PERFORMANCE TESTING OF SELF-HEALING CAPSULES IN EARLY-AGE CEMENTITIOUS MATERIAL

PERFORMANCE TESTING OF SELF-HEALING CAPSULES IN EARLY-AGE CEMENTITIOUS MATERIAL

By

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B.Sc., M.Sc.

A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree

Doctor of Philosophy

To My Parents,

Ali and Latife

Thank you for your endless unconditional love…

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TITLE:	Performance testing of self-healing capsules in early-age cementitious material
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Preface

This Ph.D. dissertation was prepared complying with the regulations of the Faculty of Graduate Studies at McMaster University for an integrated “Sandwich” thesis. The dissertation consists of 5 chapters starting with the introduction in chapter 1, followed by three distinct journal papers presented in chapters 2 to 4, and concluded with the research outcomes in chapter 5. In the subsequent paragraphs, a summary for each chapter is provided along with the corresponding research contributions.

<u>Chapter 1:</u> Presents a review of the performance of the self-healing concrete applications and the inconsistencies that drew out the objectives and motivations of this research.

<u>Chapter 2:</u> Presents a journal article titled “Performance of Capsules in Self-Healing Cementitious Material”, comprised of a review of the existing experimental and numerical studies related to the performance evaluation of self-healing capsules in cementitious material, and a finite element model developed to investigate the compatibility requirements of the capsules and concrete during concrete cracking. The paper is published in the Special Issue of *Materials - MDPI* titled "*Self-Healing Cementitious Material System*". The finite element model described in this chapter was developed by M.A. Reda in consultation with Dr. S.E. Chidiac. The paper was drafted by M.A. Reda, edited, and revised by Dr. S.E. Chidiac.

<u>Chapter 3:</u> Presents a journal article titled “Performance modelling of spherical capsules during mixing of self-consolidating concrete” aimed to evaluate the performance of capsules during concrete mixing and predict their survival rate. The paper is published in the Special Issue of *Materials - MDPI* titled "*Advanced Research Progress of Concrete*"

and is under review as of February 2023. The study's conceptualization was developed by Dr. S.E. Chidiac and implemented by M.A. Reda. The corresponding model was developed by M.A. Reda in consultation with Dr. S.E. Chidiac. The paper was drafted by M.A. Reda, edited, and revised by Dr. S.E. Chidiac.

Chapter 4: Presents a journal article titled "Performance testing of self-healing early-age concrete using restrained shrinkage" intended to evaluate the performance of the self-healing concrete system at early-age by numerically simulating the ASTM C1581 concrete's restrained shrinkage ring test considering the time-dependent concrete properties. The article is to be submitted for publication to *Cement and Concrete Composites*. The study's conceptualization was developed by Dr. S.E. Chidiac and implemented by M.A. Reda. The model was developed by M.A. Reda in consultation with Dr. S.E. Chidiac. The paper was drafted by M.A. Reda, edited, and revised by Dr. S.E. Chidiac.

Chapter 5: Provides closing remarks on the research implications and recommendations for future work.

Appendices:

Appendix A presents a conference proceeding titled "Challenges of Self-Healing Concrete Application" that summarized the recent challenges in the proposed testing methods for evaluating the properties of self-healing capsules and their efficiency in the autonomous healing system for concrete applications. The article is published in the proceedings of *"Resilient Materials 4 Life 2020 (RM4L2020)"*, Cardiff, UK.

Appendix B presents a conference proceeding titled "Properties and Performance Metrics of Healing Agents in Self-healing Concrete" intended to investigate the current polymeric self-healing agents used in concrete applications and develop a design methodology to select the suitable ones based on their application and properties. The article is published in the proceedings of the *"Canadian Society of Civil Engineering Annual Conference (CSCE2021)"*, Lecture Notes in Civil Engineering, Springer, Singapore.

Abstract

Concrete cracks are inevitable due to chemical reactions and volume changes, as well as to environmental actions and mechanical loadings. Without proper repair, these cracks allow gases, liquids, and other deleterious materials to propagate into the concrete core. As a result, healing or sealing the cracks is pivotal to mitigate the occurrence of such deterioration. Encapsulation-based autonomous self-healing has been widely investigated as a solution; however, the efficacy of this technique is highly influenced by the performance of the capsules to protect the healing agents during concrete mixing and placing, while still triggering their release when young concrete cracks.

Therefore, the objective of this study is to evaluate the performance of the self-healing capsules during concrete mixing and after hardening when the concrete undergoes volume changes due to hydration and drying. The initial stage of this research study was intended for reviewing the related literature to address the discontinuities and inconsistencies in the performance evaluation of self-healing cementitious materials. The following phases focused on testing the performance of self-healing capsules in early-age cementitious material employing fracture mechanics and finite elements techniques. The first phase focused on investigating the effectiveness of capsules in self-healing concrete at early-age providing insights into the design requirement for the success of the capsules. The second phase aimed at evaluating the performance of the self-healing capsules during concrete mixing. The correlations between the capsules' shell properties, concrete rheological properties, capsules' external forces, and capsule survival rate during concrete mixing were investigated. In the last phase, the performance of concrete containing self-healing capsules

subjected to autogenous and drying shrinkage at an early-age was evaluated by numerically simulated ASTM C1581 restrained shrinkage test. The study accounted for the time-dependent concrete's mechanical properties, and the capsule's geometrical and mechanical properties. The results of this research provided in depth understanding of the performance evaluation of self-healing capsules in cementitious material during concrete mixing and after hardening. The developed models investigated the parameters that may contribute to the performance of the self-healing capsules, which can assist in manufacturing and designing of the capsules prior to their use in self-healing cementitious material applications.

Acknowledgements

I genuinely would like to express my appreciation to my supervisor Prof. Samir E. Chidiac for all the support and guidance he provided during my PhD journey. I cannot express how blessed I feel to have such a great supervisor. Thank you for believing in my potential and providing me with a great opportunity to learn from your great knowledge, patience, wisdom, and humanity. Your continuous support and encouragement inspired and motivated me to work harder and learn smarter. I will always be proud to be a student of Prof. Samir E. Chidiac. Special thanks to my PhD committee members, Dr. Younggy Kim and Dr. Todd Hoare, for their guidance and their valuable feedback during our committee meetings. I am also appreciative to the Natural Sciences and Engineering Research Council (NSERC) of Canada for the research funding support.

To my second dad Kassem Elhalabi, my second mom Fatme Khalife, and my sister Nour thank you for all the love, care, and support you have surrounded me with. I consider myself very fortunate to have a family in Canada, who accepted me as their daughter and made me feel at home. To my mentor and brother Ahmed Yosri, my sister Shimaa Nassif, and little Laila and Nelly; thank you for always being there and for sharing every single moment with me. Thank you for believing in me and for your endless support and encouragement. To my great friend, Sylvia Mihaljevic, thank you for all the adventures and unforgettable memories we have made together. Special thanks to my dear sisters and friends who provided great support during my journey; Amany Alanany, Nourhan Hassan, Lina Elshaarawi, Nayera Waheed, May Haggag, Yara Maged, Rasha Al-Sawi, and Hana El-Gamal.

To my family, no words in this world can describe how proud I am to have the most incredible mom, Latife Abbas, and the most caring dad, Ali Reda. Without you, I would not be the same person I am today. I am grateful for all the scarifies you have made, all the prayers that lightened up my life, and all the patience in listening to my complaints all the time. To my backbone and the most caring and loving sisters, Rana, Fatme, and Zeinab thank you for your constant love, our daily talks, and for having my back through thick and thin. To my brothers, Hussein, Mohamed, and Mustafa thank you for being the best brothers one could ask for. To my childhood friend and sister who got my back my whole life, Diana Nashash, thank you for being always there for me. To my one-of-a-kind sister, Hania El-Kanj thank you for supporting me through hard and good times and understanding me without having to say a word. To my mentor and dearest sister, Eng. Anwaar El-Suraij, thank you for always being my guardian and the person whom I share every beautiful memory with. Special thanks to my brothers-in-law Daoud and Loay, and my sisters-in-law Manal, Rasha, and Amy. To my little ones; my nephews Abdelhamid, Ali Madi, Hadi, Ali Reda, and Hamza, and to my nieces Salma, Kinda, Karma, Sara, and Judy, thank you for being the light of my life and I hope I made you proud.

Finally, I would like to express my sincere appreciation for every single person who was part of this journey either by believing in me, helping and encouraging me, or remembering me in their prayers. I feel overwhelmed by the amount of love and care I have experienced in this amazing journey…

Mouna Ali Reda

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Declaration of Academic Achievement

This dissertation consists of the following research contributions:

Paper I: Reda, M.A.; Chidiac, S.E. **Performance of Capsules in Self-Healing Cementitious Material**. Materials - MDPI 2022, 15 (20), 7302. https://doi.org/10.3390/ma15207302

Paper II: Chidiac, S.E.; Reda, M.A. **Performance modelling of spherical capsules during mixing of self-consolidating concrete** – submitted to Materials – MDPI 2023, 16 (6), 2379. https://doi.org/10.3390/ma16062379

Paper III: Reda, M.A.; Chidiac, S.E. **Performance testing of self-healing early-age concrete using restrained shrinkage** – to be submitted for publication to Cement and Concrete Composites, April 2023.

Paper IV: Reda, M.A.; Guo, S.; and Chidiac, S.E. **Challenges of Self-Healing Concrete Application**. In: Resilient Materials 4 Life 2020 Conference (RM4L2020), Churchill College, Cambridge, UK, 20-23 September 2021.

Paper V: Reda, M.A.; Chidiac, S.E. **Properties and Performance Metrics of Healing Agents in Self-healing Concrete**. In: et al. Proceedings of the Canadian Society of Civil Engineering Annual Conference 2021, CSCE 2021, Lecture Notes in Civil Engineering, 248. Springer, Singapore. https://doi.org/10.1007/978-981-19-1004-3_34.

In addition to the previous publications, collaborative research was carried out that resulted in the following publications. These studies contributed to the research, yet they do not fit the research objectives.

- Guo S., Reda M.A., Chidiac S.E. Fracture of cementitious material containing spherical microcapsules. In: Resilient Materials 4 Life 2020 International Conference (RM4L2020), Churchill College, Cambridge, UK, 20-23 September 2021.
- Chidiac, S.E.; El-Samrah, M.G.; Reda, M.A.; Abdel-Rahman, M.A.E. Mechanical and radiation shielding properties of concrete containing commercial boron carbide powder, Construction and Building Materials, Volume 313, 2021, 125466, ISSN 0950-0618, https://doi.org/10.1016/j.conbuildmat.2021.125466.

Chapter 1

1 Thesis Summary

1.0 Introduction

Concrete, the most used construction material in the world, was believed to be a long-life and maintenance-free construction material [1]. However, concrete is susceptible to cracking due to chemical reactions and volumetric instability at an early age, and to environmental actions and mechanical loadings thereafter. These cracks propagate to the concrete core, providing unprotected pathways for deleterious materials. The implications have been a deteriorated built infrastructure that is costing the just USA $18 to $21 billion annually to repair or replace [2]. The "Report card" prepared by the American Society of Civil Engineers (ASCE) noted that $2.2 trillion is needed to repair and retrofit the infrastructure over five years. For Asia's infrastructure, such cost is estimated to be $2 trillion [3]. As a result, it is crucial to develop a new concrete that is either crack-free or can heal itself in the event of cracking. Many solutions have been investigated and proposed in the literature including encapsulation-based autonomous self-healing techniques. However, the efficiency of these techniques has been challenging due to the complex interactions between the capsules, healing agents, and the surrounding cementitious material. For capsules to achieve their intended function, they need to survive typical harsh conditions during concrete mixing and placing yet ensure a smooth release of the healing agents upon concrete's cracking. This study, which is numerical in nature, therefore focuses on evaluating the performance of self-healing capsules in cementitious material during concrete mixing and when concrete undergoes volume changes at an early-age. In this chapter, a summary of the current study is presented starting with the research objectives and scope, followed by a brief background focusing on the self-healing techniques, and the role of the capsules in a self-healing system. The research motivation is presented after, followed by a summary of the research contributions.

1.1 Research objectives and scope

This study aims to investigate the performance of self-healing capsules in cementitious materials. As such, numerical models employing finite elements and fracture mechanics techniques were developed to investigate the two essential roles of the self-healing capsules in: 1) surviving concrete mixing and placing conditions, and 2) rupturing due to concrete cracking, particularly due to early-age shrinkage. The developed models account for the geometrical and mechanical properties of capsules, the evolution of concrete's mechanical properties with time, and the interfacial properties between the capsule and the concrete. The scope of this study is limited to polymeric capsules in self-healing cementitious material at early-age.

1.2 Background

Concrete is made up of cement, water, aggregate, chemical and mineral admixtures. 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 cracking due to chemical shrinkage, volumetric instability, and improper placement, as well as finishing and curing. These cracks, which are narrow and shallow, are in most cases less than 3 mm wide [4]. During service, the concrete cracks when the internal stress exceeds the strength of the material. The causes can be overloading, environmental actions, and/or ground settlement. The developed cracks are generally wider and deeper than those formed at an early-age. The corresponding crack width is measured in cm. For illustration, Figure 1-1 shows the different types of cracks, along with the corresponding pattern and location.

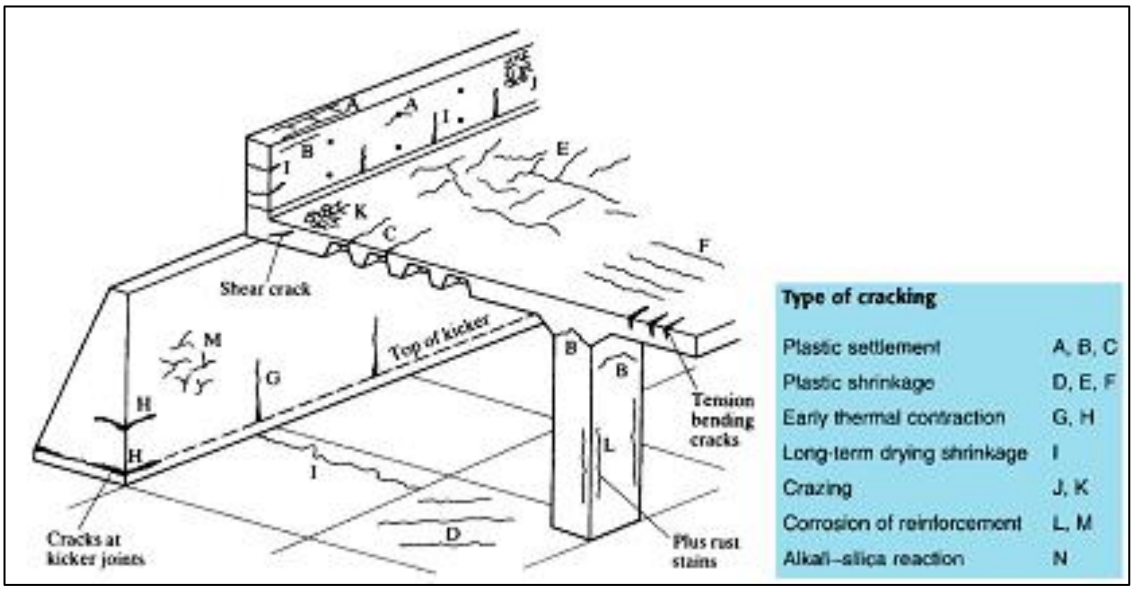

Figure 1-1 Schematic representation of the various types of cracks in concrete [5]

Although the causes of concrete cracking may differ; the consequences are nearly the same. Cracked concrete allows gases, liquids and chemicals to propagate into the concrete core. The subsequently interaction between water, gases and chemicals with Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide ($Ca(OH)_2$), the two main hydration products, results in either a chemical, physical or electrochemical deterioration mechanism. Therefore, barring the entry of these deleterious materials is necessary to prevent the deterioration of concrete. Healing or sealing concrete cracks is thus essential to mitigate, if not eliminate, the occurrence of these deterioration mechanisms.

Many materials and traditional methods have been developed for repairing cracks in concrete [6]. This includes 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 [4,7,8]. The main drawback of these repair methods, besides compatibility requirements and durability, is the timing of the repair. For reference, bridges and retaining walls are now inspected every two years whereas in the past it was on an ad-hoc basis [9]. Furthermore, cracks that are larger than 0.3 mm are repaired if detected, and finer cracks are considered too small to affect the performance or durability of concrete. When cracks are not detected, which is the norm, depending on their location within the structure and exposure, their presence will facilitate the onset and progression of various concrete deterioration mechanisms which render their repair more difficult. Moreover, repaired concrete structures are not immune as they are, for most cases, more susceptible to cracking due to the removal of concrete and introduction of new material. Lastly, the demand to minimize resources for economical and sustainability considerations is hindering concrete repair [10]. To summarize, traditional repair methods are not economical, impact the environment and continue to fail [11]. Therefore, the need for more effective and active repair systems is sought. Towards achieving a sustainable solution, biomimicry is sought to emulate nature’s time-tested strategies for self-healing concrete [12].

Concrete intrinsically heals itself as a result of a chemical reaction between unhydrated cement and water as well as between calcium hydroxide and dissolved carbon dioxide, the recrystallization of calcium hydroxide, or the precipitation of calcium carbonates [13]. In addition to the autogenous crack healing mechanism, autonomous healing can be incorporated by utilizing an extrinsic healing system within the concrete matrix. Extrinsic healing can be achieved by adding supplementary cementitious materials or mineral admixtures, microorganisms, or other healing agents that react chemically with the cementitious matrix [14–17].

1.2.1 Autogenous Healing

Autogenous healing is a passive phenomenon in concrete that can heal cracks smaller than 60 μm [17,18]. Besides the chemical mechanisms, autogenous healing as shown in Figure 1-2, can be due to physical or mechanical mechanisms. Mechanical mechanisms seal the cracks through water-borne or loose concrete particles, whereas physical sealing is by the swelling of hydration products (C-S-H gel) [16].

Autogenous healing can also be stimulated by replacing part of the cement amount in concrete with supplementary cementitious materials such as fly ash and blast-furnace slag, or by adding chemical expansive agents, swelling minerals, geomaterials, or crystalline chemical agents [12,16,17]. The existence of pozzolanic material inside the concrete helps in prompting continuous hydration and producing more hydration products inside the cracks. Whereas, expansive materials can contribute to healing the cracks in the presence of moisture due to their expanding or swelling properties. In general, the use of these materials is mainly to trigger autogenous healing. However, their healing ability is limited as once consumed in the hydration process, they won't be available for further reaction. Furthermore, expansive agents may form cracks due to their expansion inside the matrix [19]. As such, autogenous healing is limited to narrow cracks and its efficacy is conditional on the properties of the concrete and the surrounding conditions including the cementitious mix design, the hydraulic pressure, and the temperature [14,17,20]. Moreover, the presence of moisture and carbon dioxide and limiting the crack width to (< 50 – 150 μm) are necessary for autogenous healing to occur [13,21–23]. Also, it is a very slow process that might take weeks to fill in the crack and could be disturbed anytime by loading or environmental conditions [24]. Accordingly, concrete autogenous healing is best described as inconsistent and unreliable which led to the investigation of autonomous healing concrete.

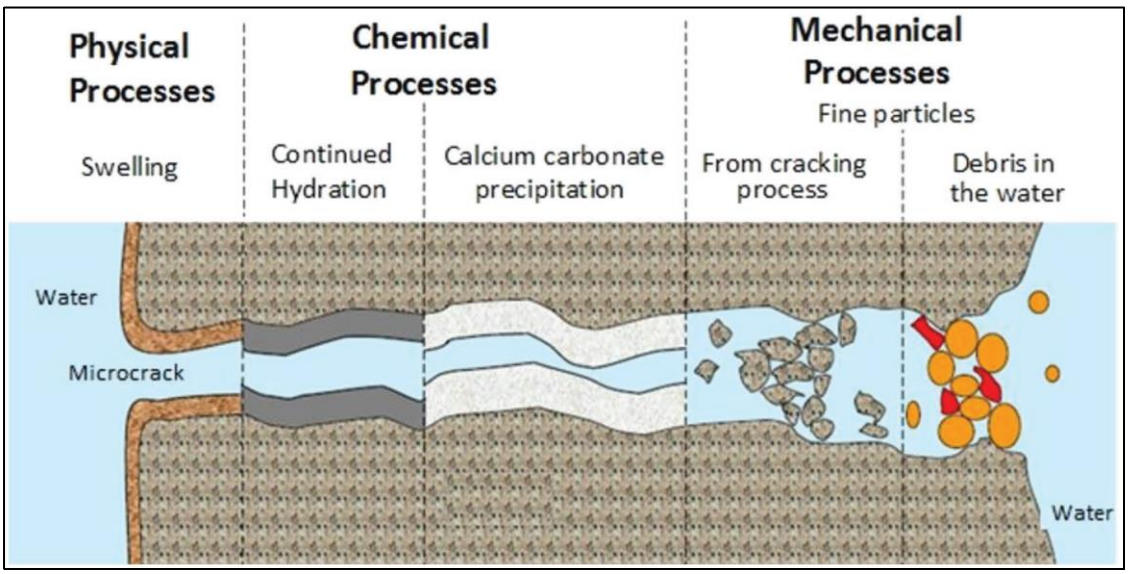

Figure 1-2 Mechanisms of autogenous healing [25]

1.2.2 Autonomous Healing

Autonomous healing involves introducing healing materials that are not intrinsic to the concrete such as bacterial or polymeric adhesive agents [23]. Microbial, or Bio-Concrete, healing depends on the biological activity of microorganisms. Alkaliphilic and spore-forming strains of bacteria, such as the Bacillus genus, are commonly used to withstand the highly alkaline conditions of concrete. Researchers used bacterial spores as they are dormant states of bacteria that protect and help the cells to withstand harsh conditions including dryness, heat, or exposure to deleterious chemicals, and enhance their shelf-life [26–28]. When proper growth conditions exist, the spores would form cells to produce calcium carbonate precipitation, which is one of the most suitable fillers for concrete due to its high compatibility with the cementitious composition [29]. This process is known as Microbiologically-Induced Calcite Precipitation (MICP) [30]. The maximum crack that can be healed by bacteria-based self-healing was found to be 970 μm [17,31]. However, healing by bacteria is a very slow process and is highly influenced by the presence of calcium cations (Ca^{+2}) and moisture [24]. Also, optimizing the nutrient media of the bacteria in concrete is still not addressed in the literature, making it very difficult to be used on a large scale [32]. Therefore, dealing with and effectively protecting the microorganisms is very challenging as many prerequisites need to be met for effective healing. As a research, the researchers started to look for alternatives such as chemical healing agents.

Chemical-based healing involves a chemical interaction with the healing agent. The healing agent in the concrete matrix will directly react with water, air, cementitious materials, or a curing agent. The reaction products will directly fill the cracks as in a one-component reaction (e.g. sodium silicate) or will need an embedded catalyst or curing agent to trigger the healing process and both should be released together to fill the cracks as in a two-component reaction (e.g. dicyclopentadiene, or epoxy).

To enhance autonomous healing, the healing agent should be protected from harsh concrete conditions during mixing and released upon crack propagation inside the cementitious matrix. This can be done via a storage medium that is either in the form of vascular networks [12,33] or in the form of protective capsules [14,23,34–36]. In the case of a vascular self-healing system, the healing agent is filled in thin hollow tubes that form a network connected to an external reservoir that supplies the healing agent. Healing using the vascular system was able to mitigate cracks up to 0.3 mm, however, these networks are difficult in casting and adversely affect the mechanical properties of concrete [16]. Besides that, the healing agent may leak out of the vessels when the cracks are wide. Therefore, the need to consider encapsulation mechanisms to protect the healing agents has been raised.

1.2.3 Encapsulation of Healing Agents

Encapsulation is the process where an active agent is coated by a polymeric shell to produce microparticles, microcapsules, and microspheres ranging from micrometers to millimeters depending on their structure [37]. The main idea of encapsulation is to seal the healing agent and only release it once the capsules are ruptured by the propagating cracks [36,38,39]. 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 [23].

