



Interfacial properties and nanostructural characteristics of epoxy resin in cement matrix



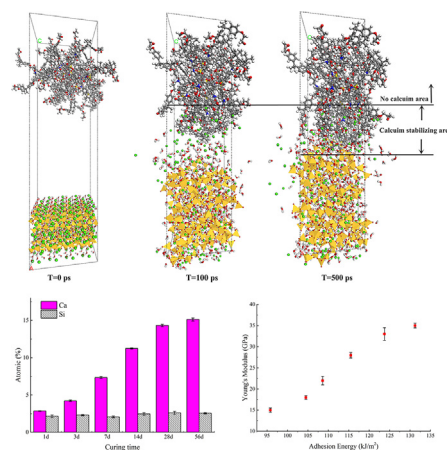
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HIGHLIGHTS

- Experimental analyses and molecular simulations were used in this study.
- Ca^{2+} ions make an electrostatic bond with hydroxyl function of resins.
- The attractive force between CSH and resin lead to an increase in Young's modulus.
- Electrostatic interaction is the main resource of adhesion energy.

GRAPHICAL ABSTRACT



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ABSTRACT

Concrete is the most utilized material all over the world. However, a vital drawback of concrete is its weak tensile properties. Thus, since 1920, many researches were focused on enhancing the tensile properties of concrete by doping resin. However, a comprehensive understanding of the mechanical performance of resin-reinforced concrete demands knowledge of resin/cement interfaces in nanoscale. In this investigation, a combination of experimental analyses and molecular simulations has been utilized to study the resin/cement interface. A novel model of calcium silicate hydrate (CSH)/resin interface was modeled according to SEM and EDX analyses. The adhesion energy of resin/CSH interface was studied at nanoscale level since adhesion energy plays an important part in the design of resin-reinforced cement composites. The relationship between Young's modulus and adhesion energy was further studied. The results show that the polarity of resin enhances the attraction of positive ions and water molecules, such as Ca^{2+} during hydration, to the resin molecules. The Ca^{2+} ions from CSH gel migrate to the interface area and make an electrostatic bond with the hydroxyl function of the resins, which is the origin of adhesion energy. Thus, the more realistic adhesion energy or even Young's modulus for resin-reinforced cement can be estimated by the actual Ca/Si ratio in CSH gel. The results are important in the further development of resin-reinforced hybrid cement composites.

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1. Introduction

Concrete, as the most utilized material all over the world, possesses great compressive strength but weak tensile performances. The cement-based concrete has an intricate structure that makes concrete a useful material as far as toughness and tensile strength, but there is room for improvement. Thus, during the past three decades, plenty of studies were concentrated on enhancing the tensile properties of cement-based concrete using a variety of chemical and physical methods [1,2]. One of the successful methods was to utilize resinous materials in concrete to achieve a composite with ductility and good tensile performance [3,4]. Nevertheless, understanding the mechanical behavior of resin-reinforced cement composite requires comprehensive knowledge of the resin/cement interface structure. Since 1920, researches of polymer-modified concrete and mortar have been conducted all over the world [5], a large number of studies have been performed on the properties of resin-reinforced cement composite [6–9]. These studies were mainly focused on the characterization of polymer under working conditions [10] and the consideration of polymer content [11], method of curing [12,13], mechanical performance [14–16] and hydration kinetics [7]. However, the structure of interfaces between resin and cement has not been studied comprehensively. Wang et al. investigated the microstructure of resin-cement interfaces using SEM photographs and found that the silane coupling agent could significantly improve interface properties of resin-cement [17]. Zhou et al. studied the debonding of concrete-epoxy interface under the coupled effect of sustained load and moisture. They developed a predictive model to describe the bond property variations of concrete-epoxy interface against long-term sustained moisture and load [18]. From nanostructure aspect, literatures [19–21] conducted molecular dynamics simulations on epoxy-concrete interfaces and founded that atomistic simulations are a powerful tool for the investigation at atomistic level to obtain adhesion energy. In the atomistic model that they built, they considered silica as concrete due to the aggregates and gluing cement hydrate all containing silica. Nevertheless, the main hydration products of Portland cement are CSH gel and portlandite, thus, the effects of Ca^{2+} ions should be considered.

