A review on Diels-Alder based self-healing polymer composites

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Abstract. Self-healing polymers are the materials which can heal the internal cracks or damages automatically without any external intervention. The concept of self-healing has been derived from the biological systems such as human bone or skin which can heal automatically. This paper reviews the self-healing polymers based on Diels-Alder reaction where diene and dienophile groups form reversible covalent bond between them in the polymer matrix. A comprehensive review on Diels-Alder based self-healing composites reinforced with nano-fillers from the last decade have been reported here. The present status followed by future scope in this area has also been discussed briefly at the end of this review.

1. Introduction
With the advancement of technologies in the recent scenario, development of advanced materials has arrived with promises of fulfilling our desire to achieve enhanced properties of materials in the aspects of quality, reliability and service lifetime. One of the most desirable requirements in the polymeric materials is mostly the recyclability or repeated use of it. Self-healing materials are polymers, metals, ceramics and their composites that when damaged by an operational use has the ability to fully or partially recover its original set of properties. The healing ability of a self-healing material provides it a longer and reliable working lifetime. There is a huge demand for self healable materials in the applications where repairing is too much challengeable. In 1996, Zhou [1] advised that the self-healing ability of living organs can be taken as reference in the design and processing of polymer composite materials.

There are mainly two critical events occurring during self-repairing of polymers: (1) physical flow of molecular segments at or near a wounded area and (2) re-bonding of cleaved bonds after mechanical damage [2]. These events may occur continuously depending upon the interplay between kinetics and thermodynamics. The healing mechanisms are mainly two types: intrinsic and extrinsic healing.

The first concept is based on the use of a healing agent in the failure zone that has the capacity to react with the matrix or to fill the crack with the material resulting from its polymerization. The first route deals with the embedding of microcapsules or hollow fibers into the polymer matrix which are previously filled with a liquid healing agent, i.e. a monomer [3–7]. When a micro-crack grows and crosses the hollow structures, the liquid healing agent is released and fills the crack. The released healing agent gets in touch with still unreacted functional groups available in the matrix and heals the crack. The limit of these healing agents is their single time healing capacity of micro-cracks healing at the same location. For this reason, Toohey [8] and Williams [9] proposed another new healing route based on a micro-vascular network similar to human blood circulatory system, which is filled with a
low viscosity healing agent. As micro-cracks are generated in the matrix, those cross through the vascular network and as a consequence, the healing agent will be delivered continuously into cracks through capillary driving force. For most of the proposed healing routes based on the polymerization of an encapsulated liquid healing agent with polymer matrix, the interaction of them with a catalyst well dispersed in the polymer matrix is required. Even though, this system can heal micro-cracks several times at the same location, the healing efficiency will depend on the consumption of catalyst within the matrix. More recently, another concept of self-healing polymer has been proposed which is based on the introduction of reversible bonds into polymer matrix architecture: (i) supramolecular bonds such as (multi-)hydrogen bonds [10,11] or host-guest structures as metal ligands [12,13] and (ii) thermo-reversible Diels–Alder (DA) bonds [14-16]. Thanks to the thermal reversible character of DA bonds, the micro-cracks can be healed as many times as required from a thermal heating and cooling cycle which allows to reform DA bonds. In this review self-healing ability of polymers and polymer composites based on the DA reaction are discussed in brief starting from the theoretical concept followed by the different literature reported in this area. Finally, some future scopes have been discussed in the field of DA based self-healing polymer composites.

2. Theoretical concept of crack healing in polymer

Wool and K O’ Connor [1] (Department of Metallurgy and Mining Engineering, University of Illinois) illustrated a theory of crack healing in polymeric materials in terms of five stages of crack healing: (1) surface rearrangement (2) surface approach, (3) wetting, (4) diffusion, and (5) randomization [2-9]. They provided a microscopic theory for healing in polymers in which mechanical properties, e.g. stress, strain, modulus and impact energy were related to time, temperature, pressure, molecular weight and constitution of the material. They developed an experimental approach to establish the relations amongst the given parameters. This experimental approach can be simply understood by the given Figure (1). [1]

![Figure 1. Evaluation of healing efficiency through experimental approach.](adapted from Ref. 1)

Healing theory developed by Wool and K O’ Connor found a wide range of applications regarding the design of self healable polymer. It also helped in finding the thermodynamic of self-healing, which suggests that the concept of self-healing is to enable a material to repair damage with minimum intervention. Based on this theory of healing, a wide range of approaches and techniques are developed to enable the self-healing properties in the polymers and their composites. Generally two approaches (a) extrinsic self-healing and (b) intrinsic self-healing are widely discussed topic in the field of self healable material. The healing performance of any materials is assessed through some experimental procedures as shown in Figure 1 [1]. Some cracks or damage is incorporated in the
virgin sample and then cracks are healed using some stimuli such as mechanical, thermal, electrical etc. and then the set of properties of healed samples are compared with that of virgin one to calculate the healing efficiency.

