his colleagues [27] utilized acrylic acid and its derivatives to modify epoxy resin, resulting in the creation of a water-based epoxy resin emulsion that possesses the ability to self-emulsify. Thirumalai [28] incorporated reactants, namely methacrylic acid and poly(methylphenylsiloxane), which possess vinyl groups at both ends of their molecules, into the epoxy resin molecule. This process resulted in the production of a self-emulsifying waterborne epoxy resin emulsion with small particles. Wu and colleagues [29] synthesized a waterborne epoxy resin emulsion by reacting polyethylene glycol with epoxy resin, along with employing physical techniques.

In summary, the preparation methods of waterborne epoxy resin have their own advantages and disadvantages. The mechanical method is simple and low cost, but the particle stability is poor and the emulsifier has residue. The phase inversion method has the advantages of simple process, high conversion efficiency, small emulsion particle size and good stability, but it requires special curing agent and high energy consumption. The emulsion of curing agent emulsification method is stable and the film performance is good. The process of preparing curing agent is complex, the cost is high and the applicability is limited. Although the chemical modification method can accurately design the structure, it may be complicated and costly.

Results: Research status of key scientific issues

Water-based epoxy resin research status at home and abroad

Epoxy resin, one of the three primary thermosetting resins employed in communications, has several benefits including minimal shrinkage after curing, strong adhesive properties, high tensile strength, and exceptional resistance to corrosion. When waterborne epoxy resin is mixed with cement, sand, curing agents, and other substances, it creates modified cement based products that have excellent adhesion, strong mechanical capabilities, long-lasting durability, and resistance to corrosion. In the 1970s, many countries have carried out research on waterborne epoxy resins, and achieved fruitful results in basic theory and application technology.

Zhao [30] used self-made high boiling alcohol lignin epoxy resin hydrophilic derivative and waterborne epoxy resin emulsion to modify cement mortar respectively, and studied its toughness. The results show that when the mass ratio of emulsifier to epoxy resin exceeds 13%, the toughness of cement mortar modified by waterborne epoxy resin emulsion is higher than that of cement mortar modified by high boiling alcohol lignin epoxy resin. Ariffin [31] conducted a study on the ratio and performance of epoxy resin emulsion modified cement mortar. The findings indicated that the compressive strength of the mortar exhibited an increase within a specific range when the party ratio rose. Guo [32] demonstrated that the absence of a curing agent resulted in a decrease in the flow and setting time of the modified mortar as the resin dose increased, owing to the elevated viscosity of the bisphenol A type epoxy resin.

Anagnostopoulos [33] selected two epoxy resin emulsions to study the hydration process, microstructure and macro properties of the modified cement slurry at four different curing temperatures and different epoxy resin content. The results show that epoxy resin emulsion can reduce the hydration heat release rate of cement slurry at the initial stage of cement hydration, slow down the hydration process, and reduce the total heat

release. The objective was to investigate the hydration process, microstructure, and macroscopic features of the modified cement pastes. The findings suggest that the epoxy resin emulsion diminishes the rate at which heat is released during the initial phases of cement paste hydration, retards the process of hydration, and reduces the overall heat release. The addition of epoxy resin does not alter the hydration products of the cement paste, which continue to be $\text{Ca}(\text{OH})_2$ and CSH gel. The epoxy resin emulsion decreases the quantity of large pores and increases the quantity of microscopic pores in the structure of the cement stone, thereby improving its resistance to corrosion.

Palanikumar [34] and other researchers introduced epoxy resin into SBR-modified mortar to investigate the impact of epoxy resin integration on the initial strength of concrete. The findings indicate that the potency of the altered mortar fluctuates depending on the specific curing conditions and polymer concentration. The modified mortar exhibits a threefold increase in compressive strength and flexural strength compared to the control sample, when subjected to the same curing conditions. Bajpai et al. [35], conducted experiments to investigate the corrosion resistance of cement-based materials by including aqueous epoxy resin and subjecting them to acid exposure in a CO_2 atmosphere. The findings demonstrated that the incorporation of 30% epoxy resin substantially enhanced the corrosion resistance of the cementitious material. Scanning electron microscopy was used to do microanalysis on the epoxy resin-modified cement based material. The analysis showed that $\text{Ca}(\text{OH})_2$ crystals in the material were linked together by polymer films, creating a strong and compact structure that is resistant to carbonation corrosion.

