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Intrinsic Self Healing Polymer Mechanism in Covalent System – A Review

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ABSTRACT: The tiny cracking or breaking of a material normally remains insignificant until it attains the macroscopic level, where the substance breaks and needs to be repaired. This is made possible by the use of self-healing polymers which have the functional characteristics of curing when a crack penetrates the material. Here in this article, we are looking at a reversible system which can revert back to its original state having the same physical properties even after crack healing. They are also referred to as externally mendable polymers because the reverting process would normally require an external stimulus for it to occur. This can be possible in the form of thermal-, photo-, or chemical-induced healing. At first such reversible interaction was made possible by utilizing covalent chemistry.

KEYWORDS : Intrinsic Self healing , Covalent Bonds, Diels -alder system

I. INTRODUCTION

Methodologies for reusing and recycling have been in practice for quite some time but the most recent of study and research have focused on materials capable of healing the cracks and damages dealt with them. Development of such materials having special grade performance has been of utmost importance owing to their ability to heal damages resulting from both physiochemical and environmental changes. Self-healing not only increases the durability and product life of a material but some materials are able to retain almost all of their strength after healing. Kennedy and Castner were the 1st to identify the thermal reversibility of Polymer materials by cyclopentadienylation and their work were the basis of other works in the future [1]. These self-healing polymers help tackle challenges those traditional materials cannot achieve like the ability to react to internal and external stimuli such as temperature, PH, mechanical stress, biological environment etc. Among many of the self-healing methods one of the most effective ways is the use of covalent bonds due to their remarkable strength and structural application giving the matrix considerable strength. Chemical routes utilizing dynamic covalent bonds like DA, disulphide bond etc. Self-healing materials can be categorized into following sections: capsule based, vascular, and intrinsic. Capsular self-healing is triggered by rupture of capsule and the healing agent along with a catalyst is discharged into the scratched area through capillary action, one of the most significant embedded microcapsule network systems was published by White et al. Who reported autonomous self-healing via the ring opening metathesis polymerization of encapsulated dicyclopentadiene which was released into an epoxy-based network loaded with a Grubbs catalyst[1]. Keller et al. Have made polydimethylsiloxane (PDMS)-based self-healing elastomers integrating two kinds of microcapsules such as resin pellet and an initiator pellet [2].

Vascular self-healing utilizes interconnected hollow channels or capillaries either 1D, 2D, 3D carries the healing agent to the cracked area. It can be refilled from a damaged area or externally which allows for multiple healing events. Bond and coworkers have managed to revise the manufacturing of hollow glass fibers and utilized fibers as the capsules for liquid healing agents [3]. The diameter of borosilicate glass fibers is ranging from 30 to 100 µm and described to have gap around 55%. These hollow fiber-based self-healing composites containing hollow fibers, can restore healing agents which in turn could heal around 97% of its basic flexural strength. In intrinsic self-healing an external stimulus triggers the healing of the material which possesses latent functionality. Intrinsic methods which need no integration of healing agents into the polymer which target out the difficulties related to the pre embedding process is more looked into nowadays. Wudl and coworkers reported a network containing self-healing characteristics under heat action through a Diels–Alder/retro Diels–Alder process [4]. Even though numerous effective healing systems triggered by various stimuli such as light, pH-value, redox agents or other heat triggered approaches have been reported, Diels–Alder (DA) healing system has become one of the most studied systems in its field. Other than the





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aforementioned approaches other scheme like – dispersion of superparamagnetic or nanomaterials that respond to electric/ magnetic field and self-repair without the addition of any discrete physical or chemical healing agents driven by interchain van der Waals interaction which forms interlocking key and lock junctions [5] in narrow composition range. With anticipation, the readers of this review are left with a rudimentary idea of the fundamentals of self-healing polymers.

II. COVALENTLY BOUND SYSTEMS

2.1 Diels alder-based polymers

The Diels alder cycloaddition reaction is one of the important and widely used reactions in organic chemistry as it converts a diene and a dienophile into a wide variety of six membered ring. The name of the reaction was coined after the two scientists Otto Paul Hermann Diels and Kurt's alder [6]. Their work was initially introduced in 1928 and thereafter in 1950 their work was awarded with Nobel prize.

