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Self-Healing Capabilities in Polymeric Materials: An Introduction to Techniques

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ABSTRACT

Polymeric materials had shown tremendous increment in its properties due to its acceptability in a wide range of engineering usage. The usage is still restricted due to its reparability and life then after. The life of repaired plastic is less. The present paper study of various type of techniques available, which can develop self-healing capabilities in polymeric materials. The main aim is to further concentrate on an idea which gives maximum improvement in engineering properties, life etc. for structural and engineering usage.

Keywords: *Self-healing, Properties, Repair, Polymeric Materials*

INTRODUCTION

Polymer is a material that serves in a variety of field and is of great importance. It can be a good replacement of metal but is limited due to number of factors. These factors include repeated need of service and maintenance or damage due to prolonged mechanical use. If life of a polymer material can be increased by some procedures, polymer will serve many functions apart from serving as a polymer. When polymer composites are used as structural composites, very few methods are available which can extend their functional life. Functional life of polymer needs to be increased and it can be done so by healing procedures. There are many healing methods but none of them is an ideal healing method. An ideal method will be one which can act quickly and directly on damaged site, thus reducing the frequency of future repairs. The way damage occurs to a composite must also be considered as repair strategies may be different for different components. For ex: For fibre breakage, replacement of fibre will be necessary while for composite fractures, sealing the crack with resin should be done. In a polymer, repair location remains the weakest point in the material and thus a favourable site for future damage to increase.

Repairing Methods for Thermosets

A plenty of methods have been employed in past to repair the composites. Consider the "hot plate welding" in this technique polymer pieces are brought into close proximity of each other at temperature above the glass transition temperature of the material, and this was sustained for enough time until interdiffusion across the crack face occurs and restores strength to the material. It has been shown, however, that the weakest point in the material remains the location where weld took place and also it becomes the favourable site for future damage [1]. For laminate composites, "resin injection" is often used to repair damage in the delamination form. This can cause problems if the crack is not accessible for injection process. "Reinforcing patch" is also used to restore strength of the material in case of fibre breakage of a laminate composite. Reinforcing patch and resin injection are sometimes used together in conjunction to restore the maximum amount of strength possible [2]. The above-mentioned methods are temporary solutions and not ideal ones as they increase the functional cost considerably as it requires constant monitoring and service of the component. Thus, a method which is cost-efficient and starts the healing process on its own, is of great interest. Also, conventional repair methods fail when shape of the component is of great complexity.

Autonomic repair or Self-healing

The concept of self-healing was proposed in the 1980s [3] as a means of healing invisible micro voids / microcracks. Self-healing materials generally are capable of substantially redeveloping its mechanical properties after the damage. Such recovery of mechanical properties can occur autonomously or with the external application of specific stimulus. This method is expected to reduce the need to constantly monitor and service the composites.

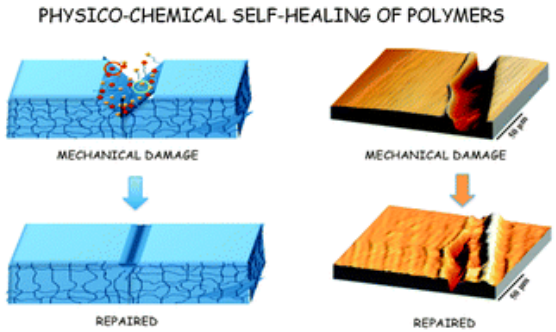

Fig 1: A schematic representing healing by polymers [4]

Techniques

The self-healing capabilities are embedded in the material system during manufacturing of the material. The techniques widely used are namely

Hollow Glass Fibres

The invention of advanced fibre-reinforced polymers (FRPs) to attain improvisation in performance in engineering structures emphasizes on the exploitation of the excellent specific strength and stiffness offered by them. On performing impact loading, poor performance was achieved due to planar nature of FRPs. It indicates their susceptibility to damage which is basically in the form of delamination. These hollow fibres offer elevated rigidity and adjustment of wall thickness and degree of hollowness allows for greater tailoring of performance. Using hollow glass fibres in composites will make it possible to achieve the required structural changes but it will also facilitate a reservoir for the containment of healing polymer. These healing polymers would flow into the damaged location for repairing them on applying mechanical stimuli.

