Self Healing Smart Polymers: Insight and Applicability

In Aerospace Industry

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Abstract:

Smart polymers are polymers which have a unique potentiality to undergo change physically or chemically in response to external stimuli's like temperature, pH, ionic concentration, light, magnetic fields, electrical fields, biological molecules and chemicals. The multi-responsive properties of smart polymer find applications in drug delivery, textiles, hydrogels, anticorrosive coatings, optical data storage, aerospace, military etc. Self-healing polymers, a type of smart polymers have an inherent ability to heal themselves like living tissues in body. This unique property leads to enhancement in its utility as composites, aerospace coatings, micro-encapsulations etc. Depending on the way of healing, self healing polymers are diversified in two categories namely intrinsic and extrinsic. Intrinsic ones heal themselves while extrinsic ones demand use of external healing agents. The development of micro-cracks in any material leads to its failure in long term. The use of self healing polymer in composites plays a vital role as it helps in healing of micro-cracks thereby increasing the service life of the composite materials. The use of self healing polymers in composites gives them light weight, good process ability, chemical stability in any atmospheric conditions. The aim of this paper is to review the aspects of selfhealing technologies and future trends in aerospace applications.

KEYWORDS: Smart polymers; Self-healing Polymers (SHP's); Polymer composites; Aerospace

1. INTRODUCTION

Smart polymers have been known to respond to the changes in the environment. This exclusive property shown by smart polymers is utilized in different fields. Different types of smart polymers respond to different environmental stimuli's. The stimuli's are temperature, pH, electric field, magnetic field, light etc. These smart polymers have an increasing demand in various industries namely drug delivery, textile, hydrogel, Coating, Aerospace as well as military(Priya James, John, Alex, & Anoop, 2014).

Among these smart polymers, the most upcoming one is self-healing polymer. They are a new class of smart polymers which have an inherent ability to heal themselves without any need of human intervention. The driving force behind the invention of these SHP's is to produce polymeric materials which would sustain shear for longer period of time and have better service life. To enhance the service life, the failure mechanism of the material needs to be understood. The major reason for the failure is nucleation and propagation of cracks in case of brittle polymers (Sheldon, 1982)and (Gamstedt & Talreja, 1999)

The self-healing phenomenon is quite similar to healing of skin wound. In case of skin wound, fibrin clot which plugs the temporary defects coupled with various biological processes leads to healing of skin. Also broken bone healing takes place by formation of fibrin clot. Internal bleeding develops

fiber mesh whose calcification and conversion to fibrous bone heals the broken bone.

without any external intervention. Some SHP's demand the use of external stimuli's like UVradiation or heat for their healing action. These are termed as extrinsic SHP's while the ones which heal without any external intervention are called as intrinsic SHP's(Yuan, Yin, Rong, & Zhang, 2008).

One of the major applications of SHP's is in the field of aerospace industry. SHP's along with fibres form composites which can be used to making aircraft or a helicopter parts. They can also be used as an anti-corrosive coating when applied as coat on the parts required for aerospace applications. The composite materials made of SHP's are lighter than the metal counterparts. The coatings of SHP's also enhance the service life of air-craft components (Teoh et al., 2010).

The main aim of this review is to broadcast the potentiality of smart polymers and specifically application of self-healing smart polymer in the field of aerospace industry.

2. SMART POLYMERS:

They are classified based on their response to stimulus as stimuli responsive polymers, temperature responsive polymers, pH responsive polymers, bio-responsive polymers and field responsive polymers. The stimuli responsive polymers undergo change in their physical and chemical properties in response to stimulus. Similarly, others also undergo abrupt change in response to stimulus. These are mainly used for drug delivery, textiles, hydrogels, anticorrosive coatings, optical data storage, aerospace, military and many more applications.

Table.1. Various stimuli and responsive materials (Priya James et al., 2014)

The self-healing topic is research driven because there is a need of autonomic repair of materials **3. SELF-HEALING POLYMERS**

(SHP's):

They are novel materials which help in avoiding catastrophic failures through their healing action. These polymers can also be broadly classified in two categories namely intrinsic or autonomic and extrinsic or non-autonomic. The extrinsic or nonautonomic require external healing agents to assist them for healing (Yuan et al., 2008).

