Self-healing polymers

Siyang Wang and Marek W. Urban ✉

Abstract | Self-healing is the capability of a material to recover from physical damage. Both physical and chemical approaches have been used to construct self-healing polymers. These include diffusion and flow, shape-memory effects, heterogeneous self-healing systems, covalent-bond reformation and reshuffling, dynamics of supramolecular chemistry or combinations thereof. In this Review, we discuss the similarities and differences between approaches to achieve self-healing in synthetic polymers, where possible placing this discussion in the context of biological systems. In particular, we highlight the role of thermal transitions, network heterogeneities, localized chemical reactions enabling the reconstruction of damage and physical reshuffling. We also discuss energetic and length-scale considerations, as well as scientific and technological challenges and opportunities.

Biological organisms have built-in repair mechanisms to prevent them from losing their functions. The repair processes in mammals and plants occur in entirely different chemical and morphological environments, yet — in a general sense — the outcomes are similar. For example, DNA damage is a fairly common event in a cell's life that may lead to DNA mutation, uncontrollable growth (cancer) or cell death. In mammals, the key components are pro-inflammatory cytokines, transforming growth factors and angiogenic factors[1,2]. Human skin self-heals via an inflammatory response of cells below the dermis by increasing collagen production, which regenerates epithelial cells and tissue. In plants, oligopeptides, oligosaccharides or other molecules induce changes that signal damage and initiate a sequence of chemical events leading to macroscopic repair[3,4]. Regardless of the individual steps in any of these processes, self-healing in living systems involves a cascade of reactions, the exact chemistries of which are far from understood.

The main approaches to self-healable polymers involve either physical or chemical events at the molecular level, although there is overlap between the two approaches (FIG. 1). Examples of physical self-healing processes are interchain diffusion[5], phase-separated morphologies[6,7], shape-memory effects[8] and the introduction of superparamagnetic nanoparticles[9]. By contrast, predominantly chemical processes include the incorporation of covalent[10–12], free-radical[13,14] or supramolecular[7,15–17] dynamic bonds. Many self-healing processes involve a combination of physical and chemical events, such as taking advantage of enhanced van der Waals forces[18], resulting in interdigitated copolymer morphologies — embedded, reactive, encapsulated fluids that burst open upon damage to fill up a wound and trigger chemical reactions of reactive agents to repair damage[19] — and cardiovascular networks[20], which use the same concept.

In this Review, we outline the physical, chemical and physico-chemical processes of self-healable polymers. We discuss how leveraging advances in synthetic materials and biological systems, while using feedback and feedforward from physico-chemical analysis and predictive computational algorithms, will lead to discoveries and technological advances. Taking self-healing materials to the next level, we discuss how exchangeable bonds triggered by thermal, chemical or other stimuli result in the development of tunable rigid or soft vitrimers.

Interchain diffusion

Early approaches for crack healing in thermoplastic polymers can be broken into five stages: segmental surface rearrangements, surface approach, wetting, diffusion and randomization[5,21]. During surface rearrangements, factors such as topography and roughness of the surfaces, chain-end distribution and molecular-weight distribution come into play. As two surfaces come together to enable subsequent molecular-level physical and/or chemical self-healing[21], they form an interface and wet each other before diffusion occurs. Various chemical rebonding techniques in thermosetting and thermoplastic self-repairing polymers have supplemented the diffusion phase[22], but differentiation between the physical and chemical processes involved is not trivial.

Mechanical damage creates interfacial regions. Local mobility and diffusion rates in damaged areas (especially in interfacial regions) are important in the self-healing process[23]. Interfacial macromolecular interpenetration was proposed in the 1960s (REF.[24]) and typical diffusion rates in solid-state polymers are 10^{-5} m min^{-1} (REF.[25]). Furthermore, full recovery of mechanical strength is approximately 0.4–0.8 times the radius of gyration[26–28],

Department of Materials Science and Engineering, Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, SC, USA.

✉*e-mail: mareku@clemson.edu*

https://doi.org/10.1038/s41578-020-0202-4

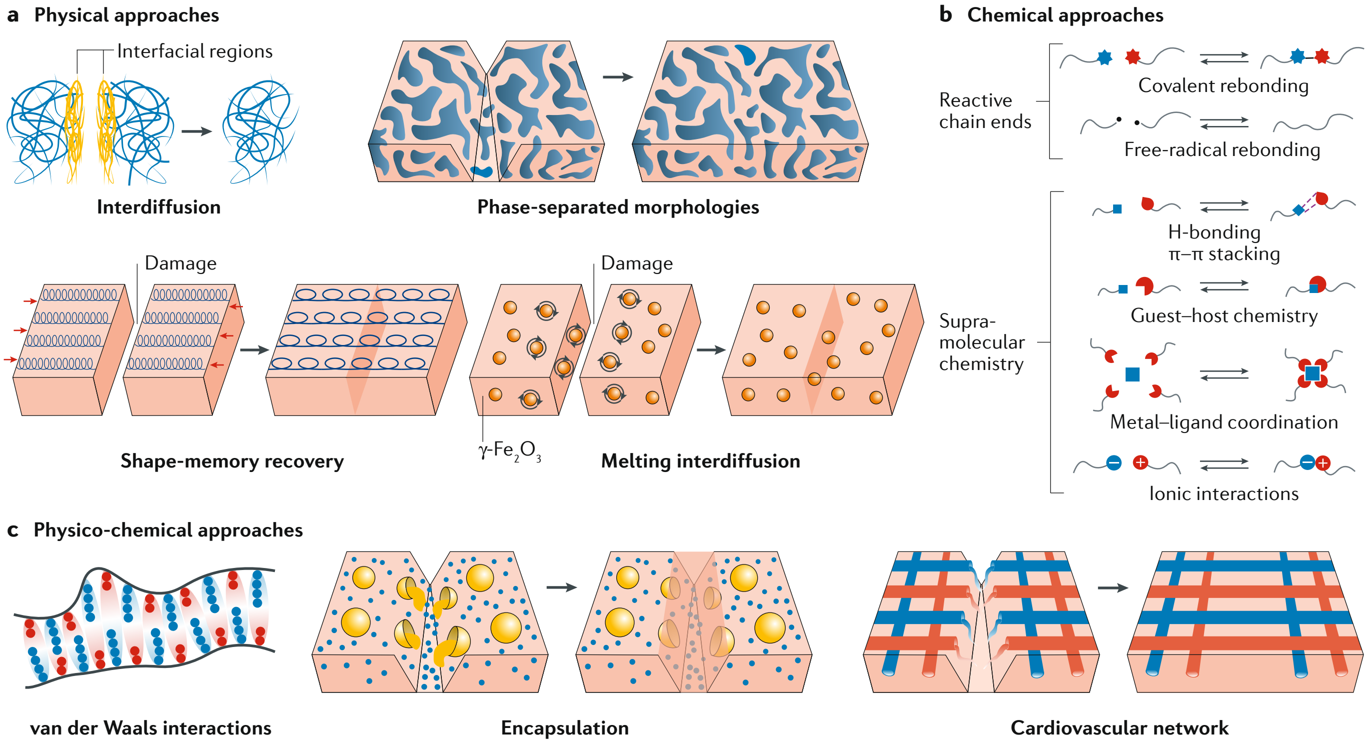


Fig. 1 | **Self-healing mechanisms. a** | Physical processes to realize self-healing include interdiffusion of polymer chains, the introduction of phase-separated morphologies, shape-memory effects and the introduction of active nanoparticles into a polymer matrix. **b** | Chemical processes to facilitate self-healing involve either introducing reactive chain ends or supramolecular chemistries. **c** | Physical and chemical processes can be combined to realize self-healing. Self-healing is achieved by incorporating enhanced van der Waals interactions, or encapsulating nanocapsules or microcapsules containing reactive liquids to heal a wound, or by mimicking cardiovascular architectures composed of hollow fibres filled with reactive chemicals to heal a polymer matrix.

and the average interdiffusion depth is expressed as a function of time $X(t)$ by

$$X(t) = X_\infty (t/T_r)^{1/4} \qquad (1)$$

where T_r is the reptation time, which is proportional to the chain molecular weight to the third power[21,28,29]. Accordingly, more flexible and shorter chains are more mobile and facilitate recovery more easily[22]. In contrast to the bulk, surface macromolecules exhibit high mobility, reflected in a lower glass-transition temperature (T_g), owing to their high degrees of freedom[21,30–32], thus facilitating enhanced diffusion. This is supported by the observation that the T_g inside a fresh cut is lower than that in an undamaged surface[33].

Fickian diffusion is enhanced above the T_g, owing to the excess free volume, driven by entanglement coupling and reptation[34–36]. However, crack healing in poly(methyl methacrylate) (pMMA) was achieved by heating above the T_g under pressure, which facilitates a recovery of the fracture stresses proportional to $t^{1/4}$, where t is the heating time[25,37]. In general, lowering the T_g enhances segmental chain mobility (which can also be achieved through the use of plasticizing solvents[25,38]), thus promoting diffusion and inducing conformational changes, but does not assure self-healing. When liquid is dispersed in a solid matrix, diffusion favours the repair process, which will be enhanced for lower-T_g networks, owing to the excess free volume. Because newly formed surfaces or interfaces resulting from damage exhibit liquid-like attributes, relatively slow diffusion rates ($\sim 10^{-3}$ m min^{-1}) are anticipated[39]. Under these conditions, the reptation model (that is, a polymer chain migrating through a tube; Eq. 1) could serve to predict topological constraints imposed on a polymer backbone by the surrounding polymer chains[37] in the bulk. However, this model may not be applicable in the surface and/or interfacial regions, where interfacial energy may dominate chain mobility.

van der Waals interactions

van der Waals interactions have been of interest for over two centuries, and the presence of van der Waals interchain forces in polymers was established decades ago. An illustrative biological system that uses van der Waals forces to adhere to any surface is gecko setae[40]. However, only recently have such interactions been recognized for their potential in designing self-healing commodity copolymers[18]. If perturbation of van der Waals forces upon mechanical damage is energetically unfavourable, interdigitated alternating or random copolymer motifs will self-heal to an energetically more favourable state. Molecular dynamics simulations showed that the formation of helix-like conformations depends on the copolymer composition and creates a viscoelastic response that energetically favours self-recovery upon chain separation, owing to 'key-and-lock' associations of the neighbouring chains. In essence, van der Waals forces stabilize neighbouring copolymers, which is reflected in enhanced cohesive-energy density (CED) values. FIGURE 2a illustrates how induced dipole interactions for alternating or random poly(methyl methacrylate-alt-ran-*n*-butyl acrylate) (p(MMA-alt-ran-nBA)) copolymers owing to directional van der Waals forces may enhance the CED at equilibrium ($\mathrm{CED_{eq}}$) of entangled and side-by-side copolymer chains. It is a challenge to measure van der Waals forces, and molecular-dynamics simulations are valuable for understanding and quantifying their role in self-healing. For that reason, various force fields for small molecules[41,42] and polymers[43,44] are useful. Although over the years they have been modified to predict polymer–polymer[45] and polymer–inorganic interactions[46], there is a need for more precise dynamic modelling of damage–repair cycles in polymers.

Shape memory

Shape-memory-assisted self-healing is commonly observed in biological systems. An example of this is wound closure in leaves, whereby, after a transversal incision, the entire leaf bends until the wound is closed. Recent studies suggest that this is governed by a combination of hydraulic shrinking and swelling, which are the main driving forces and growth-induced mechanical prestresses in plant tissues[47].

