Polymers As Concrete Healing Materials

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Abstract: Concrete is commonly used as a supporting material in the construction industry. Although it can withstand heavy loads, it is very brittle and sensitive to crack formation. Earthquakes and other environmental factors may result in the formation of cracks in the concrete structure. Penetration of chloride and atmospheric water with dissolved oxygen and carbon dioxide gasses through these cracks leads to corrosion of rebar (reinforcing steel bars). This paper is a short review of polymeric structures as concrete healing materials.

Keywords: Concrete healing, Autogenous healing, Autonomous healing, Encapsulation, Vascular approach.

1. INTRODUCTION

The fact that concrete is one of the most preferred construction materials was reflected by the global production volume of cement, which was around 4.1 billion metric tons in 2022 [1]. Its high stiffness and compressional strength, ease of production, and availability of raw materials make concrete a favorable material for buildings [2-4]. On the other hand, highly brittle characteristics of concrete can lead to crack formation at any time during its service life [5, 6]. Besides, shrinkage failures (plastic, settlement, drying), weathering, thermal stress, or various factors contribute to crack development [7-10]. The naked eye cannot detect microcracks, but environmental conditions, earthquakes (even small geological movements), cyclic and static loading can turn them into larger ones [11]. The number and size of the cracks increase the permeability of concrete, which is one of the critical parameters reducing its durability [12]. Chloride ions, carbon dioxide and oxygen dissolved in water lead to corrosion on the rebar, resulting in potential structural failures [13-15]. Therefore, many traditional maintenance and fixing methods have been implemented to avoid this type of degradation.

The effect of polymeric materials on crack healing was first reported by Malinskii in 1973 [16]. This approach was attracted considerable scientific attention in the last two decades [17-20]. Concrete self-healing methods are divided into two main categories, these are autogenous and autonomous methods [21]. In the autogenous approaches, self-healing is caused without any external intervention. On the contrary, autonomous approaches include addition of engineered admixture [22].

2. AUTOGENOUS HEALING APPROACHES

Crack width reduction is categorized as an autogenous healing approach since it does not require any external operation [23, 24]. An engineered cementitious composite (ECC) material was first reported by Li et al. in 1998. In this study, ECC contained high-modulus polyethylene fibers (with 28 and 38 µm diameters) for mechanical reinforcement and hollow glass fibers having 1.0 outer and 0.8 mm inner diameters, which was filled with ethyl cyanoacrylate glue as the sealing material. In this passive smart self-healing implementation, ECC's having 28 and 30 µm diameter polyethylene fibers gave 30 and 50 µm average crack width reduction, respectively [25]. Herbert and Li prepared cementitious composites with a polycarboxylate-based high range water reducing admixture (HRWRA) and polyvinyl alcohol (PVA) fibers [26]. The ECC specimens were monitored under natural environmental conditions in Ann Arbor (Michigan, USA) using resonant frequency (RF) and mechanical reloading to figure out the rate and degree of self-healing. The experiments showed that self-healing of the specimens could be retained under multiple damage events [26].

Superabsorbent polymers (SAP) are slightly crosslinked and highly hydrophilic three-dimensional network structures that they can absorb 4000 times their own masses [27, 28]. SAPs can retain and slowly release water in their pores and release water slowly to reduce self-desiccation shrinkage in hardening process [29]. In this method, SAP-containing slurry mixture is casted using conventional methods. SAP materials in the slurry swell slightly due to high pH (12.5-13) and ionic strength (100-450 mmol L\(^{-1}\)) [30]. It is thought that...
acrylate groups in SAPs can form bidentate complexes with calcium ions in the cementitious mixture, limiting their swelling [31-33]. In the hydration process of the cement, SAPs release the absorbed water and then shrink, producing a porous structure with pore sizes between 10 and 100 micrometers [34]. These pores, which can be regarded as macrodefects, may cause formation and propagation of cracks through them. On the other hand, when the concrete is exposed to water with low ionic content, the SAPs swell much more than they do in the cementitious slurry. The SAPs enlarge beyond the pores and penetrate the cracks. Therefore, the cracks are filled with swollen SAP and further diffusion of water is prevented. Besides, SAPs may prevent enlargement of cracks and promote autogenous healing of the concrete [34].

Kim and Schlangen prepared an ECC using Portland cement, fly ash, limestone powder, water, super plasticizer, PVA fibers (2% by volume) and SAPs. Three cementitious mixtures were prepared in three groups with different SAP contents (0%, 0.5%, and 1% by weight) and casted into molds. The control group specimens were tested in four-point bending experiments up to final failure on the 7th and 28th day after casting. The test specimens were subjected to 2mm vertical deformation on the 7th and 28th day after casting. In these preloading tests, the average crack width in the SAP-containing samples was smaller than none-containing ones. Then, samples were cured in 9 wet-dry cycles (1 hour wetting and three days drying) or lab air condition for 28 days. The cured samples were tested to failure. The four-point bending test results showed that the flexural strengths of the cured SAP-containing specimens were higher than those of the non-containing ones. The contribution of SAPs to the flexural strengths of the specimens were more profound for the water-cured samples [35].