Encapsulation is a promising approach that has been recently adopted 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 their compatibility with the cementitious matrix before applying this approach to self-healing concrete. The physical and mechanical properties of the shell material are the key to the success of the encapsulation process and the efficiency of the release of the healing agent [38,40,41]. As a crack propagates in the cementitious matrix, the microcapsules at the tip of the crack will be subjected to higher stresses leading to the rupture of the shell and the release of the healing agents to fill these cracks. Therefore, the mechanical properties including stiffness and strength of the shell should be within an acceptable range to ensure the rupture of the microcapsules without causing additional stresses at the interface between the microcapsules' shell and the cementitious matrix. Also, physical properties including the wall thickness, shape, and surface texture of the shell should be considered. The shell thickness facilitates the amount of healing agent released to the matrix. Shells with thin walls cannot survive the concrete mixing processes, whereas those with thick shells may not rupture upon cracking. In addition, the shell should be spherical to have a minimum negative effect on the mechanical properties of the cementitious matrix with a rough surface to provide an adequate bond and adhesion with the matrix. Moreover, the size should be appropriately large to provide sufficient healing agents [19,27,41–43]. Furthermore, an adequate bond between the microcapsules and the cementitious matrix, stronger than the shell itself, must exist [41,44,45]. However, this is still a challenging area that has not been studied nor tested extensively.

For the capsules to achieve their vital role, they need to withstand the highly alkaline nature of concrete. The capsules need to survive concrete mixing to protect the healing agents, otherwise, their existence in the self-healing cementitious matrix will have adverse results. Several materials have been adopted in the literature, while glass and ceramic have shown an inadequate ability to survive mixing [46–51], polymeric materials have shown promising results in terms of surviving the concrete mixing conditions while being very versatile to adjust in order to obtain the desired properties [35,51–54]. Two testing methodologies have been used to evaluate capsules' survivability; 1) Chemical stability through immersing the capsules in an alkaline solution mimicking concrete' pore solution and then investigating the survivability of the capsules visually through Scanning Electron Microscopy (SEM) [43,52–59], and 2) Mechanical stability by mixing capsules with concrete, only possible for large-sized capsule size, and then counting them manually or inspecting them visually by SEM [14,35,60,61]. Overall, previous studies revealed that there is no standard testing method to quantify the survival rate of capsules during concrete mixing and the only available ones does not necessarily reflect the statistical behavior of the whole sample. In addition, up to our knowledge, no model in the literature reported quantitatively the correlation between the concrete properties and the capsules' survival. Therefore, in this dissertation, a model was proposed to provide insights into the importance of concrete rheology in determining the survival of self-healing capsules.

The other major role of the capsules in self-healing concrete is to rupture when the concrete cracks. If the capsules debonded from their surroundings, the healing agents will not be delivered resulting in a loss of self-healing ability. The failure mode, in terms of rupture/ debond phenomena, is significantly dictated by the geometrical and mechanical properties of the capsule, the mechanical properties of the cementitious material, and the properties of the interfacial zone between the capsule and the surrounding cementitious matrix [62,63]. Experimentally, the failure mode is usually investigated visually by the SEM and optical microscope images after triggering the crack mechanically through compression and flexural tests [45,64,65]. These tests did not report the reason and the parameters that dictate such behavior. Analytically, several studies were proposed to investigate the impact of different influential parameters (e.g., the interfacial bond strength and the fracture toughness, geometrical and mechanical properties of capsules, and mechanical properties of the cementitious matrix) on the failure mode of the capsules in a self-healing cementitious matrix. These studies employed the extended finite element method (XFEM) and cohesive surface and elements techniques (CS) to model the fracture process in the concrete and the capsule [66–69]. In this dissertation, this methodology has been extended to account for the time-dependent properties of concrete, the evolution of its mechanical properties with time, and their corresponding effect on the self-healing process. Besides that, the geometrical and mechanical properties have been investigated including the radius-to-thickness ratio, elasticity modulus, rupture strength, and fracture toughness. Moreover, the interfacial properties including bond strength and interfacial fracture toughness were also considered.

1.3 Research Motivation

Based on previous background information, the research motivation was drawn from the enormity of the problem associated with concrete cracking resulting in deteriorated built infrastructure that requires billions of dollars annually to repair or replace, together with the lack of consistency of the available repair methods. Even with the promising results of encapsulation-based self-healing demonstrated in previous related studies, there are still many unanswered questions that need to be addressed in terms of the performance and efficiency of the self-healing system. Therefore, this research is intended to provide insights into the two main challenges associated with the success of the self-healing capsules in cementitious material applications:

1) Inconsistencies in the testing methods and results of the survivability of self-healing capsules during concrete mixing and placing, whether these tests are chemical or mechanical. The capsules' survival rate is usually deducted from the visual inspection of a few capsules, assuming that the sample is representative. Therefore, it is important to adopt or develop a testing method/ model that accounts for the survival rate of the capsules especially in the harsh alkaline conditions of concrete.
2) Concrete is subjected to early-age cracking due to shrinkage or thermal changes. Therefore, the performance of the self-healing system needs to be checked at early-age and accordingly the testing method used must capture the early-age cracks.

1.4 Summary of papers

This research program is developed to address the objectives of this study. The research, which is numerical in nature, comprises of three distinct journal articles and two conference proceedings integrated into the body of this dissertation and summarized in the following paragraphs:

Paper I: Performance of Capsules in Self-Healing Cementitious Material *(Published in Materials - MDPI Journal, October 2022)*

This study is intended to investigate numerically the effectiveness of capsules in healing cracked young concrete and identify some of the design requirements necessary for an effective self-healing cementitious system. This paper included a brief review of the relevant experimental and numerical studies, followed by the development of a finite element model by ABAQUS to numerically investigate the mechanical interactions between the mortar and the capsules as the mortar cracks due to dimensional changes due to hydration and/or drying. The factorial design of the experiment was developed to investigate the effect of different parameters including the geometrical and mechanical properties of the capsule, mechanical properties of two mixes of mortar at 2 days and 28 days, with and without supplementary cementitious materials, and the corresponding interfacial properties. The results of the model provide an understanding of the observed inconsistencies in the design of the capsules and the importance of the compatibility between the properties of the capsule and the surrounding cementitious matrix.

Paper II: Performance modelling of spherical capsules during mixing of self-consolidating concrete (Published in Materials - MDPI Journal, March 2023)

To our knowledge, there are no experimental or numerical methods proposed in the literature to determine the capsules' survival rate during mixing. Therefore, this paper aimed to investigate the interrelationship between shell properties and concrete rheological properties on the survivability of self-healing capsules. A two-dimensional plane strain finite element model was developed using ABAQUS to predict the survivability of self-healing capsules in a ring-pan concrete mixer. Two loading scenarios were considered: Hertz contact pressure and punching of aggregate. The external forces exerted on the capsule included the weight of the concrete layer supported by the capsule (W), centrifugal force (Fc) caused by the rotational velocity of the mixer (ω), and Bingham yield stress (τ) representing the flow of fresh concrete. The analysis includes 4 capsule geometries and 2 self-consolidating concrete mixes. To account for the variance in the capsule's geometry, statistical modelling techniques were employed to investigate the performance of the self-healing capsules and predict the survival rate within a 68% confidence interval. The results of the study reveal the importance of investigating the survivability of capsules during concrete's mixing as a prerequisite to the performance evaluation of self-healing capsules. In addition, the geometrical properties of capsule especially the radius-to-thickness ratio, rheological properties of fresh concrete, and the interaction between aggregates and capsules were found to highly influence the capsules' survivability.

Paper III: Performance testing of self-healing early-age concrete using restrained shrinkage

(To be submitted for publication in Cement and Concrete Composites)

As concrete undergoes volume changes while hardening, it is important to consider the early-age shrinkage cracks as they occur at a time when concrete is still developing its mechanical properties. Experimentally, the restrained shrinkage ring (ASTM C1581) is usually used to determine the time-dependent development of induced tensile stresses of concrete under restrained shrinkage. This paper is intended to use the ASTM concrete restrained ring test to evaluate the performance of self-healing capsules due to concrete cracking at early-age, considering: 1) the capsule's geometrical and mechanical properties, 2) the concrete's time-dependent mechanical properties, and 3) the depth of the capsule from the induced crack. Finite elements and fracture mechanics techniques were employed using ABAQUS to simulate the tensile stress development and crack initiation in the restrained concrete ring with the self-healing capsule. The results of the study have shown that the performance of the self-healing capsules at early-age are influenced by the mechanical properties of concrete, capsules' geometry, stiffness ratio of concrete to capsule, tensile-to-rupture strength ratio of concrete to capsule, and the bond strength at the capsule-concrete interface.

Paper IV: Challenges of Self-Healing Concrete Application *(Published in Proceedings of Resilient Materials 4 Life 2020 Conference (RM4L2020), September 2021)*

This study aimed at investigating the recent challenges related to self-healing capsules in concrete applications. The challenge with embedding these microcapsules for self-healing concrete is determining the shell geometrical and mechanical properties such that it can survive the concrete mixing and placement while still trigger the release of the healing agents when young concrete cracks. This paper aims to critically analyze the proposed test method for evaluating the properties of the capsules as well as their efficiency as autonomous self-healing in young concrete. The results of this review paper revealed that there is a need to develop a testing method for determining the mechanical properties of the capsules considering the confined and bonding condition of the capsules in concrete. In addition, testing the efficiency of self-healing concrete system needs to take into consideration the application (sealing or healing) and the age of concrete at testing.

Paper V: Properties and Performance Metrics of Healing Agents in Self-healing Concrete. *(Published in Proceedings of the Canadian Society of Civil Engineering Annual Conference 2021 (CSCE 2021), Lecture Notes in Civil Engineering, May 2022)*

The aim of this study is to develop a design methodology for selecting the healing agents most suited for the application. Accordingly, the healing agent properties were assessed for their viability and adequacy based on structural compatibility with the cementitious matrix. This paper, which is a critical review in scope, focused on investigating the properties of healing agents in self-healing concrete systems including the rheology and curing kinetics, mechanical properties and bond with the cementitious matrix, and healing/sealing ability. Also, it provided metrics for selecting healing agents for cementitious systems. The results revealed the suitability of epoxy resin due to its mechanical properties and flow and curing kinetics. It also highlighted on the absence of standardized testing method for evaluating the efficiency of the self-healing system.

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Chapter 2

2 Performance of capsules in self-healing cementitious material

Abstract

Encapsulation is a very promising technique that is being explored to enhance the autonomous self-healing of cementitious materials. However, its success requires the survival of self-healing capsules during mixing and placing conditions yet still trigger the release of healing agent upon concrete cracking. Review of the literature revealed discontinuities and inconsistencies in the design and performance evaluation of self-healing cementitious material. A finite element model was developed to study the compatibility requirements for the capsule and the cementing material properties while the cement undergoes volume change due to hydration and/or drying. The FE results have provided insights into the observed inconsistencies and the importance of having capsules' mechanical and geometrical properties compatible with the cementitious matrix.

Keywords: cement; self healing; capsules; FE model; compatibility

2.0 Introduction

Hydraulic cement shrinks when it chemically reacts with water to form calcium silicate hydrate (C-S-H), the glue that binds aggregates to form concrete. Early-age cracks, caused by chemical reactions, drying, and/or temperature fluctuations, vary in crack opening displacement (COD) between 10 to 100 μm [1,2]. Although fine cracks with COD less than 200-300 μm are considered too small to affect the performance and durability of concrete [3–6], many studies observed that COD between 50 to 200 μm can affect water permeability of concrete [7–10]. Accordingly, COD greater than and/or equal to 50 mm can allow entry of water and deleterious liquids to the concrete core, and thus facilitates the occurrences of concrete's chemical, physical, and/or electrochemical deterioration mechanisms. The results have been a deteriorated concrete infrastructure with an estimated repair or replacement cost between $18 and $21 billion in the United States alone [11,12]. Hence, autonomous healing, which can be achieved by adding cementing materials, microorganisms, or other healing agents that react chemically with the cementitious matrix, has been suggested and studied as a potential remedy [13–28]. The encapsulation of the healing agents has been used to protect microorganisms from the harsh conditions during mixing and cement hydration, and to protect cementitious and polymeric materials from early activation [29–54]. The capsules, which are in most cases spherical in shape and range from mm to mm [55], can be effective in sealing and/or healing cracked concrete provided they are uniformly distributed [41] and are bonded to the cement paste, and the crack opening is limited to 200 μm [20].

Healing occurs when the capsule ruptures upon intercepting a propagating crack, and the healing agent bonds the cracked surfaces. Depending on the mechanical properties and bond strength of the shell, the capsule can break during concrete mixing or placement and thus spoiling the healing agent or can debond instead of rupturing upon intercepting a crack. Accordingly, the healing effectiveness of the capsules in a cementitious matrix depends equally on the distribution and volume fraction of capsules, and on the mechanical properties, fracture energy, and interaction between the capsule and the cementitious matrix. This wicked problem is further challenged by the absence of standardized test methods for determining the performance of self-healing cementitious systems and the capsules. Consequently, the performance of self-healing cementitious systems using capsules, reported in the scientific literature, has been inconsistent [56–60].

Healing of a cracked young cementitious material poses additional challenges due to the evolution of microstructure as cement hydrates. Moreover, young cementitious material is most susceptible to cracking and these early-age cracks are the root cause of most concrete deterioration in civil infrastructure. This study, which is numerical in scope, aims to investigate the effectiveness of capsules in healing cracked young concrete and identify some of the design requirements necessary for an effective self-healing cementitious system. The paper includes a brief review of the relevant experimental and analytical studies reported in the literature, methodology developed for this investigation, analysis, and model results. Discussion of the results, which includes a comparison to the reported literature results, is subsequently presented.

2.1 Performance of self-healing cementitious system

2.1.1 Experimental studies

2.1.1.1 Capsule

The capsules in self-healing cementitious system which act as carriers for the healing agent, release the healing agent when mechanically triggered. As such, several shell materials with different healing agents have been studied as documented in Table 2-1. The role of the shell, which encapsulates the healing agent, is to protect the agent from rupturing during concrete mixing and placing, and yet cracks and facilitates the release of the agent upon concrete cracking. In brief, the capsule's mechanical properties and geometry are pivotal for the success of self-healing cementitious systems. Although several test methods have been employed to measure the mechanical properties of the capsules, as summarized in Table 2-2, there are no standard test method nor guidance on the target values for capsule properties in self-healing cementitious systems.

Table 2-1 Common shell materials and healing agents used in self-healing concrete

Shell material	Healing agent	Reference
Perspex	Epoxy Resin	[61]
Ceramic	Polyurethane (PU)	[17]
	Methyl Methacrylate (MMA)	[40]
Glass	Epoxy Resin	[61]
	Methyl Methacrylate (MMA)	[25]
	Cyanoacrylates (CA)	[26]
Borosilicate glass	Methyl Methacrylate (MMA)	[40]
	Polyurethane (PU)	[17,37,62]
	Cyanoacrylates (CA)	[15,16]
Quartz glass	Polyurethane (PU)	[49]
Urea-formaldehyde (UF)	Epoxy Resin	[38,39,52,63–65]
	Dicyclopentadiene (DCPD)	[66–70]
Melamine Urea-formaldehyde (MUF)	Epoxy Resin	[32]
	Dicyclopentadiene (DCPD)	[71]
	Epoxy Resin	[72]
Phenol-formaldehyde (PF)	Dicyclopentadiene (DCPD)	[31,33]
	Epoxy Resin	[73]
	Dicyclopentadiene (DCPD)	[74–76]
Polystyrene (PS)	Methyl Methacrylate (MMA)	[42]
	Polyurethane (PU)	[35]

Table 2-2 Properties of capsules extracted from literature

Shell Material	Average size (D) (μm)	Shell thickness (t) (μm)	Elastic Modulus (GPa)	Bursting/ Rupture stress (MPa)	Ref.
Polyurethane (PU)	50-100	1-2	0.0029	0.026	[77]
Urea-Formaldehyde (UF)	65±7 dry, 187±15 dry, 213±12 immersed	0.175±0.033	3.7±0.5, 3.6±0.4, 3.9±0.7	0.8±0.3, 0.24±0.04, 0.14±0.02	[76]
Poly-Melamine-Formaldehyde (PMF)	10-150	0.2	4.66	-	[72]
Phenol-Formaldehyde (PF)	50-200, 200-400, 400-600	29.96	2.2 ± 0.8	68.5 ± 41.6, 96.8 ± 23.5, 198.5± 31.6 mN	[31]

Single-microcapsule technique was employed by Liu et al. (1996) to measure the compressive displacement and corresponding force of Poly-Urethane (PU) capsules using micro-upsetting instruments. The single capsule started to burst when the ratio of compressed displacement to initial diameter reached 60%. The same technique was also used by Keller and Sottos (2006) to evaluate the mechanical properties of dry and immersed DiCycloPentaDiene (DCPD) filled Urea-Formaldehyde (UF) capsules. The failure, which occurred when the displacement reached 40% of the initial diameter, was due to leaked DCPD. They reported that the capsule did not burst or buckle and attributed the failure to localized damage due to the large radius of curvature. The corresponding mechanical properties were deduced from the measured load-displacement curve and membrane theory model assuming isotropic nonlinear-elastic [77] and isotropic linear-elastic material [76], respectively.

Lee et al. (2012) adopted nanoindentation technique to measure the micromechanical properties of an epoxy-filled Poly-Melamine-Formaldehyde (PMF) capsule. Using the measured load-displacement curve, the hardness and elastic modulus of the capsule were calculated. This experimental study is documented for material reference as the capsules were intended for self-healing polymers. Nanoindentation was also employed by Lv et al. (2016a) to measure the elastic modulus and rupture force of DCPD-filled Phenol-Formaldehyde (PF) capsules. The elastic modulus was deduced from the linear phase of the load-displacement curve at a displacement between 600-900 nm. The rupture force was determined at a depth of 5 mm. The same technique was also used by Lv et al. (2017) to determine the elastic modulus and hardness of the shell-cement paste interface. To simulate the interface between cement paste and PF capsules, a small piece of the shell material resin was placed on top of the cement paste sample and sealed by epoxy resin. The mechanical properties of the shell material, cement paste, and interface were measured after curing for 28 d. The elastic moduli for the cement paste, shell material, and the interface, were found to be 16 GPa, 5.5 GPa, and 4.75 GPa, respectively, and the corresponding tensile strengths were 3 MPa, 1.10 MPa, and 0.12 MPa.

Studies that were undertaken to study the performance of self-healing cementitious systems, also tested the properties of General-Purpose Polystyrene (GPPS), Acrylonitrile-Butadiene-Styrene (ABS), and High Impact-resistance Polystyrene (HIPS) capsules using compression test [79]. The test aimed to mimic the interaction between the capsules and cementitious materials. They reported that the measured load-displacement curves are not sufficient for determining the capsules' material properties as further analyses are needed to account for the effects of capsule bending resistance. This review, although brief, shows the challenges in determining the properties of the capsules and the interface between the capsules and cement paste. The results do however confirm that the shell elastic modulus and rupture stress depend on the capsule material type and geometric properties, as well as on the testing method and mechanics theory adopted to estimate the values.

The success of capsules in self-healing systems also depends on their survivability rate during harsh concrete mixing and placing conditions, and on their ability to withstand the high alkaline nature of cementitious systems. Search of the literature revealed that the survival of the capsules was deduced from visual inspection using scanning electron microscopy (SEM) images of pre-cracked hardened concrete samples [64]. Although this approach provides an indirect measurement of capsule's survivability rate, the results are yet to be proven statistically as representative of the whole sample. The SEM images before and after mixing were compared and it was observed that the capsules survived the mixing, and they have a good bond with the cement paste matrix. Furthermore, Hilloulin et al. (2015) and Lv et al. (2016b) tested the effects of alkaline environment on polymeric tubes and PF capsules, respectively. The former employed cement slurry with pH ~ 12.5-13 for a period of 7 and 14 d and measured the effect by comparing the tubes tensile strength, while the latter used $Ca(OH)_2$ aqueous solution with a pH ~ 13 for 2 d and visually inspect the capsules using SEM. The results in Hilloulin et al. (2015) revealed that the Poly(Lactic Acid) "PLA" and PS tubes did not experience change in their tensile strength after being exposed to alkaline environment, while the Poly(Methyl Methacrylate/n-Butyl MethAcrylate) "P(MMA/n-BMA)" tubes had a lower strength. On the other hand, Lv et al.

(2016b) compared the SEM images for the PF tubes, and no change was observed in the shape after exposing the capsules to alkaline environment. Although both were attempting to measure the shell chemical resistance during cement hydration period, their approach differs significantly both in exposure condition and evaluation method. The use of different test methods will automatically yield different results and inconsistencies in performance. A primary role of the capsules in self-healing system is to rupture and not debonds upon concrete cracking. The former ensures the delivery of the healing agent, while the latter results in loss of crack healing potential. Mechanical properties of cementitious material, capsule, and interfacial zone dictate to some extent the performance of self-healing system [19,31,78]. Using SEM images of a mechanically triggered crack by means of a compression test, Wang et al. (2013) observed that some UF capsules ruptured while others debonded from the 49 MPa compressive strength mortar, but did not explain what caused the difference in performance. Also using the compression test and SEM images, Dong et al. (2016) investigated the fractured surfaces of UF capsules. The images revealed that the capsules ruptured with the shell still bonded to the 55.8 MPa compressive strength cement paste. Lv et al. (2016b) used optical microscope (OM) and X-ray computed tomography (XCT) scanning technology to investigate the fractured surface of cement paste samples cured for 28 d and tested by a three-point bending test. It was observed that some of the capsules were ruptured by the crack, while the others were tightly embedded in the matrix indicating a good bond with the matrix. The study acknowledged the weak bond between the microcapsules and the matrix that needs improvement but without providing guidance. These results not only loosely and qualitatively document the performance of the capsules in cementitious matrix, but also showed that different test methods are used to evaluate the interface between the capsules and the cementitious matrix.

In summary, the capsules were tested to determine if the shell possesses the properties necessary to survive the mixing and placing of the cementitious mixture, and to crack when the cementitious matrix cracks. A range of properties has been reported for the shell's elastic modulus and rupture stress. Assuming that the test methods are repeatable and consistent, what values should the shell possess so that it can be effective in a self-healing cementitious system? Evidentially, a need exists for developing standard test methods for measuring the geometrical and mechanical properties, durability of the capsule shell, and the properties of the interfacial zone between the capsules and matrix, as well as for establishing the corresponding values that are deemed acceptable for self-healing cementitious system.

2.1.1.2 Healing system

The efficiency of a healing system is determined by the release of the healing agent and the healing of the cracks. The former is controlled by the mechanical properties of the capsules, the matrix, and their interfacial zone, whereas the latter requires that the agent flows, fills the volume before hardening, and bonds the faces of the crack. Evaluating the efficiency of healing systems is therefore complex as their performance rely on the congruent occurrence of many events. As such, indirect test methods, such as visual inspection [36,41,80], and measuring the recovery of the mechanical properties [31,32,38,39,42,52,64,70] and/or water/air tightness of the matrix [38,39,42,52,64,65], have been employed to evaluate the performance of healing system. It is evident that the absence of a standard test method and/or metric, and the use of different test methods have led to the documented inconsistencies in the performance measurement as reported in Table 2-3. The absence of a metric and/or guideline that prescribe acceptable range of shell material properties, capsule size and concentration, and healing agent properties, causes uncertainties in the healing system performance and can potentially impede its development.