This paper presented a combined numerical and experimental study on the interfacial properties of resin/cement interfaces. The atomistic model of resin/CSH interface was built using molecular dynamics (MD) method and was verified by experimental data. Since the CSH gel constitutes the most part of the final structure and is responsible for the high strength of cement-based materials [22], the influence of portlandite was not considered. During the past ten years, there were plenty of experimental investigations on CSH gel structure. In a study by Allen et al., X-ray scattering data and small-angle neutron were used to measure the solid density ($d = 2.604 \text{ mg/m}^3$) and mean formula $((\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_{1.8})$ of the nanoscale CSH gel [23]. Uzun et al. investigated the atomistic structure of CSH gel using X-ray diffraction (XRD). They suggested that CSH gel is a jennite-like structure which evolved from a tobermorite-like structure [24]. Besides, the understanding of chemical reaction occurring in CSH is very important to model the molecular structure of cement at nanoscale. Therefore, many researchers have attempted to investigate the structure of CSH gel at atomistic level [25–27]. For that matter, different methods were used to build the atomistic model of CSH gel for the sake of understanding its nanoscale properties [28,29]. Pellenq et al. constructed a molecular structure for CSH gel $((\text{CaO})_{1.65}(\text{SiO}_2)(\text{H}_2\text{O})_{1.73})$ with the stoichiometry method [30]. Bauchy et al. proposed a more realistic CSH model which based on the tobermorite crystalline [31].

There are also many experimental investigations on resin chemical properties. Fan and Yuen precisely predicted the glass-transition temperature (T_g) of an epoxy resin using MD simulation [32]. Komarov et al. utilized coarse-grain MD simulations and illustrated that T_g increases with increasing cross-linked density of resin [33]. Li et al. performed MD simulation for characterization of the thermal response of a thermoset resin, and investigated T_g and Young's modulus [34–36]. Okabe et al. recently proposed a novel curing simulation method based on MD simulation, which can reproduce curing characteristics, depending on combinations of curing agents and base resins [37].

Based on these researches, a reasonable cross-linked structure of resin was modeled in this paper to investigate the resin/cement interface properties. SEM and EDX analysis methods were carried out to create a new atomistic structure for CSH gel and its interface with resin materials. The proposed structure was analyzed and was investigated by MD simulation. The generated nanostructure of CSH utilizing the proposed model was verified by the previous nuclear magnetic resonance spectroscopy studies. Finally, the nanostructure adhesion mechanisms between resin and a layer structure of CSH gel were studied. The Ca^{2+} stabilization effect of resin and its mechanism were reported.

2. Materials and methods

In this research work, we proposed a molecular model for complex CSH gel, especially at the resin/matrix interface, with the assistance of SEM/EDX analysis. We then investigated the adhesion energies between CSH gel model and resin to understand the overall properties of resin/cement composites.

2.1. Experimental methods

2.1.1. Resin characteristics

The resin is composed of Bisphenol-A epoxy resin (BPA). The chemical structure of BPA is shown in Fig. 1a. The number of epoxy group at BPA is two, and its molecular weight is 340 g/mol. The curing agent used in this study is 4,4'-sulfonyldianiline (Fig. 1b), which molecular weight is 248 g/mol [38]. The cross-linking mechanism is shown in Fig. 2. In each epoxy group, the C—O—C bond must be broken to generate a reactive $-\text{CH}_2$ site. The $-\text{CH}_2$ site is able to cross-link with curing agents [39,40]. In the combination of curing agent and resin, the covalent bonds formed between N and C atoms due to the molecules changing their locations under proper states. If all of the potential covalent bonds are made, a 100% cross-linking density will be achieved. Although in real reactions, the cross-linking density is typically less than 100% [41].

2.1.2. Resin-reinforced cement paste

The resin-reinforced cement paste composites used in this research were manufactured by blending resin, cement powder and water to obtain homogeneous mixtures. The mixture was prepared with a specific dosage of resins for a specific composition of cement. The resin was synthesized by incorporating bisphenol-A epoxy resin and 4,4'-sulfonyldianiline at a specific ratio of 4:1. The cement was provided by Sichuan Jiahua Corporation, China. Bisphenol-A epoxy resin and polyamine epoxy curing agent were obtained from Shanghai Coating Corporation, China. The preparation of the cement paste samples is as follows: First, the weight of epoxy resin, curing agent, cement and water is measured in different vessels. Second, the epoxy resin and curing agent are mixed at a stirring rate of 2000 rpm for 60 s; while the blender is running, water is gradually added to resin solution and mixing for 60 s. After that, cement is added, and another 90 s at a rate of 4000 rpm to

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