Research progress of water-based epoxy resin modified cement based materials

Epoxy resin-modified cement based repair material is a composite material made from epoxy resin, curing agent, diluent, filler, and additives in precise proportions. During the process of hydration, the waterborne epoxy resin in the slurry gradually undergoes curing. Waterborne epoxy resin can enhance the fluidity, adhesion, acid and alkali resistance, impermeability, and corrosion resistance of cement slurry to a greater extent. Additionally, it has the ability to greatly decrease the rate of shrinkage in modified cement, making it especially well-suited for repairing and strengthening concrete structures [19]. Waterborne epoxy emulsion cement based solutions offer the added benefit of being suitable for underwater or damp substrate repairs, effectively overcoming a major obstacle in the construction industry regarding underwater repairs. This approach is convenient, ecologically sustainable, and non-toxic to humans.

To conduct research on the performance characteristics of aqueous epoxy-modified cement-based materials. Li [36] developed an underwater repair material using an

interpenetrating polymer network, which combined the reaction principles of epoxy and polyurethane. It was observed that this repair material exhibited superior physical qualities. Zhang [37] conducted a study to examine how the addition of waterborne epoxy affects the rheology, mechanical strength, bond strength, and shrinkage of cement mortars. The results suggest that the addition of waterborne epoxy resin enhances the fluidity of cement mortar, while simultaneously decreasing the amount of mixing and water needed. As the ratio of polymer to cement increases, the flexural bond strength of the material first rises and subsequently declines. The greatest adhesive strength is observed when the ratio of polymer to cement is 0.12. An excessive amount of polymer content might diminish the strength of the mortar and have a negative impact on its binding strength. Srinivasan [38] utilized aqueous epoxy resin, custom-made cement-based materials, and additives to create a fast-acting repair mortar that maintains its strength over time. They also investigated how the dose of waterborne epoxy resin affects the mechanical and shrinkage qualities of the mortar. The findings suggest that augmenting the quantity of waterborne epoxy resin within a suitable range reduces the initial compressive and flexural strength of the mortar, while notably improving the bond strength and flexural strength after 28 days, as depicted in Figs. 4(a) and 4(b). The study demonstrated that by incorporating a mixture of Pang [39] water-based epoxy resin emulsion and curing agent into cement mortar, it is possible to create a grout repair material that can be used on wet cement-based substrates. This material exhibits improved mechanical properties and enhanced resistance to chloride ion penetration and carbonation.

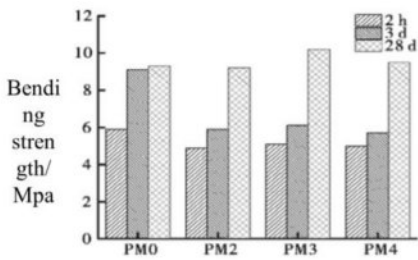
Czigány[40], a 40-year-old designer, developed three different combinations of mixing ratios for underwater repair epoxy concrete and underwater epoxy mortar. Through an examination of the mechanical properties of epoxy concrete and mortar under various mixing ratios, it was determined that the optimal epoxy resin admixture for concrete is 22.0%, while the recommended epoxy resin admixture for mortar is 23.0%. In their study, Guo [41] employed the controlled variable method to examine the mechanical properties, fluidity, and microstructure of modified concrete with varying epoxy resin coefficients. The analysis revealed that when the dosage of epoxy resin was 10 wt%, the modified concrete exhibited the highest tensile strength and tensile strain. This was attributed to the increased polymer strain, which effectively impeded the propagation of cracks and enhanced the concrete's ability to deform. Consequently, the hardness of the concrete decreased, as depicted in Fig. 4(c).

