# Self-healing by Diels-Alder cycloaddition in advanced functional polymers: A review

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## Abstract

The ability of artificial materials to be healed efficiently, mimicking the living organisms, exhibits a great deal of potential advantages that can revolutionise the operation and maintenance of materials used in various applications. Such self-healable smart materials have been extensively researched in the last few decades, leading to the development of different physical and chemical synthesis approaches. Among these methods, chemical techniques based on reversible cycloadditions or disulfide bonding provide obvious advantages in terms of repeatability, which holds prime importance in determining the commerciality of the healing approach. This review compiles the recent advances in the field of self-healing polymers where the healing ability is introduced by reversible cycloaddition reactions while focusing mainly on Diels-Alder (DA) reactions. DA is a [4+2] cycloaddition reaction where diene and dienophile pairs are used to fabricate thermally reversible crosslinked networks. These covalent bonds provide the necessary reversibility to the healing matrix and impart the desired strength to the polymeric material. There is a considerable body of recent literature where DA bonding has been employed either on its own or along with other healing mechanisms to impart self-healing to polymers. However, lack of a systematic review discussing these works makes it difficult for a beginner to cope with advancements in this field. Most early studies have focused on the healing stimuli and efficiency of healing in polymers but with this review, we would like to explore the healing thermodynamics governing the rupture–repair process in DA polymers along with the use of advanced spectroscopic techniques to study them and their applicability in thermosets, epoxy resins, biopolymers, and polymer nanocomposites. Novel applications for such advanced functional polymers, multifunctional healable polymers, and the outlook for future research, opportunities and challenges in the area are also discussed.

**Keywords:** Self-healing polymers, Diels-Alder cycloaddition, Intrinsic healing, Functional polymers, click chemistry

## 1. Introduction

Polymeric materials and their composites have been vastly used for different applications owing to their combination of favourable properties, including low cost, high chemical resistance, tunable thermal and electrical insulation, as well as light-weight. Although these materials possess attractive mechanical properties, including appropriate fatigue resistance and fracture toughness, microcracks and other structural defects can still be formed under the influence of external factors involved in their operation.[1] In the case of polymer-based composites, the formation of microcracks in the polymeric matrix deteriorates the behaviour of both the reinforcing fillers and the matrix, which directly impacts the structure's service life and jeopardizes the safety of equipment and people.[2, 3]

To overcome this, a family of polymers with self-healing characteristics and ameliorated mechanical properties have been developed. These self-healing polymeric materials can heal the microcracks and other damages, enhancing the durability and extended life span of the materials, essential or beneficial for a large variety of applications. The self-healing properties of smart polymeric materials are based on the ability of those materials to perceive and repair damages, mimicking the autonomous self-healing ability of living organisms.[4] An ideal self-healing polymer should be capable of completely healing defects of any size multiple times without the need for external stimuli. On the other hand, the properties of the polymeric material after the self-healing process should be the same or preferably better than those of the material before the healing process.[5] The influence of the self-healing property on the service life of polymeric materials is highlighted in Fig. 1. Broadly, adding a reinforcing material to the material matrix improves the properties and increases the service life to a certain extent. However, an ideal self-healing material means the material has an infinite service life and can be used without the user being concerned about mechanical damage. Healable materials that have been produced to date with covalent bonds possess higher mechanical strength but provide almost similar service life as healable materials with labile bonds.

Most of the existing self-healing polymers are able to repair themselves only in the presence of external stimuli like heat,[6, 7] mechanical force,[8, 9] light,[10, 11] electricity,[12] electromagnetic waves,[13] catalysts,[14, 15] pH stimulus,[16] oxidation-reduction[17] and/or moisture[18, 19]. Nevertheless, the literature also exists on some polymeric systems in which the self-healing process occurs autonomously[20-22].

Generally speaking, self-healing polymeric materials can be divided into intrinsic or extrinsic types based on the mechanism involved in the damage-repair process.[23] Intrinsic self-healing polymers can regain their properties immanently. In these polymers, the healing process is triggered by external stimuli, leading to a series of physical or chemical interactions at the molecular level.[24] There have been numerous studies to investigate the dynamic bonding mechanisms involved in these polymers, such as Diels-Alder bonding,[25] Michael addition[26, 27], acylhydrazone coupling[28, 29], diselenide bonding[30-33], Schiff base[34-36], hindered urea bonding[37, 38], metal-ligand coordination[39-42], cyclodextrins host-guest interactions[43, 44] and oxime bonding[45].  In contrast, the extrinsic type of the self-healing process is based on the healing chemistry that is actively embedded in the polymer matrix in the form of microcapsules[46-48] or vascular networks[49]. The latter can be sequestrated into the crack planes created by the damage, thereby restoring the material's original properties.

Polymers that can be healed extrinsically usually provide a higher level of convenience since there is no need for any external stimulus for healing. However, these polymers often lack a repeatable and consistent healing performance, which intrinsic polymers can readily provide.[50] It should be mentioned that, ideally, a reversible process that involves the formation of strong covalent bonding is required to ensure a repeatable healing process in self-healing polymeric composites. Hence, to this end, cycloaddition reactions are considered an attractive choice for building the required stimuli-responsive smart polymers.[51] Despite their intriguing characteristics, there lacks a systematic review on self-healing polymers based on cycloaddition reactions that discuss the recent trends and advances in the field. The current review article outlines the applicability of cycloaddition reactions for instilling the self-healing mechanism to the polymers, while focusing mainly on the thermally reversible Diels–Alder (DA) reaction, as explained in the next section.

## 2. [4+2] Cycloaddition for self-healing

Diels-Alder (DA) reaction is the most well-known cycloaddition mechanism, which involves a concerted pericyclic reaction to introduce reversible covalent bonding into polymers. The DA reaction is a [4+2] cycloaddition reaction between conjugated diene (electron-rich) and a substituted alkene or alkyne (electron-poor), which form a cyclohexene adduct. Alkenes or alkynes with electron-withdrawing groups (EWG) are highly suitable to disseminate this characteristic due to their ability to make existing unsaturated groups further electron-poor. DA reaction is an addition reaction and not a condensation process, i.e., all the components of the products are already present in the reactants, making it an autonomous self-contained dynamic system. DA reaction is thermally reversible, as shown in Fig. 2, for which temperature can be used to control the extent of reaction. Therefore, this mechanism is highly suitable for polymers as it does not require extreme temperatures.[52]

Various combinations of diene and dienophile have been well documented in the literature.[53] However, for any compound to work as a diene and participate in DA reaction, it should be an s-cis conformer (double bonds are cis about the single bond). S-cis conformers possess less thermodynamic stability as the smaller distance between their substituents causes steric repulsive strain in the system. Though s-trans conformers possess higher stability, substituent bonds are way too far to undergo a coordinated reaction with a dienophile.[54] Hence, compounds like furan, anthracene and cyclopentadiene, which possess s-cis in their structure, are considered very reactive as a diene, and suitable to participate in DA reaction. On the other hand, maleimide is widely used as a dienophile, and its reactivity towards the diene can be increased by introducing a partial positive charge on the $sp^2$ carbon. This is possible if the dienophile has at least one EWG-like carbonyl group (C=O) or cyano group (C≡N), which can withdraw electrons from C=C. [55]

### 2.1. Thermodynamics of self-healing in DA polymers

When a reversible polymeric network is damaged, two local processes occur at the rupture site, namely chain cleavage and chain slippage.[50] Although the chain cleavage is considered structural damage, it forms several functional groups on the surface. These functional groups can contribute to the subsequent interactions taking place in the polymer material. On the other hand, chain slippage can lead to conformational changes. The phenomena of chain slippage, chain cleavage and healing process are described graphically in Fig. 3. A polymeric system can autonomously undergo self-healing if Gibb's free energy $\Delta G \; (= \; \Delta H - T\Delta S) < \; 0$. DA reaction may be viewed entirely as a chemical bonding process for self-healing; however, physical aspects of chain flexibility and mobility also hold significant importance. Entropy changes positively from the initial state (virgin sample) to the final state (damaged sample) mainly due to the larger number of possible chain arrangements available at the newly created interfaces. Theoretically, due to positive entropy change and the higher density gradient of the chains at the interface, chain ends try to fill the void, especially when the distance between the interfaces is favourable. However, entropy changes are minimal in large polymeric chains due to limited mobility within the matrix boundaries.[23] Therefore, the flexibility of chains or glass transition temperature ($T_g$) can be considered indispensable factors for understanding the healing thermodynamics in polymers. Urban's research group suggested that the flexibility of chains will directly influence several possible chain rearrangement configurations. Therefore, Flory's flexibility parameter can be used to describe the localised entropy changes at the site of damage.[23, 56]

A self-healing polymeric lattice with $n$ polymeric chains was considered for this work by Urban and group. It was further assumed that each chain follows the self-avoiding walk model and possesses $N$ segments or repeating units. Therefore, each chain contains $(N-1)$ bonds and $(N-2)$ bond angles. To determine the influence of chain flexibility on the value of $\Delta G$, chains were assumed to be semi-flexible, and $f$ was defined as the probability of two successive bonds which were not collinear and prone to possible rotation. This implied that out of total bonds present in the lattice, $fn(N-2)$ is the number of bent bonds. Therefore, under $\partial \Delta G/\partial G=0$ condition, $f$ could be written as follows:

$$f = \frac{(z-2)e^{-\varepsilon/k_BT}}{1+(z-2)e^{-\varepsilon/k_BT}} \qquad (1)$$

where $z$ is the coordination number of the lattice unit, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\varepsilon$ is the energy difference between collinear and bent bonds. Under the assumption of no energy changes happening due to the intermolecular interactions, $\Delta G$ can be given by the equation (2).

$$\Delta G = -T\Delta S = -nRT\{ln\, N + ln(z/2e) + (N - 2)ln[1/(1-f\,)e]\} \qquad (2)$$

This method mentioned above can determine the energy change of chains where both ends are dangling. However, for chains in which one end is anchored to another chain, possessing only one free end, we will have $ln\, N = 0$. In this situation, the Gibbs free energy for tethered chains can be given as the equation (3).

$$\Delta G = -T\Delta S = -nRT\{ln(z/2e) + (N - 2)ln[1/(1-f\,)e]\} \qquad (3)$$

Considering that the threshold value of $f = K$, it leads to $\Delta G = 0$. Similarly, when $f > K$, again $\Delta G = 0$, which means the chain mobility is a spontaneous process, and healing can take place. However, when $f < K$, chains become too rigid for healing, and external energy inputs are required to overcome the thermodynamic barrier. Fig. 4 shows changes in Gibbs free energy as the function of flexibility parameter and chain length. In this graph, the plane representing $\Delta G = 0$ shows the equilibrium state of the polymer. Therefore, the healing process above this plane can occur spontaneously. On the other hand, repairs below this plane need an energy input, usually an external stimulus. The solid red curve depicts the changes in ΔG with increasing repeating units of the polymer.[23]

Since ΔH° and ΔS° for a typical Diels–Alder reaction are negative, the previously formed covalent bonds can break upon exposure of the adduct to sufficiently high temperatures, leading to the reverse reaction known as retro-DA reaction. When the adduct is cooled to lower temperatures, cycloaddition occurs again, and covalent bonds are recreated. The occurrence of a DA reaction leads to the breakage of three π-bonds, and the formation of two new sigma bonds and a π-bond, resulting in a new six-membered ring as shown in Fig. 2. DA reaction mechanism can synthesize polymers with various structural arrangements like linear, branched, and crosslinked variants. Compliance with the energy requirements of DA reaction and providing enough energy to cross the thermodynamic barrier for flexibility can be fulfilled simultaneously in the presence of an additional value of energy. This makes the DA mechanism one of the most suited contenders for self-healing polymers for which $T_g$ lies in the same range of the adduct's DA temperature.[57] The design and synthesis of various polymeric systems using the DA mechanism is a facile route due to the "click" chemistry concept employed by the reaction.[58] Thermal reversibility introduced by DA reaction has been efficiently utilised to create building blocks for thermally reversible polymeric systems.[59] This has also developed novel routes to synthesise polymeric gels with thermally reversible capabilities.[59-62] Fabricating novel degradable hydrogels[63] and thermosensitive hydrogels[64-66] based on the DA reaction opened the door for further exploration on their use in tissue engineering and drug delivery. Apart from polymer gels, sustained bonding/debonding capability of DA polymers instils the stimulus responsiveness to various materials like organic/organic hybrids[67-71], organic/inorganic hybrids[72, 73], core cross-linked and thermo-responsive micelles[74-76], multifunctional coatings [77-79], materials for data storage[80], optical polymers[72], lithography[80, 81], energy storage[82-84], contact printing[79, 85] and nano-porous films[86]. This review focuses on DA reaction as a simple and scalable tool to introduce self-healing in polymers for various applications while also suggesting some unexplored areas where these can be applied.

### 2.2. Self-healing DA Polymers based on furan-maleimide groups

As mentioned earlier, different chemicals can form DA adducts, within which the most prominent category is the Furan-Maleimide systems. The reaction between furan derivatives as diene and maleimide derivatives as dienophiles is presented in Fig. 5. The main advantage of DA reactions based on the Furan-maleimide pair is their ability to occur in a highly reversible manner under mild conditions, without any side reactions or need for catalysts. They are clean, efficient and simple in occurrence.[87]

It should be noticed that maleimide possesses two electron-withdrawing C=O groups, which makes the C=C bond from the main dienophile ring electron-insufficient, increasing the reactivity of the dienophile towards the diene. Therefore, in most early works involving Furan-maleimide based DA reactions for thermally reversible polymers, diene or dienophile was attached to the polymer chains.[61, 88, 89] This made molecular chains longer and thereby resulted in subpar chain mobility, making it highly unsuitable for applications in the field of self-healing polymers.

Wudl et al.[6] reported a self-healing polymer based on a thermally reversible DA reaction. In this work, a covalently crosslinked network (3M4F) was prepared using multifuran groups with four furan functional groups (4F) and multimaleimide monomer with three maleimide functional groups (3M). Upon heating to 150°C for 15 min, this

DA adduct displayed a debonding extent of 30%. The subsequent cooling to 80°C led to a DA reaction, and the polymer was completely cured. The adduct showed an average mending efficiency of 50% at 150°C in terms of fracture energy. The tensile strength, compressive strength, flexural strength, and compression modulus of the 3M4F polymer were superior to epoxy resins. To further enhance the self-healing properties of such polymers, alternative monomeric units with a lower melting point were introduced, which induced higher mobility in the matrix.[90] This excellent work by Chen et al. attracted further research in remendable polymers by DA reaction. Plaisted and Nemat-Nasser have qualitatively studied the polymer systems used by Chen and the team where they found that increasing the healing time over 1 hr did not affect the healing properties of the material.[91] As shown in Fig. 6, the crack completely disappears after 4 min when the sample is heated at 85 °C. Theoretically, it is supported by calculations based on the heat capacity and average thermal conductivity of polyamides, which suggests that the sample's centre should reach 85 °C within 3 min of heating. This conclusively shows that the time required for quick healing of the polymer is dictated by the chemical kinetics of the DA reaction and not by diffusion-controlled processes. Moreover, the repaired polymer was reported to have higher fracture resistance than the virgin polymer.[91]

Following this work, many self-healing polymeric systems with Furan-maleimide based DA bonding have been developed. One of the recent works features an interesting combination of Polyurethane (PU) and Polyhedral oligomeric silsesquioxanes (POSS) to introduce hydrophilicity and thermal stability to PU.[92] Furan functionalised PU was prepared using a novel chain extender by directly reacting furfurylamine with furfuryl glycidyl ether (FGE). This furan functionalised PU was grafted with Maleimide functionalised POSS by DA cycloaddition and resulted in a ultra-hydrophobic composite with a remarkable increase in its water contact angle from 84° to 141.3°. This was attributed to the cycloaddition between PU and highly hydrophobic POSS units along with increased micro- and nano- roughness. Samples with PU-POSS in a ratio of 1:36 exhibited healing efficiency >80%.

Feng et al. used ring-opening polymerization (ROP) catalysed by silicon alkoxide for FGE and carbonyl sulfide to produce a thermo-reversible triblock copolymer.[93] This furfuryl poly(thioether)-b-polysiloxane-b-furfuryl poly(thioether) copolymer not only possesses a high dielectric constant, for which it was designed but also shows tunable mechanical properties, self-healing ability and excellent shape-memory effect. This work shows a novel approach to designing self-healable advanced dielectric elastomers for actuated devices using DA chemistry.

### 2.2.1.Self-healing epoxy resins based on furan-maleimide DA reaction

Epoxy resin is one of the most well-known groups of thermosets and is widely used in several applications; for example, adhesives[94], sealants[95], paints[96], coatings and construction materials[97]. Epoxy resin is also commonly used in the electronics industry due to its excellent corrosion resistance, high resistance to heat and electricity, adhesion to many engineering materials, and desirable mechanical properties.[98] Despite these advantages, however, the disposal or recyclability of epoxy resins is challenging due to obvious environmental and economic considerations. Therefore, extending the service life of epoxy-based polymers by repeatable self-healing can tickle one of the most serious global environmental problems by reducing plastic waste.

Another environmental concern regarding polymer fabrication and processing is the involvement of various organic solvents and heating regimes. Liquid polymer precursors can offer several advantages, including the possibility of processing polymers in a solvent-free environment. It can also provide the option of using low-boiling point solvents, including propanone and methanol.[99] This permits easier removal of solvents without the involvement of high-temperature treatments, thereby preventing retro-DA reaction. The occurrence of retro-DA reaction can cause disconnection among the bonds during the solvent removal process.[88] With this in mind, Liu and Hsieh formulated furan and maleimide monomers with multiple functionalities using epoxy precursors that remain liquid at room temperature.[99] Epoxy-based compounds possess desired properties like thermal and electrical insulation and resistance towards chemicals and solvents. Fig. 7(i) shows the SEM images of the sample, demonstrating that a surface fissure can be entirely healed at 50 ºC in 24 h. This sample was intended to be used as the substrate for semiconductor silicon, where removability of the silicon part is essential for upgrading, salvaging, or reworking the components. Therefore, the ability to remove the sample from silicon wafers was tested. It was observed that the polymeric material could be removed entirely from the surface of the semiconductor material by dissolving the polymer in NMP for 1 h at 90 °C as shown in Fig. 7(ii). It is noteworthy that this sample could heal at low temperatures due to the low $T_g$ of the monomer precursors. Removability would be ideal for polymers intended for such use, however, its mechanical properties and application at higher temperature ranges could be compromised mainly due to the low Tg precursors used.

Table 1 summarises the repair performance of self-healing epoxy resins that have been fabricated utilising furan-maleimide bonding based on DA chemistry. Their properties and performance characteristics are compared based on the synthesis method, self-healing pathway, specific application, and the properties of various epoxy resins.

Furthermore, Zhang et. al proved that it is possible to synthesise thermally healable polymers using furan-functionalized alternating thermosetting polyketones and bis-maleimides, leading to a healing efficiency of almost 100%.[112] These polymers set forth some interesting properties of linear thermoplastics such as reprocessability, remeltability, and recyclability without changing their dynamic mechanical properties. This "thermoplastic" like behaviour of thermosetting polyketones is possible due to the reversible cycloaddition of the furan and maleimide functional groups on precursor chains. It is basically the bond breakage and reconnection phenomenon illusioned as remeltability. This system was also studied by altering the number of furan groups and varying the maleimide to furan molar ratios.[113] A polymeric network based on $PEAF_2M_3$ with furfuryl-telechelic poly(ethylene adipate) ($PEAF_2$) and tris-maleimide ($M_3$) was produced by Yoshie et al. [114] The rDA reaction was initiated at 145°C within 20 min. The healing efficiency of the system was recorded at 68% based on tensile strength when DA reaction was allowed to occur at 60°C for one week. Du et al.[115] reported using the reversible DA mechanism to prepare a healable linear polyurethane (PU) bearing two furan groups using 4,4-diphenylmethane diisocyanate (MDI), poly(1,4-butylene adipate glycol), DPBM and furfuryl amine. A cut was introduced on the PU film using a surgical blade, and it was heated at 120 °C. The cut was not visible after 300 s of curing. Recovery tests yielded a healing efficiency of 80% for the first cycle, and it went down by 14% for the next cycle. This work was further extended by the same group where a multi-furan monomer was prepared. This modified system could undergo self-healing at 130 °C in 300 s with a 12.4% increase in the healing efficiency as compared to the sample with two furan groups.[116]

### 2.2.2. Alternative stimuli sources

Apart from the direct heat, which is often used as a stimulus for healing, other sources can also be utilised as the energy source to stimulate the healing process, along with additional elements, such as carbon materials, enabling the utilization of those alternative sources. Furthermore, the alternative stimuli sources based on indirect heating might provide advantages such as preventing the material degradation caused by the direct heat or devising a more convenient pathway for self-healing the material depending on the specific application of the polymeric compound.

As the first example, an organic-inorganic self-healing composite material was fabricated by Park et al.[117], based on crosslinked 4F–2MEP resin and carbon fibres. The self-healing reaction was stimulated by an electric current, which generated resistive heating in the carbon fibres filler. A healing efficiency of 90% has been achieved by applying the electrical current for 3 h. Furthermore, in an interesting work by Yu et al.[118], a unique interpenetrating polymer network (IPN) was developed by a double-crosslinked hydrogel using a combination of DA reaction and acylhydrazone bond. The reversible acylhydrazone bond introduced in the DA network was a pH-responsive covalent bond and thus imparted the self-healing feature. It was observed that the single-crosslinked network (SN) sample and double-crosslinked network (DN) samples when cut into half, were able to self-heal in 3 h at ambient temperature without any external intervention. Although the healing efficiency was not reported in this work, the SN gel was mentioned to sustain its own weight. Also, the DN gel was able to bear a pulling force on the sample. The pH value was kept under 4 using HCl to demonstrate the pH responsiveness, which triggered a sol-gel transformation upon addition of TEA as shown in Fig. 8.

Towards developing advanced materials for flexible electronics, Wu et al.[119] fabricated a composite material based on PU and functionalised graphene nanosheets (FGNS). The product offered a healing efficiency of more than 96 % in terms of Young's modulus, break strength and break elongation when healed using an infrared (IR) laser. The healing mechanism is highlighted in Fig. 9, showing a photothermal-based healing process taking place in the matrix where FGNS absorb the IR radiation and release it in the form of heat. Further, Li et al.[120] utilised GO sheets' excellent microwave absorption properties of GO sheets to create a self-healing PU-based composite. The composite material produced could be healed completely under microwave irradiation in 5 min. In this case, GO sheets imparted the mechanical strength, thermal stability, and microwave healing capabilities to the sample. The PU composite was reported to show an excellent dispersion of GO inside the polymer matrix, most likely owing to the chemical bonding between the GO and polymer matrix rather than mechanical interspersion.

One of the novel mechanisms to achieve thermal triggering is magnetic hysteresis heating. It occurs when a ferromagnetic material is placed within an alternating magnetic field. Utilising this specific heating mechanism, Adzima et al.[121] developed a self-healing polymer using pentaerythritol propoxylate tris(3-(furfurylthiol)propionate) (PPTF) and 1,1′-(methylene-di-4,1-phenylene) bismaleimide (DPBM) monomers. The polymer could fully heal when exposed to a coil of strength 14.2 mT for 300 s. Hysteresis heating provides an added advantage over conventional heating due to its self-limiting nature. Once the curie temperature of a ferromagnetic particle is reached, heating would be stopped, preventing irreversible thermal degradation during the repetitive healing process.[122] Ultrasonic waves have been used to develop complex self-healing materials such as concrete[123], but it has yet not been explored for polymers using DA chemistry to the best of our knowledge. This can be further explored by using covalently bonded thermoacoustic fillers or incorporating a combination of pressure-sensitive bonds in the polymeric matrix along with DA bonds.

### 2.2.3.Self-healing biopolymers based on furan-maleimide DA reaction

Several environmental and economic challenges accompany the manufacturing process of polymeric materials from petroleum products. Consequently, a significant deal of research has focused on producing chemicals and polymeric materials from biomass, thereby taking advantage of the rich chemistry and abundance of large natural molecules available in nature. For instance, Zeng et al. [124] produced a self-healing polymeric material by the condensation polymerization approach using two bio-based monomers, namely Bis(hydroxymethyl)furan (BMF) and Poly(2,5-furandimethylene succinate) (PFS). The self-healing efficiency of the polymer without any external stimuli at room temperature was reported to be 75%. The healing performance was enhanced using a bismaleimide crosslinking solution, leading to efficiency of over 90%. Such high healing efficiency at ambient conditions had not been reported prior to this. It could be attributed to the high level of functional groups on the surface of the bio-derived materials. It was also found that a higher furan/maleimide ratio resulted in higher efficiency when self-healed or healed by solvent-assistance processes. This seems to be because the samples with low furan/maleimide ratios undergo very high crosslinking during polymerization, which hinders chain mobility. The reported sample also showed good mechanical properties. It was suggested that the healing efficiency could further improve by increasing the reaction temperatures as the chain mobility increases at elevated temperatures, thereby allowing the complete connection of furan and maleimide moieties.

