A Review on Techniques Used to Make Self-Healing Polymers

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1. Abstract

In recent times , self healing polymers have been a topic of active research . As their name suggests they exhibit an outstanding behaviour of healing whenever a crack propagates through the material . There is huge potential in them in real life applications in various fields stretching out from bioelectronics , coating and paint industry, tissue engineering to aerospace material , actuators and biomaterials . In recent years , several different and ingenious methods have been developed to synthesize self healing polymers . Our review report of this expanding field of self healing polymers is an attempt to categorise and present all techniques developed to prepare self-healing polymers .

Keywords: Polymer;Self-healing;Techniques;Healing-agent ;Crack;Material

2. Introduction

Polymers are widely used in a broad range of industries like textile, construction, aerospace, packaging and automotive because of their advantages including better resistance to chemicals than metals, light weight, broad availability, non toxic nature, etc. However, there are some problems related to long - term durability of polymeric materials for structural application.

During its prolonged usage, materials are subjected to damage or failure due to being exposed to harsh conditions. The polymers can degrade due to a number of different ways like delamination, fibre–matrix debonding, fibre fracture or microcracking of the polymer matrix[2]. Damage can be at the micro- or macro-level. A macro-level damage will break the material and a micro-level damage will bring about a change in the material's characteristics and significantly reduce the lifetime of the structure. Hence, there is a need to repair the damaged materials in time.

Researchers have been inspired by the healing processes in biological systems and have developed synthetic polymers that can repair themselves. A self-healing polymer material releases the healing agent from a specialized carrier and the healing agent repairs the crack in the material which is similar to the process of healing of fractures[3]. When the polymer is able to repair itself without requiring external stimulus, then the mending is termed as autonomic whereas when an additional treatment is required for the polymers to heal cracks, the mending is called non-autonomic[4].

Self-healing involves three steps - actuation or triggering, traveling, and repairing[5]. In the first step, the need for the healing medium to the damaged area is recognized. In the second step, the healing agent makes its way to the damaged area. In the end, the crack is repaired. The various techniques used to make self-healing polymers are presented in this review report.

Techniques for self healing can be divided based on several factors. For example, they can be divided into intrinsic self healing where polymers themselves can heal macroscopic and molecular damage or into extrinsic where the healing agent is embedded inside the polymer matrix . Another way is to organise them by the different techniques by which self healing occurs . We will follow the later in this report as this would organise all the different techniques to fall under four categories .

3. Self healing types

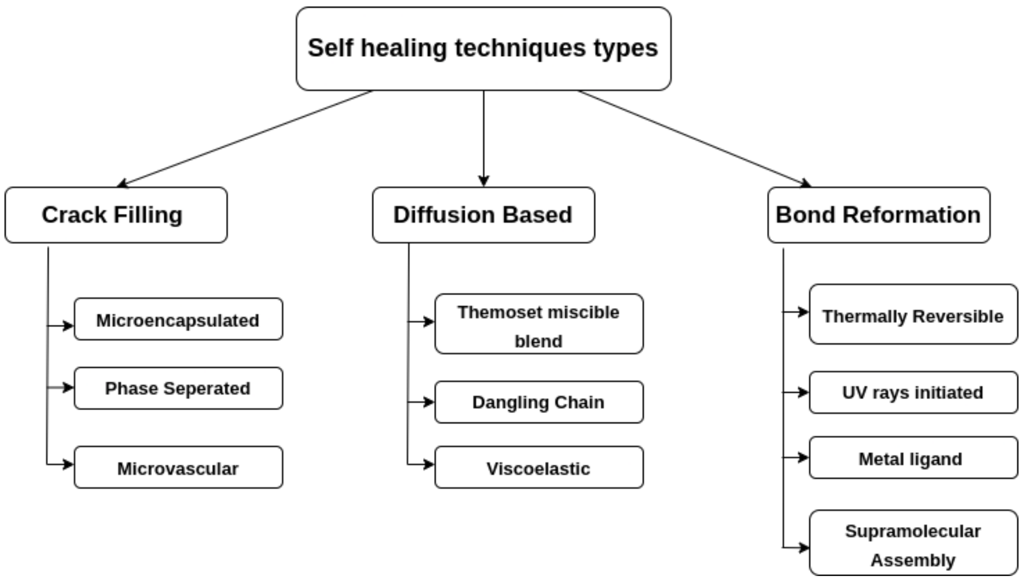

Fig 1 . Block diagram showing different techniques.

