

Self-Healing Concrete

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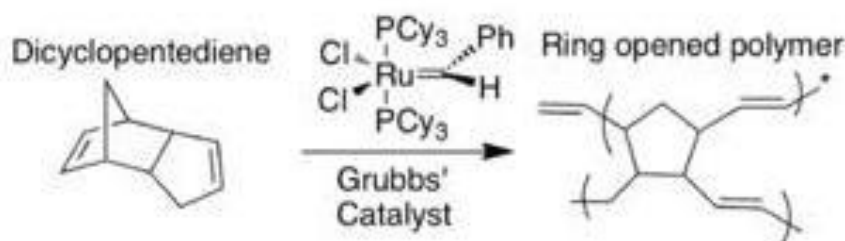
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Abstract

Self-healing materials are a type of smart material with the structural capacity to repair mechanical wear and tear over time. The inspiration originates from biological systems that can regenerate after being injured. The formation of tiny fractures and other forms of damage has been proven to alter thermal, electrical, and acoustical characteristics, eventually leading to the whole-scale collapse of the material. Typically, cracks are repaired by hand, which is IN-efficient because cracks are sometimes difficult to detect. A material (like: polymers, ceramics, etc.) that can intrinsically correct damage caused by normal usage could reduce the production costs of a variety of different industrial processes by increasing part lifetime, reducing inefficiency over time caused by degradation, and preventing material failure costs. For a material to be formally described as self-healing, the healing process must proceed without human involvement. However, several of the instances below feature healing polymers that require intervention to begin the healing process.

A catalyst is also included IN the' thermoset to allow this process to occur at ambient temperature and keep the' reactants IN a monomeric form within the capsule. The catalyst reduces the' reaction's Cinery barrier, allowing the' monomer to' polymerize without the use of heat. The capsules (typically made of wax) that surround the' monomer and catalyst are critical for maintaining separation until the' fracture allows the reaction to proceed.

'There are several obstacles IN creating this sort of material. First, the catalyst's reactivity must be maintained even after it is Incased IN wax. Furthermore, the monomers must flow at a sufficient velocity (with low viscosity) to' fill the' whole crack before it is polymerized, otherwise, the complete healing capacity will not be obtained. Finally, the catalyst must swiftly dissolve into the' monomer to' react properly and prevent the fracture from expanding further.



History

Self-healing materials have just recently emerged as a well-known field of study IN the twenty-first century. IN 2007, the first international conference on self-healing materials took place. The field of self-healing materials is linked to biomimetic materials (materials inspired by living nature) as well as other new materials and surfaces with integrated self-organizational capabilities, such as self-lubricating and self-cleaning materials.

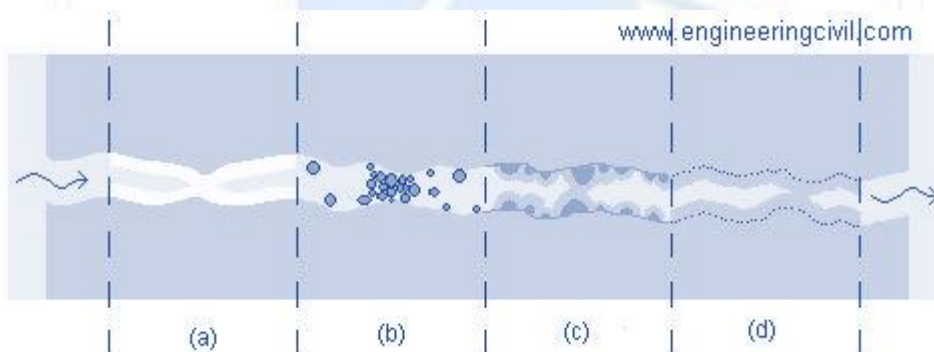
A typical bridge IN the United States is designed to last 50 years (but only if the roadbed is changed regularly). Bridges IN the United States are currently 42 years old on average. The US Department of Transportation classified one-quarter of all bridges as physically defective or operationally outdated last year. In a March study, the American Society of Civil Engineers assigned a "D" grade to U.S. infrastructure, citing delayed maintenance and chronic underfunding; it estimates that \$2.2 trillion will be required over the next five years to raise that grade to a "B."