Another biomass that attracts interest among researchers is lignin. Despite the wide availability of lignin biopolymer resources in nature, lignin is not widely used in self-healing polymers due to its structural complexity and diversity.[125] In a recent work by Buono et al.[126], a unique derivative of soda lignin was utilised. The natural material used contained around 30 wt.% lignin and maleimide moieties that were crosslinked to lignin with furan linkers to assemble a furan-maleimide-based DA polymer. Polymerization of the compound took place by a green chemistry process and did not involve the use of solvents. Moreover, the polymer sample could be healed entirely at 130 ºC. This material can be modified and assessed as a potential candidate for UV healable protecting films by taking advantage of lignin's excellent UV absorption properties.

Pectin has attracted a great deal of interest in biomedical applications due to its nontoxicity, anti-inflammation, antineoplastic activity and biospecific degradation. However, due to the presence of heteropolysaccharide branched chains that are soluble in water, its practicality has been limited. Li et al. [127] designed self-healing Pectin/Chitosan based hydrogels for drug delivery applications, and found that introducing DA chemistry in the composite not only leads to a significant improvement in the self-healing properties, but also ameliorates the cross-linking density, well-swelling, pH- and thermo-responsiveness, drugs loading efficiency, and the performance of the composite material as an efficient carrier for sustained release of drugs.

### 2.2.4. Self-healing polymer nanocomposites based on furan-maleimide DA reaction

The properties of self-healing polymers have improved significantly over the last few years due to continuous and rigorous research in this field. However, these polymers are not widely used because of their poor mechanical properties, low healing efficiency, prolonged healing time or inadequate response to external stimuli.[128] To address these challenges, carbon nanomaterials like graphene[129] and CNTs[130] have been successfully used as fillers for the polymeric matrix. Graphene possesses excellent mechanical properties, electrical/thermal conductivity, photothermal properties and excellent response to stimuli making it an ideal filler for self-healing composites.[131] Graphene derivatives can exist in three forms inside the polymeric matrix: (a) attached to the matrix by intermolecular force, (b) attached to the matrix by hydrogen bonds or host-guest interactions, and (c) crosslinked with the polymer matrix by reversible chemical bonds.[132] Graphene physically connected to the matrix by the influence of intermolecular forces hinders the healing process by limiting chain mobility.[133] Therefore, to take full advantage of graphene's unique mechanical properties, the successful interconnection of graphene materials in the polymer matrix by chemical bonds is essential. Li et al.[134] prepared a GO/PU thermally healable composite using DA reaction, where graphene oxide (GO) was chemically bonded with in-situ polymerised 4,4-diphenylmethane diisocyanate and poly(tetramethylene glycol). The composite material was heated at 150 °C for 4 h to induce rDA and slowly cooled at 65

°C, leading to the progress of DA reaction with a curing time of 24 h. Under such conditions, artificially introduced surface cuts were almost completely healed (visually) but the average healing efficiency was found to be 78% in terms of breaking stress. Meanwhile, Lin et al.[11] exploited excellent photothermal properties of graphene to devise an electrically conductive self-healing PU/graphene nanocomposite with a silver nanowire (AgNW) network inlaid in the surface layer. The composite polymeric material could be healed by 808 mm NIR irradiation with a laser density of 1.0 W cm$^{-2,}$ and the healing efficiency was reported to be above 90 %. In a recent work related to the production of GO-based self-healing composites conducted by Lee et al.[135], polymethacrylate was shown to self-heal when heated at 150 °C for 2 h followed by a heat treatment at 50 °C for 24 h. The highest efficiency obtained was 81.228% for the sample containing the highest GO content (0.030 wt%). A similar concept was adopted by Ding et al.; where Ag anchored on CNTs was used as an active filler to produce a self-healable DA PU with high strength (~15.97 MPa), high healing efficiency (~90.1%) and enhanced thermal conductivity.[136] It was found that conductivity increased because Ag nanoparticles (NPs) act as a bridge to connect CNTs and reduce the interfacial thermal resistance. Interestingly, this additional NPs loading does not interfere significantly with the chain mobility, and therefore, the self-healing ability could still be preserved. Ag NPs have also been used in other works as independent fillers to impart strength and antimicrobial properties to DA based self-healing polymers.[137]

Besides the bonding between the carbon filler and the matrix, it seems plausible that the size of the filler material could also affect the mechanical and healing properties of the composite. Lin et al.[138] used GO sheets of various sizes as shown in Fig. 10 (a-c), to reinforce the monomer and prepare PU composites based on the reaction mechanism as shown in Fig. 10 d. It was found that small-sized GO (mGO) sheets are advantageous for improving the matrix's mechanical and healing properties of the matrix. Moreover, when pristine GO (without functional moieties) was tested in nanocomposites, it was found to have inferior mechanical and self-healing properties (min. 10%) as compared to their functionalised GO counterpart. This further proves that the chemical bonds between graphene and the matrix improve mechanical properties as compared to graphene which is just physically dispersed in the polymer matrix.

Until now, most of the reported works focused on using DA reactions for intrinsic healing. However, Pratama et al. [139] developed a self-healing thermoset where DA reaction between the furan functionalised matrix and a compatible multimaleimide healing agent filled microcapsules was utilised to heal the material at room temperature. The samples were able to heal and yielded an average healing efficiency of 71%. In a similar work by Ingoglia[140], microcapsules filled with individual DA monomers were designed to initiate the DA reaction between bis(furan) and bis(Maleimide) upon cracking in the polymer matrix, initiating the release of DA monomers. The microcapsules were made from poly(urea-formaldehyde) using emulsion polymerization. Hypothetically, this approach was supposed to have several advantages because it did not involve any organic solvents, toxic components, expensive catalysts or need for external stimuli. However, the concept did not show encouraging results when self-healing was observed on a sample by encapsulating the microcapsules in a PU film. The film was scratched and left for two days under ambient conditions, but no healing was observed. The reason for unsuccessful healing was given as the inability to incorporate a high weight ratio of bis(maleimide) in the polymer films. Work in extrinsic healing by DA reaction was continued by Santos et al. [141], where they optimised the amount of DA monomer and the distribution of the microcapsules in the polymer matrix to maximise the healing efficiency. It was observed that bismaleimide with phenylacetate (PA) microcapsules having an average diameter of 150 µm provided a healing efficiency of 75% when the microcapsules loading was adjusted to 10%. Although the maleimide moieties required for the reaction increased at higher microcapsule loading, the PA solvent available at the interface also increased. Higher PA caused more plasticization at the interface, and the solvent trapped at the interface reduced the healing efficiency. Hence for healing times shorter than 2 days, the increase in capsule loading resulted in lower healing efficiency, as shown in Fig. 11. With a prolonged and thermodynamically slow healing process, PA diffused from the cut interface to the bulk of the material, thereby providing better crosslinking between furan and maleimide moieties, improving the healing. Also, in terms of mechanical strength, if the microcapsule loading was increased above 10%, fracture loads start decreasing rapidly, suggesting that loadings of 10% by weight or more are favourable for strength. Therefore, it was suggested that the microcapsule loading should be optimised to have enough furan-maleimide interlinking sites but not high enough to cause excessive plasticisation at the interface.

DA bonding is responsible for introducing a self-healing mechanism to the material; however, its role in improving mechanical/operational characteristics is insignificant and requires additional bonding mechanisms within the matrix to attain suitable properties. Sugane et al. [142] observed that when materials like furan and maleimide terminated, 8-armed star-shaped 3-caprolactone oligomers were used for self-healing matrices; the polymeric materials were mechanically incapable of retaining their shape at any temperature higher than the rDA temperature. To improve the mechanical properties, they introduced urethane bonds that possess high thermal stability and DA bonds and prepared dually crosslinked 8-armed star-shaped 3-caprolactone oligomers. The control sample with urethane bonds but without DA bonds failed to heal at standard healing conditions for this material (70 ºC for 24 h). In contrast, the sample containing DA bonds but no urethane bonds could heal itself under the same conditions but deformed due to softening. However, a dually crosslinked sample was able to heal, retain its original shape and have an efficiency of almost 90%. More information on designing tailor-made and advanced DA based homopolymers, block and graft copolymers,  dendrimers or dendronized polymers, hybrids and bioconjugates can be found in the review by Tasdelen, which can inspire novel polymeric backbones for efficient self-healing assemblies.[143]

### 2.3. Self-healing DA Polymers based on anthracene-maleimide

The thermal reversibility of DA reaction sometimes limits its use as the desired tool for high-performance engineering applications. The major limitation of using furan-maleimide moieties in the self-healing reaction is their low operating temperature as rDA bonds cleave at approximately 120 ºC.[51] At higher temperatures, the crosslinking is limited, leading to serious damage to the polymer stability and/or mechanical properties. Like the furan group, anthracene is a suitable candidate for diene due to its fixed cis conformation. Fig. 12 shows the basic cycloaddition reaction between anthracene and maleimide derivatives. Syrett et al. [144] produced PMMA with an anthracene-based DA adduct using N-(2-hydroxyethyl)maleimide to synthesise healable polymer stable at higher temperatures using 9-anthracenemethanol and 2-bromoisobutyryl bromide. Polymer with anthracene-maleimide DA adduct showed higher thermal stability than the control sample with furan-maleimide DA adduct. The polymer could be cleaved by heating to 200 ºC (rDA), and the bonds reconnected (DA) when the sample was slowly brought back to the original temperature. This proved the ability of anthracene-maleimide bonds to assist in self-healing; however, no work has investigated this material's self-healing properties or mechanical properties.

Yoshie et al. [145] synthesized a self-healing polymeric network ($PEAA_2M_3$) using a reaction between anthryl-telechelic poly(ethylene adipate) ($PEAA_2$) as anthracene source and a tris-maleimide ($M_3$) as maleimide source. A similar polymeric sample ($PEAF_2M_3$) was produced using furfuryl-telechelic poly(ethylene adipate) that has furan-maleimide DA bonding. The $PEAA_2M_3$ network exhibited higher thermal stability than $PEAF_2M_3$ due to the higher crosslinking density, similar to the results obtained by Syrett et al. [144]. A thermal stability study by in-situ ATR-IR spectroscopy while heating the sample from room temperature to 200 ºC, showed that $PEAA_2M_3$ possesses ≈ 50 ºC higher heat resistance than $PEAF_2M_3$. When the samples were given a mechanical cut and healed at 100 ºC for 7 days, a healing efficiency of 55 % could be obtained based on tensile strength and 90% based on elongation at break. This work can be easily replicated with other polymers, and in situ ATR-IR can be effectively used with other systems for analysis. Despite excellent thermal properties, DA cycloaddition with anthracene as diene and maleimide as dienophile requires high temperatures and longer reaction time to achieve a good bonding efficiency, making it unsuitable for use in materials that degrade at temperatures above 150 ºC. Moreover, due to the decomposition of individual moieties, Anthracene-maleimide DA polymers fail to exhibit higher healing efficiency.[51] Nevertheless, Heo et al. [146] prepared a self-healing polymer stable at high temperatures, with highly improved and repeatable healing ability using anthracene-maleimide moieties. 9-anthracenemethanol and N-(2-hydroxyethyl)-maleimide (HEM) were used as the source of anthracene and maleimide, respectively, and they were fully crosslinked to produce a pre-crosslinked monomer. Following that, hexamethylene diisocyanate (HDI) was reacted with the pre-crosslinked monomer in the presence of triethylamine (TEA) to break the strong hydrogen bonding in the diol precursor and prepare a viscous liquid monomer. This was essential to ensure the bulk polymer processing could be carried out without melting and in solvent-free environments. PU polymer samples by varying the pre-crosslinked monomer content (which acts as the healing agent) were prepared. A liquid monomer was used to assemble self-healing carbon fibre reinforced polymer (CFRP) composites using vacuum-assisted resin transfer moulding (VARTM). The polymer and composite displayed excellent thermal stability with no thermal degradation below 240 ºC. The PU samples with high stability also exhibited excellent self-healing properties where average first healing efficiency could reach as high as 94%. CFRP composites also showed an average first healing efficiency of up to 69%. Through mechanical testing, it was also demonstrated that pure and reinforced polymer's tensile strength, stiffness, and hardness were similar to structural epoxy and their commercially available composites. This work was the first in the Anthracene-Maleimide DA-based self-healing polymers to display high healing efficiency. Interestingly, NMR data showed that self-healing occurred through the reformation of DA adducts that were mechanically damaged and not by thermally reversible DA reactions, as usually seen with other DA polymers. This aids in high thermal stability and opens pathways for high-temperature applications.

Anthracene-Maleimide "click" partnership has been well established in earlier works; however, a newer diene-dienophile pair has recently emerged, promising ultrafast healing at lower temperatures (~130 °C) than conventional anthracene-maleimide systems. Mondal et al. [147] used reversible addition-fragmentation chain-transfer (RAFT) polymerisation to prepare 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) copolymers. The hydroxyl pendants on the methacrylate copolymers were used to attach anthracene derived fluorescent compounds followed by the DA bonding of 1,2,4-triazoline-3,5-dione (TAD) to these aromatic ends. This system showed a promising healing efficiency of ~80% when heated for 5 hrs.

### 2.4. Self-healing DA Polymers based on Cyclopentadiene

The Diels-Alder reaction yields a bridged bicyclic compound when a conjugated diene is locked in an s-cis conformation such as 1,3-cyclopentadiene. As two rings can share two nonadjacent carbons, cyclopentadienes(CPDs) can act as a diene and dienophile.[148] This seems to be advantageous when viewed from the perspective of developing self-healing composites as it can facilitate healing by a single functional component. Cyclopentadienes undergo dimerization to produce dicyclopentadienes (DCPDs), which can be converted back to cyclopentadiene through retro-DA reaction by thermal treatment, as shown in Fig. 13. [55]

The earliest work on developing thermally reversible DA polymers based on cyclopentadiene was done by Kennedy et al. [149] to produce reversible polyisobutylenes. Murphy et al. [150] successfully developed a single-component thermally re-mendable polymeric network using CPDs. In this work, DCPD dicarboxylic acid was subjected to bislactonization with a diol, resulting in a cyclic diester compound with DCPD attached. This cyclic diester compound forms a linear polymer with DCPD moieties when it undergoes ring-opening polymerization. The

CPD groups are responsible for interlinking through DA reaction and forming a crosslinked network. Self-healing is believed to occur through a rupture-repair process involving the dissociation of DA adducts by retro-DA reaction (120 ºC) and re-joining of the network by DA reaction (150 ºC). Visual inspection of the polymeric samples by optical instruments shows complete closure of the crack; however, fracture mending efficiency is found to be 40-60%. One of the monomers (monomer made with diethylene glycol) used by Murphy's group was further studied by Park et al. [151] to understand the healing processes.  The samples were cured on graphite/epoxy laminate, and healing was stimulated by electrical resistive heating.  It was observed that microcracks could heal at 70-100 ºC within a few minutes. DCPD containing chemicals have been actively used to produce resins, such as hydrocarbon resins[152] and unsaturated polyester resins[153]. This could have a great potential for developing single-component DCPD based self-healing epoxy resins with longer service life.

Interestingly, cyclopentadiene also undergoes hetero-DA reaction with dithioesters, and it has been substantially used to functionalise polymers made via RAFT polymerization.[154-157] Oehlenschlaeger et al.[158] utilised this diene-dienophile combination and prepared a self-healing system by using dyanodithioester and cyclopentadiene pair. This system displayed repetitive cyclability, did not require any external catalyst to heal and showed no damage when treated between 40-120 ºC for a short time. Samples were shown to heal completely in 10 mins at 120 ºC and 1 kN pressure in a hot press. Apart from the complete healing ability of this material under high temperatures, the mechanical properties of this material could be tuned by adjusting the healing temperature. This work was the first to report self-healing materials with such tuneable properties, making their application possible in various disciplines. Not only the properties of this polymeric network could be very easily adjusted at moderate temperatures, but it could also be done in a very short time, thereby making it more desirable for engineering applications.

### 2.5. Self-healing DA Polymers based on fulvene and cyanoolefin/dichloromaleic Acid

The main motive behind studying Fulvene based systems was to explore DA adducts with thermal reversibility at room temperature. Reutenauer et al. [159] used fulvene as a diene and cyanoolefin as a dienophile to develop a polymeric system with self-mending properties. Developing such polymeric materials was challenging as it needed precursor monomers having either two tricyanoethylenecarboxylate or two dicyanofumarate moieties. Preparing such monomers through a synthetic route is challenging due to their high sensitivity s nucleophiles. This problem was addressed by producing molecules with limited solubility. The authors designed a synthetic approach in which the monomer solubility was controlled to maintain enough supply in the solution to form the polymeric chain but low enough to easily precipitate the chains for purification. Bis(fulvene) was prepared by reacting 4-cyclopenta-2,4-dienylidenpentanoic acid and poly(ethylene glycol) (PEG 400) while DA dynamers were synthesized using bis(fulvene) and bis(tricyanoethylenecarboxylate). PEG in the form of polydispersed polyethylene spacer played an important role in obtaining polymeric chains with such high flexibility. This system exhibited excellent reversibility at room temperature. Self-healing tests were carried out by making a cut on a thin film, and the pieces were mechanically placed together at room temperature. It was observed that pieces joined together in just 10 s and were able to withstand mechanical elongation stress.

In another work, a dextran based self-healing cytocompatible hydrogel was prepared by Wei et al. [160] using fulvene-modified dextran as the base polymer and dichloromaleic-acid-modified polyethene glycol as a cross-linker. The self-healing behaviour was studied by making a cut on hydrogel disks and keeping the cut pieces joined together for 7 hrs at 37 ºC. It was observed through scanning electrochemical microscopy (SECM) and optical microscopy that segments were completely reconnected, and scratches completely disappeared in 7 hrs. Healing efficiency was determined by analysing the scratch depth at different healing times using the following equation:

$$((Depth_{0h} - Depth_{healed})/Depth_{0h}) \tag{4}$$

The healing efficiency was found to be 99%. This was the first research work that successfully used SECM for in situ analysis of the self-healing behaviour of hydrogels. This technique appears to be quite advantageous for understanding the healing mechanism and for fine-tuning the bonding characteristics to modify the healing/thermal properties. Furthermore, the use of low-temperature healing ensures that it can be easily used and repeated for temperature-sensitive materials like hydrogels. Although the synthesis route is relatively complicated compared to furan-maleimide DA adducts, this can see broad applicability in the biomedical field and can inspire such polysaccharide hydrogels that can be used as injectable carriers obviously after appropriate toxicity considerations.

There exists a colossal library of petro-based dienes such as butadiene [161], pyrrole [162] or even bio-sourced dienes such as muconic acid [163], myrcene [164], farnesene [165], cardanol [166] and sorbic acid [167]. Vegetable oils such as conjugated linoleic acid could also be used as dienes due to their high unsaturation in the alkyl chain[168]. However, most other vegetable oils do not possess the conjugated double bond necessary for cycloaddition to take place, which makes them more suitable for dienophile than diene. Furthermore, compounds such as vinyl ketone derivatives[169], itaconic acid [170], citraconic acid [171], quinones [172] and triazolines [173] are some examples of novel dienophiles that have been previously used to form DA adducts. The abundance of possible dienes, dienophiles and their combinations make the enumeration of diene-dienophile pairs inexhaustible. However, the use of such novel combinations in the synthesis of self-healing polymeric systems remains unexplored to the best of our knowledge.

## 3. **Reversible photo-crosslinking for self-healing polymers**

Apart from (4 + 2) cycloaddition, which is induced by thermal stimuli, certain other compounds like cinnamate [174-177] and coumarin [178, 179] derivatives can undergo photo-induced (2 + 2) cycloaddition reaction. During this reaction, two unsaturated groups like cinnamoyl undergo cycloaddition and form a cyclobutane ring or its derivative. This reaction can also occur in the reverse direction, resulting in the formation of original cinnamoyl structures during crack origination and propagation. [174] However, this reaction occurs only under the photo-induced stimulus and not under thermal stimulus as per Woodward-Hoffman rules due to a very high activation energy barrier under thermal control.[180] Photodimerization and photocleavage of coumarin and cinnamate are shown in Fig. 14. These cinnamoyl based polymers can undergo self-healing like DA adducts, where bonds are disconnected when cracks are induced and regenerated in the presence of a photo stimulus. Application of UV irradiation to heal the polymer provides obvious advantages of shorter healing times, higher efficiency, applicability in polymers with low Tg and ability to heal larger surface areas. [175]

Oya et al. [175] used cinnamoyl-telechelic poly(butylene adipate) (PBAC2) and a tetra-cinnamoyl linker (C4) to prepare a polymeric network that could heal under UV irradiation. Cinnamoyl functionalities of the precursor adducts were used to form the polymeric network by bonding under UV irradiation ($\lambda$ = 300–400 nm) using (2 + 2) cycloaddition. The healing behaviour of the samples was analysed by UV-vis spectroscopy. It was observed that when the crack was induced, cinnamate dimers along the interface of the crack dissociated into cinnamate monomers. When the sample was irradiated with 300-400 nm UV for 10 min at 60 ºC, it led to re-dimerization of the cinnamate monomers and crack healing could be achieved. UV-vis showed that complete chemical recovery of the polymer occurred after the UV irradiation.

Thymine based self-healing linear polymers with photo-reversible characteristics were studied by Abdallh et al. [181] Bis-butyl thymine monomers were crosslinked by irradiating UV light at 302 nm. Thymine moieties provided the polymeric matrix with photo-reversible capabilities via (2 + 2) cycloaddition. Healing was achieved by applying UV irradiation at a wavelength less than 240 nm. It was suggested that the reaction occurs due to the depolymerisation under photocleavage and UV, which reduces the $T_g$. The dropping in $T_g$ increased the chain mobility within the matrix and made the material less hard. The mechanical properties were almost entirely recovered after healing. However, $T_g$ of the healed sample was slightly lower than the virgin sample, most likely due to the misalignment of polymer chains at the healing site. This work can be used to develop temperature-sensitive polymer coatings and polymeric thin films, which can be self-healed at room temperature by UV irradiation. However, limited information is available about the mechanical characteristics of the polymer matrix before and after healing, which makes it hard to evaluate the new materials for potential applications. Moreover, analysing the repeatable healing characteristics of the sample at the same location and studying its effect on the $T_g$ would be advantageous to understanding the healing behaviour for long-term use.

Self-healing materials based on cycloaddition reactions suffer difficulty in scale-up mainly due to the use of speciality monomers/precursors. Kim et al. [182] aimed at solving the applicability issue by preparing healable microcapsules made out of homopolymers that heal a crack by initiating a photochemical (2 + 2]) cycloaddition reaction while being dispersed in any polymer matrix. Photopolymerization and suspension polymerization was used to prepare microcapsules using 1,1,1-tris (cinnamoyloxymethyl) ethane (TCE) and 1,1-di(cinnamoyloxymethyl) ethane (DCE) monomers. Each microcapsule contained TCE and DCE monomers which act as the healing agent. These microcapsules could be formed by suspension polymerization, where only the outer shells underwent polymerization because of limited light penetration. Microencapsulation offers only one-time healing at any point, mainly due to material discontinuity between the healing agents encapsulated inside the shell and the shell material, which limits their wide application. Discontinuity was resolved by using TCE-co-DCE monomers in a poly(TCE-co-DCE) shell, and it was shown through FTIR that this system was capable of repeatable healing action at a single site. The mechanism for repeatable healing is summarized in Fig. 15. This work opens pathways to create uniform polymeric matrices by utilising microencapsulation and cycloaddition reactions together. It also created a repeatable polymer network by eliminating the individual disadvantages of both approaches, which could be widely used in self-healing coatings and paints.

Utilising photo-crosslinking for self-healing polymers is not limited to (2+2) cycloaddition reactions; a considerable body of literature exhibits the use of anthracene and its derivatives to develop photo-reversible bonds based on (4+4) cycloaddition.[183, 184] In the case of (4+4) cycloaddition, two unsaturated molecules with carbon fragments are connected by four atoms to form an eight-membered ring. This cycloaddition cannot be triggered thermally due to the same reasons discussed earlier for the (2+2) cycloaddition process. (4+4) cycloaddition is considered the most reliable photo triggered reaction even when compared to (2+2) cycloaddition of coumarin and cinnamate due to its ability to remain stable against hydrolysis and isomerization reactions.[185] It also offers a facility to control the occurrence of radical polymerization when different substituents are added to positions 9 and 10. During the (4+4) cycloaddition of anthracene, generally, both head-to-head and head-to-tail dimers are produced, as shown in Fig. 16. Still, the former is not usually reported or practically used due to stability issues.[186] Anthracene and its derivatives use long-wave UV irradiation (>350 nm) to undergo  (4+4) cycloaddition, which can be reversed by exposure to short-wave UV light (<300 nm).[183]

Connal et al. prepared core crosslinked star (CCS) polymers with low $T_g$ using an orthogonal patterning technique.[187] This CCS polymer was an anthracene-functionalised poly(methyl acrylate) that displayed high photo-reversibility due to anthracene ends. These films were not studied for their healing ability, the extent of reversibility or tensile properties. However, they seem to be a suitable candidate for stable and porous self-healing films because of their reversibility and significant mechanical properties.

