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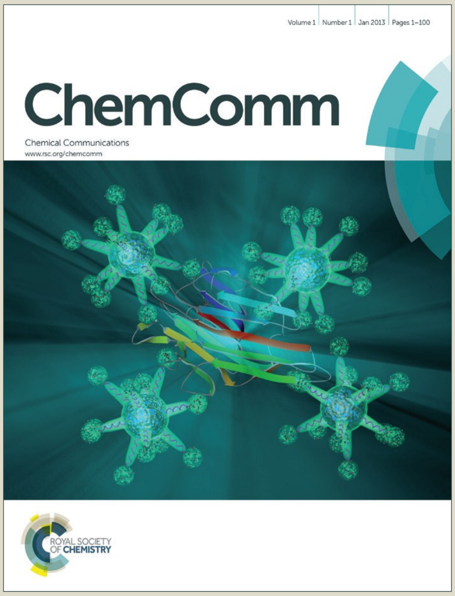

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Recent strategies to develop self-healable crosslinked polymeric networks

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Abstract

Autonomous self-healable crosslinked materials designed with built-in ability to repair physical damage and cracks can prevent catastrophic failure and thus extend the lifetime of materials. They also retain their dimensional stability, mechanical strength, thermal stability, and solvent resistance. These features promote the development of effective self-healing materials for various applications. This review summarizes recent advances in the development of novel self-healable polymeric materials, both through extrinsic methods involving the encapsulation of extra healing agents in microcapsules and through intrinsic methods utilizing the formation of reversible chemical bonds or physical interactions. Further, the outlook is briefly discussed on the important aspects for the current and future development of self-healable materials.

1. Introduction

Three-dimensionally crosslinked polymers are effective building blocks to develop a variety of novel multifunctional materials for various applications in nanoscience, biotechnology, and industrial fields.[1-9] The effectiveness of high-performance crosslinked materials is due to their dimensional stability, mechanical strength, thermal stability, and solvent resistance. Introducing the built-in ability to repair physical damage and cracks can effectively prevent catastrophic failure, thus extending the lifetime of materials. Consequently, the development of self-healing materials defined as "materials where damage automates a healing response" has currently attracted significant attention.[10, 11]

A number of strategies have been reported to develop self-healing polymers. Based on the nature of self-healing and external triggers applied, they can be classified into non-autonomous and autonomous systems. Non-autonomous self-healing polymers require external triggers such as light, temperature, and pH, whereas autonomous self-healing materials do not need any triggers to initiate the self-healing process. Alternatively, numerous strategies can be classified as intrinsic and extrinsic.[12, 13] Extrinsic self-healing involves the encapsulation of external healing agents, in the form of microcapsules or fibers, impregnated deliberately in the polymer matrix.[14, 15] When cracks or damages occur, the contents encapsulated in these containers are released to fill the disrupted parts, which then begin self-repairing either by polymerization or chemical reactions. In contrast to extrinsic self-healing occurring in a single event, intrinsic self-healing is repeatable and occurs in multiple events. Intrinsic self-healing materials are designed with reversible crosslinks, and self-healing is accomplished by bonding upon mechanical damage to the system.[16, 17] When the damage is below the critical limit, the damaged portion can be rejoined with the aid of either chemical crosslinking through dynamic covalent bond formation[18] or physical crosslinking through supramolecular (non-covalent) interactions.[19] This article reviews the recent advances in the design and development of crosslinked materials exhibiting self-healability, with a focus on the synthesis and methodology of intrinsic and extrinsic self-healing polymers reported in recent years.

2. Intrinsic self-healing methods

2.1. Reversible chemical crosslinking methods

The design of these materials involves the incorporation of dynamic covalent bonds as crosslinkages in self-healable networks. These reversible linkages are later utilized through the reformation of covalent bonds to reattach the fractured materials caused by mechanical forces (i.e. cracks or cuts). Unlike physical crosslinking methods based on supramolecular interactions, the chemical crosslinking methods utilizing reversible covalent bond formation provide higher mechanical strength and dimensional stability. These features can be advantageous in the development of tough self-healable materials. **Figure 1** illustrates several reversible dynamic linkages and chemistries that have been explored for the development of novel reversible self-healable materials.

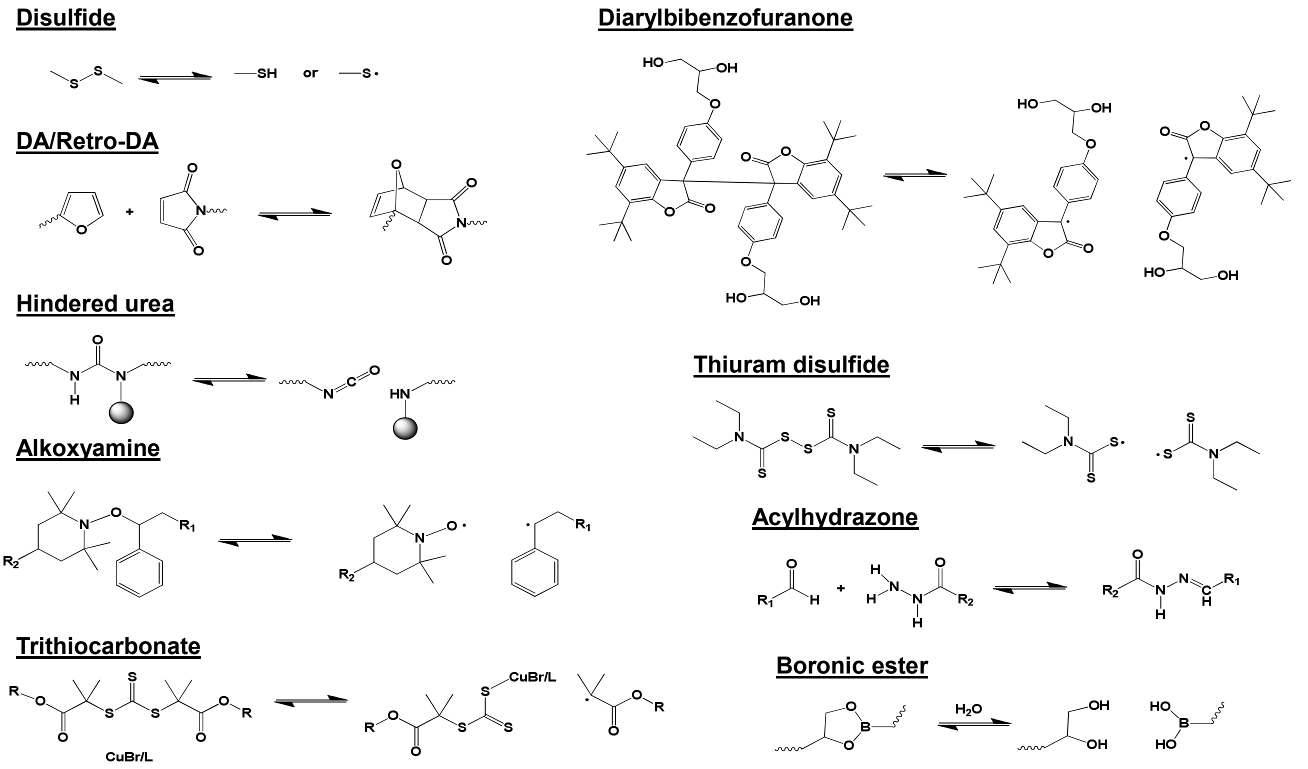

Figure 1. Reversible dynamic linkages and chemistries that have been explored for the development of novel reversible self-healable materials.

