A Review of the Encapsulation Strategy in Structural Self-healing Materials

By

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Class of 2014

Submitted to the Department of Civil and Environmental Engineering in Partial Fulfillment of the Requirements for the Degree of

Master of Engineering in Civil and Environmental Engineering
at the
Massachusetts Institute of Technology

June 2014

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Abstract

A fascinating property of the human skin is the ability to recover after suffering an injury. Bio-mimicking the process of healing after being injured when withstanding the test of time has paved the way for the advancement of self-healing materials.

After presenting an overview of the self-recovering process of the human skin, this thesis will focus on the commonalities and differences between the encapsulation of healing agents in the concrete matrix and the skin regeneration process. A methodology will then be developed to implement this strategy in structural elements, as a realistic answer to the topical issue of aging concrete facilities.

This thesis aims to explore in-depth the encapsulation strategy, which is at the forefront of the current research in innovative self-healing materials, in order to assess its efficiency in terms of structural properties and cost-effectiveness.

Thesis Supervisor: Jerome J. Connor
Title: Professor of Civil and Environmental Engineering

Acknowledgements

I would like to thank my parents for all the efforts they have spent to help me fulfilling my dream. I was able to travel and have incredibly astonishing experiences during these five past years. Every project I carried out has been dedicated to them. The year I spent at MIT was the greatest gift that was offered to me.

I would like to express my sincere gratitude to Professor J. Connor for his wise and expert guidance and for sharing his broad knowledge at all levels. The time we spent discussing about the research and about life will remain in my memory forever. Thank you for everything, Professor Connor.

Finally, this year would not have been so pleasant without my extraordinary friends in and outside of the MEng program. Thank you to my brothers Alexandre Bouaziz, Maxime Cohen, Quentin Marzari, Audren Prigent Cloitre and Alexis Turjman for this incredible year. We have had a lot of fun and every single moment we spent together was a real pleasure. Great friendships do not vanish, our friendship will remain forever.

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I. Introduction

The structural integrity of existing facilities is usually monitored through routine inspections and repair. The rehabilitation field aims to repair the structural damages affecting aging facilities. Such deterioration is then slowed using surface repairs and corrosion monitoring.

In the past decade, the building industry has taken a significant interest in engineering smart materials to alleviate issues such as excessive routine maintenance, excessive use of materials and costs. One strategy to achieve this goal is to mitigate micro scale damage through an autonomous method that senses and repairs cracks in a targeted way.

Inspired by the bio-mimicry of living bodies, some micro-strategies have aimed to provide to structural materials the ability to self-recover from damages. In particular, the skin's healing process has been a useful fully-integrated model which includes wound monitoring, healing agents transport and recovery processes. Among the strategies that are the forefront of the current research works, the encapsulation strategy, which consists into embedding capsules filled with a healing agent within the matrix of a material usually during its manufacture, has been found to be a targeted solution to bio-mimic the wound-healing process.

In order to stimulate the application of this technology at an industrial scale, this research work reviews all the recent advances made by the scientific community concerning the microencapsulation strategy. The encapsulation of healing agents is currently used in many industries such as car paintings, perfumes and fertilizers. However, such a technology is still an open end to be explored in the structural field.

This thesis is organized as followed. The first part intends to introduce the reader to the skin healing properties that are relevant to a bio-mimicry application for structural materials. The second part defines the application's scope of the encapsulation strategy, followed by the third part that focuses on the optimization of the capsules' distribution with regards to the concrete cracking. Then, the fourth part highlights the influence of embedding capsules over the mechanical properties of materials and tackles the choice of a healing agent that is adapted to concrete. Finally, the fifth part develops a cost impact approach on the life cycle of structures and presents technological improvements that may pave the way to fully auto-healing systems.

II. A brief overview of the skin healing process

1. Introduction

Human skin that is of interest for bio-mimicry applications over structural materials. The following description of its properties is not exhaustive and only presents skin features that help understand the mechanisms reproducible at a structural scale.

2. Skin description

a. Definition of the wound healing process

The Wound Healing Process is defined by the Wound Healing Society (WHS) [1] as "a complex and dynamic process that results in restoration of anatomic continuity and function". The skin healing process involves a cascade of overlapping events, starting with an injury and ending with a full or partial replacement of the injured components.

b. Composition of the skin

The human skin is made of 3 layers which are respectively from the deepest to the most superficial: the hypoderm, the derma and the epidermis. Figure 1 illustrates these layers and their components.

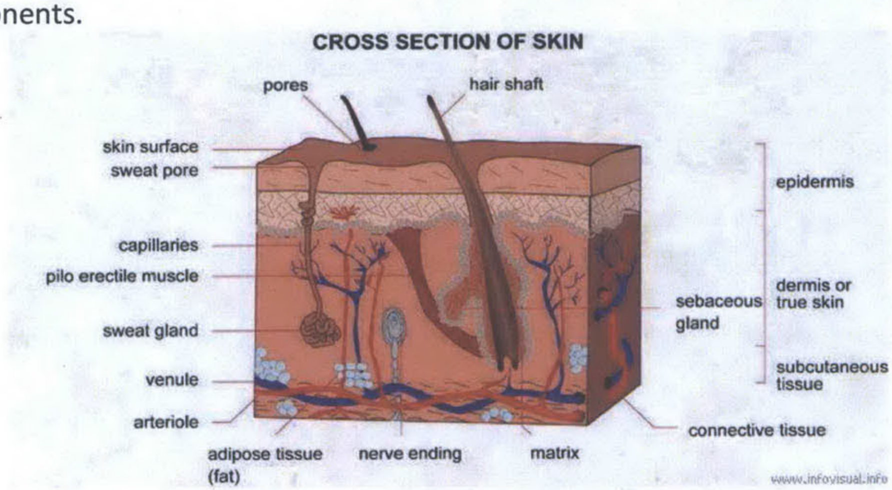


Figure 1 Skin cross section

Essentially composed of adipose tissues, the hypoderm participates in the temperature regulation of the human body. This under layer contains the majority of the blood transport system, as little as 5 cm^2 of hypoderm can include up to 5 m of thin blood vessels.

The derma contains principally fibers and provides its resistance properties to the skin. Collagen fibers contribute to skin resistance and Elastin fibers provide elasticity. This intermediary layer is also the location of numerous corpuscles that play a role in the sense of touch.

The epidermis is the thinnest layer of the skin, ranging from 60 to 100 μm. The epidermis acts as a mechanical barrier that isolates inner tissues from noxious elements and prevents blood or lymph from pouring out.

3. Definition of a wound

The wound healing process depends on the depth of the injury. Indeed, the mechanisms of wound healing differ dramatically given the layers that are affected by damages.

A wound is said to be "first degree" when the epidermis is the only damaged layer that requires a replacement.

A "second degree" wound affects both the epidermis and the derma. Some corpuscles responsible for pain impulses can be affected, which makes these wounds generally painful.

"Third degree" wounds happen when the epidermis and the derma are entirely destroyed. Many initial skin functions cannot recover due to the significant extent of the damages.

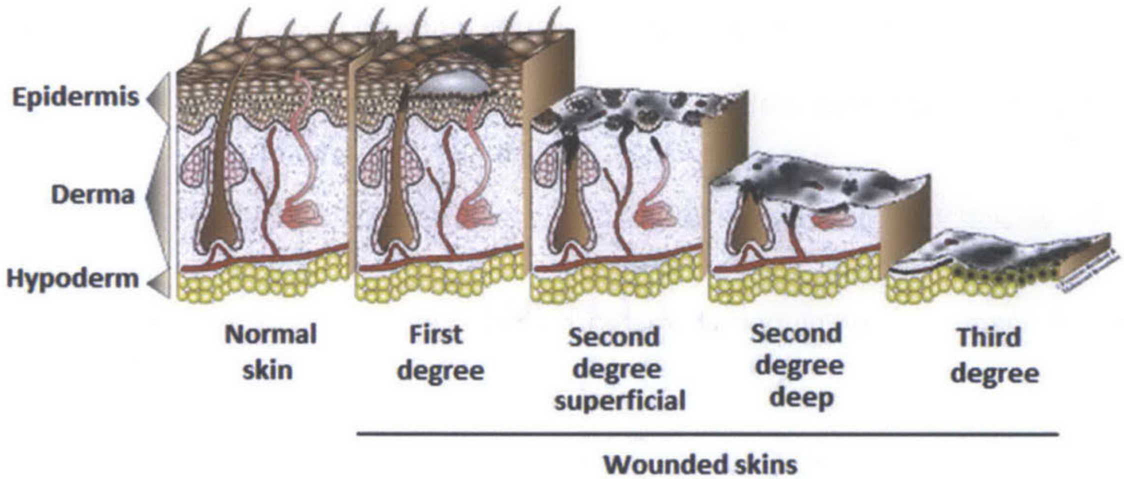


Figure 2 Representation of wound categories

Figure 2 shows the different types of wound injuries with regards to the extent of the damages.