3.1 Crack filling healing

This is a self-healing approach where autonomic repair of the polymers is done through crack filling mechanisms wherein special fluids also known as "healing agent" fills the crack and through physical and chemical process repairs it . The healing agent can include liquid catalysts, monomers or solvent solutions .

3.1.1 Microencapsulated healing agents[5]

This is one of the widely used techniques which is simple yet highly effective . In this the polymer matrix is encapsulated by microcapsules filled with a healing agent and catalyst which is either in a solid state or in a separate capsule in liquid state .

As shown in Fig[2] when a crack appears in the polymer it propagates through the matrix and breaks the capsule filled with the healing agent . After that, the healing agent comes in contact with the catalyst . After the contact polymerization reaction occurs and it shuts the crack . For this technique suitable healing agent and catalyst combination should be chosen.

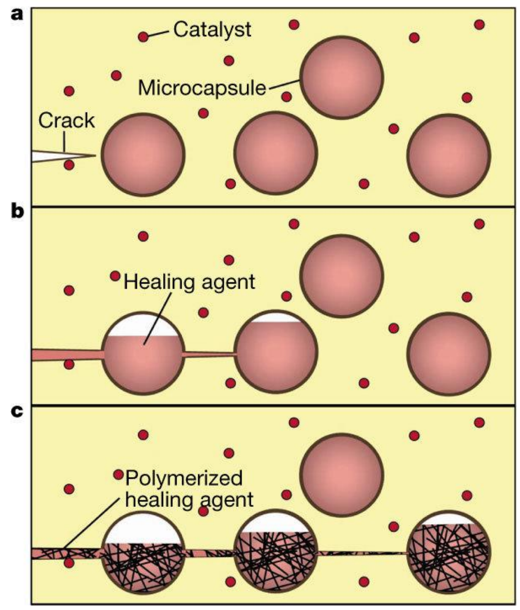

Fig 2 . Diagram showing working of encapsulated healing agent when crack appears.Reproduced from ref [7].

The common techniques which are used for the preparation of the microcapsules with the healing agent are , (a) melt dispersion , (b) preparation is situ, (c) interfacial preparation .

There are some desired material properties which should be considered while choosing the healing agent and catalyst combination .

- Both should be stable compounds over a long period of time .
- Low viscosity for the healing agent so as to facilitate its movement after capsule breakage .
- High wetting for healing agents .
- Should rapidly dissolve the catalyst .
- The polymer formed after the reaction should be highly adhesive .

The major drawback which this method suffers is that it is a single use method and cannot be used in scenarios where regular cracks occur and a periodic healing is required .

3.1.2 Phase separated healing agents

This technique directly incorporates a healing agent into the polymer where it exists in a different phase than of polymer hence the name phase separated healing agent .

After the polymer is damaged it is subjected to heating and the healing agent melts in that region filling the crack and upon cooling the polymer gets healed recovering fully from stiffness .

In this case the healing agent is also required to have a low-melting point, much lower than the melting point of the polymer .

One of the most popular healing agents is Polycaprolactone or PCL , which is a thermoplastic polymer having low melting point . Others are Polyethylene-co-methacrylic acid (EMMA) .

3.1.3 Microvascular Networks

One of the drawbacks of the previous techniques is that they are single use . To repetitively heal a large amount of healing agents is required. This led to the development of this new technique .

This technique is inspired from the capillary networks of the human blood vessels . In this the polymer contains many interconnected channels containing the healing agent . In most scenarios the channel can be linked to an external pump which is refillable and provides supply of the healing agent . As it bears so much similarity with the vascular system , hence it got the name "Microvascular Networks" .

One drawback associated with this approach is the depletion of the catalyst over time .The work is still going on to overcome this by improving the design and layout of the networks .

3.2 Diffusion based healing

This approach uses molecular diffusion of the mobile species to establish an adhesive link between the cracks and thus healing the polymer . An important thing to note is that it generally occurs at an elevated temperature (T) which is more than the glass transition temperature(Tg) of the polymer .

$$\mathbf{D \propto \sqrt{T}}$$

The rate of diffusion is directly proportional to temperature according to graham law .Hence the increased temperature results in an increase in rate of diffusion and thus better healing .