2.1.1 Furan maleimide based polymers

Furan maleimide polymers are one of the typical examples of DA reversible reactions and many researches were held since mid-20th century. Craven in 1969 was probably the first one to report his incorporation of furan -maleimide in polymers for attaining thermal reversibility [7]. Presumably the first research report of preparing DA/rDA mechanism for preparing self-healing or thermally remendable polymers was by Chen et al in 2002[8]. In the research tris maleimide (3M) and tetra furan (4F) were reacted to develop a highly crosslinked transparent organic polymer 3M4F with its ability to remend under mild condition. Preceding to this in 2003, a couple of another remendable highly crosslinked polymers 2ME4F and 2MEP4F was prepared without any solvent [4]. Liu and Hsieh in 2005 synthesized similar crosslinked polymers which exhibited high performance of thermal remendability and removability using Scanning electron microscope and other tests. Their main application was in the field of structural materials [9]. Further it was in 2007 Plaisted and Nemat-Nasser studied the recurring rupture healing properties of 2MEP4F evaluated quantitatively [10].

Copolymerization of furyl-telechelic poly (ethylene adipate) [PEA2F] and bis- and tris-maleimides by Dielsalder reaction [11]. In 2014, Rivero et al prepared furan based thermoset polyurethane in a one pot fashion [12]. Guogao Zhang and his coworkers in 2016 synthesized shape memory polymers containing furan maleimide DA moieties [13]. Self-healing ability wasn't discussed in the paper, influence of crystallization in DA reaction as well as mechanical properties were discoursed [14]. Recently in 2020 Wang et al synthesized a string of self-mending polymeric materials in reference with the reversibility of DA reaction [15]. Chen in 2020 synthesized polyureaurethane/epoxy blend coatings with furan groups terminated thermoplastic polyurea-urethanes (FTPU) which we know are capable of self-healing along with dynamic disulfide bonds combined with epoxy oligomers having hanging groups [16].



Fig 1 - Schematic depiction of the Diels-Alder based memory assisted self-healing process in a PU material based on PCL and furan-maleimide chemistry

Reprinted with permission from G. Rivero, L. T. T. Nguyen, X. K. D. Hillewaere, and F. E. Du Prez, "One-pot thermo-remendable shape memory polyurethanes," Macromolecules, vol. 47, no. 6, pp. 2010–2018, Copyright 2014 American Chemical Society.





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2.1.2 Anthracene based polymers

The number of literatures published on Anthracene based self-healing is very few. It was M. Grigoras and co-workers who in 1979 reported the synthesis of anthracene-methacrylic acid addition products, followed by their DA-polymerization, induced by thermal or by a Lewis acid (TiCl4) [17]. Anthracene substituted acrylates and methacrylate can be considered as a multi(bi)functional monomer, since they have a diene (anthryl) group and a dienophile (acrylic or methacrylic) group. This multifunctional property is described by simionescu.et al in 1985 giving high molecular weight polymers [18]. The resultant polymers have high softening points and good thermal oxidative stabilities, thereby useful in high temperature applications [17]. The synthesis and characterization process of some Diels–Alder copolymers, starting from an anthracene-based bis-diene and four bismaleimide monomers, in homogeneous solution, was presented by Grigoras and Colotin which showed that they can be copolymerized with bismaleimide derivatives by Diels–Alder cycloaddition reactions [19]. Syrett et.al used Diels–Alder mechanism to form polymerization initiators and a dimethacrylic crosslinker that leads to efficient cleavage and reformation, they developed two polymerization initiators and one cross-linker one of which showed that some anthracene derivatives can be used to modify PU films so as to endow self-healing up on them [21]. The reversibility of the particular reaction, thermal accuracy and self-healing ability of PU anthracene (puan) films were giving satisfactory self-healing ability and reinforced thermal stability.