4. The wound healing process

Depending on the type of injury, different and complex processes take place to recover (partially or completely) the initial skin properties.

a. First degree injury recovery process: a superficial treatment

This type of injury is of interest as it would be an inspiration for the treatment of micro-superficial cracks affecting concrete. The concern is more specifically addressed to the structural elements that may decay due to the appearance of micro-cracks leading to major damage such as steel reinforcement exposure in the case of reinforced concrete.

The human skin reacts to this type of injury the same way it renews itself. As the epidermis is the only layer concerned with the damage, the natural renewing of keratinocytes guarantees a total recovery of the mechanical and functional properties of the skin.

b. Second and third degree injuries: a selective self-healing response

The second degree type of injury is characterized by the destruction of the epidermis and a part of the derma. Because this kind of injury destroys corpuscles and essential nonrenewable cells, the human skin must go through a different and selective reaction according to the type of injury it experiences.

This conclusion is more significant concerning the third degree injuries, where the skin loses the majority of its components that take part in its self-healing process. An external intervention is then necessary to protect the exposed tissues.

c. The wound-healing mechanisms

This part focuses on an in-depth description of the mechanisms that occur into the wound healing process. Only a partial description of the process is presented in order to identify the main steps that can be reproduced when engineering innovative self-healing materials.

- **Vascular Response**

Regardless of the source or the location of the injury, the constriction of the vessels starts within seconds in order to stop the bleeding and to reduce the exposure to bacteria. Platelets accumulation takes place at the site of injury to form a clot. This reaction takes a few minutes and enables the blood to stay for a longer time in the injured location to provide the essential elements for the recovery process.

- **Inflammatory Response**

The inflammatory response aims to increase the early defense system of the human body against a microbial invasion. by increasing its temperature and mobilizing specific bacterial-killer white cells. White cells arrive at the injured site through the blood vessels and are in charge of ingesting injurious agents, thereby protecting the injury against bacterial invasion.

- **Proliferative Phase**

This phase involves the overlapping of collagen deposits, the tissue redevelopment and the wound contraction. Collagen is secreted to reconstruct connective tissue while capillaries and cells begin to fill the damaged space with new tissues. The wound contracts as newly formed tissue pulls wound margins inward. At this stage, the new tissue is very fragile. Skin re-growth occurs. The cells eventually begin to differentiate into various layers of the epidermis.

- **Maturation Phase**

The remodeling of the scar can continue for more than 1 year depending on the extent of the damages. New tissue can regains about two thirds of its original strength but is never as strong as the original one.

5. Conclusion

Bio mimicking the properties of the skin at a structural level requires an understanding of the wound healing mechanisms. In particular, the vascular system that provides healing agents is of interest as a tedious yet useful transport system to reproduce. The micro-entities involved in the process react in accordance with their immediate environment to provide the necessary answer to a structural perturbation. The role of changing temperature and of blood as a transport system that provides raw materials to repair the damages may be relevant for a bio-mimicry application.

III. The microencapsulation strategy

1. Definition of the scope

The previous discussion shed light on the complex processes involved in skin self-healing. This part aims to define the scope of the research work. In particular, it will define the skin properties that can be reproduced at a structural level given the recent advances in technology.

The healing technology aims to substitute for the random but global distribution of the self-healing agents in a living body. The difficulty of reproducing the vascular system at a structural level implies that the healing material should be provided locally and within a rational distribution. To do so, a relevant study carried out by Dry [2] [3] showed that internally released materials provided better physical properties recovery compared with external distribution.

Providing a global self-healing technology to cover an entire structure can be considered as an overdesign in the engineering field. In order to reduce the costs of such a global approach, the structural design field may use the existing engineering knowledge to identify the critical failure locations of a structure and locally improve their properties by implementing a self-healing technology.

This section will therefore start developing a self-healing approach within the hypothesis below:

- The global property of skin healing will be turned into a local property using the engineering design knowledge of structures

- This work focuses on a strategy that is most likely to reproduce the global randomness of the skin self-healing properties
- Given the specific difference that exists between healing a deep or a shallow injury, this work intends to propose a global strategy that will not depend on the crack location in the material.

2. Stakes of the research

Given the widespread use of concrete in the existing facilities, this study will mainly focus on strategies that enable the automatic and autonomous recovery of cement-based materials. While micro cracks are unavoidable in the design of reinforced concrete, the combination with loading cracks (especially under tensile loading) results in a significant increase of the concrete permeability. This phenomenon usually leads to a decrease in the concrete resistance against the ingress of external substances. In the end, reinforcements are exposed to corrosion and tensile strength may decrease dramatically.

Another critical stake of this research work consists in the necessary monitoring of structural damages in order to correctly assess the life span of a structure and have a better understanding of its failure modes and its cost cycle.

3. Introduction to the encapsulation strategy

Compared to the autogenic approaches, which require an external agent to heal any damages, autonomic approaches include by definition the healing agent within the matrix of the material.

The idea of having the self-healing agent in the structure is largely inspired from the bio-mimicry of the human body, with a release that occurs upon the formation of damage. Using capsules provides a mechanical barrier against an unexpected release of the healing agent. Capsules can also be distributed so that the global healing property of the material can be achieved.

Among the different works that aimed to analyze several encapsulation strategies, microencapsulation has proved to be a simple yet efficient technology. The concept of microencapsulating a material in an inert structure has been developed by White et al. [4] and has been defined as "the process of enclosing micron-sized particles of solids, droplets of liquids or gases in an inert shell, which, in turn, isolates and protects them from the external environments".

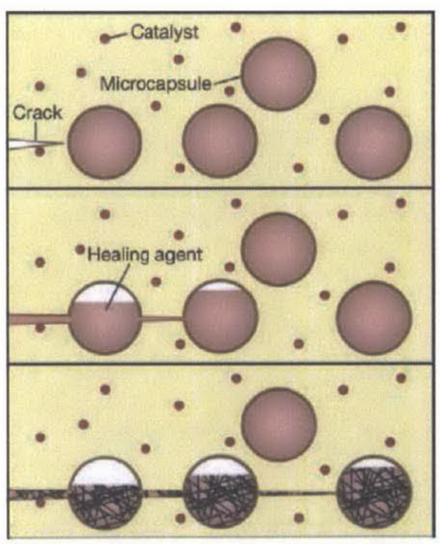


Figure 3 Microencapsulation system

As illustrated above (Figure 3), the self-healing agent is released in the matrix when a crack hits the capsule and the material spreads by capillary action into the crack space. Such a technology tackles both superficial and deep cracks. However, essential parameters need to be defined to ensure the reliability of the healing process. Among the properties to define, the capsules' shape, dimensions and distribution have been identified as critical.

IV. Distribution optimization

This part aims to understand the effect of capsules' dosage on the self-healing process.

Recently-conducted experiments intended to quantify the effect of capsules' shape and concentration on the healing efficiency after a crack.

In particular, Brown et al. [5] focused on the effect of capsules' size over the efficiency of the healing agent spread within an epoxy matrix. The main outcome of this study was the advantage of using spherical shapes due to the symmetry of the healing agent diffusion after a crack hitting a capsule.