Chen [42] conducted an experiment where they combined aqueous epoxy resin with regular silicate cement mortar and thoroughly mixed it. They observed that this resulted in a longer setting time and a significant decrease in the mechanical properties. In this experiment,

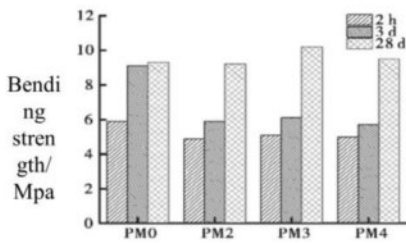
El-Hawary [43] combined slag microfine powder with modified mortar and examined the microstructure of the mortar while both materials were mixed together. The purpose was to investigate the enhancement of cement-based materials' properties and the mechanism behind it, using double-doped water-based epoxy resin and slag microfine powder. The findings indicate a substantial enhancement in both the flexural and compressive strengths of the cement-based material following the dual addition. The mechanical properties of the modified cement mortar are significantly improved by

the synergistic effects of aqueous epoxy resin and slag, which include water reduction, densification, filling, and curing crosslinking.

Kamar [44] conducted an experiment using two aqueous epoxy resins with varying amounts of two distinct epoxy equivalents to examine how they influenced the characteristics of modified cement based materials. The results indicate that the addition of waterborne epoxy resin to cement-based materials leads in the introduction of air bubbles and reduction in water content, leading to decreased density of the mortar and prolonged setting



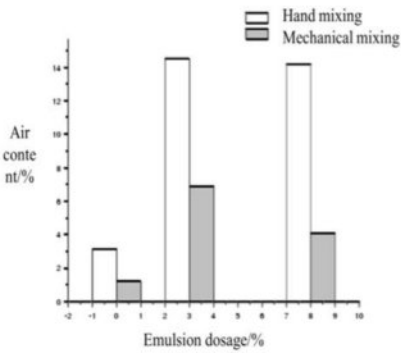
(a)



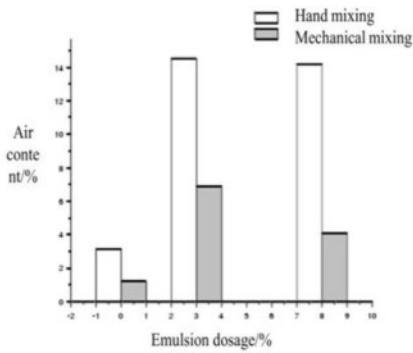
(b)

Polythene ratio	Slump/mm	Compressive strength/Mpa			Tensile strength/Mpa		Axial compressive strength/Mpa	Bending strength/MPa	Modulus of elasticity/10 ⁴ Mpa
		7d	28d	60d	28d	60d			
0	60	27.1	41.4	45.5	2.18	2.38	30.3	3.9	3.81
0.05	140	26.6	40.3	44.6	2.70	2.65	32.5	4.9	3.71
0.10	137	25.0	37.1	42.0	2.85	2.92	32.2	5.1	3.12
0.15	170	24.4	37.4	39.1	2.70	2.72	31.6	4.7	2.76
0.20	190	22.5	35.7	36.7	2.40	2.46	28.4	4.2	2.5

(c)



(d)



(e)

Fig. 4. Parameter analysis of cement mortar with different waterborne epoxy resin dosages.

time. The air content of the modified cement mortar changes depending on the mixing methods and mixing times, as depicted in Figs. 4(d) and 4(e). The initial compressive strength of the two chosen aqueous epoxy resin-modified mortars drops, but experiences a significant increase in the latter stages. The mechanical properties of the modified mortar are influenced by various curing processes. Experimental findings can identify the most effective curing method for the modified mortar.

Figure 4(a) demonstrates the impact of the amount of aqueous epoxy resin on the strength of repair mortar, as shown by reference [38]. (b) The impact of the amount of aqueous epoxy resin on the flexural strength of repair mortar is examined [38]. The study investigates the impact of different polymer contents on the performance of polymer-modified cement concrete [41]. (d) Scanning electron microscope (SEM) picture showing a polymer concentration of 10% [42]. The graph shows the variation in final setting time with the concentration of CH emulsion [44]. The study investigates the impact of different mixing methods on the air content of CH emulsion-modified mortar [44].

The above application research of waterborne epoxy resin in cement-based materials covers the influence of emulsion preparation on mortar toughness, the relationship between mix ratio and performance, the hydration and microstructure of cement slurry, as well as the improvement of mechanical properties and corrosion resistance. At present, most studies focus on the performance under certain conditions. There are some deficiencies in the research, including the lack of systematic comparison of different preparation methods, the lack of exploration of long-term durability and complex environmental performance, and the lack of in-depth research on the correlation between micro and macro performance.