2.1.1. Redox disulfide chemistry

Disulfide linkages (SS) are cleaved to the corresponding thiols either under a reducing condition in the presence of reducing agents such as phosphines or through thiol-disulfide exchange reactions in the presence of thiols.[20, 21] They can also be cleaved to the corresponding thiyl radicals under conditions such as thermal scission,[22] mechanical stress,[23] or photoirradiation.[24] Reversibly, the formed thiols or thiyl radicals are utilized to reform disulfide bonds by several reactions: oxidation of thiols, thiol-disulfide exchange reaction, and recombination of thiyl radicals. Further, disulfide linkages can be exchanged through disulfide metathesis (or disulfide rearrangement) catalyzed by phosphine,[25] tertiary amine,[26, 27] or photo-irradiation.[28] These unique redox chemistries enabling the reformation of dynamic disulfide bonds have been utilized in the design and construction of disulfide-containing self-healable materials.[29-35]

Polysulfide-crosslinked epoxy-based thermoset materials with a glass transition temperature (T_g) of -35 °C were synthesized by polyaddition via a click-type epoxy-thiol reaction of an epoxy resin bearing disulfide linkages and a polythiol. These materials are designed to have multiple disulfide linkages positioned in long side chains tethered from crosslinked networks; this enables the enhanced mobility of disulfide linkages in damaged areas (i.e. cracks or scratches). Initial cuts disappeared and mechanical strength was fully restored within 1 hr at 60 °C.[30, 31] In addition, not only the number (or density) but also the mobility of disulfide linkages available within polymeric network are important parameters that significantly influence self-healability through disulfide redox chemistry.[32]

Methacrylate-based disulfide-crosslinked materials were synthesized by atom transfer radical polymerization (ATRP) for the chain extension of a disulfide-functionalized dimethacrylate from star-shaped core-crosslinked copolymers as macroinitiators. The materials are composed of core-crosslinked stars bearing poly(butyl acrylate) arms, with the average number of arms per star-shaped core = 23, which are crosslinked with dynamic disulfide linkages at their branched peripheries. Sol-gel transition through a reduction-oxidation process allows for the preparation of reversibly disulfide-crosslinked star-polymer networks. As seen in **Figure 2**, atomic force microscopy (AFM) analysis shows a decrease in the depth of cuts over the time, suggesting the occurrence of self-healing at room temperature.[33]

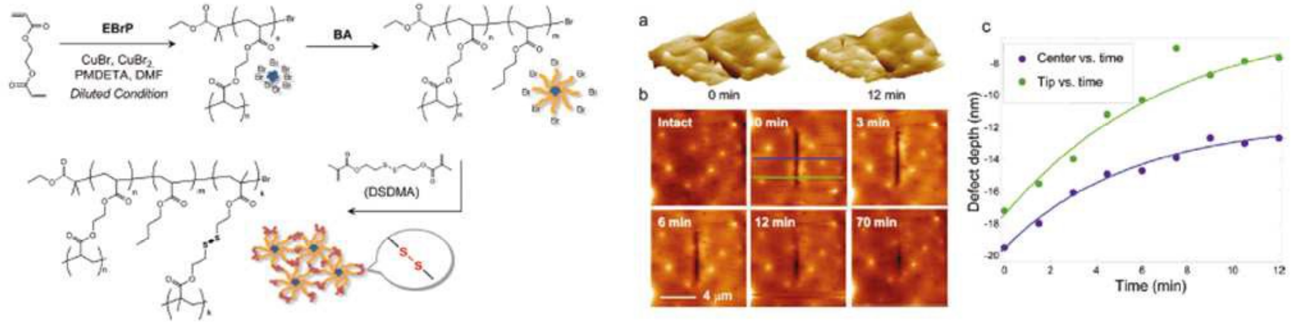

Figure 2. Chemical structure of disulfide-crosslinked star-shaped copolymer (left) and time dependent change of height mode AFM image for cut on the surface of reversibly disulfide-crosslinked star-polymer network (right): 3D images (a), 2D height mode images (b), and evolution of damage depth for 12 min at two positions (c).[33] Copyright 2012 American Chemical Society.

More recently, novel dual-sulfide-disulfide crosslinked materials (s-ssPxNs) based on linear methacrylate copolymers were developed by utilizing a combination of photo-induced thiol-ene radical addition and oxidation. As illustrated in **Figure 3**, permanent sulfide-crosslinkages retain the integrity of self-healable s-ssPxN materials with high mechanical strength upon physical damage, while dynamic disulfide crosslinkages ensure rapid and room temperature self-healing in cracks. Methacylate copolymers having pendant vinyl groups were synthesized by free radical polymerization followed by post-modification. They were then mixed with a polythiol in a non-stoichiometric balance to form lightly crosslinked networks having excess thiols (sPxNs) upon UV irradiation. Subsequent oxidation on sPxNs yielded dual s-ssPxNs with self-healable disulfide linkages. The resulting s-ssPxN networks exhibit the occurrence of rapid self-healing within 30 seconds to 30 minutes, as well as self-healing elasticity with reversible viscoelastic properties.[36]

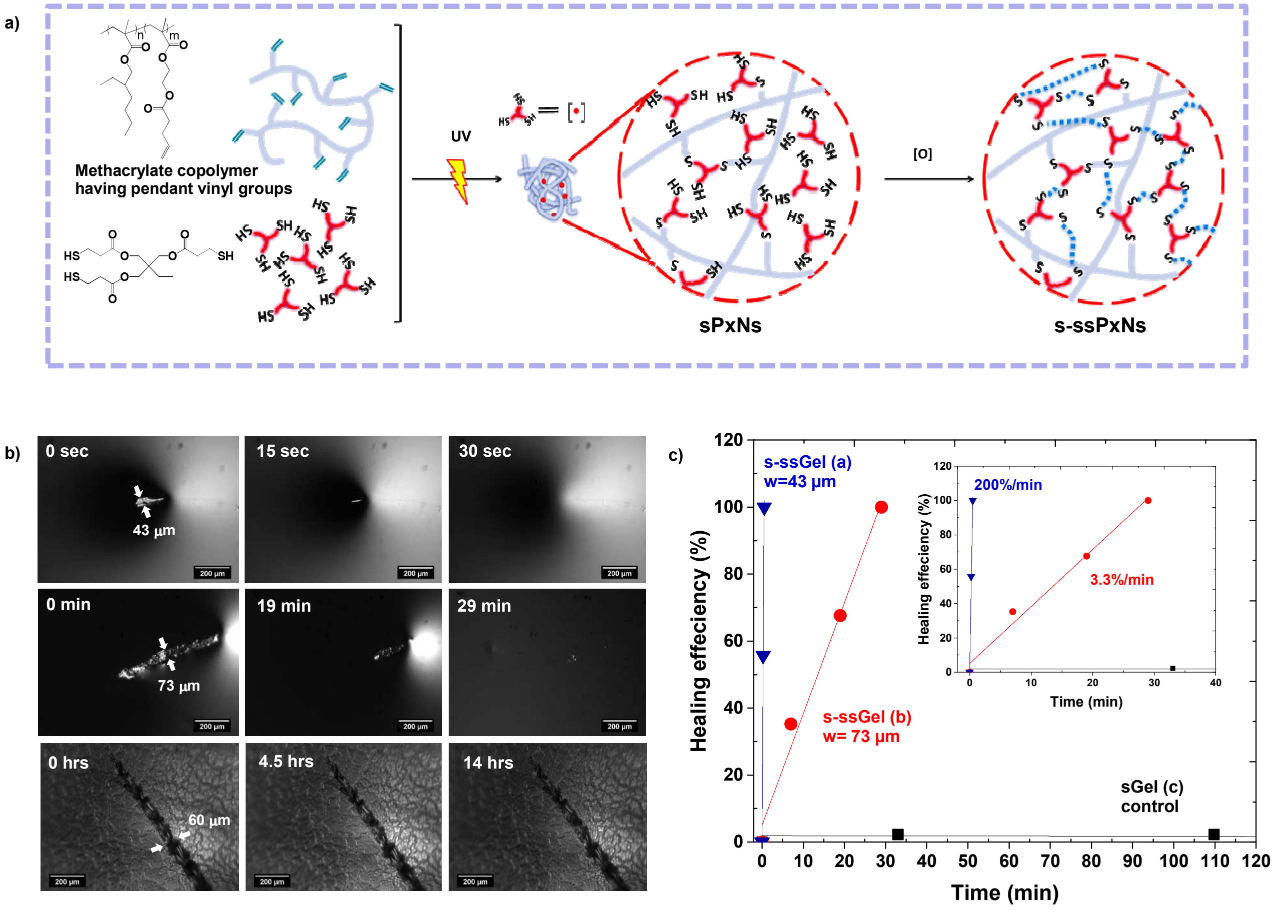

Figure 3. Illustration of a novel method utilizing click-type photo-induced thiol-ene radical addition and oxidation to synthesize dual sulfide-disulfide crosslinked networks (s-ssPxNs) (a), evolution of microscope images (b) and kinetics of self-healing (c) over time at room temperature for dual s-ssPxN with different cut sizes of 43 μm wide (upper) and 73 μm wide (middle), compared with a control of sPxN with no disulfide (bottom). Copyright 2015 Wiley Interfaces.