3.1. INTRINSIC OR AUTONOMIC SELF-HEALING:

The intrinsic or autonomic self-healing takes place in the presence of some external stimulus which is mainly heating. There are two types of healing mechanisms used for healing.

3.1.1. CHEMICAL HEALING PROCESS:

In general, healing takes place only when the reactants come in contact with each other following which diffusion and cross-linking of polymer chains takes place leading to crack healing. On crosslinking, formation of partial covalent bonds occurs by either supra-molecular forces or truly chemical forces. Permanent or rarely temporary bonds are formed in case of covalent bond driven self-healing while reversible network formation is observed in case of supra-molecular network driven healing. There is also a third category wherein healing takes place via mechano-chemical activation of molecules on subjecting mechanical forces (Binder, Dohler, & Michael, 2013).

Fig.1. Different modes of chemical interactions resulting in crosslinked network formation. (a) Covalent network formation,(b) supra-molecular network formation,(c) "switchable" network formation and (d) mechanochemical network formation (Binder et al., 2013).

3.1.2. PHYSICAL HEALING PROCESS

The physical processes are either based on molecular inter-diffusion, welding, swelling, or nano-particles.

3.1.2.1 MOLECULAR INTER-DIFFUSION:

The main steps involved are surface rearrangement, surface approach, wetting, diffusion and randomization fig.2. In this process as the polymers come in contact with each other (above their glass transition temperature (Tg)), molecular diffusion takes place and the polymer-polymer interface disappears as the crack gets healed. The craze healing only takes place at or below Tg of the polymers while for crack healing to take place the temperature must be equal to or above the Tg of the polymers (O.J. & R.P., 1987) and (R. P. & A.T., 1980) .

3.1.2.2 PHOTO-INDUCED HEALING

The healing system used in this case is a photo crosslinkable monomer along with a photo-initiator. Light of specific wavelength is used depending on the polymer. As soon as the damaged polymer is irradiated with visible light, the crosslinkable monomer crosslinks with the polymer, thus bridging the cracks. The light is able to initiate crosslinking only at the surface, hence healing efficiency for

external cracks is poor.(Wu, Meure, & Solomon, 2008)

Fig.2. Stages of self-healing mechanism. (a) Surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion and (e) randomization (R.P., Connor, & K.M., 1981)

3.1.2.3 RECOMBINATION OF CHAIN ENDS

This method is mainly used to heal molecular damages like chain scission and structural damages like loss of strength.Healing takes place in the presence of a catalyst, however, no crosslinking occurs or use of external energy source. It is applicable only for certain thermoplastics which can recombine their chains by undergoing specific healing reaction(Wu et al., 2008).

3.1.2.4 SELF HEALING BY REVERSIBLE BOND FORMATION

By inclusion of reversible bonds at normal temperatures, the chain mobility of the polymer can be used for self healing of the polymer. The damaged chains are healed by means of hydrogen bond or ionic bonds. In this method organo-siloxane based and ionomer based healing systems are used(Wu et al., 2008)

3.1.2.5 LIVING POLYMER BASED HEALING:

The free radical polymerization involving growth of polymer chains without chain transfer or termination produces living polymers. They have active functional groups capable of initiating

polymerization in presence of monomer. In case of degradation of polymers, the free radicals that are generated can recombine with the macro-radicals present at the end of polymer chains thereby healing the polymer. This type of healing is dependent on the diffusion rate of macro-radicals and Tg. The diffusion rate of the macro-radicals is less in condensed state (below the Tg of the polymer) and slows down the process of self-healing (Wu et al., 2008).

Fig.3.Mechanism of a living polymerization showing active and dormant state transformation of the polymer without chain transfer or termination (Wu et al., 2008).

3.1.2.6 NANO-PARTICLES ASSISTED SELF-HEALING:

In this method nano-particles are used for filling the cracks in the polymers and don't involve breaking or rejoining of polymer chains. The nano-particles move towards the damaged section in the polymer in response to the damage induced depletion attraction and migrate the damaging part. On cooling, a solid nanocomposite layer formation takes place which heals the polymer. Large sized nano-particles transfer the damaged surface in short time. The polymer chains in close proximity to the nano-particles extend or compress in order to avoid interaction with them and favor the aggregation of nanoparticles in the cracks (Wu et al., 2008).

