SELF-REPAIRING MATERIALS

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Summary: People have always thought that self-healing materials are science fiction, but they will become our everyday reality. We will soon see an industrial revolution in which tires, concrete or even robots will self-repair following plastic deformation. Self-healing materials are our future. From saving money and lives lost in infrastructure collapses to improving human health and longevity, self-healing materials are being used in many areas today. Research is still in its infancy, but their potential is infinite. This is true for concrete, implants, paints, or even artificial skin.

KEYWORDS: Polymers, Shape memory, Encapsulation, Repairing agent, Fatigue failure.

1. Introduction

In everyday life, the materials we use are not indestructible and are therefore subject to damage of a micro or macro structural nature. The most common damages that can occur are: ageing (with the passage of time, materials lose their original properties, and can be completely destroyed in terms of several years), wear (after continuous use of materials, they can be destroyed by the frictional forces they are subjected to), defects (no material is perfect, they have many micro defects that can lead to their sudden breakage - fatigue failure - due to the stresses and strains applied). Against the background of these problems (the third of which is the most dangerous and the hardest to find), self-repairing materials appear.

These materials, as their name suggests, are artificial materials that can repair damage that inevitably occurs during work (cracks or fissures). Although most self-repairing materials are polymers and elastomers, metals, ceramics, and cemented materials can also be used.

2. History

We can take the example of the Romans, whose buildings have survived for almost 1900 years. Geologist Mari Jackson, along with her colleagues in 2014, have made the type of mortar used for Roman structures such as the Pantheon and Colosseum. It is made by mixing volcanic ash called Pozzolane Rosse, from the Alban Hills volcano in Italy, with quicklime and water which they used to bind pieces of tufa, a rock aggregate. Lime interacted with the chemicals in the whole mixture, producing crystals that replaced the mixture. The crystals are produced continuously, thus managing to hold the mortar and the coarse aggregate together, producing a self-repairing type of material.

3. Current status

Due attention started to be given to them in 2007 at the conference on self-repairing materials. The conference, led by Professor van der Zwaag of Delft University of Technology, the Netherlands and Professor White of the University of Illinois, USA, discussed the application of concepts from the most common self-healing materials to all materials. Reaching its seventh edition in 2019, the Conference for Self-Repairing Materials, held in Yokohama, Japan, has made this topic of interest again.

4. Biomimetics in the study of self-repairing materials

Biomimetics is the act of adopting some type of pattern, system or element of nature in order to create an artificial material. Clearly, the plants and animals that surround us can encapsulate and heal wounds. For all of them there are two stages: the first stage would be self-sealing and the second stage would be self-healing. In plants, rapid self-sealing prevents the plant from becoming infected by germs, which gives it time for subsequent self-healing of the wound, which, in addition to closing the wound, also restores its mechanical properties.

In the academic literature there is documentation that these biomimetic design approaches are being used in the development of self-healing systems for polymer composites. The DIW structure can be used to essentially mimic the structure of the skin. This work has shown partial recovery of strength after fracture and could be repeated several times due to the ability to restore the grooves after use. It cannot be repeated because the polymer in the crack plane from previous healing would accumulate over a longer time.

5. Polymers in the study of self-repairing materials

Polymer is a substance made up of very large molecules formed by joining together several monomer molecules (simple unsaturated molecules). In recent times, polymers have become a basic material for products such as plastics, rubbers, films, fibers, or paints that people use to make their lives easier. The very high demand has led to an extension of their reliability and lifetime in view of a new design class of polymeric materials capable of restoring their functionality after damage or fatigue. They are divided into two different groups depending on the approach of the self-healing mechanism: intrinsic or extrinsic. Self-healing polymers follow a three-step process very similar to that of a biological response.

6. Intelligent material

Intelligent materials are a special category of materials that need to fulfil certain functions: a detection function whereby cracks are located, a processing function whereby the material decides what action needs to be taken and an actuation function whereby repair takes place. In such materials these functions can be incorporated by special devices to repair cracks, tubular vessel-like networks or special resins that cure without the presence of water. Self-repair can be of two types: passive and active.