Main challenges faced while creating this healing systems is developing a practical technique for filling repair polymers into the hollow glass fibres. All the parameters of the glass fibres are to be considered while tackling this problem. Problems such as diameter, wall thickness, and hollowness of fibre are to be considered as well. Bleay et al. [4] developed and applied a fibre filling method which involved "vacuum assisted capillary action". The selected glass fibre should also be able to withstand the composite production process without rupturing while still being able to rupture during a damage event so that healing agent can be released.

Hucker et al. [5,6] in 2004, observed that elevated compressive strength was offered by fibres of greater diameters and also giving a large reservoir to store healing agents. The second priority was to check the capacity of healing system to reach the damaged site and do the healing of the damaged site. Viscosity of the healing material and repair process kinetics greatly affected this mechanism along with the third parameter to optimize which was optimizing the density of the healing fibres in the matric, their spatial distribution and final measurements of the sample which directly altered the mechanical characteristics of the composite material. To attain good mechanical properties, adequate spacing of the repair fibres inside the composite was needed.

Though hollow glass fibres were tested and had shown tremendous improvement in properties. In addition, it was also reported that many times healing was multipoint healing, which was remarkable, but were further discarded due to their fragility and handling difficulties.

Microvascular channels

This system was invented by getting inspired from the complex microvascular systems available to us in biological systems. There are various examples such as leaf venation which closely resembles to 3-D microchannel structure systems. Because of their typical architecture, replicating these microvascular systems remains a tough challenge. This system has multiple advantages over encapsulation and hollow fibres systems. This system is capable of healing the same location in the matrix more than once. Numerous healing can be achieved by providing a continuous supply of healing agent to the matrix.

Toohey et al. [7], in 2007 reported that self-healing systems can carry out the healing of same damaged location without any external stimulus. The reported system which bio-inspired coating-substrate design supplied healing matter in matrix with a 3-D microvascular network was first embedded into the substrate. A healing combination of liquid DCPD as the healing agent and solid Grubbs catalyst to start polymerization of DCPD was used. In the test, catalyst was made into a 700 μm thick coating of epoxy which was applied to the top face of microvascular substrate and 200 μm wide channels were filled with healing agent and then sealed. Healing efficiency of 70% was achieved by this system and was able to do repeated healing for up to 7 times. The quantity of catalyst in the top layer did not have any effect on average healing efficiency per cycle but it affected the no. of cycles testing and healing could be done.

Microvascular channels in place of hollow glass fibres had shown multi cycle healing up to 7 cycles with efficiency up to 70% had been reported. The manufacturing had also become easy by improvement in lithographic technique, but the problem of blockage in channels were reported. [8,9]

Microcapsulation / Encapsulation technique

Encapsulation is the technique of preserving a material, in this case healing material, inside of a capsule. It is achieved by preserving the microencapsulated liquid healing agent and solid catalytic chemical inside polymer matrix. Upon causing damage by cracking the matrix, microcapsules release the healing agent into the matrix. All the materials used for this process need to be carefully chosen. The encapsulation process should be able to withstand the reactive healing agent and must not move out of the capsule shell as long as it is unutilised and also wall should be sufficiently resistant to processing conditions of hosts to ensure walls fractures only after composite fracture. It is usually prepared by mini-emulsion polymerization technique. The procedure involves the polymeric material's well-known oil-in-water dispersion mechanism. In most of the studies, the microcapsules are made of a urea-formaldehyde polymer that encapsulates DCPD as healing agent.

The microcapsules produced in this in-situ method have an average size of 10-1000 μm in diameter with a soft internal shell in the 160-200 nm dense range and fill material of up to 83-92 percent fluid healing solution. The mechanical rupture of the microcapsule is the sine non-qua condition necessary for regeneration method. Hence it is clearly essential to manufacture microcapsules with ideal mechanical characteristics and wall thickness.