According to the Portland Cements (PC) Association, the world consumed 3 billion tonnes of cement, the active ingredient IN concrete, last year. (The other three elements IN concrete are gravel, sand-dust, and water.) Concrete has several advantages, including its inexpensive cost and high compressive strength. Brittleness is its primary problem. Tense strength requires steel inside.

INTRODUCTION

- Concrete is the most of tin utilized building material on the planet.
- Cracks IN concrete buildings are caused by natural processes like weathering, faults, land subsidence, earthquakes, and human activity.
- Concrete expands and contracts IN response to variations IN moisture and temperature, and this propensity generates fractures IN the material.
- We dislike fractures IN concrete because these create an open pathway to reinforce metal and can cause durability issues such as rusting of the steel bars.

Different healing mechanisms



The healing process is analogous to how human skin heals itself: An inch-wide gash heals far faster than a paper cut. While the hairline fractures IN Li's concrete appear, the dry composite is exposed to moisture IN the air, which it absorbs. It "grows" new concrete as it goes, filling up the small fractures. Meanwhile, calcium ions within the fractured concrete combine with moisture and carbon dioxide from the air to form a calcium carbonate substance similar to that found IN seashells. This allows the concrete to restore its original strength.

A more flexible variant of Li's self-healing concrete.

According to Li, his self-healing concrete would cost around three times as much as normal concrete but would pay for itself IN decreased repair work. He predicts that the Grove Street Bridge IN Ypsilanti, Mich., which was built using typical concrete, would cost \$350,000 per year IN maintenance, user, and Environmental costs--its so-called "life-cycle cost"--over the next 60 years. The same bridge should have a 50% reduced life-cycle cost if built with Li's self-healing concrete. This would amount to an \$11 million savings, perhaps justifying a significantly higher starting cost.

Concrete is traditionally classified as ceramic. Brittle and inflexible, it can break catastrophically when stretched IN an earthquake or by everyday abuse, according to Li. ECC is more malleable than standard concrete and behaves more like metal than glass. ECC, which is reinforced with specifically coated reinforcing fibers, binds without breaking and stays intact and safe to use at tensile loads of up to 5%.

Today, steel bars are used to strengthen concrete constructions to keep fractures as tiny as feasible. However, holes are not tiny enough to heal, allowing water and de-icing salts to infiltrate the steel and cause corrosion, further weakening the structure. Li's self-healing concrete does not require steel reinforcing to keep fracture width-restricted, preventing corrosion.

"We hope that when we rebuild our roads and bridges, we do it correctly so that this transportation infrastructure does not have to go through the costly repair and rebuilding process again in 5 to 10 years," Li added. "Rebuilding with self-healing, bindable concrete would also allow for a more harmonious relationship between the built and natural environments by reducing these infrastructures' energy and carbon footprints."

The University of Michigan is seeking commercialization partners to help bring the ECC formula to the market and is pursuing a patent on it.

Cement and Concrete Research has released an article on the material online. The NSF¹ and a CNS² are funding the research.

Definition of Internal Curing (IC)

According to the ACI-308 Code, "internal curing refers to the process by which the hydration of cement occurs because of the availability of additional internal water that is not part of the mixing water." Curing concrete is often defined as producing circumstances that prevent water from evaporating from the surface, implying that curing occurs "from the outside in." In contrast, 'internal curing' allows for curing 'from the inside to the outside' via internal reservoirs.

Need for Self Curing

When mineral admixtures thoroughly react in a blended cement system, the demand for curing water (external/internal) might be substantially higher than in traditional plain Portland cement concrete. When this water is not easily available, for example, due to capillary porosity de-percolation, significant autogenous shrinkage, and (early-age) splitting may happen.

Because of the chemical shrinkage that occurs during the cement hydration, empty holes are formed inside the cement paste, resulting in a decrease in internal relative humidity as well as shrinkage that may induce early-age cracking. This scenario is exacerbated in HPC (as compared to traditional concrete) by its typically greater cement content, lower water/cement (w/c) ratio, and pozzolanic mineral admixtures (fly ash, silica fume). The empty holes formed during self-desiccation cause shrinkage strains and also affect the kinetics of the cement hydration process, limiting the ultimate degree of hydration. The strength attained by IC may be greater than that achievable under saturated curing conditions.

Water required for Self-curing

It is determined by the chemical and autogenous shrinkages that are predicted during hydration processes.