Hyperbranched polyglycerol with anthracene moieties(PG-An) was used to synthesise self-healing polymers based on (4+4) cycloaddition by Froimovicz et al.[188]. After introducing a surface cut on the polymer sample, 254 nm light was irradiated on the site for 15 mins to cause de-crosslinking and regenerate the macromonomer. When this material was further kept in the dark environment overnight, the PG-An sample could fill in the crack, which was attributed to its low Tg of 56 °C. Final curing of the material (crosslinking of the network) was done by irradiating with higher wavelength light (366 nm) to regenerate the polymeric network. The dendritic self-healing nanometre-size building block showcased in this work promises a potential application in hydrogels, coating, inks, and smart materials. It is essential to highlight that the healing process is repeatable, and the photo healing process could be simultaneously applied to a large area in a short duration.

Supramolecular polymers produced by employing host-guest interactions using pillar[5]arene and imidazole were investigated by Xu et al. [189]. They produced double dynamic polymeric structures containing covalent bonds based on anthracene. The advantage of producing such double dynamic polymers includes de-crosslinking by dissociating either the host-guest complexes or both the host and anthracene dimers (which can be easily controlled by the extent of heating). Since the polymers are bonded both on the molecular and supramolecular levels, their response to external stimuli is much better than conventional dynamic polymers, where the reversibility is limited either on molecular or supramolecular levels. More studies on the healing characteristics and mechanical properties would give a better idea about its potential application.

However, this work is an excellent example of smart materials where fine-tuning the responses to external stimuli is possible. This double dynamic combination of bonding could be tested on other host-guest systems.

Furthermore, a recent study produced a UV-light responsive and healable pendant using anthracene-functionalised Poly(ethylene-co-propylene), also known as EPR rubber, by coordination polymerization, which displayed a high conversion yield of ≈90% and reversibility of ≈70%. Healing efficiency based on tensile strength was calculated to be 82.9% for a sample containing 5.7 mol% anthracene.[190]

## 4. Self-healing polymers based on other reversible mechanisms

Apart from cycloaddition reactions, self-healing polymers based on the reactions initiated by disulfide groups have been investigated. Various mechanisms such as disulfide exchange[191], reduction-oxidation[192], thiol-disulfide exchange[193] and radical-mediated disulfide fragmentation[194] have been employed to produce reversible bonding. These disulfide functional moieties can either be subsumed into the main chain or attached as a cross-linker on the side chain[195]; however, the most commonly used approach is to prepare self-healing networks by using multifunctional thiols. Disulfide based reversible polymers have been reported to heal by heating[196, 197], UV light[198, 199], redox[192], pH stimulus[200]. For instance, a recent study by Guo et al. [201] demonstrated polydimethylsiloxane (PDMS) polymers which consisted of weaker H-bonds and stronger disulfide bonds. The PDMS sample was able to heal under universal conditions, including room temperature healing (healing time of 10 mins and efficiency of 93% ± 3%), refrigeration (4 °C), freezing (−20 °C), ultralow (−40 °C) temperatures, in a supercooled saline solution (30% NaCl solution at −10 °C with 89% efficiency), and strong acid/alkali environment (pH = 0 or 14 with 88% and 84% efficiency). Disulfide based self-healing polymers are favoured by the easy availability of monomeric materials and crosslinking agents, relative simplicity in fabrication and utilisation of various external stimuli. However, thiols' sensitivity to oxygen[202] has always prompted disquiet as thiols will oxidise over time and result in the loss of the self-healing ability of the material.

Supramolecular polymeric systems can contain H-bond or π-π stacking interactions within and between the chains, which reinforce and strengthen the matrix. H-bonds are reversible connections that can be ruptured when heated at temperatures (40-50 ºC) much lower than other thermally reversible bonds.[203] This is mainly because of the low binding energy of H-bond interactions (5–30 KJ mol$^{-1}$). Initially, self-healing rubber based on H-bond was reported where low Tg of rubber favoured healing at temperatures of H-bond rupture. This is ideal for thermally reversible hydrogels and low Tg polymers, which could not withstand high rebonding temperatures of the DA reactions or other covalent bonds.[204-208] However, the materials healed by hydrogen bonds possessed poor creep and solvent resistance due to the absence of necessary covalent bonds.[209] In the view to resolve this problem, hybrid supramolecular networks containing both H-bonds and covalent bonds were produced. In light of a recent work reported by Cummings et al. [210], it was corroborated that materials with stronger H-bonds (dynamic non-covalent bonds) should be favoured compared to those with more hydrogen bonds to produce materials with better mechanical properties. This can be effectively utilised in hybrid dynamic networks. π-π stacking interactions demonstrate properties similar to H-bonds and can form a network of bonds at ambient temperatures. These interactions need temperatures higher than H-bonds but lower than other covalent counterparts for debonding/bonding.[211] Some works with π-π stacking interactions have reported healing efficiency as high as 100%, but this comes at the expense of lower Tg and poor mechanical strength, which is also a problem with H-bonds.[211, 212]

Commendable work has been done in utilising multiple healing mechanisms in synergy to improvise the healing behaviour of thermosets.[213, 214] In a recent work by Xu et al., Covalent adaptable networks (CANs) were developed, which boast the easy reprocessability of thermoplastics and the excellent mechanical properties of thermosets Schiff base and DA adducts in the same matrix.[215] Schiff base provides excellent mechanical strength to the network. Meanwhile, the crosslinking density of this network decreases at higher temperatures by dissociation of DA bonds, which permits chain mobility and rearrangement of networks. This helps in smooth reprocessing and efficient self-healing. Furthermore, these CANs are postadjustable (modify properties after synthesis) as the degree of DA adduct reconnection can be controlled by heating. This unique approach shows the advantages of linking associative and dissociative dynamic chemistry for self-healing.

Singha’s group utilised double dynamic covalent bonding with DA cycloaddition and disulfide metathesis to impart some interesting properties to polymers. In one of the works, dual-healable PU was prepared using 4-aminophenyl disulfide and FGE as the chain extender.[216] PU produced by such double bonding displayed excellent tensile strength (39.5 MPa) and noteworthy self-healing efficiency (98%). In another work by the same group, a similar mechanism was utilised to impart thermal and UV-triggered self-healing to carboxylated nitrile rubber (XNBR).[217] This technique also makes recycling such rubbers quite straightforward, without significant loss in their mechanical properties.

PDMS is a widely studied polymer for self-healing applications mainly due to its wide use in medical devices, wearable electronics, waterproofing sealing, heat resistant lubricants and other useful applications. [218] DA based PDMS has been synthesised in earlier works where cycloadduct can be formed by DA (60-80 C) and broken by rDA (120-140 C).[219, 220] The main problem with such materials is the loss of their mechanical integrity above rDA temperatures, where the material begins to display flowability. To tackle this problem, Yilmaz et al. [221] synthesised a self-healable PDMS matrix with reversible DA bonding and permanent hydrosilylation. The incorporation of a permanent network by hydrosilylation maintains the mechanical integrity of the PDMS network even when the DA cycloadduct is broken. Chemical degradation and ageing under proton irradiation (by simulating geostationary environments) were studied to analyse its suitability for satellite applications where the material is not easily accessible for replacement.

## 5. Experimental and computational characterization of self-healing polymers with reversible bonds

Typically, the self-healing properties of polymers are analysed by measuring their bulk mechanical properties, such as fracture toughness and tensile strength, before and after healing.[222] This gives a beneficial insight into the healing extent and changes in the domain of physical properties. Some specialised techniques such as Tapered Double Cantilever Beam (TDCB)[223], scratch volume analysis[224], ballistic impact[225] and scratch healing analysis[226] have also been used successfully for evaluating the healing processes in polymers on a mechanical scale. However, in addition to mechanical characterization, advanced spectroscopic characterizations have been used to shed light on mechanisms of the healing process and the related mass transport phenomena in reactions that involve reversible chemical bonding. The summary of these analytical techniques is shown in Fig. 17.

The atomic force microscopy (AFM) can monitor the mass transport during healing when acquisition time is sufficient to allow for the AFM scan.[227] AFM has also been successively used to create nanoindentations by the AFM tip and then characterising the healing qualitatively.[228, 229] In contrast to AFM, several other imaging techniques such as scanning electron (SEM)[99], optical microscopy[15, 230] and optical profilometry[231] have been explored in prior studies. Although these techniques provide valuable information regarding the degree of healing, limited quantitative information can be obtained based on visual observation.

Raman[232] and infrared spectroscopy[233] are among the most commonly used techniques employed to determine local molecular events, and consequently, the progress of reversible reactions. Different forms of IR spectroscopy, such as FT-IR[113] and FTIR-ATR[124], have been successfully employed to monitor healing in DA polymers. This is usually performed by detecting the presence of reactants, intermediates, or products, and it is made possible by sufficient spatial resolution provided by these techniques. For example, Zeng et al. focused their FT-IR study on the 1700 and 1730 $cm^{-1}$ bands, representing the vibrations due to carbonyl stretching in the maleimide crosslinker and poly(2,5-furandimethylene succinate) (PFS) chain respectively. An increase in these peaks' intensity with respect to the unreacted maleimide bond at 700 $cm^{-1}$ was used to indicate the reaction’s progress.[124]

Moreover, previous works using non-resonant Raman scattering[234, 235] and Surface-enhanced Raman scattering[236] prove their potential candidacy as tools for advanced in situ monitoring of thermally reversible DA reactions.

As an alternative technique, the temperature-dependent $^{13}C$ solid-state nuclear magnetic resonance (SSNMR) spectroscopy was used by Wudl's team[6] to show the reversible DA adduct formation while heating an intrinsic type of healing polymer. SSNMR also provides useful information about the polymer chain flexibility[237], which can be escalated to understand the effect of molecular behaviour on self-healing. More advanced NMR techniques are being developed for more accurate characterization of progress in self-healing. These techniques, however, need to be further developed before wider application as standard techniques to characterise healable polymeric systems.[238, 239] For example, electron paramagnetic resonance (EPR) spectroscopy can have better time scales (μs-ps). Still, it lacks the sensitivity required to detect extremely low radical concentrations, commonly prevalent in products with higher healing times.[240, 241] Davydovich et al. [238] have successfully used Nuclear Overhauser effect spectroscopy (NOESY) and correlated spectroscopy (COSY) 2D $^{1}H$ NMR to detect self-healing in hydrophobic copolymers.

Another advancement in the field is the modification of magic angle spinning (MAS) NMR spectroscopy which is a powerful method for analysing polymeric materials. Unfortunately, the sensitivity of MAS-NMR spectroscopy is not sufficient for monitoring the healing process. However, the sensitivity of magic angle spinning (MAS) in SSNMR can be drastically improved using dynamic nuclear polarization (DNP) SSNMR spectroscopy. When SSNMR was used to investigate the structural elucidation of polymeric chain endings, it was found that signals from chain ends were scarce. However, such signals could be distinctively identified in DNP SSNMR mainly because of the enhanced sensitivity (almost by a factor of 10).[242] Characterising the chain ends is crucial for the self-healing reaction since dangling chains at the rupture site dictate the healing process occurring at the molecular level. These advanced NMR techniques have also been used to study various polymeric systems[243-246], including microporous polymers [247]. Therefore, it seems acceptable to explore these techniques further to gain a better insight into molecular events occurring at the site of rupture.

Broadband dielectric spectroscopy (BDS) is another promising technique that has also been substantially used to study the dynamics of polymeric materials.[248-250] BDS measures the dielectric properties of materials within a broad frequency range of $10^{-2}$ to $10^{9}$ Hz, and it is usually performed under isothermal or isochronal conditions. When polymeric systems are subjected to dipole polarization, motional processes occur on different timescales, frequencies, and temperatures, which highly depend on the morphology and microstructure of the polymers.[251] Therefore, this technique offers a unique approach to expressing polymer chain mobility as a function of polymer morphology or architecture, which can effectively study chain mobility at the cleavage site, particularly for composites. Hernandez et al.[252] employed BDS to investigate the self-healing in natural rubber under isothermal conditions.[252] Their results show that it is only possible to measure the dielectric signal if the sample is healing (no reliable data was obtained from cleaved samples). Also, they observed variation in the dielectric loss at the healed surface, which was attributed to nanoscopic irregularities. These results disagreed with the optical microscopy observations, which suggested the complete healing of the material. Nevertheless, there have been comments on this work in the literature, suggesting that proving the self-healing is insufficient since the crack healing in work could also be attributed to the tackiness of natural rubber.[253] Further evidence to prove the self-healing was later provided by Hernandez and his team in later work.[254] However, the authors still confirm that the reliability of BDS for evaluating the healing state requires further studies in future.

Thermal characterization techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) can also provide valuable information on molecular events that occurred in the polymeric matrix under the thermal stimulus.[146] Concerning self-healing materials, DSC combined with TGA has been used to determine the thermal stability of the materials.[135, 146, 255, 256] As breaking and reformation of reversible covalent bonds require considerable energy, the related events can be easily detected by observing the exothermic and endothermic peaks in DSC isotherms which correspond to each direction of DA cycloreversion. The temperature of rDA and DA reactions is highly dependent on the DA moieties, interfacial properties, and the polymer structure, making thermal analysis an effective approach to studying the self-healing reactions. Moreover, kinetic modelling of the DSC or microcalorimetry data can be useful to determine the optimum kinetic parameters, supporting the understanding of the reaction enthalpies and entropies.[257] Scattering techniques such as X-ray or neutron scattering offer a possibility to study the structural changes in the molecular structures as a function of temperature and time. In the past, X-ray scattering has been used to study different polymers with hydrogen bonds[258, 259] and even metallopolymers[260]; however, neutron scattering has not been applied to healing polymers. It does have great potential to study dynamic processes by real-time monitoring of the healing reaction at the molecular level, with the ability to provide more details than X-rays.[261]

Along with experimental characterisation methods, computational methods have also been used to study self-healing materials. The computational methods focus either on the prediction of healing phenomena or on providing a logical explanation of the observed healable behaviour.[262, 263] These are efficacious in determining the materials' dynamic properties during the healing process, which cannot be easily measured experimentally. When healing under the stimulus, dynamic crosslinked polymeric networks can undergo bond remodelling and interfacial chain diffusion.[33, 264] Bond remodelling conveys that the strong bonds remain intact and contribute largely to the strength of the material. However, labile bonds provide the necessary adaptability to the structure, and they are mainly responsible for self-healing.[265] Various models such as lattice spring models[266, 267] and Bell model[268, 269] have been developed to provide the necessary understanding of healing in crosslinked polymers based on bond remodelling. In the lattice spring models, particles are considered as point-like masses known as nodes, connected by Hookean springs and follow newton’s second law of motion.[270] In the Bell model, bond rupture and formation are a function of forces on each node[269].

Despite their usefulness, the healing mechanisms represented by stimuli-responsive models, like those explained above, often do not delineate any information about the loss of continuum in the matrix. Wang and co-workers[271] explained this issue by coalescence of the interpenetrating network model and network alteration theory, thereby proposing a mechanism of interfacial healing in crosslinked polymers. As the model selection would highly depend on the number of labile bonds per node-to-node interaction, the selection of the model considering the bond structure is of utmost importance.[265]

Moreover, these models also fail to explain the healing phenomena in composite materials where distribution and morphology decide the bonding characteristics. This limitation can be utilised to develop models useful to understand healing in 3D heterogeneous structures in the future. Other models such as continuum damage-healing[272] and cohesive crack growth and healing[273] have also been developed to deal with microencapsulation based extrinsic healing polymers. However, a detailed discussion on models for extrinsic healing is beyond the scope of this review.

## 6. Discussion and Outlook

Reversible cycloaddition reactions are among the most promising healing mechanisms due to their ability to efficiently heal many polymeric systems and simultaneously improve other mechanical properties by forming strong covalent bonding. Through this review, we aimed to accentuate the contribution of DA chemistry in the field of self-healing polymers by providing a complete overlook of its mechanism, thermodynamics relevant to polymeric healing, novel combinations, advanced production approaches and a cumulative guide to analyse such polymers. A combination of features that can be imparted by DA bonding includes, but is not limited to, the relative ease of manufacturing, repeatable self-healing behaviour, better mechanical properties and recyclability. Moreover, with the increasing need for smarter materials that can perform several roles, it is important to design self-healing materials with multi-functional properties. This will open the door for a set of new applications for self-healing polymers in the electronics, automotive and aerospace industries. This will also motivate profound research in stimuli-responsive healing materials, which can be translated into advanced smart materials, for example, sensor applications. Research into bio-compatible self-healing polymers shall provide a fertile ground for developing a new generation of medical implants and synthetic tissues.

DA based self-healing approaches increase the longevity of polymeric materials to a great extent. However, these techniques carry with them a fair share of constraints that limits their progress. A large portion of the research activities in this field has been carried out by using specialized monomers and precursors which are not commercially available. Also, for completing the healing reactions, new complex strategies were developed to manipulate their molecular structure, thermodynamic properties, placement of functional groups and even control the termination of chain ends. Such systems are not very likely to replace their counterparts with non-healing ability in the near future since the current polymeric materials often exhibit advantages such as low cost, simple processing, and acceptable mechanical properties. Wide commercial use of self-healing polymers would only be achieved if the commonly used commercial polymers were transformed into self-healable materials through affordable and simple technologies without scarifying the mechanical properties. It is also essential to divulge the possibility of fine-tuning materials' mechanical and healing properties under the required circumstances.

This brings us to analyse the feasibility of existing processing techniques to be escalated for producing self-healable polymeric macromolecules. The classic processing routes in polymer chemistry, such as injection moulding, blow moulding, thermoforming, and extrusion are still not fully compatible with the designed self-healing systems and needs further modifications before they can be employed for large scale production. Several approaches are currently under consideration to make the traditional polymer processing methods suitable for self-healing systems. However, with increasing demands for more complex systems such as multifunctional polymers, layer-by-layer composites, gradient materials, bioplastics, and recycled plastics, research efforts are increasingly focused on developing novel processing methods. For example, a self-healable bending soft pneumatic actuator was synthesized by forming strong covalent bonds using the DA mechanism at the multi-material interface by heat-cool cycles.[274] Some attempts are reported on using 3D printing techniques for self-healing polymers.[275] However, much research is required to enhance the efficiency and effectiveness of the healing mechanism, particularly to overcome the layer-by-layer nature of 3D printing.[276] New techniques such as photopolymerization-based 3D printing, used by Yu and his co-worker to fabricate a self-healing PDMS shoe may provide a stepping stone for large scale production of self-repairable polymer.[277] The use of cutting-edge automation techniques along with better control systems is expected to accelerate the processing technologies and produce more tailored objects. Furthermore, newer technologies like cure-on-command (including but not limited to UV curing, electron beam curing and magnetically induced curing) [278] and DA reversible thermostats (DART) 3D printing [279] could provide the necessary ladder needed for the commercialization of healable materials.

The appropriate use of material characterizations, including mechanical testing techniques, imaging, and spectroscopic methods, is essential to characterise the self-healing properties of polymers. These techniques need to be further optimised and/or developed to be able to provide sufficient sensitivity required to characterise the healing processes. For example, more studies on the structure-properties relationship are essential to understand the effect of morphology on self-healing, like the recent study by Raffa et al. [280] on DA based Styrene and Furfuryl Methacrylate composite. However, if non-destructive computational testing methods are developed, which could reliably simulate the polymer morphology, crack propagation and healing phenomena, it is not hard to envision its direct impact on time and involved costs. Developing in-situ measurement and real-time monitoring of the healing process are required and are expected to gain more attention in the future. The ex-situ characterizations currently used to investigate the self-healing materials are *"post-mortem"* in nature, meaning that the healing process is stopped after set time intervals, and samples are analysed after cooling/washing using different spectroscopic and physical techniques. However, in a dynamic process like materials healing, stopping the reaction may not be possible, and the process may continue anyway. Therefore, the ex-situ technique is missing valuable information about the intermediate steps of the healing process. Further, preparing the samples for spectroscopic or physical characterisation of functional macromolecules requires very high precision, which may result in degradation or elimination of functional groups from the chains, giving misleading information on the healing mechanism. In-situ investigations can detect structural changes during the chemical healing process. Surprisingly very limited studies can be found in the literature using in-situ techniques, like the one by Vilatela and his team, where they monitor the click chemistry healing reaction of rubber composite by continuous dynamic mechanical analysis(DMA). [281]

Although widely accepted, it is inarguable that these polymers still need external thermal stimuli for healing, restricting their applications. If such polymers can utilise a combination of low-energy weak bonds and high-energy covalent bonds in their matrix, it would be possible to achieve stimuli-free repeatable self-healing with very high efficiency. It should also be mentioned that phenomenal improvements in the properties can be achieved by adding an appropriate filler material to the matrix. However, there are still challenges in understanding the surface interactions of such materials on the microscopic level. Due to this, surface and morphological studies will become increasingly important with the rise of 2D materials as potential candidates for fillers. This enables us to incorporate DA functional groups, not just on the polymeric backbone chain but also anchored on fine materials dispersed evenly in the matrix. The recent advancements in the green and low-cost preparation of high-quality carbon nanomaterials[282], including graphene nanosheets with high electrical/thermal conductivity values[283] can provide opportunities for the development of thermally/electrically conductive self-healable polymers in future without the use of expensive noble metal NPs. The application of other 2D materials, such as MXene phases [284], transition metal chalcogenides [285] or even transition metal oxides [286] can impart valuable properties to the composite like sensing ability while also participating actively in the self-healing process. One recent example has been the incorporation of $Ti_3C_2$ MXene with self-healable polymers [287], leaving a very large number of 2D materials left to be studied for self-healing polymer applications in future.

Despite this profound research in the field of self-healable DA based polymers, not much attention has been levied to the actual reaction temperatures for DA and retro-DA reactions. These temperatures are not just based on the basic reaction mechanism but are also affected by monomeric precursors, their functionalisation, their interaction, and the thermodynamics of the DA adduct formed. A large body of literature exists where DA cycloaddition has been used to form reversible polymers; however, thermodynamic data on the reversible retro-DA is usually absent and this makes it difficult to identify their most suited area of application. For instance, anthracene cycloaddition has been studied for a long time, but there exists a huge discrepancy in the reported temperatures for retro DA reaction (ranging from 50 °C to 200 °C). This inconsistency is further fuelled by many works in this field that do not report the presence of exo and endo isomers, which are usually formed simultaneously. A better understanding of the temperature scale of diene-dienophile interactions will aid in designing polymers better tailored to specific needs. For instance, polymers for aerospace applications should be capable of healing at higher temperatures, while those required for biomedical applications need to be healed at temperatures under 40 °C.

Furthermore, the negative impact of chemicals used in these processes on the environment cannot be neglected. Most cycloaddition reactions need organic solvents and other chemicals that might be harmful to the environment. Hence, further attention should be levied to the construction of molecular systems based on the principles of green chemistry. This can be done by replacing the chemicals and reagents involved in the reaction with environment-friendly alternatives. Procuring diene and dienophile pairs from nature will lead to newer combinations of interest for polymer chemists. Natural polymeric precursors such as lignin, cellulose and even vegetable oils have been extensively studied in the past, but there is an inexhaustible library of polymers available in nature that are yet to be explored. This article provides a comprehensive overview to nurture the technological development in the field of self-healing polymers based on cycloaddition reactions which not only cater to the engineering demands but also ensure the safety of the user and environment.

## Conclusion

In this review, first, we described the possible pathways available to produce self-healing polymers and explained the importance of such healable materials on the product lifecycle. Following that, we discussed the fundamentals of DA reaction and various diene-dienophile pairs in terms of their thermodynamics, physical damage/healing phenomena, and their applications in variegated classes of polymers. Among the self-healing polymers, specific attention was paid to those polymers that exhibit healing properties based on thermal and photo-crosslinking mechanisms. The photo-activation can provide valuable opportunities since the healing process occurs in the absence of heat, which is generally more challenging to be applied. Finally, an outlook was provided on the suitable analytical and computational tools available to gain necessary insight into self-healing polymeric materials' properties and underlying healing mechanisms.

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## References

[1] Chen Y, Kushner AM, Williams GA, Guan Z. Multiphase design of autonomic self-healing thermoplastic elastomers. Nature Chemistry. 2012;4:467-72.DOI: https://doi.org/10.1038/nchem.1314.

[2] Reifsnider KL, Schulte K, Duke JC. Long-Term Fatigue Behavior of Composite Materials. In: Brien TK, editor. Long-Term Behavior of Composites. West Conshohocken, PA: ASTM International; 1983. p. 136-59.DOI: https://doi.org/10.1520/STP31820S.

[3] Mphahlele K, Ray SS, Kolesnikov A. Self-Healing Polymeric Composite Material Design, Failure Analysis and Future Outlook: A Review. Polymers. 2017;9:535.DOI: https://doi.org/10.3390/polym9100535.

