Properties and Performance Metrics of Healing Agents in Self-healing Concrete

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1 Introduction

Concrete is made up of hydraulic cement, water, aggregate, chemical admixtures, and mineral admixtures. The hydraulic cement reacts chemically with water to form an adhesive product that binds the aggregates and forms concrete. During this process, early-age concrete is susceptible to very narrow and shallow cracking due to chemical shrinkage, volumetric instability, and improper placement, finishing and curing. Cracked concrete allows gases, liquids, and other deleterious materials to enter the concrete core which in turn exacerbate concrete deterioration [36]. Therefore, healing or sealing the cracks is necessary to mitigate the occurrences of concrete deterioration mechanisms.

Many methods have been developed for repairing cracks in concrete. They include crack injection by epoxy or other polymeric materials, routing and sealing, embedment of additional reinforcement, grouting by cement or chemical grouts, or overlay and surface treatments [1, 2, 47]. The main drawback of these repair methods, besides compatibility requirements and durability, is the timing of the repair. For example, concrete bridges and retaining walls are on average inspected every two years, and fine cracks less than 0.3 mm are considered too small to be affecting the performance or durability of concrete [29]. However, field experiences have shown that these fine cracks lead to many of the observed concrete deterioration mechanisms. Therefore, there is a need for an active concrete repair system.

Concrete intrinsically heals itself as a result of chemical reactions between the unhydrated cement and water, calcium hydroxide and dissolved carbon dioxide, the

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S. Walbridge et al. (eds.), *Proceedings of the Canadian Society of Civil Engineering Annual Conference 2021*, Lecture Notes in Civil Engineering 248,
https://doi.org/10.1007/978-981-19-1004-3_34

recrystallization of calcium hydroxide, and/or the precipitation of calcium carbonates [38]. In addition to the autogenous healing, autonomous healing can be incorporated by means of an extrinsic healing system within the concrete matrix. The extrinsic healing can be achieved by adding cementing materials, microorganisms, or other healing agents that react chemically with the cementitious matrix. However, autonomous healing material needs to be protected from the harsh concrete conditions during mixing and released upon crack propagation inside the cementitious matrix. Storage medium in the form of a vascular network [30, 42] or protective capsules [3, 12, 14, 18, 28] has been employed. Encapsulation is the process where an active agent is coated by a polymeric shell. The healing agent is therefore sealed and only released once the capsules are ruptured by propagating cracks [6, 35]. Healing by microencapsulation provides a localized response when the crack propagates inside the concrete matrix, provided that the microcapsules are uniformly distributed inside the matrix [28], and the microcracks are limited to width less than 0.2 mm [16]. Encapsulation is a promising approach that has been adopted recently by many researchers in the concrete industry. However, it is important to understand the properties of the capsule shell and the healing agents along with the bond between them, and the compatibility between the healing agent and the cementitious matrix before applying this approach. This study focuses on the healing agents, specifically on developing metrics for selecting suitable healing agents, that form part of self-healing concrete systems, based on their rheological, chemical and mechanical properties.

2 Properties of Healing Agents in Self-healing Concrete Systems

The key for a successful self-healing system is highly influenced by the selection of the healing agent. Zwaag [49] defined the "ideal" healing agent as the material that is compatible with the cementitious matrix, cost-effective, and can heal the cracks completely, multiple times, and autonomously. According to Hilloulin et al. [17] and Mostavi et al. [31], the healing agent should not leak out of the capsule's shell during its shelf-life, while maintaining enough strength and compatibility with the cementitious matrix to ensure rupturing only upon cracking. Dry and McMillan [11] considered that a good healing system must have a long shelf-life, resistant to high temperatures, and must have low viscosity to flow easily into cracks and high strength enough to repair these cracks. In addition, the healing agent must form a sufficiently strong bond between the crack faces. Polymeric healing agents have been widely used in cementitious self-healing systems recently and showed very promising results in terms of healing efficiency due to their compatibility with the cementitious matrix and their flexible properties. Different polymeric materials have been encapsulated in polymeric shells through in-situ polymerization or glass tubes and used in several self-healing cementitious materials applications as listed in Table 1.

