Self-Healing of Concrete - A New Technology for a More Sustainable Future

[Extracted from website http://www.swieet2007.org.uk/files/Self Healing Concrete.pdf and http://en.wikipedia.org/wiki/Self-healing_material]

1.0 Introduction

Self-healing materials are a class of smart materials that have the structurally incorporated ability to repair damage caused by mechanical usage over time. The inspiration comes from biological systems, which have the ability to heal after being wounded. Initiation of cracks and other types of damage on a microscopic level has been shown to change thermal, electrical, and acoustic properties, and eventually lead to total failure of the material. Usually, cracks are mended by hand, which is difficult because cracks are often hard to detect. A material (polymers, ceramics, etc.) that can intrinsically correct damages caused by normal usage could lower production costs of a number of different industrial processes through longer service life, reduction of inefficiency over time caused by degradation, as well as avoidance of costs incurred by material failure. For a material to be defined as self-healing, it is necessary that the healing process occurs without human intervention. Researchers are taking both chemically and biologically-based approaches to create concrete that heals itself. Chemical approaches typically use outside or embedded water supplies to activate dry cement grains, while biologists are looking at bacteria to fill the pores.

1.1 Liquid-Based Healing Agents

Completely autonomous, synthetic self-healing material was reported in 2001 with an example of an epoxy system containing microcapsules. These microcapsules were filled with a (liquid) monomer. If a micro crack occurs in this system, the microcapsule will rupture and the monomer will fill the crack. Subsequently it will polymerise, initiated by catalyst particles (Grubbs catalyst) that are also dispersed through the system. This model system of a self-healing particle proved to work very well in pure polymers and polymer coatings.

A hollow glass fibre approach may be more appropriate for self-healing impact damage in fibre-reinforced polymer composite materials. Impact damage can cause a significant reduction in compressive strength with little damage obvious to the naked eye. Hollow glass fibres containing liquid healing agents (some fibres carrying a liquid epoxy monomer and some the corresponding liquid hardener) are embedded within a composite laminate.

1.2 Solid-State Healing Agents

In addition to the sequestered healing agent strategies described above, research into 'intrinsically' self-healing materials is also being performed. For example, supramolecular polymers are materials formed by reversibly-connected non-covalent bonds (i.e. hydrogen bond), which will disassociate at elevated temperatures. Healing of these supramolecullary-based materials is accomplished by heating them and allowing the non-covalent bonds to break. Upon cooling, new bonds will be formed and the material will potentially heal any damage. An advantage of this method is that no reactive chemicals or (toxic) catalysts are needed. However, these materials are not "autonomic" as they require the intervention of an outside agent to initiate a healing response.

1.3 Biomimetic Design Approaches

Self-healing materials are widely encountered in natural systems, and inspiration can be drawn from these systems for design. There is evidence in the academic literature of these biomimetic design approaches being used in the development of self-healing systems for polymer composites.

2.0 Self-Healing of Cementitious Composites

The development of self-healing cementitious composites is a relatively new area of research, which to this date has focused both on the natural ability of hydrates to heal cracks over time (autogenous) and artificial means of crack repair that are man-made inclusions (autonomous). The motivation for such work is to increase the durability of concrete.

The natural self-healing ability of concrete, known as autogenous healing, has been understood for around 20 years. The effect can be seen in many old structures, which have survived for such long periods of time with only limited maintenance. Cracks in old concrete structures such as Roman aqueducts and Gothic churches have been seen to heal when moisture interacts with unhydrated cement in the crack. However, in recent structures the cement content is reduced due to modern construction methods and hence the amount of available unhydrated cement is lower and the natural healing effect is reduced. The three main processes of autogenous healing are (i) swelling and hydration of cement pastes; (ii) precipitation of calcium carbonate crystals, and; (iii) blockage of flow paths due to deposition of water impurities or movement of concrete fragments that detach during the cracking process. Numerous authors in recent years have investigated various situations that affect the amount and rate of autogenic healing including the effect of temperature, degree of damage, freeze-thaw cycles and the age of the concrete. The mix composition of the mortar can also be used to enhance the autogenic behaviour, for example by including blast furnace slag into the mix. It was found that maximum healing occurred in early age concrete and specimens tested under water showed the best strength recovery, hence it was concluded that the primary healing mechanism was ongoing hydration.