2.2 Thiol Based Polymers

A tetrafunctional thiol group introduced into an epoxy resin containing disulphide group induces cross linking and the extend of self-healing depends on the concentration of the disulphide group present in the material this is because an exchange reaction between this disulphide and tetrafunctional group is accountable for self-healing characteristics. The healed material has similar elastic property as the original material [22]. It is also known that a disulfide linkage can be broken down into two thiol groups by reduction. This system can be utilized to create a wide variety of polymers which can be reversibly cross linked, where cleaving of the disulfide bridges happens under reducing conditions, and reforming of the bridges happens under oxidizing conditions [17].

Chujo et al. In 1993 were the 1st to intentionally use thiol group for reversible cross linking. They designed a redox-reversible hydrogel system based on thiol-modified poly (N acetyl ethyleneimine) and using the reversible interchange between disulfide (SS) groups and thiols (SH) [23]. Tobolsky and his coworkers showed that the introduction of disulfide and tetra sulphide bonds into the material increased the stress relaxation considerably. Tesoro et al. Used the recyclable functionality in a thermoset epoxy resin owing to the fact that a disulphide link can be broken by a reduction resulting in the formation two thiol groups and can be re-formed by an oxidation reaction [24]. Disulphide chemistry can also be used to give out a self-healing capacity in covalently bonded rubber. Pepels and coworkers conducted experiments whether the disulphide conversation proceeds through a radical mechanism or a thiol–disulphide exchange mechanism and concluded that the dominant mechanism is not the disulphide– disulphide exchange reaction, but the thiol–disulphide exchange reaction. However, the reaction is highly pH dependent [25]. The epoxy resin was anionically photopolymerized by the action of a thiol-ene system that included the prepared thiol-disulfide oligomer and the curing agent [26]. One of the most recent works in the field by Xiang et al. Reported a unique dynamic covalent click reaction between a substituted methide group (pqm) and thiol nucleophile in which the final adducts could perform dynamic exchange reaction with thiol nucleophile. They applied it to prepare cross linked Polyurethane and the resultant dynamic covalent bond showed healable property at room temperature [27].

2.3 NO based polymers

Theoretically reformation of bonds can be used effectively for healing of cracks and as a result, organic radicals have been looked at as a possible agent for mending of polymers for quite some time. N-O bond just like thiol-based system can be easily reformed and has great influence over healing of materials and they offer the significant properties of a supramolecular polymeric system, but depend on covalent bonds, as opposed to the much weaker non-covalent bonds used in the supramolecular systems [17]. Healing system using radical exchange of alkoxyamine units has been verified by Higaki et al. In 2004. It was found that the cross-linked points thermally dissociate and that the reaction system is reversible under stoichiometric control [28], [29].

2.4 Photodimerization based polymer

The photo-induced self-healing mechanism is usually seen in photosensitive molecules or functional groups such as coumarin, anthracene, trithiocarbonate units etc. Before they are introduced to a polymer chain these groups are grafted on synthetic or natural macromolecules or (co-)monomers. Chang and Aklonis analyzed the outcome of aging on the





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creep behavior of cross-linked polymer networks [30]. Coursan et al reported the Preparation of polystyrene with controlled molar mass and narrow dispersity end capped with an anthryl methyl ether group [31]. Dimerization of the polystyrene chain was observed under the irradiation of 36 nm UV light. Further when exposed at lower wavelength, the original $\dot{\omega}$ -anthryl polystyrene chains were restored.

Polyisobutylene (PIB)-based networks acquire excellent elasticity, strong adherence to substrate, good damping and barrier properties, thermal stability, and excellent chemical and solvent resistance [32]. They are found to be essentially useful for photovoltaic devices. Reversible photodimerization of coumarin moieties occurs as the resultant of UV irradiation which in turn resulted in crosslinked elastomeric films which manifested self-healing. Regardless of being a little slow, the healing of any damages was assessed to take place even under sunlight. Another noticeable work is that of Hughes, Simon and Saito in 2019, when they synthesized several photo responsive polymer networks by using two anthracene-based diamine moieties [33]. Anthracene dimer, is positioned at the center of a diamine structure, which can be used as a crosslinker for epoxy monomers. Epoxy increases the mechanical strength and crosslink density of the resulting polymer.