Table 1 Common healing agents used in self-healing cementitious systems

Healing agent	Encapsulation system	Shell material	References
Epoxy resin	Two-component	Urea–formaldehyde (UF)	[5, 8-10, 32, 45, 46]
	Two-component	Melamine urea–formaldehyde (MF)	[21, 23]
	One-component	Glass	[40]
Cyanoacrylates (CA)	One-component	Glass fiber	[22]
	One-component	Borosilicate glass	[19, 20]
Methyl methacrylate (MMA)	Three-component	Glass	[11, 41]
	Three-component	Ceramic	[41]
	Two-component	Polystyrene (PS)	[48]
Dicyclopentadiene (DCPD)	Two-component	Urea–formaldehyde (UF)	[15]
	Two-component	Poly(phenol–formaldehyde) (PF)	[24, 25]
Polyurethane (PU)	One-component	Glass	[4, 18]
	Two-component	Glass/ceramic	[26, 43]
	Two-component	Polystyrene (PS)	[17]

For achieving high self-healing efficiency, the properties of the healing agents, specifically the rheology and chemical reaction, i.e., the flow and curing properties, and the mechanical properties, i.e., the tensile strength, the stiffness, and the bond strength with the cementitious matrix need to be examined and compared to those of early age concrete. The metrics are established based on mechanical compatibility and fillability requirements.

2.1 Rheology and Cure Kinetics

The cure kinetics and the viscosity of the healing agent control its ability to flow and fill the crack opening. Viscosity of the healing agent should be low enough to fill the multiscale cracks but not too low causing it to leak from the capsule shell before cracking [19, 43]. For instance, Methyl Methacrylate has a very low viscosity that can fill very small cracks due to capillary action [48]. However, without adding thickening agent such as Polymethyl methacrylate (PMMA), it is difficult to avoid leaking from the crack [11, 41]. Similarly, Dicyclopentadiene (DCPD) has a low viscosity (<1 cPs) and requires a curing agent to initiate curing [15]. On the other side, Polyurethane (PU) has a very high curing rate and a very high viscosity (~600 cPs), thus completely filling the cracks before it hardens is difficult. [18] used a ratio 1:5 acetone to PU to reduce the viscosity to 268 cPs. The polymers' cure kinetics need to be compatible with the viscosity. If the healing agent cures rapidly,

Table 2 Flow and curing properties of polymeric healing agents

Healing agent	Viscosity (cPs)	Curing mechanism	Curing time (h)	References
Epoxy resin	250–400	Air cured	3–6	[34, 40]
Cyanoacrylates	1–10	Air or water cured	24	[19, 20, 22]
Methyl methacrylate	0.6–1	Air cured	0.5–1	[11, 41, 48]
Dicyclopentadiene	<1	Air cured	–	[15]
Polyurethane	300–800	Air or water cured	24	[17, 18, 26, 43]

it can result in a weak and discontinuous bond between the healing agent and the concrete surface. The properties of the polymeric healing agents commonly used in self-healing cementitious materials are reproduced in Table 2.

2.2 Mechanical Properties and Bond Strength with the Cementitious Matrix

The mechanical properties of the hardened healing agent are essential to ensure that the stiffness and the tensile strength are both compatible with those of the cementitious matrix to avoid re-cracking at the location of the repaired crack. Few studies considered evaluating those mechanical properties in self-healing concrete applications as listed in Table 3. In addition, the tensile strength of the healed crack should be greater than that of the surrounding concrete matrix, i.e., the bond strength being greater than the surrounding concrete mitigates the reopening of the crack. Epoxy, cyanoacrylates (CA) and Methyl Methacrylate (MMA) bond with concrete are typically examined visually using Scanning Electron Microscopy (SEM). Van Tittelboom et al. [41, 43] used MMA and noticed new cracks occurring at the repaired location which is evidence of a weak bond. Few studies tested this bond experimentally. [4] used axial tensile tests to evaluate the bond between PU and mortar. The bond strength ranged from 1.21 to 1.48 MPa, which is considered a "good" bond according to the interfacial bond strength criteria established by Sprinkel and Ozyildirim [39].

Table 3 Mechanical properties of common polymeric healing agents

Healing agent	Tensile strength (MPa)	Elastic Modulus (GPa)	Elongation (%)	References
Epoxy resin	22	4.00	79	[23, 34, 40]
Cyanoacrylates	20	1.26	2–3	[19, 20, 27]
Polyurethane	2	–	550	[18]

2.3 Effect of Cement Hydration on the Healing Agent

Thao et al. [40] evaluated the effect of concrete curing temperature on the hardening reaction of epoxy resin. The encapsulated epoxy samples were heated gradually in a water bath up to 77.5 °C over a period of one week before using them in mortar samples. The results showed that the bond strength is still higher than the surrounding matrix and that no visible cracks were observed after heating. Van Tittelboom et al. [41, 43] injected two-component MMA healing agent in cracked mortar samples and cured the samples for 14 days in a high pH environment. The samples were subjected to a three-point-bending test after 14 days. The strength regain was found to decrease after 48 h which is evidence of the degradation of the healing agent due to high pH. Accordingly, the effects of concrete alkalinity and curing conditions on the stability and hardening of the healing agent needs to be evaluated to avoid any degradation in the bond.