The simplest way of self-healing is to ensure that extra dry cement in the concrete exposed on the crack surfaces can react with water and carbon dioxide to heal and form a thin white scar of calcium carbonate. Calcium carbonate is a strong compound found naturally in seashells. In the lab, the material requires between one and five cycles of wetting and drying to heal.

There have been a number of healing agents proposed. However, these are generally 'off the shelf' agents, making them relatively low cost and readily available. This suits the nature of their use in large bulk material such as concrete. To date, the most common healing agents proposed are epoxy resins, cyanacrylatates, and alkali-silica solutions. There are a number of pre requisites that an agent must possess including, a suitably low viscosity to ensure a wider repair area and a sufficiently strong bond between crack surfaces and that there should be adequate capillary forces to draw the agent into the crack.

2.1 Materials

2.1.1 Epoxy Resin system

In epoxy resin system, a low viscosity epoxy resin in an organic film pipe that melts at 93°C. Upon formation of a crack, sensed via a strain gauge, there is a reduction in electrical conductivity and hence increased resistance and temperature. This increased temperature melts the organic supply tube and cures the epoxy resin after it has flowed into the crack.

2.1.2 Cyanoacrylates

Commonly known as super glues, cyanoacrylates are a one part system that, in the presence of moisture, react and cure very rapidly forming a bond often stronger than the material it is bonding, i.e. concrete. Hence the healed crack is actually stronger than the surrounding material itself. This system showed that if a system is damaged and healed and then damaged again, a new crack will form around the healed crack. The use of cyanoacrylates in concrete is further enhanced by them being an acidic solution, which due to the concrete's alkaline environment causes yet quicker healing.

2.1.3 Alkali-Silica Solutions

Alkali-silica solutions have also been utilized as healing agents mainly; in the presence of oxygen, the solution causes hydration and hence bonding of the original crack faces. Although this system produces lower bond strength, it causes less material compatibility problems than the previous two systems.

The above described healing agents require a method to encapsulate them in the cementitious matrix until they are required for healing. The above 1-component healing agents are preferable than 2-component healing agents because of incomplete mixing of the different components. But the 1-component healing agent has a shorter shelf life period. 2-component polyurethane healing agent has been used quite successfully. Several methods have been proposed including the use of micro-capsules, a continuous glass supply tube and capillary tubes, which are embedded in the concrete.

2.2 Method of Encapsulatation

2.2.1 Hollow Tube Approach

Fragile glass capillaries or fibers are embedded within a composite material. The resulting porous network is filled with monomer. When damage occurs in the material from regular use, the tubes also crack and the monomer is released into the cracks. Other tubes containing a hardening agent also crack and mix with the monomer causing the crack to be healed. The diameter of the tube is 20-70 μm and the material for tube is urea formaldehyde or gelatin. Capillary tubes used in the medical profession for blood testing have been embedded in concrete as encapsulating vessels for ethyl cyanoacrylate healing agent. Experiments have that despite some localized debonding between the tube and cement matrix, the system was successful in sensing crack propagation and actuating accordingly healing the crack. Finally, continuous glass supply pipes which have the advantage of being able to vary the healing agent and supply additional healing agent have proven successful in healing larger fractures. The issue with such a system, however, is that care must be taken in placing the glass tubes and hence is not suitable for cast in-situ concrete.