[4] Garcia SJ. Effect of polymer architecture on the intrinsic self-healing character of polymers. European Polymer Journal. 2014;53:118-25.DOI: https://doi.org/10.1016/j.eurpolymj.2014.01.026.

[5] Schmets A, Zaken G, Zwaag S. Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science2007.

[6] Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, et al. A Thermally Re-mendable Cross-Linked Polymeric Material. Science. 2002;295:1698-702.DOI: https://doi.org/10.1126/science.1065879.

[7] Luan Y-G, Zhang X-A, Jiang S-L, Chen J-H, Lyu Y-F. Self-healing Supramolecular Polymer Composites by Hydrogen Bonding Interactions between Hyperbranched Polymer and Graphene Oxide. Chinese Journal of Polymer Science. 2018;36:584-91.DOI: https://doi.org/10.1007/s10118-018-2025-y.

[8] Yanagisawa Y, Nan Y, Okuro K, Aida T. Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking. Science. 2018;359:72-6.DOI: https://doi.org/10.1126/science.aam7588.

[9] Yue Y, Liu N, Ma Y, Wang S, Liu W, Luo C, et al. Highly Self-Healable 3D Microsupercapacitor with MXene–Graphene Composite Aerogel. ACS Nano. 2018;12:4224-32.DOI: https://doi.org/10.1021/acsnano.7b07528.

[10] Thakur S, Karak N. Tuning of sunlight-induced self-cleaning and self-healing attributes of an elastomeric nanocomposite by judicious compositional variation of the TiO2–reduced graphene oxide nanohybrid. Journal of Materials Chemistry A. 2015;3:12334-42.DOI: https://doi.org/10.1039/C5TA02162F.

[11] Lin C, Sheng D, Liu X, Xu S, Ji F, Dong L, et al. NIR induced self-healing electrical conductivity polyurethane/graphene nanocomposites based on Diels−Alder reaction. Polymer. 2018;140:150-7.DOI: https://doi.org/10.1016/j.polymer.2018.02.036.

[12] Huang L, Yi N, Wu Y, Zhang Y, Zhang Q, Huang Y, et al. Multichannel and Repeatable Self-Healing of Mechanical Enhanced Graphene-Thermoplastic Polyurethane Composites. Adv Mater. 2013;25:2224-8.DOI: https://doi.org/10.1002/adma.201204768.

[13] Li J, Liu Q, Ho D, Zhao S, Wu S, Ling L, et al. Three-Dimensional Graphene Structure for Healable Flexible Electronics Based on Diels–Alder Chemistry. ACS Applied Materials & Interfaces. 2018;10:9727-35.DOI: https://doi.org/10.1021/acsami.7b19649.

[14] Toohey KS, Sottos NR, Lewis JA, Moore JS, White SR. Self-healing materials with microvascular networks. Nature Materials. 2007;6:581-5.DOI: https://doi.org/10.1038/nmat1934.

[15] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. Nature. 2001;409:794-7.DOI: https://doi.org/10.1038/35057232.

[16] Cong H-P, Wang P, Yu S-H. Stretchable and Self-Healing Graphene Oxide–Polymer Composite Hydrogels: A Dual-Network Design. Chemistry of Materials. 2013;25:3357-62.DOI: https://doi.org/10.1021/cm401919c.

[17] Xiang Z, Zhang L, Li Y, Yuan T, Zhang W, Sun J. Reduced Graphene Oxide-Reinforced Polymeric Films with Excellent Mechanical Robustness and Rapid and Highly Efficient Healing Properties. ACS Nano. 2017;11:7134-41.DOI: https://doi.org/10.1021/acsnano.7b02970.

[18] Cheng H, Huang Y, Cheng Q, Shi G, Jiang L, Qu L. Self-Healing Graphene Oxide Based Functional Architectures Triggered by Moisture. Adv Funct Mater. 2017;27:1703096.DOI: https://doi.org/10.1002/adfm.201703096.

[19] Yang S, Liu J, Pan F, Yin X, Wang L, Chen D, et al. Fabrication of self-healing and hydrophilic coatings from liquid-like graphene@SiO2 hybrids. Composites Science and Technology. 2016;136:133-44.DOI: https://doi.org/10.1016/j.compscitech.2016.10.012.

[20] D'Elia E, Barg S, Ni N, Rocha VG, Saiz E. Self-Healing Graphene-Based Composites with Sensing Capabilities. Adv Mater. 2015;27:4788-94.DOI: https://doi.org/10.1002/adma.201501653.

[21] Kim C, Ejima H, Yoshie N. Polymers with autonomous self-healing ability and remarkable reprocessability under ambient humidity conditions. Journal of Materials Chemistry A. 2018;6:19643-52.DOI: 10.1039/C8TA04769C.

[22] Li Ra, Fan T, Chen G, Zhang K, Su B, Tian J, et al. Autonomous Self-Healing, Antifreezing, and Transparent Conductive Elastomers. Chemistry of Materials. 2020;32:874-81.DOI: 10.1021/acs.chemmater.9b04592.

[23] Yang Y, Urban MW. Self-healing polymeric materials. Chemical Society Reviews. 2013;42:7446-67.DOI: https://doi.org/10.1039/C3CS60109A.

[24] Bai Y, Chen Y, Wang Q, Wang T. Poly(vinyl butyral) based polymer networks with dual-responsive shape memory and self-healing properties. Journal of Materials Chemistry A. 2014;2:9169-77.DOI: https://doi.org/10.1039/C4TA00856A.

[25] Ehrhardt D, Mangialetto J, Bertouille J, Van Durme K, Van Mele B, Van den Brande N. Self-Healing in Mobility-Restricted Conditions Maintaining Mechanical Robustness: Furan–Maleimide Diels–Alder Cycloadditions in Polymer Networks for Ambient Applications. Polymers. 2020;12:2543.DOI: https://doi.org/10.3390/polym12112543.

[26] Yang Z, Wang F, Zhang C, Li J, Zhang R, Wu Q, et al. Bio-inspired self-healing polyurethanes with multiple stimulus responsiveness. Polymer Chemistry. 2019;10:3362-70.DOI: https://doi.org/10.1039/C9PY00383E.

[27] Chakma P, Rodrigues Possarle LH, Digby ZA, Zhang B, Sparks JL, Konkolewicz D. Dual stimuli responsive self-healing and malleable materials based on dynamic thiol-Michael chemistry. Polymer Chemistry. 2017;8:6534-43.DOI: https://doi.org/10.1039/C7PY01356F.

[28] Chang R, Wang X, Li X, An H, Qin J. Self-Activated Healable Hydrogels with Reversible Temperature Responsiveness. ACS Applied Materials & Interfaces. 2016;8:25544-51.DOI: https://doi.org/10.1021/acsami.6b08279.

[29] Huang X, Wang X, Shi C, Liu Y, Wei Y. Research on synthesis and self-healing properties of interpenetrating network hydrogels based on reversible covalent and reversible non-covalent bonds. Journal of Polymer Research. 2021;28:1.DOI: https://doi.org/10.1007/s10965-020-02155-9.

[30] Suzuki N, Takahashi A, Ohishi T, Goseki R, Otsuka H. Enhancement of the stimuli-responsiveness and photo-stability of dynamic diselenide bonds and diselenide-containing polymers by neighboring aromatic groups. Polymer. 2018;154:281-90.DOI: https://doi.org/10.1016/j.polymer.2018.09.022.

[31] Ji S, Cao W, Yu Y, Xu H. Dynamic Diselenide Bonds: Exchange Reaction Induced by Visible Light without Catalysis. Angew Chem Int Ed Engl. 2014;53:6781-5.DOI: https://doi.org/10.1002/anie.201403442.

[32] Ji S, Cao W, Yu Y, Xu H. Visible-Light-Induced Self-Healing Diselenide-Containing Polyurethane Elastomer. Adv Mater. 2015;27:7740-5.DOI: https://doi.org/10.1002/adma.201503661.

[33] Xu H, Suzuki N, Takahashi A, Ohishi T, Goseki R, Xie X-M, et al. Structural reorganization and crack-healing properties of hydrogels based on dynamic diselenide linkages. Science and Technology of Advanced Materials. 2020;21:450-60.DOI: https://doi.org/10.1080/14686996.2020.1783967.

[34] Li H, Bai J, Shi Z, Yin J. Environmental friendly polymers based on schiff-base reaction with self-healing, remolding and degradable ability. Polymer. 2016;85:106-13.DOI: https://doi.org/10.1016/j.polymer.2016.01.050.

[35] Mo C, Xiang L, Chen Y. Advances in Injectable and Self-healing Polysaccharide Hydrogel Based on the Schiff Base Reaction. Macromol Rapid Commun. 2021;42:2100025.DOI: https://doi.org/10.1002/marc.202100025.

[36] Dai X, Du Y, Wang Y, Liu Y, Xu N, Li Y, et al. Stretchable Self-Healing Polymeric Networks with Recyclability and Dual Responsiveness. ACS Applied Polymer Materials. 2020;2:1065-72.DOI: https://doi.org/10.1021/acsapm.9b01073.

[37] Kim GY, Sung S, Kim MP, Kim SC, Lee S-H, Park YI, et al. Reversible polymer networks based on the dynamic hindered urea bond for scratch healing in automotive clearcoats. Applied Surface Science. 2020;505:144546.DOI: https://doi.org/10.1016/j.apsusc.2019.144546.

[38] Wang S, Yang Y, Ying H, Jing X, Wang B, Zhang Y, et al. Recyclable, Self-Healable, and Highly Malleable Poly(urethane-urea)s with Improved Thermal and Mechanical Performances. ACS Applied Materials & Interfaces. 2020;12:35403-14.DOI: https://doi.org/10.1021/acsami.0c07553.

[39] Liu Y, Tang Z, Wang D, Wu S, Guo B. Biomimetic design of elastomeric vitrimers with unparalleled mechanical properties, improved creep resistance and retained malleability by metal–ligand coordination. Journal of Materials Chemistry A. 2019;7:26867-76.DOI: https://doi.org/10.1039/C9TA10909A.

[40] Wang S, Ma S, Li Q, Xu X, Wang B, Huang K, et al. Facile Preparation of Polyimine Vitrimers with Enhanced Creep Resistance and Thermal and Mechanical Properties via Metal Coordination. Macromolecules. 2020;53:2919-31.DOI: https://doi.org/10.1021/acs.macromol.0c00036.

[41] Sánchez-Morán H, Ahmadi A, Vogler B, Roh K-H. Oxime Cross-Linked Alginate Hydrogels with Tunable Stress Relaxation. Biomacromolecules. 2019;20:4419-29.DOI: https://doi.org/10.1021/acs.biomac.9b01100.

[42] Niu X, Wang F, Kui X, Zhang R, Wang X, Li X, et al. Dual Cross-linked Vinyl Vitrimer with Efficient Self-Catalysis Achieving Triple-Shape-Memory Properties. Macromol Rapid Commun. 2019;40:1900313.DOI: https://doi.org/10.1002/marc.201900313.

[43] Xiong H, Li Y, Ye H, Huang G, Zhou D, Huang Y. Self-healing supramolecular hydrogels through host–guest interaction between cyclodextrin and carborane. Journal of Materials Chemistry B. 2020;8:10309-13.DOI: https://doi.org/10.1039/D0TB01886D.

[44] Sugane K, Shibata M. Self-healing thermoset polyurethanes utilizing host–guest interaction of cyclodextrin and adamantane. Polymer. 2021;221:123629.DOI: https://doi.org/10.1016/j.polymer.2021.123629.

[45] Collins J, Nadgorny M, Xiao Z, Connal LA. Doubly Dynamic Self-Healing Materials Based on Oxime Click Chemistry and Boronic Acids. Macromol Rapid Commun. 2017;38:1600760.DOI: https://doi.org/10.1002/marc.201600760.

[46] Safaei F, Khorasani SN, Rahnama H, Neisiany RE, Koochaki MS. Single microcapsules containing epoxy healing agent used for development in the fabrication of cost efficient self-healing epoxy coating. Progress in Organic Coatings. 2018;114:40-6.DOI: https://doi.org/10.1016/j.porgcoat.2017.09.019.

[47] Handique J, Dolui SK. Microencapsulated self-healing polymers via controlled, surface initiated atom transfer radical polymerization from the surface of graphene oxide. Journal of Polymer Research. 2018;25:217.DOI: https://doi.org/10.1007/s10965-018-1603-6.

[48] Sun C, Yarmohammadi A, Isfahani RB, Nejad MG, Toghraie D, Fard EK, et al. Self-healing polymers using electrosprayed microcapsules containing oil: Molecular dynamics simulation and experimental studies. Journal of Molecular Liquids. 2021;325:115182.DOI: https://doi.org/10.1016/j.molliq.2020.115182.

[49] Zhu Y, Ye XJ, Rong MZ, Zhang MQ. Self-healing glass fiber/epoxy composites with polypropylene tubes containing self-pressurized epoxy and mercaptan healing agents. Composites Science and Technology. 2016;135:146-52.DOI: https://doi.org/10.1016/j.compscitech.2016.09.020.

[50] Willocq B, Odent J, Dubois P, Raquez J-M. Advances in intrinsic self-healing polyurethanes and related composites. RSC Advances. 2020;10:13766-82.DOI: https://doi.org/10.1039/D0RA01394C.

[51] Liu Y-L, Chuo T-W. Self-healing polymers based on thermally reversible Diels–Alder chemistry. Polymer Chemistry. 2013;4:2194-205.DOI: https://doi.org/10.1039/C2PY20957H.

[52] Yang B, Gao S. Recent advances in the application of Diels-Alder reactions involving o-quinodimethanes, aza-o-quinone methides and o-quinone methides in natural product total synthesis. Chemical Society reviews. 2018;47:7926-53.DOI: https://doi.org/10.1039/c8cs00274f.

[53] Francesco Fringuelli AT. Thermal Diels–Alder Reaction. The Diels–Alder Reaction2001. p. 29-97.DOI: https://doi.org/10.1002/0470845813.ch2.

[54] Carey FA, Sundberg RJ. Concerted Cycloadditions, Unimolecular Rearrangements, and Thermal Eliminations. Advanced Organic Chemistry: Part B: Reactions and Synthesis. Boston, MA: Springer US; 2007. p. 473-617.DOI: https://doi.org/10.1007/978-0-387-71481-3_6.

[55] Bruice PY. Organic chemistry. 7 ed. Upper Saddle River, N.J.: Pearson Education Limited; 2014.

[56] Flory PJ, Gee G. Statistical thermodynamics of semi-flexible chain molecules. Proc R Soc Lon Ser-A. 1956;234:60-73.DOI: https://doi.org/10.1098/rspa.1956.0015.

[57] Gandini A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. Progress in Polymer Science. 2013;38:1-29.DOI: https://doi.org/10.1016/j.progpolymsci.2012.04.002.

[58] Kolb HC, Finn MG, Sharpless KB. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. Angew Chem Int Ed Engl. 2001;40:2004-21.DOI: https://doi.org/10.1002/1521-3773(20010601)40:11<2004::AID-ANIE2004>3.0.CO;2-5.

[59] Kawamoto K, Grindy SC, Liu J, Holten-Andersen N, Johnson JA. Dual Role for 1,2,4,5-Tetrazines in Polymer Networks: Combining Diels–Alder Reactions and Metal Coordination To

Generate Functional Supramolecular Gels. ACS Macro Letters. 2015;4:458-61.DOI: https://doi.org/10.1021/acsmacrolett.5b00221.

[60] Imai Y, Itoh H, Naka K, Chujo Y. Thermally Reversible IPN Organic−Inorganic Polymer Hybrids Utilizing the Diels−Alder Reaction. Macromolecules. 2000;33:4343-6.DOI: https://doi.org/10.1021/ma991899b.

[61] Chujo Y, Sada K, Saegusa T. Reversible gelation of polyoxazoline by means of Diels-Alder reaction. Macromolecules. 1990;23:2636-41.DOI: https://doi.org/10.1021/ma00212a007.

[62] Pramanik NB, Nando GB, Singha NK. Self-healing polymeric gel via RAFT polymerization and Diels–Alder click chemistry. Polymer. 2015;69:349-56.DOI: https://doi.org/10.1016/j.polymer.2015.01.023.

[63] Kirchhof S, Brandl FP, Hammer N, Goepferich AM. Investigation of the Diels–Alder reaction as a cross-linking mechanism for degradable poly(ethylene glycol) based hydrogels. Journal of Materials Chemistry B. 2013;1:4855-64.DOI: https://doi.org/10.1039/C3TB20831A.

[64] Yu F, Cao X, Li Y, Zeng L, Zhu J, Wang G, et al. Diels–Alder crosslinked HA/PEG hydrogels with high elasticity and fatigue resistance for cell encapsulation and articular cartilage tissue repair. Polymer Chemistry. 2014;5:5116-23.DOI: https://doi.org/10.1039/C4PY00473F.

[65] Wei H-L, Yang Z, Zheng L-M, Shen Y-M. Thermosensitive hydrogels synthesized by fast Diels–Alder reaction in water. Polymer. 2009;50:2836-40.DOI: https://doi.org/10.1016/j.polymer.2009.04.032.

[66] Wang G-F, Chu H-J, Wei H-L, Liu X-Q, Zhao Z-X, Zhu J. Click synthesis by Diels-Alder reaction and characterisation of hydroxypropyl methylcellulose-based hydrogels. Chemical Papers. 2014;68:1390-9.DOI: https://doi.org/10.2478/s11696-014-0574-2.

[67] Burmeister D, Ahrens L, Opitz A, Ligorio G, Hermerschmidt F, Jänsch D, et al. Utilizing Diels–Alder "click" chemistry to functionalize the organic–organic interface of semiconducting polymers. Journal of Materials Chemistry C. 2020;8:3302-7.DOI: https://doi.org/10.1039/C9TC06180K.

[68] Shibata M, Teramoto N, Akiba T, Ogihara M. High-performance hybrid materials prepared by the thermo-reversible Diels–Alder polymerization of furfuryl ester-terminated butylene succinate oligomers and maleimide compounds. Polymer Journal. 2011;43:455-63.DOI: https://doi.org/10.1038/pj.2011.14.

[69] Raut SK, Mondal P, Parameswaran B, Sarkar S, Dey P, Gilbert R, et al. Self-healable ultrahydrophobic modified bio-based elastomer using Diels-Alder 'click chemistry'. European Polymer Journal. 2021;146:110204.DOI: https://doi.org/10.1016/j.eurpolymj.2020.110204.

[70] Yeh C-M, Lin C-H, Han T-Y, Xiao Y-T, Chen Y-A, Chou H-H. Disulfide bond and Diels–Alder reaction bond hybrid polymers with high stretchability, transparency, recyclability, and intrinsic dual healability for skin-like tactile sensing. Journal of Materials Chemistry A. 2021;9:6109-16.DOI: https://doi.org/10.1039/D0TA10135D.

[71] Chennapuram M, Subba Reddy UV, Seki C, Okuyama Y, Kwon E, Uwai K, et al. Hybrid-Type Squaramide-Fused Amino Alcohol Organocatalysts for Enantioselective Diels–Alder Reactions of 3-Hydroxy-2-Pyridones with Maleimides. European Journal of Organic Chemistry. 2017;2017:4633-41.DOI: https://doi.org/10.1002/ejoc.201700830.

[72] Adachi K, Achimuthu AK, Chujo Y. Synthesis of Organic−Inorganic Polymer Hybrids Controlled by Diels−Alder Reaction. Macromolecules. 2004;37:9793-7.DOI: https://doi.org/10.1021/ma0400618.

[73] Lee YH, Ko WC, Zhuang YN, Wang LY, Yu TW, Lee SY, et al. Development of Self-Healable Organic/Inorganic Hybrid Materials Containing a Biobased Copolymer via Diels-Alder Chemistry and Their Application in Electromagnetic Interference Shielding. Polymers. 2019;11.DOI: https://doi.org/10.3390/polym11111755.

[74] Bapat AP, Ray JG, Savin DA, Hoff EA, Patton DL, Sumerlin BS. Dynamic-covalent nanostructures prepared by Diels–Alder reactions of styrene-maleic anhydride-derived copolymers obtained by one-step cascade block copolymerization. Polymer Chemistry. 2012;3:3112-20.DOI: https://doi.org/10.1039/C2PY20351K.

[75] Barthel MJ, Rudolph T, Crotty S, Schacher FH, Schubert US. Homo- and diblock copolymers of poly(furfuryl glycidyl ether) by living anionic polymerization: Toward reversibly core-crosslinked micelles. J Polym Sci Pol Chem. 2012;50:4958-65.DOI: https://doi.org/10.1002/pola.26327.

[76] McElhanon JR, Zifer T, Kline SR, Wheeler DR, Loy DA, Jamison GM, et al. Thermally Cleavable Surfactants Based on Furan−Maleimide Diels−Alder Adducts. Langmuir. 2005;21:3259-66.DOI: https://doi.org/10.1021/la047074z.

[77] Vauthier M, Jierry L, Martinez Mendez ML, Durst Y-M, Kelber J, Roucoules V, et al. Interfacial Diels–Alder Reaction between Furan-Functionalized Polymer Coatings and Maleimide-Terminated Poly(ethylene glycol). The Journal of Physical Chemistry C. 2019;123:4125-32.DOI: https://doi.org/10.1021/acs.jpcc.8b10533.

[78] Pratama PA, Peterson AM, Palmese GR. Diffusion and Reaction Phenomena in Solution-Based Healing of Polymer Coatings Using the Diels–Alder Reaction. Macromol Chem Phys. 2012;213:173-81.DOI: https://doi.org/10.1002/macp.201100407.

[79] Gevrek TN, Ozdeslik RN, Sahin GS, Yesilbag G, Mutlu S, Sanyal A. Functionalization of Reactive Polymeric Coatings via Diels–Alder Reaction Using Microcontact Printing. Macromol Chem Phys. 2012;213:166-72.DOI: https://doi.org/10.1002/macp.201100406.

[80] Gotsmann B, Duerig U, Frommer J, Hawker CJ. Exploiting Chemical Switching in a Diels–Alder Polymer for Nanoscale Probe Lithography and Data Storage. Adv Funct Mater. 2006;16:1499-505.DOI: https://doi.org/10.1002/adfm.200500724.

[81] Adzima BJ, Kloxin CJ, DeForest CA, Anseth KS, Bowman CN. 3D Photofixation Lithography in Diels–Alder Networks. Macromol Rapid Commun. 2012;33:2092-6.DOI: https://doi.org/10.1002/marc.201200599.

[82] Sparks BGT, P F; Poling, B E. Storing solar energy by liquid phase Diels-Alder reactions. AIChE Symp Ser; (United States)1981.

[83] Sparks BG, Poling BE. Energy storage capacity of reversible liquid-phase Diels Alder reaction between maleic anhydride and 2-methyl furan. Aiche J. 1983;29:534-7.DOI: https://doi.org/10.1002/aic.690290403.

[84] Yang S, Du X, Deng S, Qiu J, Du Z, Cheng X, et al. Recyclable and self-healing polyurethane composites based on Diels-Alder reaction for efficient solar-to-thermal energy storage. Chemical Engineering Journal. 2020;398:125654.DOI: https://doi.org/10.1016/j.cej.2020.125654.

[85] Thongsomboon W, Sherwood M, Arellano N, Nelson A. Thermally Induced Nanoimprinting of Biodegradable Polycarbonates Using Dynamic Covalent Cross-Links. ACS Macro Letters. 2013;2:19-22.DOI: https://doi.org/10.1021/mz300628s.

[86] Glassner M, Blinco JP, Barner-Kowollik C. Formation of nanoporous materials via mild retro-Diels–Alder chemistry. Polymer Chemistry. 2011;2:83-7.DOI: https://doi.org/10.1039/C0PY00267D.

[87] Li F, Li X, Zhang X. Dynamic Diels–Alder reactions of maleimide–furan amphiphiles and their fluorescence ON/OFF behaviours. Organic & Biomolecular Chemistry. 2018;16:7871-7.DOI: https://doi.org/10.1039/C8OB01944D.

[88] Goussé C, Gandini A, Hodge P. Application of the Diels−Alder Reaction to Polymers Bearing Furan Moieties. 2. Diels−Alder and Retro-Diels−Alder Reactions Involving Furan Rings in Some Styrene Copolymers. Macromolecules. 1998;31:314-21.DOI: https://doi.org/10.1021/ma9710141.

[89] Canary SA, Stevens MP. Thermally reversible crosslinking of polystyrene via the furan–maleimide Diels–Alder reaction. Journal of Polymer Science Part A: Polymer Chemistry. 1992;30:1755-60.DOI: https://doi.org/10.1002/pola.1992.080300829.

[90] Chen X, Wudl F, Mal AK, Shen H, Nutt SR. New Thermally Remendable Highly Cross-Linked Polymeric Materials. Macromolecules. 2003;36:1802-7.DOI: https://doi.org/10.1021/ma0210675.