An important point of the difference between the crack filling and diffusion technique is that while in the former the healing agent fills the gap between the crack , in the later diffusion takes from a part of the damaged surface to another . Hence this is used mainly for surface healing .

3.2.1 Thermoset/thermoplastic miscible blend

Developed by **Hayes and a co-worker**[5] ,in this technique a type of polymer known as thermoplastic (**polybisphenol-A-co-epichlorohydrin**) polymer was picked out from a blend which was homogeneous in nature with thermoset including both type that is before and after the curing process .This was disintegrated into a composite which is made up of two component constituting of thermoset epoxy resin and E-glass/epoxy made with help of conventional lay-up methodologies.

On applying tensile force or impact , a quick thermal treatment result in substantial reduction in delamination region and it rises in extension at failure with fracture toughness with taking impact strength also into consideration.On applying temperature of 100 to 140uC in thermal treatment it results in melt permeating and filling in damaged area of the thermoplastic.

With the variation in thermoplastic polymer loadings the amount of healing and healing itself also varied ,its level differed with plastic loading and healing temperature . When we get ideal circumstances it shows around 70 % recovery of virgin characteristics.

3.2.2 Dangling chain diffusion

This technique makes use of the 'dangling chains' which are the segments of the chains whose one end is not attached to the main polymer branch . These chains branch out of the main branch of the polymer and span throughout the surface to repair any damage .

The chains exhibit segmental interdiffusion which is in many ways similar to that of liquids . The mode of healing differs from physical interactions such as interlocking to chemical reactions .

In this case the healing heavily depends on the quantity of the dangling chains and their lengths . Also this method is effective at room temperature .

3.2.3 Viscoelastic healing

This type of healing uses the viscoelastic characteristic of some polymers . This technique was demonstrated by Kalista and co-workers . The energy released during the impact results in temporarily creating a melt and then due to inherent viscoelastic behaviour it physically closes the deformations .

Addition of the ionomeric clusters along with the chain and treating the damaged area with heat results in an increase in capability of the polymer to heal.

3.3 Bond reformation

This technique is used in polymers containing particular bonds that are reversible in response to mild external factors such as light,heat and pH, etc.[5]. These distinctive polymers are often known as *dynamers* or *mendomers*, meaning a group of polymers that can be mended by heating. These mendomers can potentially repair themselves repeatedly in a manner that the original polymer can be restored fully at micro-structure.

3.3.1 Thermally reversible self-healing

A thermally reversible reaction such as Diels–Alder (DA) occurring between a diene and a dienophile, is used to carry out self healing using the heat as an external agent .

The temperature range of approx. 90 °C to 120°C, that takes place in controlled retro-Diels–Alder (rDA) reaction of furan/maleimide derived polymers is too low for thermal degradation to compete with the cycloreversion, but can be used for some formation purposes[5].The DA product that is formed by this addition reaction mainly causes random bond breakage in the diene and dienophile bond. Therefore the fragmented diene and dienophile parts must be again brought together in a solid state Dies Alder reaction so that healing occurs at the molecular level .

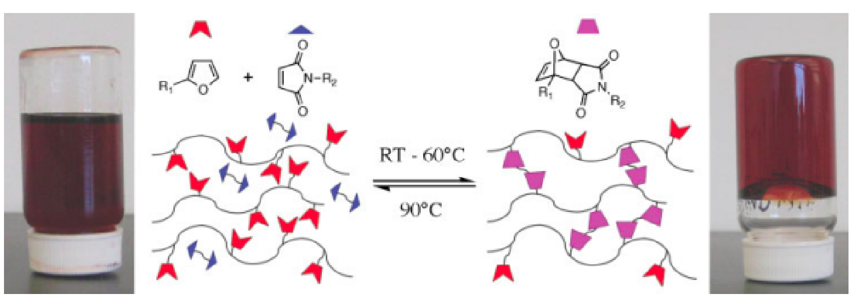

Fig 3 .Thermally reversible self healing . Right vial shows polymer gel and the right vial shows liquid polymer on application of heat . Reaction is shown in the top center . Change in polymer network is shown bottom center . Reproduced from ref [8]

The DA reaction can occur even at room temperature without needing any external reagent,helping in manufacturing in bulk quantities.