Theory: Research on the mechanism of water-based epoxy resin modification of cement based materials

Fundamentals of the action of epoxy emulsion in cement mortar

Many effects of waterborne epoxy resin on the properties of cement-based materials are due to its unique mechanism of action. Extensive research has been conducted on the process of waterborne epoxy resin in cement based materials since the 1940s. Several fundamental theories of modification have been proposed, including diffusion theory, adsorption theory, mechanical theory, and electrostatic theory. The primary focus of this research is on the first three theories [45].

Diffusion theory

The molecules in the water-based epoxy resin create a mutual diffusion phenomenon under the condition of Brownian motion or oscillation of the chain segments. The higher the bonding temperature and the longer the

contact time, the greater the diffusion effect and the stronger the bond.

Adsorption theory

The water-based epoxy resin molecule diffuses to the surface of the treated object. In this process, it is affected by factors such as temperature rise and contact pressure. When the epoxy resin is sufficiently close to the two molecules of the treated object, the molecules will attract each other, so it has a certain bonding strength.

Mechanical theory

Mechanical theory suggests that the adhesive must penetrate into the voids on the surface of the object to be adhered to, to exclude the air adsorbed at its interface, and, after curing, to produce mechanical bonding, in order to produce bonding.

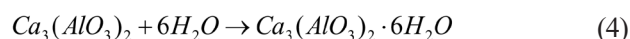
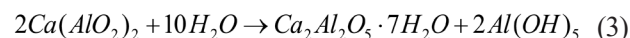
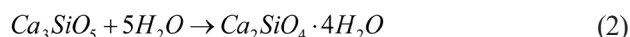
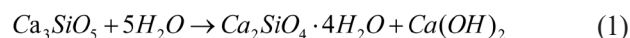
Role of cement on epoxy emulsion

Following the process of cement hydration, the slurry undergoes an increase in alkalinity. Waterborne epoxy resin has the ability to disperse or dissolve in water and undergo polymerization in an alkaline environment at room temperature, resulting in the formation of cross-linked macromolecules. This greatly enhances the efficiency of both newly mixed and cured mortars.

Hydration and microstructure analysis

Researchers have extensively examined and discussed the mechanism of polymer modification. They have also studied many models based on morphology and structure. Among these models, the Ohama model [46] and Konietzko model [47] are particularly well-known and widely accepted.

Both models indicate that the addition of polymer to cement slurry results in the dispersion of the polymer within the slurry. As the process of cement hydration becomes stronger, the amount of water present in the cement slurry drops steadily as a result of both hydration and evaporation. Once the water content in the polymer emulsion reaches a specific threshold, it undergoes a transformation and produces a film with strong adhesive properties. During this process, the cement undergoes a slow transformation through hydrolysis and hydration, which are intricate chemical reactions. These reactions involve:



The two models, Ohama and Konietzko, propose different explanations for the structure formed by the polymer and latex film with cement hydration products. Ohama suggests a three-dimensional mesh structure, while Konietzko suggests a three-dimensional interpenetrating network. The modification method is

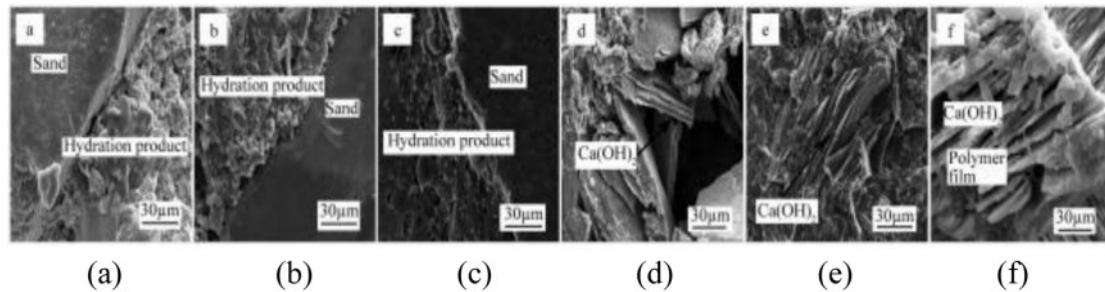


Fig. 5. SEM of cement mortar with different epoxy/cement ash contents [48].