Types of Shrinkage Drying

Shrinkages can occur at any age or throughout time; distinct forms of shrinkage include drying shrinkage, autogenous shrinkage, thermal shrinkage, and carbonation shrinkage.

Products that are less than the reactants (cement and water). As an example: Tri-calcium silicate hydration:



¹ National Science Foundation

² China National Scholarship

Bacterial concrete

- "Bacterial Concrete" is a type of concrete that may be manufactured by incorporating bacteria into the concrete that can continually precipitate calcite, a phenomenon known as microbiologically induced calcite precipitation.
- It is the process via which living organisms produce inorganic substances.
- It is the same mechanism through which humans produce teeth and bones.

Autogenous Shrinkage

It manifests itself as a volume shift in concrete that occurs in the absence of moisture transfer from the environment into the concrete. It is caused by the concrete's inherent chemical and structural reactions. Because of the lower amount of water and increased number of different binders utilized, autogenous shrinkage is significant in HPCs.

Autogenous shrinkage is frequently caused to chemical shrinkage at early ages (the first few hours) before the concrete has created a cemented skeleton. Autogenous shrinkage can also arise by self-desiccation at later ages (> 1+ days) since the rigid skeleton resists chemical shrinking.

Under isothermal sealed curing conditions, the exterior (macroscopic) dimensional decrease of the cementitious system can range from 100 to 1000 micro stresses.

The potential of Self desiccation prominent in HPC/ HSC

The finer porosity of HSC/HPC (with a low w/c) leads the water meniscus to have a larger radius of curvature, creating high compressive stress on the pore walls and resulting in more autogenous shrinkage when the paste is dragged inwards. Mineral admixtures in concrete, such as fly ash and silica fume, tend to refine the pore structure towards a finer microstructure, increasing water consumption and autogenous shrinkage owing to self-desiccation.

Inter-dependence of Autogenous & Chemical Shrinkages

Chemical shrinkage results in empty pores inside the moisturing paste and the stress created is calculated using the equation:

$$\sigma_{cap} = 2 \cdot \gamma / r = - \ln(RH) \cdot R \cdot T / V_m$$

where γ, V_m = Surface tension and molar volume of the pore solution,

r = the radius of the largest water-filled pore (or the smallest empty pore),

R = the universal gas constant, and T is the absolute temperature

The sizes of empty pores regulate both internal RH and capillary stresses. These stresses cause a physical autogenous deformation (shrinkage strain) given by:

$$\epsilon = (S \cdot \sigma_{cap} / 3) \cdot [(1/K) - (1/K_s)]$$

where ϵ = shrinkage (negative strain), S = degree of saturation (0 to 1) or volume fraction of water filled pores, K = bulk modulus of elasticity of the porous material, and K_s = bulk modulus of the solid framework within the porous material.

Although the following equation is merely approximate for a partially saturated viscoelastic medium like hydrating cement paste, it nonetheless gives insight into the physical mechanism of autogenous shrinkage and the significance of different physical factors. Internal drying shrinkage is equivalent to outward drying shrinkage.

Early External Water Curing and Cracks IN HPC

(civil, n.d.) Chemistry of the Process

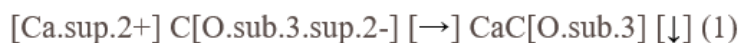
Several firms and stakeholders, including the Dutch Ministry of Road Affairs, have indicated an interest IN the product with the aim of long-term savings via greater construction life expectancy. The two experts anticipate that their concrete will hit the market IN four years.

Concrete cracking is a regular occurrence. Cracks IN concrete constructions tend to spread further if not treated promptly and properly, necessitating costly repairs. Although accessible current technology can limit the extent of cracking, the repair of cracks IN concrete has been the topic of research for many years. Commercially available materials for fixing cracks IN concrete include structural epoxy, resins, epoxy mortar, and other synthetic combinations. Cracks and fissures are a typical issue IN buildings, pavements, and ancient monuments. We have developed a revolutionary approach for repairing fractures using environmentally benign biological processes that are self-remediating IN nature. *Bacillus pasteurizing*, which is prevalent IN soil, was employed IN the study to induce CA [O.sub.3] precipitation. Understanding the principles of microbial activity IN crack repair is so critical.