2.1.2. Diels-Alder (DA)/retro-DA chemistry

DA reaction is a thermally-induced [4+2] cycloaddition of a diene and a dienophile. Furan group and maleimide groups are generally used as typical diene and dienophile, respectively. The resulting DA adduct undergoes a cleavage reaction (called retro-DA reaction) at high temperatures, re-generating the corresponding diene and dienophile. They then reform DA linkages. This reversible

DA/retro-DA reaction has been utilized for the development of thermally-induced, self-healable materials. Various approaches that have been explored can be classified based on the chemical structures of polydienes and polydienophiles for step-growth polymerization through polyaddition.

Approach I utilizes the direct polyaddition of small molecules of polydienes and polydienophiles at a moderate temperature (≈ 60-80 °C).[37, 38] As illustrated in **Figure 4**, thermally remendable crosslinked materials were synthesized by polyaddition of a four-arm furan-labeled monomer (4F) and a three-arm maleimide-labeled monomer (3M). The rate of polymerization increased with an increasing DA reaction temperature. For the resulting DA-crosslinked materials, the healing efficiency of cracks through retro-DA reactions was 50% at 150 °C and 41% at 120 °C.[37] Single-component DA-crosslinked polymeric materials were synthesized by polyaddition of a bifunctional monomer functionalized with cyclopentadiene acting as both diene and dienophile. The monomer was generated by the retro-DA reaction of the corresponding dicyclopentadiene-based monomer. The mending efficiency of the network was 40-60%.[39] These materials were further used to enhance interlaminar properties in epoxy-based composites. An introduction of a plasticizer into DA-crosslinked materials can enhance the reformation efficiency of DA-adducts followed by retro-DA reaction. For example, the use of benzyl alcohol as a plasticizer allows for the improvement of self-healing recovery in DA-crosslinked materials composed of a polyfunctional furan and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BM). Such enhancement is attributed to an increase in free volume and molecular mobility of the polymeric network.[40] Details on the synthesis and self-healing of DA-based crosslinked materials have been summarized in a review.[41]

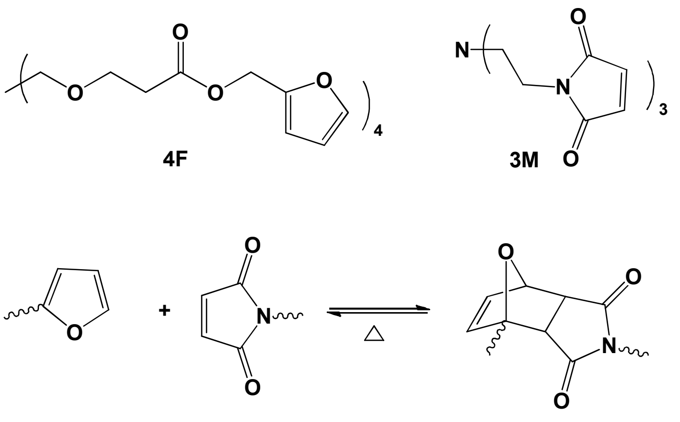

Figure 4. Illustration of polyaddition through DA reaction of a four-arm furan-labeled monomer (4F) and a three-arm maleimide-labeled monomer (3M) to form DA-crosslinked materials.[37]

Approach II involves the synthesis of polymethacrylates bearing pendant furan groups by chain-growth polymerization of a methacrylate functionalized with a furan group. Random copolymers having pendant furan groups were synthesized by controlled radical polymerization methods including ATRP[42-44] or reversible addition fragmentation chain transfer (RAFT) polymerization.[45] The resulting copolymers were crosslinked with BM through DA reactions. FT-IR technique was used to investigate thermal reversibility of the resulting DA-crosslinked networks by monitoring a decrease in a peak for furan rings (1010 cm^{-1}) for DA reaction and a disappearance of a peak for C=C vibration (1630 cm^{-1}) for retro-DA reaction. The DA linkages were disrupted to the corresponding diene and dienophile at 100 °C, and then restored upon cooling down to room temperature. Scanning electron microscopy images show that the distinctive cracks made on the surface of networks were completely healed upon heating at 120 °C for 4 hrs.[44] Further, ABA-type triblock copolymers consisting of a soft poly(2-ethylheyxyl acrylate) in the middle (B block) and a glassy and hard poly(furfuryl methacrylate) at the ends (A blocks) were synthesized by ATRP. The resulting polymers formed DA-crosslinked networks in the presence of BM crosslinker. Similar results of thermally-driven self-healing behavior on damaged films were observed (**Figure 5**).[46]

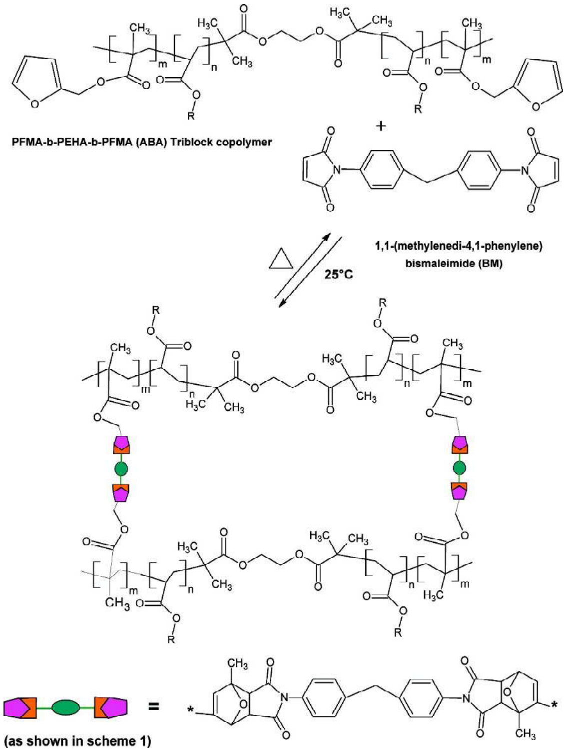

Figure 5. Schematic illustration of DA and retro-DA reaction occurred in reactive mixtures consisting of a ABA triblock copolymer having pendant furfuryl groups with 1,1′-(methylenedi-4,1-phenylene)bismaleimide for thermally-driven self-healing.[46] Copyright 2010 American Chemical Society.