In 2007, the impact of microcapsule diameter and crack size on the efficiency of self-healing products was also studied by

Rule et al. [10]. They used epoxy-based fabric comprising the catalyst components of Grubb's catalyst particles and microencapsulated DCPD. The liquid volume that microcapsule was capable of carrying to the crack face was shown to be linear with microcapsule diameter for a given weight fraction of microcapsules. The size of microcapsules also plays a role in the system's performance, in terms of composite's toughness and nature of the interaction between microcapsule and polymer matrix. Depending on these relationships, the size and weight fraction of microcapsules can be rationally selected to provide ideal regeneration of a specific fracture size.

However, as observed by Williams et al. [11], the density of the shell wall is mainly autonomous of production parameters and is generally between 160-200 nm. But during the encapsulation procedure, slight adjustment can be made to change the resulting microcapsules. The size of microcapsule is regulated primarily by the agitation rate during the encapsulation phase. Typical rate of agitation reported was 200-2000 rpm [11].

Brown et al. [12] observed in 2004 that maximum toughening of the smaller microcapsules occurs at lower concentrations simultaneously Rule et al. [10] in 2007 observed that samples consisting of large microcapsules shows better performance than those with small microcapsules at the same weight fraction, assumed to be because of quantity of healing agent present in the sample. Later on, it was found that best healing of the composites was achieved in a sample consisting of 10 wt.% of 385 μm capsules which results to 4.5 mg of the healing agent being supplied per unit area of crack. The quantity of healing agent which can be delivered to the crack area was measured on the basis of size of microcapsule size and wt. fraction.

Quantification of improvement

Healing of a polymeric material refers to healing of various mechanical properties which directly or indirectly play a significant role in deciding the functional life of the material. Wool and O'Connor [13] described a method which describes the extent of healing in polymeric systems for a range of properties. This method has been most commonly adopted and also used for comparing "healing efficiency" of different self-healing polymeric systems. One basic standard practice to assess the healing ability of polymers is by comparing the fracture toughness both before healing and after healing the composites. The healing efficiency is η,

$$\eta\ (\%)\ = \frac{K_{IC}^{healed}}{K_{IC}^{Virgin}}\ *100$$

Where k(healed) is the fracture toughness of healed specimen and k(virgin) is the fracture toughness of virgin specimen.

Crack healing efficiency (η) can be defined as the ability of a treated sample to recover fracture toughness [13]

$$\eta\ = \frac{K_{IC}^{healed}}{K_{IC}^{Virgin}}$$

Evaluation of the fatigue crack propagation behaviour was done by following the protocols mentioned by Brown et al. [12] who defined healing in terms of life extension factor.

$$\eta_d\ = \frac{N_{healed} - N_{control}}{N}$$

Where $N_{healed\ is}$ the total number of cycles to failure for a self-healing specimen and $N_{control}$ is the total number of cycles to failure for a similar sample without healing.

As per investigations, successful healing is considered as one in which lost stiffness is restored due to damage induced by cyclic loading rather than changes in crack growth rate or absolute fatigue life.

Limitations

The method of encapsulating healing material has one limitation which is, once if it gets used, healing won't take place from the same capsule as healing material has been exhausted by healing process and it won't be available for next cycle of healing. While there are other feasible options to make healing possible in the next consecutive cycles. Microvascular healing system is capable of healing the material in multiple cycles but it also has a limitation of complex manufacturing process. Repairing is a time-consuming process and immediate healing will not happen. Protecting coating is also at risk of getting damaged during the repairing being done.

Scope

Material degradation occurs at the nanoscale level and then propagating to microscopic level which ultimately affects the strength and durability of the material. And durability remains a topic of great importance for today's structural complexities and to overcome it, it will be preferable to stop and overcome damage at nanoscale level and restoring the mechanical characteristics which is possible by developing material which is capable of doing healing itself at nanoscale level.

Carbon Nanotubes (CNT) are generally preferred as an ideal filler material for reinforcement of mechanical structures and molecular storage device. This is because a greater amount of interfacial area is available due to small size of CNTs. CNTs are of great interest and promising results have been displayed already by CNTs. But CNTs cannot be still used as Nano reservoirs for the self-healing purpose.

Dynamic tests can be conducted to evaluate more mechanical properties to suggest future usage of material. Modelling of materials can be done after knowing all the properties of microcapsules because insertion of molecules into CNTs is a typical procedure.

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