Fig.4.Schematic diagram of movement of nanoparticle during growth of crack in thermoplastics (Wu et al., 2008)

3.1.3 HEALING EFFICIENCY OF INTRINSIC SYSTEMS

Polymers have shown up to 100 percent healing efficiency, with PMMA systems being the most extensively studied. The various healing methods mentioned above are suited for systems of differing healing agents and materials.

The temperature of healing is another important parameter which needs to be considered. The temperature of operation should be comparable with the temperature of the system. Or, it should be possible to induce the necessary temperature during maintenance to provoke the self healing phenomenon

3.2 EXTRINSIC OR NON-AUTONOMOUS SELF-HEALING:

In this case the polymer matrix does not have the ability to heal itself. There is a necessity of employing and embedding external healing agents. Capillary effect helps in healing of crack by release of healing agents in the plane of crack formation. In this type of healing, even the type of container plays an important role. The mode of repairing action varies with different types of container used. This type of healing is applied in pipelines, microcapsulation process and micro-vascular networks(Yuan et al., 2008).

3.2.1. HOLLOW GLASS FIBRES:

The self healing in case of pipelines is achieved when pipelines are filled with polymerizable medium which flows through the affected areas and heals them by elimination of cracks. An important criterion in this case is that the polymerizable medium must be fluid at healing temperature. In hollow glass tubes and fibers, generally epoxy is used along with hardener as a two-pack system. The epoxy resin is applied directly to the hollow fiber tube while hardeners are incorporated in microcapsules. The efficiency of healing depends on the parameters of the hollow pipes and thickness of the composite as well as energy of impact.

Fig.5. Schematic diagram of repair concept for polymer matrix composites using pre-embedded hollow tubes (Yuan et al., 2008)

3.2.2. MICRO-ENCAPSULATION:

In this process there is dispersion of solid-catalyst particles along with microcapsules which have healing agent within them in the polymer matrix. As the cracks are formed they propagate into the bulk of the matrix where they interact with the microcapsules filled with healing agent. The interaction leads to rupture of the microcapsules which releases healing agent in the gaps thereby leading to contact between healing agent and the catalyst supporting cross-linking polymerization which helps in binding the surface of the cracks (R.P. et al., 1981).

Fig.6. Microencapsulation Design (R.P. et al., 1981)

Table.3. Literature summary of chemicals used for self healing investigated for the microencapsulation approach (Brown et al., 2005)

3.2.3 MICRO-VASCULAR NETWORKS:

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It is similar to microencapsulation process but here the matrix, catalyst and healing agent are made of same material. The difference is that the crosslinking no longer takes place in spheres instead it takes place in three dimensional networks of microchannels. The matrix here is made of brittle epoxy which leads to areas of lower stress concentration making crack propagation towards more compliant regions located at the interface of matrix and microchannels. The healing mechanism remains same (Jinglei, Keller, Moore, White, & Sottos, 2008)

Fig.7. Micro-vascular network and Crack propagation (Jinglei et al., 2008)

a) The shell material of the catalyst microcapsules is put between square brackets;

b) Healing efficiency obtained using manual injection of healing agents is put between brackets; healing efficiencies higher than 100% indicate a healed network that fails at a higher load value than the original matrix network; multiple healing cycle values are not added to allow comparison between the different delivery systems; c) Meltable particles are added to the matrix

4 POTENTIAL APPLICATTIONS

Applications of self-healing materials are expected to cover almost entirely all industries in future. The very few applications that have been developed to date are mainly in the building industries, automotive, and aerospace. One such example is of Nissan Motor Co. Ltd who have commercialized world's first self-healing clear coat for surfaces of car and the trade name of this product is ''Scratch Guard Coat''. The self healing coat is hydrophobic and it repaired scratches on the coated car surfaces and was effective for a period of three years. While Bayer Material Science developed two component polyurethane clear coats. That coating healed scratches under the influence of sunlight or heat and these coatings were based on the use dense polymer networks having flexible linkages(Ghosh, 2009). Self healing materials are also used in a wide range of paints, coatings and adhesives. Self-healing coatings can prove useful for metallic components like steel so as to improve their service life and to reduce maintenance costs.