Approach III involves the synthesis of liner polymers having pendant furan groups by post-modification of polybutadiene,[47, 48] polyamides,[49] or polyketones[50] with furfuryl amine. For example, furan-functionalized polyketones were synthesized by Paal-Knorr reaction of the polyketones with furfuryl amine. The resulting polyketones were then mixed with BM to form DA-crosslinked materials at 50 °C. Repeatable self-healing of the materials through retro-DA reaction was observed at 110 °C within <30 min.[50]

Other approaches have also been reported to synthesize self-healable materials; including DA-crosslinked networks based on epoxy resin by polyaddition[51, 52] and DA-labeled block copolymer at the block junction by ATRP.[13]

2.1.3. Hindered urea chemistry

Urea bonds bearing a bulky group on the nitrogen atom can dissociate into the corresponding isocyanate and amine; they then reversibly form the urea bonds.[53] This dynamic hindered urea chemistry has been explored in the development of catalyst-free, low-temperature crosslinked self-healing of poly(urethane-urea) containing hindered urea bonds (HUBs). As illustrated in **Figure 6**, the HUBs in cuts were involved in the reverse process of typical urea bond formation, leading to the occurrence of autonomous repairing for 12 hrs at 37 °C.[54] This chemistry has been further explored to synthesize hydrolyzable polyureas bearing HUBs.[55]

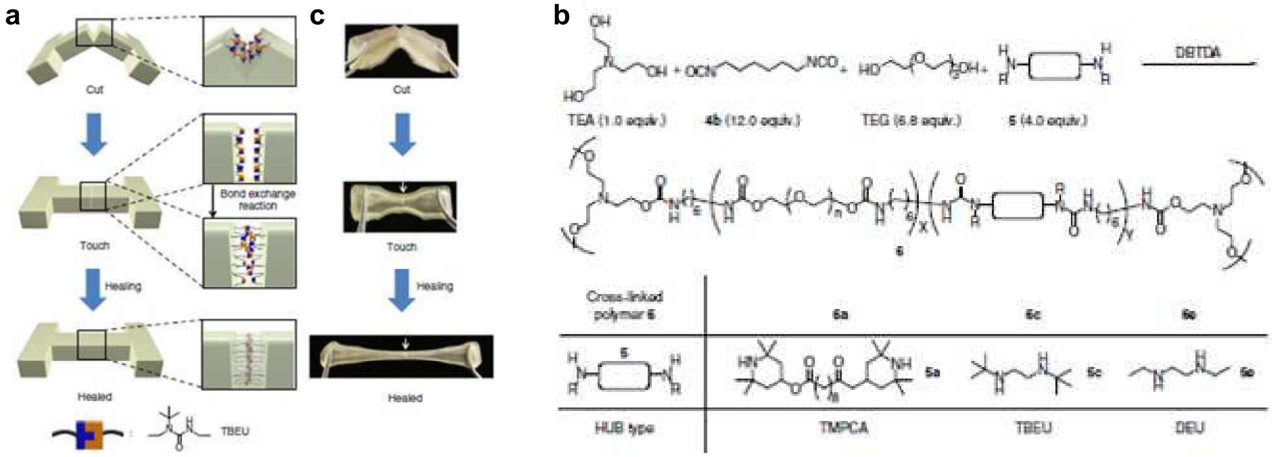

Figure 6. Schematic illustration of self-healing process (a), chemical structures and ratios of components used for the synthesis (b), and selected snapshots during the course of self-healing experiments of HUB-based crosslinked poly(urethane-urea) materials (c). TMPCA: 2,2,6,6,-tetramethylpiperidinylcarboxyamide, TBEU: 1-(t-butyl)-1-ethylurea, and DEU: 1,1-diethylurea.[54] Copyright 2014 Nature Publishing Group.

2.1.4. Other reversible chemistry

Thiuram disulfide (TDS) moieties were introduced into polyurethane-based crosslinked materials. When exposed to visible light, TDS units underwent radical reshuffling with neighboring TDS units to reform disulfide bonds through radical transfer reaction or radical crossover reaction. This disulfide reshuffling induced self-healing on damaged areas. Their self-healing behavior was followed by cutting a cylindrical sample into two pieces, which were contacted under visible light at room temperature. After 24 hrs, the ruptured pieces were re-annealed together, exhibiting similar mechanical properties as before the physical damage.[56] In addition, alkoxyamine,[57, 58] diarylbibenzofuranone (a dimer of arylbenzofuranone),[59] trithiocarbonate,[60] acylhydrazone,[61-63] and imine,[64] as well as olefin metathesis,[65] boronic ester,[66-68] and coumarin dimer[69] have also been explored for the development of intrinsic self-healing materials.

2.2. Reversible physical crosslinking methods

The methods utilize non-covalent interactions, typically hydrogen bonding, π-π, metal complexation, ionic, and host-guest interactions. The formed physical crosslinks are easily disrupted in response to external stimuli such as pH, temperature, heat, and mechanical stress. Such physical disruptions are restored to their original interactions due to the unique reversibility of the physical crosslinks.

2.1.1. Hydrogen bonding interactions

Hydrogen bonding strategy for the development of self-healable supramolecular materials requires the introduction of hydrogen bonding motifs as donors and acceptors into polymers as in pendant chains, in arms, or at chain ends. Widely-explored hydrogen bonding motifs include 2-ureido-4-pyrimidinone (Upy)[70] and secondary amide groups. Thymine/2,6-diaminotriazine,[71] urea moieties,[72] and carboxylic acids[73, 74] have also been used. These groups enable the formation of reversible supramolecular crosslinking networks through their intermolecular hydrogen bonding. Upon physical damages, the supramolecular crosslinks are disrupted; however, they can be reformed because of their unique reversibility. Monofunctional and difunctional Upy-conjugated poly(ethylene glycol) (UPy-PEG) was synthesized by a facile conjugation of UPy and PEG. The mixture of these conjugates self-assembled in water to form fibril-embedded hydrogels. Their structural and mechanical properties, as well as self-healability, were regulated by varying the ratios of monofunctional to crosslinking difunctional UPy-PEG.[75]

A concern for most self-healable materials utilizing hydrogen bonding interactions is their weak mechanical strength due to the use of soft polymers as self-healable matrix. A promising strategy that has been proposed to overcome this challenge is the incorporation of hard domains into soft supramolecular polymeric matrix containing hydrogen bonding motifs. The presence of hard domains provides toughness and mechanical strength, while soft matrix promotes the mobility of hydrogen bonding groups for self-healing. For example, well-controlled bottle brush polymers were synthesized by a combination of free radical polymerization and ATRP. They consist of polystyrene (PS) backbone (high T_g) as a hard phase and polyacrylate amide (PA-amide) brushes (low T_g) as a soft phase. The brush polymers collapsed into core-shell nanostructures, which further assembled to two-phase nanostructures. They consist of hard polystyrene domains microphase-separated in a soft matrix, which contains secondary amide groups that are capable of forming dynamic supramolecular networks, having both hydrogen bond donor and acceptor functionalities. The resulting supramolecular assembly was reversibly broken and reformed, affording spontaneous self-healing behavior (**Figure 7**).[76] Diblock copolymers synthesized by RAFT polymerization consist of a hard PS block and a soft poly(n-butyl acrylate) (PBA) block, functionalized with an UPy motif at one end, thus forming PS-PBA-UPy. Dimerization of two UPy units allowed for the synthesis of well-controlled ABA triblock copolymers, thus forming PS-b-PBA-(UPy-UPy)-PBA-b-PS. These copolymers formed a microphase-separated thermoplastic elastomers of hard PS domains in PBA soft matrix with reversible hydrogen bonding interactions to afford dynamic self-healing properties.[77] Similar approaches have also been reported, including ABA triblock copolymers with pendant amide groups in the A blocks,[78] core-shell particles having amide groups in arms,[79] and polyurethanes having UPy groups.[80]