[91] Plaisted TA, Nemat-Nasser S. Quantitative evaluation of fracture, healing and re-healing of a reversibly cross-linked polymer. Acta Materialia. 2007;55:5684-96.DOI: https://doi.org/10.1016/j.actamat.2007.06.019.

[92] Behera PK, Mondal P, Singha NK. Self-Healable and Ultrahydrophobic Polyurethane-POSS Hybrids by Diels–Alder “Click” Reaction: A New Class of Coating Material. Macromolecules. 2018;51:4770-81.DOI: 10.1021/acs.macromol.8b00583.

[93] Feng Z, Guo J, Cao X, Feng G, Chen Z, Zhang X-H. A thermo-reversible furfuryl poly(thioether)-b-polysiloxane-b-furfuryl poly(thioether) triblock copolymer as a promising material for high dielectric applications. Polymer Chemistry. 2022;13:1376-86.DOI: 10.1039/D2PY00043A.

[94] Kishi H, Fujita A, Miyazaki H, Matsuda S, Murakami A. Synthesis of wood-based epoxy resins and their mechanical and adhesive properties. J Appl Polym Sci. 2006;102:2285-92.DOI: https://doi.org/10.1002/app.24433.

[95] Gao W, Bie M, Liu F, Chang P, Quan Y. Self-Healable and Reprocessable Polysulfide Sealants Prepared from Liquid Polysulfide Oligomer and Epoxy Resin. ACS Applied Materials & Interfaces. 2017;9:15798-808.DOI: https://doi.org/10.1021/acsami.7b05285.

[96] David R, Raja VS, Singh SK, Gore P. Development of anti-corrosive paint with improved toughness using carboxyl terminated modified epoxy resin. Progress in Organic Coatings. 2018;120:58-70.DOI: https://doi.org/10.1016/j.porgcoat.2018.03.013.

[97] Capricho JC, Fox B, Hameed N. Multifunctionality in Epoxy Resins. Polymer Reviews. 2020;60:1-41.DOI: https://doi.org/10.1080/15583724.2019.1650063.

[98] Jin F-L, Li X, Park S-J. Synthesis and application of epoxy resins: A review. Journal of Industrial and Engineering Chemistry. 2015;29:1-11.DOI: https://doi.org/10.1016/j.jiec.2015.03.026.

[99] Liu Y-L, Hsieh C-Y. Crosslinked epoxy materials exhibiting thermal remendablility and removability from multifunctional maleimide and furan compounds. J Polym Sci Pol Chem. 2006;44:905-13.DOI: https://doi.org/10.1002/pola.21184.

[100] Li J, Zhang G, Deng L, Jiang K, Zhao S, Gao Y, et al. Thermally reversible and self-healing novolac epoxy resins based on Diels–Alder chemistry. J Appl Polym Sci. 2015;132:n/a-n/a.DOI: https://doi.org/10.1002/app.42167.

[101] Peterson AM, Jensen RE, Palmese GR. Room-Temperature Healing of a Thermosetting Polymer Using the Diels−Alder Reaction. ACS Applied Materials & Interfaces. 2010;2:1141-9.DOI: https://doi.org/10.1021/am9009378.

[102] Tian Q, Yuan YC, Rong MZ, Zhang MQ. A thermally remendable epoxy resin. Journal of Materials Chemistry. 2009;19:1289-96.DOI: https://doi.org/10.1039/B811938D.

[103] Dello Iacono S, Martone A, Pastore A, Filippone G, Acierno D, Zarrelli M, et al. Thermally activated multiple self-healing diels-alder epoxy system. Polymer Engineering & Science. 2017;57:674-9.DOI: https://doi.org/10.1002/pen.24570.

[104] Coope TS, Turkenburg DH, Fischer HR, Luterbacher R, van Bracht H, Bond IP. Novel Diels-Alder based self-healing epoxies for aerospace composites. Smart Materials and Structures. 2016;25:084010.DOI: https://doi.org/10.1088/0964-1726/25/8/084010.

[105] Zolghadr M, Shakeri A, Zohuriaan-Mehr MJ, Salimi A. Self-healing semi-IPN materials from epoxy resin by solvent-free furan–maleimide Diels–Alder polymerization. J Appl Polym Sci. 2019;136:48015.DOI: https://doi.org/10.1002/app.48015.

[106] Urdl K, Weiss S, Christöfl P, Kandelbauer A, Müller U, Kern W. Diels-Alder modified self-healing melamine resin. European Polymer Journal. 2020;127:109601.DOI: https://doi.org/10.1016/j.eurpolymj.2020.109601.

[107] Guo Y-k, Li H, Zhao P-x, Wang X-f, Astruc D, Shuai M-b. Thermo-reversible MWCNTs/epoxy polymer for use in self-healing and recyclable epoxy adhesive. Chinese Journal of Polymer Science. 2017;35:728-38.DOI: https://doi.org/10.1007/s10118-017-1920-y.

[108] Handique J, Dolui SK. A thermally remendable multiwalled carbon nanotube/epoxy composites via Diels-Alder bonding. Journal of Polymer Research. 2019;26:163.DOI: https://doi.org/10.1007/s10965-019-1804-7.

[109] Guo Y, Zou D, Zhu W, Yang X, Zhao P, Chen C, et al. Infrared induced repeatable self-healing and removability of mechanically enhanced graphene–epoxy flexible materials. RSC Advances. 2019;9:14024-32.DOI: https://doi.org/10.1039/C9RA00261H.

[110] Li Q-T, Jiang M-J, Wu G, Chen L, Chen S-C, Cao Y-X, et al. Photothermal Conversion Triggered Precisely Targeted Healing of Epoxy Resin Based on Thermoreversible Diels–Alder Network and Amino-Functionalized Carbon Nanotubes. ACS Applied Materials & Interfaces. 2017;9:20797-807.DOI: https://doi.org/10.1021/acsami.7b01954.

[111] Khan NI, Halder S, Wang J. Diels-Alder based epoxy matrix and interfacial healing of bismaleimide grafted GNP infused hybrid nanocomposites. Polymer Testing. 2019;74:138-51.DOI: https://doi.org/10.1016/j.polymertesting.2018.12.021.

[112] Zhang Y, Broekhuis AA, Picchioni F. Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers? Macromolecules. 2009;42:1906-12.DOI: https://doi.org/10.1021/ma8027672.

[113] Toncelli C, De Reus DC, Picchioni F, Broekhuis AA. Properties of Reversible Diels–Alder Furan/Maleimide Polymer Networks as Function of Crosslink Density. Macromol Chem Phys. 2012;213:157-65.DOI: https://doi.org/10.1002/macp.201100405.

[114] Yoshie N, Watanabe M, Araki H, Ishida K. Thermo-responsive mending of polymers crosslinked by thermally reversible covalent bond: Polymers from bisfuranic terminated poly(ethylene adipate) and tris-maleimide. Polymer Degradation and Stability. 2010;95:826-9.DOI: https://doi.org/10.1016/j.polymdegradstab.2010.01.032.

[115] Du P, Liu X, Zheng Z, Wang X, Joncheray T, Zhang Y. Synthesis and characterization of linear self-healing polyurethane based on thermally reversible Diels–Alder reaction. RSC Advances. 2013;3:15475-82.DOI: https://doi.org/10.1039/C3RA42278J.

[116] Du P, Wu M, Liu X, Zheng Z, Wang X, Joncheray T, et al. Diels–Alder-based crosslinked self-healing polyurethane/urea from polymeric methylene diphenyl diisocyanate. J Appl Polym Sci. 2014;131:n/a-n/a.DOI: https://doi.org/10.1002/app.40234.

[117] Park JS, Darlington T, Starr AF, Takahashi K, Riendeau J, Thomas Hahn H. Multiple healing effect of thermally activated self-healing composites based on Diels–Alder reaction. Composites Science and Technology. 2010;70:2154-9.DOI: https://doi.org/10.1016/j.compscitech.2010.08.017.

[118] Yu F, Cao X, Du J, Wang G, Chen X. Multifunctional Hydrogel with Good Structure Integrity, Self-Healing, and Tissue-Adhesive Property Formed by Combining Diels–Alder Click Reaction and Acylhydrazone Bond. ACS Applied Materials & Interfaces. 2015;7:24023-31.DOI: https://doi.org/10.1021/acsami.5b06896.

[119] Wu S, Li J, Zhang G, Yao Y, Li G, Sun R, et al. Ultrafast Self-Healing Nanocomposites via Infrared Laser and Their Application in Flexible Electronics. ACS Applied Materials & Interfaces. 2017;9:3040-9.DOI: https://doi.org/10.1021/acsami.6b15476.

[120] Li J, Zhang G, Sun R, Wong C-P. A covalently cross-linked reduced functionalized graphene oxide/polyurethane composite based on Diels–Alder chemistry and its potential application in healable flexible electronics. Journal of Materials Chemistry C. 2017;5:220-8.DOI: https://doi.org/10.1039/C6TC04715G.

[121] Adzima BJ, Kloxin CJ, Bowman CN. Externally Triggered Healing of a Thermoreversible Covalent Network via Self-Limited Hysteresis Heating. Adv Mater. 2010;22:2784-7.DOI: https://doi.org/10.1002/adma.200904138.

[122] Ahmed AS, Ramanujan RV. Curie temperature controlled self-healing magnet–polymer composites. Journal of Materials Research. 2015;30:946-58.DOI: https://doi.org/10.1557/jmr.2015.59.

[123] In C-W, Holland RB, Kim J-Y, Kurtis KE, Kahn LF, Jacobs LJ. Monitoring and evaluation of self-healing in concrete using diffuse ultrasound. NDT & E International. 2013;57:36-44.DOI: https://doi.org/10.1016/j.ndteint.2013.03.005.

[124] Zeng C, Seino H, Ren J, Hatanaka K, Yoshie N. Bio-Based Furan Polymers with Self-Healing Ability. Macromolecules. 2013;46:1794-802.DOI: https://doi.org/10.1021/ma3023603.

[125] Eraghi Kazzaz A, Hosseinpour Feizi Z, Fatehi P. Grafting strategies for hydroxy groups of lignin for producing materials. Green Chemistry. 2019;21:5714-52.DOI: https://doi.org/10.1039/C9GC02598G.

[126] Buono P, Duval A, Averous L, Habibi Y. Thermally healable and remendable lignin-based materials through Diels – Alder click polymerization. Polymer. 2017;133:78-88.DOI: https://doi.org/10.1016/j.polymer.2017.11.022.

[127] Li D-q, Wang S-y, Meng Y-j, Guo Z-w, Cheng M-m, Li J. Fabrication of self-healing pectin/chitosan hybrid hydrogel via Diels-Alder reactions for drug delivery with high swelling property, pH-responsiveness, and cytocompatibility. Carbohydrate Polymers. 2021;268:118244.DOI: https://doi.org/10.1016/j.carbpol.2021.118244.

[128] Islam S, Bhat G. Progress and challenges in self-healing composite materials. Materials Advances. 2021;2:1896-926.DOI: https://doi.org/10.1039/D0MA00873G.

[129] Zhu Y, Yao C, Ren J, Liu C, Ge L. Graphene improved electrochemical property in self-healing multilayer polyelectrolyte film. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2015;465:26-31.DOI: https://doi.org/10.1016/j.colsurfa.2014.10.035.

[130] Willocq B, Bose RK, Khelifa F, Garcia SJ, Dubois P, Raquez JM. Healing by the Joule effect of electrically conductive poly(ester-urethane)/carbon nanotube nanocomposites. Journal of Materials Chemistry A. 2016;4:4089-97.DOI: https://doi.org/10.1039/C5TA09793B.

[131] Li G, Xiao P, Hou S, Huang Y. Graphene based self-healing materials. Carbon. 2019;146:371-87.DOI: https://doi.org/10.1016/j.carbon.2019.02.011.

[132] Chee WK, Lim HN, Huang NM, Harrison I. Nanocomposites of graphene/polymers: a review. RSC Advances. 2015;5:68014-51.DOI: https://doi.org/10.1039/C5RA07989F.

[133] Zhao L, Jiang B, Huang Y. Functionalized graphene-reinforced polysiloxane nanocomposite with improved mechanical performance and efficient healing properties. J Appl Polym Sci. 2019;136:47725.DOI: https://doi.org/10.1002/app.47725.

[134] Li J, Zhang G, Deng L, Zhao S, Gao Y, Jiang K, et al. In situ polymerization of mechanically reinforced, thermally healable graphene oxide/polyurethane composites based on

Diels–Alder chemistry. Journal of Materials Chemistry A. 2014;2:20642-9.DOI: https://doi.org/10.1039/C4TA04941A.

[135] Lee WJ, Cha SH. Improvement of Mechanical and Self-Healing Properties for Polymethacrylate Derivatives Containing Maleimide Modified Graphene Oxide. Polymers. 2020;12.DOI: https://doi.org/10.3390/polym12030603.

[136] Ding S, Zhang J, Zhou L, Luo Y. Promoting healing progress in polymer composites based on Diels-Alder reaction by constructing silver bridges. 2021;32:1239-50.DOI: https://doi.org/10.1002/pat.5173.

[137] Wang H, Yan R, Zou Y, Xing D, Zhong K. Light-driven self-healing polyurethane based on PDA@Ag nanoparticles with improved mechanical and antibacterial properties. Journal of Materials Chemistry B. 2022;10:1085-93.DOI: 10.1039/D1TB02710G.

[138] Lin C, Sheng D, Liu X, Xu S, Ji F, Dong L, et al. Effect of different sizes of graphene on Diels-Alder self-healing polyurethane. Polymer. 2019;182:121822.DOI: https://doi.org/10.1016/j.polymer.2019.121822.

[139] Pratama PA, Sharifi M, Peterson AM, Palmese GR. Room Temperature Self-Healing Thermoset Based on the Diels–Alder Reaction. ACS Applied Materials & Interfaces. 2013;5:12425-31.DOI: https://doi.org/10.1021/am403459e.

[140] Ingoglia BT. Microencapsulation of Diels-Alder Monomers in Self-Healing Materials. Kaleidoscope. 2014;11.

[141] Santos SC, La Scala JJ, Palmese GR. Effect of Microcapsule Content on Diels-Alder Room Temperature Self-Healing Thermosets. Polymers. 2020;12.DOI: https://doi.org/10.3390/polym12123064.

[142] Sugane K, Yoshioka Y, Shimasaki T, Teramoto N, Shibata M. Self-healing 8-armed star-shaped ε-caprolactone oligomers dually crosslinked by the Diels-Alder and urethanization reactions. Polymer. 2018;144:92-102.DOI: https://doi.org/10.1016/j.polymer.2018.04.045.

[143] Tasdelen MA. Diels–Alder “click” reactions: recent applications in polymer and material science. Polymer Chemistry. 2011;2:2133-45.DOI: https://doi.org/10.1039/C1PY00041A.

[144] Syrett JA, Mantovani G, Barton WRS, Price D, Haddleton DM. Self-healing polymers prepared via living radical polymerisation. Polymer Chemistry. 2010;1:102-6.DOI: https://doi.org/10.1039/B9PY00316A.

[145] Yoshie N, Saito S, Oya N. A thermally-stable self-mending polymer networked by Diels–Alder cycloaddition. Polymer. 2011;52:6074-9.DOI: https://doi.org/10.1016/j.polymer.2011.11.007.

[146] Heo Y, Malakooti MH, Sodano HA. Self-healing polymers and composites for extreme environments. Journal of Materials Chemistry A. 2016;4:17403-11.DOI: https://doi.org/10.1039/C6TA06213J.

[147] Mondal P, Jana G, Behera PK, Chattaraj PK, Singha NK. A new healable polymer material based on ultrafast Diels–Alder ‘click’ chemistry using triazolinedione and fluorescent anthracyl derivatives: a mechanistic approach. Polymer Chemistry. 2019;10:5070-9.DOI: 10.1039/C9PY00499H.

[148] Briou B, Améduri B, Boutevin B. Trends in the Diels–Alder reaction in polymer chemistry. Chemical Society Reviews. 2021;50:11055-97.DOI: https://doi.org/10.1039/D0CS01382J.

[149] Kennedy JP, Castner KF. Thermally reversible polymer systems by cyclopentadienylation. II. The synthesis of cyclopentadiene-containing polymers. Journal of Polymer Science: Polymer Chemistry Edition. 1979;17:2055-70.DOI: https://doi.org/10.1002/pol.1979.170170715.

[150] Murphy EB, Bolanos E, Schaffner-Hamann C, Wudl F, Nutt SR, Auad ML. Synthesis and Characterization of a Single-Component Thermally Remendable Polymer Network: Staudinger and Stille Revisited. Macromolecules. 2008;41:5203-9.DOI: https://doi.org/10.1021/ma800432g.

[151] Park JS, Takahashi K, Guo Z, Wang Y, Bolanos E, Hamann-Schaffner C, et al. Towards Development of a Self-Healing Composite using a Mendable Polymer and Resistive Heating. J Compos Mater. 2008;42:2869-81.DOI: https://doi.org/10.1177/0021998308097280.

[152] Park J-H, Kong W-S, Lee S-H, Lee JW, Yoon HG, Lee BY. Characterization and application of propylene grafted hydrogenated dicyclopentadiene hydrocarbon resin. International Journal of Adhesion and Adhesives. 2016;68:326-32.DOI: https://doi.org/10.1016/j.ijadhadh.2016.04.002.

[153] Wu Y, Li K. Acrylated epoxidized soybean oil as a styrene replacement in a dicyclopentadiene-modified unsaturated polyester resin. J Appl Polym Sci. 2018;135:46212.DOI: https://doi.org/10.1002/app.46212.

[154] Inglis AJ, Nebhani L, Altintas O, Schmidt FG, Barner-Kowollik C. Rapid Bonding/Debonding on Demand: Reversibly Cross-Linked Functional Polymers via Diels−Alder Chemistry. Macromolecules. 2010;43:5515-20.DOI: https://doi.org/10.1021/ma100945b.

[155] Zhou J, Guimard NK, Inglis AJ, Namazian M, Lin CY, Coote ML, et al. Thermally reversible Diels–Alder-based polymerization: an experimental and theoretical assessment. Polymer Chemistry. 2012;3:628-39.DOI: https://doi.org/10.1039/C1PY00356A.

[156] Guimard NK, Ho J, Brandt J, Lin CY, Namazian M, Mueller JO, et al. Harnessing entropy to direct the bonding/debonding of polymer systems based on reversible chemistry. Chemical Science. 2013;4:2752-9.DOI: https://doi.org/10.1039/C3SC50642H.

[157] Oehlenschlaeger KK, Guimard NK, Brandt J, Mueller JO, Lin CY, Hilf S, et al. Fast and catalyst-free hetero-Diels–Alder chemistry for on demand cyclable bonding/debonding materials. Polymer Chemistry. 2013;4:4348-55.DOI: https://doi.org/10.1039/C3PY00476G.

[158] Oehlenschlaeger KK, Mueller JO, Brandt J, Hilf S, Lederer A, Wilhelm M, et al. Adaptable Hetero Diels–Alder Networks for Fast Self-Healing under Mild Conditions. Adv Mater. 2014;26:3561-6.DOI: https://doi.org/10.1002/adma.201306258.

[159] Reutenauer P, Buhler E, Boul PJ, Candau SJ, Lehn JM. Room temperature dynamic polymers based on Diels-Alder chemistry. Chemistry (Weinheim an der Bergstrasse, Germany). 2009;15:1893-900.DOI: https://doi.org/10.1002/chem.200802145.

[160] Wei Z, Yang JH, Du XJ, Xu F, Zrinyi M, Osada Y, et al. Dextran-based self-healing hydrogels formed by reversible diels-alder reaction under physiological conditions. Macromol Rapid Commun. 2013;34:1464-70.DOI: https://doi.org/10.1002/marc.201300494.

[161] Dewar MJS, Olivella S, Stewart JJP. Mechanism of the Diels-Alder reaction: reactions of butadiene with ethylene and cyanoethylenes. Journal of the American Chemical Society. 1986;108:5771-9.DOI: 10.1021/ja00279a018.

[162] Jo YY, Lee AS, Baek K-Y, Lee H, Hwang SS. Thermally reversible self-healing polysilsesquioxane structure-property relationships based on Diels-Alder chemistry. Polymer. 2017;108:58-65.DOI: https://doi.org/10.1016/j.polymer.2016.11.040.

[163] Settle AE, Berstis L, Rorrer NA, Roman-Leshkóv Y, Beckham GT, Richards RM, et al. Heterogeneous Diels–Alder catalysis for biomass-derived aromatic compounds. Green Chemistry. 2017;19:3468-92.DOI: 10.1039/C7GC00992E.

[164] Hornung CH, Álvarez-Diéguez MÁ, Kohl TM, Tsanaktsidis J. Diels–Alder reactions of myrcene using intensified continuous-flow reactors. Beilstein Journal of Organic Chemistry. 2017;13:120-6.DOI: 10.3762/bjoc.13.15.

[165] Orzolek BJ, Rahman MA, Iovine PM. Synthesis of Biorenewable Starch–Farnesene Amphiphilic Conjugates via Transesterification of Terpene-Derived Diels–Alder Adducts. ACS Sustainable Chemistry & Engineering. 2018;6:13562-9.DOI: 10.1021/acssuschemeng.8b03771.

[166] Kathalewar M, Sabnis A. Epoxy resin from cardanol as partial replacement of bisphenol-A-based epoxy for coating application. Journal of Coatings Technology and Research. 2014;11:601-18.DOI: 10.1007/s11998-014-9570-2.

[167] Malshe VC, Phadke JP, Jadhav MA. Diels-Alder adduct of sorbic acid and methyl ester of soyabean oil as substitute to conventional dimer acids. Pigment & Resin Technology. 2013;42:15-23.DOI: 10.1108/03699421311288724.

[168] Nagao K, Yanagita T. Conjugated fatty acids in food and their health benefits. Journal of Bioscience and Bioengineering. 2005;100:152-7.DOI: https://doi.org/10.1263/jbb.100.152.

[169] Kong L, Han X, Jiao P. Catalytic asymmetric Diels–Alder reactions involving aryl vinyl ketones. Chemical Communications. 2014;50:14113-6.DOI: 10.1039/C4CC06837H.

[170] Lejeail M, Fischer HR. Investigations on the replacement of bismaleimide by the bio-based bisitaconimide for recyclable thermoset composites based on thermo-reversible Diels-Alder cross-links. European Polymer Journal. 2020;131:109699.DOI: https://doi.org/10.1016/j.eurpolymj.2020.109699.

[171] Gaina V, Gaina C. AB monomers: II, synthesis and polymerization of AB monomers containing citracon- or maleimide and allylphenyl groups. Designed Monomers and Polymers. 2007;10:91-104.DOI: 10.1163/156855507779763621.

[172] Molinari A, Oliva A, Reinoso P, del Corral JMM, Castro MA, Gordaliza M, et al. Cytotoxic–antineoplastic activity of hydroquinone derivatives. European Journal of Medicinal Chemistry. 2002;37:177-82.DOI: https://doi.org/10.1016/S0223-5234(01)01329-0.

[173] Banert K, Schumann P. Diastereoselective Tandem Diels-Alder Macrocyclizations Starting from Sorbyl or Sorboyl Derivatives. Synlett. 2008;2008:535-8.

[174] Chung C-M, Roh Y-S, Cho S-Y, Kim J-G. Crack Healing in Polymeric Materials via Photochemical [2+2] Cycloaddition. Chemistry of Materials. 2004;16:3982-4.DOI: https://doi.org/10.1021/cm049394+.

[175] Oya N, Sukarsaatmadja P, Ishida K, Yoshie N. Photoinduced mendable network polymer from poly(butylene adipate) end-functionalized with cinnamoyl groups. Polymer Journal. 2012;44:724-9.DOI: https://doi.org/10.1038/pj.2012.18.

[176] Hu L, Cheng X, Zhang A. A facile method to prepare UV light-triggered self-healing polyphosphazenes. Journal of Materials Science. 2015;50:2239-46.DOI: https://doi.org/10.1007/s10853-014-8786-y.

[177] Froimowicz P, Klinger D, Landfester K. Photoreactive Nanoparticles as Nanometric Building Blocks for the Generation of Self-Healing Hydrogel Thin Films. Chemistry (Weinheim an der Bergstrasse, Germany). 2011;17:12465-75.DOI: https://doi.org/10.1002/chem.201100685.

[178] Ling J, Rong MZ, Zhang MQ. Coumarin imparts repeated photochemical remendability to polyurethane. Journal of Materials Chemistry. 2011;21:18373-80.DOI: https://doi.org/10.1039/C1JM13467A.

[179] Ling J, Rong MZ, Zhang MQ. Photo-stimulated self-healing polyurethane containing dihydroxyl coumarin derivatives. Polymer. 2012;53:2691-8.DOI: https://doi.org/10.1016/j.polymer.2012.04.016.

[180] Mandal DK. Chapter 5 - Cycloadditions 2: Stereochemistry of [4+2] and [2+2] Cycloadditions. In: Mandal DK, editor. Pericyclic Chemistry: Elsevier; 2018. p. 191-268.DOI: https://doi.org/10.1016/B978-0-12-814958-4.00005-2.