based on the formation of a three-dimensional network structure by the epoxy resin molecules. This structure closely encloses the hydration products of the cement, resulting in an interpenetrating network. This enhances the density and durability of the repair material. Fig. 5 illustrates the alterations in microstructure. Fig. 5 displays: (a) Regular cement mortar; (b) Cement mortar with a 2% epoxy resin to cement ratio; (c) Cement mortar with a 4% epoxy resin to cement ratio; (d) Scanning Electron Microscope (SEM) image of the hydration product of Ca(OH)_2 in regular cement mortar; (e) SEM image of the hydration product of Ca(OH)_2 in cement mortar with a 2% epoxy resin to cement ratio; (f) SEM image of the hydration product of Ca(OH)_2 in cement mortar with a 4% epoxy resin to cement ratio [48].

Figure 5 clearly illustrates that ordinary cement mortar contains numerous pores and has a less compact structure. However, the inclusion of epoxy resin significantly enhances the connection between the cement paste and the sand particles, resulting in a stronger bond between them. The density of the epoxy resin/cement ash structure in the (2%) cement mortar body is greater than that of the conventional cement mortar body and the epoxy resin/cement ash structure in the (4%) cement mortar body. It demonstrates that using an appropriate epoxy resin can decrease the porosity of cement-based repair materials and enhance their flexural strength. However, it will also lead to a decrease in compressive strength. This reduction in compressive strength is due to the fact that the modulus of elasticity of a single epoxy resin is smaller than that of cementite. Fig. 5(d), (e), (f) illustrates the presence of a polymer film on the hydration product Ca(OH)_2 in epoxy modified cement mortar. Additionally, the epoxy resin emulsion has the ability to alter the morphology of Ca(OH)_2 . The Ca(OH)_2 crystals in ordinary cement mortar are weak and cannot withstand the rearrangement pressure of the hydration products. Ca(OH)_2 crystals exhibit enhanced resistance to rearrangement pressure when epoxy resin is present in the slurry. Researchers have proposed that the inclusion of polymers can induce the formation of a well-organized layered structure in the hydration product Ca(OH)_2 [49]. The polymer films situated between the Ca(OH)_2 layers function as interlayer adhesives, enhancing the crystal

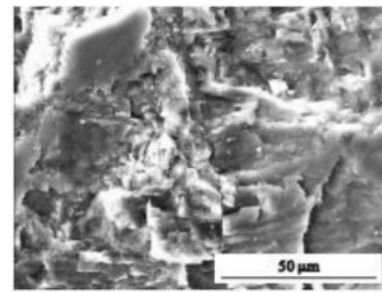


Fig. 6. SEM photos of 10% polymer [41].

structure and enhancing the performance of the cement mortar. Huang Zhiqiang [41] observed by ESEM that the resin is adsorbed on the surface of the cement hydration product and forms a dense polymer film with the cement matrix and aggregate, but the polymer cannot be mixed in excess, as shown in Fig. 6.

The polymer in the cement mortar enhances the adhesion, permeability, and other qualities of the mortar through its curing and film forming mechanism. The polymer film is created through the process of water evaporation, leading to the aggregation and bonding of particles. The process of curing and film generation is depicted in Fig. 7.

It was found by scanning electron microscopy that when the content of styrene-butadiene latex was small,

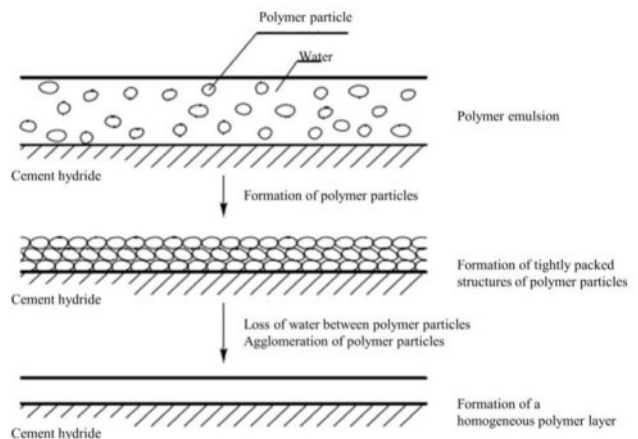


Fig. 7. Simplified model of polymer curing to film [44].

Table 3. Microstructure research results of epoxy resin modified cementitious repair materials.