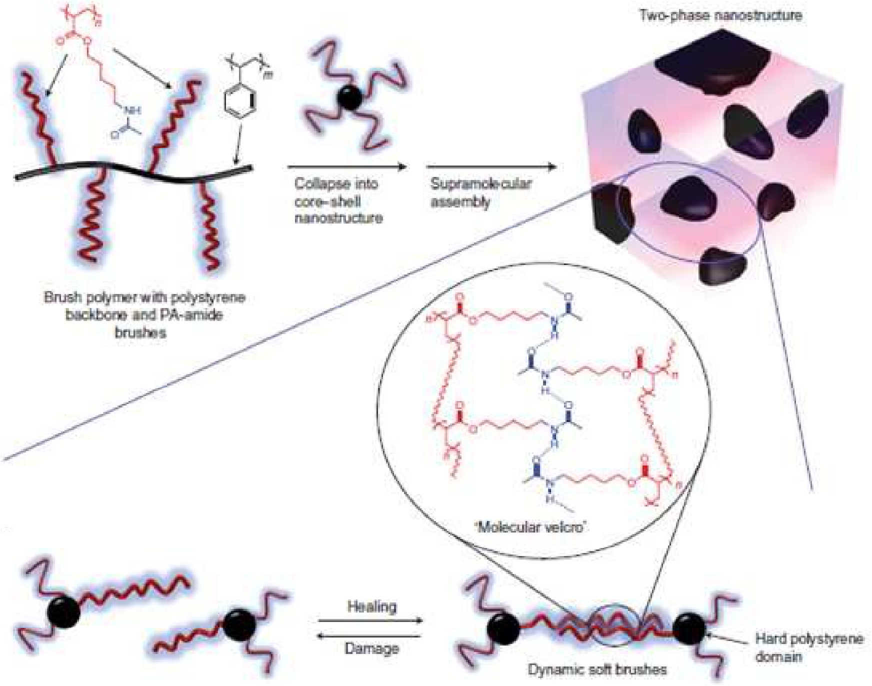

Figure 7. Schematic illustration of hydrogen-bonding brush polymer consisting of polystyrene backbone (high T_g) as a hard phase and polyacrylate amide brushes (low T_g) as a soft phase and its supramolecular assembly to form two-phase microstructures, consisting of hard polystyrene domains microphase-separated in soft matrix containing secondary amide groups that are capable of forming dynamic supramolecular networks.[76] Copyright 2014 Nature Publishing Group.

2.1.2. π-π interactions

Self-healing through dynamic π-π stacking utilizes aromatic units, mostly pyrene moieties as π-electron-rich residues and diimide units, as π-electron-deficient residues. The two residues form complexes adopting chain-folded conformation through π-π stacking interactions. These supramolecular interactions can be disrupted and reoriented upon thermal response. As a consequence, physical damages are subsequently healed. As a typical example, **Figure 8** illustrates a polymer blend consisting of a chain-folding polydiimide (1) and a telechelic polyurethane with pyrenyl end groups (2). The reactive blend yielded supramolecular crosslinked material induced by π-π stacking with thermal reversibility. Self-healing behavior was observed at temperatures >50 °C.[81, 82] Further, the design of new monomers with multiple aromatic units[83] or the introduction of cellulose nanocrystals (CNCs)[84] and gold nanoparticles (AuNPs)[85] enhanced mechanical strength of the self-healable networks.

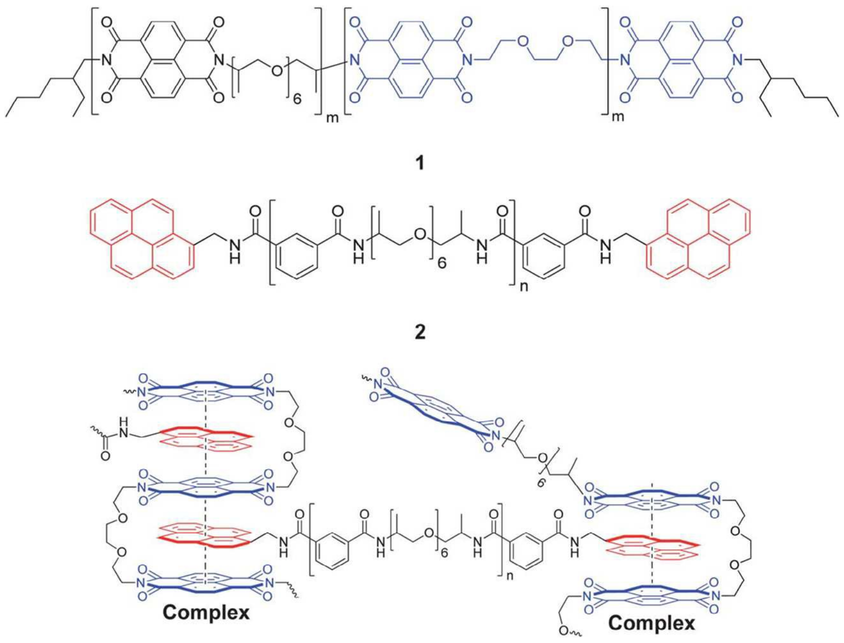

Figure 8. Illustration of π-π interaction between a polydiimide and a pyrenyl end-capped polymer.[85] Copyright 2013 Royal Society of Chemistry.

2.1.3. Metallo-supramolecular interactions

This method utilizes metal-ligand interactions where polymeric ligands are designed to have ligand motifs that bind to metal ions at the chain ends or in the side chains. Upon the incorporation of metal ions, such as Zn, Fe, Co, and Ni, linear supramolecular polymer or supramolecular crosslinked network can be formed through specific metal-ligand interaction. These interactions can be disrupted physically, thermally, or upon UV irradiation. Subsequent restoration of such interaction can induce self-healing behavior of the material.

2,6-Bis(1′-methylbenzimidazolyl)pyridine (Mebip) and its oxy-derivatives[86] have been used as a ligand motifs that bind to zinc ions. For example, poly(ethylene-co-butylene) copolymers having Mebip ligands at their termini were synthesized and interacted with Zn ions through metal-ligand interactions to form metallo-supramolecular polymers (**Figure 9**). The resulting network had relatively high mechanical strength with storage modulus (G′) $\approx 10^7$ Pa. After exposure to UV, the Mebip-Zn interactions were electronically excited. The absorbed energies were converted into heat to induce the dissociation of network. When UV-light was off, the metal-ligand interactions were reassembled, leading to the occurrence of self-healing.[87] An introduction of CNCs into the supramolecular mixture reinforced mechanical properties (G′ $\approx 10^8$ Pa at higher concentration of Zn^{2+}).[88] In addition, poly(butyl acrylate-co-methyl methacrylate) bearing pendant Mebip units were synthesized. An addition of Zn metal ions resulted in the formation of metallo-supramolecular crosslinked network containing hard metal-ligand rich-domains phase-separated in soft polyacrylate phases. The healing process was observed both optically and thermally. Further unique triple shape memory transitions were studied at different temperatures.[89]

Other ligand motifs have also been explored for the development of metallo-supramolecular self-healable materials, including 2,6-bis(1,2,3-triazole-4-yl)pyridine (BTP),[90-92] imidazole,[93] tyrosine,[94] polyethyleneimine,[95] triazole,[96] and terpyridine.[97, 98]

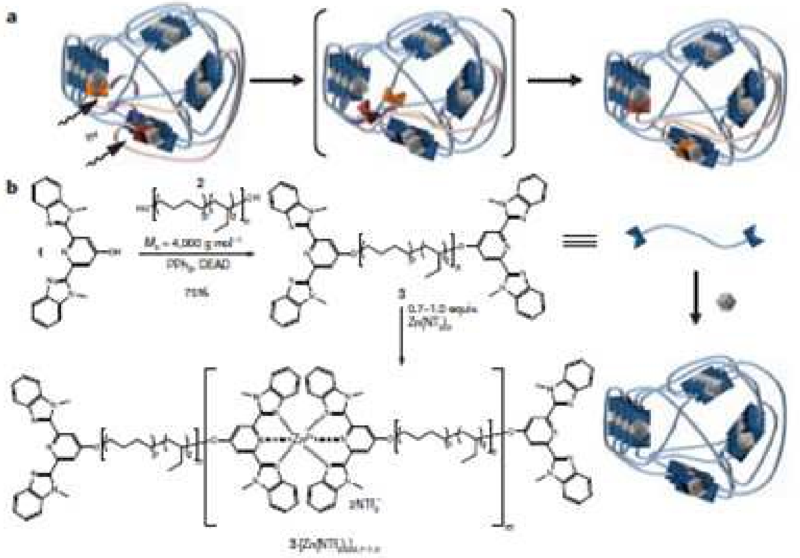

Figure 9. Schematic illustration of metal-ligand interaction between Mebip units and Zn ions[87]. Copyright 2011 Nature Publishing Group.

2.1.4. Ionic interactions

This method toward reversible physical self-healing utilizes ionic crosslinking between anionic polymers and cationic species as metal ions, small molecules, or macromolecules. The formed ionic crosslinking networks can be broken when physically disrupted and subsequently restored in response to change in stimuli at an ambient condition.

