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# Study on the effect of waterborne epoxy resins on the performance and microstructure of cement paste

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## HIGHLIGHTS

- The morphology studies of resin networks and pore structures on three-dimension.
- The chemical and mineralogical study of cement paste with two types of waterborne epoxy resins.
- The chemical and fracture model of NEP and EEP modified cement is provide.
- Elaborated how the crystal size and content of $Ca(OH)_2$ are affected.

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## ABSTRACT

Concrete repairing, rehabilitation and prolonging the effective service-life of structures plays an important role in building field worldwide. The polymer-modified cementitious material dominated by different resins has been widely applied in repairing and reinforcing, wherein the epoxy resin is a material with excellent comprehensive properties. The waterborne resin gets a better compatibility and coupling effects with the cement hydration. In this paper, the effect of two waterborne epoxy resins on the hydration of cement and the microstructure of paste have been studied. The mechanical properties, mesoscopic morphologies after mixing and curing, the hydration products, chemical bonds and three-dimensional structures of the cement paste with emulsion type epoxy resin (EEP) and non-emulsion type epoxy resin (NEP) (with content of 5%–80% wt.) are studied by optical microscopy, field emission scanning electron microscopy, X-ray diffractometer, Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray computed tomography. The results show that EEP and NEP have a significant effect on the formation of portlandite crystals at an early stage. NEP is more effective than EEP on the toughening effect with the content of 40% wt. The stress–strain curve of non-emulsion epoxy cement paste (NEPC) manifests an obvious secondary step, and the fracture strain value rises from 0.6% to 1.2–1.3% which proves the NEP enhances the resistance to cracking. The resin in NEPC mainly consists of a layered network structure with the continuous phase in the transverse direction.



## 1. Introduction

Cement is always playing an important role as a construction material because of its excellent cost-effective ratio and good moldability in the architectural history. On the other hand, however, the structural characteristics of cement also bring the construction a disadvantage which is brittle to strain or deformation [1,2]. The deterioration of concrete and occurrence of cracks often appear in stress concentration areas (steps, joints, edges and corners etc.) as well as the cyclic deformation zone (sections exposed to the corrosive environment, freezing and thawing, pavements, decks and wharfs etc.). Concrete repairing and prolonging the useful service-life of reinforced concrete structures is an important issue in building field worldwide [3]. In 2007, more than $9 million for damage reparation of MacArthur Maze bridge, which included $4.3 million for demolishing and about $2 million for traffic control has been spent by US government. It has taken 26 days to finish all the construction work and reopen the Maze to the traffic. The total economic impact to the San Francisco Bay Area has been evaluated for $6 million a day [4,5]. However, the conventional cement-concrete material reparation is limited by the brittleness, poor

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cohesiveness and impermeability of the material itself, this issue, therefore, cannot be solved economically and fundamentally [6–8]. To achieve a higher ductility and cohesiveness of mortar and concrete, researchers have proposed a variety of methods, such as using reinforcement steels, blending fibers or polymers [9–11]. A systematic and holistic approach to durability must place equal emphasis on the structural design, selection of materials, mixture proportions, and processing methods that protect the soundness of a concrete structure in the exposure environment [12]. The polymer-modified cementitious material dominated by different resins has been widely applicated in building and construction repairing, wherein the epoxy resin is a material with excellent comprehensive properties [9,13]. As its molecule is with a variety of active groups, for instance, hydroxyl and epoxy groups, epoxy resin can react or well integrate with many other synthetic resins. Besides, the functional groups show different properties. For example, carbon chain shows flexibility, methyl shows toughness, ether bond shows chemical resistance, benzene ring shows heat resistance and hardness, and hydroxyl shows adhesive properties etc. [14–17]. In addition, incorporation of resins in cement based material has also been reported a certain extent of improvement in workability e.g. fast setting (which eliminate the need for road plates), wide temperature range (some of them are below freezing point), minimal failures, adhesive to most materials and good durability [18–20].

Although the addition of resin into cement-based materials can bring a variety of excellent performance, limited by the inherent characteristics of the resin, the use of resins still exposes many problems which are shown as follows:

1. Cost. Resins are much more costly than cement.
2. Mixing and handling. When the single or multi-component resins are mixed with cement, the condensation time, fluidity, viscosity control and cleaning process is relatively complex.
3. Safety. Since the resin is generally solvent-based polymer which is flammable, explosive and with high VOC content etc. [21], largely using resin in construction will bring considerable adverse impacts on the transportation, the environment and the health of workers.
4. Coupling effects. Polymer and cement-based materials are incompatible, the solvent which will affect the cement hydration. Thus, the chemical reaction still need to be further studied.

