Title: *Different Techniques and Methods of Self Healing for* Proceedings of the 6th International Workshop on Structural Health Monitoring 2007

Authors: Bo Xu, Ph.D. Student, Department of Civil and Environmental Engineering, University of Alabama in Huntsville, Huntsville, AL 35899. Houssam A. Toutanji, Professor of Civil Engineering, Department of Civil and Environmental Engineering, University of Alabama in Huntsville, Huntsville, AL 35899. John A. Gilbert, Professor of Mechanical Engineering, Department of Mechanical and Aerospace Engineering, University of Alabama in Huntsville, Huntsville, AL 35899. Kirk Biszick, Ph.D. Student, Department of Mechanical and Aerospace Engineering, University of Alabama in Huntsville, Huntsville, AL 35899.

**ABSTRACT**

A number of self healing materials and structures have been developed to automatically sense damage and respond to it via self repair. The basic concept is that a damaged structure is repaired by materials already contained within it, analogous to the biological healing process in living organisms. The approach typically takes advantage of the outstanding properties of reinforced materials to substantially improve a composite structure’s resistance to delamination and crack propagation. The ability to restore materials’ performance without affecting overall properties leads to a safer, more reliable, and longer lasting composite system. Since no external monitoring or human intervention is required, the system requires less maintenance potentially resulting in lower overall cost.

This paper reviews and compares different self healing techniques and methods while making recommendations on those most suitable for infrastructure. Employing hollow fibers (both single and crosslinking), for example, typically results in more strength as compared to systems built using microcapsules. The importance of adhesives and their effects on smart self-healing materials and structures will also be discussed. A good adhesive, for example, should be multipart with a compressible volume. Ideally, it should have the potential to be injected into narrow cracks, be water resistant, possess good bonding properties, and capable of transferring stresses well.
INTRODUCTION AND BACKGROUND

Detecting and repairing of damage are major problems for the polymer matrix composites and cement materials used in advanced structures. Macroscopic damages in the surface of the matrix can be detected visually and typically repaired onsite by hand, but the damages such as matrix micro-cracking, fiber-matrix debonding and delamination are extremely difficult to detect and even more difficult to repair. Self healing material has the ability of automatic sensing and self repairing, which offer the potential for a substantial improvement in resistance to delamination propagation, allowing outstanding properties of reinforced material to be fully exploited.

The use of functional components stored inside composite materials to restore physical properties after damage has been advocated by several workers. Dry and Dry et al. [1-5] developed the concept of a biological self healing method on cement matrices. The self healing design is the release of liquid repair components from inside the hollow vessels distributed within the concrete specimen into the matrices after sustaining damage. The methyl and methacrylate liquid were stored inside the hollow porous polypropylene fibers within the concrete, release into the crack to reduce concrete permeability and regain the strength.

Li et al. [6] developed the self-repairing concept and applied it to cement material. Controlled microcracking was offered by a strain-hardening engineered cement composite (ECC). The capillary effect was first introduced as a method of filling a hollow glass fiber with healing agent.

Issa et al. [7] restored structural integrity and increased the compressive strength and stiffness of cracked concrete test cubes by gravity filling of cracks using a low viscosity gel-type epoxy resin system.

The application of a self-repairing concept to fiber reinforced polymer composite materials has been researched by several researchers. Zako et al. [8] introduced a method of embedding a small grain particle-type epoxy particle with a diameter of 50μm in a glass/epoxy composite laminate. To repair the damage, the specimen was heated to 120 °C and maintained at this temperature for 10 minutes. In this process, the embedded particles in the matrix can melt by heat and flow to repair the crack. The bending test and tensile fatigue test showed that the stiffness was recovered in the repaired specimen.

White et al. [9] reported a structural polymeric material with the ability of self healing. The reaction polymerizes dicyclopentadiene (DCPD) at room temperature in several minutes to yield a tough and highly crosslinked polymer network. DCPD-filled microcapsules (50±200 mm) with an urea-formaldehyde shell were prepared using standard microencapsulation techniques. The microcapsule shell provides a protective barrier between the catalyst and DCPD to prevent polymerization during the preparation of the composite. The material incorporates a microencapsulated healing agent that is released upon crack intrusion. Polymerization of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces. The fracture experiments yield as much as 75% recovery in toughness.

Bleay et al. [10] conducted the studies with composite material. The glass fiber acting both reinforcement and containers for repair resins was investigated in the study. One and two parts epoxy resin system were investigated. A selection of the impacted specimens was examined by introducing X-ray opaque dye penetrate into the impacted
region and taking X-radiographs to detect the damage. Further more, Pang et al. [11] developed the hollow fiber reinforcement with large internal volume to maximize the storage capacity.