3. Extrinsic self-healing approaches

This is also termed as ‘Autonomous Healing’ system. In this approach, healing agents are captured or encapsulated in hollow fibers [17,18], microspheres [19,20] and other containers [21]. During the operational phase, crack or break induced in the polymer causes the release of healing agents to perform the healing operation. Theory of crack healing [1] as discussed in previous section play a major role in this type of healing. This type of healing approach follows the five stages of healing as discussed earlier. Extrinsic self-healing approach is again divided into two groups: capsule based and vascular based. The healing agents are encapsulated through the micro-encapsulation or vascular network as shown in Figure 2 [22]. Whenever, a crack damages these containers, healing agents are released in the crack path; polymerization occurs and finally heals the crack. The major disadvantage of capsule based healing is its single time healing capability. On the other hand, embedding vascular network containing healing agent in the polymer matrix is a key challenge for the researcher in perspective of their fabrication.

4. Intrinsic self-healing approaches

Intrinsic self-healing also termed as stimuli-responsive self-healing involves some external stimuli (Thermal, photochemical, electrical and moisture activation) to trigger the healing process, which is most accomplished by a bond-breaking and bond-rebuilding process as shown in Figure 3 [23]. Various reaction mechanisms are utilized to enable the intrinsic healing in polymers. Some examples are irradiation-induced cycloaddition [24], metathesis reactions [25], photothermal ring-opening reactions [26], photothermal metal–ligand complexation [27], and redox-triggered host–guest complexation and decomplexation reactions [28,29]. Reversible covalent bonding based on DA reaction for intrinsic healing is further discussed in the subsequent sections.

Figure 2. (a) capsule based and (b) vascular based self-healing mechanism. [adapted from ref. 22].

Figure 3. Schematic representation of intrinsic self-sealing by external stimuli; thermal, photochemical, electrical and moisture activation. [adapted from ref. 23]
Reversible covalent bond possesses high bonding strength than supramolecular bonds which makes it a good candidate for developing self-healing materials. Factors which possess the significant role in the designing of self-healing materials are the dissociation and association rates of reversible bond as well as the chain mobility. Self repairing covalent bonds are categorized in four group: (1) reversible cyclo-addition reactions, (2) exchange reactions, (3) stable free radical mediated reshuffling reactions, and (4) heterocyclic compounds/carbohydrates facilitated bond deformations. Covalent self repairing bonds require high activation energy, which is a major drawback with this type of healing reactions. For example in Diels-Alder (DA) reaction, activation temperature required for healing is 120°C [30]. High temperature exposure may not be desirable for polymers because of the glass transition temperature of polymer can be within 100°C.

5. Diels-Alder [4+2] cycloaddition reaction

Diels-Alder reaction is named after the scientists Otto Paul Hermann Diels and Kurt Alder. They firstly described it in 1928, for which work they were awarded Nobel Prize in Chemistry in 1950 [31]. It is a [4+2] cycloaddition organic reaction between a conjugated Diene and a substituted Alkene also termed as Dienophile to form a substituted Cyclohexene as shown in Figure 4.

![Figure 4](image-url)

**Figure 4.** Reaction mechanism of Diels-Alder reaction and an example based on this reaction using furan as Diene group and maleimide as Dienophile group.
Figure 5. Intrinsic self-healing mechanism. (a) three approaches of intrinsic self-healing (1) Reversible bonding based on Diels-Alder–retro-Diels-Alder reaction (2) chain entanglement (2) Non covalent bonding. Stage of intrinsic healing is composed of (1) development of self-healing polymer, (2) characterization, (3) triggering (4) evaluation of healing efficiency [adapted from ref. 22].

Diels-Alder reaction is governed by orbital symmetry consideration; so it is also termed as a \([4\pi S+2\pi S]\) cyclo-addition which shows that the reaction proceeds through the superficial interaction (an interaction which is thermally allowed as a \(4n+2\) cycloaddition) of a \(4\pi\) electron system (Diene structure) with a \(2\pi\) electron system (Dienophile structure). The "Click" characteristics of DA reaction make it easy for polymer design and synthesis. DA reaction is thermally reversible in nature i.e. DA adduct could undergo a reverse reaction when the temperature reached at a level favourable for Retro DA (reverse DA reaction). In Retro DA reaction, DA adducts break into the Diene and Dienophile group involved in the DA reaction.

The first self-healing polymer based on the thermo reversible DA reaction was reported by Chen and co-workers [30]. Their system was based on the cyclo-addition of a multi-furan monomer containing four furan groups (4F) and a multi-maleimide monomer consisting of three maleimide functionalities (3M) as shown in Figure 4. The resulting covalent cross-linked network (3M4F) displayed reversibility upon heating to 150°C for 15 min, leading to a cleavage of about 25% of the DA adduct (retro-DA). Upon cooling to 80°C and subsequent curing at this temperature, the broken bonds were allowed to fully reconnect. By virtue of this special behaviour, self-healing experiments were performed by cutting the sample into two pieces. After damage, the two cut surfaces were brought closely into contact, heated to 150°C to allow the retro-DA reaction and, finally, cooled to room temperature. The average healing efficiency was found to be about 50% of the original fracture energy. A year later the same authors improved their work by the utilization of low-melting point monomers, which feature a higher mobility in the resulting cross-linked network [32]. Thereby, the self-healing efficiency could be increased to about 80%. The intrinsic self-healing approach has been schematically shown in Figure 5 [22].