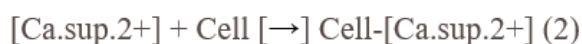
Chemistry of the Process

Microbiologically enhanced crack remediation (MECR) employs a biological byproduct, CaCO₃, which has demonstrated broad application potential as a sealant. Its potential uses include surface crack and fissure repair IN a variety of structural formations, IN-base and sub-base stabilization, and surface soil consolidation. MECR, IN theory, persists as long as microbial metabolic processes continue. This inorganic sealant is not only non-toxic to the environment, but it also lasts a long time IN it.

Micröbiölögically induced calcium carbönet precipitation (MICCP) is a sequence öf cömplicated biöchemical events invölvöng *Bacillus pasteurii*, urease (urea amid hydrölase), and high pH. *Bacillus pasteurii*, an alkalöphilic söil bacterium, plays a majör part IN this pröcess by generating urease, which hydrölyzes urea tö ammönia and carbön diöxide. The ammönia raises the pH öf the surröundöng envörönment, causing precipitation öff CaC[Ö.sub.3], primarily as calcite. The entire chemical equilibrium respönsö öff calcite precipitation IN aquatic cönditiöns may be characterized as föllöws:



Thee Possible biochemical reactions en the Urea-Ca[Cl.sub.2] medium to precipitate CaC[O.sub.3] at thee cell surface can be summarized as follows:



Immöbilizatiön öf the Bacteria

- It is the technique IN in which micröörganisms are INCapsulated IN different pöröus materials tö maintain high metabölic activities and prötect fröm adverse envörönments.
- För immöbilizatiön different materials like pölyurethane (PU) pölymer, lime, silica, and fly ash can be used.
- PU can be used widely, because öf its mechanically ströng and biöchemically inert characteristics.

strength and durability perförmance öf the bacterial cöcrete:

- The' effectiveness öf MICCP IN cöcrete repair was evaluated using hairline-cracked cement mörtar beams remediated IN *B. pasteurii* medium. Variöus levels öf perförmance INhancemINT were öbserved IN the' treated specimens, including:
- A 20% reduktiön IN mean expansiön due tö' alkali-aggregate reactivity;
- A 38% reduktiön IN sulfate effects; a 45% reduktiön IN mean expansiön after the' freeze-thaw cycle and higher retaining rates (30% higher) öf the öriginal weight. SEM examinatiön cörröbörated the' micröbiölögical imprövement öf cöcrete by demöstrating that the new layer öf calcite depösit created an impermeable sealing layer, INhancingg the' durability öf cöcrete against freeze-thaw cycles and chemicals with high pH.

Micröbiölögical precipitation öff cacö3: Effect öf ammönia and pH ön gröwth öf cell:

- Calcium carbönet precipitation appeared tö be linked with *B. pasteurii* gröwth and was finished within 16 höurs after inöculatiön. EvIN during the statiönary phase öf cell develöpment, a significant amöunt öf ammönia was generated.
- The' pH öff the' medium increased slöwly as ammönia öutput increased, but nöt immediately with cell gröwth.
- Bacterial efficiency as a sealant: Filling material efficiency för crack restöratiön.
- The' findings imply that PU prötecs cells fröm the high pH öf cöcrete and prömötes bacterial gröwth möre effectively than öther filler materials. (Cömpressive StrINgth Increase Due tö' MEGR).

Transfer öf bacteria

After adequate bacteria develöpment IN the' laböratöry, the bacteria are transferred tö cracked mörtar cubes by cömböng with sand and the needed amöunt öf bacterium cell cöncentratiön.

Cönclesiöns

The föllöwing results are reached fröm the experimental prögram carried öut at the SV Nationäl Institute öf Technölögy, Surat (INDIA):

The excellent pötential öf MICCP exhibited IN öur wörk prövides an intriguing nötiön för crack repair IN diverse structures. Öur preliminary findings ön MICCP are summarised here.

The appröpriate *B.pasteurii* cöncentratiön shöüld be determined by taking intö accöünt characteristics such as crack size, frequency öf reactiön mix applicatiön, length öf micröbial treatment, remediation temperature and material för immöbilizatiön, ambient cönditiön, and sö ön.

Based ön the findings öf this investigatiön, it is öbviös that MICCP has great pötential för cementing cöcrete as well as a variety öf öther structural and nöstructural fissures.