2.4 Sealing and Healing Ability

Polymeric agents can heal, seal, or heal and seal the cracked concrete surfaces. Healing refers to restoring or upgrading the mechanical properties of the cracked concrete, and sealing implies plugging the crack without restoring the mechanical properties. For the agent to heal cracked concrete, its mechanical properties including stiffness and strength should be compatible with those of the concrete matrix in a way that both materials bond together and the load can transfer along the repaired crack [44]. However, if the stiffness and strength of the agent are less than those of the concrete, i.e., it cannot share the load, yet it plugs the crack and regain gas and liquid tightness, then the agent is considered a sealing agent. The ductility and elongation of the polymer are essential for sealing and healing. Agents that cure to form a brittle material with low elongation such as CA can be used to heal static cracks, while those that cure to form flexible or semiflexible ductile materials with low tensile strength such as PU are more efficient in sealing the cracks [37]. The literature reveals that most polymeric healing agents do not act as efficient healer, but they have a demonstrated crack bridging and sealing ability. Dong et al. [8–10] used epoxy resin and observed that the cracks were sealed through SEM images, and that high amount of nitrogen and carbon were found in the healed area. CA showed promising results as a healing agent [19, 22], however, more evidence is needed to confirm its watertightness, durability, and crack bridging efficiency. Yang et al. [48] observed partial gas permeability and strength gain when using MMA, but others questioned MMA bond strength [41, 43]. Lv et al. [24, 25] showed DCPD sealing ability in barring the ingress of aggressive aqueous chemicals into the cementitious matrix. Others have identified PU as a sealing material commonly used to improve watertightness of cracked areas [26, 41, 43].

Several studies tested the durability or mechanical strength recovery of self-healing cementitious systems as summarized in Table 4. As shown, the majority focused on the mechanical strength recovery. It is worth noting that there are no standardized test method or protocol to evaluate the performance or durability of healing agents. As such, it is extremely difficult to compare the documented performance of healing agents.

Table 4 Performance evaluation of polymeric healing agents commonly used in the literature

Healing agent	Criteria	Properties	References
Epoxy resin	Mechanical properties	• Stiffness has decreased • Ultimate load has increased • Flexural strength has increased by 32%	[40]
	Mechanical properties & durability	• Compressive strength has increased by 9% • Flexural strength has increased by 3% • Chloride permeability recovery rate is 100%	[46]
	Mechanical properties & durability	• Chloride diffusion coefficient has increased by 20% • Compressive strength has increased by 10–13% • Capillary porosity has dropped by 15%	[8–10]
Cyanoacrylates	Mechanical properties	• Stiffness has increased slightly	[22]
	Mechanical properties	• Stiffness has increased • Ductility has improved • Ultimate load has increased	[19, 20]
Methyl methacrylate	Durability	• Water permeability has improved	[41]
	Mechanical properties & durability	• Gas permeability coefficient has decreased to 66.8% • Toughness has improved	[48]
Dicyclo-pentadiene	Mechanical properties	• Stiffness has increased by 30% • Compressive strength has increased	[15]
	Mechanical properties	• Compressive strength decreased by 32% • Ductility has improved	[24, 25]
Polyurethane	Mechanical properties	• Flexural strength increased up to 30%	[18]

(continued)

Table 4 (continued)

Healing agent	Criteria	Properties	References
	Mechanical properties and durability	• Capillary absorption has decreased by 50% • Strength regain is 96%	[4]
	Mechanical properties and durability	• Flexural strength increased up to 62% • Stiffness has increased up to 64% • Water permeability coefficient has decreased	[43]
	Durability	• Chloride penetration has increased by increasing crack width	[26]

3 Metrics for Selecting Healing Agents

The properties of the healing agent including its bond strength with the surrounding cementitious matrix need to be compatible with both early age and mature concrete properties. For reference, the mechanical properties of concrete with w/c = 0.39 as it ages are listed in Table 5. Of significance is the ratio of concrete stiffness at 1 day to 28 days compared to strength.