Mookhoek's [6] research work focused on the influence of a crack's size in the healing process, which, according to the viscosity of the healing agent, can considerably influence the healing outcome. However, this parameter may not be of interest as the crack size in concrete cannot be efficiently controlled but only limited to a maximum value.

However, only few recent studies tried to elaborate a methodology that allow a more efficient application of microencapsulation at a global scope. To figure out the analytical impact of the shape, Zhong et al. [7] developed a numerical approach that links between the random distribution of capsules into the matrix of a structural element and the probability of an embedded capsule to being hit by a crack. This quantitative approach intended to define an optimal dosage of pre-embedded capsules in concrete in order to reach a predefined healing level of cracks. The next part will focus on the analysis of the numerical model developed by Zhong et al.

1. The 2D probabilistic approach model

Zhong et al. [7] research work focused on the probability of a developing crack hitting a capsule in a two-dimensional and three-dimensional matrix model. The purpose of their study was to find an optimal analytical dosage procedure to implement the self-healing strategy.

The capsules were supposed to be equally dispersed and the geometric theory of probabilities was used to develop their model. The crack location was considered as a random parameter in the matrix.

Resulting from a convex geometry analysis, the probability of randomly distributed crack(s) meeting a circular capsule was found to be:

$$p = \frac{\pi(\pi R^2 + 2Rl)}{\pi ab - 2(a+b)l + l^2}$$

where *a* and *b* correspond to the sizes of the 2D-sample, *l* to the length of the crack and *R* to the radius of the capsule.

For a square sample region model (*a*=*b*), the probability could be expressed as:

$$p = \frac{\pi(\pi R^2 + 2Rl)}{\pi a^2 - 4al + l^2}$$

Supposing then that the self-healing material is a homogeneous matrix, *m(T)* was defined as the number of capsules in the square sample region T:

$$\lim_{m,a \to \infty} \frac{m(T)}{a^2} = \sigma$$

The probability of hitting exactly n capsules was then given by:

$$P_n(m,a) = \binom{m}{n} p^n (1-p)^{m-n}$$

which results in:

$$P_n = \lim_{m,a\to\infty} P_n(m,a) = \frac{(\sigma(\pi R^2 + 2Rl))^n}{n!} e^{-\sigma(\pi R^2+2Rl)}$$

Therefore it was concluded that the number of circular capsules hit by a crack randomly occurring in the sample region follows a Poisson probability distribution. Given this distribution's mathematical properties, $\sigma(\pi R^2 + 2Rl)$ also corresponds to the mean number of capsules hit by one random segment crack. This observation leads to the following result, describing the probability that at least one capsule is hit by a crack occurring in the sample region:

$$P = 1 - e^{-\sigma(\pi R^2+2Rl)}$$

Isolating the "area fraction of capsules" parameter $A_A = \pi R^2 \sigma$, a formula that describes the necessary dosage of capsules A_A was determined,

$$A_A = \frac{\pi R}{\pi R + 2l} \ln(\frac{1}{1-P})$$

Therefore, by targeting a the probability P of a crack hitting a capsule, the analytical approach developed by Zhong et al. [7] allows one to calculate a probabilistic dosage in a 2D model.

2. The 3D probabilistic approach model

The same approach was adopted to develop a 3D model and evaluate the necessary dosage in a finite volume of material. Based on the assumptions made by Bejan et al. [8] and Zemskov et al. [9], penny-shaped cracks (green in Figure 4) were considered randomly dispersed in a random distribution of spherical capsules (red in Figure 4).

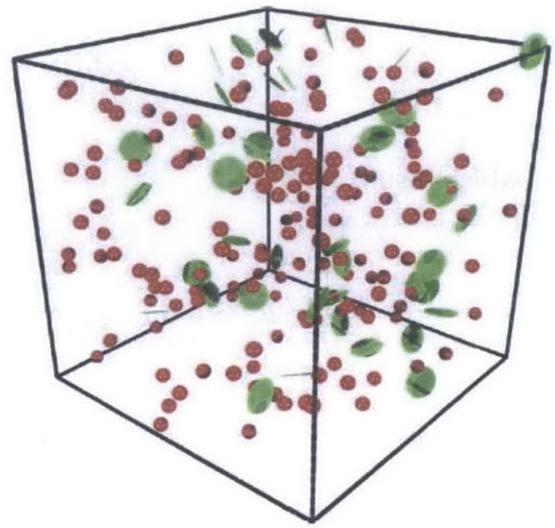


Figure 4 Self-healing system of spherical capsules embedded in the matrix subject to penny-shaped cracks

For randomly distributed capsules governed by a number density λ, the probability that a random crack meets a capsule was found to be:

$$P = 1 - e^{-\lambda\left(\frac{4}{3}\pi R^2 + \pi^2 R^2 l + 2\pi R l^2\right)}$$

By introducing the parameter "volume fraction of capsules" $V_V = \frac{4}{3}\pi R^3 \lambda$, Zhong et al. [7] were also able to define an analytical approach to calculate the necessary dosage of capsules in a 3D model after defining a probability P of a crack hitting a capsule:

$$V_V = \frac{\ln \frac{1}{1-P}}{1 + \frac{3\pi l}{4R} + \frac{3l^2}{2R^2}}$$

3. Shape optimization

Instead of supposing a spherical shape of the capsules, this part aims to explore other geometries that can improve the healing process. Indeed, the geometry optimization is an open issue due to its complexity. The problem might imply to consider the following 3 parameters in the optimization process:

- optimizing the shape in terms of hitting probability
- optimizing the size of the capsules to have a minimal impact on the material strength
- optimize the fluid diffusion after a crack hits a capsule

a. <u>Shape and size optimization</u>

A further study conducted by Jung [10] highlighted the experimental observation that spherical capsules allow smaller transport distance of the healing material in an open crack than a cylindrical shape (elongated capsules). The experiments with elongated capsules resulted in a significant improvement of the recovery process than by using spherical capsules, with enhanced physical properties such as a better compressive strength and permeability.

Inspired by these results, the similar probabilistic approach was conducted by Zhong et al. [7] to evaluate the hitting probability of a penny-shaped crack (green in Figure 5) affecting a cylindrical capsule (red in Figure 5). The hitting probability was then defined by:

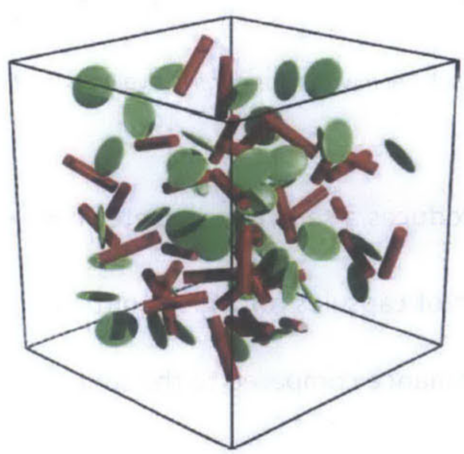


Figure 5 Self-healing system of cylindrical capsules

$$P = 1 - e^{\left[-\lambda\left(\pi h R^2 + \frac{\pi^2 l R}{2}(H+R) + \frac{\pi l^2}{2}(h+\pi R)\right)\right]}$$

where h and R are respectively the length and the basic radius of a cylindrical capsule.

The volume fraction V_V of cylindrical capsules was then found to be given by:

$$V_V = \frac{\ln\left(\frac{1}{1-P}\right)}{1 + \frac{(\tau+1)\pi}{2\tau}x + \frac{(\tau+\pi)}{2\tau}x^2}$$

with $\tau = \frac{h}{R}$ and $x = \frac{l}{R}$.

b. Analytical comparison between cylindrical and spherical capsules

The curves below (see Figure 6) summarize the differences between cylindrical and spherical capsules.