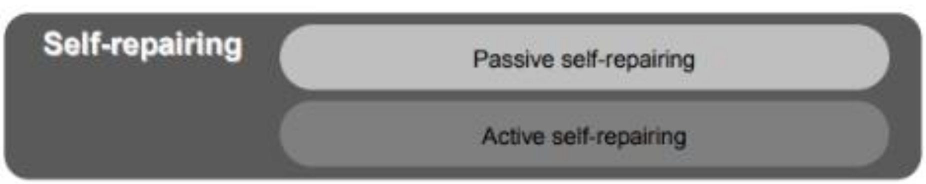

Fig. 1. Types of self-healing mechanisms [1]

7. Passive self-repairing

Passive self-repair is the process by which damage is repaired by releasing a repair agent from capsules inserted into the material composition. This basic concept was proposed by the Agency for Science and Technology in 1989.

A first study was carried out by Dry in 1994. A crack in a brittle cement concrete caused by overheating of the material was repaired by releasing capsules containing brittle glass fibers. The bonding agent (the glass fiber capsules) can be and thus fill the crack.

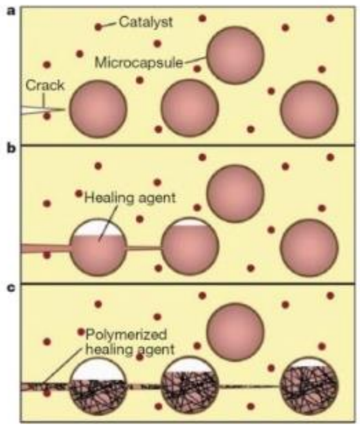

Fig. 2. Example of passive self-repair [2]

In 1998, the composition of PSS-ECC self-healing cement was investigated. In this case, the bonding agent is brittle fiber tubes containing ethyl acrylate. In this study, the importance of the value range in which the repair agent works was emphasized. Thus, the dimensions must be within a few tens of microns, otherwise the adhesive agent will not be sufficient. For larger cracks, thick hollow glass tubes are needed, but they reduce the mechanical properties of the material. The drive mechanisms must also be considered. Thus, the maximum width should be less than the inner diameter of the glass fiber.

Another study conducted in 2004 attempted to recover not mechanical properties but water permeability. Fragile glass tubes embedded in a HPFRCC matrix were used as a repair agent. The graph below shows the relationship between maximum width and water permeability. The results show that at widths less than 0.2 mm, due to the viscosity of the repair agent, self-healing was more ineffective than for cracks larger than 0.2 mm.

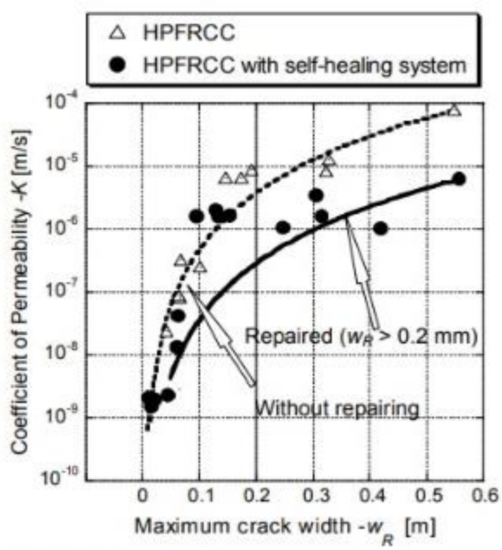

Fig. 3. Dependence of permeability on maximum crack width [3]

8. Active self-repairing

Because of the brittle capsules used in passive self-repair, the use of such materials on site is much more difficult. So new materials have been tried.

In 2003, Sakai proposed the use of a shape memory alloy (SMA) to close cracks.

The "shape memory" phenomenon is present in certain alloys with reversible martensite transformation in which the structural constituent has a thermoelastic character. A product made of an alloy can be deformed from an initial shape with a thermally stable configuration to another shape with a thermally inconsistent configuration. This product can be said to have a shape memory because it can return from a thermally unstable configuration to its original, thermally stable configuration when heated, i.e., it can be said to remember its original shape. Metallic alloys with the property of returning to their original shape is the result of the fact that they exhibit a reversible transformation from a current state to a martensitic state when the temperature changes. As this is a relatively new field of advanced technology, the data on the production of these materials and their applications are far from being sufficiently well known, although a great deal of research is being carried out internationally in this area, with results being published after the new products have come onto the market.