In synthetic polymers, the shape-memory effect was discovered in the 1940s and first used in dental materials (methacrylic ester resin)[48]. In the 1960s, this discovery was followed by the development of heat-shrinkable polyethylene in films, tubing and other applications[49,50]. The response of shape-memory materials to external stimuli was largely neglected as part of self-healing processes. However, if designed properly, polymers can 'memorize' a permanent shape that can be manipulated to create a temporary form, and, under suitable conditions triggered by external or internal stimuli (for example, heat, light or deformation), transform back to the memorized permanent shape. Such responses manifest in conformational changes and/or chain contractions, which are typically entropy-driven, resulting in mass flow and self-healing[51]. One example is light-activated shape-memory polymers, which use one wavelength of light for photocrosslinking, while a second wavelength cleaves the photocrosslinked bonds to enable reversible switching between elastomers[52]. Another example is pretensioned shape-memory alloy wires[53] or fibres[54] in

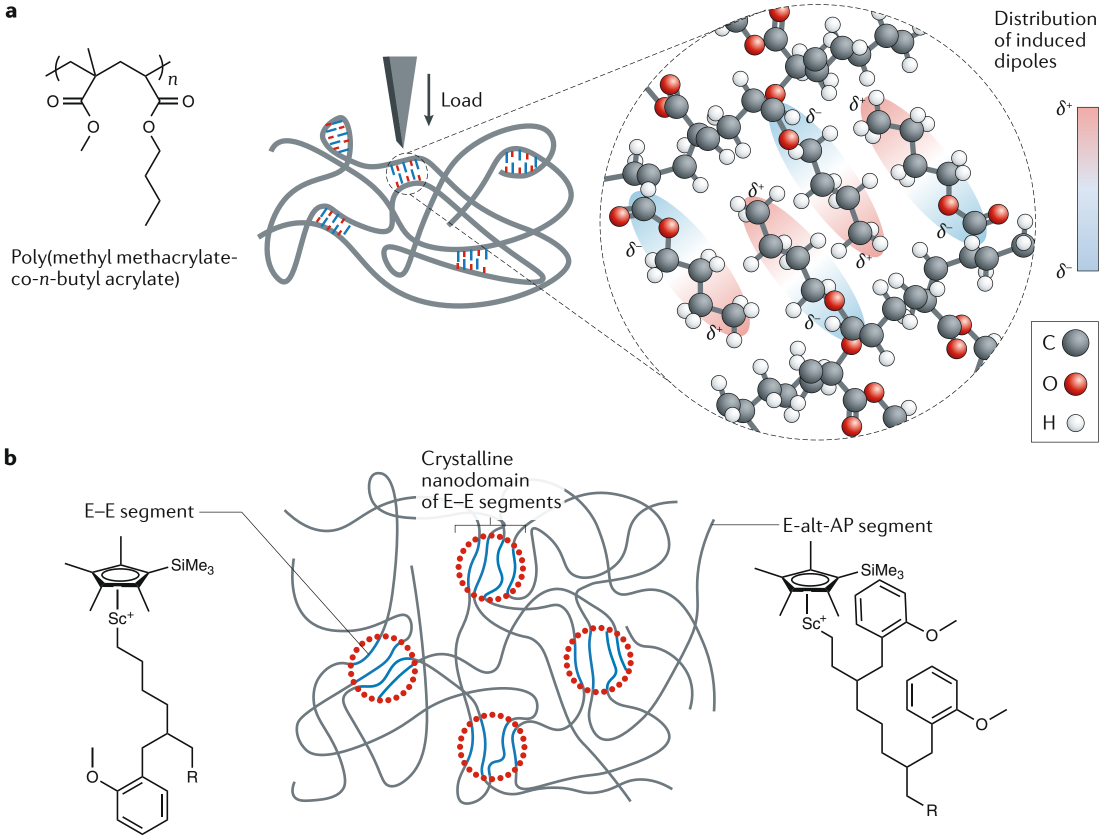


Fig. 2 | **Self-healing through van der Waals forces or the shape-memory effect. a** | Key-and-lock configuration in self-healing poly(methyl methacrylate-co-*n*-butyl acrylate) copolymer. Self-healing occurs in a narrow compositional range for copolymer topologies that are preferentially alternating with a random component and is attributed to favourable van der Waals forces between the polymer chains, forming key-and-lock interchain junctions. **b** | A self-healing and phase-separated copolymer system comprising ethylene(E)-alt-anisyl propylene (AP). Copolymers with glass-transition temperatures below room temperature are self-healable; however, the shape-memory effect is observed for copolymers with glass-transition temperatures around or above room temperature. Panel **b** (left) adapted with permission from REF.[59], ACS.

a polymer matrix. Upon activation at elevated temperature, self-healing occurs owing to forces pulling crack surfaces towards each other.

Incorporating soft and hard segments into one copolymer can lead to phase-separated morphologies. For example, a material that combines rubber elasticity and thermoplastic stiffness will expand the applications of copolymers owing to enhanced mechanical properties represented by enhanced storage and loss moduli. If stiff and tough polymers are combined with dynamic and flexible macromolecular assemblies facilitating mobility, self-healing can be achieved[7]. Such materials have been made that respond to external stimuli, including temperature, electrical or magnetic fields[55], solution concentration[56] or light[57]. Notably, the action of the shape-memory effect during self-healing restores entropic energy upon the release of the force creating damage to fill an open wound in the material.

The shape-memory effect can be determined quantitatively in a single dynamic mechanical analysis that enables determination of stored conformational entropy in polymers that exhibit a T_g and a rubbery plateau[58]. Although the majority of polymers exhibit some kind of shape-memory effect, they do not necessarily self-heal. An attempt was made to relate shape memory to self-healing by copolymerizing ethylene and anisyl-substituted propylenes using a sterically demanding half-sandwich scandium catalyst[59]. This study showed nanodomain phase separation and self-healability for copolymers with T_g below room temperature, in particular, in aqueous environments (FIG. 2b); however, when the T_g was tuned near or above room temperature, the shape-memory effect was observed. This raises several questions, including the extent to which viscoelasticity above the T_g contributes to self-healing; how enhanced chain mobility near T_g affects self-healing locally and globally; how far from the damage area polymer chains 'feel' conformational changes; and the role of interfacial energy in self-healing near the damaged regions[60]. In attempts to address these questions, two mechanisms of self-healing were identified: first, viscoelastic shape memory driven by stored conformational entropy upon damage, which is recovered to facilitate self-healing, and, second, surface-energy-driven or surface-tension-driven processes that reduce newly generated surface areas created upon damage by shallowing and widening wounds until healed[61].

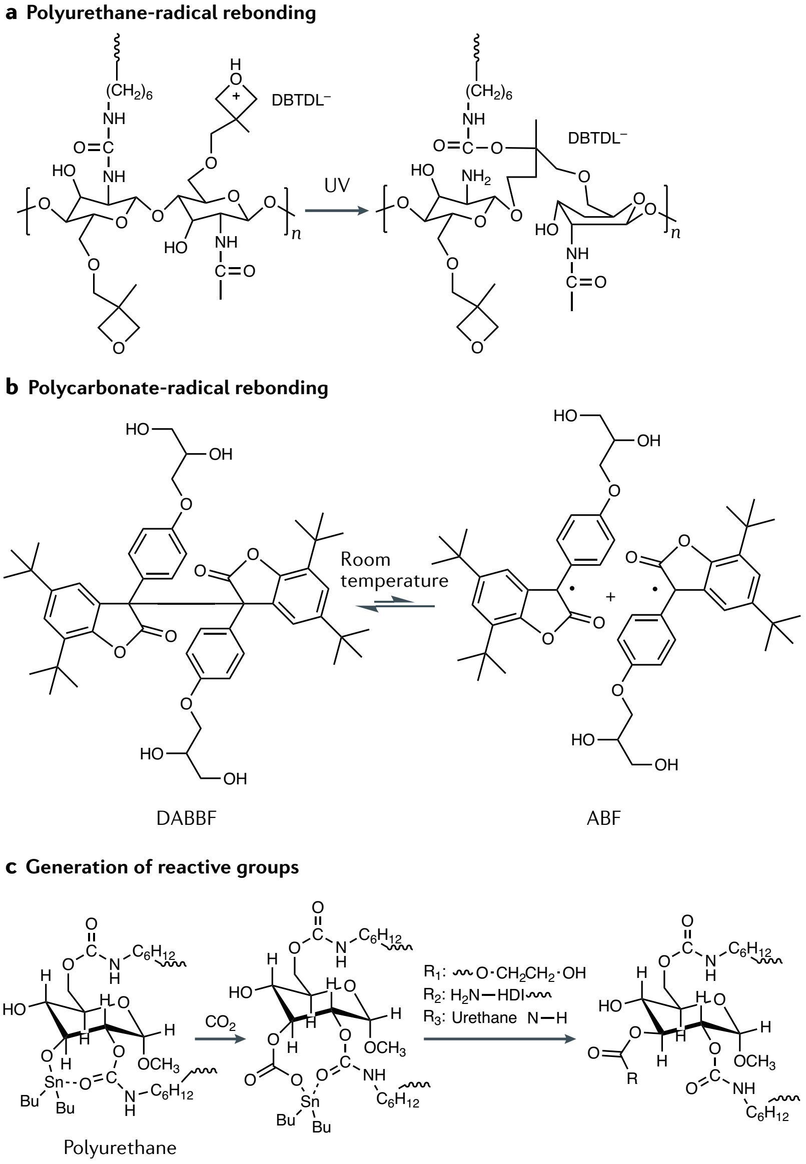
Heterogeneous self-healing systems

Although interest in homogeneous self-healing polymers via interchain diffusion dates back to the early 1980s, heterogeneous systems were not conceptualized and developed until the 2000s. The encapsulation of reactive fluids that are released upon damage and, hence, fill and repair the damaged area is one of the first examples of self-healing heterogeneous systems[19] (FIG. 1c). Initial studies involved catalysed reactions of ring-opening metathesis polymerization of dicyclopentadiene in the presence of a ruthenium catalyst[19]. This approach has been reviewed elsewhere[62,63]. The presence of nanocapsules and microcapsules with reactive ingredients that, upon cracking, fill in the damaged area resembles blood clotting in a wound, but a technological challenge is achieving high stability of the capsules during processing and overcoming the limitation of one-time self-repair. A somewhat analogous concept to develop fibre-reinforced composites that retard failure is based on cardiovascular networks in which hollow fibres filled with reactive ingredients serve as delivery systems of chemicals to the wounded area. For this application, self-healing microfibres with core–shell geometry containing encapsulated binary epoxies are promising materials[64]. These fibres can be formed by coaxial nozzles that encapsulate epoxy resin and crosslinker in separate cores. Upon damage, epoxy and crosslinker are released from the cores of damaged fibres and self-heal. This approach is conceptually exciting if 'used' self-healing agents could be replenished after damage.

Polymers in a molten state — owing to their low viscosity and flow — may also serve as glue to repair mechanical damage. Because of interfacial diffusion in the molten state, incorporating superparamagnetic γ-Fe_2O_3 nanoparticles into a polymer matrix facilitates repair under the application of an oscillating magnetic field[9]. As a result, the polymer matrix–nanoparticle interfacial regions melt, facilitating polymer flow and the permanent repair of physically separated polymer surfaces. Embedding physically responsive nanoparticles or microparticles has several technological advantages, particularly in materials where damage repair does not permit the use of electromagnetic radiation, heat or other stimuli. It may also be advantageous in fibre-reinforced composites, where damage may not be easily detectable and accessible, such as fibre–matrix interfaces.

Long-range sensing and signalling are intriguing properties of biological systems, but challenging to achieve in synthetic materials. One approach to address this challenge is to fabricate a Diels–Alder bond-containing polyurethane backbone with electrically conductive carbon nanotubes (CNTs), where the dynamics of Diels–Alder bond reformation enables self-healing and the CNTs confer electrical conductivity[65]. In this case, when electric potential is applied to a damaged specimen, the difference in electrical resistance between the damaged and undamaged areas results in temperature differentials reflected in infrared spectroscopy thermal images, thus providing crack diagnostics. This type of composite material can also be equipped with strain-sensing capability and has potential technological applications in electronic strain sensors as an alternative to ceramic piezoelectric devices. Based on these studies, we envision that electrically, thermally or optically conductive fibres embedded into a polymer matrix may lead to a new generation of self-healing materials. An early example is CNTs dispersed in vitrimer-based epoxy, which can facilitate self-healing using photothermal energy to activate transesterification reactions[66].

Multiphase heterogeneous polymeric materials can be produced by copolymerizations. Similar to phase-separated polyurethane containing a combination of soft and hard segments, self-healing can be achieved in copolymers by combining hard polystyrene backbones with soft polyacrylate amide (PAAm) pendant groups carrying multiple H-bonding sites[7].



a **Polyurethane-radical rebonding**

b **Polycarbonate-radical rebonding**

c **Generation of reactive groups**

Fig. 3 | **Reformation of covalent bonds. a,b** | Free-radical rebonding[13,14]. **a** | Upon mechanical damage of an oxetane-substituted chitosan precursor incorporated in a two-component polyurethane network, four-membered oxetane rings open to create two reactive ends. Upon exposure to ultraviolet (UV) light, chain scission of the chitosan occurs, which crosslinks with the reactive oxetane ends, thus repairing the network. **b** | Diarylbibenzofuranone (DABBF), a dimer of arylbenzofuranone (ABF) and known antioxidant, was used as a dynamic reversible covalent bond capable of self-healing at room temperature in the dark. **c** | Generation of reactive amines[10] capable of self-healing. When methyl-α-D-glucopyranoside (MGP) molecules react with hexamethylene diisocyanate (HDI) and polyethylene glycol (PEG), crosslinked MGP–polyurethane networks are formed, which self-repair in air. DBTDL, dibutyltin dilaurate.

This approach relies on localized variations in T_g introduced by phase-separated high-T_g polystyrene and low-T_g PAAm segments, which facilitates network remodelling through hydrophobic and hydrophilic interactions. Taking this concept further, triblock copolymers can be prepared, benefiting from the elastomeric properties of microphase-separated thermoplastic block copolymers with the reversible H-bonding[67]. This is an example of how localized compositional heterogeneities can be used in designing self-healing polymer networks. It is worth noting, however, that commercial styrene and acrylic copolymers are non-self-healable. To achieve self-healing, the chemical make-up of the copolymer, control of the copolymer topologies and the processing conditions are crucial. For example, it was shown for PAAm that phase separation may induce gel–glass-like transitions using a combination of good and poor solvents[68]. In addition, phase-separated supramolecular architectures can also facilitate self-healing, as demonstrated for acrylic or styrene-based triblock copolymers[69].

H-bonding can also be used to achieve self-healing in heterogeneous systems. For example, bio-derived carboxyl cellulose nanocrystals can be used to construct H-bonding interactions with chitosan-decorated epoxy natural rubber latex, where carboxyl cellulose nanocrystal molecular chains comprise rich carboxylic and hydroxyl groups. Moreover, chitosan molecular chains provide abundant amino, acetamide and hydroxyl groups, interacting with each other via H-bonding[70]. Using condensation polymerization, elastomers composed of polytetraethylene and tetraethylene glycol have been prepared that are highly stretchable, tough and capable of self-healing[71]. The key interaction responsible for these properties is quadrupole H-bonding.