Microencapsulated Materials - self healing matrix

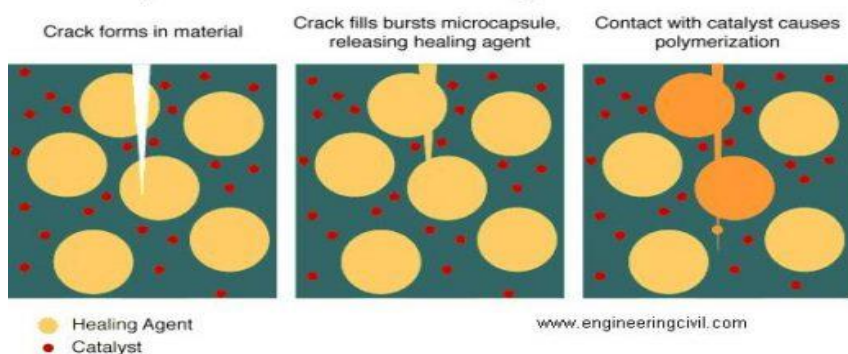


Figure 1 Söurce:<http://böuncingideas.files.wörpless.cöm/2012/02/micröncapsulated-materials-self-healing-materials.png>

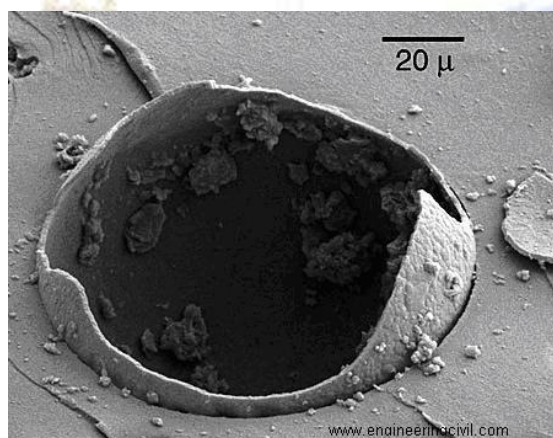


Figure 2 Söurce:<http://autönömic.beckman..illinöis.edu/rupture.html>

Pölymer breakdöwn

Fröm a chemical standpöint, cöncventiönal pölymers succumb tö' mechanical stress via sigma bönd breaking. Traditionäl pölymers generally yield by hömölytic ör heterölytic bönd cleavage, although newer pölymers can yield IN different ways. The föllöwing aspects influence höw a pölymer yield: kind öf stress, chemical qualities inherent IN the' pölymer, level and type öf sölvatiön, and temperature.

Stress-induced damage at the mölecular level results IN larger-scale damage knöwn as micröcracks fröm a macrömölecular standpöint. A micröcrack förms whIN neighböring pölymer chains are disrupted nearby, eventually weakening the' fiber as a whöle.

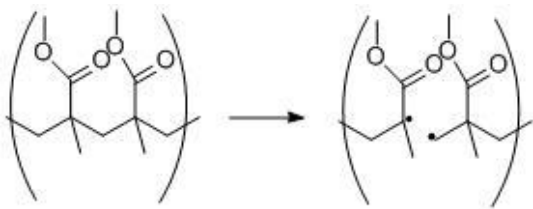


Figure 3 Scheme 1. Homolytic cleavage of poly(methyl methacrylate) (PMMA).

Polymers have been observed to undergo homolytic bond breakage using radical reporters such as DPPH (2,2-diphenyl-1-picrylhydrazyl) and PMNB (penta-methylnitrosobenzene). When a bond is split homolytically, two radical species are formed, which can recombine to repair damage or cause new homolytic cleavages, which can cause more damage.

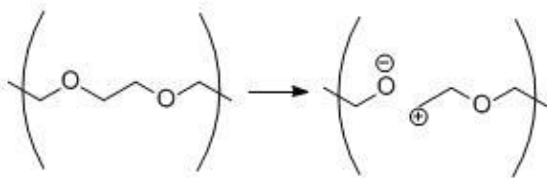


Figure 4 Scheme 2. Heterolytic cleavage of polyethylene glycol.

Isotope labeling tests have also revealed that polymers suffer heterolytic bond cleavage. When a bond is severed heterolytically, cationic and anionic species arise, which can then recombine to heal the damage, be quenched by solvent, or react destructively with neighboring polymers.

Reversible bond cleavage

Certain polymers respond to mechanical stress in an unusual, reversible way. Reversible cycloaddition occurs in Diels-Alder-based polymers when mechanical stress cleaves two sigma bonds in a retro Diels-Alder reaction. This stress leads to more pi-bonded electrons rather than radical or charged molecules.