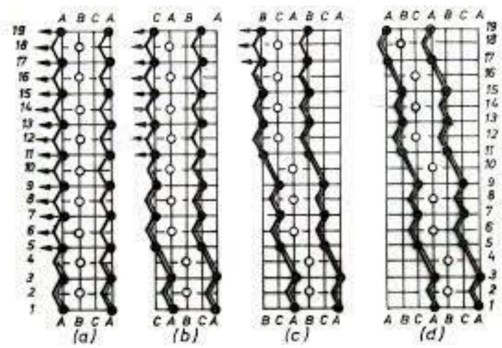

Fig. 4. Successive stages in the transformation of a shape memory material [4]

Nishiwaki in 2006 developed a new approach that can be called "active self-healing system". Following cracks in the concrete that trigger electrical stimuli from a sensor, self-repair starts automatically. The system consists of a conductive composite for self-diagnosis of cracks, made of a thermoplastic film and a resin as a repair agent. The self-diagnostic composite is used to monitor cracks like a sensor. The sensor can, in the absence of any deformation, monitor the deformation using the conductive path with dispersed particles. Around a larger crack detected by the sensor, the electrical resistance of the sensor increases because part of the electrically conductive path around the crack is cut off. With the sensor, selective heating can be achieved around the crack. Knots were installed on the surface of the self-diagnostic composite, and between them the composite was covered with a polyethylene film. Thus, this foil eliminated the bond between concrete and composite and the width of the crack was related to the deformation measured with a certain accuracy.

9. Reversible polymers

Polymers don't always need internal performative systems, such as embedded capsules or vascular tubes, to repair internal wounds. Some of them break apart to reveal what we might think of as highly "reactive" heads or fragments that naturally try to rejoin. Driven by either light or heat, these stray fragments naturally try to rejoin with other nearby molecules, reversing the damage and repairing the material. Some break off to expose their electrically charged ends, giving the broken fragments a built-in electrostatic attraction. Damage occurs when electrostatic forces pull the fragments together, allowing the material to repair itself. Sometimes all you need to repair damage is a little heat.

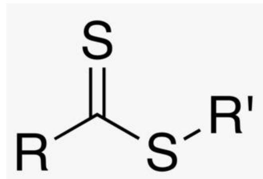

Fig. 5 Shows a reversible polymer fragment [5]

10. Photopolymerization

A team of researchers at the University of Southern California's Viterbi School of Engineering has developed a self-repairing material using the light-curing technique. By chemically modifying a resin, it became self-repairing, and by solidifying it using light, the desired shape is achieved.

By reacting a group called thiols with thiol-oxidizing agents, they obtain sulfides, a group that can repair itself. This is the basis of photopolymerization.

Wang explains: "When we gradually increase the amount of oxidant, the self-healing property becomes stronger, but the photopolymerization behavior is reduced. There is a competition between these two behaviors. And eventually we found the ratio that allows fast regeneration and relatively fast photopolymerization."

The researchers have shown that in just a few hours (depending on the volume of the object) it is fully regenerated. For example, a cube with a side of 17.5 mm^2 can completely self-heal in just two hours at a temperature of 60 degrees Celsius. By increasing the temperature, the material can repair itself faster.

11. Applications

Self-repairing materials have numerous applications in everyday life from industry to medicine. We can imagine how buildings, bridges or even asphalt can close cracks on their own, how cars damaged at low speeds can be repaired, and how even a common paint scratch on a car no longer requires a service visit. We can experiment with self-repairing car linings and even implants or artificial skin that mimic their natural counterparts. Accidents during work could also be avoided, leading to lower repair costs and safer working conditions for human operators.

12. Conclusions

Now that we've discovered self-healing materials, let's look at some of the advantages and disadvantages of these. The advantages of self-repairing materials are their longer lifetime, lower maintenance time, which allows for higher productivity, fewer accidents during operation and improved quality of life through their use in the medical field.

As regards passive self-repair, one problem is the impossibility of repairing larger cracks. Also, the incorporation of self-repairing components into the mats and ceramics is a laborious and still rudimentary process. Finally, after repair some materials may have their physical, chemical, and mechanical properties affected.

Thus, although much more research is needed in this area, due to the multitude of applications they can achieve, we can expect a real revolution in these materials.

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