Criteria proposed in the literature to evaluate the performance of repair materials in concrete structures that were based on compatibility requirements as in Table 6, can be examined while developing the metric. By comparing the mechanical properties of epoxy resin and CA, given in Table 3, with those of the concrete, it is evident that

Table 5 Mechanical properties of concrete with w/c = 0.39 [33]

Age (day)	Compressive strength (MPa)	Young's modulus (GPa)	Tensile strength (MPa)
1	24.80	26.20	2.52
2	27.44	27.63	2.79
3	29.92	28.86	2.90
7	35.70	31.70	3.50
28	46.34	35.39	4.12

Table 6 General requirements of patch repair materials for compatibility [13]

Property	Relationship of repair material (R) to concrete substrate (S)
Modulus in compression, tension, and flexure	R ~ S
Strength in compression, tension, and flexure	$R \geq S$

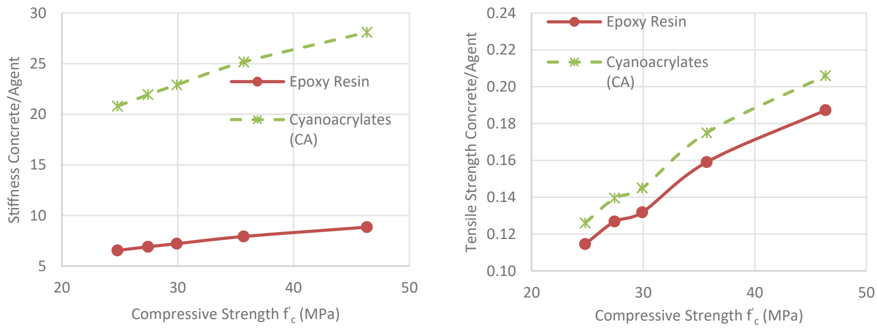

Fig. 1 Mechanical properties of concrete with age and polymeric healing agents

the tensile strength of the healing agents is much greater than that of concrete, while the stiffness is much lower. According to the criteria listed in Table 6, the healing agents do not satisfy the mechanical compatibility requirements and therefore are expected to perform poorly as repair material. Test results have shown the opposite, implying that these criteria are not transferable to self healing concrete. Since the healing occurs at the micro scale, it is preferable for the healing agent to have lower stiffness as not to attract load, and higher tensile strength and bond as to transfer the load without rupturing and debonding. Moreover, elongation of healing agent is important to accommodate movements due to environmental actions or others. Accordingly, it is recommended that the stiffness of healing agents be lesser than that of concrete, strengths including bond strength be greater than those of concrete, and elongation of the healing agents be at least twice the crack opening.

Although concrete is most susceptible to cracking at early age, it is vital that the agent provides healing throughout the concrete service life. Figure 1 illustrates the dependence of the stress at the interface between the hardened healing agent and the surrounding concrete matrix on the healing agent and the age of concrete. This implies that the properties of concrete at early age and 28 days need to be examined [7].

4 Discussions and Conclusions

This study aims to assess the performance of polymeric healing agents for the use in self-healing systems based on their rheological and mechanical properties. Qualitative assessment of the performance of the common polymeric healing agents used in self-healing system is presented in Table 7. Comparing the assessment to the suggested mechanical properties presented earlier, it can be deduced that epoxy resin has the desired mechanical properties. Moreover, the viscosity and curing time of epoxy resin are acceptable for flowing and filling microcracks. Flow rate is inversely proportional to viscosity.

Table 7 Assessment of performance of common polymeric healing agents

Healing agent	Encapsulation system	Viscosity	Strength	Stiffness	Elongation
Epoxy resin	I, II	Low	High	Low	Average
Cyanoacrylates (CA)	I	Very low	High	Low	Very low
Methyl methacrylate (MMA)	II	Very low	–	–	–
Dicyclopentadiene (DCPD)	II	Very low	–	–	–
Polyurethane (PU)	I, II	High	Low	-	Very high

The properties of cyanoacrylates and other polymers need to be modified to meet the criteria set for healing agents. Specifically, the healing agent stiffness must be lower and the strength higher than that of concrete, the elongation has to be about 100%, and the ratio of curing time to viscosity has to be large enough to ensure adequate flow rate to fill the microcracks. Moreover, the evaluation needs to consider the concrete properties at both early age and at 28 days. In conclusion, the absence of standard test methods for evaluating the performance and durability of self-healing concrete poses real challenge in developing self-healing concrete systems and that the proposed criteria are provided as a guideline.

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