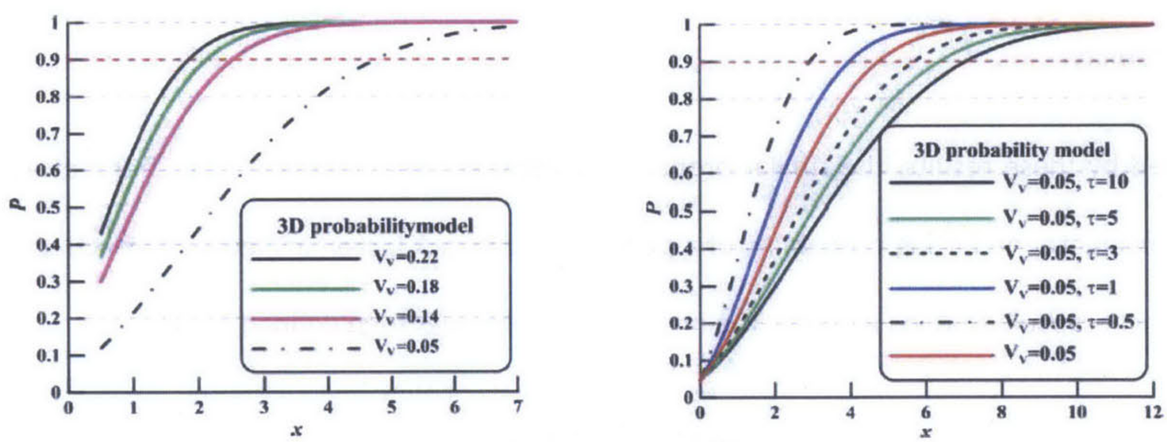


Figure 6 Plot of intersecting probability P with x for different volume fraction of spherical capsules (left) and cylindrical capsules (right)

Using cylindrical capsules introduces a second parameter $\tau = \frac{h}{R}$ that influences substantially the necessary volume fraction of capsules for a given hitting probability. This parameter can be used to improve the performance compared to the spherical capsules' model.

For instance, for a given ratio $x = \frac{l}{R} = 4$, a spherical capsules' volume fraction of 5% reaches a hitting probability of 0.8. For the same ratio and volume fraction in the cylindrical capsules case, the hitting probability varies from 0.6 to 1 depending on the value of $\tau = \frac{h}{R}$. In particular, the highest probability is reached with the smallest value of τ ($\tau = 0.5$), which may indicate that a better result is obtained when increasing the number of capsules and reducing their size.

Compared to spherical capsules, using elongated capsules enable one to reach higher hitting probabilities if sized correctly. However, in the same crack condition (same x value), reducing the size of the capsules (by reducing τ) to increase their number and reach higher hitting probabilities has a drawback on the amount of used material. Considering smaller elongated capsules with the same volume fraction induces higher capsules' surfaces and therefore higher amounts of raw materials and higher costs.

As a conclusion, from a purely statistical point of view, choosing between spherical and cylindrical capsules is an open optimization problem that offers a diversified set of solutions. In particular, this part highlighted that elongated capsules are not automatically providing better hitting probabilities than spherical ones. An additional geometric and cost analysis optimization would give a broader view of what an ideal dosage would be.

V. Mechanical properties

This part aims to explore the mechanical behavior of the capsules when hit by a crack. The failure mode of the capsules as well as the mechanical consequences of incorporating capsules in a rigid material will be highlighted.

1. Crack-Capsule interaction

Microcapsules are required to exhibit specific mechanical characteristics to be used as a storage system. Capsules must rupture under the stress implied by an approaching crack and release their content in the crack upon rupture.

Adding capsules should also have a minimal impact on the mechanical performances of the composite when facing a loading situation.

a. Finite Element Analysis

To address the issue of capsule rupture, a finite element analysis has been conducted by the Department of Aeronautical and Astronautical Engineering at the University of Illinois. The analysis was performed on a single hollow spherical microcapsule under the two conditions described below (see Figures 7 and 8).

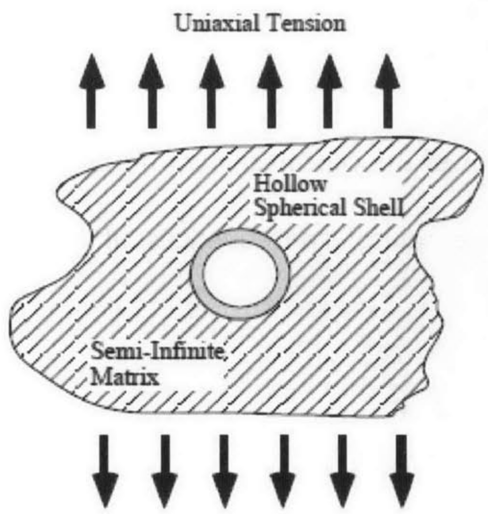


Figure 8 Tensioned system with no crack

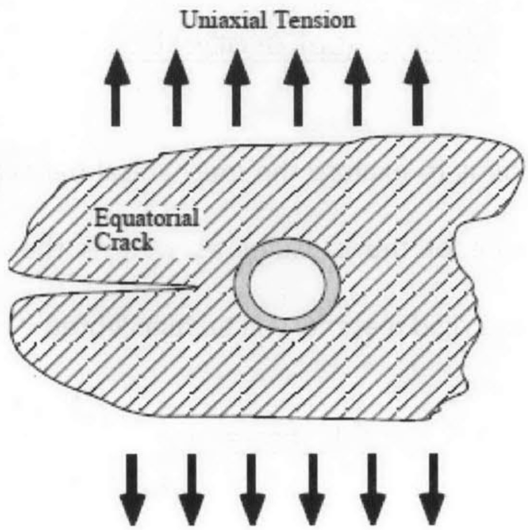


Figure 7 Tensioned system with a crack reaching the capsule

In this experiment carried out by Geubelle et al. [4], both conditions involved tensile loading and hollow spherical shells of 2 microns wall thickness (see Figure 9).

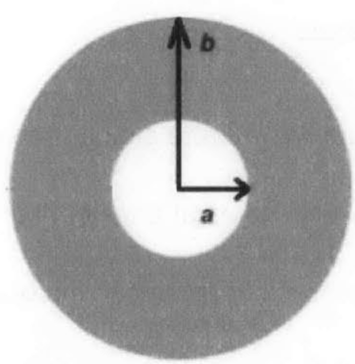


Figure 9 3M and Cannon Capsules (a=13 microns, b=15

The first situation had no crack in its matrix and served as a reference. The second experimental condition involved a crack in a cubic sample of epoxy material, the mechanical properties of which are provided in the table below (see Figure 10).

Material Property	Value
E_{mat} (Young's modulus of matrix)	3.2 GPa
E_{sph} (young's modulus of shell)	4.4 GPa
ν_{mat} (Poisson's ratio of matrix)	0.33
ν_{sph} (Poisson's ratio of shell)	0.33

Figure 10 Mechanical properties of the capsules and the epoxy matrix

Polyoxymethylene urea (PMU) microcapsules, which are available in the industry, have been used in the following study. The 3D samples have then been modeled as 10-node meshed tetrahedron elements in ANSYS 5.2, with appropriate boundary conditions. A far-field tensile stress of 1.0 MPa was applied at the edge of the matrix box.

The results of this study have been represented on stress contour plots on the shell material. In particular, the comparison between the two experimental situations suggested that an approaching crack induced higher stress in the capsule's shell. The maximum stress locations were assumed to be the potential rupture positions. Plots below represent the observations (See Figures 11 and 12).