The data in Table 2-3, which presents a representative sample of proposed healing systems and performance test methods, not only reveal their diversity but also show the inconsistencies in the design of the healing system specifically the size and content of the capsules and their compatibility to the cementitious mixture composition. Nonetheless, the following observations have been deduced:

i. Capsules formed using UF are found to range between 10 to 1000 mm in diameter, 0.2 to 8 mm in thickness, and 8 to 39 in the ratio of radius to thickness except for the capsules that were used by Gilford et al. (2014) whose ratio is 107 to 5000. Both the radius to thickness ratio and diameter of the capsules affect their ability to withstand forces, to develop a mechanical bonding, as well as to effectively deliver the healing agent. The spectrum provides little information and thus confidence on what geometrical properties the capsules need to possess for an effective self-healing system.

ii. UF encapsulating epoxy resin [38,39,52,64,65], Dicyclopentadiene (DCPD), Sodium Silicate [70], and Calcium Nitrate Tetrahydrate [41], have been added to the mortar with varying mixture composition and properties. The reported 28-day mortar compressive strength ranges from 28 to 56 MPa, and the flexural strength from 8.4 to 10.6 MPa. The cementitious mix design is seldom documented in these studies and only some studies reported the mechanical properties of the hardened mixture. The ratio of water to cement and cement to sand, the cement content, capsule content, and other additives are found to significantly vary among the documented studies without any rational to the design.

iii. Capsules contents are found to range between 0.5 to 12% of the cement content. The broad range of the capsules content used in these studies combined with the absence of any rational to designing self-healing system can discourage the concrete construction industry from experimenting with self-healing system.

iv. UF, MUF, and PF are used for encapsulation with UF being the most common, and epoxy resin, DCPD, Sodium Silicate, and Calcium Nitrate Tetrahydrate used as healing agents with epoxy being the most common. The diverse chemical composition and properties of the healing agents provide options but with no justification or guidance on how to select the healing agents.

v. Test methods not only vary in scale from recovery of mechanical properties and transport properties to recovery of matrix microstructure which includes pores size distribution and porosity, but also the varying ages at which matrix was pre-cracked and tested. These variabilities raise many questions; Is there a difference in material response between mechanically and chemically triggered cracks, i.e., between cracks induced by external loads versus those caused by dimensional changes? Does the cementitious material degree of hydration affect the healing efficiency of the system, specifically the capsule bond strength? The aim of these performance tests appears to test the mechanical and/or durability recovery of mature concrete and provide zero measure of the healing performance at an early age when the cementitious system is most vulnerable to cracking.

vi. Healing performance indicators of the systems appear to be all over the place where the following measures have been reported: average recovery rate, recovery rate, healing rate, crack healing ratio, and healing ratio. For reference, rate is a measure of two unlike units and should not be used to compare two measurements of the same units. Alternatively, the ratio can provide a measure of the healed system to the uncracked system. Moreover, the reported experimental measurements are concerning as without a measure of certainty in the form of standard deviation, there is zero confidence in their measured values.

The previous studies revealed that using capsules in self-healing cementitious systems without understanding the properties required to ensure compatibility with the cementitious matrix, without a defined aim of the self-healing system being sealing or healing, and without a clear definition of efficiency would lead to inconsistencies in the results perhaps even for the same type of capsules.

Table 2-3 Performance of self-healing system in concrete applications

Healing agent	Shell material	Performance criteria	Capsule size (μm)	Capsule content (%)	Pre-loading condition	Curing conditions and testing age	Testing methodology	Reference
Epoxy resin	UF	Mechanical properties & Durability	73-309	3, 6, 9	30%, 50%, 70% of maximum compressive/ flexural strength	Pre-cracked after curing for 28 day (RH> 90%, 20 °C), then left to heal for 3 d (same curing conditions)	- Compressive strength test - Three-point bending test - RCM test	[38]
Epoxy resin	UF	Mechanical properties & Durability	45-185	3, 6, 9	60% of maximum compressive strength	Pre-cracked after curing for 28 day (RH> 90%, 20 °C), then left to heal for 7 d (cured in a box at temp.< 50 ^{o}C)	- Compressive strength test - DMA test - MIP test	[52]
Epoxy resin	UF	Mechanical properties & durability	132, 180, 230	2, 4, 6, 8	60% of maximum compressive strength	-	- Compressive strength test - RCM test	[39]
Epoxy resin	UF	Mechanical properties & durability	132, 180, 230	2, 4, 6, 8	30-70% of maximum compressive strength	Cured for 60 d in the curing chamber (95 ± 5% RH, 20 ± 2 ^{o}C), then pre-cracked and left to heal at a temperature of 30-60 ^{o}C for 3d, 5d, 7d, 14d and 28d	- Compressive strength test - RCM test - MIP test	[64,65]
DCPD and Sodium Silicate	UF	Mechanical properties	75-1000	0.5, 1.0, 2.5, 5.0 (Sodium Silicate), 0.25 (DCPD)	70% of maximum compressive strength.	Steam cured for 7 d at 20-25 ^{o}C, then reloaded three cycles before left to heal in curing room for 48 h	- Compressive strength test	[70]

Calcium Nitrate Tetrahydrate	UF	Visual and crack width	22-59	0.5, 0.75	Flexural damage up to sudden change in the displacement	Cured for 28 d (95% RH), oven-dried for 3 d (60 °C), then pre-cracked, water immersed for 7, 21, 42 d, and oven-dried again for 3 d (60 °C)	- ESEM/ EDS	[41]
Sodium Silicate	Double-walled PU/UF	Visual and crack depth	-	2.5, 5	Flexural damage up to load of 500 kg	Cured water for 7 d, pre-cracked then left to heal for 2 weeks	- PUNDIT device	[36]
Epoxy resin	MUF	Mechanical properties	10-1800	1, 2, 4	30, 60, 80% of maximum load resistance	Cured for 28 d (≥95% RH, 20 ± 2 ºC), left to heal for 2 hours after pre-cracked, then tested up to failure	- Three-point bending test	[32]
DCPD	PF	Mechanical properties	50-600	4-12	Loaded up to failure	Cured for 28 d in wet chamber (25 ºC, 95% RH)	- Compressive strength test	[31]
MMA	PS	Mechanical properties & durability	4.15	1.5	80% of maximum compressive strength	Cured in wet chamber for 28 d (≥95% RH, 20 ± 2 ºC. Samples of 1d and 28 d are pre-cracked, rest for 24 h, then cured for another 24 h in vacuum-dried room (for permeability)/ subjected to cyclically loading between 25-95% of maximum compressive strength (for fatigue)	- Gas permeability test using liquid methanol - Fatigue test under uniaxial compression cyclic loading	[42]
CSA	PS	Visual and crack volume	200-500	5	Up to compressive strength of 11 MPa	Cured for 28 d in curing chamber, then pre-cracked and immersed in water for 21, 42, 63, 84 and 105 d	- X-ray µCT and SEM/ EDS	[80]

2.1.2 Numerical studies

Several studies proposed analytical/numerical models to investigate the fracture behavior of the capsules in self-healing systems and evaluate the suitability of their mechanical and geometrical properties and their interactions with the cementitious matrix. Gilabert et al. (2015) developed a 2D model to investigate the effect of the interfacial bond strength on the stress concentration around a cylindrical capsule embedded in a cracked linear elastic concrete matrix subjected to uniform uniaxial far-field stress. The interface was represented by a linear cohesive zone model. Perfect and imperfect bonds were investigated with different ranges of shell-to-matrix stiffness ratio, capsule thicknesses, and strength ratio. The results revealed that debonding of the capsule is controlled by the strength ratio namely bond strength to far-field stress, geometric ratio i.e., capsule thickness to radius, and elastic properties ratio of capsule to concrete. The effect of interfacial fracture energy on the capsule debonding behavior was also investigated [82]. The results showed that the fracture energy does not influence the initiation of debonding and that fracture energy greater than 0.5 J/m^2 has no effect on debonding. However, it affects the brittleness of the process of failure. Model of three-point bending test employing extended finite element method (XFEM) and cohesive surface techniques (CS) was used to investigate the effect of inserting tubular glass capsules on the overall beam's strength, and to study the capsule size and interfacial properties vis-a-vie capsule rupture [83]. The results revealed that the bond strength needs to be at least 2 MPa to ensure the rupture of the capsule, and that by increasing the ratio of the capsule thickness to radius to 0.23, the minimum bond strength required to ensure capsule rupture increases to 5 MPa, which is considered high for a polymer-mortar interface. Li et al. (2017) developed a finite element model using XFEM technique and cohesive zone to simulate crack propagation in a matrix and the potential of capsule debonding. They concluded that debonding depends on the strength ratio between the capsule and the interface. The effect of fracture strength at the interfacial transition zone (ITZ) of a circular capsule with different core-shell thicknesses on the rupturing of the capsule was investigated using a 2D numerical model [85]. The crack path was pre-initiated as a zero-thickness cohesive element through the concrete matrix. They concluded that the probability of capsule rupture is highly influenced by the capsule shell thickness, and when the fracture properties of the interface are equal to the mortar matrix, the probability of capsule rupture increases. A follow-up study was undertaken to study the effects of varying the fracture strengths between capsule, mortar, and the interface on the crack initiation and propagation [86]. The results revealed that having similar fracture strength for the capsule and mortar with higher interfacial strength ensure crack propagation through the capsule.

The results from the numerical studies, although limited, confirm the significance of the capsule geometric properties and compatibility between the capsule, mortar, and interface bond strength, on the performance of self-healing cementitious system. Moreover, these results highlight the significance of mortar properties on the self-healing performance, specifically when considering early age cracking of cementitious material.

2.2 Methodology

An experimental program was developed using factorial design of experiments [87] to numerically investigate the mechanical interactions between the mortar and the capsules as the mortar cracks due to dimensional changes. The geometrical and mechanical properties of the capsule, and the properties of the mortar and the interface between the mortar and the capsules as a function of age and composition were studied. Two mortar mixes, one mix without supplementary cementing materials (SCM) at age 2 and 28 d, and one mix with SCM consisting of 22% ground granulated blast furnace slag (GGBFS) and 8% silica fume (SF) as cement replacement at age 2 d, were considered for this study. The corresponding mortar mixture composition and properties are given in Table 2-4. The mortar compressive strength was estimated using the model proposed by Chidiac et al. (2013), the modulus of elasticity and tensile strength using the models of ACI 318M (2019) and Onken and Rostasy (1994), and the fracture toughness using the models of Gustafsson (1985) and Hillerborg (1985). The values adopted for the shell geometry and material, and for the interface were selected based on the data reported in the literature and reproduced in Table 2-5. The factorial design, which uses the variables presented in Table 2-6, led to 96 combinations that were analyzed using the commercial finite element program ABAQUS [93].

Table 2-4 Mortar mixture composition and properties

Constant Values			
w/c		0.3	
Cementing (kg/m^3)		550	
Sand/cementing		3	
Variables Values			
Mortar age (day)	2	2	28
SCM (% of cement)	0	22%GGBFS+8%SF	0
f'_c (MPa)	24.1	17.0	50.8
E_m (GPa)	30	30	39
f_{tm} (MPa)	1.6	1.3	4.0
G_m (J/m^2)	30	20	60

Table 2-5 Capsule and interface properties

	Variable	**Values used**	**Range in literature**	**References**
Shell geometry	R_s (μm)	50, 60, 100	5-1000	[85], [86], [83], [70], [66], [32], [31,33]
	t_s (μm)	1, 2, 3, 8	1-200	[78], [86], [81], [83], [38,52], [94], [31,33]
Shell properties	E_s (GPa)	4	2.25-12	[95], [78], [85], [86], [81], [83], [38,52], [76], [32], [96,97], [72], [31,33], [96,97], [98], [99], [100], [101], [102]
	f_{rs} (MPa)	30, 50	23-90	[83], [35], [98], [99], [100], [101], [102]
	G_s (J/m^2)	100	40-500	[85], [83], [103], [96,97], [104], [105] [100], [101]
	ν_s	0.3	0.3-0.36	[95], [85], [86], [83] [96,97], [98], [101]
Interface properties	σ_{bi} (MPa)	0.9-3.4	0.1-15	[78], [85], [86], [81], [83], [106], [35], [107], [108], [109], [110], [111]
	G_i (J/m^2)	20-80	0.1-100	[85], [86], [81], [83]

Table 2-6 Variables considered in the DoE

Variables	Range			Star Point
2d Mortar without SCM				
R_s (mm)	0.06	0.1		0.05
t_s (mm)	0.002	0.003	0.008	0.001
E_s (GPa)	4			
f_{rs} (MPa)	30	50		
G_s (J/m^2)	100			
σ_{bi} (MPa)	1.1	1.3		
G_i (J/m^2)	20	50		
2d Mortar with SCM				
R_s (mm)	0.06	0.1		0.05
t_s (mm)	0.002	0.003	0.008	0.001
E_s (GPa)	4			
f_{rs} (MPa)	30	50		
G_s (J/m^2)	100			
σ_{bi} (MPa)	0.9	1.0		
G_i (J/m^2)	20	50		
28d Mortar without SCM				
R_s (mm)	0.06	0.1		0.05
t_s (mm)	0.002	0.003	0.008	0.001
E_s (GPa)	4			
f_{rs} (MPa)	30	50		
G_s (J/m^2)	100			
σ_{bi} (MPa)	2.9	3.4		
G_i (J/m^2)	40	80		

2.2.1 Finite element model

A 2-D plane strain finite element model was constructed for this analysis. The idealized model, which is shown in Figure 2-1, consisted of a 50 mm by 30 mm rectangular shape mortar matrix with a single spherical capsule centrally located 25 mm below the top surface, an interface layer around the capsule, and a centrally positioned crack path. Accordingly, three interfaces were considered, mortar-to-mortar interface for where the mortar cracks, capsule-to-mortar interface representing the zone binding the mortar and the capsule, and the capsule-to-capsule interface for where the capsule ruptures. Moreover, two boundary conditions were used, a roller at the bottom surface and a horizontally moving rigid boundary at the two vertical edges of the matrix. The latter simulates the effects of dimensional change, specifically shrinkage.

The progressive meshing was used in this study to balance computational efforts and discretization errors. The element size ranged from 2.6 μm around the capsule interface to 1.6 mm at the far edges of the mortar matrix. The generated finite element mesh along with a zoomed-in mesh on the area surrounding the capsule are shown in Figure 2-2. For reference, 720 and 12300 CPE8 elements were used to model the capsule and the matrix, respectively.

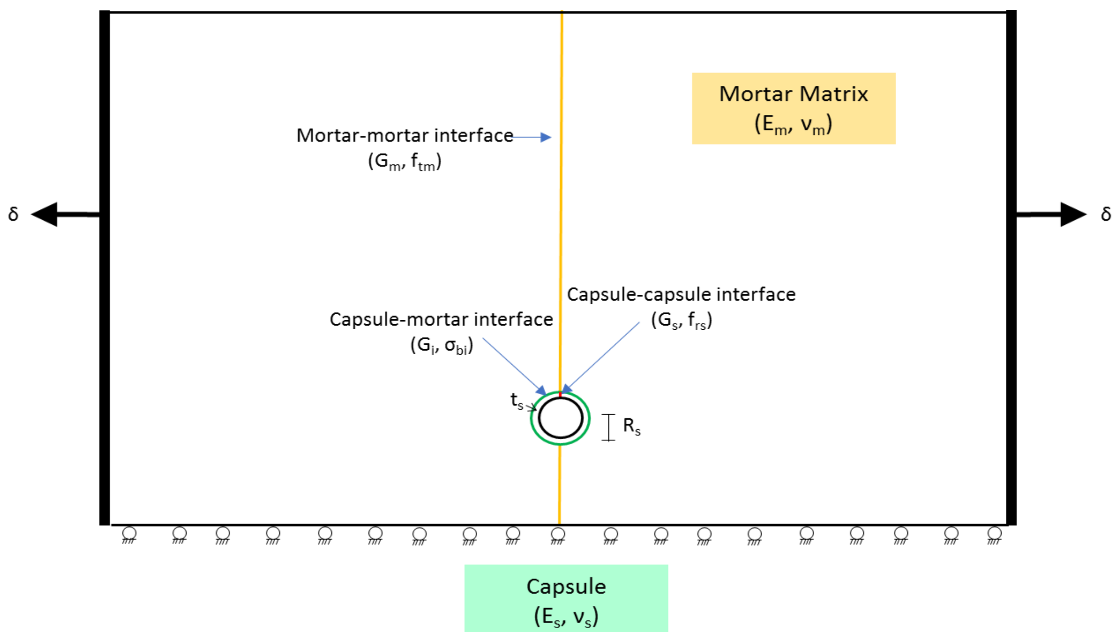


Figure 2-1 FE model schematic view including geometry, boundary conditions, and loading conditions

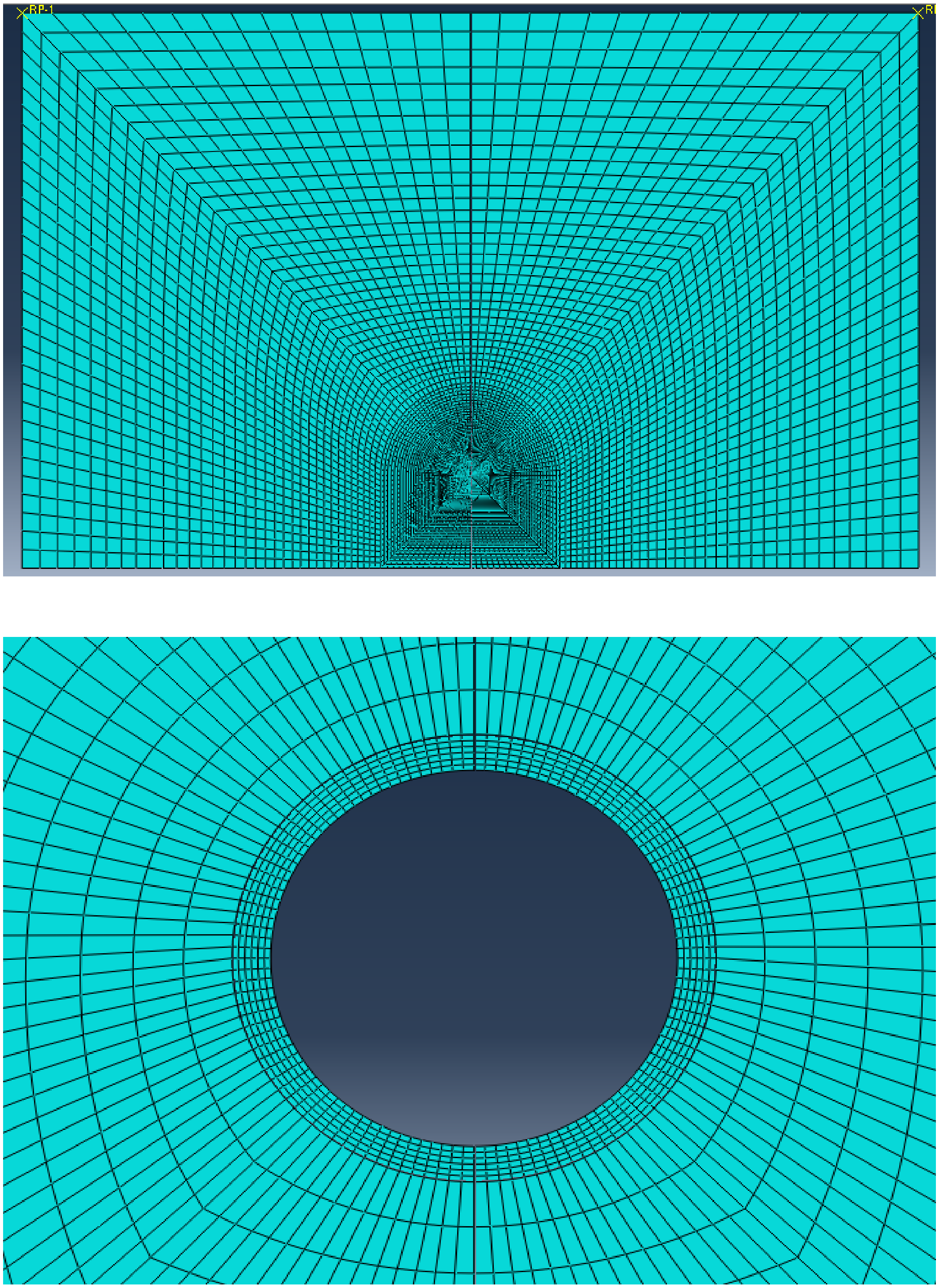


Figure 2-2 Finite element mesh of the mortar (top) and the area around the capsule (bottom)

2.2.2 Damage model

Abaqus cohesive interface surfaces were used to capture the damage as the rigid boundaries move horizontally to simulate the effects of dimensional changes [93]. The elements are used to connect any two surfaces whose separation is governed by a traction-separation law, specifically the matrix-matrix interface, capsule-matrix interface, and capsule-capsule interface, as illustrated in Figure 2-1. The traction-separation behavior, described in Figure 2-3, is assumed to be linear elastic until the initiation of damage. Damage is initiated when the stress has reached the bond strength of the capsule-matrix interface, the maximum tensile strength of mortar at the mortar-mortar interface, and the maximum rupture strength of the capsule at the capsule-capsule interface. Thereafter, damage will evolve based on energy dissipation principles and is governed by the interface fracture toughness (G). Moreover, the model assumes that 80% of the capsule surface area is bonded to the surrounding matrix, yielding a 20% reduction in the bond strength between the mortar and the capsule.

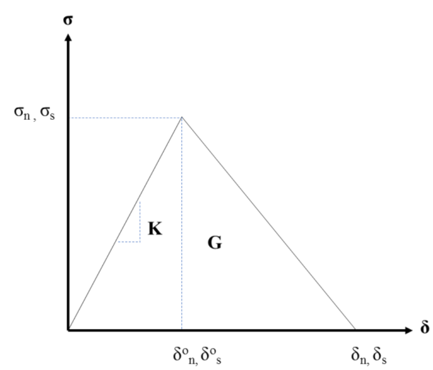


Figure 2-3 Bilinear traction-separation law [93]

2.3 Results, analyses, and discussion

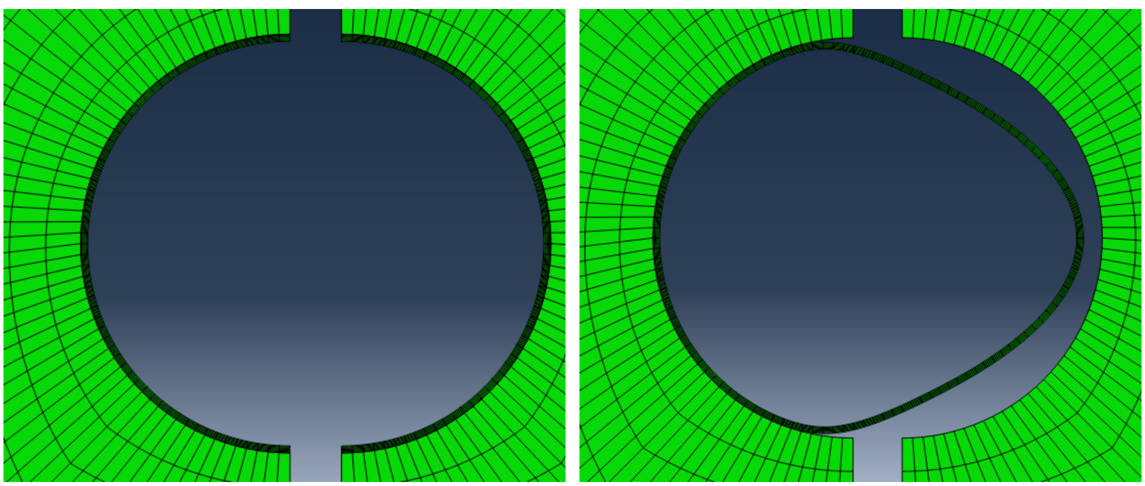
The results from the finite element analyses, in the form of failure mode, and crack mouth opening displacement (CMOD) are reproduced in Table 2-7. The two failure modes, Rupturing (R) of the shell and Debonding (D) of the capsule, which were captured by the finite element model, are shown in Figure 2-4. Figure 2-5 shows the relationship between CMOD and the capsule failure modes for the three mortar mixes. The observed trend clearly indicates that the relationship between the capsule and the mortar is very much influenced by the properties of the mortar. Comparing the mortar mixes without SCM at 2d and 28d, the CMOD values are different reflecting the strength development but also the pattern is different. At 2d, rupturing as the mode of failure is dominant for 33% of the capsules at smaller crack opening but as the crack widens, the mode of failure becomes unpredictable with debonding being more predominant. At 28d, rupturing as the mode of failure is dominant for 66% of the capsules and is over a broader range. As the crack continues to widen, debonding of the capsule becomes the dominant mode of failure. These results are significant in more than one way, first the age of the mortar or the mechanical property of the mortar dictates the interaction between the capsule and the mortar, and second the size of the crack at 28d dictates the capsule predominant mode of failure. The latter is significant for the cases where mortar is pre-cracked to study the efficiency of the self-healing system. Comparing the mortar mixes with and without SCM at 2d, one observes a different pattern. The CMOD values reflect the weaker mortar at 2d. Moreover, the mode of failure is different for SCM mixes where rupturing is dominant at both ends whereas those without SCM show a transition from one mode to the other. This indicates that the response is very complex for weaker mortar reflecting the early age.