COMPARISON OF ADHESIVE STORAGES

Techniques and methods developed regarding the storage of the adhesive in the self-healing system can be divided into two categories. The first is polypropylene or glass fiber as the storage of the healing agent (Dry et al. [2-5]). When loading, the fiber breaks and the healing agent is released into the cracks or the delaminated area. The chemicals then polymerize or harden, bonding the crack faces. The second category is microcapsules as the media to store the adhesive in the matrices (White et al. [19]). When loading, the microcapsule shell breaks by the crack propagation and the chemical is released into the cracks or the delaminated area. Polymerization of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces. Usually glass fiber is used in the self-healing of cement material while the microcapsule is used in the composite material. Comparing the two methods, researchers such as Bleay et al. [10] and Pang et al. [11] believe that the hollow fibers both single fiber and crosslinking is a good method; the fibers are not only used to carry the adhesive agent but also work as the reinforcement in the matrix to improve the strength of the material. Bleay et al. tried to use small fibers to minimize any detrimental effect associated with large diameter fibers while Pang et al. used large size fibers in order to maximize the storage capacity.

Typical Examples of Using Fibers

Dry et al. [5] investigated whether the performance of bending strength and material integrity of a typically reinforced cement composite may be improved through the release of “healing” chemicals, such as adhesives, from hollow fibers into cracks induced by loading. Test performed on two sets of 1x1x6 in. concrete prism specimens. Sample set #1 contained 24 steel-reinforcing fibers (0.5 mm diameter) and 16 adhesive-filled glass fibers (1.0 mm inside diameter and 1.5 mm outside diameter) running the length of the prisms. Sample set #2, the control set, contained 24 metal-reinforcing fibers and 16 of the same repair fibers, but the fibers were empty. Each specimen was loaded in three-point bending over a 5 in. span until fracture at which point the repair fibers broke releasing the adhesive agent into the concrete matrix. The adhesive was given 7 days to set. Each specimen then was loaded again in three-point bending (See Figure 1). For specimens in set #1 (adhesive filled), the slope of the load–displacement graphs for the first bending event and the second bending event are parallel, indicating an equal rate of displacement for applied loads. This, however, is not true for specimens in set #2 (the control set containing the empty repair fibers). The shallower slope of the second bending event indicates a greater displacement for applied loads than in the first (See Figure 1). This behavior is attributed to the decrease in strength from cracking in the first bending test. The rounded peaks of the diagrams for sample set #1 reveal a more elastic failure than is indicated by the sharp points of the diagrams for the controls in sample set #2.
Additionally, samples in set #1 carried a greater load in the second bending test than in the first. This was not the case for the controls. Presumably, cracks repaired in the adhesive-repaired test samples are stronger than the original matrix. The adhesive acts to reinforce and strengthen the concrete.

![Figure 1. Load-displacement for each sample for first and second three-point bend test [6]](image)

**Typical Example of Using Microcapsule**

DCPD-filled microcapsules (50±200 mm) with a urea-formaldehyde shell were prepared using standard micro encapsulation techniques (White et al. [9]). The microcapsule shell provides a protective barrier between the catalyst and DCPD to prevent polymerization during the preparation of the composite. Polymerization of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces. The fracture experiments yield as much as 75% recovery in toughness. Observations by optical and scanning electron microscopy confirmed the healing concept (See Figure 2).

![Figure 2. The autonomic healing concept [9]](image)
A representative load-displacement curve for a self-healing composite sample is plotted in (See Figure 3) demonstrating recovery of about 75% of the virgin fracture load. The average critical load for virgin self-healing samples containing microspheres was 20% larger than the average value for the neat epoxy control samples, indicating that the addition of microspheres and catalyst increases the inherent toughness of the epoxy.

![Load-displacement curve for self-healing composite](image)

Figure 3. Healing efficiency is obtained by fracture toughness testing of tapered double-cantilever beam (TDCB) specimens [9]

**COMPARISON OF THE ADHESIVES USED IN CEMENT MATRICES**

Dry [2] tried the liquid methyl methacrylate first in his active mode. This approach is in response to human intervention and therefore is active. When low heat is later applied to the matrix, a wax coating on the fibers is melted and the methyl methacrylate moves out into the dried matrix. The heat is raised, and the methyl methacrylate polymerizes (See Figure 4). This is not a real self healing adhesive because it needs human intervention to complete the healing process. Later he tried a passive design by using the release of crack-adhering adhesives from hollow glass fibers into concrete to fill cracks. Loading, which causes micro cracking in the matrix, breaks the fibers allowing the chemical to be released and flow into micro cracks. Compared to the active model, this model can automatic sensing and release chemical into the matrix without any external control, hence it is an economical system which has advantages on cost saving.