2.2.2 Microcapsule Healing

This method is similar in design to the hollow tube approach. Monomer is encapsulated and embedded within the thermosetting polymer. When the crack reaches the microcapsule, the capsule breaks and the monomer bleeds into the crack, where it can polymerize and mend the crack (Fig. 1)

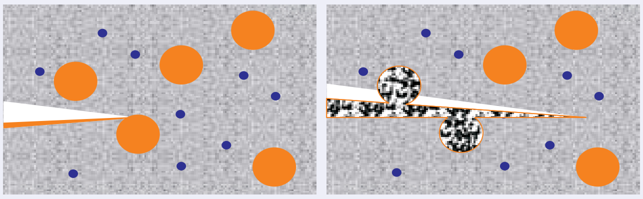

Fig. 1: Depiction of crack propagation through microcapsule-embedded material

Orange circles - Monomer microcapsules

Blue dots - Catalyst

In order for this process to happen at room temperature, and for the reactants to remain in a monomeric state within the capsule, a catalyst is also imbedded into the thermoset. The catalyst lowers the energy barrier of the reaction and allows the monomer to polymerize without the addition of heat. The capsules (often made of wax) around the monomer and the catalyst are important to maintain separation until the crack facilitates the reaction. Microcapsules have the advantage that the concrete can react to diffused cracking in multiple locations, although once a capsule has "been utilized" it cannot be refilled and it remains a void in the concrete.

3.0 Cementitious-Shape Memory Polymer Composite System

Another system being developed at Cardiff University combines both the autogenous healing and autonomous principles in that it makes use of a man-made system to enhance the natural autogenic healing and repair cracks in concrete. The system incorporates shape memory polymers into the cementitious matrix to place the crack in the most favourable conditions for autogenous healing to occur.

The cementitious-shape memory polymer composite system being developed at Cardiff University is base on polyethylene terephthalate (PET) polymer material. Shape memory polymers are semi-crystalline polymers which have a predefined shape memorised in their material structure. In the case of the proposed system the memorised state is a shorter specimen than the current material, so that upon activation the specimen will contract or shrink and in a restrained condition generate a shrinkage force.

Upon crack formation the system seen in Figure 2 will be triggered. The shape memory polymer, which is anchored within a cavity in the cementitious matrix, is activated via heating. Heating can be in the form of direct heat or electrical current via an increase in temperature due to high ohmic resistance. Upon activation the shape memory effect or shrinkage occurs and due to the restrained nature of the tendon, a tensile force is generated. This tensile force in turn imparts a compressive force to the cementitious matrix at the crack location and hence the crack closes. Autogenous healing then occurs and is enhanced by the crack being put into this compressive state.

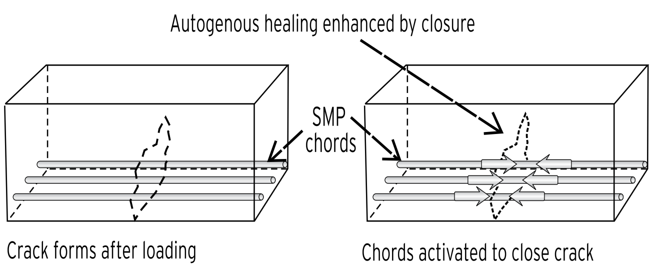

Fig.2: Shape-memory polymer-cementitious composite

4.0 Inorganic Self-Healing Material

Another inorganic self-healing material is being developed at the University of Rhode Island, where micro-encapsulated sodium silicate healing agents of small amount (about 2%) are directly embedded into a concrete matrix. When tiny stress cracks begin to form in the concrete, the capsules rupture and release the healing agent into the adjacent areas. The sodium silicate reacts with the calcium hydroxide naturally present in the concrete to form a calcium-silica-hydrate product to heal the cracks and block the pores in the concrete. The chemical reaction creates a gel-like material that hardens in about one week. The special feature of this material is that it can have a localized and targeted release of the healing agent only in the areas that really need it. Figure 3 shows one such concretre matrix embedded with micro-encapsulated sodium silicate healing agent for self-healing, which additionally acts for waterproofing.

Fig. 3: Concrete matrix embedded with a micro-encapsulated sodium silicate healing agent

In tests comparing a standard concrete mix to concrete containing two percent sodium silicate healing agent, sodium silicate healing mix recovered 26 percent of its original strength (after being stressed to near breaking) versus just 10 percent recovery by the standard mix. This healing agent could also act as a corrosion inhibitor. The release of the agent will result in corrosion inhibition by two mechanisms. First, the reduced water transport due to the filled pores and reduced interconnectivity within the matrix may result in less moisture reaching the metal and ultimately less corrosion. Also, silicates can deposit on the surface to form a protective film, which may also help with reducing the corrosion rate of the steel rebars. The effectiveness to use as additional corrosion inhibitor is still in research stage.