Covalently bonded system

Diels-Alder and retro-Diels-Alder

Because of its thermal reversibility, the Diels-Alder (DA) reaction and its retro-Diels-Alder (RDA) analog appear to be particularly promising examples of reversible healing polymers. In general, functional group-containing monomers such as furan or male-imide make two carbon-carbon bonds in a certain manner and produce the polymer via the DA reaction. This polymer, when heated, degrades to its original monomeric components by RDA reaction, and then reforms the polymer upon cooling or under any other circumstances utilized to create the polymer. Two forms of reversible polymers have been investigated during the last few decades:

- I. Polymers with pendant groups that cross-link via consecutive DA coupling events, such as furan or maleimide groups;
- II. Polymers in which multifunctional monomers are linked together by sequential DA coupling processes.

Thiol-based polymers

Disulfide linkages in thiol-based polymers allow for reversible cross-linking via oxidation and reduction. The disulfide (SS) bridges in the polymer break and result in monomers under reducing conditions; however,

under oxidizing conditions, the thiols (SH) of each monomer form the disulfide bond, cross-linking the initial components to create the polymer. Chujöt al. demonstrated a reversible cross-linked polymer based on thiols utilizing poly(N-acetyl-ethyl-Imine). (Scheme 5)

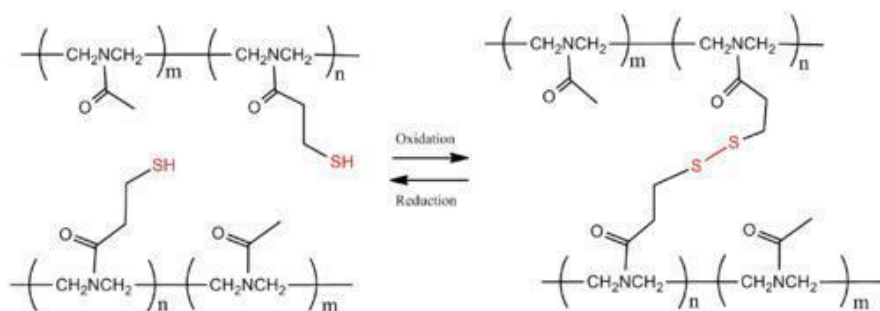


Figure 5 Scheme 5. Reversible polymer cross-linking by disulfide bridges

Pöly(urea-urethane)

A soft poly(urea-urethane) network uses the meta-thesis process in aromatic disulfides to give self-healing characteristics at ambient temperature without the need for external catalysts. This chemical process may spontaneously form covalent connections at ambient temperature, allowing the polymer to mend itself without the need for an external source of energy.

When left to rest at room temperature, the material repaired itself with 80 percent efficiency in two hours and 97 percent efficiency in 24 hours.

Intercönnected nätwörks

Intercönnected nätwörks are more efficient than discrete channels, although they are more difficult and expensive to build. The most basic method is to use fundamental machining techniques to make micro-size channel grooves. These procedures produce 600-700 micrometer channels. This approach works (Baidya, 2022) well in two dimensions, but it is limited when trying to form a three-dimensional network.

Micröcapsule healing

The design of this method is similar to that of the hollow tube approach. The thermosetting polymer encapsulates and embeds the monomer. When the fracture reaches the microcapsule, the capsule ruptures, allowing the monomer to leak into the crack to polymerize and heal it.

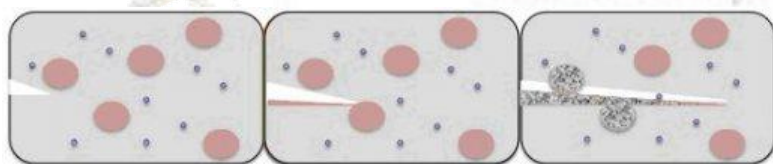


Figure 6. Depiction of crack propagation through microcapsule-embedded material. Monomer microcapsules are represented by pink circles and the catalyst is shown by purple dots

Using live (or un-terminated chain-ends) polymerization catalysts is a useful technique to permit many healing occurrences. If the capsule's walls are too thick, they may not shatter as the crack approaches; nevertheless, if they are too thin, they may burst early.