Covalent-bond reforming

Free-radical recoupling can reform covalent bonds in polyurethanes and polycarbonates cleaved by mechanical damage (FIG. 3a,b). The number of free radicals formed in these processes may vary depending upon their stability; for example, in polyurethanes modified by oxetanes or oxolanes, the C–O cleavage results in fairly stable free radicals. In such cases, kinetic factors are important in self-healing: if free radicals or other reactive groups remain reactive for sufficient time after bond cleavage, the chain ends terminated with free radicals will react before they are quenched by oxidative processes. Thus, stability and reactivity are important considerations. Mechanical damage resulted in cleavage of a constrained four-membered ring oxetane generating stable free radicals[33], and self-healing upon mechanical damage of a crosslinked polyurethane network can be achieved by exposing the damaged area to 302-nm ultraviolet (UV) radiation[13] (FIG. 3a). Although mechanistically and kinetically different, self-healing was also realized with oxolane–chitosan macromonomers introduced to polyurethane networks[72]. In polycarbonates produced by heat-induced reactions and diisocyanate-terminated poly(propylene glycol)[14], mechanical damage generates the arylbenzofuranone radicals produced upon the dissociation of tetrahydroxy-functionalized diarylbibenzofuranone (DABBF). For these radicals to facilitate the rebonding of polycarbonate radical (FIG. 3b), the radicals must have low or no sensitivity to oxygen to avoid radical quenching via free-radical reactions with molecular oxygen[73], which impede self-healing. A similar approach was developed for the reformation of polycarbonate networks by adding a base (Na_2CO_3) to introduce additional ester reactions[74]. Subsequent substitutions between phenoxide and phenyl–carbonyl chain ends along with CO_2 recombination facilitates the repair of polycarbonate network.

Adduct (exo or endo) formation between furan (diene) and maleimide (dienophile) groups can also facilitate self-healing, owing to covalent rebonding[75,76]. In these studies, mechanical activation of a DABBF-based scissile using dynamic covalent mechanophores was covalently attached to the surface of cellulosic nanocrystals. The mechanically activated radicals recombined much more slowly than those formed by DABBF monomers and DABBF-containing polymers in the other environments, such as solutions, bulk and gels[77]. Free-radical stability and self-healing has also been explored in self-healable alkoxyamines prepared by click chemistry, in which UV irradiation cleaved polymer crosslinks, followed by recombination of radical species[78]. Similarly, multifold nitroxide-exchange reactions between trialkoxyamines and trinitroxide monomers form covalently crosslinked dynamic self-healable network with a tunable degree of crosslinking[79]. The uniqueness of this approach is the reversibility driven by concentration changes of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radicals.

The Calvin cycle — a biological process that converts light energy into sugars — is a sequence of reactions that includes the fixation of carbon dioxide and various enzymatic reactions[80]. This sequence of reactions is driven by forming and reforming reactive groups. Achieving the fixation of carbon dioxide using synthetic materials has also been realized and, similarly, enables the reformation of bonds and the renewal of materials[10]. These materials are capable of self-repair in the presence of atmospheric carbon dioxide and water by generating reactive amine functionalities that react to reform urethane and carbonate linkages. More specifically, methyl-α-D-glucopyranoside (MGP) reacts with hexamethylene diisocyanate trimer and polyethylene glycol (PEG) to form crosslinked MGP–polyurethane networks[10] (FIG. 3c).

As described earlier, thermal energy and electromagnetic radiation are commonly used to initiate self-healing. It is often difficult to determine if electromagnetic radiation alone causes self-healing or if energy absorption results in temperature changes, thus leading to the same net effect — network repair. This energy conversion influences the reversibility and efficiency of self-healing reactions in reversible crosslinking via Diels–Alder reactions (for example, in epoxies[12,81–83], bismaleimides[84,85], polyurethanes[86,87], anthracene–maleimide-based polymers[88,89], caprolactones[90,91], poly(ethylene oxide)[92], polyesters[93], crosslinked polylactic acid[94] and acrylics[95,96]). Retro-Diels–Alder reactions offer a disconnection between diene and dienophile, but elevated temperatures reconstruct the covalent bonds to repair the crack[12] (FIG. 4a). The photochemical [2+2] cycloaddition of a 1,1,1-tris-(cinnamoyloxy-methyl) ethane (TCE) monomer can be used for self-healing reactions to form cyclobutane structures via the reversibility of cyclobutene to C=C bond conversion[97] (FIG. 4b). In this example, the cycloaddition reaction[98] capitalizes on the C–C bond cleavage of cyclobutane rings between TCE monomers induced by mechanical damage, resulting in the formation of the original cinnamoyl groups; however, healing occurs because of the reversibility of cyclobutane crosslinks of TCE via [2+2] photocycloaddition upon UV exposure. A low-temperature reversible

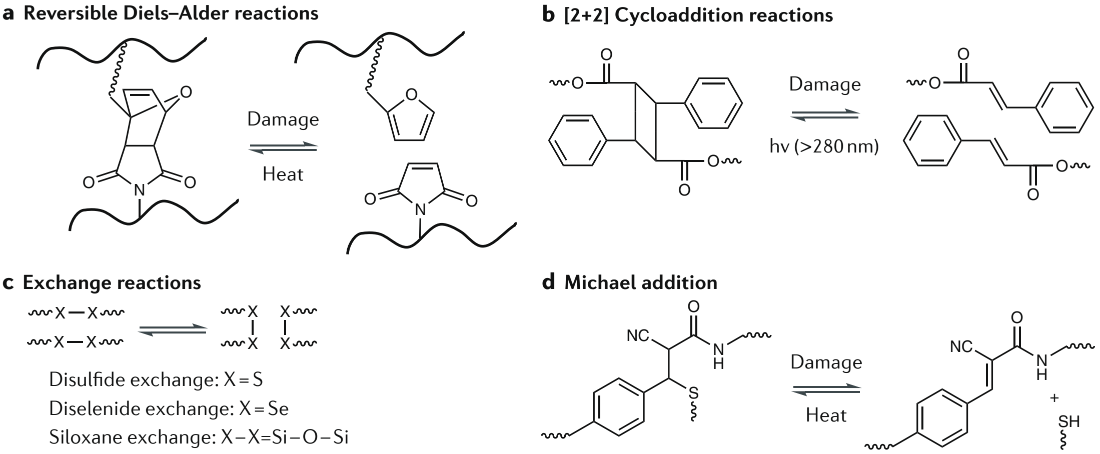


Fig. 4 | **Reversible reactions enabling reformation of covalent bonds. a** | Thermally reversible Diels–Alder reaction of furan and maleimide moieties forms a highly crosslinked network that is thermally reversible by the retro-Diels–Alder reaction[12]. **b** | Cycloaddition reactions can be used to photocrosslink cinnamate monomer, such as 1,1,1-tris-(cinnamoyloxy-methyl)ethane, and uncrosslink to original cinnamoyl groups, thus facilitating crack healing[97]. **c** | Three different exchange reactions can lead to self-healing. Disulfide-exchange reactions enable self-healing of *n*-butyl acrylate-based star polymers by attaching bis(2-methacryloyloxyethyl) disulfide to the arm end, resulting in a crosslinked star polymer[106]. The presence of disulfide functional groups enabled cleavage, owing to reduction reactions at the chain ends with thiol groups. Diselenide-exchange reactions[113] (dynamic diselenide bonds incorporated into polyurethanes facilitate visible-light-assisted self-healing materials). Siloxane-exchange reactions[116] can serve in self-healing of silicone-based polymers. Under stress, siloxane bonds in the silicone networks are cleaved, but the addition of either acid or base will catalyse stress relaxation, resulting in self-healing, **d** | Michael-addition reaction[115] between a trithiol and a bisbenzylcyanoacetamide derivative forms a self-healable dynamic network above 60 °C.

system using acid-activated dithioesters as dienophiles in hetero-Diels–Alder reactions with cyclopentadiene[99] has slow self-healing kinetics in the absence of a catalyst, but when hetero-Diels–Alder contains cyanodithioester, a catalyst is not required[100]. Using cyanodithioester and cyclopentadiene building blocks, healing can be accelerated at 120 °C (REF.[101])). It is also well established that Diels–Alder reactions can be catalysed by antibodies and RNA[102], which offers the possibility of using these reactions in chemical biology. The dynamics of Diels–Alder bonds for self-healing in polyurethane and CNT composites was also used in electrically conductive networks[65].

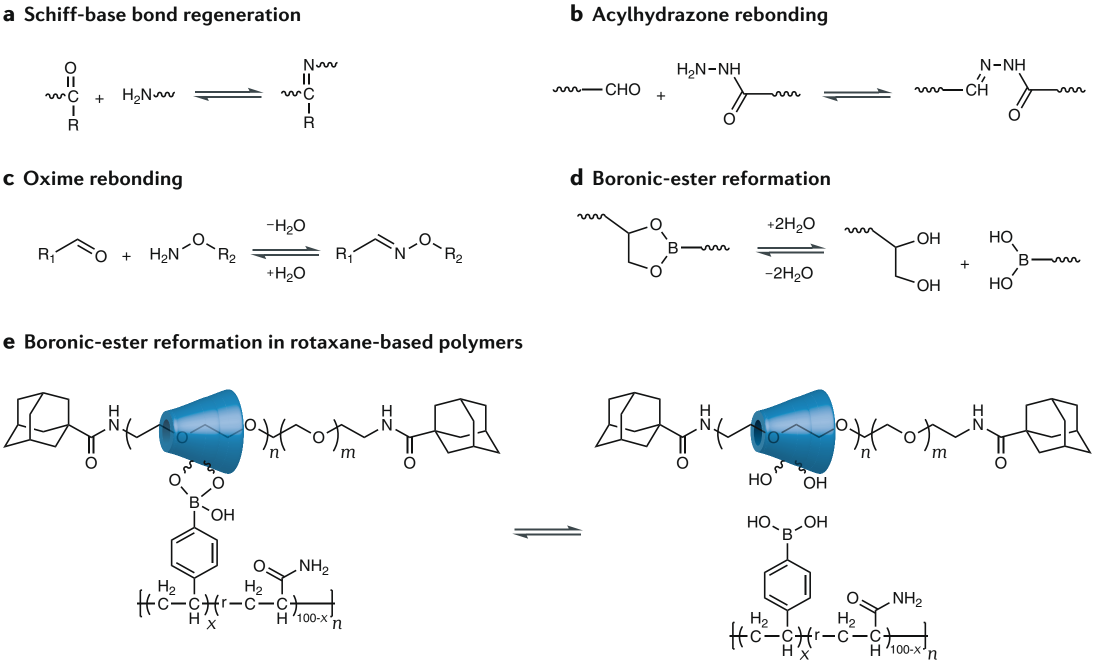
Sulfur and selenium chemistry, which is vital in biological systems, also enables self-healing. Particularly, the robust nature of thiol–ene chemistry has led to many synthetic opportunities[103,104]. For example, features of reversible reshuffling reactions of S–H and S–S bonds have been used in trithiocarbonates, in which copolymerization of *n*-butyl acrylate and a trithiocarbonate crosslinker resulted in high mobility of polymer segments, triggering homolysis of C–S bonds[105]. The reversible nature of S–S bonds, that is, reduction to form two thiol (S–H) groups, and oxidation to restore the disulfide (S–S) linkages, can be effectively used in self-healing[106] (FIG. 4c). Introducing reversible disulfide (S–S) crosslinks into covalently crosslinked networks can be achieved by poly(*n*-butyl acrylate)-grafted star polymers[107]. In this example, the polymer networks originate from crosslinked cores composed of poly(ethylene glycol diacrylate) and macroinitiators for the consecutive chain extension of bis(2-methacryloyl) oxyethyl disulfide. In another example, photoinduced thiol–ene click-type radical addition, which generates lightly sulfide-crosslinked polysulfide-based networks with an excess of thiols, and the subsequent oxidation of these thiols enables the formation of dynamic disulfide crosslinks to yield dual sulfide–disulfide crosslinked networks with fast self-healing rates[108]. Triblock copolymers with a centre poly(ethylene oxide) block and dithiolane blocks crosslinked with dithiol also enable self-healing by reversible ring opening of the pendent 1,2-dithiolanes via disulfide exchange between 1,2-dithiolanes and dithiols[109]. Bis(4-aminophenyl) disulfide can also be effectively used as a dynamic crosslinker in self-healing poly(urea–urethane) elastomers without the use of a catalyst[110]. Disulfide chemistry was also used in self-healable polyurethanes[111]. An advantage of disulfide-exchange reactions is that S–S bonds are capable of dynamic rearrangements upon heat, UV light and redox conditions, and, when incorporated into low-T_g gel networks, temperature-reversible self-healing can be achieved. The concept of disulfide links incorporated in a rubber network resulted in the restoration of mechanical properties at moderate temperatures (~60 °C)[112], but the main challenge is to achieve self-healing in higher-T_g networks. Applying the same exchange concept, a series of diselenide bond-containing polyurethane elastomers was prepared[113]. Aromatic diselenides have also been incorporated into polyurethane networks using a para-substituted amine diphenyl diselenide, resulting in faster self-healing than the corresponding disulfide-based materials and reprocessability at temperatures as low as 100 °C (REF.[114]). Reversible thiol–ene click reactions have also been used in a Michael-addition reaction, in which trithiol was reacted with a bisbenzylcyanoacetamide derivative to generate a self-healable dynamic polymer network above 60 °C (REF.[115]) (FIG. 4d).