Table 2-7 Results of the FE

Run	R_s (mm)	t_s (mm)	f_{rs} (MPa)	σ_{bi} (MPa)	G_i (N/mm)	Failure Mode	CMOD (μm)
1	0.06	0.003	30	1.1	0.02	D	5.187
2	0.10	0.003	30	1.3	0.02	D	5.148
3	0.06	0.008	30	1.1	0.02	D	5.296
4	0.10	0.008	30	1.3	0.02	D	5.145
5	0.06	0.003	50	1.1	0.02	D	5.142
6	0.10	0.003	50	1.3	0.02	D	5.108
7	0.06	0.008	50	1.1	0.02	D	5.258
8	0.10	0.008	50	1.3	0.02	D	5.180
9	0.06	0.003	30	1.1	0.05	D	5.156
10	0.10	0.003	30	1.3	0.05	D	5.121
11	0.06	0.008	30	1.1	0.05	D	5.267
12	0.10	0.008	30	1.3	0.05	D	5.112
13	0.06	0.003	50	1.1	0.05	D	5.170
14	0.10	0.003	50	1.3	0.05	D	5.164
15	0.06	0.008	50	1.1	0.05	D	5.297
16	0.10	0.008	50	1.3	0.05	D	5.147
17	0.06	0.003	30	0.9	0.02	D	4.218
18	0.10	0.003	30	1.0	0.02	D	4.221
19	0.06	0.008	30	0.9	0.02	D	4.371
20	0.10	0.008	30	1.0	0.02	D	4.216
21	0.06	0.003	50	0.9	0.02	D	4.207
22	0.10	0.003	50	1.0	0.02	D	4.188
23	0.06	0.008	50	0.9	0.02	D	4.286
24	0.10	0.008	50	1.0	0.02	D	4.204
25	0.06	0.003	30	0.9	0.05	D	4.192
26	0.10	0.003	30	1.0	0.05	D	4.236
27	0.06	0.008	30	0.9	0.05	D	4.242
28	0.10	0.008	30	1.0	0.05	D	4.193
29	0.06	0.003	50	0.9	0.05	D	4.228
30	0.10	0.003	50	1.0	0.05	D	4.213
31	0.06	0.008	50	0.9	0.05	D	4.230
32	0.10	0.008	50	1.0	0.05	D	4.227
33	0.06	0.003	30	2.9	0.04	D	9.523
34	0.10	0.003	30	3.4	0.04	R	8.132
35	0.06	0.008	30	2.9	0.04	D	9.578
36	0.10	0.008	30	3.4	0.04	D	9.556

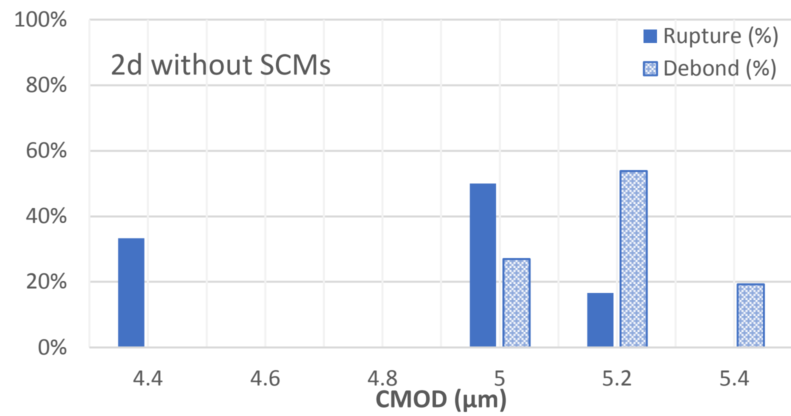
37	0.06	0.003	50	2.9	0.04	D	9.629
38	0.10	0.003	50	3.4	0.04	R	9.025
39	0.06	0.008	50	2.9	0.04	D	9.744
40	0.10	0.008	50	3.4	0.04	D	9.515
41	0.06	0.003	30	2.9	0.08	R	9.886
42	0.10	0.003	30	3.4	0.08	R	8.158
43	0.06	0.008	30	2.9	0.08	D	9.614
44	0.10	0.008	30	3.4	0.08	D	9.504
45	0.06	0.003	50	2.9	0.08	D	9.564
46	0.10	0.003	50	3.4	0.08	R	9.056
47	0.06	0.008	50	2.9	0.08	D	9.639
48	0.10	0.008	50	3.4	0.08	D	9.552
49	0.10	0.002	30	1.3	0.02	R	5.115
50	0.10	0.002	50	1.3	0.02	D	5.270
51	0.10	0.002	30	1.3	0.05	R	5.139
52	0.10	0.002	50	1.3	0.05	D	5.202
53	0.10	0.002	30	1.0	0.02	R	4.219
54	0.10	0.002	50	1.0	0.02	D	4.261
55	0.10	0.002	30	1.0	0.05	R	4.167
56	0.10	0.002	50	1.0	0.05	D	4.255
57	0.10	0.002	30	3.4	0.04	R	9.479
58	0.10	0.002	50	3.4	0.04	R	9.726
59	0.10	0.002	30	3.4	0.08	R	9.714
60	0.10	0.002	50	3.4	0.08	R	9.649
61	0.06	0.002	30	1.1	0.02	D	5.170
62	0.06	0.002	50	1.1	0.02	D	5.168
63	0.06	0.002	30	1.1	0.05	D	5.179
64	0.06	0.002	50	1.1	0.05	D	5.161
65	0.06	0.002	30	0.9	0.02	D	4.195
66	0.06	0.002	50	0.9	0.02	D	4.188
67	0.06	0.002	30	0.9	0.05	D	4.267
68	0.06	0.002	50	0.9	0.05	D	4.232
69	0.06	0.002	30	2.9	0.04	R	8.031
70	0.06	0.002	50	2.9	0.04	D	9.602
71	0.06	0.002	30	2.9	0.08	R	8.014
72	0.06	0.002	50	2.9	0.08	D	9.627
73	0.10	0.001	30	1.3	0.02	R	4.546
74	0.10	0.001	50	1.3	0.02	R	5.112
75	0.10	0.001	30	1.3	0.05	R	4.549
76	0.10	0.001	50	1.3	0.05	R	5.208
77	0.10	0.001	30	1.0	0.02	R	3.846
78	0.10	0.001	50	1.0	0.02	R	4.791
79	0.10	0.001	30	1.0	0.05	R	3.838
80	0.10	0.001	50	1.0	0.05	R	4.757

81	0.10	0.001	30	3.4	0.04	R	7.370
82	0.10	0.001	50	3.4	0.04	R	8.111
83	0.10	0.001	30	3.4	0.08	R	7.376
84	0.10	0.001	50	3.4	0.08	R	8.099
85	0.05	0.008	30	1.1	0.02	D	5.189
86	0.05	0.008	50	1.1	0.02	D	5.238
87	0.05	0.008	30	1.1	0.05	D	5.154
88	0.05	0.008	50	1.1	0.05	D	5.179
89	0.05	0.008	30	0.9	0.02	D	4.242
90	0.05	0.008	50	0.9	0.02	D	4.236
91	0.05	0.008	30	0.9	0.05	D	4.219
92	0.05	0.008	50	0.9	0.05	D	4.216
93	0.05	0.008	30	2.9	0.04	D	9.678
94	0.05	0.008	50	2.9	0.04	D	9.597
95	0.05	0.008	30	2.9	0.08	D	9.728
96	0.05	0.008	50	2.9	0.08	D	9.785

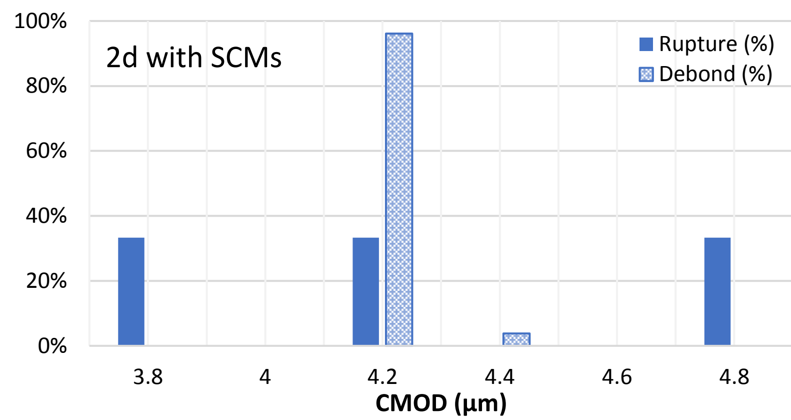


(a) (b)

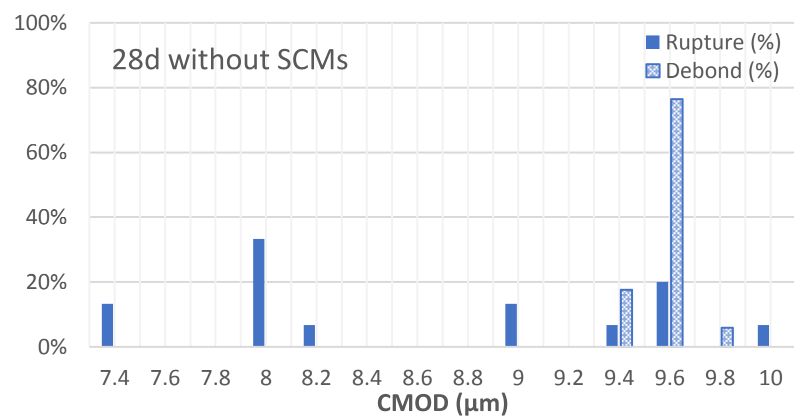
Figure 2-4 Capsule failure modes: (a) Rupturing, (b) Debonding



(a)



(b)



(c)

Figure 2-5 CMOD and capsule failure modes for the three mortar mixes, (a) 2d without SCMs, (b) 2d with SCMs, and (c) 28d without SCMs

Further examination of the results reveals the interactions between the capsule geometry and property, and the mortar property. For the 2d mixes without SCMs, and moving from low to high CMOD values, the following observations are deduced: 1) Large capsules with thin shell and low rupture strength are for most cases rupturing; 2) For the smaller capsule and thicker shell or high rupture strength, debonding is the predominant mode of failure; 3) There was no dominant failure pattern observed when the capsule rupture strength, the bond strength, and the capsule geometry are found to have equally competing values. The 2d mixes with SCMs experienced similar behavior but with lower CMOD values, notably: 1) Large capsules with thin shell always experienced rupturing despite their rupture strength; 2) Capsules with higher rupture strength need large CMOD value to fail without altering the mode of failure being rupture or debond; 3) Small capsules with thicker shell will most likely debond. And, for 28d mixes without SCMs, the predominant mode of failure is rupturing of the shell at the high CMOD values including thicker shell and smaller capsules except for those with a low capsule radius-to-thickness ratio, specifically 6 to 20. This observation includes the capsules with very thick shell of 8 μm.

Comparing the model results to the observations made from experimentally reported data on self-healing mortar, one can provide insights into the inconsistencies in the system performance. First, examining the geometry of the capsules it was deduced from the model that most of the capsules whose radius to thickness ranged from 6 to 20 debonded, 20 to 30 debonded or ruptured depending on the capsule rupture strength, and from 33 to 100 ruptured. This implies that the diameter of the capsule, without considering the other geometrical properties such as thickness, and without considering the rupture strength of the capsule is not a sufficient measure to predict the response of the capsule. It should be noted that the capsule used in the model ranged from 100 to 200 μm in diameter and 1 to 8 μm in thickness. Closer examination of Wang et al.'s [38] experimental results reveals that the employed capsules had a radius to thickness ratio ranging from 4 to 38, and that some capsules were ruptured whereas others debonded when tested at 28 d. These experimental observations support the deduced model results where rupturing as the prevalent mode of failure occurs when the ratio is between 33 and 100. Likewise, Lv et al. [33] reported that some of the capsules were ruptured by the crack, whereas others remained intact in the cement paste. Again, their capsules' radius to thickness ratio ranged from 0.20 to 45. Dong et al. [64] noted that the capsules ruptured when tested but unfortunately made no mention of the capsules debonding or of the capsules thickness. Second, the mechanical properties of the mortar when pre-cracked, which are dictated by the age and composition of the mixture, and the crack width are found to highly affect the capsule mode of failure. These observations further explain the inconsistencies in the performance of self-healing mortar. Third, the absence of a standard test that accounts for the properties of the mortar and capsule, and a clear methodology for pre-cracking and testing performance of self-healing mortar have added to the uncertainty in the body of knowledge.

2.4 Conclusions

The results from the analytical study and the review of the literature yield the following conclusions:

1) There is a need for developing standard test methods to measure the capsules geometry, being diameter and thickness, and mechanical properties, and the mechanical properties of the interface between the mortar and the capsule.
2) There is a need for developing standard test methods for measuring the survival rate of capsules during mixing and placing of concrete as a pre-requisite to determining efficiency of the self-healing cementitious system.
3) There is no clear definition of self-healing efficiency nor a define method for measuring self-healing efficiency of mortar and other cementitious systems.
4) Inconsistencies in the reported self-healing mortar performance are attributed to the inter-relationship between the geometry of the capsules, the properties of the capsules, the properties of the mortar, and the pre-crack width induced in the mortar.
5) The capsules' radius to thickness is found to significantly affect the capsule mode of failure.
6) The crack opening affects the capsule failure mode differently depending on the age and composition of the mortar, and properties of the capsule.
7) The age of the mortar is important when testing self-healing system especially when mortar is susceptible to cracking at early age.

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Chapter 3

3 Performance modelling of spherical capsules during mixing of self-consolidating concrete

Abstract

Autonomous healing is a very promising technique in self-healing concrete systems. For capsules to achieve their anticipated performance, they should survive concrete harsh mixing conditions, yet rupture upon concrete cracking. At present, there are no standard test methods, experimentally or analytically, for determining the capsule survival rate during mixing. This study investigates the correlation between the capsules' shell properties, concrete rheological properties, capsules' external forces, and capsule survival rate during concrete mixing. Finite element and statistical modelling techniques were employed to evaluate the capsule performance and predict the survival rate of capsules during concrete mixing with 68% confidence. The results revealed capsules' radius-to-thickness ratio between 30 and 45 are likely to survive concrete mixing and yet still rupture upon concrete cracking.

Keywords: self-healing; capsule survival rate; FE Model; probability; rheological properties; concrete; concrete pan mixer

3.0 Introduction

Encapsulation, which is employed to protect the healing agent during the mixing and casting of fresh concrete, and to release the agent upon cracking of hardened concrete [1,2], is a promising technique for autonomous self-healing concrete systems [3–22]. For the capsules to achieve their objective, the shell's mechanical and geometrical properties need to be compatible with those of the concrete matrix. Ideally, the shell needs to be ductile to endure the harsh concrete mixing conditions and brittle to rupture upon concrete cracking. Different shell materials have been investigated and tested in the literature including glass [5,21–29], ceramic [21,29], and polymers [2–4,9,12,14–16,18,19,30–41]. Test results revealed that glass and ceramic have low survivability during mixing [42,43], whereas polymers have “switchable” mechanical properties with a higher survival ratio [13,44–47]. The robustness of capsules to survive mixing conditions require not only to resist the shear forces applied by the concrete mixer but also the punching stress exerted by the aggregates [47–49]. The review of the literature revealed that there are no standard test methods for measuring the performance of capsules in terms of survivability during concrete mixing and placing. The studies documented in the literature, which are presented next, show inconsistencies in the results as different test methods and measuring techniques are used to assess the performance. Moreover, capsules’ survival rate during mixing is found to be highly influenced by the geometrical and mechanical properties of the shell, concrete rheological properties, and speed and type of the concrete mixer. As such, a need exists to develop standard testing protocols to evaluate the performance of capsules in self-healing cementitious materials during the mixing and placing of concrete. This study aims to address this need by investigating analytically the relationship between the shell's geometrical and mechanical properties, concrete rheological properties, and the survival rate of the self-healing capsules. Numerical and statistical models are employed to predict the capsule survival probability with 68% confidence during mixing. The paper includes five parts: introduction; a brief literature review of the test methods used to evaluate the survivability of capsules during concrete mixing; the methodology proposed to determine the survivability of capsules in concrete during mixing which includes material properties, idealized model of capsules during mixing, and design of experiment; the model results, and analysis and discussion of the results; and conclusions.

3.1 Literature Review – A brief

The survivability of capsules during concrete mixing is pivotal to the effectiveness of self-healing concrete systems. Being the vessel for the healing agents, if the capsules were ruptured during mixing, then their presence in the self-healing cementitious matrix becomes detrimental to the concrete mechanical properties of the concrete matrix. Among several encapsulation materials investigated in the literature for their suitability in self-healing concrete applications, glass and ceramic have shown limited ability to survive mixing conditions and needed protection techniques to enhance their ductility [25,29,47,48,50,51], while polymeric materials have shown promising results in surviving concrete mixing [13,44–47].

The review of the literature revealed two testing methodologies have been adopted to investigate the survivability of self-healing capsules; 1) Chemical stability [3,13,38,45,46,49,52–54], and 2) Mechanical stability [22,44,55,56]. The survivability of the capsules is determined by either manually counting the number of intact capsules and/or by visually inspecting the capsules' morphology using optical microscope and Scanning Electron Microscopy (SEM) [16,31,57–59].

The chemical stability test, which consists of immersing the capsules in a high pH solution mimicking concrete pore solution followed by a mechanical test, aims to ensure that the capsules' mechanical properties are not altered by the concrete pore solution using SEM. The tensile strength of PLA, PS and P(MMA-n-BMA) tubes were tested before and after immersing in cement slurry with a pH of 12.5 to 13 for 7 to 14 days. The results have shown that only P(MMA/n-BMA) tubes' strength was lower [3,53]. Others investigated the chemical resistance of soda glass capsules by filling the capsules with a traceable fluorescent dye and immersing them in a solution with a pH of 12. They reported no leakage or observed change in the physical properties [52]. Lv et al. [38] and Giannaros et al. [49] immersed phenol-formaldehyde (PF) dicyclopentadiene (DCPD)-filled microcapsules and sodium silicate-filled poly-urea and Gelatin-gum Arabic capsules, respectively, in saturated calcium hydroxide solution for 48 h, and confirmed through SEM images that the capsules maintained their morphology. Kanellopoulos et al. [13] and Al-Tabbaa et al. [46] tested the chemical stability of dry and hydrated Gelatin-acacia gum microcapsules by immersion for 2 months in sodium hydroxide solution with pH of 11.5, 12.5, and 13.5. Using SEM and optical microscope images, the capsules were found to remain spherical. Also, Mao et al. [54] confirmed the survivability of the sodium silicate microcapsules with polyurea shell for oil well cement application by immersing some capsules in a saturated calcium hydroxide solution with pH of 13 at 80 ^{o}C for 14 days, and others in a cement slurry. SEM images of capsules in saturated solution or the thin cement paste layer extracted from the cement slurry showed that the capsules survived the mixing process.

Testing the mechanical stability during mixing was reported for large-size capsules with visual count employed to determine the number of intact capsules. The developed tests consist of mixing the fresh concrete, then sieving it under running water to capture the surviving capsules. Hu et al. [22] mixed 10 glass cylindrical capsules that are 8 mm inner diameter, 1 mm thick, and 30 mm long, and filled with polyurethane healing agent, with cement mortar in a mixing pan at a speed of 65 rpm for 3 min and reported a survival rate of 90 to 100%. Gruyaert et al. [55] mixed 10 ethyl cellulose (EC) cylindrical capsules of 3 mm inner diameter, 1 mm thick, and 50 mm long, and 10 glass EC-coated capsules of 1.7 mm inner diameter, 0.3 mm thick, and 25 to 50 mm long, using 3 different concrete batches in a concrete mixer for 2 min at 140 rpm followed by 1 min at 285 rpm. The results revealed 100% capsule survival when 25% plasticizer was used to the mix, 40 to 90% survival for 10% plasticizer for EC capsules, and 80-90% survival for glass-EC coated capsules. Sinha et al. [56] mixed 20 polylactic acid (PLA)-based biomass elongated elliptical capsules with 12 concrete batches in a revolving drum tilting mixer. To account for the effect of the capsules' geometry, a range of sizes between 5 to 19.05 mm and thicknesses of 0.4 to 2 mm was used with aspect ratio varying between 1:1:1, 1.5:1:1, and 2:1:1, to mimic gravel and sand sizes used in the concrete mix. The standard concrete mixing protocol was first used, then the capsules were added to the mix and mixed for an additional 5 min. Capsules of smaller size and higher aspect ratio were found to perform better, specifically the survival ratio of 9.5 mm capsules with an aspect ratio of 2:1:1 and 0.4 mm thick was 95 to 100%. Araújo et al. [44] mixed the dry components of concrete for 1 min, added the water and mixed for another 1 min, then added the Poly (methyl methacrylate) capsules and mixed for 2 additional min. Three sets of cylindrical capsules' sizes and thicknesses were used, 6.5±0.3 mm, 0.7±0.1 mm, 5.9±0.6 mm, 0.4±0.1 mm, and 5.8±0.3 mm, 0.2±0.1 mm, with 50 mm length. They concluded that capsules with thicker walls have a higher survival rate.

From the previous studies, the following observations can be deduced:

i. Standardized tests to evaluate the survivability of capsules during concrete mixing are needed.
ii. Test results show that capsules have the required chemical resistance to survive in high alkaline concrete pore solution.
iii. Capsules survival rate, being due to chemical and/or mechanical tests, is deduced from visual inspection of few capsules and assuming that the sample is representative of the whole sample. One needs to establish the statistical properties of the sample before accepting such an approach.
iv. The type of mixer, speed of mixing, mixing time, and mixing technique varied between different studies, which makes it difficult to compare the results even for the capsules made with the same material.
v. Concrete rheological properties affect the capsules' survivability rate.
vi. Capsules in mortar have a higher survivability than those added to concrete.
vii. Capsules with smaller diameter and thicker walls have a higher survival rate.

3.2 Methodology

Finite element and statistical modelling techniques were employed for determining the survivability of polymeric capsules in a concrete mixer. Experiments carried out by the authors and data reported in the literature were used to quantify the rheological properties of fresh concrete, and the mechanical and geometrical properties of polymeric capsules, respectively. It was postulated that the rheological properties of concrete and the rotational speed of the mixer affect the shearing stress and normal stress exerted on the capsules during mixing, respectively. Standard deviation was the measure used to account for the variability in the capsules' geometrical and mechanical properties. Design of experiment technique (DOE) was employed to study the relationship between the input variables and the capsules' survival rate which was predicted with 68% confidence. Details of the material properties, model development, and DOE are provided next.