Compared to the single-component adhesive, a multi-component adhesive has more stability and long longevity because it is activated at a later date. Dry and McMillan [3] used a three-part methylmethacrylate (MMA) adhesive system in their study. The MMA adhesive system has been used to bond and resurface cracked concrete bridge decks [3]. The monomer can also resist extreme temperatures between -20 and +160 °F. The monomer and its initiators have the viscosity of water, so the can flow into small cracks. This system consists of a MMA monomer and two separate catalysts or initiators containing cobalt and peroxide. When mixed, the initiators cause a polymerization reaction in the monomer that hardens to a consistency of plexiglas in 30
The three-part adhesive system is made up of 100 parts MMA, 4 parts cumine hydroperoxide and 2 parts cobalt neodecanoate, the latter two components being the initiators that cause the MMA to polymerize or harden. In commercial practice, the two initiators must be mixed into the MMA separately. If the initiators are mixed together without the MMA, it will cause an explosive reaction. For this reason, it is not possible to put the three-part liquid MMA adhesive system into concrete beam samples because the mixture is chemically unstable. The three-part system was reduced to a two-part system by pre-mixing either of the initiators with the MMA, assuming it would not immediately polymerize. When the third remaining component was added to this mixture, it polymerized into a very hard Plexiglas-like substance within an hour. Also, they used hollow tunnels coated with a brittle sealer as a delivery system. Rounded steel rods were cast in concrete beam samples and pulled out after 24 hrs of curing. They left small tunnels through the length of the sample. The insides of the tunnels were coated with a thin layer of water seal and capped using brass pipe fittings set in the concrete at the ends of the beam. The larger tunnels were loaded with the cobalt/MMA solution. A single small tunnel was made with a 1.8” diameter steel rod that was located in the center of the beam width and 3/8” above the large tunnels (See Figure 5). This small tunnel was loaded with the cumine hydroperoxide initiator and contained approximately 15% of the column of the larger tunnels. The beam samples had a 1.8” triangular notch set in the middle underside of the beam. This was made to guarantee consistent crack location in all samples.

Figure 4. Design for timed release of polymerizeable chemicals to repair cracks and fill pores by melting of the coating on porous fibers [2]
The MMA adhesive system worked very well. The two liquids leaked out into the cracks and entirely filled them with a solid Plexiglas-like matrix within 24 hrs. Test results from the three-point bend test are recorded plotting kN of force against mm of deflection. The adhesive repaired beam carried more load in the second test (+130%), while the two controls carried 117% and 65%. When standardized to 1 mm of deflection the results show even more strength gain from the adhesive repaired specimens. The conclusion is that the MMA adhesive bond restored strength and made the beam more flexible.

Letsch [12] explored the repair of cracks with dynamically changing crack width using the injection of an epoxy resin containing microballoons. Incompressible repair materials either caused the crack to reopen or new cracks to occur in the same vicinity. Therefore, Letsch stated that a successful repair material must have the following characteristics: (1) a compressible volume, (2) be possibly injected into narrow cracks, (3) good bonding properties and watertight, and (4) be able to transfer stresses. By mixing microballoons containing compressible gases into epoxy resins, he formed a new type of repair material. The ability of the microballoons to compress and expand allowed the crack to become narrow or wide without disrupting the bond between the epoxy resin and the concrete; thus, insuring stress transfer and bar protection against exposure to air despite crack movement.

Dry et al. [4] focused on the effect of various adhesives used for self-repair on the concrete considering factors such as stress transfer capability, varying crack width, and damping. They compared the cyanoacrylate (superglue) with the foam adhesive and the empty polypropylene beads which are able to compress and expand. The experiment results showed that specimens with stiffer adhesives, such as cyanoacrylate or cyanoacrylate with beads, have an improvement in both loading and deflection due to crack repair and the old cracks did not reopen. The foam materials and beads rendered the adhesives to be able to compress and expand more, so that the bond between the epoxy resin and the concrete is maintained.

Issa and and Debs [7] restored structural integrity and increased the compressive strength and stiffness of cracked concrete cube specimens by gravity filling of cracks using a low viscosity gel-type epoxy resin system. A two-component system (resin and hardener), low viscosity liquid used to fill and seal cavities and cracks in the structural
elements. It was found that cracks caused a reduction in compressive strength of up to 41% whereas the epoxy gravity filling method, when properly applied, restored the compressive strength by decreasing the reduction in strength down to only 8.23%.

CONCLUSION

Smart self healing materials have the ability to detect and repair damages whenever and wherever are generated inside the material. They overcome the difficulties in detecting and repairing the internal damages by using conventional methods. This would make the material safer, more reliable, longer lasting, and require less maintenance resulting in significant cost reduction.

A successful adhesive should have a compressible volume, be possibly injected into narrow cracks, have good bonding properties and watertight, and be able to transfer stresses. A multi-component adhesive has more chemical stability than a single-component adhesive.

Hollow fibers both single fiber and crosslinking is a good functional component as it can not only carry the adhesive agent but also work as the reinforcement in the matrix to improve the strength of the material. However, their self-healing effectiveness was shown to be limited by the amount of healing resin that could be stored internally. Microcapsule can reduce the mechanical property of material if used in large quantity.

REFERENCES