Self-healing polymers can also used for medicinal applications. Self-healing polymers that are biocompatible can help to achieve long-term service life of artificial teeth, artificial bones, pacemakers, hip and knee replacements, dental materials, and other medical devices. Recently developed selfhealing rubber can be used efficiently in the toy industry. It can also find application in manufacturing of sporting goods. Large numbers of consumers are willing to pay high price for highquality boats and surfboards, fishing equipment, skis, helmets and other protective gear, tennis rackets, and many other such sports related equipment. This technology could improve the quality of all these products. It can be successfully used in electrical applications as well. Polymer composite electronic components and circuit boards can suffer from electrical and mechanical failures if progress of micro cracking is not stopped. This selfhealing technology could help to counter such failures.

Another industrial segment where uses of selfhealing materials are foreseen is in the aviation industry. Application of composites in aircrafts has developed significantly in recent years. Composites reinforced with hollow fibers are a possible way to recover cracking or damages. Even in space applications, self-healing polymers have found great applications.

5. AIRCRAFT APPLICATIONS:

5.1. FRACTURE GROWTH RETARDATION OF POLYMER COMPOSITES:

There are various factors responsible for crack formation like thermal, environmental and chemical. Apart from these factors, the major factors are cyclic and impact fatigues. The crack propagation is the first step to failure. Cracks usually propagate when the energy required for generation of new surfaces in the material is lesser than the energy released during crack. In order to stop the crack from propagating, the energy released must be dissipated in the loaded material(Wu et al., 2008).

5.1.1 INTRINSIC CRACK PROPAGATION RETARDATION

The growth of cracks can be retarded in an intrinsic way by using monomer and curing system in varying proportion which help in relieving the stresses in the material thereby enhancing the intrinsic property of the new material. This way of crack retardation has very little role in healing of damaged materials (Wu et al., 2008).

5.1.2. EXTRINSIC CRACK PROPAGATION RETARDATION

In this method the energy is dissipated of away from the tip of the propagating crack through mechanical change behind the tip of the crack. Additives serve the purpose of extrinsic toughening agent when they are elongated or compressed in the hole or gap which is behind the tip of the crack (Wu et al., 2008)

5.2. CONVENTIONAL METHODS FOR HEALING OF CRACKS IN POLYMER COMPOSITES:

\The commonly used techniques for crack healings are patching, welding and in-situ curing of the resins (Wu et al., 2008).

5.2.1. PATCHING:

In this method the material which gets damaged is replaced by a new material. The patch is attached by either using adhesives or by mechanical fastening. The patch can be attached by direct attachment to the damaged part, removal of damaged part followed by attachment of new part or by removal of damaged part and the addition of new part followed by addition of patches. The regaining of property is highly dependent on the compatibility between the patch and the material, thickness of the patch and the interface between the patch and the material.

5.2.2. WELDING:

In this process the damaged surfaces fuse or rejoin by means of chain entanglements between the polymer chains. The process of rejoining takes place by surface rearrangement, surface approach, wetting and diffusion. The process may get hampered owing to inaccurate welding temperature, solvents and poor chemical bonding between the surfaces of the polymer. It can be used for thermoplastic as well as thermoset polymers.

5.2.3. IN-SITU CURING:

In this process the damage is recovered by crosslinking with a new resin. It is similar to the patching process. In these processes a non cured resin can be added along with adhesive as a patch

which then gets cured with the polymer material thereby repairing the damage.

5.3. NEED FOR SELF HEALING:

The concept of self-healing can be broadly applied in the field of aerospace technology. Fibre reinforced plastic composites are widely used in the aircraft industries. These composites are unable to maintain the structural integrity of the parts under high loading. This leads to formation of microcracks in the components which go unnoticed. These cracks propagate and result in fracture. The use of self-healing polymers either in the form of composite or coating will help in healing of microcracks which lead to failure of the material in long run. Also since polymer composites are lighter than conventional ones, the use of self-healing polymer will not only heal the cracks but will also make the composite less heavy. One of the major applications in the aircraft industry is in making of helicopter blades.