Silicone-based polymers — owing to their dynamic network rearrangements — are perhaps the most technologically promising, yet least explored, self-healing materials[116]. For example, tetramethylammonium-silanolate-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(heptamethylcyclotetrasiloxanyl)ethane produced a polymer that could self-heal, owing to its ethylene bridges and active silanolate end groups[117]. Perhaps one of the most attractive features of silicone-based materials with self-healing properties are energy[118,119] and biomedical[120] applications. Of particular interest are self-healing dielectric-silicone-based elastomers that exhibit high dielectric permittivity. These properties can be achieved using an interpenetrating polymer network of silicone elastomer and ionic silicone polymers[121]. The latter are crosslinked through proton exchange between amines and acids, and are able to self-heal after electrical breakdown or mechanical damage. The self-healing is attributed to the reassembly of the ionic bonds during damage. Self-healing in silicone-based polymers was also accomplished using thiol-functionalized silicone oils containing silver[122] and magnetic Fe_3O_4 nanoparticles containing mussel-inspired metal-coordination bonds with dopamine molecules[123,124].

Taking self-healing further, latexes synthesized via a simple colloidal process undergo not only self-healing but also colour changes in the damaged area[125]. The synthesis of these materials was accomplished by emulsion copolymerization of a small fraction of photochromic monomer (spirooxazine) into methyl methacrylate and *n*-butyl acrylate copolymers. Upon mechanical damage, colourless damaged areas become red and, upon exposure to electromagnetic radiation, not only does self-healing occur but also the red colour in the damaged area reverts to its original colourless appearance. During repair, which is initiated by visible light, the spirooxazine rings close; however, the neighbouring copolymer segments form intermolecular H-bonding that forces the copolymer backbone to remain in an extended conformation. This network is an example of how combining covalent bonding and supramolecular chemistry may lead to self-healing and sensing.

Dynamic covalent-bond reformation

The interest in covalently bonded self-healable hydrogels is driven by its biomedical applications, which range from regenerative medicine to drug and protein delivery systems or tissue–material barriers. Self-healing in hydrogels can be achieved using reversible Schiff-base linkages[126]. For example, such hydrogels can be formed from the reaction of OH-PEG with 4-formylbenzoic acid and, subsequently, glycol chitosan[127] (FIG. 5a). In this case, a large dynamic strain (300%) can change the elastic modulus from approximately 1.5 kPa to 10 Pa and



a Schiff-base bond regeneration

b Acylhydrazone rebonding

c Oxime rebonding

d Boronic-ester reformation

e Boronic-ester reformation in rotaxane-based polymers

Fig. 5 | **The dynamic reformation of covalent bonds. a** | Schiff-base rebonding reaction[127]. **b** | Acylhydrazone rebonding[108,130]. **c** | Oxime rebonding[131]. **d** | Radical thiol–ene click chemistry is initiated by light, which enables the reversible formation of boronic esters to yield self-healable polymers[135]. **e** | Self-healing polymer gels are formed by crosslinked polyrotaxane and poly(acrylamide) with reversible boronate linkages[142].

induce gel–sol transitions. When implanted into the central nervous system, neurosphere-like progenitors proliferate in the hydrogel and differentiate into neuron-like cells, causing neural repair. Schiff-base networks can also be integrated with dynamic reversible acylhydrazone via acylhydrazines and aldehyde functionalities into Diels–Alder crosslinked networks[128]. A hybrid self-healing hydrogel system combining Schiff-base and amine reactions with micelles exhibits rapid self-healing, extensibility and compressibility for wound-dressing applications[129].

Hydrozenes (C=N-X)[108,130] (FIG. 5b) and oximes[131] (FIG. 5c) are commonly used conjugates labile to hydrolysis. Keto-functional copolymers can be prepared by conventional radical polymerization of *N*,*N*-dimethylacrylamide (DMAA) and diacetone acrylamide (DAA)[131]. The resulting water-soluble copolymers (p(DMAA-stat-DAA)) can be chemically crosslinked with difunctional alkoxyamines to obtain hydrogels via oxime formation and sol–gel transitions induced by the addition of excess monofunctional alkoxyamines to promote competitive oxime exchange under acidic conditions at 25 °C. The dynamic nature of oxime functionalities facilitates reversible self-healing. Similarly, polyurethane-like dynamic covalent polymers (poly(oxime-urethanes)) with self-healing at 120 °C can be prepared[132].

Boronic acids form a variety of dynamic covalent bonds[133]. This can be achieved, for example, through dehydration of boronic acids to form boroxines by reversible hydrolysis[134]. The boroxine–boronic acid equilibrium can be shifted by adjusting the temperature, adding a Lewis base or changing the water concentration. However, the property that makes boronic acids unique in the context of self-healing is their ability to form reversible dynamic covalent bonds with diols to form cyclic boronate esters. For example, photoinitiated radical thiol–ene click chemistry was used to form hydrogels capable of repeated healing under ambient conditions[135] (FIG. 5d). In another approach, combining reversible and dynamic boronate ester and disulfide chemistries facilitated the development of pH-responsive, glucose-responsive, redox-responsive and self-healable properties in hydrogels[136]. Self-healable hydrogels can also be prepared by covalent transesterification reactions of boronic acid with diols[137]. These boronate-ester-crosslinked hydrogels are capable of self-healing under neutral and acidic conditions, owing to the presence of an intramolecular coordinating boronic-acid monomer, 2-acrylamidophenylboronic acid[138]. Synthetic hydrogels functionalized with boronic acid can also be used as matrices for 3D cell culture[139], and those generated by boronic-ester and disulfide-exchange chemistry can self-heal in response to several stimuli[136].

In addition to boronic acid and boronate ester, self-healing gels with dynamic covalent bonds can be formed from a range of other reactive groups. For example, alkoxyamines with dynamic covalent bonds can facilitate self-healing, although the sensitivity of atmospheric oxygen at elevated temperatures (90–130 °C) leads to C–ON bond dissociations[140]. Another approach is the photoinduced [2+2] cycloaddition of cinnamoyl groups to reversibly form cyclobutene-derivative polymer gels[97]. This mechanism is driven by trithiocarbonate units that undergo reshuffling reactions; these units are particularly attractive as photoinitiators in reversible addition–fragmentation chain transfer (RAFT) polymerization[105]. This concept was expanded to self-healing networks using trithiocarbonate as photoresponsive units to achieve remarkable self-healing properties[141]. The latter is an excellent example of how covalently crosslinked polymers, through light stimulation and macroscopic fusion of separate pieces, synchronize self-healing events. Moreover, polyrotaxanes crosslinked by reversible bond reformation between ring molecules and vinyl polymers using boronic linkages are another example of rapid self-recovery upon damage[142] (FIG. 5e). Hydrogels with double networks were also developed to achieve toughness comparable to that of rubber[143], but many applications require the material to withstand repeated loading–unloading cycles in a short time, along with self-healing upon injury. To tackle this challenge, polyurethane-based hydrogels with enhanced dipole–dipole and H-bonding interactions were prepared[144]. These materials have superior mechanical properties to conventional double-network hydrogels and are also capable of self-healing.

Supramolecular dynamic chemistry

Supramolecular chemistry is non-covalent bonding represented by hydrogen bonding, metal–ligand coordination, π–π, ionic, guest–host and van der Waals interactions[145,146]. Although these interactions are relatively weak compared with covalent bonding, collectively, they form mechanically strong and very dynamic systems. Many biological assemblies are based on the principles of supramolecular chemistry. Accordingly, supramolecular processes are typically bottom-up and involve non-equilibrium states.

The field of supramolecular chemistry has been around for several decades[147,148] and is attractive for development of self-healing materials because of its reversibility, directionality and sensitivity. In contrast to covalent bonding, networks held together with non-covalent bonds can be remodelled reversibly — from fluid-like, low-density and high-free-volume states to solid-like, low-free-volume, elastic and plastic networks. Supramolecular polymers usually exhibit low T_g, which results in soft polymers, making them popular in the development of hydrogels. Hydrogels based on supramolecular chemistry have been used in applications such as injectable bioimplants, printable biological compounds and artificial skin.

In this section, we cover the different supramolecular interactions and chemistries used to produce self-healing materials, namely, those based on H-bonding, metal–ligand, ionic, host–guest and π–π interactions.

Designs based on H-bonding. H-bonding is typically among the strongest of non-covalent interactions and its directionality and high per-volume concentration confers acceptable mechanical strength. Owing to these attributes and reversibility, it can be used in self-healing of thermoplastic polymers[149,150]. For example, high-segmental-mobility polyisobutylenes functionalized with thymine and 2,6-diaminotriaine end groups assemble into strong rubber-like materials by forming triple hydrogen bonds (FIG. 6a). When supramolecular polyisobutylene networks are equipped with directional associative end groups, tunable dynamic behaviour, including self-healing, can be achieved[151]. Combining four hydrogen bonds offers high association constants[152,153]. An example of this is a functional unit of urea isopyrimidone with enhanced association strength between units when incorporated in polysiloxanes, polyethers and polyesters[154–156]. In contrast to bis-urea H-bonding, which leads to crystallization or clustering, resulting in brittle materials, applying thiourea moieties leads to zigzag H-bonded arrays, which eliminate unfavourable crystallization[157]. The dense H-bonds between thiourea appear to be ideal to crosslink low-molecular-weight polymers to achieve tough, room-temperature self-healable materials. In another example, dual-amide H-bonds doped with poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT–PSS) offer another venue for fabrication of self-healing hydrogels[158], whereas integrating DNA-grafted polypeptides and DNA linkers provides reversible DNA recognition for self-healing[159]. Also, sacrificial H-bonding was introduced by incorporation of secondary amide side chains into olefin-containing networks to achieve self-healing[160].

As a consequence of dynamic association–dissociation, H-bonding plays a role in tuning mechanical properties. Supramolecular polymers based on bifunctional ureidopyrimidinone derivatives behave like mechanically stable, high-molecular-weight thermoplastic polymers; however, their mechanical properties, such as Young's modulus and tensile strength, exhibit a strong temperature dependence, owing to H-bonding dissociations[161]. Along the same lines, polysiloxane elastomers containing a mixture of strong and weak H-bonding (FIG. 6b) offer tunable mechanical properties, including stretchability, toughness and autonomous self-healing ability, even under water[162]. Owing to the presence of H-bonding of different strengths, these self-healable elastomers can distinguish external signals of different strength, thus opening the possibilities for applications in human–machine interactions.

Fatty diacids and triacids from renewable resources have been used in a two-step synthetic route (FIG. 6c) to form self-healing networks by bringing together two cut ends at room temperature, without external heat[15]. Condensation polymerization of acid groups with an access diethylenetriamine and subsequent reactions with urea involving amidoethyl imidazolidone, diamidoethyl urea and diamido tetraethyltriurea groups resulted in an oligomer mixture with excessive H-bonding. In another example, which took advantage of variable-strength H-bonding and segmental mobility of hydrogels, self-healing could be switched on or off by adjusting temperature or pH[163].

Using the crosslinker 2-ureido-4-pyrimidone-4-hydroxybutyl acrylate (UPyHCBA), which consists of an acrylic head, a hydrophobic alkyl spacer connected by carbamate and a 2-ureido-4-pyrimidone tail, both hydrophobic association and H-bonding can be achieved. Sodium dodecyl sulfate micelles can provide a hydrophobic environment for the UPyHCBA