6. Present and future scopes

Introduction of self-healing ability in polymeric composites has been growing significantly and in the recent years, a lot of work is done in this field. In polymeric composite materials, generally fillers such as rigid nanoparticles, nanotubes or fillers do not contribute in self repairing process. Self healable matrix phase can only show self repairing ability in the composites. Generally, fracture occurs either in matrix phase or at the interface of matrix and nano fillers. To enhance the reliability and service lifetime of the polymeric composites, researchers have started to enable the self-healing ability at the interface of nano composites. To create a strong interface, surface modification of nanoparticles has developed in the field of nanocomposites. These modified surfaces generate amine [33], carboxylic acid [34], hydroxyl [35], furfuryl [36] groups which can react with the matrix phase to form interfacial region. One can develop self repairing ability at the interfacial region using suitable combination of functional group present at modified surface of nano fillers and reactive group of matrix phase. A dynamic bonding through DA based reaction at the interface can be utilized for introducing the self-healing ability. Figure 6 illustrates self repairing ability that can be developed at the interface of nano composites. Table 1 shows the different DA reaction approach reported by scientists for self-healing at the interface of nanofiller and matrix phase containing Diene and Dienophile group attached or mixed with it.
Figure 6. Dynamic interfacial self-healing in nanocomposites: dissociation of interfacial bonding under shear forces and reforming cleaved interactions [adapted from ref. 37]

Pratama et al. [43] demonstrated room temperature self-healing of thermosetting resin based on Diels-Alder reaction. Three different maleimide based thermosets were encapsulated in urea-formaldehyde shell and Furfuryl glycidyl ether were mixed in the epoxy resin and a self-healing DA adducts was synthesized in the matrix phase. About 95% healing efficiency were found due to incorporation of 0.3 wt.% microcapsules. The major disadvantage of this work was single step healing as the healing agent contained in the capsules was consumed after first cycle of healing. Turkenburg et al. [44] demonstrated multiple times healing of epoxy matrix by introducing furfuryl and maleimide functional groups in the matrix phase. They have successfully achieved five times healing cycle in the epoxy matrix. In another report, Park et al. [45] investigated self-healing property of polymer composites modified with bis-maleimide tetrafluor (2MEP4F). Curing of DA adduct was done by using electrical resistive heating. About 90% and 86% healing efficiency of the composites were found after 1st and 2nd time healing respectively. Thus, from the above discussion, it can be expected that DA based self-healing polymer composites stimulated with electricity, light and magnetic field will be the smart and advanced polymeric materials in future.

In summary, theoretical concepts of crack healing and interaction with nature may help to develop an effective and efficient way for enabling self-healing property in materials. In the field of remotely triggered self-healing polymers, a wide research scope is available. Elimination of toxic agents used for incorporation of healing ability and developing environmental friendly self-healing materials should be the ultimate goal in this field. Also commercial self-healing materials are unexplored till now which encourage the scientific community to do lot of research in future to make it commercialized.

Table 1. Interface healing based on Diels-Alder reaction

| Nano-filler          | Surface Reactive Groups | Matrix Reactive Groups | Surface Matrix DA Reaction | Ref.  |
|----------------------|-------------------------|------------------------|---------------------------|-------|
| Nano-silica Cage     | ![nano-silica cage](image) | ![matrix reactive groups](image) | ![surface matrix DA reaction](image) | [38]  |
| Glass Fiber          | ![glass fiber](image)    | ![matrix reactive groups](image) | ![surface matrix DA reaction](image) | [39]  |
| Carbon Fiber         | ![carbon fiber](image)   | ![matrix reactive groups](image) | ![surface matrix DA reaction](image) | [40]  |
| Silica Nanoparticle  | ![silica nanoparticle](image) | ![matrix reactive groups](image) | ![surface matrix DA reaction](image) | [41]  |
7. Conclusion

Investigation on self-healing polymeric materials is exciting and interesting field for the scientists because of the increasing demand of smart materials. This review is mainly focused on the concept of self-healing and application of Diels-Alder reaction mechanism for self-healing in polymeric materials. Extrinsic self-healing (capsule-based and vascular network based self-healing) and intrinsic self-healing (reversible Diels-Alder based self-healing) are the main two types of self-healing approaches. Capsule based self-healing concept has the limitation in regards to the single time self-healing and vascular network has the limitation in regards to complexity in synthesis, design and reinforcement in the polymer matrix. But, Diels-Alder based self-healing can overcome such limitations. Though, several numbers of publications have been reported on multiple times self-healing capability of Diels-Alder based self-healing polymers, but the major disadvantages are poor mechanical and thermal performance. The objective of this review was to represent the Diels-Alder based crack healing concept and to show a journey of development in this field, so that a systematic development pattern in this field can be introduced to the readers.

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