Multivalent ferric ions were used to form ionically-crosslinked self-healable materials with chemically-crosslinked hydrogels based on poly(acrylic acid) having pendant COOH groups[99, 100] and catechol-functionalized polyallylamine.[101] As seen in **Figure 10**, the ionically-crosslinked hydrogels with relatively low storage modulus ($G' \approx 10^4$ Pa) exhibit autonomous self-healing through dynamic bonding of physical crosslinking and migration of ferric ions.[99] Cationic macromolecules (oligomers or polymers) have been used.[102, 103] One example is high-water-content moldable hydrogels consisting of sodium poly(acrylic acid), with a multivalent G3-dendrimer functionalized with terminal guanidiuium ion groups in the presence of clay nanosheets.[102] Other ionically crosslinked hydrogels were prepared by ionic interactions of poly(allylamine) mixed with multivalent anions such as tripolyphosphate,[104] or poly(N,N-dimethylacrylamide) with clay particles.[105]

Layer-by-layer approaches of anionic and cationic species through ionic interactions have also been explored. The resulting multi-layered hydrogels exhibit self-healing; further, healability was promoted by swelling and hydration in the presence of moistures.[106-110]

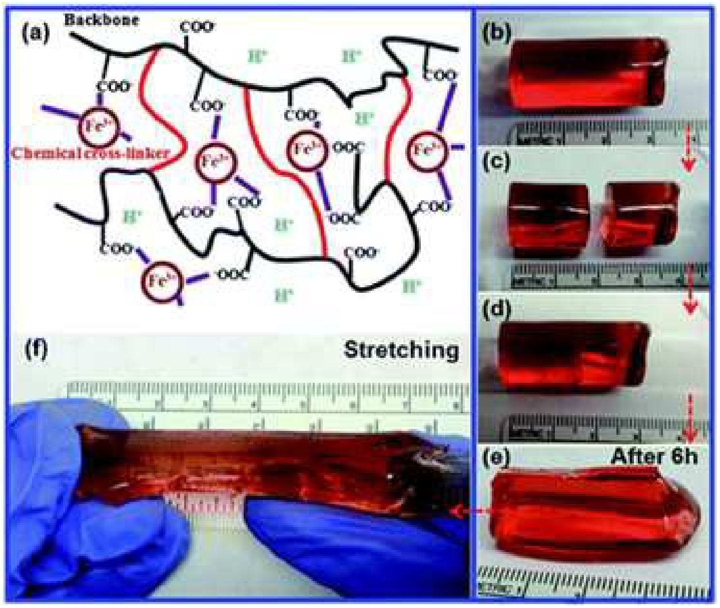

Figure 10. Schematic illustration of ionically-crosslinked hydrogels of poly(acrylic acids) with ferric ions (a) and digital images showing the occurrence of autonomous self-healing through dynamic bonding of physical crosslinking (b-f).[99] Copyright 2013 Royal Society of Chemistry.

2.1.5. Host-guest interactions

Specific interlocking host-guest interactions are reversibly disassembled in response to stimuli such as redox potential, pH, and temperature. Such reversibility has been explored in the design of self-healing polymeric materials in the form of supramolecular hydrogels, nanofibers, and organo-gels. Details on synthesis and self-healing through host-guest interactions have been described in a review.[111]

Cyclodextrin (CD) moieties as host molecules and ferrocene (Fc) moieties as guest molecules have been used. Uncharged Fc moieties formed strong complexes with CD moieties in host-guest manner. On the other hand, charged Fc moieties upon oxidation induced the dissociation of host-guest complexes which can be restored under a reductive condition.[112-114] Poly(acrylic acid) (PAA) was modified with CD, forming PAA-CD, and with Fc, yielding PAA-Fc. As illustrated in **Figure 11**, the mixture of PAA-CD and PAA-Fc formed supramolecular hydrogels through host-gust interactions. Upon oxidation and reduction of Fc moieties, these two pieces were rejoined and the crack was sufficiently healed to form one gel after standing for 24 hrs.[112] Two types of oligo(ethylene glycol) terminated with CD and Fc were synthesized and mixed at a 1/1 mole ratio of host/guest units to form supramolecular fibrous nanostructures in aqueous solution due to interlocking host-guest interactions. Transmission electron microscopy images show self-degradation of nanofibrous structure upon oxidation and reassembly of degraded fibers upon reduction within 2 hrs.[114]

Crown ether-based molecular recognition has been explored for the synthesis of self-healable materials.[115, 116] For example, copolymers based on poly(methyl methacrylate) having pendant crown ether units as host moieties was synthesized. These host moieties were crosslinked with alkyl dialkylammonium guest moieties, forming crosslinked organogels. A few minutes after their macroscopic damages, the occurrence of self-healing on cuts was visible to the naked eye. Further, the self-healable gels show repeatable restoration of G′ and G″.[115]

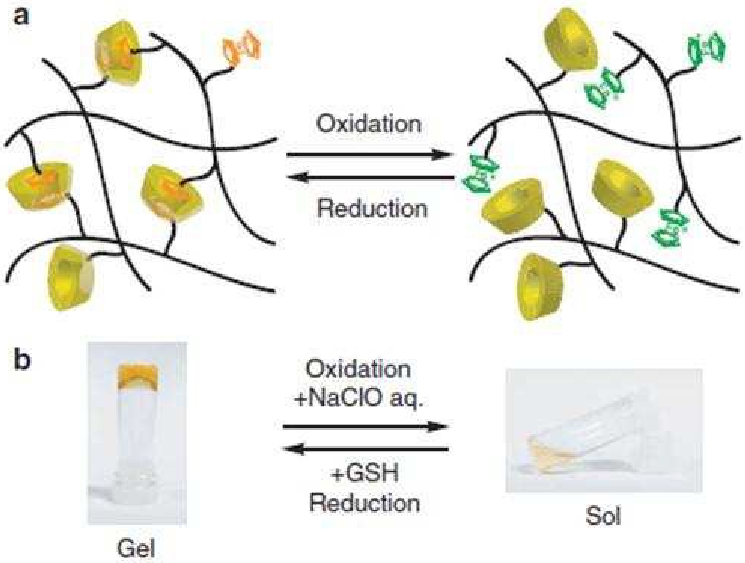

Figure 11. Schematic illustration of host-guest interactions between PAA-CD and PAA-Fc to form self-healble suparmolecular hydrogels (a) and their digital images showing gel-sol transition .[112] Copyright 2011 Nature Publishing Group.

3. Extrinsic self-healing methods

In contrast to intrinsic self-healing systems, where materials themselves are self-healable through reversible chemical reactions or physical interactions, extrinsic self-healing systems contain external healing agents such as monomers, catalysts, or crosslinkers in the forms of capsules, fibers, or vasculatures. These reactive containers are impregnated in polymeric matrix. When crack or damage occurs, the healing agents are released into cracks from ruptured containers to heal the materials by a designed polymerization or a chemical reaction. Extrinsic self-healing materials can be categorized into two self-healing systems: capsule-based and microvascular. This section focuses on only capsule-based extrinsic self-healing materials. Details for microvascular systems are summarized in review and recent publications.[117, 118]

Capsule-based extrinsic self-healing systems require the design of micron-sized capsules that sequester either healing agents or catalysts. Microcapsules, in most cases, are embedded in polymeric matrix (or coatings) that contain healing agents that are needed for self-healing. Upon the rupture of the microcapsules via puncture or crack in the matrix, the sequestered healing agents flow into crack planes via capillary action and mix with other healing agents for polymerization or crosslinking to plug crack planes. A number of parameters have to be considered in the design and synthesis of microcapsules for effective microcapsule-based self-healing. These parameters include not only size (micron to nano) and uniform distribution of capsules but also mechanical strength and miscibility of shells with matrix. The shells should be designed to be strong enough to retain the integrity of capsules embedded in the dried matrix layer. Typical shell-forming polymers include urea-formaldehyde, melamine-formaldehyde, and polyurethane resins. They are generally prepared by *in situ* and interfacial encapsulation techniques utilizing the occurrence of polymerization at interfaces of droplets in an oil-in-water (o/w) emulsion. Several strategies using well-known polymerization methods and chemical reactions have been explored to develop capsule-based extrinsic self-healing materials.