In order to solve the above problems, waterborne resins have been invented to reduce flammability and toxicity [22,23]. In general, waterborne resins are modified-resins with hydrophilic groups, in the form of particles of different size, dispersed in the water as a continuous phase (which are mostly emulsion). Much of the literature focus on the influence of resin on hydration and carbonation of cement. Kong et al. investigated the interactions between styrene-acrylate emulsions and cement with emphasis on the charge properties of the polymer particles, which showed that the polymer emulsions retard cement hydration by delaying effect represented by a delayed hydration peak and the slowing down effect characterized by a reduced main hydration peak during the acceleration period [22]. M.U.K. Afridi et al. studied morphologically the effects of carbonation on $Ca(OH)_2$ crystals in unmodified mortar and polymer modified mortars (PMMs) and conclude that $Ca(OH)_2$ crystals formed in unmodified mortar were weak, unable to withstand stresses generated due to carbonation-related shrinkage and therefore cracked on exposure to $CO_2$ [24]. Emulsion modified cement paste systems show that the hydration of cement is delayed while a certain amount of $Ca(OH)_2$ are generated and hydrolysis and crosslinking in the high alkaline environment are further reacted [24,25]. For the mechanical properties, it is commonly reported that the elastic modulus, ductility and flexural properties of polymer modified cementitious material are significantly improved, while the results of compressive strength are different [26,27]. Additionally, epoxy resin is suitable to polymer-cement paste system because usually when the concentration of epoxy groups is lower than the one of NH groups, side reactions do not occur. The epoxy-amine reaction is, therefore, suitable for the synthesis of model networks and furtherly to improve the compatibility with the cement matrix [19,28].

In the existing literature, most of the waterborne resins, especially waterborne epoxy resins, have been studied around the emulsion type, while few studies have been conducted on the non-emulsion type waterborne epoxy resins. Compared with non-emulsion, the emulsion has a simpler preparation process, but the shelf life is shorter (2 years for non-emulsion and less than 1 years for emulsion) and the storage environment has higher requirements. Besides, the morphology studies of resin networks and pore structures so far focused mainly on two-dimension [29]. Therefore, in this study, two different types of waterborne epoxy resins (emulsion type and non-emulsion type) have been added to the cement paste with different contents. The mechanical properties, mesoscopic morphologies after mixing and curing, hydration products, chemical bonds and the three-dimensional structures of the different substrates are studied by optical microscopy, field emission scanning electron microscopy (SEM), X-ray diffractometer (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-ray computed tomography (X-CT).

## 2. Experimental

### 2.1. Materials

The materials used in this study were Portland cement 52.5 type and two different waterborne epoxy resins which were emulsion type epoxy resin (EEP resin) and non-emulsion type epoxy resin (NEP). The emulsion type epoxy resin matches with the polyamine curing agent (CA-e) while non-emulsion type epoxy resin matches modified complex compounds of multi-phenol curing agent (CA-n). Both two epoxy resins are bisphenol A diglycidyl ether type epoxy resin and water soluble after mixing with the corresponding curing agent (shown in Fig. 1a). The superplasticizer used in the experiments is a polycarboxylic acid type water reducing agent with water reduction of 40%. The chemical composition of the cement is shown in Table 1, while the properties of the epoxy resins and hardeners are followed in Table 2 and Fig. 1(b).

### 2.2. 2Methodology

#### 2.2.1. Mix proportions

Firstly, the cement and water were mixed with a constant water to cement (W/C) ratio of 0.29 into a paste (1% wt. of superplasticizer was dissolved in water in advance). Then, epoxy resin was mixed with the matched curing agent into a mixture. Secondly, resin mixture was mixed with paste with different polymer to cement (P/C) ratios by weight immediately. Each mixing procedure was stirring for 1 min at a speed of 600 rpm. Finally, the resin-cement mixtures were poured into the molds (2 cm*2cm*2 cm and 2 cm*2 cm*8 cm respectively) and vibrated for 10 s, then placed into a curing condition of 98% RH at 25 °C. The mix proportions of samples are listed in Table 3.

#### 2.2.2. Fourier transforms infrared spectra (FTIR) and Raman spectroscopy

FTIR of 7d and 28 d paste samples were tested by a FTIR spectrometer (Nicolet 5700) with wave number range of 400–4000 $cm^{-1}$ and resolution of 0.1 $cm^{-1}$. To conduct the FTIR, 1 mg paste