3.2.1 Material and Geometrical Properties

Two self-consolidating concrete (SCC) mixes, designed to have a minimum slump flow of 600 mm, were used in this study. A ring-pan mixer [60] was used for mixing the SCC mixes. The composition and measured properties of the two mixes are given in Table 3-1. Portland-Limestone cement (CSA type GUL) and ground granulated blast furnace slag (GGBFS) were provided by Lafarge Holcim, Canada. The corresponding physical and chemical properties are presented in Table 3-2. High-range water-reducing admixture (HRWRA), Glenium© 7700 [61] and viscosity modifying admixture (VMA), MasterMatrix© VMA 362 [62], were added to the mixes to achieve the design slump flow. Regarding the coarse aggregates, the nominal maximum aggregate size, specific gravity, bulk density, and absorption are 14 mm, 2.74, 1544 kg/m3, and 1.58%, respectively. The fineness modulus, specific gravity, bulk density, and absorption of fine aggregate are 2.88, 2.71, 1746 kg/m3, and 1.28%, respectively. The bulk density, specific gravity, and absorption of coarse and fine aggregates were determined in accordance with ASTM C127-15 [63] and ASTM C128-15[64], respectively. The slump flow and density were measured in accordance with ASTM C1611-18 [65] and CSA A23.2-4C:14[66], respectively. RheoCAD 500, a concrete rheometer developed by CAD Instruments [67] along with the Bingham material model [68–70] were used to estimate the rheological properties of SCC mixes.

Table 3-1 Self-Consolidating Concrete mix design used in the FE model

Mixture Proportion	**SCC Mix #1**	**SCC Mix #2**
Water-to-Cementing Materials Ratio, w/cm	0.32	0.32
GUL (% mass of cm)	100	70
GGBFS (% mass of cm)	0	30
Cementing Content (kg/m^3)	450	450
Volume Fraction of Coarse Aggregate, V_{CA} (m^3/m^3)	0.30	0.25
Volume Fraction of Fine Aggregate, V_{FA} (m^3/m^3)	0.35	0.40
HRWRA, (% mass of cm)	0.84	0.69
Fresh Properties		
Density, ρ (kg/m^3)	2451	2416
Slump flow, S_f (mm)	638	680
Viscosity, μ (Pa.s)	49	78
Yield Stress, τ_0 (Pa)	40	16

Table 3-2 Physical and chemical properties of cement used in the study [71]

Oxides, Compounds	Composition (% mass)	
	GUL	GGBFS
CaO	61.3	36.9
SiO_2	18.0	36.2
Al_2O_3	4.4	10.4
Fe_2O_3	2.8	0.6
MgO	2.9	11.9
K_2O	0.5	0.5
Na_2O	0.2	0.4
Na_2O_{eq}	0.6	0.8
SO_3	3.6	2.7
TiO_2	0.3	1.1
MnO	2.9	0.5
Free CaO	1.1	
Limestone	11.5	
Loss on Ignition	5.5	0.8
Total	96.8	101.2
C_3S	47	
C_2S	16	
C_3A	7	
C_4AF	8	
Specific Surface Area, Blaine (m^2/kg)	468	475
Specific Gravity	3.15	2.92
Compressive Strength, 28d (MPa)	41.7	

For the capsule, two values for the diameter and thickness were considered along with a single value for the rupture strength and fracture energy as given in Table 3-3. Standard deviation, which was estimated from the work of Wang et al. [9], was included to account for the variability in the capsules' geometry and rupture strength. The capsules' rupture strength and fracture energy were deduced from data reported in the literature for polymeric shell material [72].

Table 3-3 Capsule properties used in the FE model

Variables	Mean±Standard Deviation	
Diameter of Capsule, D_s (mm)	0.2±0.057	0.5±0.142
Shell Thickness, t_s (mm)	0.002±0.0006	0.003±0.0008
Rupture Strength of Capsule, f_{rs} (MPa)	30.0 ± 2.5	
Fracture Energy, G_s (J/m^2)	100	

3.2.2 Finite Element Model

The idealized model, which is schematically shown in Figure 3-1, consists of a single capsule located at the bottom and outer edge of the concrete mixer. This scenario afforded the inclusion of all the external forces exerted on the capsule, namely the weight of the concrete (W), the centrifugal force (F_c) caused by the rotation of the mixer, and the shear force (τ) due to mixing and flow of fresh concrete.

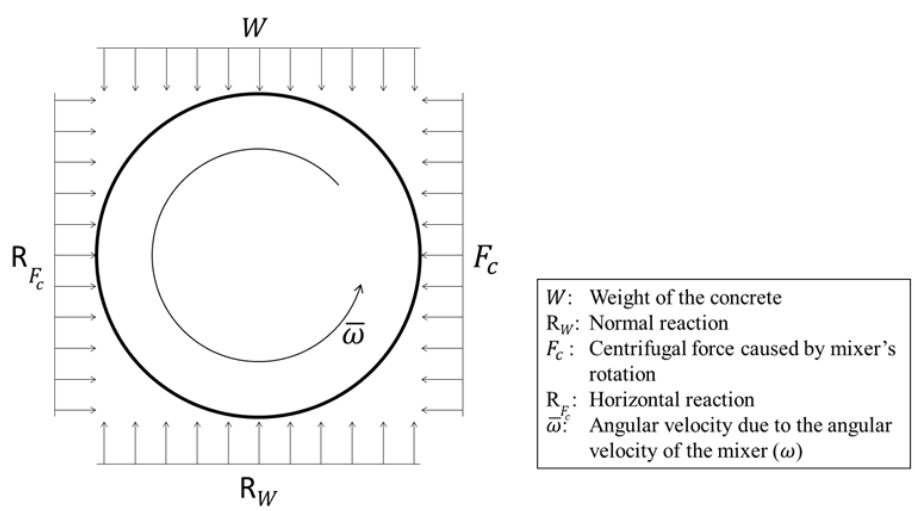

Figure 3-1 Schematic model of a single capsule in a concrete mixer

The weight (W) corresponding to the concrete layer atop the capsule can be estimated by

$$W = \rho \frac{\pi}{4} D_s^2 t_c g \tag{1}$$

in which ρ is the density of the fresh concrete (kg/m^3), D_s the diameter of the capsule (m), t_c the thickness of the concrete layer atop the capsule (m), and g the gravitational acceleration (m/s^2). The thickness of the concrete layer is deduced from the size of the mixer and its maximum concrete yield.

The centrifugal force (F_c) caused by the rotation of the mixer is estimated by

$$F_c = \rho \frac{\pi}{4} D_s^2 \left(\frac{d_m}{2}\right)^2 \omega^2 \tag{2}$$

in which d_m is the diameter of the mixer (m), and ω the angular velocity of the mixer (rad/s). For the LIEBHERR ring-pan mixer Type R [60] used in this study, the mixer nominal capacity, outer diameter, and rotational velocity is 1 m^3 of concrete, 2.425 m, and 26 rpm, respectively.

The forces, W and F_c, can be applied over the surface area of the capsule or as a point force. The former represents the contact pressure between the concrete paste and the capsule, and the latter represents the punching of the capsule by an aggregate. The contact surface is modelled in accordance with Hertzian contact pressure, where

$$P(r) = P_o \left(1 - \frac{r^2}{D_s^2}\right)^{1/2} \tag{3}$$

in which P_o being the maximum contact pressure corresponding to W and F_c over the surface area of the capsule (MPa), r the radial distance (m), and D_s the diameter of the capsule. Hertzian contact model has been used to characterize the response of microcapsules tested under compression in several self-healing studies [73–75].

The likelihood of an aggregate punching a capsule, increases with the decrease in concrete paste thickness. As such, a model developed by Chidiac et al. [76] is employed to determine the average-paste-thickness (APT) of the 2 SCC mixes. The APT model is reproduced below, where

$$APT = -\frac{1}{2}\left(D_{fa} + \frac{\phi_{ca}D_{fa}^2}{\phi_{fa}D_{ca}} + \frac{\phi D_{fa}^2(1-\phi_{max})}{\phi_{fa}\phi_{max}D}\right) + \frac{1}{2}\sqrt{\left(D_{fa} + \frac{\phi_{ca}D_{fa}^2}{\phi_{fa}D_{ca}} + \frac{\phi D_{fa}^2(1-\phi_{max})}{\phi_{fa}\phi_{max}D}\right)^2 + \frac{4}{3}\frac{(\phi_{max}-\phi)}{\phi_{max}}\frac{D_{fa}^2}{\phi_{fa}}} \quad (4)$$

and $D = \left(\frac{{D_{ca}}^3\phi_{ca}+{D_{fa}}^3\phi_{fa}}{\phi_{ca}+\phi_{fa}}\right)^{1/3}$ (5)

in which D, D_{fa}, and D_{ca} are the mean diameters of the total aggregate gradation, fine aggregate gradation, and coarse aggregate gradation corresponding to 50 % passing, respectively. ϕ,$\phi_{fa,}$ ϕ_{ca}, and ϕ_{max} are volume fraction of aggregates, fine aggregates, coarse aggregates, and maximum packing density of aggregates, respectively. The volume fraction of fine and coarse aggregates, along with ϕ_{max},ϕ/ϕ_{max}, D, and APT for the 2 mixes are reported in Table 3-4. The results, which show that the capsule diameter is significantly larger than the APT, indicate that there is a maximum likelihood of capsules being punched by aggregates.

Table 3-4 Aggregates volume fraction and APT measurements

Mix #	ϕ_{fa}	ϕ_{ca}	ϕ_{max}	ϕ/ϕ_{max}	D (mm)	APT (mm)
1	0.35	0.30	0.78	0.83	6.56	0.11
2	0.40	0.25	0.77	0.84	6.18	0.10

The mixing of fresh concrete begins when the shear stress (τ) exceeds the concrete yield stress (τ_0) and increases linearly with the concrete plastic viscosity (μ) and shear strain rate ($\dot{\gamma}$) as given by Bingham model [68–70], where

$$\tau = \tau_0 + \mu\dot{\gamma} \quad (6)$$

The concrete Bingham properties represented by the yield stress and plastic viscosity were measured experimentally and reported in Table 3-1. The shear strain rate ($\dot{\gamma}$) is assumed uniform and calculated using the following relationship

$$\dot{\gamma} = \frac{\omega\left(\frac{d_m}{2}\right)}{t_c} \quad (7)$$

An idealized 2-D plane strain finite element (FE) model was developed for this analysis using the commercial finite element program ABAQUS [77]. The FE model, which is shown in Figure 3-2, consists of a single spherical capsule surrounded by three contact surfaces representing the bottom and side edge of the mixer and the concrete atop the capsule. The contact interface between the mixer wall and the capsule outer layer is modelled as a surface friction with a static friction coefficient of 0.34 [78]. The top contact interface represents the cohesive structure of the fresh concrete atop the capsule. The three loads shown being vertical, horizontal, and circumferential represent the weight of the concrete atop the capsule, the centrifugal force, and the shear load, respectively. The FE mesh consists of an 8-node biquadratic plane strain quadrilateral (CPE8) with 4 elements along the thickness of the capsules and 1:1 aspect ratio.

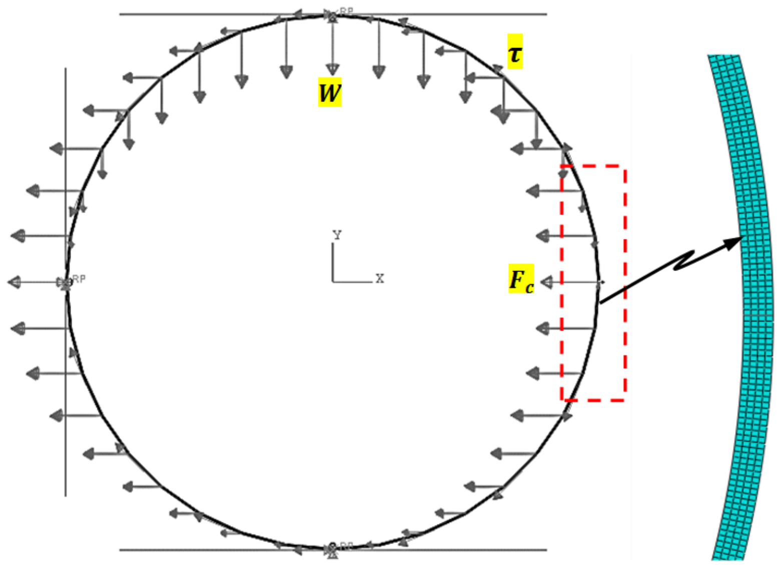

Figure 3-2 FE model includes geometry, boundary & loading conditions, and mesh.

The cohesive interface surface model, developed by ABAQUS [77], was employed to capture the fracture of the capsule surface. The interface was placed along the horizontal direction passing through the diameter of the shell. Damage initiates when the nominal stress reaches the rupture strength of the capsule and propagates based on the energy dissipation governed by the fracture toughness (G) [72].

3.2.3 Design of Experiments

The analysis was carried out using DOE technique to determine the interaction between the input parameters and the output, specifically the survival of the capsule. Two diameters and two thicknesses of the capsule were included. Additionally, the mean plus and minus one standard deviation were analyzed for the capsule geometry and the capsule rupture strength. Moreover, 2 loadings were considered to account for the interaction between the capsule and concrete paste and the capsule and aggregate. The analyses carried out are summarized in Table 3-5.

Table 3-5 DOE developed for this study

D_s (mm)	t_s (mm)	Mix #1			Mix #2		
		Centrifugal Stress (kPa)	Weight (kPa)	Shear Stress (kPa)	Centrifugal Stress (kPa)	Weight (kPa)	Shear Stress (kPa)
Loading Scenario #1: Hertz Contact Pressure							
0.200±0.057	0.002±0.0006	8.68	1.69	1.02	8.56	1.67	1.57
0.500±0.142	0.003±0.0008						
Loading Scenario #2: Aggregate Punching							
0.200+0.057	0.002±0.0006	1.796	1.69	1.02	1.771	1.67	1.57
0.200	0.002±0.0006	1.091			1.075		
0.200-0.057	0.002±0.0006	0.561			0.553		
0.500+0.142	0.003±0.0008	11.226			11.066		
0.500	0.003±0.0008	6.818			6.721		
0.500-0.142	0.003±0.0008	3.504			3.454		

3.3 Results, Analysis, and Discussion

The results revealed two potential failure modes for the capsule as shown in Figure 3-3. The first mode is due to stretching and/or rupturing of the capsule shell caused by the pressure from surrounding concrete paste, and the second mode is due to punching of the capsule shell caused by the aggregates. The criteria for the first failure mode are the elongation of the shell and the rupture strength of the material. The criterion for the second failure mode is the rupture strength of the material. For reference, the rupture strength of the capsule, f_{rs} = 30.0±2.5 MPa, and the elongation limit of the urea-formaldehyde shell is 0.75±0.08% [79].

The FE analyses, which yielded the shell state of stress and strain as well the survivability of the capsule to squeezing and stretching by concrete paste and pinching by aggregates, are summarized in Table 3-6. CSMAXSCRT is a variable in ABAQUS that indicates whether the contact stress damage initiation criterion has been satisfied at the contact point with a value of Zero for an undamaged surface to One for the initiation of damage [77]. The results also include the maximum contact pressure, the maximum true logarithmic strain, and the observed failure mode.

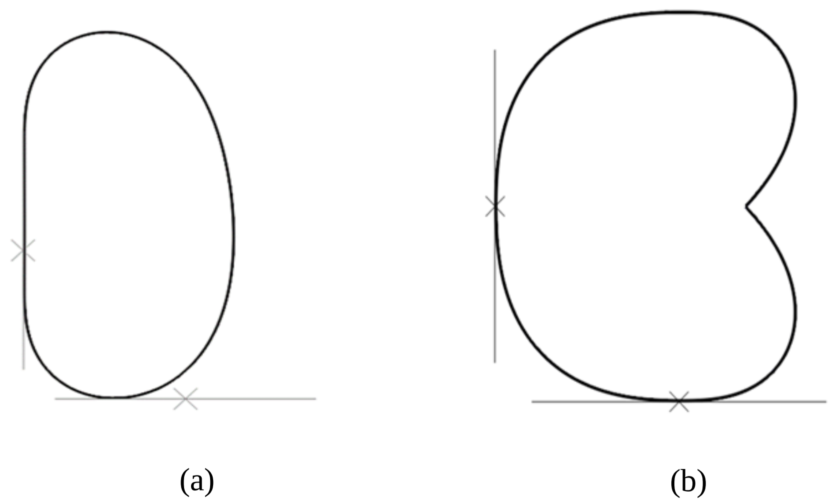

Figure 3-3 Capsule failure modes deduced from the FE analysis, (a) Stretching and/or rupturing, (b) Punching

Table 3-6 FE results including observed capsule performance

Mix #1		**Loading scenarios**							
		Contact Pressure					Point Load		
D_s (mm)	t_s (mm)	CSMAX SCRT	Pressure (MPa)	Performance	Log Strain (%)	Performance	CSMAX SCRT	Pressure (MPa)	Performance
0.257	1.4	0.8	24.27	Survived	0.55	Survived	1.0	34.11	Ruptured
0.257	2.0	0.6	17.83	Survived	0.50	Survived	1.0	42.11	Ruptured
0.257	2.6	0.4	12.60	Survived	0.31	Survived	1.0	37.75	Ruptured
0.200	1.4	0.7	20.21	Survived	0.59	Survived	1.0	41.68	Ruptured
0.200	2.0	0.4	12.81	Survived	0.32	Survived	0.9	32.53	Survived
0.200	2.6	0.3	8.07	Survived	0.19	Survived	0.5	18.64	Survived
0.143	1.4	0.4	13.27	Survived	0.33	Survived	0.7	23.87	Survived
0.143	2.0	0.2	7.02	Survived	0.17	Survived	0.3	11.58	Survived
0.143	2.6	0.1	4.19	Survived	0.10	Survived	0.2	7.026	Survived
0.642	2.2	0.5	16.22	Survived	0.54	Survived	1.0		Ruptured
0.642	3.0	0.8	23.13	Survived	0.48	Survived	1.0		Ruptured
0.642	3.8	0.8	25.36	Survived	0.61	Survived	1.0	41.19	Ruptured
0.500	2.2	0.7	19.52	Survived	0.44	Survived	1.0		Ruptured
0.500	3.0	0.9	26.49	Survived	0.60	Survived	1.0	37.22	Ruptured
0.500	3.8	0.6	19.20	Survived	0.53	Survived	1.0	44.62	Ruptured
0.358	2.2	0.9	26.02	Survived	0.59	Survived	1.0	36.52	Ruptured
0.358	3.0	0.6	16.81	Survived	0.45	Survived	1.0	51.59	Ruptured
0.358	3.8	0.4	11.76	Survived	0.29	Survived	1.0	52.44	Ruptured

Mix #2		**Loading scenarios**							
		Contact Pressure					Point Load		
D_s (mm)	t_s (mm)	CSMAX SCRT	Pressure (MPa)	Performance	Log Strain (%)	Performance	CSMAX SCRT	Pressure (MPa)	Performance
0.257	1.4	0.8	24.39	Survived	0.55	Survived	1.0	33.74	Ruptured
0.257	2.0	0.9	26.09	Survived	0.76	Ruptured	1.0	41.42	Ruptured
0.257	2.6	0.6	18.24	Survived	0.47	Survived	1.0	37.25	Ruptured
0.200	1.4	0.9	27.71	Survived	0.70	Ruptured	1.0	36.31	Ruptured
0.200	2.0	0.6	18.56	Survived	0.48	Survived	0.9	32.15	Survived
0.200	2.6	0.4	12.02	Survived	0.29	Survived	0.5	18.48	Survived
0.143	1.4	0.6	19.19	Survived	0.50	Survived	0.7	23.69	Survived
0.143	2.0	0.4	10.55	Survived	0.25	Survived	0.3	11.46	Survived
0.143	2.6	0.2	6.37	Survived	0.15	Survived	0.2	6.964	Survived
0.642	2.2			Survived		Survived	1.0		Ruptured
0.642	3.0			Survived		Survived	1.0		Ruptured
0.642	3.8	0.9	27.10	Survived	0.61	Survived	1.0	34.55	Ruptured
0.500	2.2	0.7	22.28	Survived	0.76	Ruptured	1.0	31.96	Ruptured
0.500	3.0	0.9	26.76	Survived	0.60	Survived	1.0	33.41	Ruptured
0.500	3.8	0.9	25.98	Survived	0.74	Ruptured	1.0	43.74	Ruptured
0.358	2.2	0.9	26.09	Survived	0.59	Survived	1.0	43.17	Ruptured
0.358	3.0	0.8	22.67	Survived	0.65	Survived	1.0	55.53	Ruptured
0.358	3.8	0.6	17.01	Survived	0.44	Survived	1.0	51.42	Ruptured

Assuming the results follow a normal distribution, the capsule probability of failure based on a 68% confidence level was analyzed using the finite element results and the corresponding material properties. The three failure modes were analyzed separately and the results in the form of probability of failure (P_f) are presented in Table 3-7. The overall P_f was determined on the assumption that 90% of the capsules are surrounded by concrete paste and 10% by aggregates. From the results of Table 3-7, the probability of failure of the two capsule sizes, specifically 0.2 mm and 2.0 mm, and 0.5 mm and 3.0 mm, for mixes 1 and 2, are 6.6%, 11.2%, 8.7%, and 11.3%, respectively. Recalculating the overall P_f with the assumption that 100% of the capsules are surrounded by concrete paste and 0% by aggregates, the results become 0.0%, 1.3%, 2.6%, and 1.9%, respectively. These results reveal that 1) the rheological properties of the concrete mix affect the survivability of small size capsules and that the effect decreases with an increase in capsule diameter, 2) the survivability of the capsule decreases as the capsule size increases regardless of the rheological properties of concrete, 3) the interaction of aggregates with the capsules significantly affect the survivability of the capsules, and 4) on average, 90% of the capsules are expected to survive the mixing of concrete for a material rupture strength of 30±2.5 MPa and elongation limit of 0.75±0.08%.

Table 3-7 Capsule probabilities of failure

Mix #1			**Probability of Failure (%)**			
D_s (mm)	t_s (mm)	$D_s/2t_s$	Contact pressure		Point Load	Total
			Rupturing	Stretching	Rupturing	
0.257	1.4	92	1.1	0.4	95.0	9.8
0.257	2.0	64	0.0	0.1	100.0	10.0
0.257	2.6	49	0.0	0.0	99.9	10.0
0.200	1.4	71	0.0	1.6	100.0	10.0
0.200	2.0	50	0.0	0.0	84.4	8.4
0.200	2.6	38	0.0	0.0	0.0	0.0
0.143	1.4	51	0.0	0.0	0.7	0.1
0.143	2.0	36	0.0	0.0	0.0	0.0
0.143	2.6	28	0.0	0.0	0.0	0.0
0.642	2.2	146	0.0	0.3	100.0	10.0
0.642	3.0	107	0.3	0.0	100.0	10.0
0.642	3.8	84	3.2	3.2	100.0	12.9
0.500	2.2	114	0.0	0.0	100.0	10.0
0.500	3.0	83	8.0	2.5	99.8	12.3
0.500	3.8	66	0.0	0.2	100.0	10.0
0.358	2.2	81	5.6	1.6	99.5	11.4
0.358	3.0	60	0.0	0.0	100.0	10.0
0.358	3.8	47	0.0	0.0	100.0	10.0
Mix #2			**Probability of Failure (%)**			
D_s (mm)	t_s (mm)	$D_s/2t_s$	Contact pressure		Point Load	Total
			Rupturing	Stretching	Rupturing	
0.257	1.4	92	1.2	0.3	93.3	9.6
0.257	2.0	64	5.9	57.6	100.0	15.3
0.257	2.6	49	0.0	0.0	99.8	10.0
0.200	1.4	71	18.0	27.4	99.4	26.1
0.200	2.0	50	0.0	0.0	80.5	8.1
0.200	2.6	38	0.0	0.0	0.0	0.0
0.143	1.4	51	0.0	0.0	0.6	0.1
0.143	2.0	36	0.0	0.0	0.0	0.0
0.143	2.6	28	0.0	0.0	0.0	0.0
0.642	2.2	146	0.0	0.0	100.0	10.0
0.642	3.0	107	0.0	0.0	100.0	10.0
0.642	3.8	84	12.3	3.1	96.6	12.5
0.500	2.2	114	0.1	55.5	100.0	10.1
0.500	3.0	83	9.7	2.4	91.4	11.3
0.500	3.8	66	5.4	45.8	100.0	14.9
0.358	2.2	81	5.9	1.6	100.0	11.4
0.358	3.0	60	0.2	8.5	100.0	10.2
0.358	3.8	47	0.0	0.0	100.0	10.0

Figure 3-4 displays the probability of failure calculated for the capsules' radius to thickness for both concrete mixes. The effects of capsules' geometry and rheological properties of the concrete mix are evident. The results show that for capsules whose radius-to-thickness ratio is greater than 45, their probability of failure increases from 0 to 10%. Moreover, the combined effect of the concrete rheological properties and the capsules' geometry on the capsules' survivability is complex. For mix #2, an increase from 10% to 26% is observed for the capsules whose radius-to-thickness ratio range between 60 to 80, and an increase from 10% to 13% is observed for both mixes for the capsules whose radius-to-thickness ratio range between 80 to 90. In general, the capsules' survivability decreases to 90% once the capsule radius-to-thickness ratio is greater than 45. This finding agrees well with a previous recommendation for capsules' radius-to-thickness ratio ranging between 30 to 100 for rupturing instead of debonding upon cracking of hardened concrete [72]. Based on these results, the recommendations are amended to capsules' radius-to-thickness ratio of 30 to 45 for surviving concrete mixing and yet still rupture upon cracking of hardened concrete.