3.1. Ring opening metathesis polymerization (ROMP)

The first generation of microcapsule-based self-healing materials has utilized living ROMP.[119] Microcapsules of dicyclopentadiene (DCPD) in urea-formaldehyde shells (50 - 200 μm) were prepared by a general protocol for interfacial encapsulation method. Hydrophobic DCPD monomers were emulsified in the presence of ethylene maleic anhydride copolymers in aqueous solution containing urea. Under agitation, an addition of formaldehyde yielded microcapsules, which were isolated and air-dried. As illustrated in **Figure 12a**, the formed DCPD-containing microcapsules were embedded in epoxy-based matrix formulated with a first-generation Grubb's catalyst. When mechanical damage occurred, self-healing was triggered by the rupture of microcapsules, releasing DCPD into the cracks and driven by capillary force. The released DCPD was mixed with ruthenium-based Grubb's catalyst to be polymerized via ROMP at room temperature within minutes (**Figure 12b**). The crack-healing efficiency of these epoxy composites was assessed by fracture test using a tapered double cantilever beam specimen. As seen in **Figure 12c**, the self-healable composites required greater load for the fracture, compared with control composite with no self-healable microcapsules.[120] The effect of ruthenium catalysts[121] and stereoisomers of DCPD[122] on self-healing kinetics have been further explored.

Several approaches to maximize self-healing efficiency for the epoxy materials have been explored. Wax-protected catalysts in microspheres enabled the improvement of poor dispersibility of catalysts in epoxy matrix.[123, 124] The size of microcapsules is critical in that the amount of DCPD delivered to the cracks linearly increased with their size. Self-healing reached maximum levels when sufficient DCPD is available to entirely fill the cracks.[125] In contrast to micron-sized capsules, nanometer-sized capsules can be beneficial in thin films or microelectronic coatings, which usually have cracks on smaller length scales. Emulsion (or miniemulsion)-solvent evaporation methods allow for the synthesis of submicron-sized capsules containing Grubb's catalyst[126] and nanocapsules containing self-healing agents.[127]

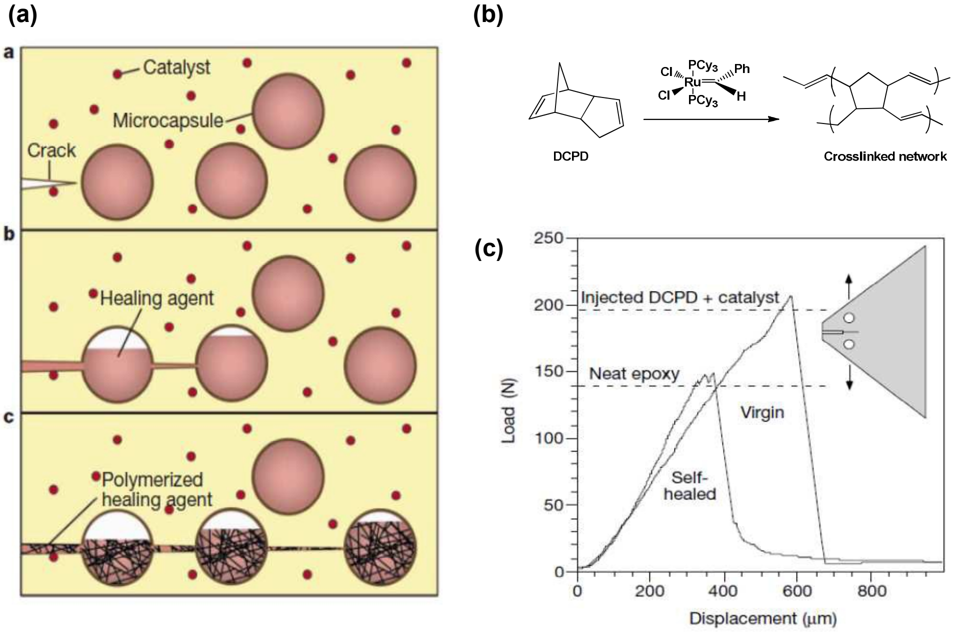

Figure 12. Pictorial depiction of healing mechanism of urea-formaldehyde microcapsule (a), healing chemistry utilizing ROMP of DCPD in the presence of Grubb's catalyst (b), and healing efficiency is obtained by fracture toughness testing of tapered double-cantilever beam (TDCB) specimens (c).[120] Copyright 2001 Nature Publishing Group.

3.2. Controlled radical polymerization (CRP)

ATRP is a versatile and powerful CRP technique that allows for the synthesis of well-controlled (co)polymers with narrow molecular weight distribution.[128, 129] As illustrated in **Figure 13**, ATRP has been explored to heal damage. Microcapsules of glycidyl methacrylate in melamine-formaldehyde shells were dispersed in matrix consisting of poly(methyl methacrylate) terminated with Br groups (PMMA-Br) prepared via ATRP. When the microcapsules were ruptured, the released glycidyl methacrylate (GMA) was chain-extended through ATRP from PMMA-Br ATRP macroinitiators mediated with Cu species at ambient temperatures to form PMMA-b-PGMA diblock copolymers. Such chain extension via ATRP enabled self-healing.[130] RAFT polymerization has also been utilized in self-healing. Similarly, polystyrene prepared via RAFT polymerization was mixed with melamine-formaldehyde microcapsules containing GMA. Upon the rupture, GMA was polymerized from polystyrene macroinitiator under a RAFT polymerization condition on damage, offering the recovery of impact strength.[131]

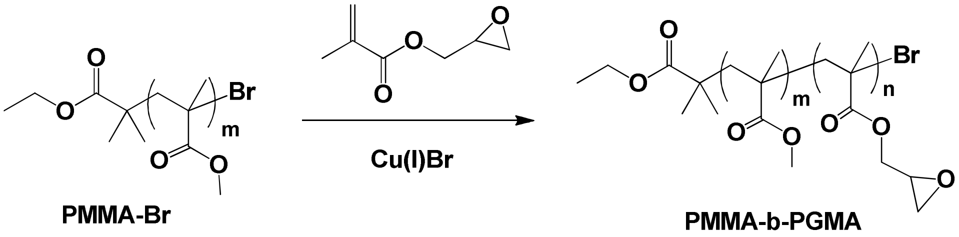

Figure 13. Illustration of ATRP of GMA from PMMA-Br macroinitiator for microcapsule-based extrinsic self-healing.

3.2. Azide-alkyne click chemistry

Small molecular weight alkynes and three-arm star polyisobutylene azides were encapsulated separately in phenol-formaldehyde microcapsules; they were impregnated in high molecular weight polyisobutylene matrix containing Cu(I) species. As illustrated in **Figure 14**, azide-alkyne click reaction in the presence of Cu(I) species was triggered to heal cracks when microcapsules were ruptured upon impact releasing sequestered alkyne and azide.[132]