Photo-tunable self-healing behavior has its promising advantages in smart functional coating of photovoltaic device and designing flexographic imaging plate materials. Within the scope of this application, Joseph et al exhibited a design for a sequence of non-polar polymers incorporated with photodimerizable coumarin fractions that endure intra/inter chain reaction

with UV radiation. The native polymers showed intrinsic and autonomic healing behavior at ambient temperature [34]. Following the similar mechanism Zhao et al synthesized a biosource self-healing coating. A novel photo-healable material was prepared using photoinitiated thiol epoxy mechanism [35]. To develop self-healing materials for physical application, Photo remendable polymer networks were constructed by Ling et al using isophorone diisocyanate, polyethylene glycol and photo-reversible fraction 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin [36]. Yet another work based on coumarin which has been used as an intrinsic self-healing material due to its ability to undergo $[2\pi+2\pi]$ photocycloaddition. Wong et al embedded coumarin derivatives into bio-based polyurethanes [37]. The photocycloaddition reaction of coumarin upon UV radiation is capable of promoting it as self-healing agent and thereby enhancing its mechanical strength. Potential applications of this polymer include production of solar wafer.

2.5 Hindered urea bonds

Polymers which contain dynamic covalent bond exhibit many dynamic properties which include self-healing, malleability and shape memory. Overcoming this particular drawback, Ying et al developed the plan of dynamic hindered urea bonds (hubs) (which are bulky groups attached to Nitrogen of urea) [38]. It has a wide range of applications such as design and synthesis of polyurea and poly(urethane-ureas), coating materials, fiber, adhesive etc. In polymer industries, which are capable of catalyst-free dynamic property change and independent repairing at low temperature. Young et al reported the synthesis of a sequence of polyacrylate urethane urea networks containing hindered urea groups [39]. The main purpose of the synthesis was to be used as an application in automotive clearcoats. As the contents in the HU adducts were changed, the properties of clear coats were also shifted. Further in 2017, Park et al prepared remendable polymers (ptb-HDI and ptb-IPDI) containing hindered urea bonds by free-radical copolymerization followed by crosslinking with diisocyanates [40].

2.6 Acylhydrazone based

Among all the interactions we have discussed until now, acylhydrazone based self-healing linkages have gained enormous attention due to the fact that it can repair hydrogels without stimulations [41]. Acylhydrazone bond is a dynamic covalent bond as mentioned and they are synthesized by the condensation reaction of an aldehyde group and a non-basic organic compound called hydrazide. Guo et al did a noticeable work where they synthesized ketone-based polymers based on commercially available diacetone acrylamide (DAAM) by a reversible addition–fragmentation chain transfer (RAFT) polymerization technique [42]. The polymers could react with hexane dihydrazide yielding hydrogels. The hydrogels possess self-healing ability and undergo reversible sol–gel transition by the alternation of the pH, due to the ketone-based DCB properties. Sun et al reported the research of thermo-responsive hydrogels based on dynamic acylhydrazone formation which were found to be self-healable and PH-sensitive [43]. Qiao et al demonstrated the preparation of a self-healing alginate hydrogel, based on dynamic acylhydrazone and multiple hydrogen bonds, through a rapid one-step reaction of PEG dibenzaldehyde and adipic dihydrazide-modified alginate [44].





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III. CONCLUSION

Significant developments of intrinsic self-healing polymers and materials have been reviewed in this paper. This realm of smart materials has a bright future in the upcoming millennium. Chen and Wudl had a very important role in bringing the self-healing technology to the research world [4], [8]. Although Diels Alders approach is still considered a milestone in the field of intrinsic mechanism, many other reversible networks like hydrogen bonded, photodimerization, biologically inspired etc. have also played an important part in setting up a high bar. The main disadvantage of intrinsic self-healing is that there is always the need for manual intervention. Shape memory assisted self-healing is now being reported, yet there's a rapid need of much more development to this. In addition, the monomers are expensive to use for large scale applications. This review also encourages the researchers to compare the pros and cons among different mechanisms of self-healing polymers like capsular, vascular and intrinsic. The future of the intrinsic self-healing polymers depends on the development of automated mechanisms along with shape memory assistance, where there will be discovery of advanced chemicals and novel material.

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