[181] Abdallh M, He P, Hearn MTW, Simon GP, Saito K. Light-Switchable Self-Healing Dynamic Linear Polymers: Reversible Cycloaddition Reactions of Thymine-Containing Units. Chempluschem. 2019;84:333-7.DOI: https://doi.org/10.1002/cplu.201900079.

[182] Kim S, Kim B-H, Oh M, Park DH, Lee S. Repeatable Crack Self-Healing by Photochemical [2 + 2] Cycloaddition of TCE-co-DCE Monomers Enclosed in Homopolymer Microcapsules. Polymers. 2019;11:104.DOI: https://doi.org/10.3390/polym11010104.

[183] Han D, Lu H, Li W, Li Y, Feng S. Light- and heat-triggered reversible luminescent materials based on polysiloxanes with anthracene groups. RSC Advances. 2017;7:56489-95.DOI: https://doi.org/10.1039/C7RA12201B.

[184] Dong S, Ong A, Chi C. Photochemistry of various acene based molecules. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2019;38:27-46.DOI: https://doi.org/10.1016/j.jphotochemrev.2018.12.002.

[185] Kuhl N, Bode S, Hager MD, Schubert US. Self-Healing Polymers Based on Reversible Covalent Bonds. In: Hager MD, van der Zwaag S, Schubert US, editors. Self-healing Materials. Cham: Springer International Publishing; 2016. p. 1-58.DOI: https://doi.org/10.1007/12_2015_336.

[186] Sieburth SM, Cunard NT. The [4 + 4] cycloaddition and its strategic application in natural product synthesis. Tetrahedron. 1996;52:6251-82.DOI: https://doi.org/10.1016/0040-4020(95)01077-7.

[187] Connal LA, Vestberg R, Hawker CJ, Qiao GG. Fabrication of Reversibly Crosslinkable, 3-Dimensionally Conformal Polymeric Microstructures. Adv Funct Mater. 2008;18:3315-22.DOI: https://doi.org/10.1002/adfm.200800333.

[188] Froimowicz P, Frey H, Landfester K. Towards the Generation of Self-Healing Materials by Means of a Reversible Photo-induced Approach. Macromol Rapid Commun. 2011;32:468-73.DOI: https://doi.org/10.1002/marc.201000643.

[189] Xu J-F, Chen Y-Z, Wu L-Z, Tung C-H, Yang Q-Z. Dynamic Covalent Bond Based on Reversible Photo [4 + 4] Cycloaddition of Anthracene for Construction of Double-Dynamic Polymers. Organic Letters. 2013;15:6148-51.DOI: https://doi.org/10.1021/ol403015s.

[190] He Z, Niu H, Li Y. UV-Light Responsive and Self-Healable Ethylene/Propylene Copolymer Rubbers Based on Reversible [4 + 4] Cycloaddition of Anthracene Derivatives. Macromol Chem Phys. 2020;221:2000096.DOI: https://doi.org/10.1002/macp.202000096.

[191] Fortman DJ, Snyder RL, Sheppard DT, Dichtel WR. Rapidly Reprocessable Cross-Linked Polyhydroxyurethanes Based on Disulfide Exchange. ACS Macro Letters. 2018;7:1226-31.DOI: https://doi.org/10.1021/acsmacrolett.8b00667.

[192] Bapat AP, Ray JG, Savin DA, Sumerlin BS. Redox-Responsive Dynamic-Covalent Assemblies: Stars and Miktoarm Stars. Macromolecules. 2013;46:2188-98.DOI: https://doi.org/10.1021/ma400169m.

[193] Pepels M, Filot I, Klumperman B, Goossens H. Self-healing systems based on disulfide–thiol exchange reactions. Polymer Chemistry. 2013;4:4955-65.DOI: https://doi.org/10.1039/C3PY00087G.

[194] Fairbanks BD, Singh SP, Bowman CN, Anseth KS. Photodegradable, Photoadaptable Hydrogels via Radical-Mediated Disulfide Fragmentation Reaction. Macromolecules. 2011;44:2444-50.DOI: https://doi.org/10.1021/ma200202w.

[195] Eom Y, Kim S-M, Lee M, Jeon H, Park J, Lee ES, et al. Mechano-responsive hydrogen-bonding array of thermoplastic polyurethane elastomer captures both strength and self-healing. Nature Communications. 2021;12:621.DOI: https://doi.org/10.1038/s41467-021-20931-z.

[196] Qu Q, Wang H, He J, Qin T, Da Y, Tian X. Analysis of the microphase structure and performance of self-healing polyurethanes containing dynamic disulfide bonds. Soft Matter. 2020;16:9128-39.DOI: https://doi.org/10.1039/D0SM01072C.

[197] Lin H-K, Liu Y-L. Reactive Hybrid of Polyhedral Oligomeric Silsesquioxane (POSS) and Sulfur as a Building Block for Self-Healing Materials. Macromol Rapid Commun. 2017;38:1700051.DOI: https://doi.org/10.1002/marc.201700051.

[198] Zhao D, Du Z, Liu S, Wu Y, Guan T, Sun Q, et al. UV Light Curable Self-Healing Superamphiphobic Coatings by Photopromoted Disulfide Exchange Reaction. ACS Applied Polymer Materials. 2019;1:2951-60.DOI: https://doi.org/10.1021/acsapm.9b00656.

[199] Fu Q, Yan Q, Zhou M, Xie W, Fu H. Study on UV/sunlight curable self-healing topological polysulfide polymer network based on disulfide exchange. Polym Advan Technol. 2021;32:2252-61.DOI: https://doi.org/10.1002/pat.5259.

[200] Rodriguez-Docampo Z, Otto S. Orthogonal or simultaneous use of disulfide and hydrazone exchange in dynamic covalent chemistry in aqueous solution. Chemical Communications. 2008:5301-3.DOI: https://doi.org/10.1039/B808725C.

[201] Guo H, Han Y, Zhao W, Yang J, Zhang L. Universally autonomous self-healing elastomer with high stretchability. Nature Communications. 2020;11:2037.DOI: https://doi.org/10.1038/s41467-020-15949-8.

[202] Bagiyan GA, Koroleva IK, Soroka NV, Ufimtsev AV. Oxidation of thiol compounds by molecular oxygen in aqueous solutions. Russian Chemical Bulletin. 2003;52:1135-41.DOI: https://doi.org/10.1023/A:1024761324710.

[203] Golkaram M, Fodor C, van Ruymbeke E, Loos K. Linear Viscoelasticity of Weakly Hydrogen-Bonded Polymers near and below the Sol–Gel Transition. Macromolecules. 2018;51:4910-6.DOI: https://doi.org/s10.1021/acs.macromol.8b00772.

[204] Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature. 2008;451:977-80.DOI: https://doi.org/10.1038/nature06669.

[205] Montarnal D, Cordier P, Soulié-Ziakovic C, Tournilhac F, Leibler L. Synthesis of self-healing supramolecular rubbers from fatty acid derivatives, diethylene triamine, and urea. Journal of Polymer Science Part A: Polymer Chemistry. 2008;46:7925-36.DOI: https://doi.org/10.1002/pola.23094.

[206] Montarnal D, Tournilhac F, Hidalgo M, Couturier J-L, Leibler L. Versatile One-Pot Synthesis of Supramolecular Plastics and Self-Healing Rubbers. Journal of the American Chemical Society. 2009;131:7966-7.DOI: https://doi.org/10.1021/ja903080c.

[207] Liu Y, Zhang K, Sun J, Yuan J, Yang Z, Gao C, et al. A Type of Hydrogen Bond Cross-Linked Silicone Rubber with the Thermal-Induced Self-Healing Properties Based on the Nonisocyanate Reaction. Industrial & Engineering Chemistry Research. 2019;58:21452-8.DOI: https://doi.org/10.1021/acs.iecr.9b03953.

[208] Phadke A, Zhang C, Arman B, Hsu C-C, Mashelkar RA, Lele AK, et al. Rapid self-healing hydrogels. Proc Natl Acad Sci U S A. 2012;109:4383-8.DOI: https://doi.org/10.1073/pnas.1201122109

[209] Herbst F, Döhler D, Michael P, Binder WH. Self-Healing Polymers via Supramolecular Forces. Macromol Rapid Commun. 2013;34:203-20.DOI: https://doi.org/10.1002/marc.201200675.

[210] Cummings SC, Dodo OJ, Hull AC, Zhang B, Myers CP, Sparks JL, et al. Quantity or Quality: Are Self-Healing Polymers and Elastomers Always Tougher with More Hydrogen Bonds? ACS Applied Polymer Materials. 2020;2:1108-13.DOI: https://doi.org/10.1021/acsapm.9b01095.

[211] Okano N, Osaki M, Ikura R, Takashima Y, Yamaguchi H, Harada A. Bulk Copolymerization of Host–Guest Monomers with Liquid-Type Acrylamide Monomers for

Supramolecular Materials Applications. ACS Applied Polymer Materials. 2020;2:1553-60.DOI: https://doi.org/10.1021/acsapm.9b01220.

[212] Zhang M, Xu D, Yan X, Chen J, Dong S, Zheng B, et al. Self-Healing Supramolecular Gels Formed by Crown Ether Based Host–Guest Interactions. Angew Chem Int Ed Engl. 2012;51:7011-5.DOI: https://doi.org/10.1002/anie.201203063.

[213] Wang Z, Liang H, Yang H, Xiong L, Zhou J, Huang S, et al. UV-curable self-healing polyurethane coating based on thiol-ene and Diels-Alder double click reactions. Progress in Organic Coatings. 2019;137:105282.DOI: https://doi.org/10.1016/j.porgcoat.2019.105282.

[214] Yang S, Zhao J, Chen S, Zhao J. Flexible Self-healing Cross-linked Polyamides Synthesized Through Bulk Michael Addition, Polycondensation, and Diels-Alder Reaction. Chemical Research in Chinese Universities. 2021.DOI: 10.1007/s40242-021-1202-7.

[215] Xu X, Ma S, Wang S, Wang B, Feng H, Li P, et al. Fast-Reprocessing, Postadjustable, Self-Healing Covalent Adaptable Networks with Schiff Base and Diels–Alder Adduct. 2022:2100777.DOI: https://doi.org/10.1002/marc.202100777.

[216] Behera PK, Raut SK, Mondal P, Sarkar S, Singha NK. Self-Healable Polyurethane Elastomer Based on Dual Dynamic Covalent Chemistry Using Diels–Alder “Click” and Disulfide Metathesis Reactions. ACS Applied Polymer Materials. 2021;3:847-56.DOI: 10.1021/acsapm.0c01179.

[217] Sarkar S, Banerjee SL, Singha NK. Dual-Responsive Self-Healable Carboxylated Acrylonitrile Butadiene Rubber Based on Dynamic Diels–Alder “Click Chemistry” and Disulfide Metathesis Reaction. 2021;306:2000626.DOI: https://doi.org/10.1002/mame.202000626.

[218] Wolf MP, Salieb-Beugelaar GB, Hunziker P. PDMS with designer functionalities—Properties, modifications strategies, and applications. Progress in Polymer Science. 2018;83:97-134.DOI: https://doi.org/10.1016/j.progpolymsci.2018.06.001.

[219] Yan Q, Zhao L, Cheng Q, Zhang T, Jiang B, Song Y, et al. Self-Healing Polysiloxane Elastomer Based on Integration of Covalent and Reversible Networks. Industrial & Engineering Chemistry Research. 2019;58:21504-12.DOI: 10.1021/acs.iecr.9b04355.

[220] Wang J, Lv C, Li Z, Zheng J. Facile Preparation of Polydimethylsiloxane Elastomer with Self-Healing Property and Remoldability Based on Diels–Alder Chemistry. 2018;303:1800089.DOI: https://doi.org/10.1002/mame.201800089.

[221] Yilmaz D, Lansade D, Lewandowski S, Perraud S, Llevot A, Carlotti S. Combination of permanent hydrosilylation and reversible Diels–Alder reactions for self-healing poly(dimethylsiloxane) materials with enhanced ageing properties. Materials Today Chemistry. 2022;24:100860.DOI: https://doi.org/10.1016/j.mtchem.2022.100860.

[222] Bode S, Enke M, Hernandez M, Bose RK, Grande AM, van der Zwaag S, et al. Characterization of Self-Healing Polymers: From Macroscopic Healing Tests to the Molecular Mechanism. In: Hager MD, van der Zwaag S, Schubert US, editors. Self-healing Materials. Cham: Springer International Publishing; 2016. p. 113-42.DOI: https://doi.org/10.1007/12_2015_341.

[223] Brown EN, Sottos NR, White SR. Fracture testing of a self-healing polymer composite. Experimental Mechanics. 2002;42:372-9.DOI: https://doi.org/10.1007/BF02412141.

[224] Meurer J, Hniopek J, Ahner J, Schmitt M, Popp J, Zechel S, et al. In-depth characterization of self-healing polymers based on π-π interactions. Beilstein journal of organic chemistry. 2021;17:2496-504.DOI: https://doi.org/10.3762/bjoc.17.166.

[225] John Varley R, van der Zwaag S. Development of a quasi-static test method to investigate the origin of self-healing in ionomers under ballistic conditions. Polymer Testing. 2008;27:11-9.DOI: https://doi.org/10.1016/j.polymertesting.2007.07.013.

[226] Vega JM, Grande AM, van der Zwaag S, Garcia SJ. On the role of free carboxylic groups and cluster conformation on the surface scratch healing behaviour of ionomers. European Polymer Journal. 2014;57:121-6.DOI: https://doi.org/10.1016/j.eurpolymj.2014.05.005.

[227] Brancart J, Scheltjens G, Muselle T, Van Mele B, Terryn H, Van Assche G. Atomic force microscopy–based study of self-healing coatings based on reversible polymer network systems. Journal of Intelligent Material Systems and Structures. 2014;25:40-6.DOI: https://doi.org/10.1177/1045389x12457100.

[228] Yoon JA, Kamada J, Koynov K, Mohin J, Nicolaÿ R, Zhang Y, et al. Self-Healing Polymer Films Based on Thiol–Disulfide Exchange Reactions and Self-Healing Kinetics Measured Using Atomic Force Microscopy. Macromolecules. 2012;45:142-9.DOI: https://doi.org/10.1021/ma2015134.

[229] Kötteritzsch J, Stumpf S, Hoeppener S, Vitz J, Hager MD, Schubert US. One-Component Intrinsic Self-Healing Coatings Based on Reversible Crosslinking by Diels–Alder Cycloadditions. Macromol Chem Phys. 2013;214:1636-49.DOI: https://doi.org/10.1002/macp.201200712.

[230] Billiet S, Hillewaere XKD, Teixeira RFA, Du Prez FE. Chemistry of Crosslinking Processes for Self-Healing Polymers. Macromol Rapid Commun. 2013;34:290-309.DOI: https://doi.org/10.1002/marc.201200689.

[231] Perepelkin NV, Martin-Martinez JM, Kovalev AE, Borodich FM, Gorb SN. Experimental testing of self-healing ability of soft polymer materials. Meccanica. 2019;54:1959-70.DOI: https://doi.org/10.1007/s11012-019-00965-w.

[232] Zedler L, Hager MD, Schubert US, Harrington MJ, Schmitt M, Popp J, et al. Monitoring the chemistry of self-healing by vibrational spectroscopy – current state and perspectives. Materials Today. 2014;17:57-69.DOI: https://doi.org/10.1016/j.mattod.2014.01.020.

[233] Otts DB, Zhang P, Urban MW. High Fidelity Surface Chemical Imaging at 1000 nm Levels: Internal Reflection IR Imaging (IRIRI) Approach. Langmuir. 2002;18:6473-7.DOI: https://doi.org/10.1021/la025684y.

[234] Karabacak M, Çoruh A, Kurt M. FT-IR, FT-Raman, NMR spectra, and molecular structure investigation of 2,3-dibromo-N-methylmaleimide: A combined experimental and

theoretical study. Journal of Molecular Structure. 2008;892:125-31.DOI: https://doi.org/10.1016/j.molstruc.2008.05.014.

[235] Kim T, Assary RS, Curtiss LA, Marshall CL, Stair PC. Vibrational properties of levulinic acid and furan derivatives: Raman spectroscopy and theoretical calculations. J Raman Spectrosc. 2011;42:2069-76.DOI: https://doi.org/10.1002/jrs.2951.

[236] Joo SW. pH-Dependent Surface-enhanced Raman Scattering Analysis of Maleimide and Succinimide on Ag Nanocolloidal Surfaces. B Korean Chem Soc. 2008;29:1761-4.DOI: https://doi.org/10.5012/bkcs.2008.29.9.1761.

[237] Hong Y-l, Miyoshi T. Solid-State NMR Characterization of Polymer Chain Structure and Dynamics in Polymer Crystals. In: Palsule S, editor. Encyclopedia of Polymers and Composites. Berlin, Heidelberg: Springer Berlin Heidelberg; 2021. p. 1-17.DOI: https://doi.org/10.1007/978-3-642-37179-0_27-1.

[238] Davydovich D, Urban MW. Water accelerated self-healing of hydrophobic copolymers. Nature Communications. 2020;11:5743.DOI: https://doi.org/10.1038/s41467-020-19405-5.

[239] Schmidt-Rohr K, Spiess HW. CHAPTER THREE - High-Resolution NMR Techniques for Solids. In: Schmidt-Rohr K, Spiess HW, editors. Multidimensional Solid-State NMR and Polymers. San Diego: Academic Press; 1994. p. 69-134.DOI: https://doi.org/10.1016/B978-0-08-092562-2.50008-4.

[240] Hinderberger D. EPR Spectroscopy in Polymer Science. In: Drescher M, Jeschke G, editors. EPR Spectroscopy: Applications in Chemistry and Biology. Berlin, Heidelberg: Springer Berlin Heidelberg; 2012. p. 67-89.DOI: https://doi.org/10.1007/128_2011_236.

[241] Nevejans S, Ballard N, Miranda JI, Reck B, Asua JM. The underlying mechanisms for self-healing of poly(disulfide)s. Physical Chemistry Chemical Physics. 2016;18:27577-83.DOI: https://doi.org/10.1039/C6CP04028D.

[242] Ouari O, Phan T, Ziarelli F, Casano G, Aussenac F, Thureau P, et al. Improved Structural Elucidation of Synthetic Polymers by Dynamic Nuclear Polarization Solid-State NMR Spectroscopy. ACS Macro Letters. 2013;2:715-9.DOI: https://doi.org/10.1021/mz4003003.

[243] Gizatullin B, Neudert O, Stapf S, Mattea C. Dynamic Nuclear Polarization Fast Field Cycling Method for the Selective Study of Molecular Dynamics in Block Copolymers. Chemphyschem : a European journal of chemical physics and physical chemistry. 2017;18:2347-56.DOI: https://doi.org/10.1002/cphc.201700539.

[244] Pinon AC, Schlagnitweit J, Berruyer P, Rossini AJ, Lelli M, Socie E, et al. Measuring Nano- to Microstructures from Relayed Dynamic Nuclear Polarization NMR. The Journal of Physical Chemistry C. 2017;121:15993-6005.DOI: https://doi.org/10.1021/acs.jpcc.7b04438.

[245] Viger-Gravel J, Berruyer P, Gajan D, Basset J-M, Lesage A, Tordo P, et al. Frozen Acrylamide Gels as Dynamic Nuclear Polarization Matrices. Angew Chem Int Ed Engl. 2017;56:8726-30.DOI: https://doi.org/10.1002/anie.201703758.

[246] Brownbill NJ, Sprick RS, Bonillo B, Pawsey S, Aussenac F, Fielding AJ, et al. Structural Elucidation of Amorphous Photocatalytic Polymers from Dynamic Nuclear Polarization Enhanced Solid State NMR. Macromolecules. 2018;51:3088-96.DOI: https://doi.org/10.1021/acs.macromol.7b02544.

[247] Blanc F, Chong SY, McDonald TO, Adams DJ, Pawsey S, Caporini MA, et al. Dynamic nuclear polarization NMR spectroscopy allows high-throughput characterization of microporous organic polymers. Journal of the American Chemical Society. 2013;135:15290-3.DOI: https://doi.org/10.1021/ja408074v.

[248] Mijović J, Lee H, Kenny J, Mays J. Dynamics in Polymer−Silicate Nanocomposites As Studied by Dielectric Relaxation Spectroscopy and Dynamic Mechanical Spectroscopy. Macromolecules. 2006;39:2172-82.DOI: https://doi.org/10.1021/ma051995e.

[249] Hernández M, Carretero-González J, Verdejo R, Ezquerra TA, López-Manchado MA. Molecular Dynamics of Natural Rubber/Layered Silicate Nanocomposites As Studied by Dielectric Relaxation Spectroscopy. Macromolecules. 2010;43:643-51.DOI: https://doi.org/10.1021/ma902379t.

[250] Hernández M, Ezquerra TA, Verdejo R, López-Manchado MA. Role of Vulcanizing Additives on the Segmental Dynamics of Natural Rubber. Macromolecules. 2012;45:1070-5.DOI: https://doi.org/10.1021/ma202325k.

[251] Kremer Friedrich SA. Broadband Dielectric Spectroscopy. New York: Springer; 2003.

[252] Hernández M, Grande AM, van der Zwaag S, García SJ. Monitoring Network and Interfacial Healing Processes by Broadband Dielectric Spectroscopy: A Case Study on Natural Rubber. ACS Applied Materials & Interfaces. 2016;8:10647-56.DOI: https://doi.org/10.1021/acsami.6b02259.

[253] Das A, Le HH, Vuorinen J, Heinrich G. Comment on "Monitoring Network and Interfacial Healing Processes by Broadband Dielectric Spectroscopy: A Case Study on Natural Rubber". ACS Applied Materials & Interfaces. 2017;9:14547-51.DOI: https://doi.org/10.1021/acsami.6b16045.

[254] Hernández M, Grande AM, van der Zwaag S, García SJ. Reply to Comment on "Monitoring Network and Interfacial Healing Processes by Broadband Dielectric Spectroscopy: A Case Study on Natural Rubber". ACS Applied Materials & Interfaces. 2017;9:14552-4.DOI: https://doi.org/10.1021/acsami.7b02617.

[255] Dahlke J, Kimmig J, Abend M, Zechel S, Vitz J, Schubert US, et al. Quantification of the scratch-healing efficiency for novel zwitterionic polymers. NPG Asia Materials. 2020;12:13.DOI: https://doi.org/10.1038/s41427-019-0190-2.

[256] Schäfer S, Kickelbick G. Double Reversible Networks: Improvement of Self-Healing in Hybrid Materials via Combination of Diels–Alder Cross-Linking and Hydrogen Bonds. Macromolecules. 2018;51:6099-110.DOI: https://doi.org/10.1021/acs.macromol.8b00601.

[257] Cuvellier A, Verhelle R, Brancart J, Vanderborght B, Van Assche G, Rahier H. The influence of stereochemistry on the reactivity of the Diels–Alder cycloaddition and the implications for reversible network polymerization. Polymer Chemistry. 2019;10:473-85.DOI: https://doi.org/10.1039/C8PY01216D.

[258] Herbst F, Seiffert S, Binder WH. Dynamic supramolecular poly(isobutylene)s for self-healing materials. Polymer Chemistry. 2012;3:3084-92.DOI: https://doi.org/10.1039/C2PY20265D.

[259] Yan T, Schröter K, Herbst F, Binder WH, Thurn-Albrecht T. Nanostructure and Rheology of Hydrogen-Bonding Telechelic Polymers in the Melt: From Micellar Liquids and Solids to Supramolecular Gels. Macromolecules. 2014;47:2122-30.DOI: https://doi.org/10.1021/ma402007f.

[260] Bode S, Bose RK, Matthes S, Ehrhardt M, Seifert A, Schacher FH, et al. Self-healing metallopolymers based on cadmium bis(terpyridine) complex containing polymer networks. Polymer Chemistry. 2013;4:4966-73.DOI: https://doi.org/10.1039/C3PY00288H.

[261] Ruocco N, Dahbi L, Driva P, Hadjichristidis N, Allgaier J, Radulescu A, et al. Microscopic Relaxation Processes in Branched-Linear Polymer Blends by Rheo-SANS. Macromolecules. 2013;46:9122-33.DOI: https://doi.org/10.1021/ma4014498.

[262] Chen X, Zhu J, Luo Y, Chen J, Ma X, Bukhvalov D, et al. Molecular dynamics simulation insight into the temperature dependence and healing mechanism of an intrinsic self-healing polyurethane elastomer. Physical Chemistry Chemical Physics. 2020;22:17620-31.DOI: https://doi.org/10.1039/D0CP03013A.

[263] Arab B, Shokuhfar A. Molecular dynamics simulation of cross-linked urea-formaldehyde polymers for self-healing nanocomposites: prediction of mechanical properties and glass transition temperature. Journal of Molecular Modeling. 2013;19:5053-62.DOI: https://doi.org/10.1007/s00894-013-1996-4.