Research worker	Performance enhancement mechanism /research content	Research findings
Zhong Shiyun, Wang Peiming [54]	Study on the morphology and structure of modified mortar before and after the study of silicate	A significant quantity of polymers was discovered in the interfacial transition zone of polymer-modified concrete, resulting in the formation of a robust network structure.
Senthilkumar K.M [55]	Study of the capillary structure of epoxy-modified pastes	The proposed polymer discontinuous film fills the capillary pores in hardened cement paste, reducing the size of big pores and increasing the size of small pores. This leads to an improvement in the mechanical characteristics of the paste.
Ohama Y[56]	Changes in morphology of phenylpropylene emulsion-modified cement paste at various ages observed by scanning electron microscopy	The findings indicate that the polymer undergoes a curing process, forming a thin layer on the surface of the cement particles. This, in turn, causes the modified cement mortar to develop cracks at the overlapping areas.
ARIFIN N F[57]	Microstructural morphology of epoxy resin emulsion cement mortar using scanning electron microscopy (SEM)	SEM microscopic analysis revealed that the addition of epoxy hindered the formation of crystals in the cement. Furthermore, the epoxy underwent crosslinking and curing within the cement, resulting in the entanglement of hydration products with the polymer. This process enhanced the structural morphology of the cement stone.
Jo B W [58]	Investigation of the effect of different dosage of epoxy resin on the microstructure of cement mortar by using electron microscope	The findings indicate that the addition of an optimal quantity of epoxy resin enhances the microstructure of cement mortar.
Agavrioloaie L [59]	Analysis of the effect of waterborne epoxy resin and fly ash on cement hydration products by scanning electron microscopy	The findings indicate that the modified mortar achieves ideal mechanical properties when composed of 10% fly ash and 10% epoxy resin. Additionally, the inclusion of epoxy resin enhances the adhesion and corrosion resistance of the cement mortar, albeit at the expense of reduced flexural strength.
Camille A. Issa [60]	Experimental study of epoxy repairing of cracks in concrete	Studies indicate that the addition of a 9% epoxy resin emulsion can significantly enhance the mechanical characteristics and corrosion resistance of slag cement.

the polymer mainly existed in the form of particles, and the local network structure was formed by particle accumulation [50]. The results of this study also confirmed the Puterman and Malorny structural model. Puterman and Malorny believe that not all polymers modify cement-based materials by film-forming, and when the minimum film-forming temperature of the polymer emulsion is higher than the experimental temperature, it cannot form a film and can only be modified in the form of particles [51]. In their investigation, Su et al. [52] employed ESEM to examine the structural changes of phenylpropylene emulsion-modified cement pastes at various stages of development. They discovered that the polymer adheres to the surface of the cement particles, creating a coating and filling the microcracks in the mortar. In their study, Sakai et al. [53] utilized scanning electron microscopy to examine the microstructure of polymer emulsion and powder modified cement mortar. They observed that the polymer exists as individual particles, and it is hypothesized that these latex particles have the ability to create a film emulsion. This emulsion

film is primarily found in a uniform distribution within the hardened cement paste, as well as on the surface of the aggregates.

Structural modelling of epoxy-modified cement paste

Considering the findings from the aforementioned investigations, we suggest a structural model for epoxy-modified cement mortar, as depicted in Fig. 8. This model combines Ohama's model [46] and Konietzko's model [47].

Epoxy resins exist in cured slurries in three different forms, each having different levels of impact on the structure and properties of the changed slurry. To begin with, epoxy resin particles are enclosed within the hydration products, resulting in the formation of adhesive forces between them. This not only enhances the robustness of the network structure of hydration products in the slurry, but also decelerates the pace of cement hydration. Furthermore, the epoxy resin particles tend to cluster together at the capillary pores, obstructing

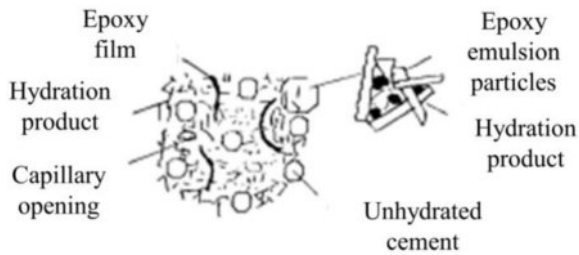


Fig. 8. Structural modelling of epoxy-modified cement mortar [55].

them and establishing a strong bond with the walls of the pores. This enhances the overall compactness of the slurry, diminishes its permeability, and consequently enhances its resilience and numerous operational attributes. Furthermore, the non-uniform spread of the epoxy film enhances the adhesive force of the hydration products on both surfaces of the film, mitigates the occurrence of small cracks due to shrinkage, and augments the strength and resistance to permeability of the modified slurry.