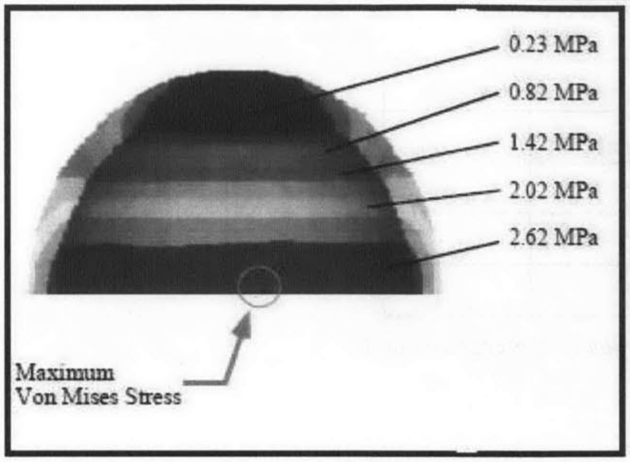


Figure 11 Shell contour stresses resulting from the 3D finite element model under tension without a crack

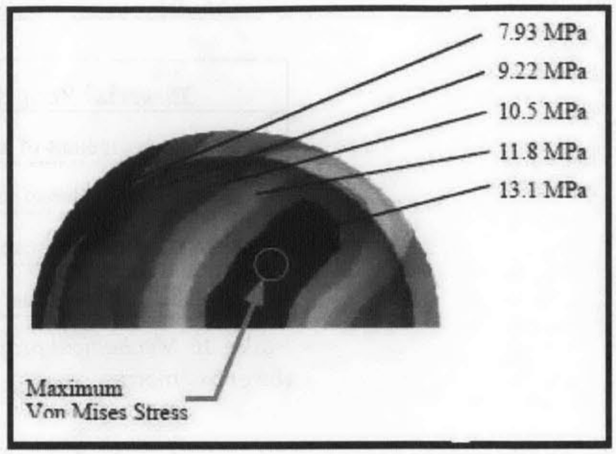


Figure 12 Shell contour stresses resulting from the 3D finite element model under tension with a crack

The interaction between the crack and the interface shell/matrix has proved to be critical when considering the design of the microspheres. However, a validation of the finite element analysis still needs to be conducted.

Using a biological microscope and a scanning electron microscope proved to be a successful approach to observe the plastic zone developing around the propagating crack. Spheres proved to fail ahead of the crack tip, as shown on Figures 13 and 14.

However, none of the observation of the fractured surfaces resulted in a significant proof that the capsules experienced either a breakage or an interface failure (de-bonding phenomenon). The observation of the spheres during the experiment revealed the occurrence of a cavitation phenomenon before the breakage. The cavitation occurring when the crack propagates in an elastomeric material and approaches a rigid barrier was interpreted as being the failure mode of the spheres. However, no quantitative result could be evaluated due to the complexity and the scale of the phenomenon.

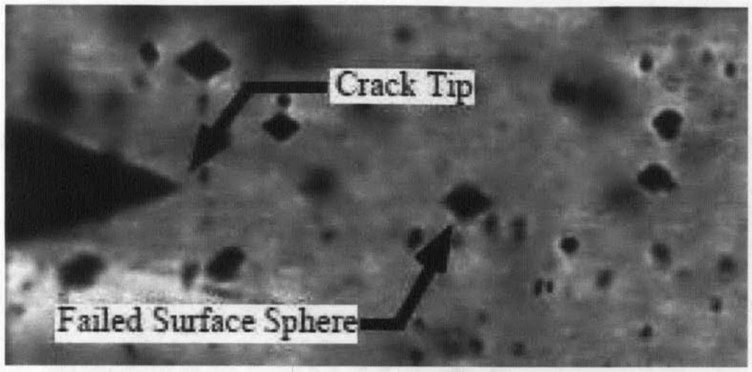


Figure 13 Failure process observed with a biological microscope

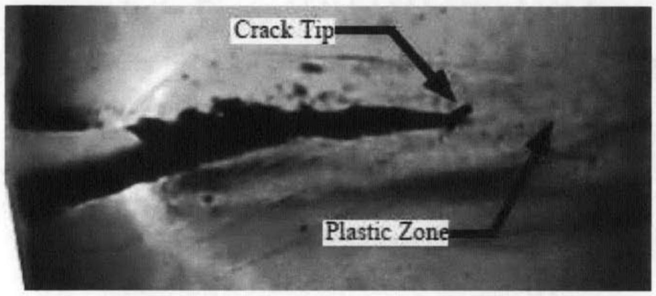


Figure 14 Failure process observed with a biological microscope: plastic zone developing ahead of the crack

The observation of the cavitation process (see Figure 15) instead of a slipping/de-bonding phenomenon confirmed an operational adhesion between the capsules and the matrix. Adhesion is a critical point to ensure the effective breakage of the capsules.

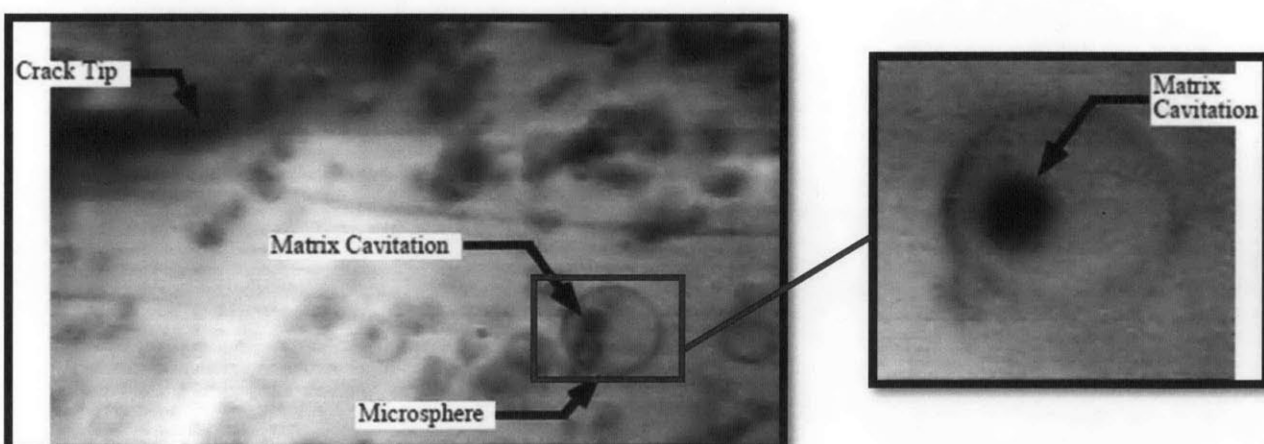


Figure 15 Cavitation in capsule with an approaching crack

b. Elastic modulus and stiffness determination

The effect of microspheres on the mechanical properties of concrete was investigated by Jung [10]. In particular, the effect of adding microspheres on the elastic modulus of the composite material was assessed depending on the volume fraction of microcapsules.

Using samples of DCPD polyester with different volume ratios of embedded microcapsules, a tensile test was conducted. The collected data (see Figures 16 and 17) suggested that the elastic modulus is a decreasing function of the volume fraction of capsules.

	Young's Modulus (GPa)	
Volume Fraction	Mean Value	Standard Deviation
0%	3.55	0.17
5%	2.95	0.12
10%	2.89	0.08
18%	2.66	0.08
25%	2.46	0.07
30%	2.08	0.07

Figure 16 Table representing the evolution of Young's Modulus in terms of volume fraction of capsules

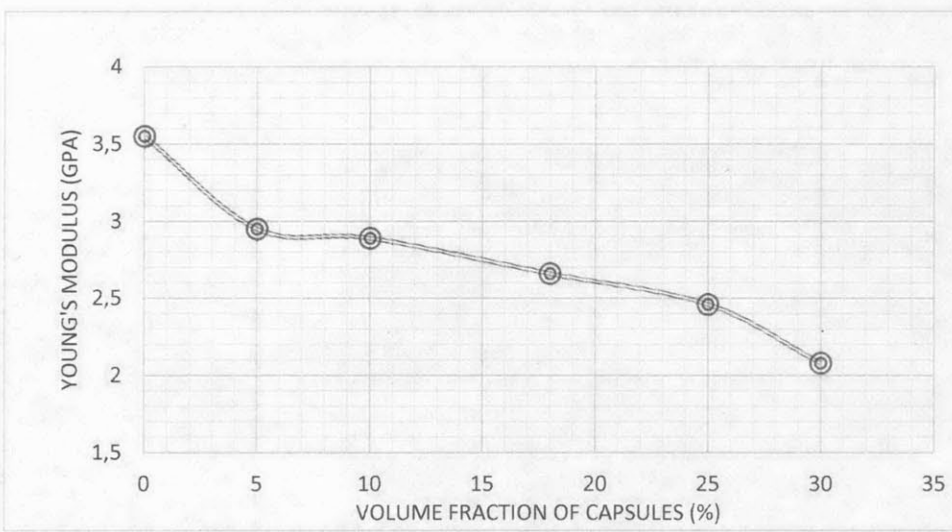


Figure 17 Plot representing the evolution of Young's Modulus in terms of the volume fraction of capsules

However, none of the existing theoretical models of capsules incorporation have proved to fit with the experimental results of tensile tests. Due to the high number of influencing variables, many explanations can be suggested to justify the inaccuracy of the predictions.