[264] Sattar MA, Patnaik A. Design Principles of Interfacial Dynamic Bonds in Self-Healing Materials: What are the Parameters? Chem Asian J. 2020;15:4215-40.DOI: https://doi.org/10.1002/asia.202001157.

[265] Javierre E. Modeling Self-Healing Mechanisms in Coatings: Approaches and Perspectives. Coatings. 2019;9:122.DOI: https://doi.org/10.3390/coatings9020122.

[266] Buxton GA, Care CM, Cleaver DJ. A lattice spring model of heterogeneous materials with plasticity. Modelling and Simulation in Materials Science and Engineering. 2001;9:485-97.DOI: https://doi.org/10.1088/0965-0393/9/6/302.

[267] Balazs AC. Modeling self-healing materials. Materials Today. 2007;10:18-23.DOI: https://doi.org/10.1016/S1369-7021(07)70205-5.

[268] Bell GI. Models for the Specific Adhesion of Cells to Cells. Science. 1978;200:618-27.DOI: https://doi.org/10.1126/science.347575.

[269] Salib IG, Kolmakov GV, Gnegy CN, Matyjaszewski K, Balazs AC. Role of Parallel Reformable Bonds in the Self-Healing of Cross-Linked Nanogel Particles. Langmuir. 2011;27:3991-4003.DOI: https://doi.org/10.1021/la104609t.

[270] Duki SF, Kolmakov GV, Yashin VV, Kowalewski T, Matyjaszewski K, Balazs AC. Modeling the nanoscratching of self-healing materials. J Chem Phys. 2011;134:084901.DOI: https://doi.org/10.1063/1.3556744.

[271] Yu K, Xin A, Wang Q. Mechanics of self-healing polymer networks crosslinked by dynamic bonds. Journal of the Mechanics and Physics of Solids. 2018;121:409-31.DOI: https://doi.org/10.1016/j.jmps.2018.08.007.

[272] Barbero EJ, Greco F, Lonetti P. Continuum Damage-healing Mechanics with Application to Self-healing Composites. Int J Damage Mech. 2005;14:51-81.DOI: https://doi.org/10.1177/1056789505045928.

[273] Ponnusami SA, Krishnasamy J, Turteltaub S, van der Zwaag S. A cohesive-zone crack healing model for self-healing materials. International Journal of Solids and Structures. 2018;134:249-63.DOI: https://doi.org/10.1016/j.ijsolstr.2017.11.004.

[274] Terryn S, Roels E, Brancart J, Van Assche G, Vanderborght B. Self-Healing and High Interfacial Strength in Multi-Material Soft Pneumatic Robots via Reversible Diels–Alder Bonds. 2020;9:34.

[275] Ligon SC, Liska R, Stampfl J, Gurr M, Mülhaupt R. Polymers for 3D Printing and Customized Additive Manufacturing. Chemical Reviews. 2017;117:10212-90.DOI: https://doi.org/10.1021/acs.chemrev.7b00074.

[276] Serex L, Bertsch A, Renaud P. Microfluidics: A New Layer of Control for Extrusion-Based 3D Printing. Micromachines (Basel). 2018;9:86.DOI: https://doi.org/10.3390/mi9020086.

[277] Yu K, Xin A, Du H, Li Y, Wang Q. Additive manufacturing of self-healing elastomers. NPG Asia Materials. 2019;11:7.DOI: https://doi.org/10.1038/s41427-019-0109-y.

[278] Javadi A, Mehr HS, Sobani M, Soucek MD. Cure-on-command technology: A review of the current state of the art. Progress in Organic Coatings. 2016;100:2-31.DOI: https://doi.org/10.1016/j.porgcoat.2016.02.014.

[279] Yang K, Grant JC, Lamey P, Joshi-Imre A, Lund BR, Smaldone RA, et al. Diels–Alder Reversible Thermoset 3D Printing: Isotropic Thermoset Polymers via Fused Filament Fabrication. 2017;27:1700318.DOI: https://doi.org/10.1002/adfm.201700318.

[280] Raffa P, Kassi A, Gosschalk J, Migliore N, Polgar LM, Picchioni F. A Structure-Properties Relationship Study of Self-Healing Materials Based on Styrene and Furfuryl Methacrylate Cross-Linked via Diels–Alder Chemistry. 2021;306:2000755.DOI: https://doi.org/10.1002/mame.202000755.

[281] Yue HB, Fernández-Blázquez JP, Beneito DF, Vilatela JJ. Real time monitoring of click chemistry self-healing in polymer composites. Journal of Materials Chemistry A. 2014;2:3881-7.DOI: https://doi.org/10.1039/C3TA14961G.

[282] Kamali AR. Production of Advanced Materials in Molten Salts. Green Production of Carbon Nanomaterials in Molten Salts and Applications. Singapore: Springer Singapore; 2020. p. 5-18.DOI: https://doi.org/10.1007/978-981-15-2373-1_2.

[283] Kamali AR. Eco-friendly production of high quality low cost graphene and its application in lithium ion batteries. Green Chemistry. 2016;18:1952-64.DOI: https://doi.org/10.1039/C5GC02455B.

[284] Zhang K, Sun J, Song J, Gao C, Wang Z, Song C, et al. Self-Healing Ti3C2 MXene/PDMS Supramolecular Elastomers Based on Small Biomolecules Modification for Wearable Sensors. ACS Applied Materials & Interfaces. 2020;12:45306-14.DOI: https://doi.org/10.1021/acsami.0c13653.

[285] Sajedi-Moghaddam A, Saievar-Iranizad E, Pumera M. Two-dimensional transition metal dichalcogenide/conducting polymer composites: synthesis and applications. Nanoscale. 2017;9:8052-65.DOI: https://doi.org/10.1039/C7NR02022H.

[286] Motora KG, Wu C-M, Chang C-C, Liao J-H. NIR Light Stimulated Self-Healing Reduced Tungsten Oxide/Polyurethane Nanocomposite Based on the Diels−Alder Reaction. 2021;306:2100438.DOI: https://doi.org/10.1002/mame.202100438.

[287] Zou Y, Fang L, Chen T, Sun M, Lu C, Xu Z. Near-Infrared Light and Solar Light Activated Self-Healing Epoxy Coating having Enhanced Properties Using MXene Flakes as Multifunctional Fillers. Polymers-Basel. 2018;10:474.DOI: https://doi.org/10.3390/polym10050474.

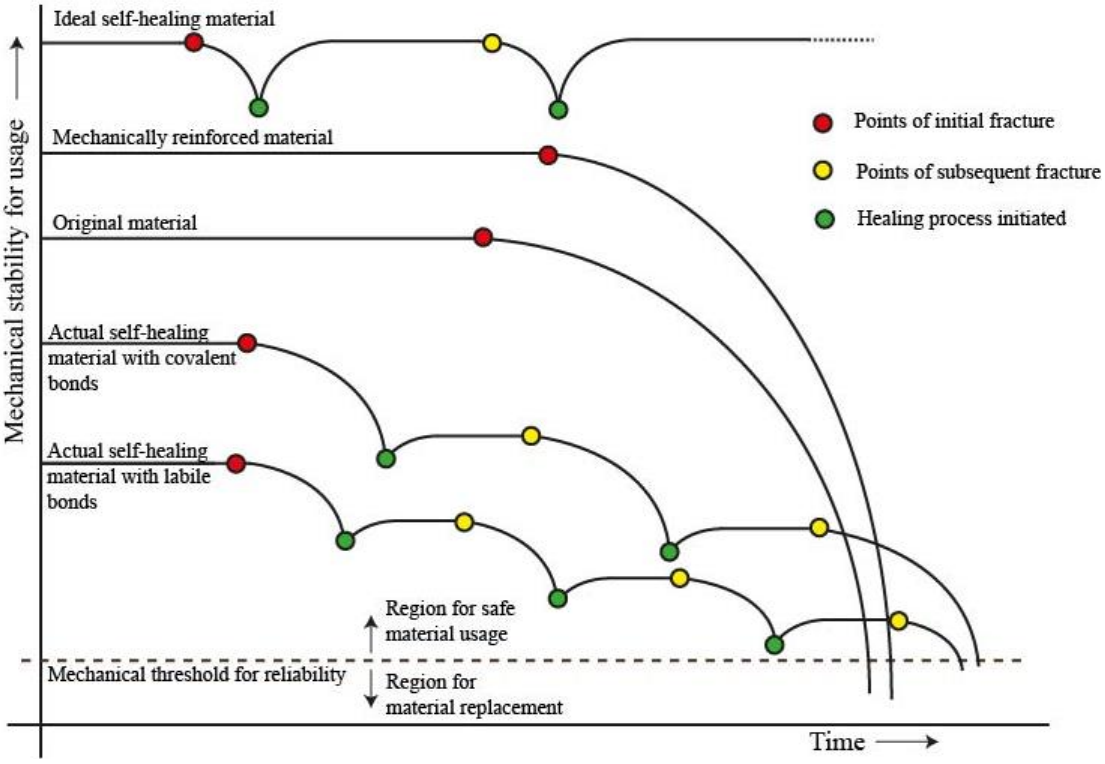

Fig.1 The schematic representation of the serviceable lifetime of materials with and without incorporating self-healing properties.

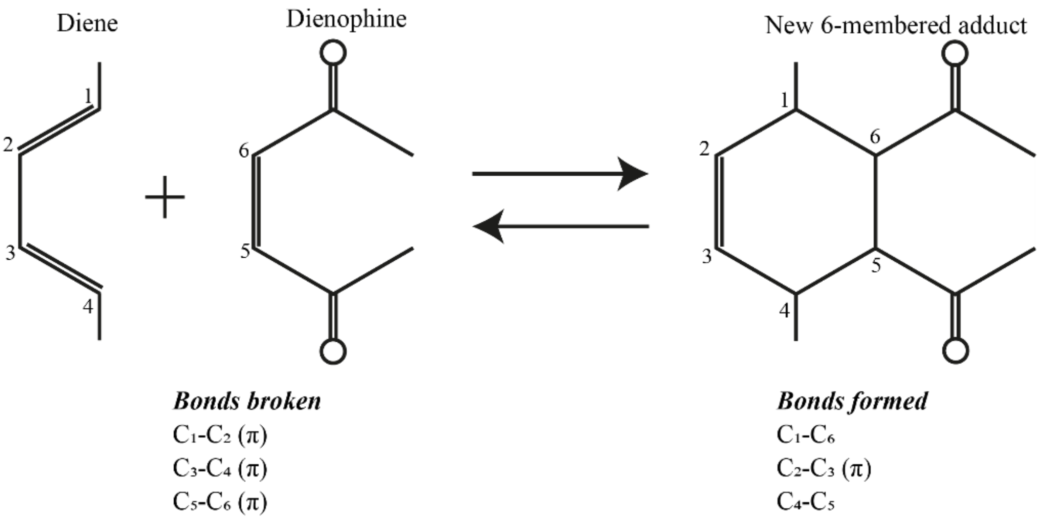

Fig. 2 Stereochemistry of Diels-Alder reaction.

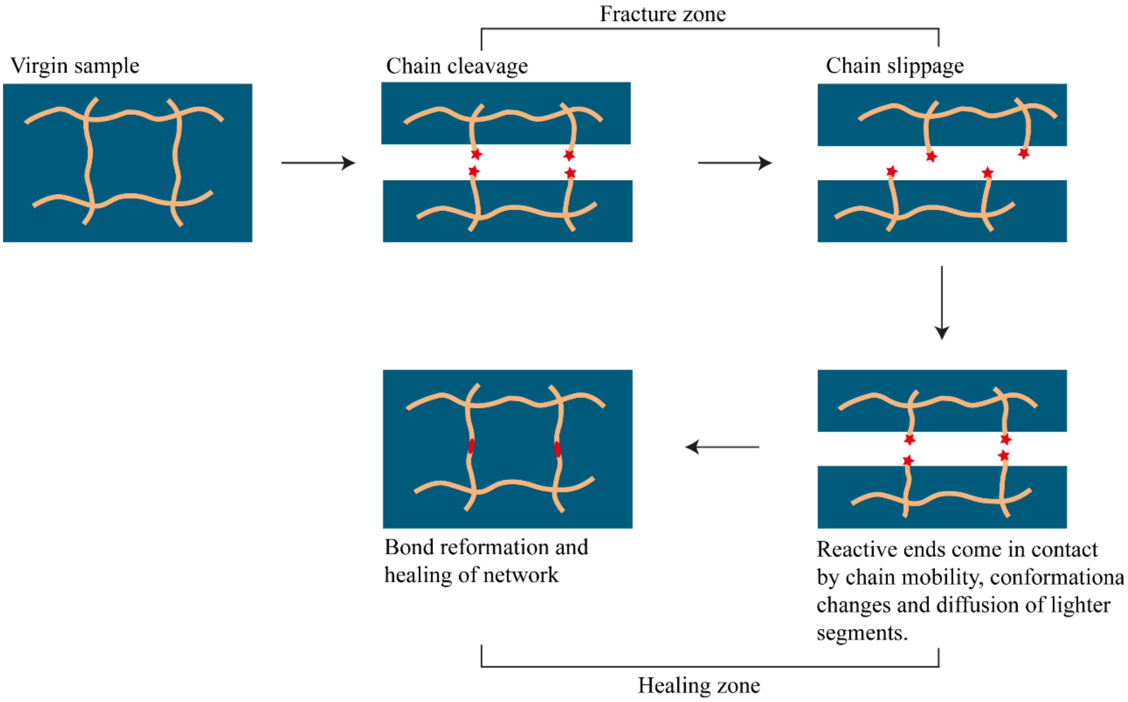

Fig. 3 Chain cleavage and chain slippage in the polymer matrix

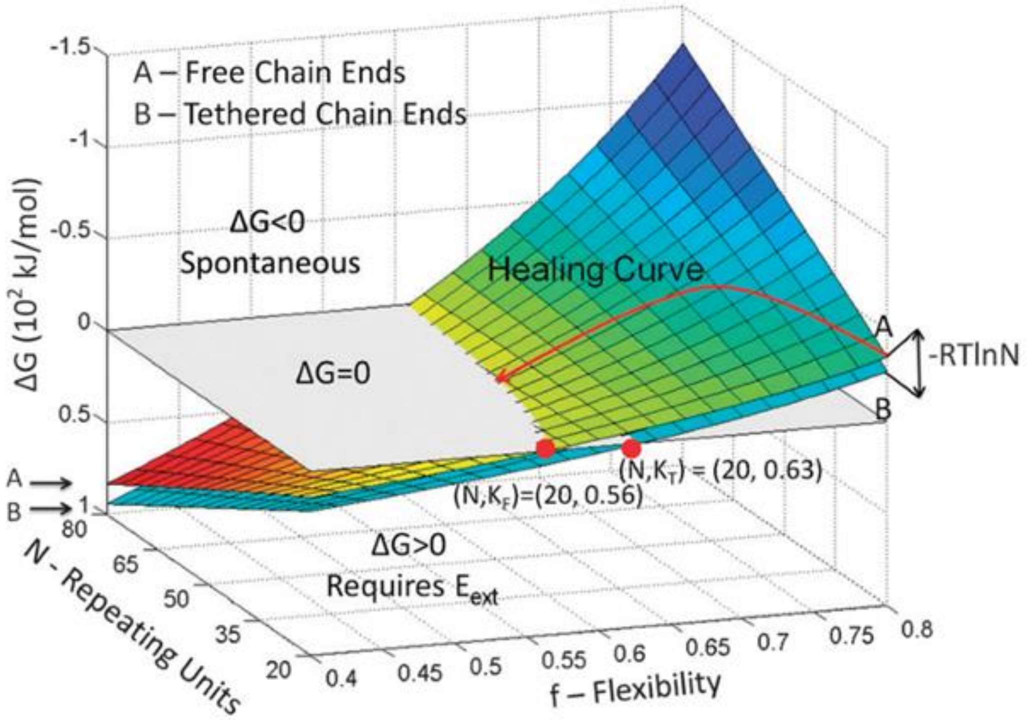

Fig. 4: Changes in Gibbs free energy as a function of repeating units and Flory's flexibility parameter. Republished with permission of Royal Society Of Chemistry, from Ref. [23]; permission conveyed through Copyright Clearance Center, Inc.

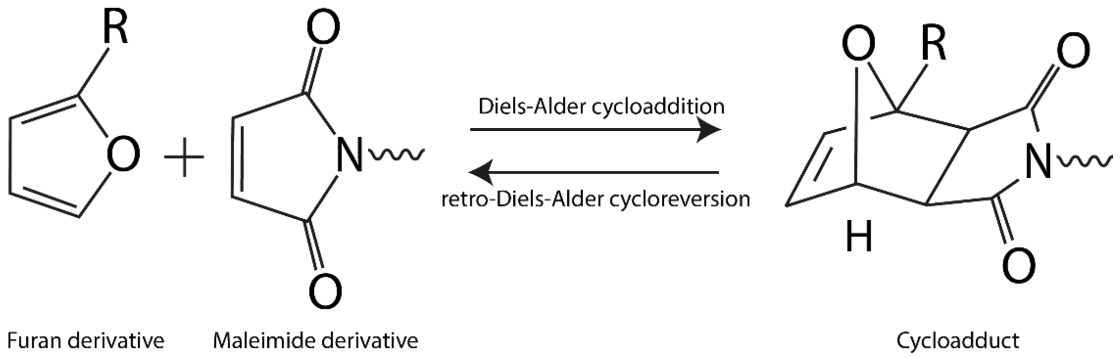

Fig. 5 Furan-Maleimide based DA reaction

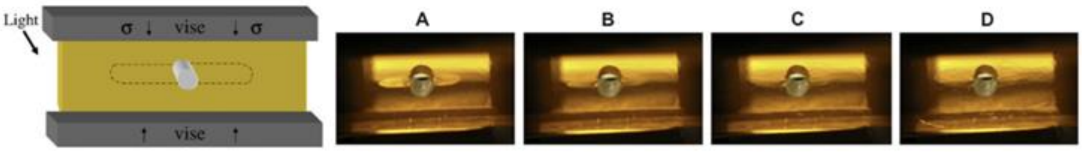

Fig. 6. In-situ photos of representative healing treatment of 2MEP4F occurring at 85 ºC. The left panel shows the orientation of the sample with respect to the camera. The right panels show the sequence of photos during the treatment: (A) 0 min; (B) 2 min; (C) 4 min; and (D) 15 min. Reprinted from Ref. [91] with permission from Elsevier.

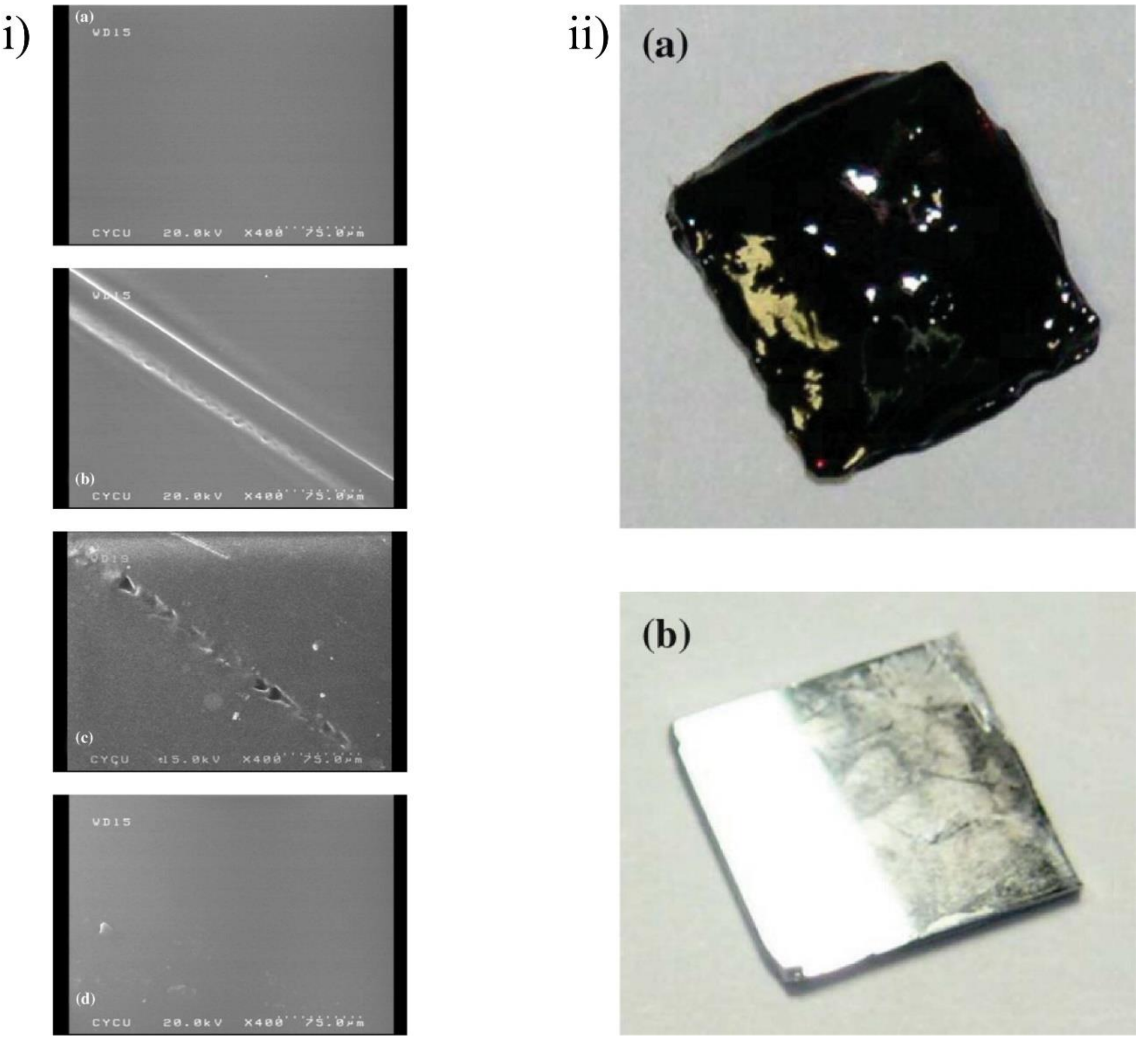

Fig. 7 Epoxy-based self-healing polymers used on Silicon substrate i) The assessment of the remendability of the epoxy-based self-healing polymers. SEM micrographs of (a) the pristine crosslinked adducts, (b) knife-cutting sample, (c) thermally self-repaired sample (50 °C; 12 h), and (d) thermally self-repaired. ii) Removability of epoxy (a) Trimaleimide-Trifuran adduct encapsulated silicon wafer. (b) This sample was washed with NMP at 90 °C, after which the polymer was removed. Reprinted from Ref. [99] with permission from John Wiley and Sons.

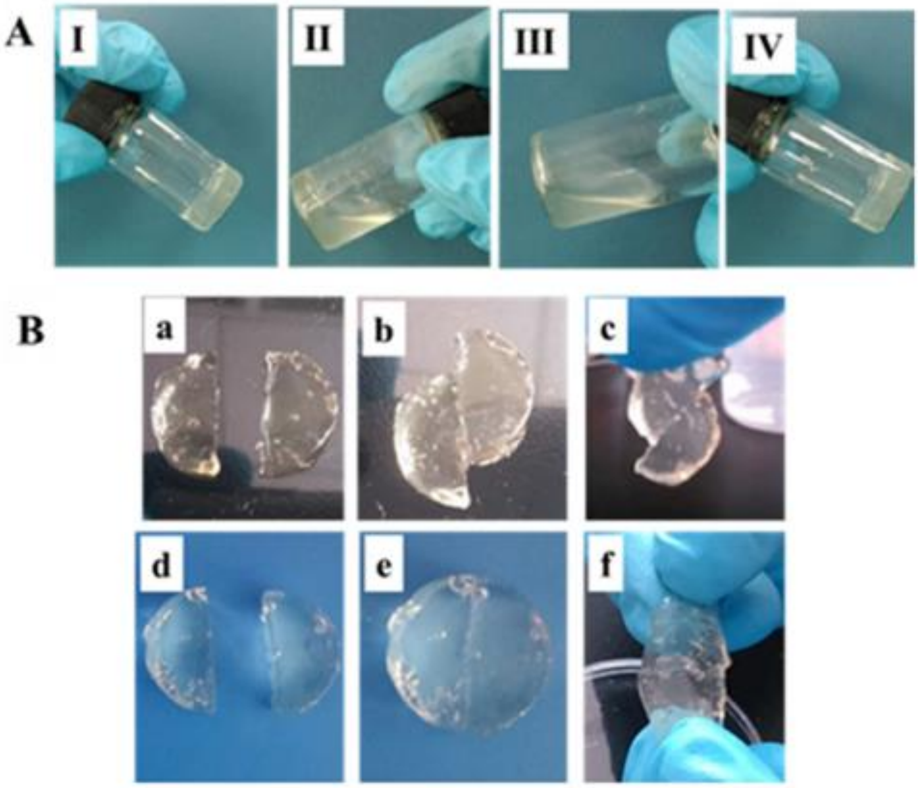

Fig. 8 The self-healing interpenetrating polymer network (IPN) with pH-responsive covalent bonds. (A) Sol−gel transition property of single-crosslinked network (SN) hydrogel used in the self-healing polymer: (I) SN hydrogel; (II) the hydrogel (1 mL) 10 min after adding 40 μL HCl; and (III) after 20 min; (IV) 25 min after adding 66 μL TEA into the solution self-healing. (B) The self-healing property of SN (a−c) and DN (d−f) hydrogel. Reprinted (adapted) with permission from [118]. Copyright 2015 American Chemical Society.