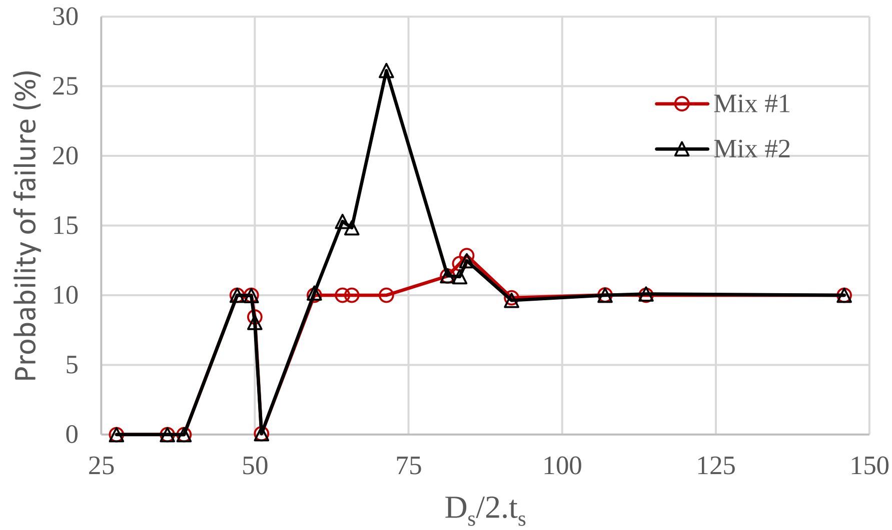

Figure 3-4 Capsule radius-to-thickness probability of failure

The FE results are found to agree with Souza and Al-Tabbaa experimental data [59]. Their SEM images revealed that the acrylate shell of the capsules' radius-to-thickness ratio of 6.3 and 27.5 survived concrete mixing. Kanellopoulos et al. [13]used Gelatin-acacia gum capsules and reported that capsules whose radius-to-thickness of about 50 debonded from the cement paste prisms after testing under a three-point-bending test, while the smaller capsules whose radius-to-thickness less than 30 showed better bonding with the surrounding matrix [13]. These experimental findings further support our amended recommendation of using capsules whose radius-to-thickness ratio is between 30 to 45 to ensure their survivability during concrete mixing and yet still rupture upon cracking of hardened concrete.

3.4 Conclusions

This paper presents a finite element model for studying the survivability of capsules during concrete mixing. The model considers all possible interactions between the capsules and the surroundings, as well as accounts for the geometry of the capsules and the rheological properties of the concrete. The capsules' probabilities of failure were determined using statistical models and assuming a normal distribution. Accordingly, the following conclusions are drawn:

(1) A handful of papers have studied the survivability of capsules during mixing as part of a self-healing concrete system.

(2) The capsules' radius-to-thickness ratio highly influences the survivability of the capsules during concrete mixing.

(3) Rheological properties of fresh concrete affect the survivability of small size capsules and that effect decreases with an increase in capsule diameter.

(4) Interaction between aggregates and capsules adversely affects the survivability of capsules.

(5) Capsules whose radius-to-thickness ratio is greater than 45, their probability of failure increases from 0 to 10%.

(6) The combined effect of concrete rheological properties and capsules geometry on the capsules‘ probability of failure increases to 26% for mix #2 when the capsules' radius-to-thickness ratio is between 60 to 80, and 13% for mix #1 and mix #2 when the capsules radius-to-thickness ratio is between 80 to 90.

(7) The capsules' survivability decreases to 90% when the capsules' radius-to-thickness ratio is greater than 90 regardless of the concrete rheological properties.

The recommendations are to design self-healing concrete system with capsules' radius-to-thickness ratio between 30 to 45 to survive concrete mixing and yet still rupture upon cracking of hardened concrete, and that the development of a standard test needs to account for the capsule geometry and material properties, the concrete rheological properties, the concrete mix design specifically the APT and the aggregate content and angularity, and the speed of the mixer. Lastly, the findings, conclusions, and recommendations are specific to the variables investigated in this study.

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Chapter 4

4 Performance testing of self-healing early-age concrete using restrained shrinkage

Abstract

Performance of self-healing concrete at early-age was evaluated numerically by simulated ASTM C1581 restrained shrinkage test that accounts for the concrete's time-dependent mechanical properties, and capsule's geometrical and mechanical properties, and depth. Concrete shrinkage strain and mechanical properties were measured experimentally. Finite element modelling and fracture mechanics techniques were employed to simulate the concrete volume change due to autogenous and drying shrinkage and to calculate the corresponding concrete state of stress and crack development in a restrained shrinkage ring containing self-healing capsules. The performance of self-healing capsules in early-age concrete was found to depend on concrete's mechanical properties and geometry, stiffness ratio of concrete-to-capsule, tensile-to-rupture strength ratio of concrete-to-capsule, and the bond strength at the capsule-concrete interface. Presuming that all the capsules will remain intact while the concrete hardens is inaccurate.

Keywords: self-healing capsules; FE Model; concrete; shrinkage ring test; restrained shrinkage

4.0 Introduction

Concrete is prone to early-age cracking due to chemical reactions, and changes in its temperature and water content [1–4]. While cement is hydrating, its microstructure is evolving with time and so are its volume and mechanical properties. When the tensile stresses due to the volume change exceed the concrete's tensile strength, cracking occurs. The width of concrete early-age cracks ranges from micrometers to a few millimeters, which is sufficient to facilitate the onset and progression of various concrete deterioration mechanisms. These cracks, which occur frequently and are seldom addressed, compromise the durability of exposed concrete and the sustainability of concrete infrastructure [5–8].

Several standard test methods have been developed to assess concrete's susceptibility to early-age cracks due to restrained shrinkage such as uniaxial shrinkage tests [9–11], plate/ slab tests [12–14], and ring tests [15–17]. Among these tests, the restrained shrinkage ring test, which is shown in Figure 4-1, has gained wide acceptance because it allows the quantification of tensile stresses as well as the age of concrete cracks. The test accounts for chemical, autogenous, drying, and thermal shrinkage. Details of the test procedures are documented in ASTM C1581/C1581M − 18a [18].

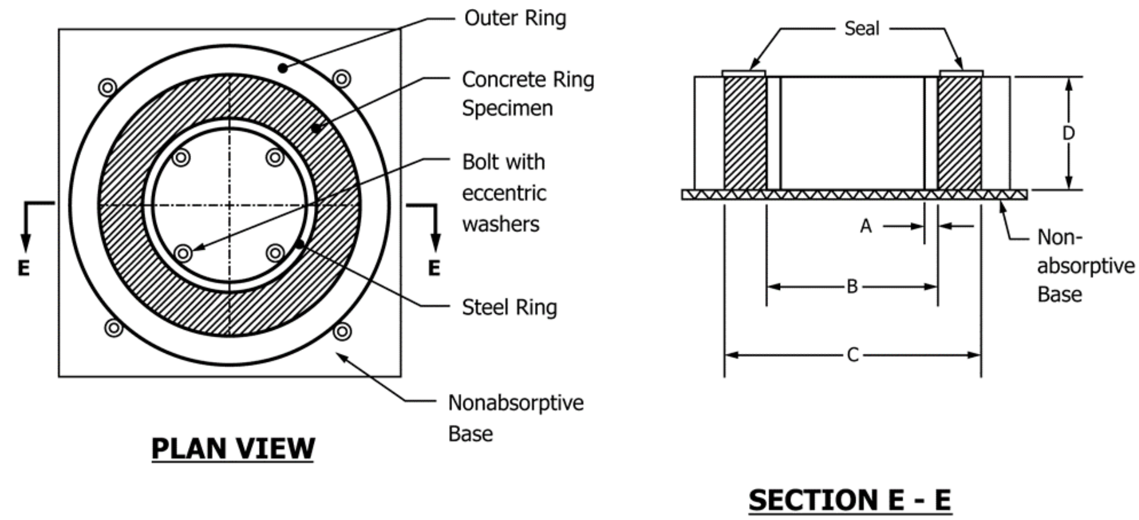

Figure Dimensions	SI Units	Inch-Pound Units
A	13 ± 1 mm	0.50 ± 0.05 in.
B	330 ± 3 mm	13.0 ± 0.12 in.
C	405 ± 3 mm	16.0 ± 0.12 in.
D	150 ± 6 mm	6.0 ± 0.25 in.

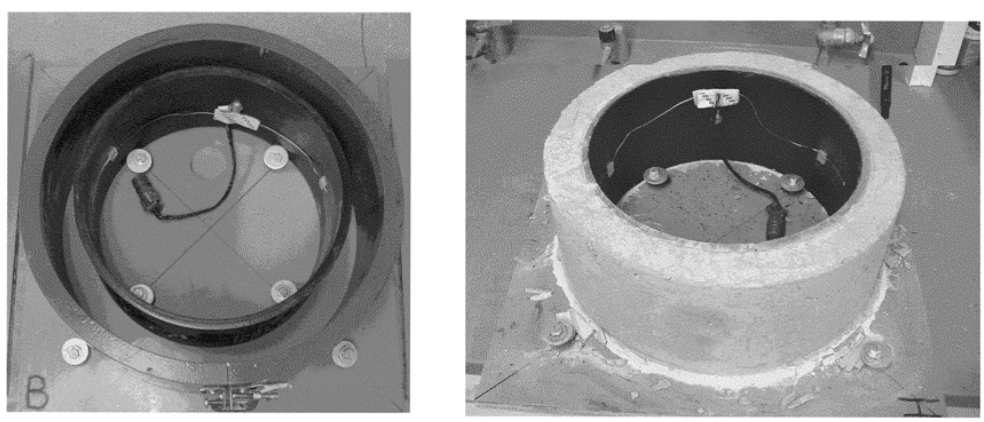

Figure 4-1 Restrained shrinkage ring test, extracted from [18]

Numerous researchers have modelled the restrained shrinkage ring test during its development and thereafter to investigate the effects of ring dimensions and geometric shape on concrete's stress development and crack initiation [19–22]. Dong et al. [23] developed a 3-D finite element (FE) model to investigate the influence of concrete ring thickness on the crack initiation location and the corresponding stress distribution across the thickness. Two thicknesses mimicking thin and thick rings were compared, 37.5 and 75 mm, respectively. The results revealed that the concrete's cracking is highly influenced by the thickness of the ring, where the crack initiates at the outer drying surface of the thick ring, while it initiates from the inner circumference of the thin ring, yet this needs to be verified experimentally. Zhou et al. [24] also developed a 3-D model to investigate the suitability of using elliptical rings and the influence of the geometrical factor, that is the ratio between the largest to the smallest semi-axes (a/b) on the stress development. It was found that if a/b is 2-3, the crack initiates in a shorter time than circular and other elliptical rings. In addition, changing the geometrical factor affects the location of crack initiation, where for a/b=1.2 the crack was initiated between the major and the minor axes, for a/b = 1.5 many cracks were initiated on the major axis and between the major and the minor axes, and for a/b=2-2.5 the crack was observed close to the vertex on the major axis. In the previous studies, the time-dependent mechanical properties of the concrete were measured experimentally and reproduced using regression models. Khan et al. [25] accounted for the tensile creep in their model and included the effective elastic modulus method. A 2-D model was developed to evaluate the effect of the degree of restraint of the shrinkage ring on the induced tensile stresses in early-age concrete, and concluded that the higher the degree of restraint, the higher the induced tensile stresses leading to faster crack initiation. Zhang et al. [26] adopted the same approach and developed a 2-D axisymmetric model to simulate the time-dependent tensile stresses in a restrained ring. Thermal strain fields and age-adjusted effective modulus were considered to account for the effects of both restrained shrinkage and tensile creep. The FE model results, specifically the initiation of the first crack, were validated using experimentally measured data of 21 concrete mixes with strength ranging between 25-100 MPa. In summary, FE models of restrained shrinkage ring were found to successfully simulate the time-dependent tensile stress development and cracks in early-age concrete. The review of the literature revealed that these shrinkage test methods, being laboratory or numerical models, have not been extended to evaluate the performance of self-healing concrete systems due to early-age cracking [7]. Few documented studies on repairing early-age cracks added unprotected bacteria, i.e., without carriers/encapsulations, to the mixture thinking that the capsules might withstand concrete cracking, preventing the initiation of self-healing at an early age [27,28]. Most if not all self-healing concrete studies that added healing capsules to their concrete mix do not investigate or discuss the status of the healing capsules during the concrete hydration period. Researchers have either presumed that the capsules remain intact and/or were not aware of the interactions between the capsules and the hardening concrete, and therefore ultimately not accounting for its impact on the overall performance of self-healing concrete. This paper aims to address this knowledge gap by investigating the interactions between capsules and hardening concrete.

4.1 Methodology

Standard test methods were developed for determining the susceptibility of concrete mixtures to early-age cracking. ASTM C1581 [18], which is the restrained-ring shrinkage test, affords the measurement of induced tensile stress in concrete as it hardens as well as the determination of the age at cracking. Numerical simulations of concrete tested using ASTM C1581 have reproduced the induced tensile stress history and corresponding early-age cracking as documented in the literature. Accordingly, numerical modelling of concrete containing self-healing capsules tested using the ASTM C1581 shrinkage test was selected for this investigation. Moreover, the characterization of the concrete properties at early-age and corresponding ASTM C1581 test results will be part of the performance of self-healing capsules in concrete investigation. The design parameters were employed to numerically investigate the interaction between the mechanical properties of the concrete, the geometrical and mechanical properties of the capsules, and the interface between the concrete and the capsules.

4.1.1 Concrete's properties

Two 40 MPa concrete mixes, one without ground granulated blast furnace slag (GGBFS) and the second one with 60% GGBFS referred to as Mix 1 and Mix 2, respectively, were used in this study. General Purpose (GP) cement was used to prepare all concrete mixes following the Australian Standard AS3972 type GP [29]. The concrete mix design and the cementing material chemical composition are reproduced in Table 4-1 and Table 4-2, respectively. Crushed basalt coarse aggregate with a maximum size of 10 mm and Sydney fine sand with a maximum nominal size of 2.36 mm, were used for the concrete mixes. Superplasticizer, Master Glenium SKY 8100, was used to control the concrete slump [30].

Table 4-1 Concrete mix design

Sample ID	GP Cement (kg/m^3)	GGBFS (kg/m^3)	Coarse Aggregates (kg/m^3)	Fine Aggregates (kg/m^3)	Super-plasticizer (ml/m^3)	Water-to-binder (w/b)
Mix 1	450	0	966	790	600	0.43
Mix 2	180	270	981	803	600	0.37

Table 4-2 Chemical composition of cementing material

Oxides, Compounds	Composition (% mass)	
	GP Cement	**GGBFS**
SiO_2	18.8	36.6
Al_2O_3	5.0	10.2
Fe_2O_3	2.8	0.4
CaO	63.8	42.9
MgO	1.0	6.7
Na_2O	0.3	0.3
K_2O	0.7	0.4
TiO_2	0.3	0.5
SO_3	3.0	1.3
Mn_3O_4	-	0.3
Compressive Strength, 28d (MPa)	>45	

The experimental program, which was carried out by Zhang et al. [26], includes the measurements of concrete compressive strength (f'_c), modulus of elasticity (E_m), and split tensile strength (f_{tm}) with time using AS1012.9 [31], AS1012.17 [32], and AS1012.10 [33] respectively, as well as the concrete time-dependent tensile creep coefficients and the age it cracked using ASTM C1581 test method. The measured concrete's modulus of elasticity was adjusted to account for the creep coefficient using Bažant's model [34]. The corresponding age-adjusted effective modulus (E_{meff}) is given by

$$E_{meff}(t,t_0) = \frac{E_m(t_0)}{1+\chi(t,t_0)\,\phi(t,t_0)} \tag{1}$$

in which $E_m(t_0)$ is the concrete modulus of elasticity at the age of the first loading t_0, $\phi(t,t_0)$ the creep coefficient at time *t* for concrete loaded at t_0, and $\chi(t,t_0)$ the ageing coefficient at time *t* for concrete first loaded at t_0. The corresponding concrete properties used in this study are reproduced in Table 4-3. The concrete fracture toughness (G_m) was estimated using the model proposed by Bažant and Becq-Giraudon [35] with the Poisson's ratio (ν_m) equal to 0.18. The properties of the concrete-capsule interface, specifically the bond strength (σ_{bi}) and the fracture toughness (G_i) were estimated to be 70% of those of concrete [7]. These properties are reproduced in Table 4-3 for Mix 1 and 2.

Table 4-3 Time-dependent concrete and concrete-capsule interface properties

Mix 1							
Age (days)	f'_c (MPa)	E_m (MPa)	E_{meff} (MPa)	f_{tm} (MPa)	G_m (J/m^2)	G_i (J/m^2)	σ_{bi} (MPa)
1	17	22700	22700	2.08	54	38	1.45
2	30.5	24920	20091	2.78	70	49	1.95
3	32.2	27840	19955	2.86	72	50	2.00
7	34.7	33080	18751	2.97	74	52	2.08
28	40.7	36270	14851	3.22	80	56	2.25
Mix 2							
Age (days)	f'_c (MPa)	E_m (MPa)	E_{meff} (MPa)	f_{tm} (MPa)	G_m (J/m^2)	G_i (J/m^2)	σ_{bi} (MPa)
1	8.5	18340	18340	1.47	41	29	1.03
2	15.6	22680	18388	1.99	54	38	1.39
3	21.6	25250	19543	2.34	63	44	1.64
7	29.3	28560	20850	2.73	72	50	1.91
28	37.7	31670	16026	3.09	81	57	2.17

4.1.2 Capsules' properties

The capsules' geometry includes 2 diameters and 2 thicknesses as well as their variability, specifically one standard deviation [36]. The capsule's modulus of elasticity, rupture strength, Poisson's ratio, and fracture energy were deduced from Reda and Chidiac [7]. The corresponding properties are given in Table 4-4.

.

Table 4-4 Capsule properties and position

Variables	**Mean±Standard Deviation**	
Diameter, D_c (mm)	0.2±0.057	0.5±0.142
Shell Thickness, t_c (mm)	0.002±0.0006	0.003±0.0008
Distance from the surface to capsule, d (mm)	5	10
Modulus of Elasticity, E_c (GPa)	4.0	
Rupture Strength, f_{rc} (MPa)	30.0	
Fracture Energy, G_c (J/m^2)	100	
Poisson's Ratio, ν_c	0.3	

4.1.3 Design of Experiments

The numerical experiments were designed to investigate the interactions between the capsule geometry, the capsule mechanical properties, the concrete properties, and the properties of the interface between the capsules and the surrounding concrete, on the performance of the self-healing capsule in early-age concrete. The capsule depth, being the distance from the concrete surface where the crack initiates to the center of the capsule was also investigated. The variables, which are given in Table 4-5, resulted in 48 and 12 runs for Mix 1 and Mix 2, respectively. Star points, as noted in Table 4-5, were added to study the effects of the capsule's properties on its overall performance.

Table 4-5 Design of experiment used in the FE Model

Mix # 1				
	Variable	**Range**		**Star points**
Shell geometry	D_c (mm)	0.2±0.057	0.5±0.142	
	t_c (mm)	0.002±0.0006	0.003±0.0008	
Capsule position	d (mm)	5	10	
Shell mechanical properties	E_c (GPa)	4		6, 7, 10
	f_{rc} (MPa)	30		60, 90
	G_c (N/mm)	0.1		

Mix # 2		
	Variable	**Range**
Shell geometry	D_c (mm)	0.5±0.142
	t_c (mm)	0.003±0.0008
Capsule position	d (mm)	5
Shell mechanical properties	E_c (GPa)	4
	f_{rc} (MPa)	30
	G_c (N/mm)	0.1

4.2 Finite Element Model

The concrete's restrained shrinkage ring can be idealized as a 2-D axisymmetric FE model, or a 2-D plane strain model and one-quarter of the plane section due to double symmetry as shown in Figure 4-2. The latter model, which was used in this study, includes the steel ring, the interface layer between the steel and the concrete, the concrete, and the spherical capsule. The outer and inner radii of the concrete ring are 170 mm and 135 mm, respectively, and the outer and inner radii of the steel ring are 135 mm and 130 mm, respectively [18,25,26,37,38]. For this study, three interfaces were embedded in the FE model to investigate the performance of the self-healing capsules due to early-age concrete cracking. The first interface is a concrete-to-concrete interface representing the initiation and propagation of cracks in concrete, the second interface is referred to as the capsule-to-capsule interface representing the initiation and propagation of cracks in capsules, and the third interface is between the capsule and the concrete. All three interfaces were modelled as cohesive surfaces with their corresponding damage models to simulate the development and propagation of cracks [7].

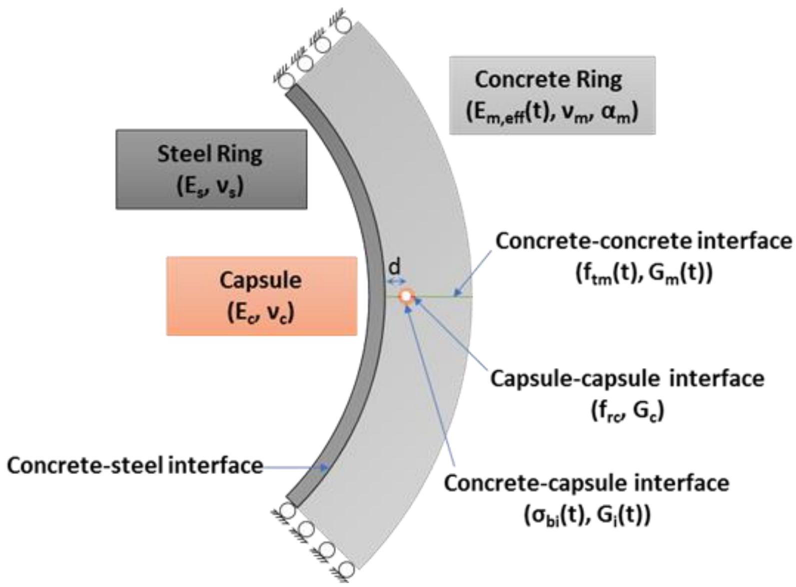

Figure 4-2 Idealized model of the restrained shrinkage ring

ABAQUS cohesive surface separation is governed by the traction-separation law where the behavior of the material is assumed to be linear elastic until the initiation of damage as depicted by Figure 4-3 [39]. In this study, damage, which is represented by a crack, will initiate when the nominal stress reaches the tensile strength at the concrete-concrete interface, the rupture strength at the capsule-capsule interface, or the bond strength at the concrete-capsule interface. Afterwards, the damage will evolve based on energy dissipation principles and is governed by the interface fracture toughness (G). The interface between the concrete and steel ring is modelled as frictionless in the tangential direction and hard contact boundary in the normal direction. The double symmetry boundary condition is modelled using rollers.