First, the distribution of the capsules may not be homogeneous. Ensuring a small spread of the experimental results and multiplying the number of measures should ensure a better statistical accuracy of the measures.

Secondly, the theoretical models do not take into account the local phenomena due to the diaphragm represented by the shell of the capsule. Such a complex issue may open the way to many research topics on modeling friction and energy dissipation when cracking a spherical shell in a rigid environment, or on analyzing the interactions between separate microcapsules when a crack propagates in their immediate environment.

Lastly, none of the existing models take into account the presence of the healing agent in the capsule when predicting the mechanical behavior of the composite material. In fact, the healing agent may behave as an incompressible liquid when pressure is high, and may participate in a volume conservation effect that may strengthen the capsules' resistance against a crack tip.

2. Healing Agent

The use of embedded capsules has been preferred due to its cost-effectiveness and efficiency within every layer of the concrete matrix. This solution does not require a real-life monitoring technology to locate the occurrence of the cracks. Moreover, if the concrete is cast in optimal mixing conditions, it is a reasonable assumption to suppose that the capsules may have a homogeneous distribution in the concrete matrix.

However, the critical nature of the self-healing agent to be incorporated in the capsules is still an open end to explore. The healing agent needs to satisfy numerous conditions when cracking occurs:

- An ideal self-healing agent is supposed to have the viscous properties that enable it to migrate into a crack after a capsule cracking.
- The chemical properties of it need to allow a hardening that would result in a post-healing recovery of strength in case of crack reopening.
- The mechanical properties of a post-cracking sample of concrete should be equal to or greater than the initial properties of it.
- The healing agent needs to have a long-term durability and a compatibility with the matrix over the lifetime of the structure.

Several healing agents will be compared in the following section. Each type of agent will be judged using various parameters, such as initial cost, strength and life span among others.

a. <u>Further-hydration-based strategies</u>

Further hydration can provide an integrated way to recover from a crack by simply hydrating the unhydrated cementitious components in the concrete matrix. It is the result of a chemical reaction between the air and any water that seeps into the cracks, creating then calcium carbonate or calcium hydroxide. Microcapsules can then contain the water that will be engaged in a hardening reaction inside of the concrete.

An experiment was conducted at the Microlab of Delft University to test the healing method of hydration. The products generated to fill in the cracks from further hydration were C–S–H gels, which are the same components involved in the hydraulic bonding effect of cement in the concrete matrix. The chemical reaction of hydration is presented below:

$$C3S + H2O \rightarrow CSH + CH$$

Thus, a good compatibility was expected to ensure optimal mechanical properties. However, the healing efficiency tends to be more unpredictable as the matrix properties become an influencing factor. From a cost viewpoint, this solution proves to be the less expensive but further investigation needs to be conducted to ensure its efficiency.

A research conducted by Naciri [11] at the IRC laboratory of Paris aimed to find an experimental approach to initiate a dosage of the unhydrated cement in crushed concrete samples, using thermo-gravimetric analysis. The results showed a significant variation in the quantities of C-S-H formed after rehydrating the samples, depending on the nature and their origin. Therefore implementing this strategy might imply externalities in the cost cycle of the concrete, as the recycling process will need additional traceability information.

A research conducted by Pelletier et al. [12] resulted in significant experimental outcomes about self-healing concrete's strength. The capsules used were made of polyurethane and filled with a sodium silicate solution.

Concrete samples were prepared by following the specifications of ASTM C-109, with 65% mass of C-109 sand, 24% mass of Type I/II Portland cement and 11% in mass of water.

Microcapsules were then dosed at 2% of volume in the composite self-healing mixture. Then samples were cast in molds of dimensions 160x40x20 mm for flexural strength tests and 500x500x500 mm for compressive strength tests. Full curing was achieved by containing the samples submerged in water and a 95% humidity environment for 28 days.

For flexural strength, the three-point-bend test was used, following the ASTM C348-97 (see Figure 18). The specimen was then loaded at a rate of 0.25mm/min without reaching the full failure of the sample, so that it could go through the same process after letting time for the healing effect to take place.

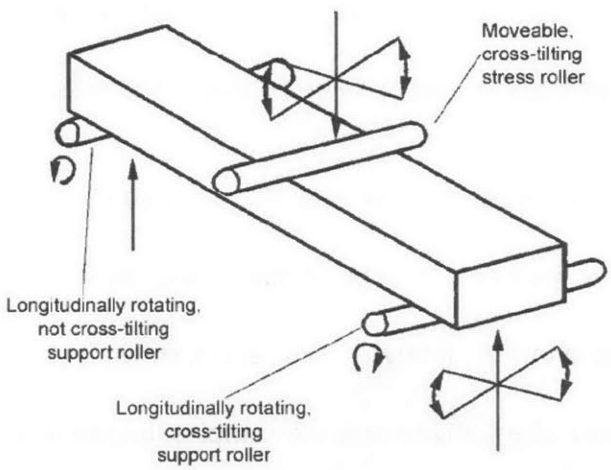


Figure 18 Three-Point Bend Test

For the compressive strength, following the ASTM C109, the strain rate was about 1mm/min and the sample was first cracked then retested.

The healing agent was released in the concrete matrix when the capsules were ruptured by propagating cracks. A chemical reaction occurred between the calcium hydroxide in the cement and the sodium silicate agent. C-S-H gel was then produced and the hardening of the residual unhydrated cement was activated to fill the cracks. The C-S-H ((CaO.SiO2).H2O) allowed the recovery of strength in the samples. The relevant chemical reaction is displayed below:

$$Na2O \bullet SiO2 + Ca(OH)2 \rightarrow (CaO \bullet SiO2) \bullet H20 + Na2O$$

Results of the experiments conducted by Pelletier et al. [12] are listed in Figures 19, 20 and 21 and represented for a comparison purpose in Figures 22 and 23.

Sample	Control. strength (ksi)	With 2% vol. microcapsules (ksi)
1	2.279	2.253
2	2.283	2.307
3	2.247	2.875
4	2.244	2.579
5	2.276	2.718

Figure 19 Compressive strength after cracking with 2% volume fraction of capsules

Sample	Initial Max Load, N	Max Load After Damage, N	Recovered, %
1	512.9	46.7	9.11
2	490.7	57.55	11.7
3	541.9	76.6	14.1
4	470.6	66.4	14.1
5	525.8	69.6	13.2

Figure 20 Flexural recovery with no capsules

Sample	Initial Max Load, N	Max Load After Damage, N	Recovered, %
1	495.7	124.4	25.1
2	416.7	85.9	20.6
3	476.6	125.2	26.2
4	513.8	127.5	24.8
5	528.2	130.5	24.7

Figure 21 Flexural recovery with 2% volume fraction of capsules

Figure 22 shows that flexural capacity after the initial cracking is almost doubled in the samples containing capsules compared to the control samples. This result tends to confirm that the microencapsulation has significant results on the mechanical properties of structural elements. Figure 23 confirms that the 2% volume fraction of capsules does not reduce the compressive strength of the concrete. An interesting experiment to extend these results would be to compare the tensile strength between the capsuled sample and the control one.