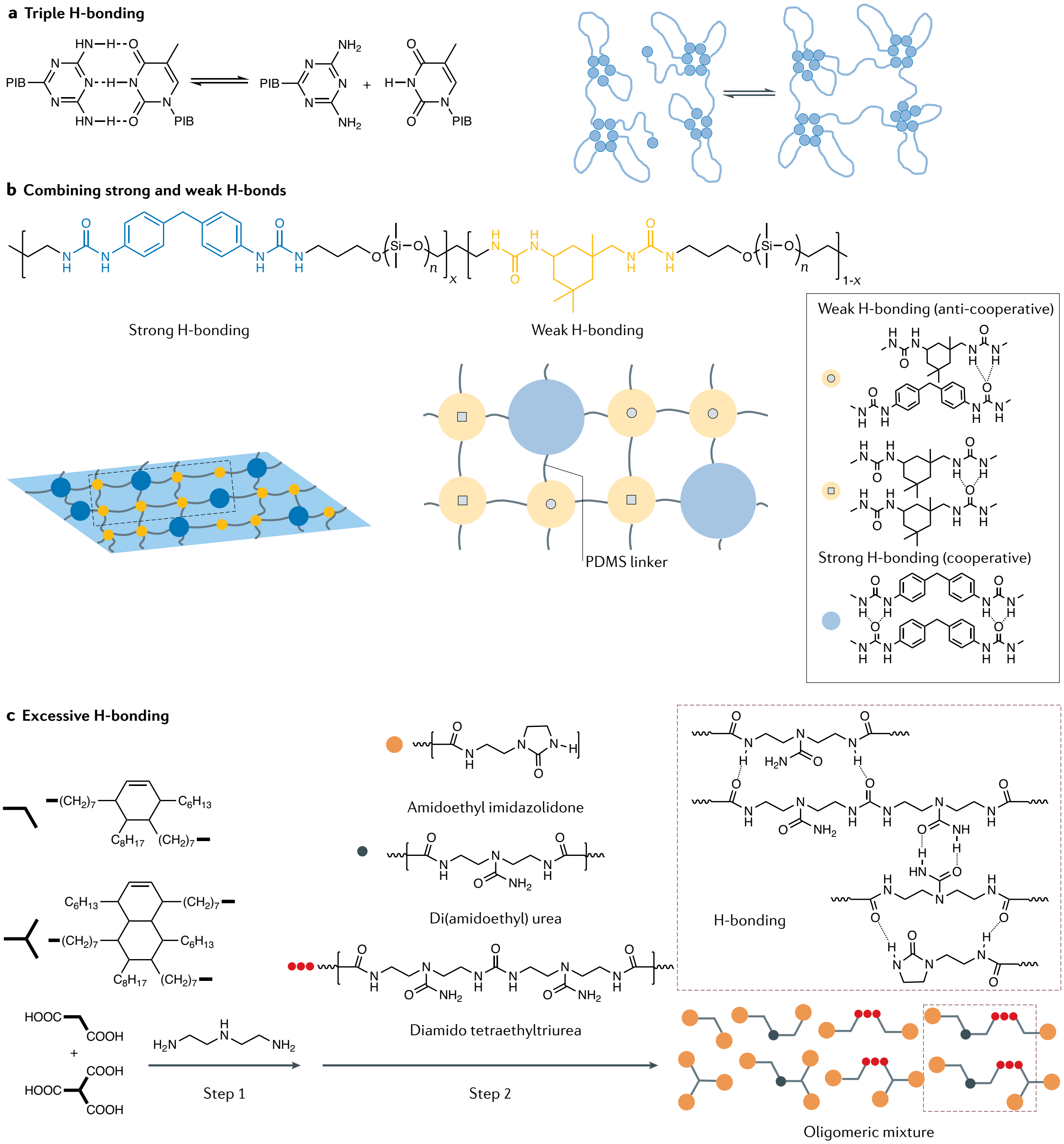


Fig. 6 | **Examples of hydrogen bonding in self-healing polymers. a** | Triple H-bonds between thymine and 2,6-diaminotriaine form self-healable supramolecular networks. **b** | The combination of strong and weak hydrogen bonding in polydimethylsiloxane (PDMS)–4,4′-methylenebis(phenylurea) form self-healable networks. **c** | A mixture of fatty diacid and triacid reacts with diethylenetriamine to form self-healable copolymers. Subsequent reactions with urea form oligomeric networks with strong hydrogen bonds. PIB, polyisobutylene. Panel **a** adapted with permission from REF.[151], RSC. Panel **b** adapted with permission from REF.[162], Wiley-VCH. Panel **c** adapted from REF.[15], Springer Nature Limited.

prepared by micellar polymerization of UPyHCBA and acrylamide[164]. Another useful self-healing mechanism is the formation of urea–water clusters in urea-based polyurethanes in the presence of moisture[165].

Metal–ligand interactions. When metal ions and appropriate ligands — either at the end of a polymer chain or as a pendent group — are brought together, they form a coordination complex, linking the polymer chains together. Metal–ligand complexes have advantages associated with their ability to coordinate different metal ions and ligand substitutes, thus leading to different association strengths. When mechanical forces are applied, such complexes dissociate, and their reformation results in self-healing. Another appealing feature is minimal or no side reactions during repeated damage–repair cycles. Reversibility upon mechanical damage is facilitated by metal-ion–ligand dissociations, with reforming triggered by exposure to electromagnetic radiation or elevated temperatures.

Exemplifying a temperature-responsive system, when hydroxyl ethylene diamine triacetic acid is used to control the molecular weight and crosslinker density in the presence of terpyridine–Ru, temperature changes decouple Ru metal from the ligand, resulting in bonding and debonding[166]. In a metallosupramolecular system, the terpyridine–Fe^{2+} complexation pair with poly(alkyl methacrylate) accomplishes self-healing at elevated temperature[167], although, in this case, the elevated temperatures may lead to adverse effects, such as polymer degradation. In a chemically different, photoresponsive metallosupramolecular system, polymers comprising an amorphous poly(ethylene-co-butylene) core with 2,6-bis(1-methylbenzimidazolyl)pyridine ligands can form metal–ion binding, which, upon mechanical damage, can be mended through exposure to light[16] (FIG. 7a). Because exposure to UV light causes the metal–ligand coordination to be electronically excited via the absorption process, the desorption of energy may lead to heat dissipation and temporary cleavage of the metal–ligand linkages. Other examples of the formation of self-healing complexes are N-heterocyclic carbenes and transition metals[168]. However, a drawback of these examples is the substantial external energy input required.

It is important to match the electronic network properties and excitation sources when designing self-healing polymer networks using metal–ligand coordination chemistry. An example of this is polyethylenimine–copper supramolecular polymer networks with reversible UV-induced self-healing by the reformation of Cu–N coordination bonds[169]. This system experiences virtually no temperature change during exposure to electromagnetic radiation, providing high photon efficiency without side reactions. The network undergoes square-planar-to-tetrahedral ($D_{4h} \rightarrow T_d$) symmetry changes at the C_2H_5N–Cu coordination complex centre without side reactions facilitated by charge transfer between σ(N) bonding and $d_{x2\text{-}y2}$(Cu) antibonding orbitals. Combining the properties of polyurethane and polydimethylsiloxane (PDMS) networks into one supramolecular and covalently crosslinked system catalysed by $CuCl_2$, this system reforms both coordination and covalent bonds[170].

Other pathways to self-healing in metal–ligand coordination systems are shown in FIG. 7b,c. For example, a self-healing dielectric elastomer has been synthesized using 2′-bipyridine-5,5′-dicarboxylic amide as ligand and Fe^{2+} and Zn^{2+} with various counter anions in which metal–ligand coordination serve as crosslinking sites in non-polar PDMS[171] (FIG. 7b). The kinetically labile coordination between Zn^{2+} and bipyridine endows fast self-healing under ambient conditions. In the second example, the coordination between Fe^{3+} and catechol ligands resulted in a pH-induced crosslinked self-healing polymer with near-covalent elastic moduli[172] (FIG. 7c). The uniqueness of this approach is the ability of mono-catechol–Fe^{3+}, bis-catechol–Fe^{3+} or tris-catechol–Fe^{3+} formation at different pH values, thus providing control of crosslinking without Fe^{3+} precipitation[173]. Incorporating Eu–iminodiacetate coordination with hydrophilic poly(*N*,*N*-dimethylacrylamide)[174] and dynamic ionic interactions between carboxylic acid groups of poly(acrylic acid) (PAA) and ferric ions[175] or polyelectrolytes[176] are other examples of self-healable hydrogels[177,178].

Nature offers opportunities for designing self-healing systems. Inspired by catechol-containing biopolymers that mimic sea-mussel adhesives, crosslinked hydrogels were prepared by the complexation of branched catechol-derivatized PEG with 1,3-benzenediboric acid. This material exhibits tunable, covalently bonded gel behaviour under alkaline pH, but dissociates into a viscous liquid under neutral and acidic conditions[168,179]. It has been used in surface modifications of synthetic polyacrylate and polymethacrylate materials with mussel-inspired catechols, which resulted in self-healing initiated and accelerated by H-bonding between interfacial catechol moieties[180].

Finally, tuning the strength of metal–ligand interactions has implications for the dynamic mechanical properties of supramolecular elastomers. For example, when 2,6-pyridinedicarboxamide ligands are incorporated along PDMS backbones, complexation of the polymer with Fe(III) (FIG. 7d) results in an elastic material that self-heals at room temperature. This behaviour is attributed to the bonding energies of Fe(III)–$N_{pyridyl}$, Fe(III)–N_{amido} and Fe(III)–O_{amido}, which may range from strong to weak. The weaker bonds are responsible for energy dissipation on stretching and on-demand self-healing, whereas the metal ions maintain their location near the ligands, thus resulting in stronger interactions and rapid bond reformation[181].

Host–guest interactions. Guest–host chemistry is commonly used in fabricating hydrogels. For example, hydrophobic cavities in β-cyclodextrin can accommodate a variety of guest moieties[182–185]. If one surface contains a cyclodextrin host and the other guest molecules, host–guest interactions will result in bonding[17]. The supramolecular polymers shown in FIG. 8a are equipped with multipoint molecular recognition sites achieved by various water-soluble polymer backbones modified with β-cyclodextrin hosts and hydrophobic adamantine as the guest at the side chain. This simple method produces a transparent, flexible and tough hydrogel that self-heals in both wet and dry states[186]. Because of their amenability to chemical modifications and biocompatibility, supramolecular hydrogels composed of modified hyaluronic acid with either adamantane or β-cyclodextrin are able to rapidly form intermolecular host–guest bonds[187,188]. The mechanical properties of this system can be tuned by changing the concentration and ratio of the guest-to-host moieties.

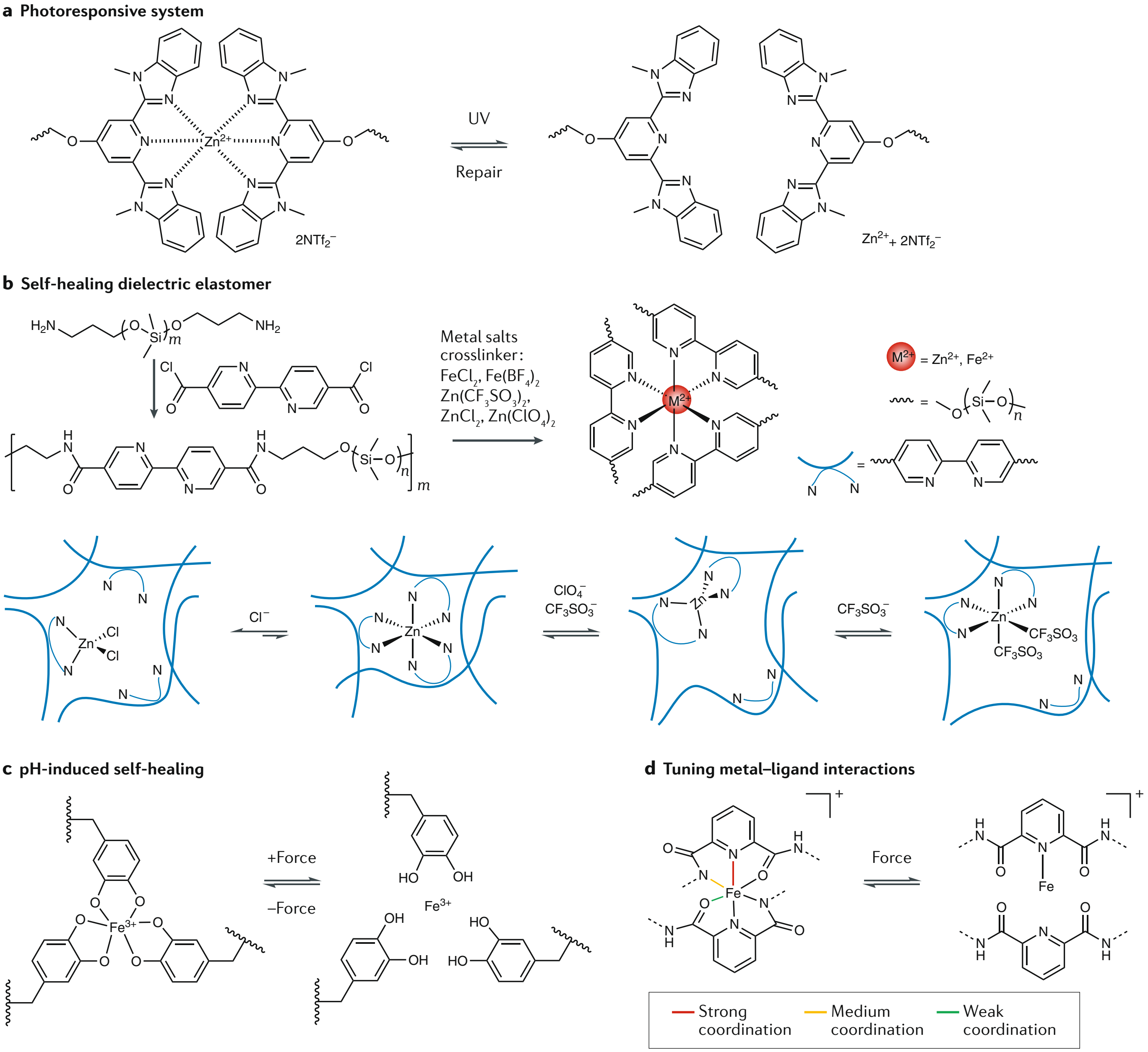


Fig. 7 | **Self-healing using metal–ligand coordination chemistry. a** | Coordination of Zn(NTf)$_2$ and 2,6-bis (1-methylbenzimidazolyl)pyridine ligands responsible for self-healing in poly(ethylene-co-butylene)[16]. **b** | Synthetic route to prepare Zn^{2+}- or Fe^{2+}-containing crosslinked polydimethylsiloxane networks and a schematic illustration of the dynamic interactions within the Zn^{2+}–ligand complex, counter anions polymer system under mechanical stress[171]. **c** | Reversible tris-catechol–Fe^{3+} complex[172]. **d** | Reversible coordination complexes with 2,6-pyridinedicarboxamide ligands and Fe(III) centre as crosslinker for self-healable polydimethylsiloxane network[181].