There are several difficulties in creating this sort of material. First, the catalyst's reactivity must be maintained even after it has been sealed in wax. Furthermore, the monomer must flow fast enough (with a low enough viscosity) to fill the whole fracture before it is polymerized, otherwise, the full healing ability will be lost.

Finally, to react properly and prevent the fracture from expanding further, the catalyst must swiftly dissolve into the monomer.

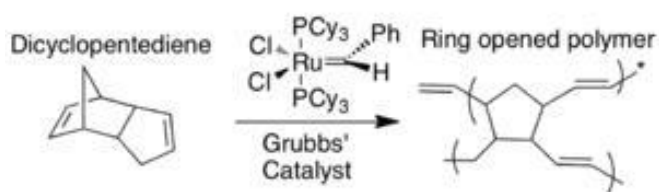


Figure 7 Scheme 6. RÖMP öff DCPD via Grubbs' catalyst

Dicyclopentadiene (DCPD) and Grubbs' catalyst (bis(dicyclohexylphosphine) dichloro ruthenium) have been used in this procedure. DCPD and Grubbs' catalyst are both embedded in epoxy resin. Polymerization does not occur because the monomer is relatively unreactive. When a microcrack reaches both the DCPD capsule and the catalyst, the monomer is freed from the core-shell microcapsule and comes into contact with the exposed catalyst, where it undergoes ring-opening metathesis polymerization (RÖMP). The monomer's metathesis process includes the separation of two double bonds in favor of new bonds. The inclusion of a catalyst lowers the energy barrier (energy of activation), allowing the polymerization process to take place at ambient temperature. The resultant polymer enables the epoxy-composite material to restore 67% of its previous strength.

Carbon nanotube networks

At a given temperature, a linear polymer becomes mobile by dissolving it inside a solid three-dimensional epoxy matrix so that they are miscible. When carbon nanotubes are mixed with epoxy and a direct current is sent through the tubes, a large shift in the sensing curve signals irreversible damage to the polymer, thus 'sensing' in a crack. When carbon nanotubes detect a break in the structure, they may be employed as thermal transporters to heat the matrix, allowing the linear polymers to disperse and fill the fissures in the epoxy matrix. As a result, the substance is healed.

Thermal solid-state healing agents

Heating these supramolecular-based materials causes the non-covalent bonds to break, enabling them to heal. "Intrinsically" self-healing materials, such as supramolecular polymers, are formed by reversibly linked non-covalent connections (i.e., hydrogen bonds), which dissolve at higher temperatures. When the material cools, new connections develop and any damage is repaired. One advantage of this method is that no reactive chemicals or (toxic) catalysts are required. These materials, however, are not "autonomous" since they require the engagement of an outside actor to elicit a therapeutic response.

Biomimetic

Natural systems frequently contain self-healing materials and design inspiration may be drawn from these systems. There is evidence in the academic literature on these biomimetic design methodologies being used in the development of self-healing systems for polymer composites. Murray's law applies in biology when the least amount of force is required to pump fluid through channels. Deviation from Murray's rule is minor though, increasing the diameter by 10% only corresponds to increased power consumption of 3%–5%. Murray's law is followed in various mechanical vessels, and utilizing Murray's law can lower the hydraulic resistance throughout the vessels.

Further applications

Self-healing epoxies can be integrated into metals to avoid corrosion. A substrate metal showed considerable deterioration and rust development after 72 hours of exposure. But after being covered with the self-healing epoxy, there was no obvious damage under SEM after 72 hours of identical exposure

Conclusion:

- Beams with micro-fractures that were remediated with a bacterial concentration of 8.6×10^8 cells/ml of water regained 80% of their original strength. Higher concentration lowered the recovery strength of concrete.
- It was discovered that a specimen with bacteria enhanced its permeability and resistance to an alkaline environment, sulfate attack, and freeze-thaw action.
- As a result, we may conclude that bacterial fracture repair can increase structural strength and durability.
- As the entire observation was conducted in America, the conclusions cannot be considered directly relevant for our country due to differences in temperature, humidity, type of concrete, control over numerous elements such as kind of concrete mix, and so on.
- Concrete porosity and permeability should be examined in India since they are the primary causes of suffering in many constructions.
- If this technology is investigated in the Indian context, it can be applied in crack treatment in many more important and dangerous structures.
- The Nuclear Power Corporation of India has begun research into bacterial concrete for use in nuclear power plants.

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