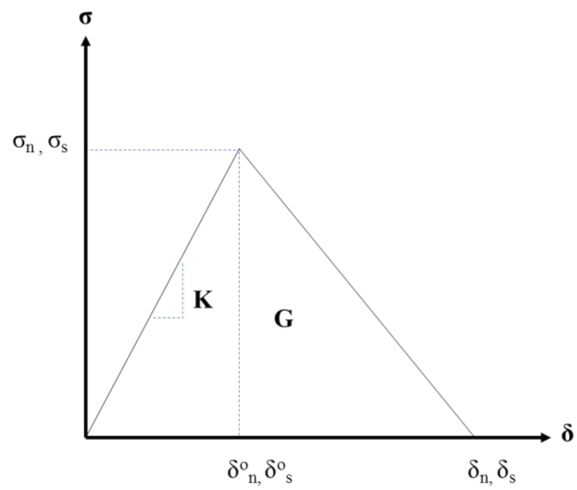

Figure 4-3 Bilinear traction–separation law [39]

The FE mesh, consisting of 8-node plane strain quadrilateral elements (CPE8), was generated using progressive meshing to balance computational effort and discretization errors. The model includes 420 elements for the capsule, 2,260 elements for the steel ring, and 20,080 elements for the concrete. The element size ranges from 11 μm around the capsule to 2.5 mm at the far edges of the concrete. The FE mesh is shown in Figure 4-4.

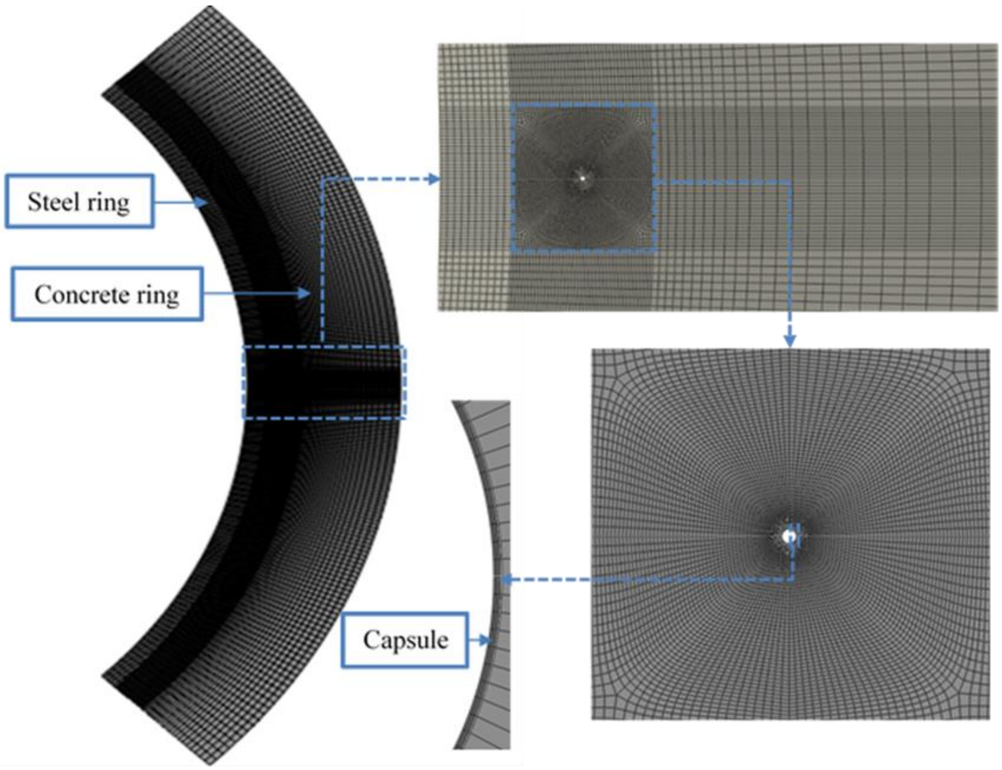

Figure 4-4 FE mesh of the idealized restrained shrinkage ring with self-healing capsule

The simulation using the finite element accounts for the cement chemical reaction, specifically the volume's change due to shrinkage and the evolution of material properties. Thermal strain, which accounts for dimensional change like shrinkage strain, is adopted in this study to simulate the effects of shrinkage on concrete containing self-healing capsules. Accordingly, the temperature field is provided along with a fictitious thermal expansion as follows,

$$T(t) = \frac{\varepsilon_{sh}(t)}{\alpha} \tag{2}$$

in which $T(t)$ is the calculated temperature field as a function of time, α the fictitious linear thermal expansion, and $\varepsilon_{sh}(t)$ the experimentally measured shrinkage strain with time. The measured free shrinkage is reproduced in Figure 4-5. The strain field per time step was assumed to be constant across the thickness. The time-step was explicit, i.e., controlled by ABAQUS, to ensure model convergence.

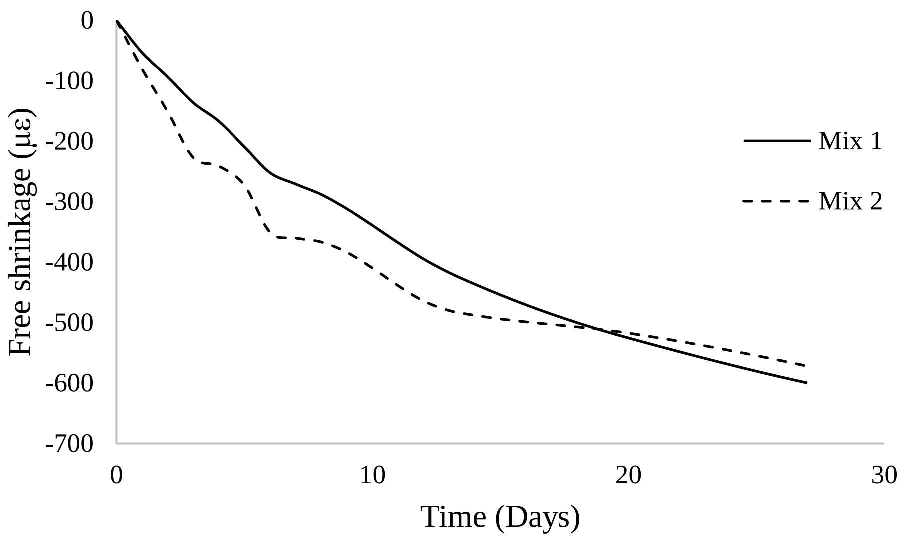

Figure 4-5 Free shrinkage versus time for Mix 1 and Mix 2 [26]

4.3 Results, Analyses, and Discussion

The results from the finite element analyses, in the form of failure modes and the age at which failure occurred, are reproduced in Table 4-6. The two failure modes, rupturing of the shell and debonding of the capsule, which were captured by the FE model, are shown in Figure 4-6. In addition to visual observation, the progression of damage was tracked using CSMAXSCRT, which yields when damage evolution was initiated [39]. A value of 1 identifies a completely damaged element.

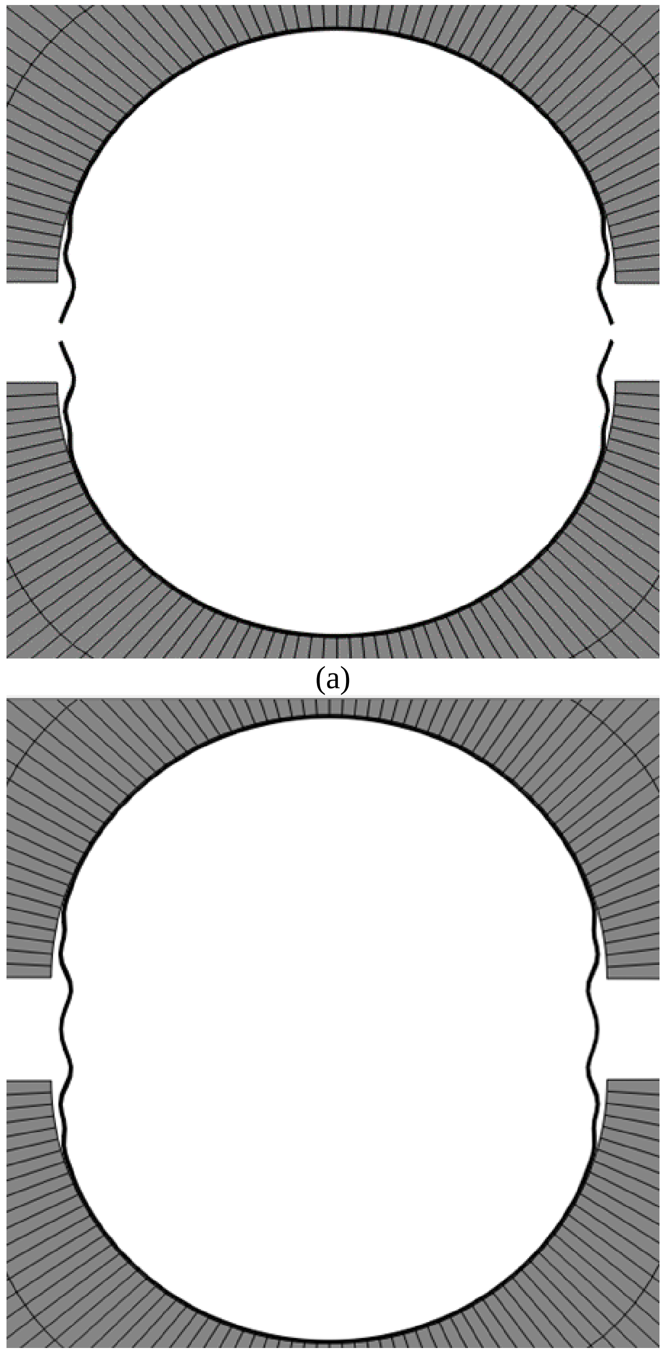

Figure 4-6 Capsule failure modes: (a) Rupturing, (b) Debonding

Table 4-6 FE results including the observed performance of the self-healing capsule

	D_s (mm)	t_s (µm)	$D_s/2t_s$	d (mm)	Capsule behavior	Time at capsule failure initiation (Day)
Mix # 1	0.36	2.2	83	5	Ruptured	21.63
	0.36	3.0	60	5	Debonded	-
	0.36	3.8	47	5	Ruptured	23.93
	0.5	2.2	116	5	Ruptured	20.64
	0.5	3.0	83	5	Ruptured	24.30
	0.5	3.8	65	5	Ruptured	21.92
	0.64	2.2	148	5	Ruptured	20.61
	0.64	3.0	107	5	Ruptured	21.71
	0.64	3.8	83	5	Ruptured	24.04
	0.36	2.2	83	10	Ruptured	21.50
	0.36	3.0	60	10	Debonded	-
	0.36	3.8	47	10	Ruptured	23.62
	0.5	2.2	116	10	Ruptured	19.93
	0.5	3.0	83	10	Ruptured	20.83
	0.5	3.8	65	10	Ruptured	21.49
	0.64	2.2	148	10	Ruptured	23.65
	0.64	3.0	107	10	Ruptured	24.61
	0.64	3.8	83	10	Ruptured	25.68
	0.14	1.4	50	5	Debonded	-
	0.14	2.0	36	5	Debonded	-
	0.14	2.6	28	5	Debonded	-
	0.2	1.4	69	5	Debonded	-
	0.2	2.0	50	5	Debonded	-
	0.2	2.6	39	5	Ruptured	24.04
	0.26	1.4	89	5	Ruptured	20.19
	0.26	2.0	64	5	Ruptured	22.78
	0.26	2.6	50	5	Ruptured	25.70
Mix # 2	0.36	2.2	83	5	Did not fail	-
	0.36	3.0	60	5	Ruptured	10.49
	0.36	3.8	47	5	Debonded	-
	0.5	2.2	116	5	Ruptured	9.85
	0.5	3.0	83	5	Ruptured	10.28
	0.5	3.8	65	5	Debonded	-
	0.64	2.2	148	5	Ruptured	10.18
	0.64	3.0	107	5	Ruptured	9.38
	0.64	3.8	83	5	Ruptured	12.04

A comparative analysis was carried out to provide insights and interpretations of the FE results. The comparison includes: 1) the mechanical properties of concrete, 2) the interfacial bond strength between the capsule and the concrete, 3) the geometrical and mechanical properties of the capsule, and 4) the depth of the capsules from the concrete initial crack.

Concrete's mechanical properties

The FE analysis yielded the same results observed experimentally where the 60% GGBFS cement replacement, Mix 2, cracked at a younger age in comparison to Mix 1. Examination of the concrete mixes' mechanical properties evolution with time, shown in Figure 4-7, indicates that the tensile strength of Mix 2 is developing much slower than Mix 1 whereas the difference in the evolution of elastic modulus is much smaller. For Mix 1, the concrete started to crack at ~ 6 days, and the capsules started to rupture at ~20-25 days, depending on their geometrical and mechanical properties. While for Mix 2, the crack initiated at ~2.5 days, and the capsules started rupturing at ~9-12 days. These results are in agreement with previously reported results [7] that revealed the significance of concrete age and properties when testing self-healing systems.

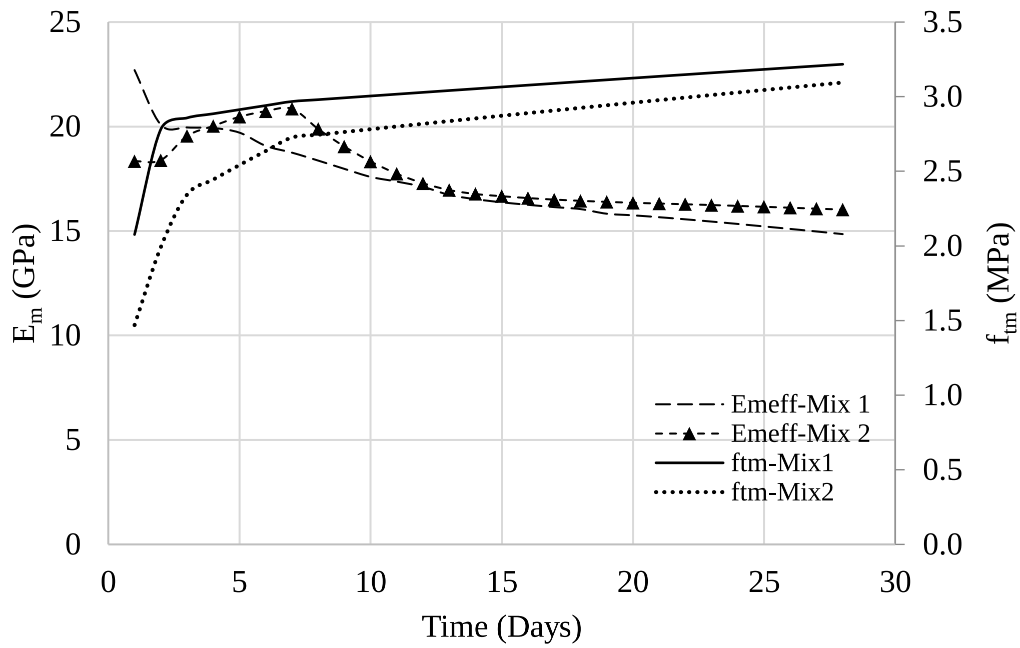

Figure 4-7 Development of mechanical properties of concrete, reproduced from [26]

A closer examination of the FE results shows the interaction between the concrete properties with those of the capsule. At a depth of 5 mm, the capsule embedded in Mix 2 debonded when the diameter was 0.36 and 0.5 mm, and a thickness of 3.8 µm, whereas the capsule in Mix 1 debonded for the case where the capsule diameter was 0.36 and 3.0 µm thick. The capsule was found to rupture in all the other cases. This indicates that the relative strength of the interfacial bond and the shell affects the mode of failure. Examining the geometry of the capsule, specifically $D_s/2t_s$, debonding was found to occur when the ratio is between 47 and 65 but also depends on the bond strength. As the capsule becomes thicker, the likelihood of debonding increases, especially for the capsules with a smaller diameter.

Capsule-concrete bond strength

The effect of the interface bond strength on the capsule performance was investigated by increasing the strength of the capsule that ruptured, specifically the capsule with a diameter of 0.36 mm diameter and 3.8 μm thick embedded in Mix 1, by 30%. The mode of failure was found to shift from rupturing to debonding of the capsule. This result provides insights into the interaction between the concrete and capsule properties and the significance of that interaction.

Capsules' geometry

The capsules' geometry, specifically the diameter and thickness, was statistically investigated by accounting for their variability at a 68% confidence interval. The capsule diameters of 0.2±0.057 mm and 0.5±0.142 mm, and thicknesses of 0.002±0.0006 and 0.003±0.0008mm embedded in Mix 1, and capsule diameters of 0.5±0.142 mm, and thicknesses of 0.003±0.0008mm embedded in Mix 2, were studied. The results from Mix 1 revealed that larger diameter capsules, 0.5±0.142 mm, are found to have higher occurrences of rupturing in comparison to the smaller diameter capsules, 0.2±0.057 mm. With closer examination of the results and the capsule's mode of failure, one observes that thin shell capsules are more likely to stretch and then debond rather than rupture, whereas thicker shell capsules for the same diameter are more likely to rupture. These results reveal that the capsule's mode of failure depends on the load shared between the concrete and the capsule. For relatively stiff capsules, the load sharing results in the rupturing of the capsules whereas for flexible capsules, there is no load sharing and the capsule stretches and debonds. Combining this finding with the one deduced from the concrete properties, it becomes evident that the performance of the capsules not only depends on the geometry of the capsule and the relative stiffness of the capsule to concrete but also the relative strength of the bond and the shell.

Capsules' mechanical properties

The effect of the capsules' mechanical properties on the overall performance of the capsules was further investigated by varying the relative stiffness of the concrete to that of the capsule. Results, given in Table 4-7, reveal that the capsule ruptures at an earlier time when their relative stiffnesses and shell thicknesses were decreased while maintaining the same diameter. As one decreases further their relative stiffness, the mode of failure changes from rupturing to debonding. This finding further supports that the load shared between concrete and capsule influences the mode capsules fail.

Table 4-7 Ratio of concrete-to-capsule stiffness versus capsules performance

	Time of rupture (Days)		
	Capsule diameter (mm), Capsule thickness (µm)		
	0.64,3.8	0.64,3.0	0.64,2.2
E_m/E_c=5.0	24.04	21.71	20.61
E_m/E_c=3.3	21.73	21.72	20.08
E_m/E_c=2.8	18.30	21.69	**Debonded**
E_m/E_c=2.0	**Debonded**	**Debonded**	

Similarly, concrete tensile strength to capsule rupture strength was investigated to determine its significance on the performance of the capsules. The results, shown in Table 4-8, reveal that a decrease in their relative strength changes the mode of failure from rupturing to no failure. Moreover, changing the capsule thickness while maintaining the same diameter and relative strength yielded an earlier rupture time. As the relative strength decreases, the bond strength decreases and the capsules either debond or survive with partial failure. The results indicate that capsules can rupture after being stretched as observed for the case of $f_{tm}/f_{rc} = 0.05$ with a 0.26 mm capsule diameter and thickness of 1.4 mm. Moreover, an examination of CSMAXSCRT values, given in Table 4-8, reveals that the capsules that did not rupture are found to accumulate damage. For the capsules that did not rupture, it is observed that a decrease in the relative strength and shell thickness yields an increase in the accumulated damage. These observations imply that the capsule resistance to rupture, which depends on its rupture strength and geometry, affects the capsule failure mode. This finding is consistent with the previous observations.

Table 4-8 Ratio of concrete tensile strength to capsule rupture strength versus capsules performance

	Time of rupture (Days)					
	Capsule diameter (mm), Capsule thickness (μm)					
	0.64,3.8	0.64,3.0	0.64,2.2	0.26,2.6	0.26,2.0	0.26,1.4
f_{tm}/f_{rc} =0.1	24.04	21.71	20.61	25.70	22.78	20.19
f_{tm}/f_{rc} =0.05	**Did not rupture**	**Did not rupture**	**Did not rupture**	**Did not rupture**	**Did not rupture**	25.70
f_{tm}/f_{rc} =0.03	**Did not rupture**	**Did not rupture**	**Did not rupture**	**Did not rupture**	**Did not rupture**	**Did not rupture**
	CSMAXSCRT					
	Capsule size (mm), Capsule thickness (μm)					
	0.64,3.8	0.64,3.0	0.64,2.2	0.26,2.6	0.26,2.0	0.26,1.4
f_{tm}/f_{rc}=0.1	1.00	1.00	1.00	1.00	1.00	1.00
f_{tm}/f_{rc}=0.05	**0.58**	**0.67**	**0.82**	**0.59**	**0.74**	1.00
f_{tm}/f_{rc}=0.03	**0.39**	**0.46**	**0.54**	**0.39**	**0.49**	**0.75**

Capsules' depth

The effect of the capsule's depth on its performance was investigated by moving the capsule from 5 mm to 10 mm from the concrete surface in Mix 1. The results showed no change in the mode of failure. This finding needs further investigation as the assumed uniform shrinkage strain along the thickness of the concrete ring may have biased the response.

4.4 Conclusions

This numerical study investigated the interactions between the capsules and hardening concrete using the restrained shrinkage ring test and determined their impacts on the long-term performance of self-healing capsules in concrete. Accordingly, the following conclusions are drawn:

(1) The finite element model of restrained shrinkage ring provides insights into the performance of self-healing capsules in early-age concrete.

(2) The performance of capsules in a self-healing system is highly influenced by the capsule geometry, the relative stiffness of concrete and capsule, the ratio of concrete tensile strength to the capsule rupture strength, and the bond strength at the interface between the capsule and the concrete.

(3) The time-dependent mechanical properties of early-age concrete alter the performance of self-healing capsules even for those with the same geometrical properties.

(4) The performance of self-healing capsules due to early-age cracking is too complex for establishing simple design criteria.

(5) Standard test methods are needed to measure the capsules' geometrical and mechanical properties, and the mechanical properties of the concrete and capsules interface, as they strongly influence the performance of self-healing capsules in early-age concrete.

(6) Presuming that all the capsules will remain intact while the concrete hardens is inaccurate.

(7) Performance of self-healing capsules as early age concrete cracks needs to be quantified as it is pivotal to designing an efficient self-healing concrete system.

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Chapter 5

5 Conclusions

The research presented in this dissertation aimed at investigating the performance of self-healing capsules in cementitious material in terms of survivability during concrete mixing and rupturing upon interaction with concrete's shrinkage cracking at an early-age.

The first paper presented in chapter 2 focused on addressing the inconsistencies in the performance of self-healing capsules and the corresponding testing methods/ models adopted in the literature to evaluate the efficiency of such capsules. It also consisted of a finite element model developed to provide insights into the observed inconsistencies and addressed the compatibility requirements between the capsule and the surrounding concrete matrix. Reviewing the literature and the results of the numerical model revealed the following:

- There is a need to develop or adopt standardized tests to evaluate the mechanical properties of self-healing capsules considering the surrounding conditions of the concrete matrix.
- It is important to develop testing methods to evaluate the concrete-capsule interfacial properties including the fracture toughness and bond strength and their effect on the performance of the capsules in the self-healing system.
- It is important to predict the survivability of self-healing capsules during concrete mixing prior to evaluating the performance of the capsules in self-healing concrete applications.

- The self-healing efficiency definition is still questionable and there is a lack of understanding and consensus on what is considered an efficient self-healing system.
- The geometrical ratio of the radius-to-thickness of the self-healing capsules was found to significantly affect the performance of the self-healing capsules and the corresponding failure mode.
- Before assessing the performance of the capsules in the self-healing concrete system, it is crucial to assess the status of the capsules at early-age concrete cracking as concrete is vulnerable to early-age shrinkage cracks.