Disussion: Water-based epoxy resin modified cement based materials application research progress

Based on the above analysis, it can be seen that waterborne epoxy resin modified cement-based materials have a series of excellent properties due to their unique microstructure and special hydration reaction mechanism, which are widely used in many fields such as construction, bridge and water conservancy. The research and development of waterborne epoxy resin modified cement-based materials has shown excellent performance in the repair of many degraded concrete components, which is also the reason for its rapid development.

Application of waterborne epoxy-modified cement based materials on roads

Traditional concrete paving materials possess certain benefits, such as minimal susceptibility to temperature changes and exceptional strength. However, they also exhibit drawbacks, including significant brittleness, limited toughness, and inadequate durability. These shortcomings can result in premature cracking and other related issues. A novel road construction and maintenance material can be created by blending sulfo-aluminate cement, water-based epoxy, and additives. This material exhibits exceptional compressive strength, flexural strength, and bond strength. This material exhibits exceptional road performance and durability, hence enhancing the longevity of pavements and presenting significant prospects for its application.

Current status of domestic and foreign research

Professor Shen Aiqin has created polymer-modified cement-based materials that possess outstanding qualities

for repairing cement concrete pavements. Several universities and research institutes have conducted extensive study and obtained notable outcomes [61, 62]. Saccani et al. [63]. developed a rapid repair mortar for cement concrete pavement using custom-made cement-based materials, water-based epoxy resin, and fibers as the primary components. This formulation enhanced the flexural strength and bond strength of the modified materials, while also exhibiting exceptional toughness, minimal shrinkage, and long-lasting durability. Guo [64] conducted a study on the introduction of aqueous epoxy resin-modified cement into asphalt mixes in order to create a semi-rigid composite material. The findings suggest that the addition of epoxy resin can greatly enhance the mechanical characteristics of asphalt concrete pavement materials, making this composite material superior to regular asphalt mixtures. Ai [65] examined the practical use of modified epoxy resin cement-based materials for repairing damaged concrete pavements. The study also evaluated the effectiveness of using a thin layer of epoxy resin mixture as a cover after the repair. The results indicate that these materials are highly effective for repairing both pavements and thin layers of concrete pavements. Rod [66] employed epoxy resin to enhance the properties of rubber-modified asphalt. The resulting modified asphalt exhibited a deformation recovery rate that was over 50% higher than that of the original asphalt. This improvement enables the modified asphalt to better withstand the impact of traffic loading. Xu Ouming [67] conducted a series of studies on the performance of waterborne epoxy modified emulsified asphalt mixtures for pothole repair in asphalt pavements. The findings indicated that the incorporation of waterborne epoxy resins enhanced the initial strength of the mixtures and reduced the time required for curing. Additionally, the emulsified asphalt mixtures maintained favorable storage properties even after a certain period of time. Fowler [68] and other researchers discovered through trials that concrete mixes treated with epoxy have the ability to cure quickly within a brief timeframe, resulting in the rapid construction of highways.

Many of the above scholars have achieved results in the field of waterborne epoxy resin for pavement materials, and developed polymer-modified cement-based materials that can improve pavement performance. However, the research is insufficient, the comparison of different preparation processes is not systematic, the long-term and complex environmental performance research is scarce, and the micro and macro correlation research is weak.

Application of water-based epoxy resin-modified cement based materials in well cementing

Due to the growing demand for natural gas and oil in China, the depth of oil and gas wells has reached several thousand meters in recent years. In order to withstand the challenging conditions of the downhole environment,

which is known for its elevated temperature and pressure, it is necessary to use cementing materials that possess exceptional strength, permeability, toughness, and longevity. Presently, epoxy has garnered significant attention in the cementing sector for its exceptional mechanical qualities and resistance to corrosion [69, 70] Due to the diligent work of numerous researchers, notable advancements have been achieved in enhancing the mechanical characteristics of aqueous epoxy resin and cement composites used in cementing applications.