On the basis of Diels-Alder chemistry between the multi furan and multi maleimide, Chen, Murphy, Peter, Tian and others developed adaptable polymers for various purposes.

3.3.2 Ultra Violet rays initiated self-healing[5]

The bond can also be reformed by radiations instead of heat with the help of UltraViolet rays commenced self healing.The oxolane–chitosan–polyurethane (OXO–CHI–PUR) chain exhibits this property of self healing when exposed to UV light.

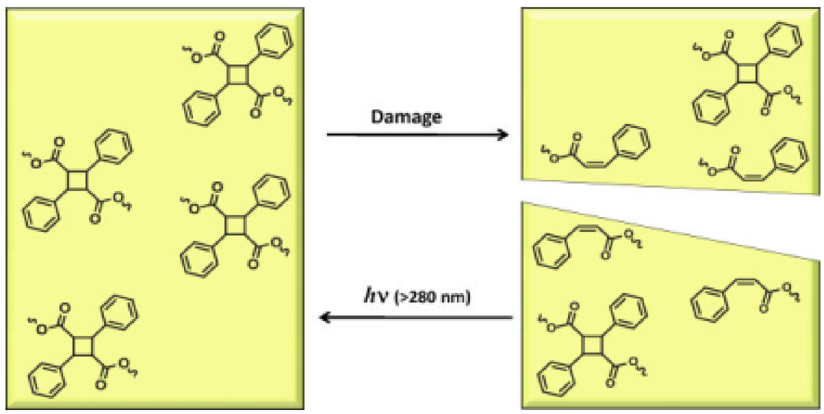

Fig4 . Effect of UV rays on oxolane–chitosan–polyurethane chain .Reproduced from ref. [5] .

The main application of this type of polymer is in aerospace . UV responsive microcapsules are embedded in the polymer. The outer shell consisting of pure $TiO2$ gets degraded due to UV radiation. Due to this degradation, some microcapsules get ruptured and the healing agents are released to get the cracks repaired. [6]

3.3.3 Metal–ligand dissociation/association healing

This technique is useful to reverse mechanical damage under ambient conditions, without any external factor. This type of polymer is formed by dynamic metal-ligand interactions carried out in a soft matrix of a two phase brush polymer system. The metal and ligand (for e.g. zinc and imidazole) are selected in such a way that they have enough affinity to reform rapidly.

3.3.4 Healing via supramolecular assembly

In this type of technique of healing, the polymers are considered which are made up of supramolecular self-assembly. Now, these types of polymer are also known to carry out self healing behavior. As we know that the connection between molecules of polymer is mainly dependent upon non-covalent bonds which give us the assurance of omnipresent molecular structure which is a requirement of possessing a weak link throughout the backbone of a given polymer.

4. Conclusion

This report gives an insight into different types of approaches and methods to construct self-healing polymers at both micro and macro level. The types of approaches used for self-healing discussed here, crack filling, diffusion based and bond reformation can build polymers for typical applications. The polymers developed for self-healing with improved properties make them advantageous to be used for various purposes in industries. Some of the healing techniques discussed can be used to heal the material only once or only for surface healing or needs to possess a certain thermodynamic affinity between the components for self-reformation of the polymer. Other drawbacks include economic challenges for manufacturing of these materials, long term retention of healing properties of the substance, elasticity, and stability in different environmental conditions.

With advancement in technology, the present healing mechanism of the polymers will definitely improve to evolve present techniques into procedures to establish fully efficient, autonomic repair, mechanically improved self-healing polymers, with a significant operating temperature range and mimicking biochemical processes. Self-healing polymers could be potentially a source of sustainable development.

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Contribution

A.B. - contributed in Abstract and Introduction sections .
R.T.- contributed in section 3.1 Crack filling healing .
C. - contributed in subsections 3.2.1 and 3.2.2 of section 3.2 Diffusion based heating .
M.S. - contributed in subsections 3.3.1 and 3.3.2 of section 3.3 Bond Reformation .
K. - contributed in subsections 3.2.3 , 3.3.3 and 3.3.4 .
U.R. -contributed Conclusions,Acknowledgements and figures used in the report .

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