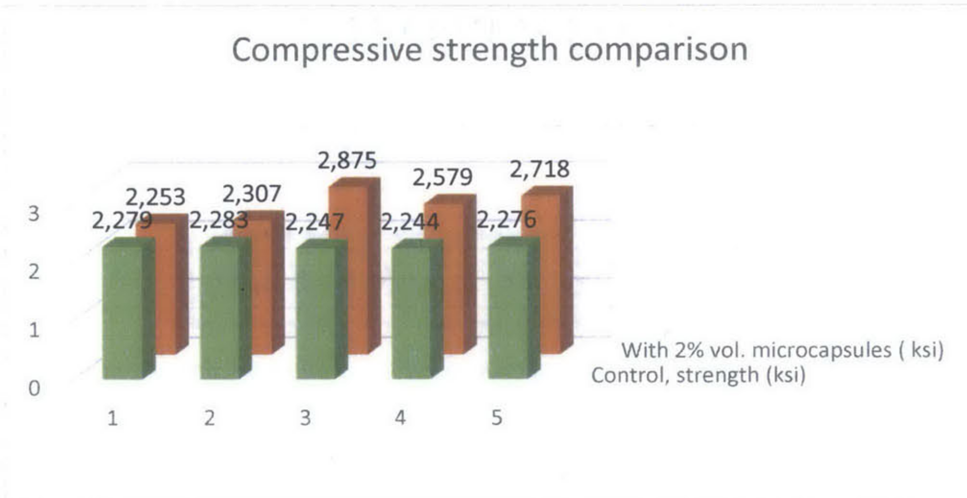


Figure 22 Flexural recovery rate comparison between no capsules samples and 2% volume fraction of capsules

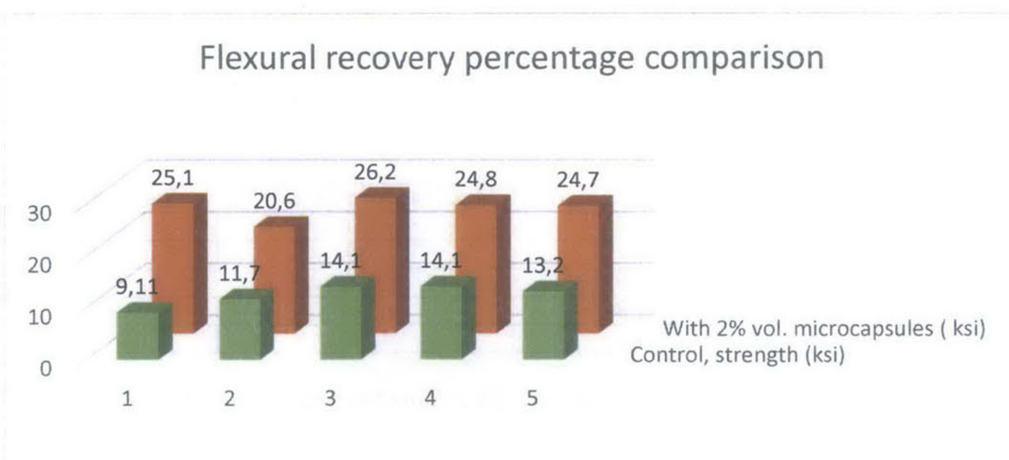


Figure 23 Compressive strength comparison between no capsules samples and 2% volume fraction of microcapsules

b. Cyanocrylates approach

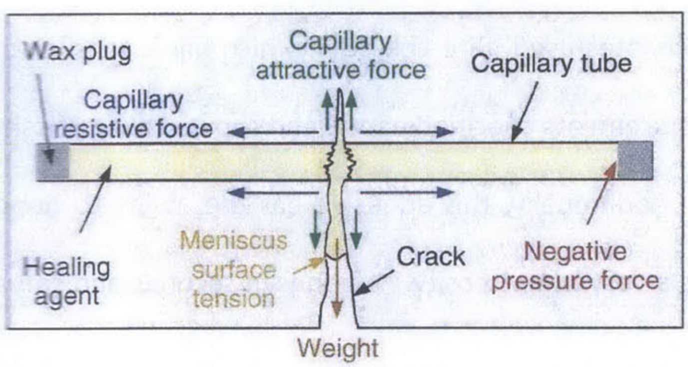
Cyanoacrylates are systems that react as glues. They have very low viscosities and can cure within minutes after their activation. Cyanocrylates can also reach sufficient levels of strength to resist crack reopening and be compatible with cementitious matrix. In addition to that, cyanocrylates can be encapsulated and are a suitable, readily available and cost effective solution.

However, the cyanoacrylates' property of curing too quickly may reduce their dispersion in structural elements' matrix. Therefore, experiments have been performed at Cardiff University since 2006 to test the feasibility and the results of embedding brittle cyanocrylate-filled capsules in concrete beams. The crack width, the migration of the adhesive and the strength recovery were recorded to compare both the pre crack and the post healing properties of the composite.

One of the two cyanoacrylates used, Rite Lok EC-5, which has a tensile strength of 2.9 ksi, met successfully the requirements specified above and showed a significant recovery of the mechanical properties. Additionally, this adhesive has the ability to bond to a significant range materials and has a very low viscosity. It bonds in seconds and can achieve full bond strength in 24 hours.

Four self-healing beams and two control beams were used in the experiment, each experiencing a point load in the center (See Figures 24 and 25). Two self-healing beams contained one layer of tubes and two others contained two layers of tubes. The tubes in all four self-healing beams were filled with the Rite-Lok EC5 adhesive and with ink dye to trace the flow of the adhesive in the tested samples.

(a)



(b)

Figure 24 (a) Ink Seepage in Material (b) Forces Acting on Adhesive

The results showed that the beams with two layers of tubing experienced significant self-healing action, which is proven by the extent of ink penetration.

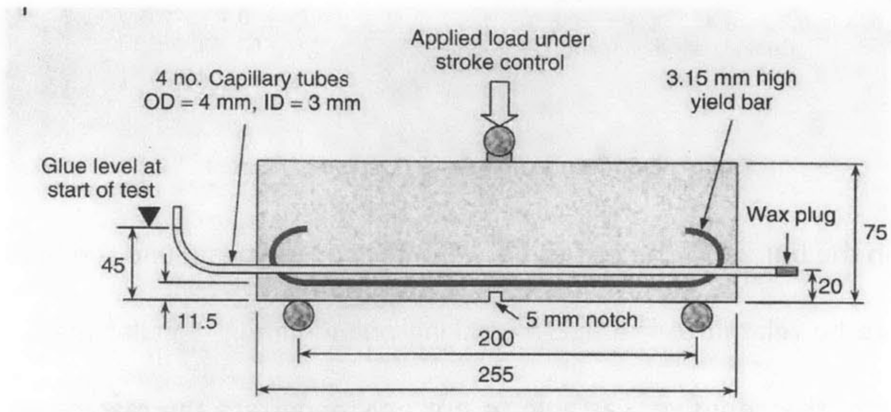


Figure 25 Beam Loading protocole

Figure 26 shows the deflection and Crack Mouth Opening Displacement (CMOD) of the self-healing beams being compared to the mean of the control beams. Point a, in Figure 26b, shows the stiffness of the two control beam. Point b shows that a higher force is necessary to open the crack diameter with the same amount in the self-healing beam than in the control one. This can be assumed to be the effect of the cyanoacrylates crack healing. Point c shows that an even greater force was required to create the same deflections and crack diameters after 24 hours of healing. This effect may be the consequence of the Rite-Lok EC5's hardening time window.