Another well-known host is cucurbit[8]uril (FIG. 8b), which has high molecular weight and sufficient chain entanglement for physical crosslinking, and can accept two guests, naphthyl and viologen[189]. Some seminal studies using self-assembled peptides have demonstrated the potential of these interactions in biomedical applications[190,191]. At low concentration (2.5 mol%), dynamic cucurbit[8]uril-mediated non-covalent crosslinking yields extremely stretchable and tough supramolecular polymer networks, exhibiting remarkable self-healing capability at room temperature. These ionically conductive and transparent networks can be stretched to 100 times their original length and hold objects 2,000 times their own weight[192]. Although this example and those above are remotely related to self-healing, if applied in the host–guest environments, potential applications in self-healing of materials are feasible.

Ionic interactions. Ions have a key role in many biological processes. For example, molecular motors are powered by chemical processes that result in the swelling and shrinkage of macromolecular segments, thus causing motion. These processes are often attributed to the imbalance between osmotic and entropic forces resulting from stored energy between electrostatic repulsions and negatively charged filaments. Ionic interactions also influence polymer networks and are primarily manifested by the formation of ionomers[193]; however, only some ionomers self-heal. For example, poly(ethylene-co-methacrylic acid) (pEMAA) and polyethylene-*g*-poly(hexylmethacrylate)[194] (pEHMA) self-repair (FIG. 9a) under ambient conditions and at elevated temperatures upon projectile puncture testing[195]. Moreover, a ballistic puncture in low-density polyethylene does not heal, whereas a puncture in pEMAA does[194]. This is a two-stage process whereby projectile impact disrupts the ionomeric network and the heat generated by friction during damage is transferred to polymer matrix surroundings, resulting in a localized melt state. The molten polymer surfaces fuse via interdiffusion to seal the puncture, followed by rearrangement of the ionic clustered regions and long-term network relaxation.

As a consequence of electrostatic interactions, macromolecules carrying opposite charges form neutrally charged polyelectrolyte complexes. Stiff and self-healing gels can be fabricated with the polyelectrolyte complexation of polyamines with phosphate-bearing multivalent anions[196] (FIG. 9b). Self-healing is also exhibited in polyelectrolyte complexes synthesized from (PAA)/poly(allylamine hydrochloride) (PAH) pairs and NaCl, with the self-healing efficiency increasing with NaCl concentration[197] (FIG. 9c). In this case, self-healing originates from the disturbance of ionic interactions by adding salt, resulting in enhanced chain mobility.

Although ionic bonds may be more difficult to break than covalent bonds, they can be disrupted by introducing strong electrostatic interactions (for example, dissociations upon addition of water or adding strong polar salts or solvent). Therefore, the addition of water, salt or polar solvents will influence self-healing. In the presence of water, polyelectrolyte multilayered assemblies also exhibit self-healing upon mechanical damage. An example of this is polyampholyte self-healing hydrogels

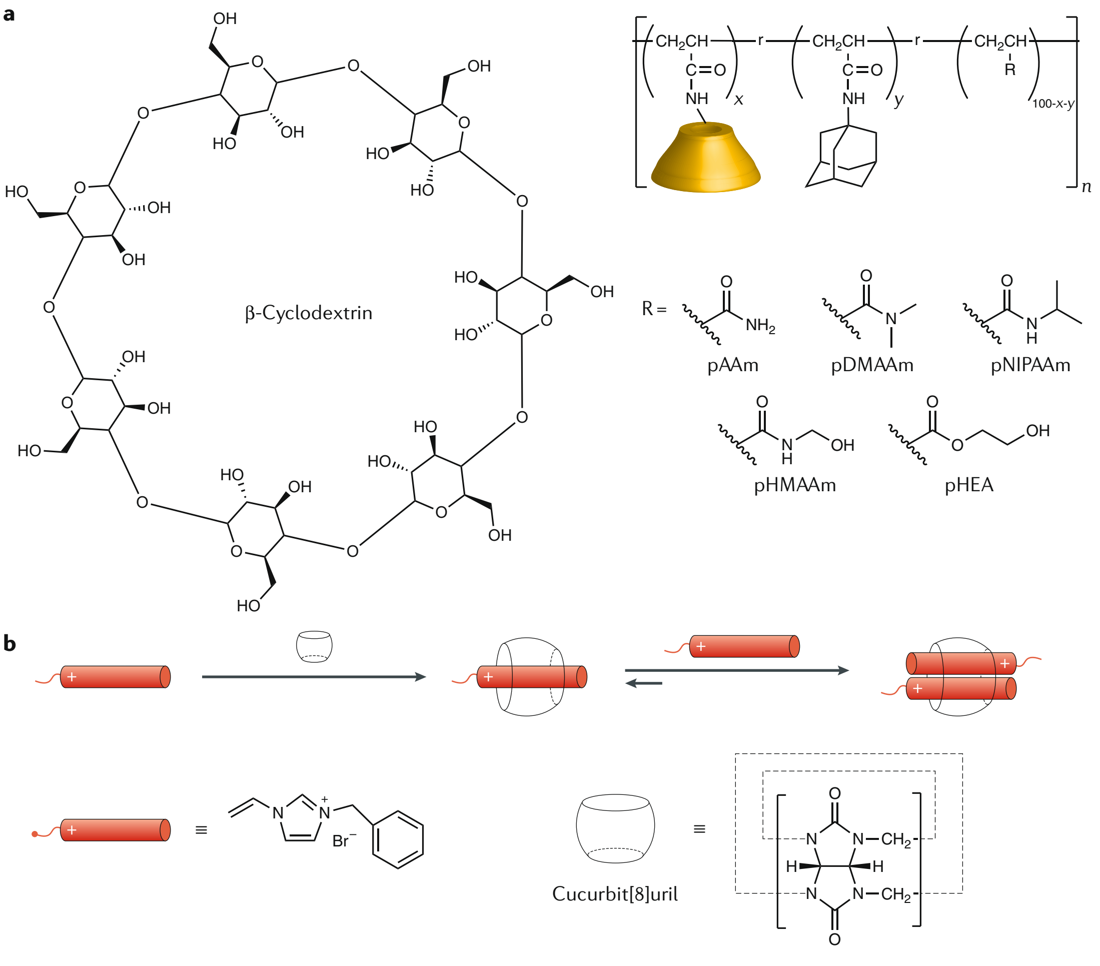


Fig. 8 | **Host–guest chemistry in self-healing systems. a** | Water-soluble polymer backbones modified with β-cyclodextrin as host and hydrophobic adamantine as guest at the side chain. Polymers selected to form the water-soluble backbone of the system include poly(acrylamide) (pAAm), poly(*N*,*N*-dimethylacrylamide) (pDMAAm), poly(*N*-isopropylacrylamide) (pNIPAAm), poly(hydroxymethylacrylamide) (pHMAAm) and poly(hydroxyethylacrylate) (pHEA)[186]. **b** | Stepwise formation of ternary host–guest supramolecular complexation between cucurbit[8]uril and guest molecule with macrocyclic host cucurbit[8]uril and polymerizable guest molecules (1-benzyl-3-vinylimidazolium) and acrylamide[192]. Panel **b** adapted with permission from REF.[192], Wiley-VCH.

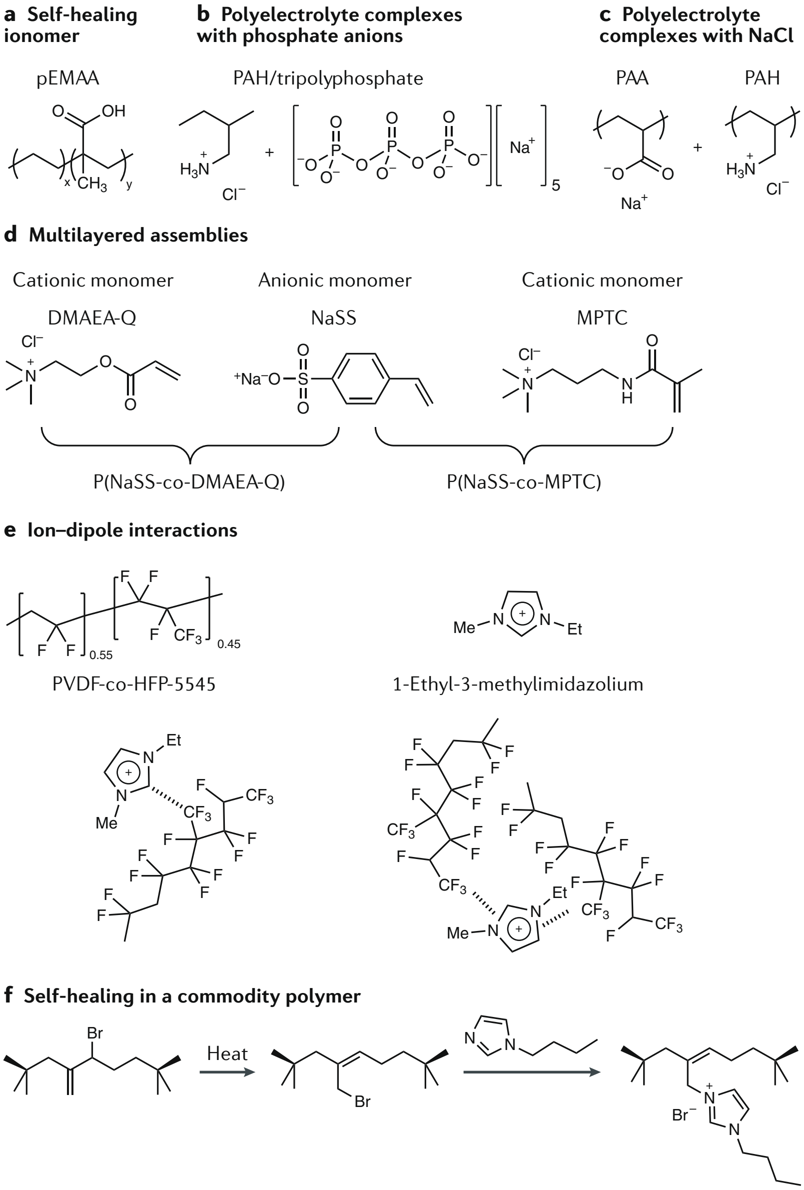


Fig. 9 | **Examples of ionic interactions applied in self-healing. a** | An early example of a self-healing ionomer, namely, poly(ethylene-co-methacrylic acid) (pEMAA)[194]. **b** | Polyelectrolyte complexes with phosphate anions, for example, poly(allylamine hydrochloride) (PAH)/tripolyphosphate ionic gel[196]. **c** | Polyelectrolyte complexes can be formed by ultracentrifugation with NaCl, for example, poly(acrylic acid) (PAA)/PAH[197]. **d** | Chemical structures of anionic monomer sodium 4-styrenesulfonate (NaSS), cationic monomers acryloyloxyethyltrimethyl ammonium chloride (DMAEA-Q) and [3-(methacryloylamino)propyl]trimethylammonium chloride (MPTC) used for synthesizing polyampholyte hydrogels, p(NaSS-co-DMAEA-Q) and p(NaSS-co-MPTC)[198]. **e** | Ionic conductor fabrication using ion–dipole interactions between poly-(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) and 1-ethyl-3-methylimidazolium, where PVDF-co-HFP is the polar polymer network comprising VDF (which is crystalline and less polar) and HFP (which is amorphous and highly polar)[200]. **f** | Reversible ionic transformation between the bromine functionalities of bromobutyl rubber and ionic imidazolium bromide groups results in self-healing rubber material[201].

(90% healing efficiency) and tougher hydrogels (0.2 MPa stress at break)[198] (FIG. 9d). In this system, high density of weak bonds facilitates bond reforming, but the softness enhances contact across the interface, thereby increasing the self-healing efficiency. In another example, star-shaped PEG chains functionalized with alendronate form reversible crosslinked networks when triggered by Ca ions[199]. Mechanically and electrically self-healing hydrogels can be obtained using dynamic ionic interactions between carboxylic groups of PAA and ferric ions[178]. Moreover, stretchable, transparent, self-healable ionic conductors can be formed based on ion–dipole interactions[200] (FIG. 9e). In these systems, the polar polymer network is usually composed of poly-(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP). This copolymer, which contains two building units, VDF (crystalline and less polar) and HFP (amorphous and highly polar), is capable of room-temperature self-healing without external stimulus.

Moving towards commodity self-healable polymers, ionic interactions may be important in the optimization and modification of commercial rubber. Commercially popular and inexpensive butyl rubber can be modified into a self-healing product by ionic modifications without the addition of conventional curatives or vulcanizing agents. For example, the mechanical properties of bromobutyl rubber (which is conventionally sulfur-cured) can be improved by transforming its bromine functionalities into ionic imidazolium bromide groups (FIG. 9f), resulting in reversible ionic associations that exhibit physical crosslinking[201]. In summary, ionic interactions in polymers may provide a unique opportunity for the development self-healable commodity materials.