As such, the second phase of the study presented in chapter 3 of this dissertation employed finite element and statistical techniques to develop a model that can efficiently predict the survivability of self-healing capsules during concrete mixing. The model accounted for different interactions between the capsules and their surroundings including the rheological properties of fresh concrete, and the geometrical and mechanical properties of capsules. This phase of the study revealed that:

- There is a need to develop a standard testing method to evaluate the survivability of capsules during concrete mixing, considering the rheological properties of the concrete mix, the type and speed of the mixer, and the aggregate content and shape.
- The geometrical ratio of radius-to-thickness of the self-healing capsules has a significant impact on the survivability of the capsules during mixing.
- Rheological properties of fresh concrete should be considered in evaluating the survivability of capsules during mixing, and their effectiveness decreases with larger capsules.

- The survival of capsules is highly influenced by whether they are punched by the surrounding aggregates or sheared due to the interaction with the surrounding paste.
- The probability to rupture due to interaction with aggregates negatively impacts the survival rate.
- The probability of failure of capsules whose radius-to-thickness ratio is greater than 45, increases from 0 to 10%. Regardless of the rheological characteristics of the concrete, the capsules' survival drops to 90% when their radius-to-thickness ratio exceeds 90.
- Capsules with a radius-to-thickness ratio of 30 to 45 were found to survive concrete mixing, yet rupture upon concrete cracking.

The third phase of the study presented in chapter 4 investigated the adequacy of adopting the restrained shrinkage ring to evaluate the performance of self-healing capsules at concrete early-age shrinkage cracks. The study employed finite element techniques to develop a model that represents the effect of adding a self-healing capsule on stress development in a restrained shrinkage ring. The following conclusions have been drawn:

- The restrained shrinkage ring can be used to evaluate the performance of self-healing capsules at an early age.
- It is essential to investigate the status of the capsules due to early-age cracking before assessing the efficiency of the self-healing system.
- The performance of capsules in a self-healing system is highly influenced by the radius-to-thick ratio, the stiffness ratio between the concrete and the capsule, the ratio of the tensile strength of the concrete to the rupture strength of the capsule, and the bond strength at the interface between the capsule and the concrete.

- Mix composition and the mechanical properties of the concrete were found to alter the behavior of the self-healing capsules even for the same geometrical properties.
- There is a need to develop a testing method to evaluate the mechanical properties of the capsules and the interfacial properties before incorporating them into concrete self-healing systems.

Recommendations for Future Work

<u>Recommendations for experimental work</u>

- A Standard test to evaluate the efficiency of self-healing concrete is needed.
- A testing method to evaluate the mechanical properties of the capsules and the capsule-concrete interfacial properties in self-healing concrete is needed.
- Develop a testing method to quantify the survival of self-healing capsules during concrete mixing and to validate the survival of the capsule model.
- Evaluate the adequacy of the restrained shrinkage ring to evaluate the performance of a self-healing concrete system at an early-age.

<u>Recommendations for numerical modelling</u>

- The models in this study can be expanded to account for varying capsule sizes and thicknesses, a wider range of concrete properties including tensile strength, modulus of elasticity, and fracture toughness, and a wider range of interfacial properties such as the bond strength and fracture toughness of the capsule-concrete interface. A sensitivity analysis needs to be conducted to evaluate the effect of all parameters.
- Develop a dynamic model that accounts for the rotation of the concrete mixer to investigate the survival of self-healing capsules during concrete mixing.

- The concrete shrinkage in the restrained shrinkage ring model was assumed to be uniform across the wall, therefore, the shrinkage strain fields were applied with zero gradient. To better mimic the shrinkage behavior of concrete, the model needs to allow for gradient change in the shrinkage strain fields in the ring.
- To better mimic the crack initiation and propagation in the concrete matrix, the model can be further expanded to integrate cohesive elements within the mesh to predict the crack location.
- Examine the effects of capsules agglomeration on the model results.

Appendices

A. Challenges of Self-Healing Concrete Application

Abstract

Concrete, the most used construction material in the world, is susceptible to cracking as an inevitable natural phenomenon. It could occur in the plastic and hardened states as symptoms of volumetric stability issues, environmental actions, or mechanical loading of concrete elements. Without proper repair, cracks continue to grow and affect the performance, durability, and mechanical properties of concrete structures. The concept of self-healing and self-repairing naturally is being studied for concrete. Although cracks have been shown to heal in concrete either autogenously or autonomously, the field application of self-healing concrete remains challenging. Micro-encapsulation, which is one of the most promising technique in self-healing, faces similar challenges starting with the lack of consistent and standard test method to evaluate the healing efficiency of the microcapsules and of the system.

This study examines the postulated test methods in the literature pertaining to the effects of adding microcapsules on the properties and performance of concrete. Particularly, the distribution, number, and geometry of the microcapsules are investigated as well as the compatibility requirements of the material and system. The study will note the strengths and weaknesses of current test methods as well as identify the necessary test requirements for evaluating the healing efficiency and efficacy of microcapsules in concrete.

A.1. Introduction

Concrete, the most used construction material in the world, emerged in the early 1900's as a durable and maintenance-free construction material. However, concrete is susceptible to cracking at early age due to chemical reactions and volumetric instability. Without proper repair, crack openings provide deleterious gases and liquids pathways to the concrete core that compromise the performance and longevity of concrete structures. Self-healing, observed in nature and successfully developed for metals and polymers, has emerged as an option for concrete. Although cracks with very small openings in concrete have been shown to heal autogenously, the results are inconsistent and environment dependent. The application of autonomous healing, which is a possible alternative, is challenging.

Encapsulation, which involves the sealing of healing agents in microcapsules whose release is controlled by either a mechanical or environmental trigger, provides the vessels for autonomous self-healing concrete. The challenge with embedding these microcapsules for self-healing concrete is determining the shell geometrical and mechanical properties such that it can survive the concrete mixing and placement while still trigger the release of the healing agents when young concrete cracks [1,2]. This paper aims to critically analyze the proposed test method for evaluating the properties of the capsules as well as their efficiency as autonomous self-healing in young concrete.

A.2. Methodology and testing procedures

Microcapsules geometrical and mechanical compatibility requirements

The geometrical properties of the capsule, such as shape, size, surface morphology, and ratio of shell thickness to capsule diameter, influence the mechanical and fracture behavior of the capsule as well as its durability. The size of the capsule should be large enough to host the healing agents, yet not too large to adversely affect the mechanical and transport properties of concrete. The capsules' diameter used in self-healing concrete ranges between 10-1000 μm, while the capsules' diameter ranges between 100 and 200 μm in self-healing polymers industry [3]. For reference, the diameter of air-entrained voids in concrete is between 10 and 100 μm, and with every 1% increase in air content yields 5 to 6% decrease in the concrete compressive strength [4]. A spherically shape capsule is preferred as it mitigates geometric discontinuities due to sharp edges and presents the least effects on the mechanical properties of the matrix. The morphology of the outer shell, specifically its roughness, is also due to the enhanced mechanical bond. Proper sizing of the capsule also requires a delicate and complex balance between the diameter that controls the storage capacity and the ratio of shell thickness to diameter of the capsule that controls the survivability and trigger of the capsule [5].

The mechanical trigger of capsules during the initiation or propagation of cracks in concrete is essential for healing to occur. Accordingly, the stiffness and strength of the capsule shell relative to those of the matrix are important. Ratio of matrix stiffness to that of the capsule controls the distribution of stress and ratio of their strength affects the fracture plane. As presented with these 4 scenarios of incompatibility, the properties of the capsule and matrix need to be equal: A stiffer and stronger capsule will attract more load and results in debonding of the capsule; A softer and stronger capsule will not attract the load and if cracking is in the vicinity of the capsule it will cause the interface to debond or the plane near the interface to crack, most likely will not lead to a crack in the vicinity of the capsule; A stiffer and weaker capsule will most likely not survive the rigorous mixing and placing of concrete; A softer and weaker capsule may survive the initial mixing and placing of concrete, however it may not fracture unless it is stretched which is not likely in concrete. Moreover, the bonding strength of the capsule to the matrix needs to be greater than the mechanical trigger of the capsule.

Microcapsules strength and stiffness properties

Characterization of the capsule's properties is yet to be standardized. Different test methods have been proposed in the literature to evaluate the stiffness and strength of a single capsule. These tests include Liu et al. [6] who tested polyurethane microcapsules by compressing a single capsule between two parallel glass plates until the capsule started to burst, Keller and Sottos [7] who tested the mechanical properties of poly(urea-formaldehyde) capsules by compressing a single-capsule, Lee et al. [8] who used nanoindentation and a cone tip of approximately 3 μm radius to measure the micromechanical properties of the capsule, and Lv et al. [9] who also used nanoindentation to evaluate the mechanical properties of phenol-formaldehyde shell-interlayer-cement paste zone (SIC). The corresponding results are summarized in Table A-1.

Microcapsules healing efficiency

Testing the healing efficiency of capsules in concrete poses a multitude of challenges as one needs to account for the maturity of the concrete and the type of healing. The compatibility between the capsule mechanical properties and the matrix and the bonding strength are a necessary requirement for the mechanical trigger to work. Recognizing that the properties of concrete evolve with maturity, especially at its early age, the enforcement of the compatibility requirements is very difficult if not impossible. Moreover, the healing can have two performance requirements, sealing the crack to restore the concrete water and gas tightness or repairing the crack to restore the concrete stiffness and strength. As a priori, the test method must account for these specificities before it can be applied. Therefore, the properties of the shell and the healing agent must be selected accordingly.

Table A-1 Microcapsule shell properties

Shell Material	**Average size (*D*) (μm)**	**Shell thickness (*t*) (μm)**	***t/D***	**Elastic Modulus (GPa)**	**Rupture stress (MPa)**
Poly(urethane) (PU) [6]	50-100	1-2	~ 0.02	0.0029	0.026
Urea-formaldehyde (UF) [7]	58-225	0.175±0.033	~ 0.001	3.7±0.2	0.24±0.04 (D=187±15 μm)
Melamine-formaldehyde (MF) [8]	50-150	0.2	~ 0.003	4.66	1.5
Phenol-formaldehyde (PF) [5], [9]	50-600	29.96	~ 0.1	2.2 ± 0.8	1.37 ± 0.3 (D=200–400μm)

Proposed test methods to evaluate the healing efficiency do not appear to account for the type of healing and the age of the concrete. Most test methods employ either the 3-point or 4-point flexural test or a compressive test to induce cracking in the concrete sample and then measure the healing effectiveness by measuring the flexural or compressive strength recovery of the sample [10–12]. The testing approach reported in the literature is problematic for many reasons. First, these tests do not reproduce the predominant failure mechanism caused by shrinkage at early age and environmental loading at a later age. Second, the sequences of the test and test results need to be time dependent to assess both the healing efficiency of the capsules in concrete. Thirdly, these tests are missing the most important problem in concrete, shrinkage due to hydration or drying which occurs when the concrete is very young. In brief, new testing methodology is needed to evaluate the efficiency of capsules in early and later age, and for sealing or structural repairing the concrete.

A.3. Preliminary results and discussion

To illustrate some of the issues raised with the current testing methods, the geometrical and mechanical properties of the prevalent polymeric capsules used in concrete for autonomous healing, documented in Table A-1, are compared with the evolving properties of concrete that are reproduced in Table A-2 for water to cement ratio w/c equals to 0.33 [13]. For reference, the shrinkage strains and corresponding stresses developed in concrete were estimated according to CEB [14] and reproduced in Table A-1. Comparing the stress values to the capsule rupture strength of Table A-1, the likelihood of rupturing the capsules due to shrinkage is very high but not high enough to crack the concrete as per the tensile strength. These results suggest that the capsules will rupture inside the concrete even if the concrete does not crack.

Table A-2 Mechanical properties of concrete with w/c = 0.33 [13]

Age (h)	Young's modulus (GPa)	Tensile strength (MPa)	Shrinkage stress (MPa)
6	15.4	0.83	0.59
12	28.1	2.49	1.08
24	31.2	3.32	1.20
48	35.1	4.02	1.35
72	35.4	4.19	1.36
168	36.2	4.34	1.39
672	40.3	5.30	

The addition of surface drying strains to the shrinkage strains will most likely cause the concrete to crack at the exposed surface. From fracture mechanics, a magnification of 1.8 in the stress values can develop at the tip of the crack. Accordingly, the stress values would be large enough to rupture the capsules provided the bonding strength between the capsule and the matrix are not lower to cause debonding of the capsule.

The mechanical properties of concrete evolve as concrete matures. A plot of the ratio of concrete stiffness at different ages to that of the capsules, shown in Figure A-1, reveals an increase in the first 24h with the magnitude depending on the material used to form the capsules. These results show that the state of stress in the vicinity of the capsule will be different for the different polymeric material and age of concrete [15]. A plot of the ratio of concrete tensile strength to that of the capsule rupture strength, shown in Figure A-1, reveals that cracking can occur in the matrix for the cases where ratio is close to one, i.e. at early age. Therefore, a proper characterization of the capsule material properties is pivotal to ensure that the capsules rupture when it intercepts a crack. Moreover, testing the performance of the healing system needs to be carried out at the most critical age of concrete.

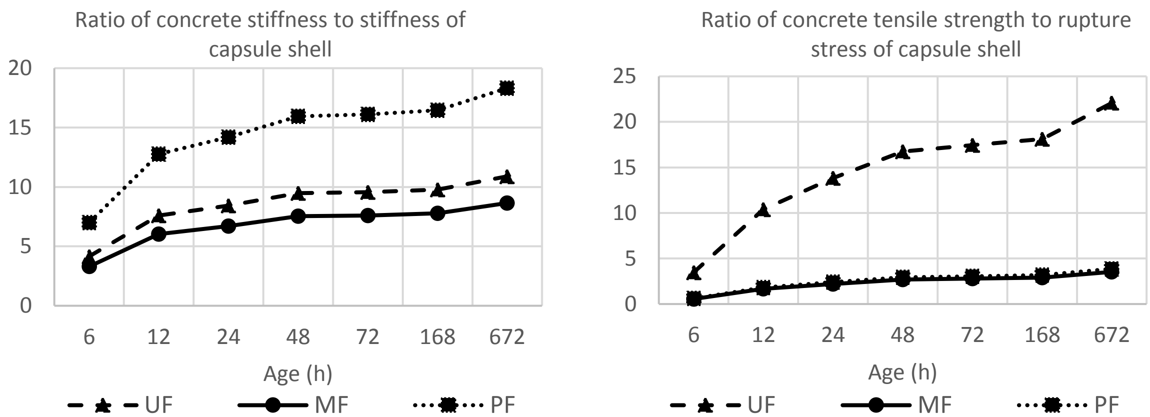

Figure A-1 Mechanical properties of concrete with age and polymeric capsules

Table A-3 documents the reported increase in the recovered mechanical properties of concrete due to self-healing for 2 different capsules. Although the results are appealing, they are most likely difficult to reproduce in the laboratory and in the field for the following reasons.

Table A-3 Mechanical recovery of self-healing cementitious materials

Shell material	Average size (*D*) (μm)	Shell thickness (*t*) (μm)	*t/D*	Recovered property	Recovery
Urea-Formaldehyde [16], [17]	80-1000	0.14-0.20	~0.002	Elastic modulus	11-30%
	132-230	-	-	Compressive strength (pre-damage of 60% σ_{max})	10%
Melamine urea-formaldehyde [10]	10-1000	1.1~1.3	~0.003	Normalized flexural strength (pre-damage of 30% f_{max})	1.8

In addition to the concerns raised previously, the healing efficiency of capsules in concrete also depends on the flow properties and hardening kinetics of the healing agent as well as the testing environment. The former is critical for the healing agent to flow and fill the crack before it hardens. The environment of the laboratory where the tests are carried out to assess the healing efficiency of the capsules in concrete is not representative of the concrete inner and outer environment, i.e. the moisture condition and temperature within the concrete and the environment surrounding the concrete will be different. These environmental conditions affect the flow, hardening kinetic and bonding strength of the healing agent.

A.4. Conclusions

The results from this study reveals the followings:

1) Testing the mechanical properties of the capsules need to account for the confined and bonding condition of the capsules in concrete.
2) Mechanical and geometric properties of the capsules must be compatible with those of the concrete at early age to mitigate cracks due to shrinkage.
3) Capsule mechanical trigger is a balance between the mechanical properties of the concrete and the capsule and the bond strength at the interface between the capsule and concrete.
4) Flow properties, hardening kinetic and bond strength of the healing agent need to be characterized for different temperature and moisture conditions.
5) Test method for determining the efficiency of self-healing concrete needs to be specific to the type of healing, age of concrete and root causes of the cracks.
6) Current test methods for the capsules and healing efficiency fail to meet their objectives.

Acknowledgment

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

Abstract

Self-healing concrete is evolving throughout the years to address concrete's shortcomings, specifically the development of cracks due to low tensile strength. Encapsulation, a technique first developed for self-healing polymers, has been adapted to self-heal concrete. The success of encapsulation to autonomously self-heal cementitious material is highly influenced by the mechanical properties of the cementitious material, mechanical and geometrical properties of the capsules, as well as various properties of the healing agent. The aim of this study is to develop a design methodology for selecting the healing agents most suited for the application. Accordingly, the healing agent properties will be assessed for their viability and adequacy based on structural compatibility with the cementitious matrix. The healing agent properties of polymers include rheology, chemical kinetics, bond strength, stiffness, and crack-bridging of hardened agent.

B.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 [1]. 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 (ACI-Committee-224 2007; Woodson 2009; Allen, Edwards, and Shaw 2005). 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 [5]. 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 recrystallization of calcium hydroxide, and/or the precipitation of calcium carbonates [6]. 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 [7,8] or protective capsules [9–13] 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 [14,15]. 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 [10], 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.

B.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 (2007) 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. (2015) and Mostavi et al. (2015), 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 (1996) 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 B-1.

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.

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 [21,22]. For instance, Methyl Methacrylate has a very low viscosity that can fill very small cracks due to capillary action [23]. However, without adding thickening agent such as Polymethyl methacrylate (PMMA), it is difficult to avoid leaking from the crack [20,24]. Similarly, Dicyclopentadiene (DCPD) has a low viscosity (< 1 cPs) and requires a curing agent to initiate curing [25]. 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. Hu et al. (2018) 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, 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 B-2.

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

Healing Agent	Encapsulation system	Shell material	References
Epoxy resin	Two-component	Urea-formaldehyde (UF)	[26–32]
	Two-component	Melamine urea-formaldehyde (MF)	[33,34]
	One-component	Glass	[35]
Cyanoacrylates (CA)	One-component	Glass fiber	[36]
	One-component	Borosilicate glass	[22,37]
Methyl Methacrylate (MMA)	Three-component	Glass	[20,24]
	Three-component	Ceramic	[24]
	Two-component	Polystyrene (PS)	[23]
Dicyclopentadiene (DCPD)	Two-component	Urea-formaldehyde (UF)	[25]
	Two-component	Poly(phenol-formaldehyde) (PF)	[38,39]
Polyurethane (PU)	One-component	Glass	[9,40]
	Two-component	Glass/ ceramic	[21,41]
	Two-component	Polystyrene (PS)	[18]

Table B-2 Flow and curing properties of polymeric healing agents

Healing Agent	Viscosity (cPs)	Curing mechanism	Curing time (hours)	References
Epoxy resin	250-400	Air cured	3 – 6	[35,42]
Cyanoacrylates	1 – 10	Air/ water cured	24	[22,36,37]
Methyl Methacrylate	0.6 – 1	Air cured	0.5 – 1	[20,23,24]
Dicyclopentadiene	< 1	Air cured	-	[25]
Polyurethane	300 – 800	Air/ water cured	24	[9,18,21,41]

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 B-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. (2011) used MMA and noticed new cracks occurring at the repaired location which is evidence of a weak bond. Few studies tested this bond experimentally. Van Belleghem et al. (2018) 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 [43].

Table B-3 Mechanical properties of common polymeric healing agents

Healing Agent	Tensile Strength (MPa)	Elastic Modulus (GPa)	Elongation	References
Epoxy resin	22	4.00	79%	[33,35,42]
Cyanoacrylates	20	1.26	2 – 3%	[22,37,44]
Polyurethane	2	-	550%	[9]

Effect of cement hydration on the healing agent

Thao et al. (2009) 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 ^{o}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. (2011) 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.

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 [45]. 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 [46]. 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. (2016; 2013; 2017) 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 [22,36], however, more evidence is needed to confirm its water-tightness, durability, and crack bridging efficiency. Yang et al. (2011) observed partial gas permeability and strength gain when using MMA, but others questioned MMA bond strength (Van Tittelboom et al. 2011). Lv et al. (2016) 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 water-tightness of cracked areas (Maes et al. 2014; Van Tittelboom et al. 2011).

Several studies tested the durability or mechanical strength recovery of self-healing cementitious systems as summarized in Table B-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 B-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%	[35]
	Mechanical properties & durability	• Compressive strength has increased by 9% • Flexural strength has increased by 3% • Chloride permeability recovery rate is 100%	[31]
	Mechanical properties & durability	• Chloride diffusion coefficient has increased by 20% • Compressive strength has increased by 10 – 13% • Capillary porosity has dropped by 15%	[26–28]
Cyanoacrylates	Mechanical properties	• Stiffness has increased slightly	[36]
	Mechanical properties	• Stiffness has increased • Ductility has improved • Ultimate load has increased	[22,37]
Methyl Methacrylate	Durability	• Water permeability has improved	[24]
	Mechanical properties & durability	• Gas permeability coefficient has decreased to 66.8% • Toughness has improved	[23]
Dicyclo-pentadiene	Mechanical properties	• Stiffness has increased by 30% • Compressive strength has increased	[25]
	Mechanical properties	• Compressive strength decreased by 32% • Ductility has improved	[38,39]
Polyurethane	Mechanical properties	• Flexural strength increased up to 30%	[9]
	Mechanical properties and durability	• Capillary absorption has decreased by 50% • Strength regain is 96%	[40]

Mechanical properties and durability	• Flexural strength increased up to 62% • Stiffness has increased up to 64% • Water permeability coefficient has decreased	[24]
Durability	• Chloride penetration has increased by increasing crack width	[41]

B.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 B-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 B-6, can be examined while developing the metric. By comparing the mechanical properties of epoxy resin and CA, given in Table B-3, with those of the concrete, it is evident that 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 B-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 B-1illustrates 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 [47].

Table B-5 Mechanical properties of concrete with w/c = 0.39 [48]

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 B-6 General requirements of patch repair materials for compatibility [49]

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

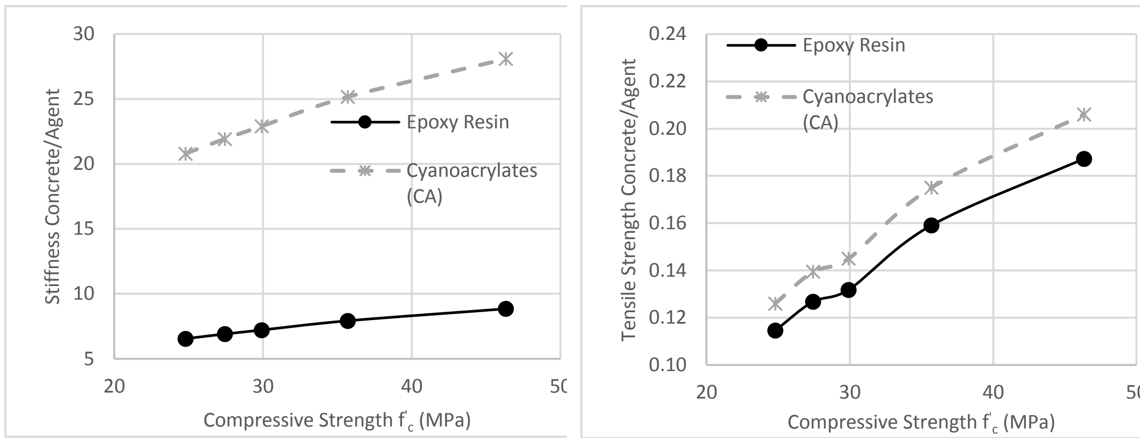

Figure B-1 Mechanical properties of concrete with age and polymeric healing agents

B.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 B-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 B-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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