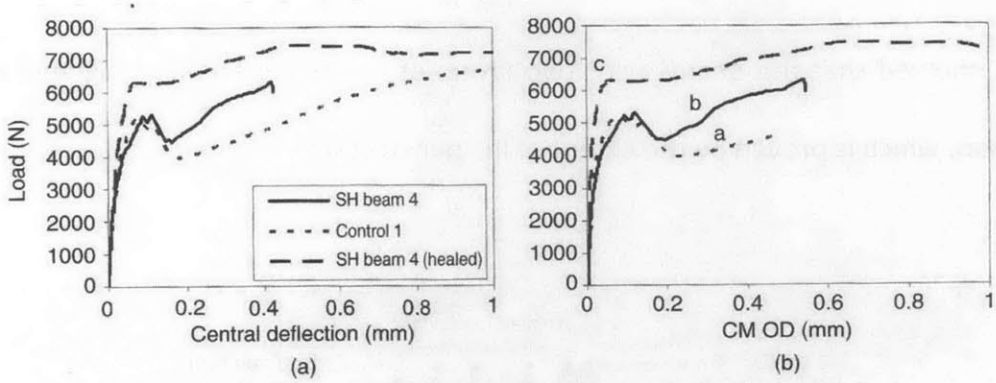


Figure 26 Deflection and Crack Opening of a Beam

The decrease in the bumps of the curves between the control beam and the healing samples was assumed to be related to the micro-cracking phenomenon. Smaller amplitudes of the bumps show that the adhesive was able to not only penetrate the macro-cracks but also help seal some of the micro-cracking that the beams had underwent. Additionally, the ink stain locations in the concrete prove that the adhesive was able to fight gravity due to capillary forces and rise into crack locations before hardening.

c. <u>Epoxy-resin based strategy</u>

Another method to repair cracked concrete involves epoxy-resins. Tests using this material were performed by Alexander et al. [13] by injecting the healing epoxy-resin directly into cracks using syringes.

Two component epoxy resins, which were separately stored adjacent to one another within a cementitious matrix, were studied by Mihashi et al. [14]. However, it was concluded that insufficient mixing of the two different released resins resulted in a poor polymerization degree and therefore poor mechanical performance of the adhesive. This solution might therefore not be relevant for microencapsulation healing application, due to the curing of the epoxy that is necessarily initiated by mixing the two compounds. The mixing did not take place even when the two components were sealed together in an air tight tube and mixed. Other attempts included putting each compound in a separate tube but the results showed that the epoxy did not mix well to seal the entire crack. Additionally, the relatively high viscosity of these materials were not suitable in case of small crack widths.

VI. Technological improvements and cost impact

1. Development of a new approach

The first part of this research emphasized the way the human body does not specifically pre-locate the area of damages but has developed a global healing system that provides an adaptive answer to injuries.

In a structural application, an ideal self-healing system would therefore "sense" the damage and trigger the release of the healing agent at the right location. The idea behind the use of microcapsules was to avoid the cost of a trigger due to the engineering knowledge of structures, which can help locating critical areas that should contain capsules. This approach helped reducing the cost of implementation of this technology.

However, a monitoring system can be used to locate the cracks and decide whether the capsules system should be activated or not, given the scale of the damages or the impact of them on the mechanical properties of a structural element. Such an integrated system would represent the next step for the encapsulation strategy. A consequence of this approach is that the capsules design would then be specific to match the requirements of this system and would be different from the bio-mimicry approach presented in the previous sections.

2. A sensing technology

A structural self-healing monitoring system has been developed by J.Connor and S.Laflamme at the Department of Civil an Environmental Engineering of the Massachusetts Institute of Technology in partnership with Potsdam University researchers. Based on a skin system that recovers structural elements, the “sensing skin” can monitor concrete cracks continuously and cost-efficiently.

The sensing skin was made of stretchable polymer (thermoplastic elastomer) that worked as a capacitor (thanks to titanium dioxide for electrical capacitance) providing a high sensitiveness to strain. Because of its softness, the sensing skin proved perfectly adapted to any structural geometry.

Depending on the type of cracks that one would like to detect, the sensing skin distribution can be fully adapted. In particular, shear cracks can be ideally detected by placing patches of sensing skin diagonally on the surface while flexural cracks would better detected using horizontal patches on a horizontal structure.

Linked to a computer system that detects any small modification in the capacitance of the skin, this system proved to be efficient in detecting surface cracks.

3. Cost-efficiency of the self-healing technology

An enhanced service life of concrete structures will reduce the demand for new constructions. This, in turn, results in the use of less raw materials and an associated reduction in pollution, energy consumption, and carbon dioxide production due to the mixing of concrete and emissions from construction vehicles. Statistics show the large amount of money that society spends on concrete bridge repair, which has been estimated at about $5.2 billion per year in the United States and reconstruction of bridges has been estimated between $20 billion and $200 billion alone. Comprehensive life cycle analyses indicate that the indirect costs due to traffic jams and associated lost productivity are more than 10 times the direct cost of maintenance and repair.

The performance and cost of regular structures over time are compared to that of self-healing structures. In Figures 27a and 27b, line A represents a normal structure and line B represents a high quality structure. It can be seen that the higher quality structure undergoes fewer repairs over time but has a slightly higher initial cost. Figures 28 is corresponding performance and cost diagrams for self-healing structures.

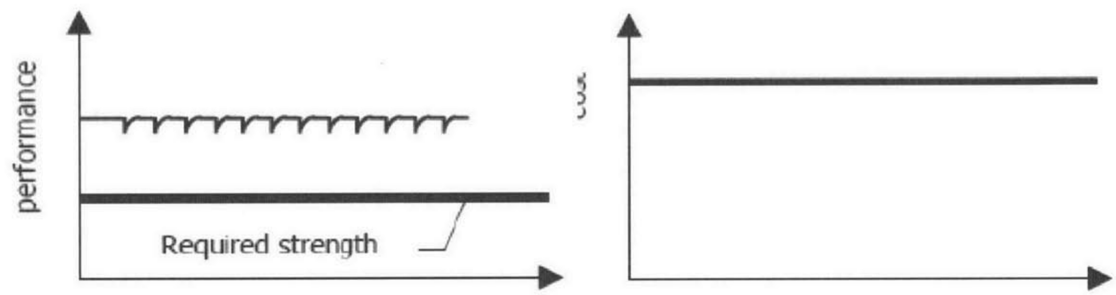


Figure 27 Performance and costs of a structure made with self-healing material (concrete) with elapse of time

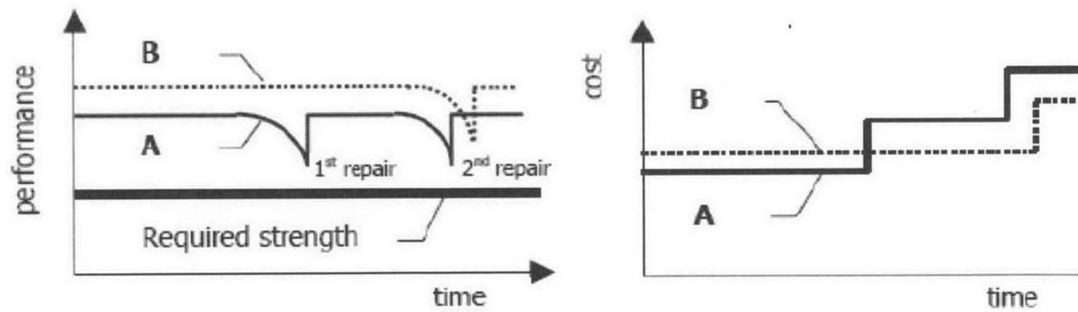


Figure 28 Performance and costs with elapse of time for normal and high quality structures.

The higher initial cost is balanced by the reduction of additional costs because due to maintenance. The construction industry is also responsible for almost 50% of the CO2 production, and it is therefore an absolute priority to enhance the longevity of the built infrastructures and reduce the impact on the environment.

VII. Conclusion

In this contribution the focus has been on self-healing of concrete through cast-in capsules. This, however, is only one possible concept. For example, hybrid concepts are conceivable as well, whereby an external trigger activates cast-in healing components. For all alternatives it holds that the implementation phase requires thorough studies on the building process. In the case of encapsulation, the most adapted industry would be for prestressed concrete cast off-site. Prestressed concrete structural elements are very sensitive and more expensive than regular reinforced concrete. Therefore a healing system would be very valuable in their life and cost cycles. Casting off-site enables a better control of the ratio of capsules and a better mixing of the concrete.

Encapsulation has proved to be efficient at a laboratory scale. Considering taking this technology to the industrial step would however create new challenges such as the transportation and the maintenance of the capsules, the accuracy and the control of the capsules dosage and the concrete homogeneous pouring without being vibrated.

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