5.0 Catalyst-Free Self-Healing Material System

A new catalyst-free, self-healing material system developed by researchers at the University of Illinois offers a far less expensive method and the new self-healing system incorporates chlorobenzene microcapsules, as small as 150 microns in diameter, as an active solvent. The expensive, ruthenium-based Grubbs' catalyst, which was required earlier, is no longer needed. By removing the catalyst from the material system, a simpler and more economical alternative could be developed for strength recovery after crack damage has occurred. Self-healing of epoxy materials with encapsulated solvents can prevent further crack propagation while recovering most of the material's mechanical integrity. During normal use, epoxy-based materials experience stresses that can cause cracking, which can lead to mechanical failure. Autonomous self-healing is a process in which the damage itself triggers the repair mechanism to retain structural integrity and extend the lifetime of the material. This system of self-healing system is simple, very economical and potentially robust.

In the researchers' original approach, self-healing materials consisted of a micro-encapsulated healing agent (dicyclopentadiene) and Grubbs' catalyst embedded in an epoxy matrix. When the material cracked, microcapsules would rupture and release the healing agent, which then reacted with the catalyst to repair the damage. In their new approach, when a crack forms in the epoxy material, microcapsules containing chlorobenzene break. The solvent disperses into the matrix, where it finds pockets of unreacted epoxy monomers. The solvent then carries the latent epoxy monomers into the crack, where polymerization takes place, restoring structural integrity. In fracture tests, self-healing composites with catalyst-free chemistry recovered as much as 82% of their original fracture toughness. The new catalyst-free chemistry has removed the barriers to cost and level of difficulty.

6.0 Biotechnological Approach of Self-Healing

One further and very interesting method of producing self-healing concrete is being developed at Delft University in The Netherlands, which makes use of mineral producing bacteria. The various types of bacteria being used are *Bacillus cohnii*, *Bacillus pasteurii*, *Bacillus lentus*, *Bacillus sphaericus* (Fig. 4) and *Pseudomonas aeruginosa*.

Fig. 4: *Bacillus sphaericus* Bacteria used for self-healing of concrete

In this system, the bacteria act as a catalyst and transform a precursor compound into a suitable filler material, such as calcium carbonate-based mineral precipitates. A microscopic view of one such bacteria treated concrete is shown in Figure 5.

The filler material then acts as a type of bio-cement, which effectively seals newly formed cracks. The bacteria approach is also being developed at Jadvpur University, Kolkata.

Fig. 5: Microscopic view of bacteria treated concrete

7.0 Conclusion

Cracks in concrete buildings, roads, and sidewalks are common and often require costly plugging. Approximately half of the ₹ 56,000 crore spent on construction work in the UK per annum is allocated to repair and maintenance of existing structures, many of which are concrete structures. As per the estimate of the Construction Industry Development Council (CIDC), New Delhi, ₹ 32,000 crore is required to rebuild India's damaged concrete structures. But if concrete could detect cracking and heal itself, then there would not only be significant cost savings, but also an environmental benefit as well since concrete production accounts for significant amount of the world's carbon dioxide emissions.

Self-healing of cracks is possible only up to certain limit. Most of these materials and technology are in research stage, which needs further studies before being applied in the practical field.

Glue From Bacteria Can 'Knit' Cracks In Concrete

[Reported from The Times of India, Mumbai Edition dated 22nd November, 2010 page 19]

London: A genetically-modified bacteria has been developed by British scientists, which can knit together cracks in concrete structures by producing a special glue.

As per the research study at the Newcastle University, the microbe, can self-heal the very fine cracks to produce a mixture of calcium carbonate and bacterial glue which combine with filamentous bacteria cells to 'knit', the structure together. The bacteria used was Bacilala Filla to prolong the life of the structures, which are costly to build. It can also reduce the emissions of carbon dioxide as concrete production accounts for around 5% of emissions by which this can reduce environmental impact. **PTI**