Snoeck et al. used cross-linked polyacrylate potassium salt as SAP material (1%, 2%, and 4% by weight of the cement) [36]. The other ingredients of the cementitious mixture were ordinary Portland cement, fly ash, silica sand, a polycarboxylate superplasticizer, and PVA fibers (2% by volume). The samples were deformed 28 days after casting by applying flexural stress on a four-point bending test equipment up to 7 mm vertical displacement, where the PVA fibers reached their maximum strain. The first-cracking strength of the sample having 1% SAP gave similar results with the reference sample having no SAP. Whereas the increasing amount of SAP in the mixture had adverse effects on the flexural strength of the samples due to a decrease of the surface area. The cracked specimens were cured at three different conditions for 28 days: exposing to wet/dry cycles, storing in air at relative humidity of 60% or 90%. When the samples were subjected to aqueous environment during wet/dry cycles, SAP-containing samples demonstrated better self-healing ability than the reference sample without SAP. Besides, the degree of self-healing in terms of regain in peak strength increased as the content of the SAP was increased and reached up to 120% for the samples having 4% SAP. The enhanced self-healing was attributed to internal curing due to further hydration and precipitation of CaCO₃. The precipitation of CaCO₃ was facilitated by PVA microfibers and cracks with up to 138 micrometer width were closed completely. Furthermore, exposure to an environment with relative humidity of 90% and 60% resulted in self-healing of SAP-containing samples. Whereas the reference specimens didn’t show any self-healing in humid environments.

3. AUTONOMOUS HEALING APPROACHES

Autonomous self-healing approaches require addition of additives and use of specific techniques to transfer them into cementitious mixture.

3.1. Encapsulation

Encapsulation is one the most used method to transfer healing agents into the concrete matrix [37]. There are some basic requirements for the capsule materials and healing agents. The shell of the capsules should be compatible with the chemicals inside the capsules and with cementitious mixture and withstand external mechanical effects during concrete preparation and casting [38, 39]. When concrete was exposed to crack generating flexural or compressional stress, the capsules should be broken, and the healing material should be released into the cracks. The healing agents in the capsules should have adequate viscosity to allow their penetration through the cracks and to prevent their leakage from the concrete during curing [40, 41]. The efficiency of encapsulation healing mechanism depends on the capsule diameter, shell thickness, and surface texture [42].

The use of encapsulation method for self-healing of concrete was reported by Carolyn Dry in 1994 [43]. In this study, methyl methacrylate monomer in hollow porous polypropylene capsules was used as the healing agent. The monomer was released into the voids and cracks upon slight heating of concrete. The heat was increased, and methyl methacrylate
polymerized, resulting in the increased flexural strength of the concrete. Li et al. [25] and Joseph et al. [42] employed cyanoacrylate adhesive as the healing agent and glass fibers and reservoirs, respectively, for the encapsulation purposes. Van Tittelboom et al. [44] and Karaïkos et al. [45] employed polyurethane-based healing material and glass or ceramic cylindrical capsules.

The composition and shape of the capsule is very important. The capsules with too thick and flexible walls may not break when some cracks develop around them. On the other hand, thin walls or ones made from fragile materials may rupture while preparing the cementitious mixture before the formation of cracks. White et al. prepared urea-formaldehyde capsules filled with dicyclopentadiene (DCPD) monomer via standard microencapsulation techniques [46]. The cementitious mixture contained Grubbs’ catalyst which shows high metathesis activity. Besides, it has high tolerance towards a wide range of functional groups as well as oxygen and water [47–49]. The shells of the capsules provided a protective barrier between the Grubb’s catalyst and the monomer during the preparation of the composite.

Dong et al. [50] developed a model work to simulate effect of shell thickness on the release rate of the microcapsules. The microcapsules contained sodium monofluorophosphate and microcrystalline cellulose were mixed into Polysorbate 80. The microspheres were prepared via extrusion–spheronization method. Then, polystyrene microcapsules with different thicknesses were formed around the microspheres by spray drying. The authors used Ca(OH)₂ solutions at different pH levels to simulate a cementitious environment. They reported that the microcapsules are promising for achieving smart release control in alkaline media. Mostavi et al. produced microcapsules with double shell layers using polyurethane and poly(urea-formaldehyde) resins to prevent encapsulation failures during concrete mixing. Inside the shells, sodium silicate was contained as the healing material [51].

3.2. Vascular Mechanism

Vascular approach is another elegant method developed for self-healing of concrete. In this method, very thin hollow tubes or tubular networks have been used to transfer healing materials to the vicinity of cracks, like vascular system in the human body [52, 53]. Since they are provided from an external system by human intervention, multiple healing agents can practically be used [43, 52]. The vascular approach was first proposed by Dry in 1994 [43]. Polypropylene fiber tubes had been installed in the concrete before it was hardened. Then, cracks were developed intentionally, and methyl methacrylate monomer was drawn into the tubes, therefore into the concrete, by a vacuum system. Then, concrete was heated mildly and the wax around the tubes is melted, letting the monomer to diffuse into the cracked concrete. Finally, the temperature was increased to polymerize the monomer. The method reported by Nishiwaki et al. does not require human intervention [54]. This approach included the use of RuO₂-containing sintered electrically conductive paste and organic film pipe with healing agent inside. When a crack developed by an applied stress, the conductive material near the crack was deformed and electrical conductivity was reduced. Then, electrical resistivity was increased and temperature around the crack was risen depending on the magnitude of the injected current. When the organic film pipe was heated, the healing material was released to the cementitious mixture.

4. CONCLUSION

The self-healing of the cementitious matrix is a very complex phenomenon, involving chemical and physical processes. Healing of concrete occurs via combination of various pathways. The hydration of un-hydrated materials, increase in their volumes and then make bonding with the crack walls, reducing the void space and thus water permeability. The healing efficiency of the methods depends on both chemical and physical interaction between cementitious matrix and the healing agents. Mechanical tests are not efficient enough to understand what is happening inside the cracks. Therefore, reproducibility of the applied healing techniques is rather limited.

REFERENCES