5.4. HEALING SYSTEMS:

The extrinsic self healing systems are more widely used where the healing agent fills the cracks. The intrinsic ones are not much in use. They basically heal on the principle of Diels-Alder reaction.The composite materials have self healing polymers reenforced with either Hollow glass fibre (HGF), Carbon fibre (CFRP) or Glass fibres (GFRP). The composites are most often made of thermosetting polymers. These self-healing composites are light in weight, have high strength and show good degree of stiffness. All these properties make them highly efficient and sustainable in the field of transport and especially in the field of aircraft applications (Tan et al., 2008).The conventionally used materials in aerospace industry can be depicted in Fig 8.

Fig.8. Materials conventionally used in aircrafts ("Mechanical Engineering Blog," n.d.).

5.5. TESTING OF COMPOSITES FOR DETERMINING THEIR PROPERTIES

Healing of a polymeric material can be referred to the recovery of various properties such as surface smoothness, tensile strength, and fracture toughness. Various tests were carried out to determine optimum combination of host material and healing system to be used for aerospace application. Substrates were subjected to different healing conditions so as to study their healing efficiency. Table 5 provides brief information of some developments achieved. It can be observed that both thermosetting and thermoplastic materials were studied for self healing and the research was found to be more focused on thermosettingcomposite-based systems in recent years (Aïssa, Therriault, Haddad, & Jamroz, 2012).

Table.5. External healing composite systems (Aïssa et al., 2012).

S.H.Teoh et.al (2010) (Teoh et al., 2010) have reported the studies carried out to determine the optimum flexural strength of the self healing composite that can be used on parts like aircraft's composite structures. The double layer unidirectional hollow glass capillary tubes of external diameter of $1.5 - 1.6$ mm were used and the self healing capability of the epoxy composite was determined based on flexural strength using three point bend test (ASTM D790) at various healing regimes. It was observed that mechanical strength was restored by the self healing agent within the hollow glass capillary tubes. When the doubled layer healed hollow glass fibre laminate was subjected to a healing regime of 3 weeks, an increase in the healed strength of 27% was seen as compared to damaged baseline laminate.

 Similar work was reported by Willy. C.K.Tan et.al (2008) (Tan et al., 2008) using single layer of unidirectional thicker hollow glass fibre. It was observed from the flexural 3 point bend test that there was 47.6% increase in the healed strength of the healed hollow fibre laminate as compared to the damaged baseline laminate. From the above results it can be concluded that flexural strength of a single layered unidirectional thicker hollow glass fibre is greater than the flexural strength of the double layer unidirectional hollow glass capillary tubes. In both the cases, mechanical strength is restored by the self healing composite. This restored mechanical strength of the self healing composite proves that it has potential to be used on actual composite parts such as aircraft's composite structures

 Self-healing polymers are applied in airplanes as an autonomous process. The non-autonomous process would fail to be fruitful in aircraft materials because it will be difficult to get access to ultraviolet light during flight. It is necessary for the healing to be spontaneous. Fiber-reinforced polymer (FRP) composites can be used in various areas such as the tailfin, wings, nose or fuselage of the plane. The hollow capsules break open thereby leading to leaking out of the resin and hardener. The composite is healed by this process. Most of these particles after getting healed once have about 90% of their original strength

5.6. BENEFITS OVER CONVENTIONAL METHODS:

There are various benefits of using self-healing polymers in aircrafts. It is possible to fix small damages. Self-healing materials can also be of help to mechanics who can remove parts based on their life cycles and not according to a schedule. No mechanical testing will be required. Despite the parts being more expensive initially, knowing when to replace them will help to save money in the long run and thereby be cost effective.

This technology will make aircrafts safer when compared to other materials.

6. CONCLUSION

 The field of healable materials has reached exciting cross-roads. There is now an international effort towards a common end goal of autonomic reversibly healable materials, and the research being done covers many new avenues to afford such intelligent materials. From repairable aircraft composites to damage-resistant coatings and healable automobile brake pads, the potential applications for these materials are limited solely by the imagination of scientists and engineers.

 It is our hope that this review serves as a comprehensive summary of the work accomplished thus far in the area of stimuli-responsive self healable materials, as well as an exploration of the latest research to be published and a glimpse into possible future directions for this research to take. It is sure that this wonderful field of self-healing materials will continue to grow beyond the technologies reviewed.

7. FUTURE TRENDS:

This is a path breaking technology which yet needs to be commercialized at a cheaper cost. It can then be implemented in cell phones, armored military vehicles, and automotive applications and will become available for our daily uses.

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