π–π interactions. π–π interactions are often viewed as an extension of coordination chemistry. As the name implies, these interactions are facilitated by π orbitals, which are strongly dependent on chemical structure and stereochemistry. π–π interactions are well-documented in many biological studies of peptides, interactions of aromatic side groups in proteins, and nucleic acids or DNA. Using a combination of π–π, metal-coordination chemistry and/or H-bonding, several self-healing elastomers have been developed. For example, combining Pt···Pt and π–π interactions between a cyclometalated platinum(II) complex and a PDMS backbone enables high stretchability and self-healing[202]. Composites with metal nanoparticles can also be commonly applied. For example, the blend of pyrene-functionalized polyamide (π-electron donor), polydiimide (π-electron acceptor) and pyrene-functionalized gold nanoparticles can produce thermally induced π–π stacking interactions between functionalized gold nanoparticles and the polymer matrix, resulting in self-healing[203]. Combining π–π and H-bonding interactions can lead to thermally triggered, self-healable, tweezer-shaped structures consisting of bis-pyrenyl end groups and naphthalene-diimide chains, along with a non-tweezer combination of naphthalene-diimide end groups and mono-pyrenyl groups[204]. Incorporating an ionic moiety into the same π–π stacking system may provide technological opportunities for the development of conductive self-healing polymers, such as a cathode in lithium–sulfur batteries[205].

Regardless of the chemical reactions involved in the self-healing of polymers, the main challenge is the ability of the network to rearrange upon mechanical damage. With a few exceptions — such as some heterogeneous networks[206] — recent studies have focused on low-T_g

polymers. Another challenge is to achieve self-healing in higher-T_g polymers, in which the limited free volume diminishes the segmental mobility of macromolecular chains and diffusion is unfavourable. Thus, the presence of localized low-T_g and high-T_g components may be necessary for achieving self-healing in functional materials.

Vitrimers

Vitrimers are a relatively new class of synthetic material that resemble enzymatic cleavage of linkers in biological systems. Their characteristic feature is exchangeable covalent bonds, which, upon cleavage, can reshuffle[207,208]. The exchange may be triggered by thermal, chemical or other stimuli, and rigidity and plasticity are tunable[209]. Vitrimers form covalent networks capable of changing their topology through thermoactivated bond-exchange reactions (FIG. 10a). At high temperatures, they flow and behave like viscoelastic liquids; however, at low temperatures, slow exchange reactions result in thermoset-like properties. The network rearrangements impart high mechanical recyclability and the ability to undergo thermal healing, as well as rapid stress relaxations, which are not found in conventional crosslinked thermoset polymers. These networks can also exhibit shape-memory properties, allowing for autonomous arrangement into complex shapes through dynamic crosslinks by the introduction of exchangeable chemical bonds. A unique property of epoxy-based vitrimers is that their T_g can be controlled by tuning the rates of transesterification[210] (FIG. 10b). An alternative to transesterification is catalyst-free transamidation exchange reactions. Because amide groups are thermodynamically more stable than esters, the resulting vitrimer networks are less susceptible to hydrolysis[208] (FIG. 10c).

Another attractive class of vitrimers is based on bis(cyclic carbonate)s, which can react with triamines or hydroxyl groups[211] (FIG. 10d). Using transamination reactions (FIG. 10e), vinylogous urethane networks can be produced via the condensation reaction between acetoacetates

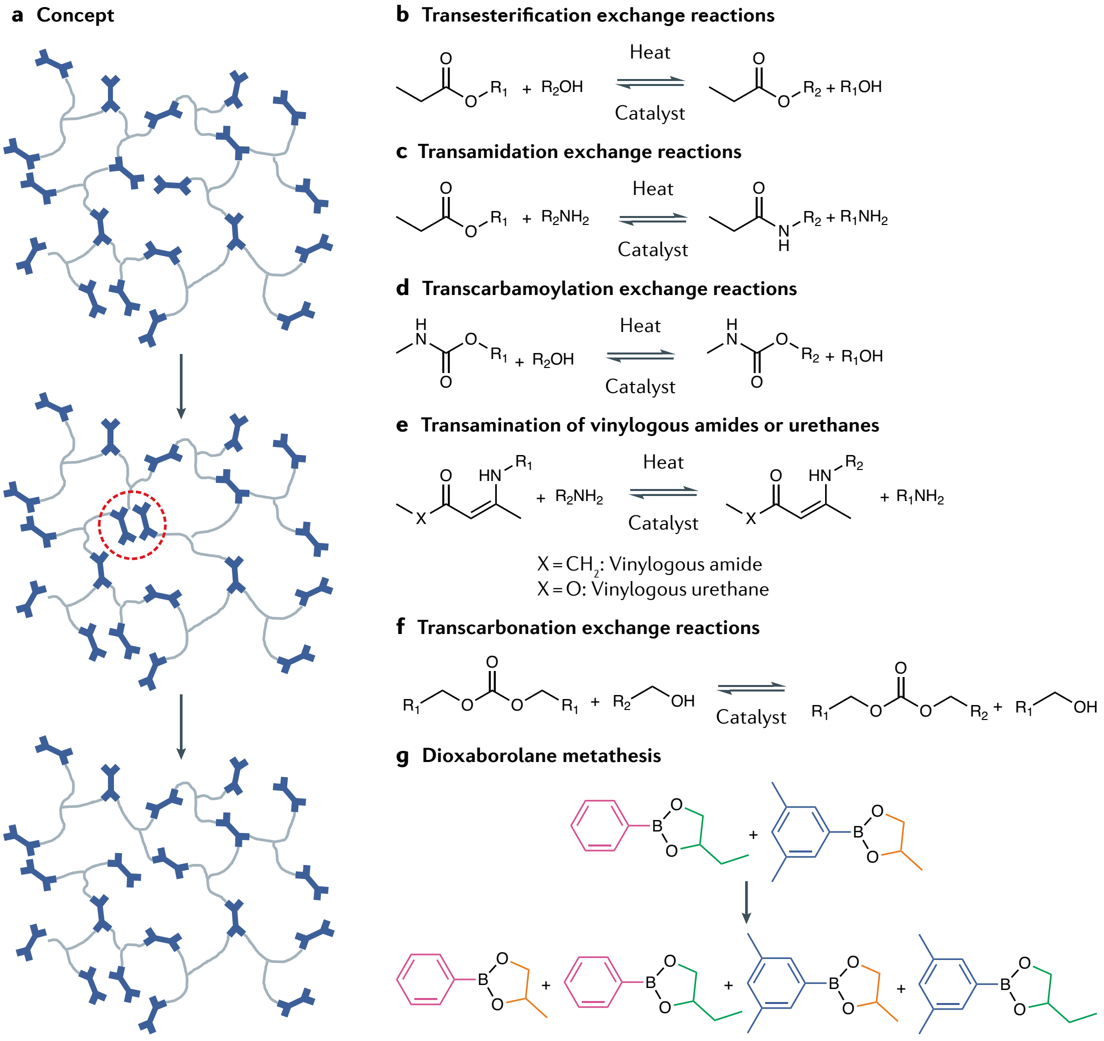


Fig. 10 | **Vitrimer systems. a** | General concept of topological rearrangements through exchange reactions in vitrimers. **b** | Transesterification of hydroxy-ester networks[207]. **c** | Transamidation exchange reactions in polyhydroxyurethane networks[208]. **d** | Transcarbamoylation reactions leading to polyhydroxyurethanes[211]. **e** | Transamination of vinylogous amides or urethanes[208]. **f** | Transcarbonation reactions leading to polycarbonates[212]. **g** | Dioxaborolane metathesis reactions[213]. Panel **a** reprinted with permission from REF.[207], AAAS.

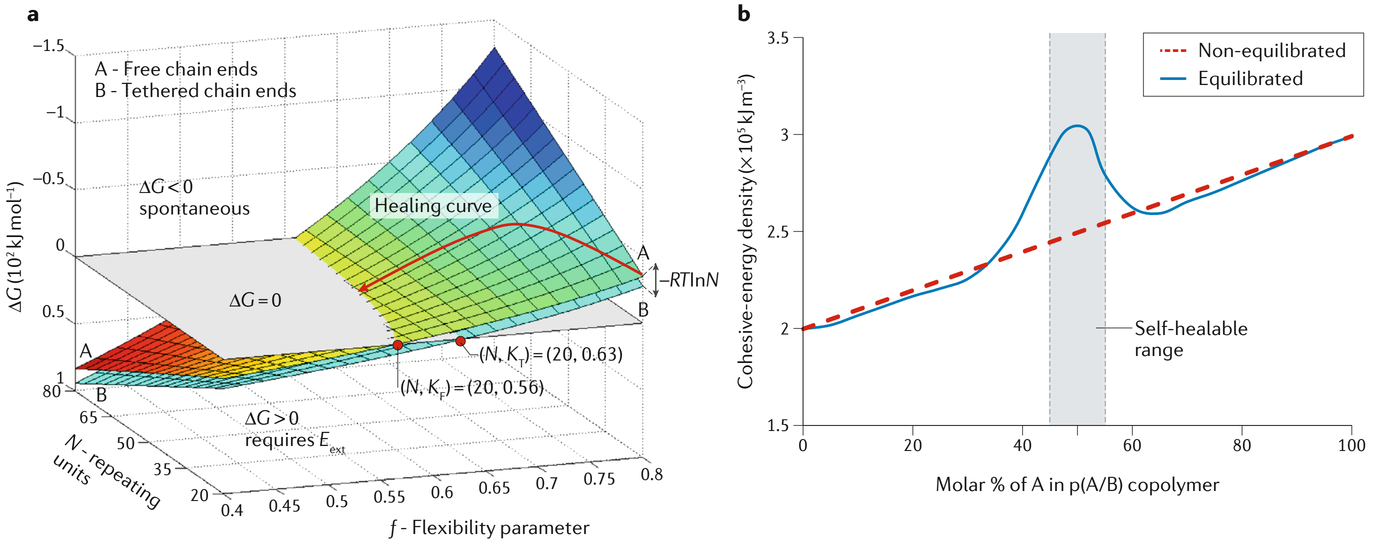


Fig. 11 | **Energy considerations of self-healing. a** | A plot of the change in Gibbs free energy ($\Delta G = -T\Delta S$) as a function of the number of segments (*N*) in a polymer chain and the flexibility parameter (*f*) for free and tethered chain ends (surfaces A and B, respectively). At equilibrium, $\Delta G = 0$. The space above this plane ($\Delta G < 0$) represents spontaneous repair, whereas below it ($\Delta G > 0$), self healing will not occur. The red dots mark the critical *f* values for free (K_F) and tethered (K_T) chain ends for $N = 20$. The solid red curve shows how ΔG is influenced by *N*. E_{ext} is the external energy input. **b** | Cohesive-energy density (CED) as a function of molar ratio for non-equilibrated and equilibrated copolymers. Panel **a** adapted with permission from REF.[22], RSC.

and amines[208]. The bisacetoacetate monomers can be prepared from readily available diol monomers and their combination with commercially available polyamine monomers allows tunability of the mechanical properties of the poly(vinylogous urethane) polymers. Another example of a vitrimer system is the reaction of bis(cyclic carbonate) and diols[212] (FIG. 10f). The problem, however, with the aforementioned examples is their need for a catalyst. By contrast, polyhydroxyurethane vitrimers can be formed without a catalyst[211], as can those formed via metathesis reactions of dioxaborolanes[213] (FIG. 10g).

Vitrimers can either be introduced to other polymer networks or have additives added to them to improve their properties. For example, vitrimer-based liquid-crystalline elastomers exhibit processability owing to monodomain alignments, thus allowing robust construction of actuators with complex 3D structures; however, the stability of these elastomers needs to be improved[214]. Introducing oligoaniline into vitrimer networks resulted in a covalently crosslinked material that can respond to heat, light, pH, voltage, metal ions and redox chemicals[215]. This material exhibited shape memory, self-healing, recyclability, electrochromism and adsorption of metal ions. As mentioned earlier, CNTs embedded in common vitrimers are able to remotely trigger localized transesterification[66] and, more interestingly, induce fast exchange reactions in crosslinked liquid-crystalline elastomers, thus allowing spatial control of the alignment and fabrication of dynamic 3D constructs in a short time[216].

The main challenge is designing self-healable polymers with high thermal resistance. These materials typically exhibit high T_gs. However, in the design of vitrimer polymers, two transitions should be taken into account: T_g (glassy to rubbery state) and topology-freezing transition (T_v) (viscoelastic solid to viscoelastic liquid), both controlled by crosslink density, monomer rigidity, the kinetics of exchange reactions and the concentration of exchangeable bonds[217]. The presence of the two transitions is an opportunity for developing self-healable polymers using the exchange-reactions concept. One can envision that, if localized damage generates a sufficient amount of heat to reach a T_v, thus triggering exchange reactions, self-healing may occur for high-T_g polymers, as long as local damage generates sufficient segmental chain mobility to facilitate, for example, wound closure.

Energetic considerations

During the damage–repair cycle, a polymer's response is in non-equilibrium state. One example is phase-separated morphologies, where each phase responds at different rates to damage, thus resulting in gradients of local volume expansion and different rates of filling the empty space. To understand these processes, knowledge of the rates of response for each phase is required. Assuming that mechanical damage causes chain cleavage or slippage near newly created surfaces, loose chain ends may or may not reform. A Gibbs free energy (ΔG) < 0 will favour recombination if the entropy (ΔS) > 0. Assuming that the damage–repair cycle is a transition from a non-equilibrium to an equilibrium state achieved by a series of infinitely small equilibrated steps described by the recoupling lattice model[22,218], chain flexibility — macroscopically reflected by the T_g — will influence the number of chain configurations. To predict self-healing, a recoupling lattice model (FIG. 11a) can be used. This relates Flory's flexibility parameter to the number of repeating units needed for a given ΔG (REF.[219]). Self-repair is favourable when the enthalpy (ΔH) < 0, implying that exothermic processes are dominated by macromolecular miscibility and favourable intermolecular and intramolecular chains (defined by the Flory–Huggins parameter[218]).