Progress of research at home and abroad

Yue Lei [33] examined the hydration process, micromorphology, hydration products, and corrosion resistance of resin-cement pastes made from two epoxy resins (N1 and N2) at temperatures of 30 °C, 70 °C, and 150 °C without the presence of a curing agent. The findings indicate that the inclusion of epoxy resin does not alter the cement hydration process. Furthermore, the impact of N1 resin on cement hydration is more significant compared to N2 resin. The primary hydration products of the modified cement remain predominantly $\text{Ca}(\text{OH})_2$ and CSH gel. Additionally, the epoxy resin is present in the form of an epoxy film within the cement structure, effectively filling the internal pores. The addition of epoxy resin can enhance the corrosion resistance of cement stone and bolster its strength. In their study, Song et al. [71] examined the impact of incorporating aqueous epoxy resin and hardener on the mechanical characteristics of oil well cement stone. The findings demonstrated that the addition of 60% aqueous epoxy resin to cement stone resulted in a substantial 47% enhancement in compressive strength and an impressive 98% improvement in tensile strength over a period of 28 days, as compared to oil well cement stone. Microstructural analysis revealed that an elevated concentration of aqueous epoxy resin enhances the strength and hardness of the cement stone. Li and colleagues examined the impact of incorporating aqueous epoxy resin on the physical characteristics of oil well cement [72]. The experimental findings indicated that the flowability of cement, when mixed with waterborne epoxy resin, remained similar in comparison to unaltered cement. However, the modified cement mixture, containing 10% waterborne epoxy resin, exhibited a significant 52% increase in shear strength of cementite after 24 hours. Gretz and Plank [73] and other researchers conducted studies involving the addition of epoxy resin to oil well cement. The results shown that this addition prolongs the hydration process of the cement and reduces the formation of hydration products. Consequently, the likelihood of early cement cracking is effectively reduced. FERNANDEZ.R [74] investigated the performance of resin cement slurry using varying quantities of waterborne epoxy resin. The experimental findings demonstrated that the addition of 10% resin content to the cement stone resulted in a remarkable 142.2% enhancement in compressive strength and a significant 124.8% improvement in tensile strength after

28 days, as compared to the unmodified slurry. The introduction of epoxy resin caused a delay in the process of cement hydration, nevertheless, the resulting products of hydration remained unaltered. Moreover, it greatly enhanced the pore structure of the cement stone used in oil wells. Wang [75-77] and colleagues conducted a study on the doping of uncured epoxy resin into oil well cement slurries. They discovered that increasing the quantity of epoxy resin enhanced the mechanical properties of cementite. However, insufficient doping resulted in a decrease in the elastic modulus and compressive strength.

The incorporation of epoxy resin into cement system can improve the strength, toughness and corrosion resistance of cement stone, change the hydration process without changing the main hydration products, and optimize the pore structure. The research mainly focuses on specific scenarios such as oil well cement, lacks the comparison of epoxy resins with different preparation processes, and lacks in-depth research on long-term performance and micro-macro correlation mechanism in complex environments.

Conclusions

Water-based epoxy resin is a polymer that consists of at least two epoxy groups in each molecule. It is used in modified cement-based repair materials to provide high strength, strong adhesion, low shrinkage, and excellent corrosion resistance. This material has great potential for use in structural reinforcement repair projects in the construction field. However, there are still several shortcomings that need to be addressed. Future research should focus on overcoming these shortcomings, which can be summarized into seven main research directions.

(1) The research will also focus on the anti-aging and service life extension of aqueous epoxy modified concrete during construction.

(2) Further study is required to determine the most suitable polymers for diverse building applications, with the aim of selecting more cost-effective options.

Waterborne epoxy resin modified cement-based materials should be evaluated in terms of their potential for energy conservation and environmental sustainability.

(4) Investigating the underwater repair operation of aqueous epoxy resin modified mortar is a promising research avenue.

(5) Investigating the design direction of performance structure in polymer cement based materials.

(6) Investigating the impact of cement on the performance of water-based epoxy resin modified mortar.

(7) In engineering practice, the objective is to examine how the strength of the base to be restored affects the bonding performance of aqueous epoxy resin modified cement based materials.

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