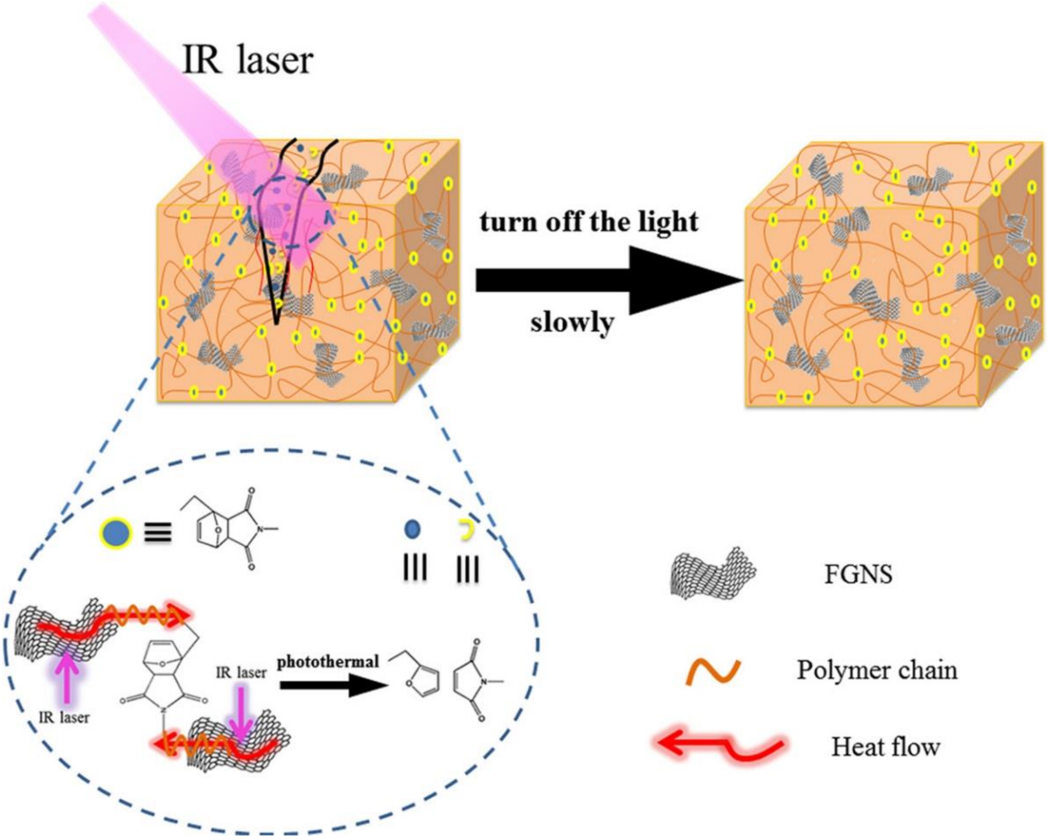

Fig. 9 Illustration of the self-healing process of FGNS-PU-DA nanocomposite influenced by IR laser irradiation. Graphene acts as a conducting medium for photothermal conversion which provides a stimulus for healing. Reprinted (adapted) with permission from [119]. Copyright 2017 American Chemical Society.

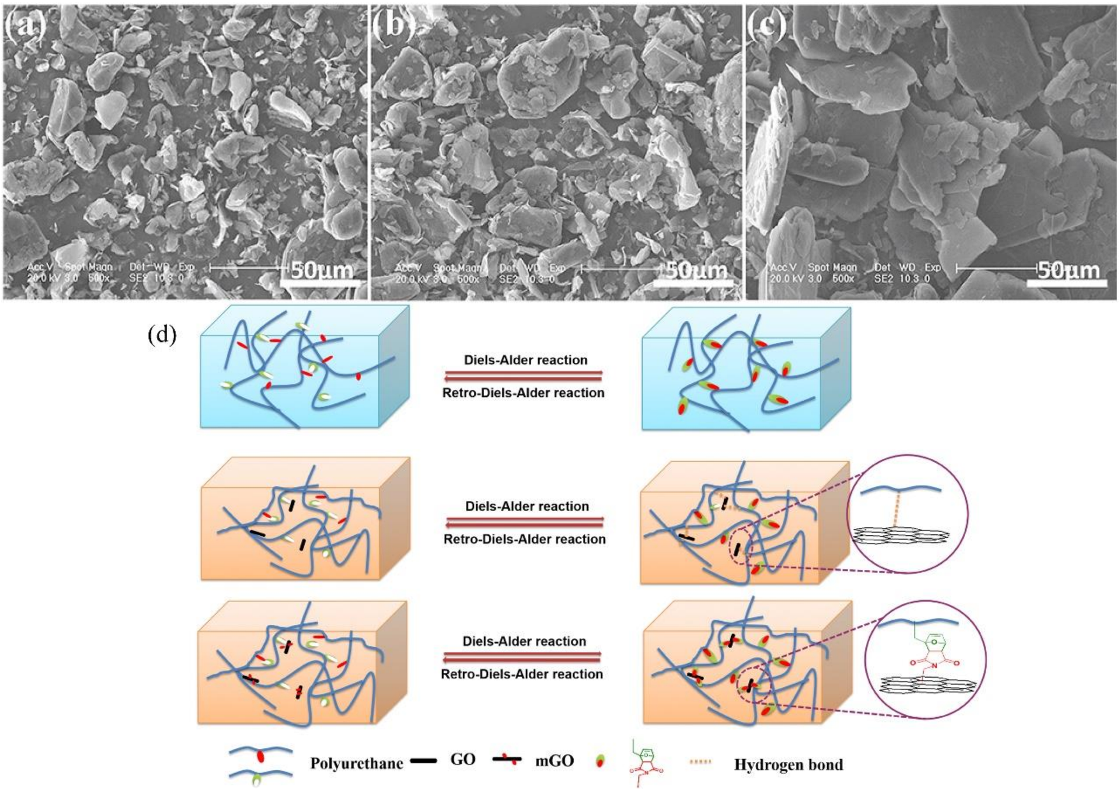

Fig. 10 (a,b, c) SEM images of different sizes of GO, and (d) their influence as filler in the mechanism involved in the preparation of PU composites. Reprinted from Ref. [138] with permission from Elsevier.

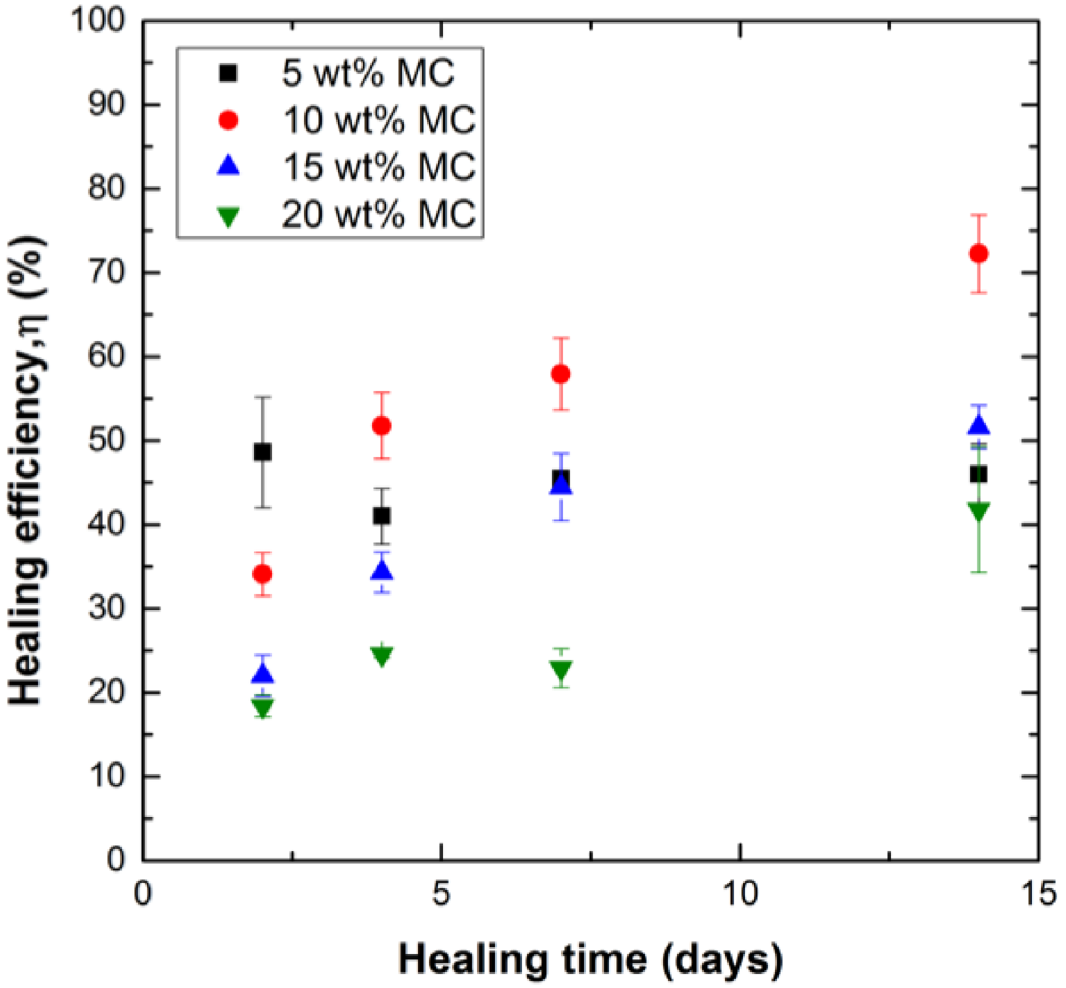

Fig. 11 Healing efficiency, η (%) vs. healing time (days) for modified fracture toughness samples with varying microcapsule content. Adapted from Ref. [141]

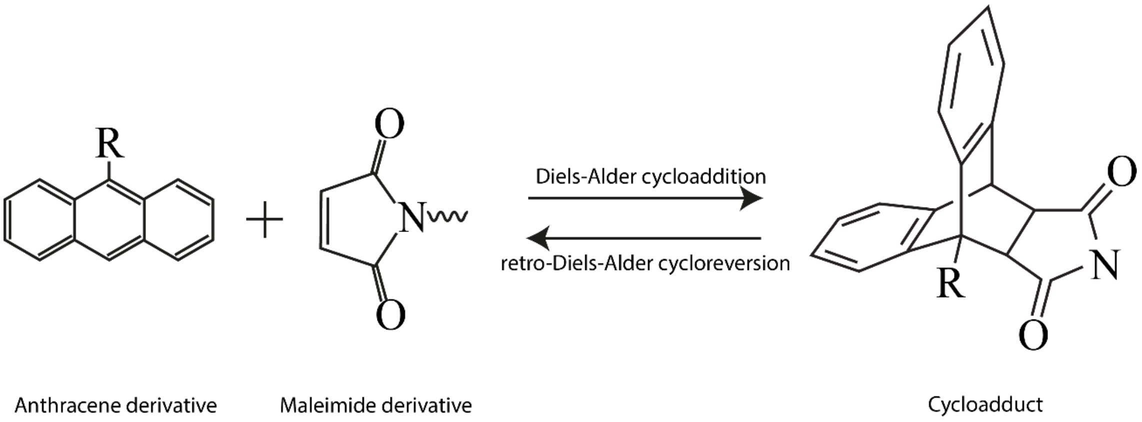

Fig. 12 Anthracene-Maleimide based DA reaction

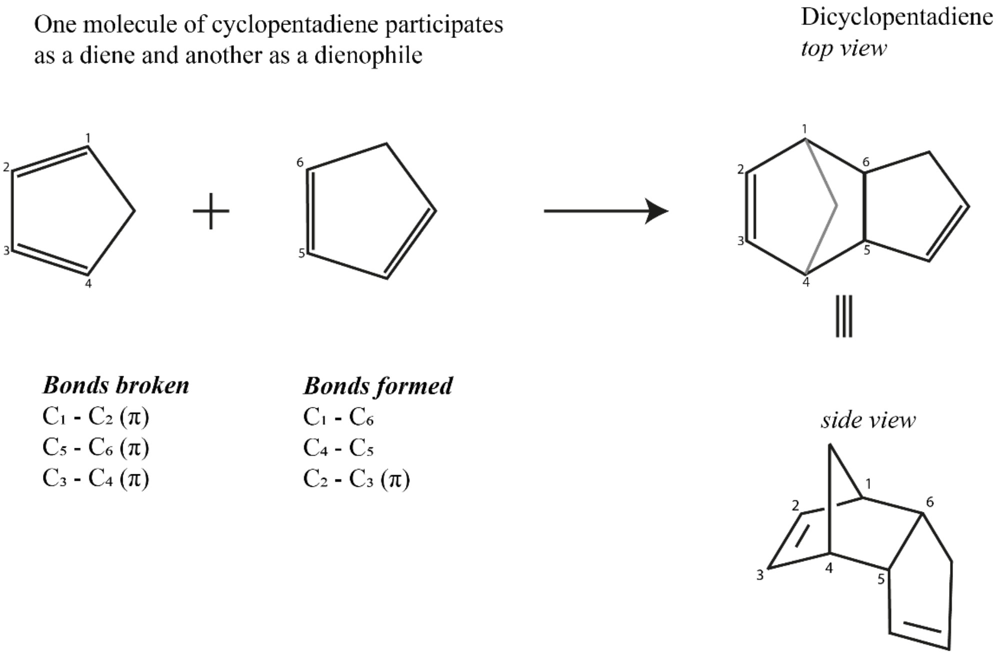

Fig. 13 Reaction mechanism of DA reaction based on cyclopentadiene

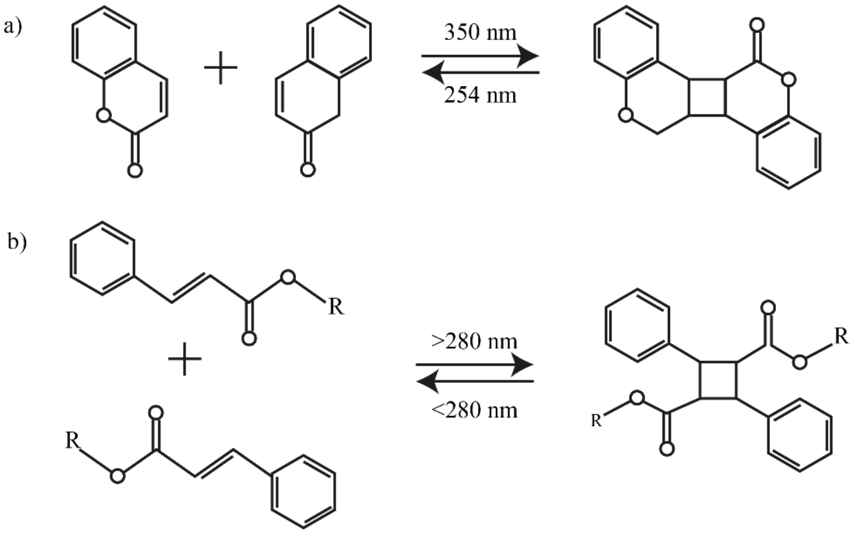

Fig. 14 Photodimerization and photocleavage of (a) coumarin and (b) cinnamate

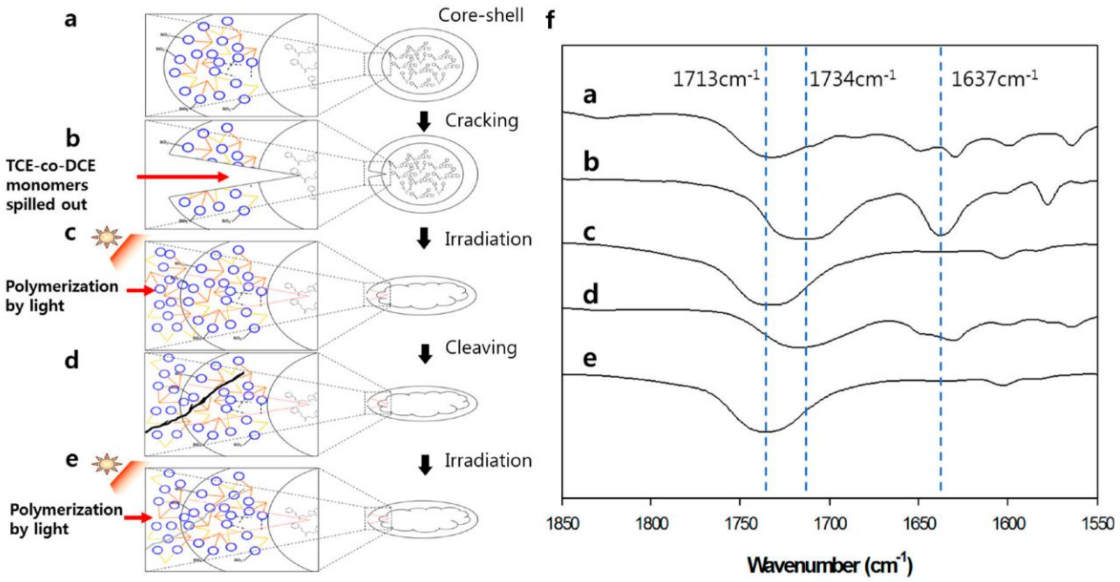

Fig. 15 Repeatability of self-healing. (a-e) Schematics of core-shell-like microcapsules to repeatedly heal the crack. (f) FT-IR spectra for each step of repeated cracking and healing process shown in (a-e) Adapted from Ref. [182]

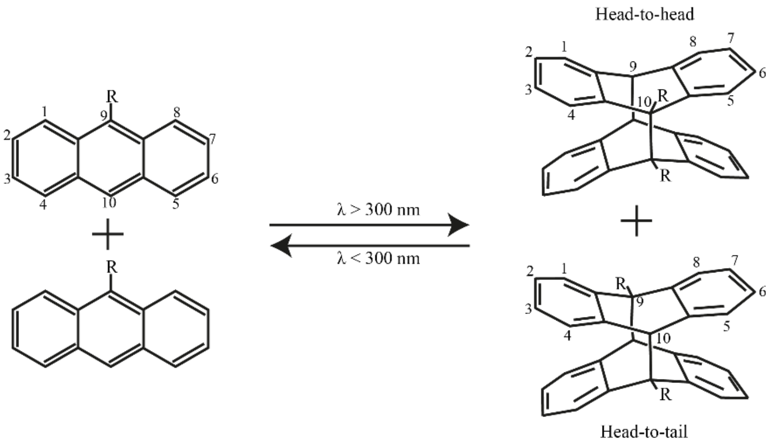

Fig. 16 (4+4) cycloaddition of anthracene

|  | **Analytical Technique** | **Determine mechanical/ chemical properties** | **Measure healing efficiency** | **Identify mechanism of healing** | **Smaller samples can be analysed** | **Non-destructive** |
|---|---|---|---|---|---|---|
| **Mechanical Testing Techniques** | TDCB | ✓ | ✓ | ✗ | ✗ | ✗ |
|  | Tensile Testing | ✓ | ✓ | ✗ | ✗ | ✗ |
|  | Scratch healing | ✗ | ✓ | ✓ | ✓ | ✓ |
|  | Fracture mechanics | ✓ | ✓ | ✓ | ✗ | ✗ |
|  | Ballistic impact | ✗ | ✓ | ✗ | ✗ | ✗ |
|  | Scratch volume | ✗ | ✓ | ✗ | ✓ | ✓ |
|  |  |  |  |  |  |  |
| **Thermal Characterization and Scattering Techniques** | DSC | ✓ | ✗ | ✓ | ✓ | ✓ |
|  | TGA | ✓ | ✗ | ✗ | ✓ | ✗ |
|  | X-ray scattering | ✓ | ✗ | ✓ | ✓ | ✓ |
|  | Neutron scattering | ✓ | ✗ | ✓ | ✓ | ✓ |
|  |  |  |  |  |  |  |
| **Imaging Techniques** | Optical microscopy | ✗ | ✓ | ✓ | ✓ | ✓ |
|  | Optical profilometry | ✗ | ✓ | ✓ | ✓ | ✓ |
|  | SEM | ✗ | ✓ | ✓ | ✓ | ✓ |
|  | AFM | ✓ | ✓ | ✓ | ✓ | ✓ |
|  |  |  |  |  |  |  |
| **Other Spectroscopic Techniques** | IR | ✓ | ✗ | ✓ | ✓ | ✓ |
|  | Raman | ✓ | ✗ | ✓ | ✓ | ✓ |
|  | SSNMR | ✓ | ✗ | ✓ | ✗ | ✓ |
|  | DNP SSNMR | ✓ | ✗ | ✓ | ✗ | ✓ |
|  | EPR | ✓ | ✗ | ✗ | ✓ | ✓ |
|  | COSY | ✓ | ✗ | ✓ | ✗ | ✓ |
|  | NOESY | ✓ | ✗ | ✓ | ✗ | ✓ |
|  | BDS | ✓ | ✓ | ✓ | ✓ | ✓ |

Fig. 17 Summary of analytical techniques to study self-healing in intrinsic polymers.

ü shows that the method is suitable and verified in the literature

û indicates that the technique is unsuitable or lacks sufficient evidence to prove its suitability

Table 1. Properties of various self-healing epoxy resins fabricated based on furan-maleimide DA adduct

| **System** | **Self-healing Pathway** | **Self-healing efficiency** | **Healing conditions** | **Preparation method** | **Original mechanical properties** | **Suitable application** | **Reference** |
|---|---|---|---|---|---|---|---|
| Novolac epoxy resin | Heat | - | 130 ºC (10 min) + 60 ºC (2 h) | Solution mixing | Storage modulus: 2.37 GPa | Electronics, packaging | [100] |
| DGEBA-FGE-PACM | Healing agent | 70% | Thermally: 90 °C (1 h); Agent: 10 µL DMF + 25 °C (12 h) | Solution mixing | Fracture toughness: 920 $Jm^{-2}$, Tangent modulus of elasticity: 3.3 GPa | Load bearing applications | [101] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| DGFA-DPMBMI | Heat | 77% | 125 ºC (20 min) + 80 ºC (72 h) | Solution mixing | Young’s modulus: 2.5 GPa, Tensile strength: 53 MPa, Elongation at break: 1.5 %, Flexural modulus: 4.6 GPa, Flexural strength: 110 MPa | Adhesives, binder, coatings | [102] |
| DGEBA | Heat | 83.80% | 120˚C (30 min)+ 90˚C (24 h) | Solution mixing | Elastic modulus: 4.89 GPa | Adhesives, coatings and structural applications | [103] |
| DGEBA | Heat | Highest at 122 % | 150 °C (5 min) 3 times | Solution mixing and batch extrusion | - | FRP composites | [104] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| DGEBA-FFR-BMI | Heat | Semi-IPN and DA polyadduct samples: 80 and 95% | 130 ºC (30 min ) + 60 ºC (12 h) | Solution mixing | Flexural strength: Semi-IPN: 96.96 Mpa, DA polyadduct: 5.675 MPa | Shape memory materials | [105] |
| Melamine | Heat | - | 120 °C, 65 °C (15) min | Solution mixing | - | Surface coating in wood-based materials | [106] |
| DPMBMI-Carbon nanotube(CNT) | Heat | 103.4% ± 14.3% | 120 °C (30 min) | Solution mixing | Highest Shear Modulus: 2.12 MPa | Adhesives, binder, coatings | [107] |
| EpF- Multi-walled CNT (MWCNT) | Heat | 79.82% | 140 °C (16 h) | Solution mixing | Tensile strength: 70.3 Mpa, Elongation at | Smart materials in electronic and | [108] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | break: 8.2%, Toughness: 3 MJ/m$^3$ | engineering fields. | |
| FGE-DPMBMI-GNS | Infrared Lamp | Higher than 85% | IR irradiation at 0.2 Wcm$^{-2}$ (20 min) | Solution mixing | Maximum tensile modulus:14.52±0.45 MPa | Transport industries, electronics | [109] |
| $NH_2$-MWCNTs/DA-epoxy | NIR light | 77% | Visible light healing (30 s) | Solution mixing and batch extrusion | Tensile strength: 22.1 MPa | Adhesives, binder, coatings | [110] |
| B-GNPs in HPM | Heat | 87±5 % | 130 °C (2 h) to form retro-DA bonds+80 °C (2 h) | Solution mixing | Tensile strength: 5.63 ± 0.24 MPa Tensile modulus: 1651 ± 125 GPa | Polymer nanocomposites for engineering applications | [111] |