In copolymers, the composition determines the CED — the minimal amount of energy required to remove (or add) a macromolecular chain from a surrounding network. CED values plotted as a function of the copolymer composition predict a linear dependence in the non-equilibrated state (FIG. 11b). These predictions show that when the molar fraction of A in the p(A/B) copolymer (A with higher T_g and B with lower T_g) increases, the CED values gradually increase, owing to the larger content of B units in the chain. However, when the system is equilibrated, taking into account composition-dependent conformations, a maximum CED value is reached in the vicinity of the self-healing composition[18]. The maximum molar ratio corresponds to copolymer conformations that preferentially exhibit helical configurations (self-healing is typically not observed for other copolymer compositions or for homopolymer blends of the same compositions). One can envision a copolymer backbone with a helical topology as a spring, which, upon compression, is distorted. When an external force is released, the 'spring' decompresses, bringing the cleaved ends together to self-heal. If low T_g was the only driving force for self-healing, compositions with the higher B content would also exhibit self-healing characteristics; however, they do not and, instead, they may form sticky, flowing films. These materials are commercially known as pressure-sensitive adhesives.

Polymer-chain separation or rupture — an outcome of physical damage — creates isolated chain ends, which can be in a form of loose chain ends, free radicals (depending on the polymer) or other reactive groups. The repair process begins longitudinally along the bottom of a scratch owing to energetically favourable interactions, manifested by lower near-surface T_g. During this process, a percolation transition (that is, the minimum threshold of reconnected ends or recombined chains) occurs after a given number of macromolecules are connected longitudinally. The driving force is high interfacial energy in the smaller-curvature areas at the bottom of a scratch[220], which leads to close physical proximity, high segmental mobility and entropic energy storage during damage. If the interfacial energy and entropy can be recovered during repair, the material will autonomously self-heal.

If polymer chains are in extended conformations, mechanical damage may lead to their compression. Upon release of an applied force, decompression driven by stored entropic and interfacial energies of spring-like copolymer segments will restore their initial state. The spring model of the shape-memory effect resulting from entropy storage during mechanical damage may also explain the driving force for self-healing behaviour; however, validation requires quantitative analysis. In fact, the maximum storable strain (and, thus, shape-memory storage capacity) can be accurately predicted using the junction density (that is, chemical or physical crosslinks) and shape-memory factor[221].

We anticipate that high-junction-density polymers (that is, those with a high number of entanglements and high molecular weight) will self-heal via shape-memory effects owing to their ability to store entropic energy, but that low-junction-density polymers will self-heal as a consequence of surface-tension effects. For example, in thermoresponsive polyurethanes formed via the Diels–Alder reaction between furan and maleimide moieties, the shape-memory effect facilitated self-healing without the need for an external force (in contrast to other self-healing polymers)[86]. Expanding the application temperature range to 130 °C and thermal stability to 250 °C (compared with 60 °C for more common self-healing polymers based on polycaprolactone[222]) makes these materials particularly attractive.

Self-healing is a local phenomenon with macroscopic consequences. If polymer components exhibit localized, endothermic, stimuli-responsive transitions[223,224] below the T_g at or near the damaged surface, macromolecular flow will occur[225,226] and repair may occur. In the presence of localized heterogeneities, such as in elastomers, concurrent H-bonding and covalent-like bonded polyvalent clusters introduce balance between the steady state and non-equilibrium states[15]. The term autonomous self-healing is often used to emphasize self-healing under ambient conditions, which implies a bulk phenomenon. However, the local dynamics of macromolecular segments, reactivity of reactive components (such as catalysts or reactive groups) and/or stereospecificity are responsible for temperature-dependent entropic and enthalpic contributions to the Gibbs free energy, leading to self-healing.

From molecular to microrepair

Self-healing in biological systems occurs across all length scales. At the molecular level, biological systems use metabolic processes, such as in autophagy, to self-heal[227]. Self-healing materials can have similar metabolic character if 'outdated' or degradation products are replaced by new components, eliminating undesirable by-products. A problem is that side reactions may lead to undesirable products and are not easily controllable. However, combining the attributes of two or more self-healing motives in synthetic materials may lead to autonomous self-healing with a metabolic character. The future of self-healing polymer networks may comprise controllable supramolecular networks or van der Waals interactions, which do not generate side reactions or involve covalent rebonding.

At the atomic scale of the covalent bond length in synthetic and natural materials, cleavage of aliphatic chains leads to the formation of CH or CH_2 free radicals, or slippage of polymer chains. For chain cleavage, simple geometrical considerations indicate that, relative to terminal $-CH_3$ represented by sp^3 hybridization, CH and CH_2 free radicals adopt more directional sp and sp^2 hybridizations. The distances between the free radicals to initiate coupling are roughly 2.35–3.44 Å, and an energy of ~20 kcal mol^{-1} is typically required. When radical coupling occurs, the bonding distances decrease to 0.95–1.60 Å and the energy required decreases to ~10 kcal mol^{-1}. For radical recoupling to occur, interchain diffusion should occur, which is often driven by the access of interfacial energy in the damaged area and the T_g-dependent kinetics of interdiffusion (Eq. 1).

At the nanometre scale of skeletal muscle fibres, mesogenic precursors are activated in the site of an injured fibre, leading to the proliferation of myoblasts, which repair damage by differentiating into multinucleated myocytes[2]. By analogy with supramolecular self-healing chemistry, satellite and myelomonocytic cells also contribute to repair processes, in which dysferlin acts as a Ca^{2+} sensor of the muscle membrane damage, triggering vesicle fusion and directing Ca^{2+} along the membrane to seal the lesion by sending messages to neutrophils for repair[3,4].

An example of cascading processes at the micrometre and millimetre scales are skin-injury wounds, which penetrate into the dermis layer of skin, to which the red blood cells transfer as a result of rupture of blood vessels. Platelets and inflammatory cells or cytokines rush to the site of the injury and receptors signal the event by activating fibroblasts and other connective-tissue cells to deposit collagen. As a result, new tissue at the injury site and wound healing occurs[5]. The cascading processes leading to such self-healing (not just in mammals but also in plants) brings a different perspective to designing self-healing in synthetic materials. However, it is necessary to answer fundamental questions of how localized individual reactions are capable of generating cascading microscale responses leading to macroscale self-healing. This requires the measurement of the molecular-level events — usually inside a scratch — responsible for self-healing of materials.

Tools for studying self-healing

Self-healing is typically measured by bulk mechanical analysis, in which properties before and after damage are assessed (ideally, these should match). Although useful, this analysis does not reveal the molecular processes responsible for self-healing. To identify mass transport during the damage–repair cycle, atomic force microscopy may be useful if acquisition times are fast enough to capture self-healing. The same is applicable to optical microscopy.

Many self-healing mechanisms are not trivial to study experimentally. For detecting local molecular events, the most sensitive spectroscopic tools are infrared[228] and Raman spectroscopy[229], which provide satisfactory spatial resolution. By contrast, electron paramagnetic resonance[230] and NMR spectroscopy[231,232], in particular, nuclear Overhauser effect spectroscopy (NOESY) and correlated spectroscopy (COSY) 2D ^{1}H NMR exhibit decent sensitivity but insufficient spatial resolution. A promising approach for monitoring self-healing events in polymers is dynamic nuclear polarization (DNP) NMR spectroscopy, if it were applied to assess conformational changes of dangling chain ends at the interfacial regions generated during damage. In fact, the DNP approach has the potential to improve the sensitivity of ^{1}H NMR spectroscopy up to ~660-fold. Solid-state DNP ^{13}C spectroscopy has been used in microporous organic polymers[233] but requires an external bis-nitroxide radical-polarizing agent. Other intrinsic radicals as polarizing agents can also be used[234,235].

Computational research is increasingly important to predict or explain observed self-healing behaviour. For example, the rolling motion of microcapsules was modelled using Brownian dynamics on an adhesive-coated substrate to design particle-filled microcapsules that heal cracks in the substrate[236]. To model fracture and self-healing, most models adopt continuum-damage approaches in which cracking and healing are considered as the degradation and recovery of materials properties. By contrast, cohesive-zone approaches treat damage as a discrete event, allowing explicit modelling of crack evolution[237], including simulation of property recovery over repeated healing events. Looking forwards, there are opportunities for using and developing computational models that could tackle 3D self-healing in heterogeneous systems. Collectively, computer simulations and modelling are useful for answering many of the puzzling questions that are not easily experimentally measured, particularly for predicting dynamic materials properties[238–240].

Outlook

The past couple of decades have brought remarkable advances in the controllable synthesis of self-healing polymers and the development of ‘living-like’ programmable polymeric materials. The synthetic capabilities afforded by continuously improving polymerizations provide access to new, controlled-architecture macromolecules with precision placement of the functionality needed for self-healing. New strategies for installing self-healable moieties into existing commodity polymers have further expanded the preparation toolbox. Further manipulation of molecular weight and molecular-weight distribution, molecular architecture, functional-group placement and precise copolymer compositions will yield self-healing polymers with new properties. However, the technological success of self-healing polymers will depend on how commodity (co)polymers can be cost-effectively converted into their self-healable counterparts via precisely controllable and affordable polymerization processes, and how the structural understanding can be translated into specific functionalities and applications.

In addition to one-time and repeated-cycle self-healing, there are opportunities and challenges in the development of sequential and parallel reactions that may lead to physical remodelling at macroscopic scales. Localized heterogeneous macromolecular networks capable of transient communication and signalling of damage that enable synchronous macroscopic rearrangements will become increasingly important in the development of self-healing materials. Localized T_g gradients and associated local stimuli-responsive transitions[241,242] will become crucial for achieving reasonable self-healing kinetics. It is interesting to note that some of the observations and questions from the late 1970s and early 1980s remain unanswered. For example, for pMMA slightly above T_g, a diffusional interpenetration of chain segments occurs, but after short penetration times (~5 min), fracture toughness is regained in short-term experiments, but long-term properties cannot be restored[243].

The ultimate challenge will be to produce polymer networks with metabolic and anabolic characteristics, whereby synchronized events between sequential or concurrent self-healing paths occur. An approach in this direction is combining phase-separated supramolecular and covalent bonding with hydrophilic and hydrophobic interactions. For example, learning from nature, when a protein composed of a hydrophobic packed interior and hydrophilic exterior is placed in an aqueous environment and exposed to hydrostatic pressure (or cutting), water molecules are forced into the protein interior by filling cavities and breaking up the hydrophobic structure[244,245]. When the forces are removed, hydrophobic interactions prevail and the protein regains its structural and functional features. There are opportunities for further advances when hydrophobic and hydrophilic interactions in synthetic polymers compete during the damage–repair cycle. Similar to biological systems, the key to controlling these macromolecular interactions is precise molecular DNA-like sequencing. From a macroscopic view, the formation of self-knotted polymer-chain topologies promises the ability of self-healing of fibres in composites.

Applications of self-healing polymers are likely to be found in agriculture, the food industry, medicine, transportation, recycling and upcycling. All these sectors face challenges to meet new requirements and regulations, and polymers with upcycling and self-healing attributes may become a new standard for many industries. Despite the urgency of agricultural needs, our understanding of how plants and other species transport nutrients to their destinations in vivo is still largely unanswered. Similarly, there are many unanswered or unasked questions in self-healing polymers. One such question is how the shape and symmetry of a structure will determine the arrangements of the building blocks enabling self-healing through internal actuation mechanisms leading to macroscopic reconfiguration of the materials. The challenge is how to implement internal directional actuation mechanisms while retaining physical and chemical stability. If answered, technological advances may enable new strategies for materials developments. It is not hard to envision that hip or other body part replacements may have extended lifetimes when self-healing materials are used. Biological sensing and signalling pathways are mediated by interfacial processes linked to biological growth and development. One can envision that self-healing will be crucial for interactions between synthetic and biological systems. To achieve this, we need to better understand the molecular processes that govern biosynthetic signalling and decision-making processes in synthetic materials. Using the analogy of metabolic processes in cells, we envision that, if repeating units of a copolymer represent a heritable genetic identity derived during its growth, different interfacial interactions (the 'genotype') will lead to different materials 'phenotypes'.

Overall, the outcomes will be less energy used and less waste generated. Self-healable polymers with more tunable time-sensitive properties are needed; a grocery bag does not have to last more than a day or two, but paint on a bridge or vehicle needs to last much longer. An ultimate goal of future studies should lead to the development of organism-like materials with encoded molecular features that dictate their growth and structural assembly in response to the environment. Organism-like materials will consist of elements responsible for autonomous and adaptive properties enabling the creation of synthetic integrated systems and devices.

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Acknowledgements

This work was supported by the National Science Foundation under awards DMR 1744306 and partial OIA-1655740. The J.E. Sirrine Foundation Endowment at Clemson University is also acknowledged for partial support of this work.

Author contributions

S.W. wrote and edited the article. M.W.U. conceptualized, wrote and edited the article.

Competing interests

The authors declare no competing interests.

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