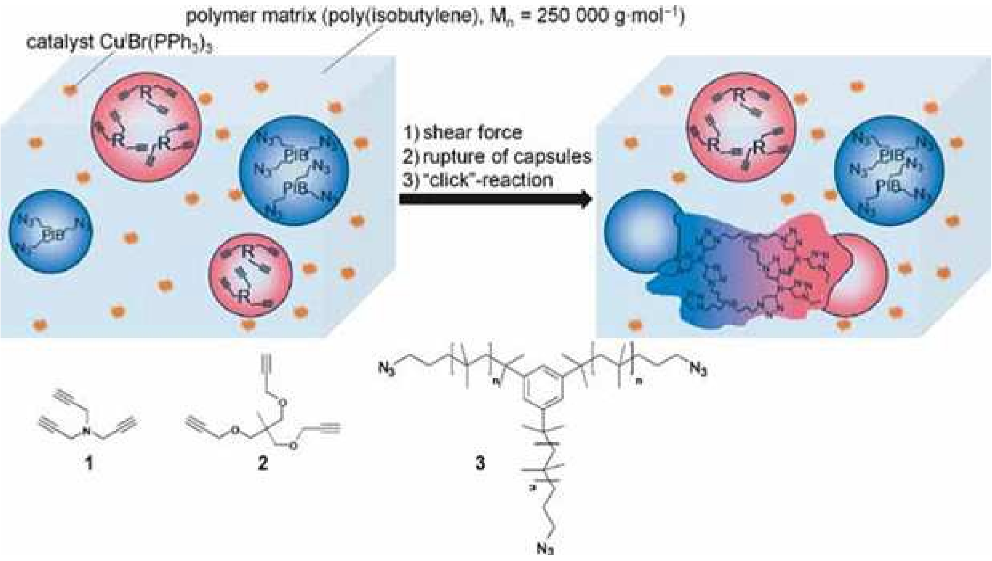

Figure 14. Design and extrinsic self-healing of polyisobutylene matrix embedded with microcapsules of small molecular weight alkynes and three-arm star polyisobutylene azides separately via azide-alkyne click reaction in the presence of Cu(I) species.[132] Copyright 2011 Wiley Interfaces.

3.2. Polyaddition

A number of unique chemistries have been explored; **Figure 15** illustrates typical examples. In addition to the use of ROMP described above, epoxy-amine reaction has been utilized for the development of self-healable epoxy-based materials. Reports describe the design and use of microcapsules containing solvent/reactive epoxy in urea-formaldehyde shell,[133] epoxy/mercaptan in melamine-formaldehyde shell,[134] and reactive amine in polyurethane shell.[135] These reactive microcapsules were embedded in self-healable epoxy composites and ruptured to be able to cure epoxy. Transition metal-catalyzed hydrosilylation has been explored to develop polydimethylsiloxane (PDMS)-based self-healing materials.[136, 137] Particular materials contained siloxane-based healing agents phase-separated in vinyl ether matrix and polyurethane microcapsules containing di-n-butyl tin dilaurate catalyst. Upon the damage, capsules were broken to release tin catalysts. Tin-catalyzed polyaddition of hydroxyl-terminated PDMS with polydiethoxysiloxane in the contact with tin catalysts resulted in self-healing.

One of the drawbacks of most extrinsic self-healing systems via ROMP, controlled radical polymerization, and tin-catalyzed polyaddition is associated with the presence of catalysts. These drawbacks include catalyst availability, cost, and environmental toxicity, as well as stability, materials processing, and residual catalysts remaining in materials. Recently, catalyst-free extrinsic self-healing systems have been reported. A system utilizes polyaddition through the formation of urea linkages in the presence of moisture. Polyurethane-based microcapsules containing reactive isocyanates such as isophorone diisocyanate[138] or an isocyanate-rich polyurethane prepolymer[139] were prepared by an interfacial encapsulation technique in O/W emulsion. Another system utilizes a photo-induced chain-growth polymerization.[140, 141] A vinyl-functionalized PDMS and a photo-initiator were encapsulated in urea-formaldehyde microcapsules. Upon the crack, photo-crosslinking of the released reagents from the microcapsules occurred to attain photo-induced self-healing. These materials could be useful for self-healing anticorrosion and protection coatings.

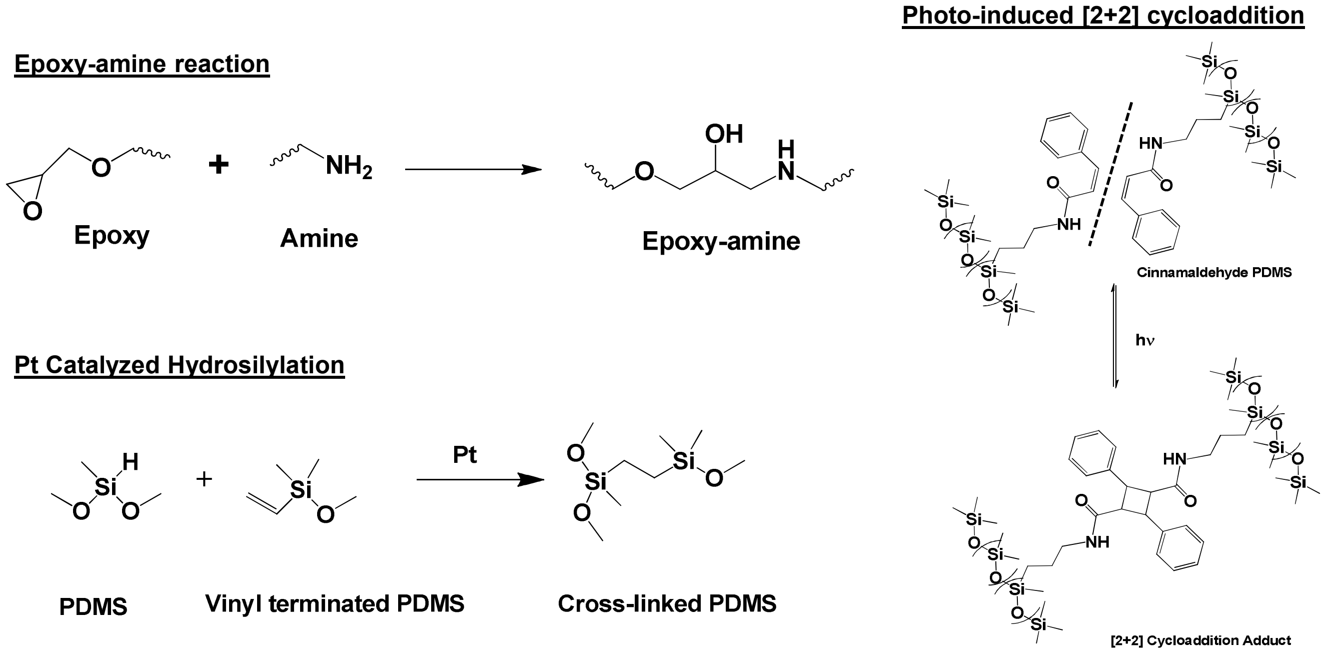

Figure 15. Illustration of various polyaddition mechanisms for the development of novel extrinsic self-healing materials.

4. Conclusion

Recent advances in the development of intrinsic and extrinsic methods to synthesize novel self-healable polymeric materials are summarized. Extrinsic self-healing methods utilize the encapsulation of extra healing agents such as monomers, crosslinkers, and catalysts in capsules-like structures. Upon damage, the encapsulated healing agents are released to fill the fractured parts where polymerization takes place to heal the cracks. Even though most methods can heal large damaged areas, they exhibit a single event of self-healing due to the depletion of the encapsulated healing agents. In contrast, intrinsic self-healing methods utilize reversible (or dynamic) chemical crosslinking through the formation of dynamic covalent bonds and non-covalent crosslinking through supramolecular interactions. Numerous approaches to synthesize reversible, repeatable self-healing networks have been proposed; however, most intrinsic self-healing systems require initiation by external stimuli such as temperature, pH, light, or chemicals.

Future design and development of effective self-healing materials that can be used in a wide range of biomedical and industrial applications require a high degree of control over properties. They include i) the occurrence of multiple self-healing events, ii) the minimal or no use of external stimuli, iii) the unchanged integrity of original materials upon multiple healing cycles, and iv) the high mechanical strength while also maintaining dynamic physical or chemical interactions. Numerous crosslinked systems are built on soft polymeric materials such as hydrogels and organogels. Most of them exhibit great self-healability; however, they still suffer from various applications requiring high mechanical strength. In an attempt to enhance toughness while retaining self-healability for supramolecular materials, an innovative design featuring the incorporation of hard domains or nanoparticles into soft matrix has been explored. Nevertheless, more studies should be focused on the development of tough self-healing polymeric materials. Further, most self-healing materials that have been reported utilize single dynamic interactions: future designs could explore the occurrence of self-healing through dual or multiple interactions.

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