

Intrinsically Self-Healing Polymers: From Mechanistic Insight to Current Challenges

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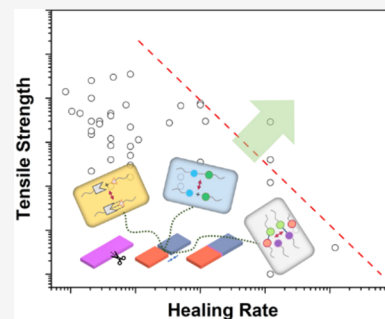
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ABSTRACT: Self-healing materials open new prospects for more sustainable technologies with improved material performance and devices' longevity. We present an overview of the recent developments in the field of intrinsically self-healing polymers, the broad class of materials based mostly on polymers with dynamic covalent and noncovalent bonds. We describe the current models of self-healing mechanisms and discuss several examples of systems with different types of dynamic bonds, from various hydrogen bonds to dynamic covalent bonds. The recent advances indicate that the most intriguing results are obtained on the systems that have combined different types of dynamic bonds. These materials demonstrate high toughness along with a relatively fast self-healing rate. There is a clear trade-off relationship between the rate of self-healing and mechanical modulus of the materials, and we propose design principles of polymers toward surpassing this trade-off. We also discuss various applications of intrinsically self-healing polymers in different technologies and summarize the current challenges in the field. This review intends to provide guidance for the design of intrinsic self-healing polymers with required properties.



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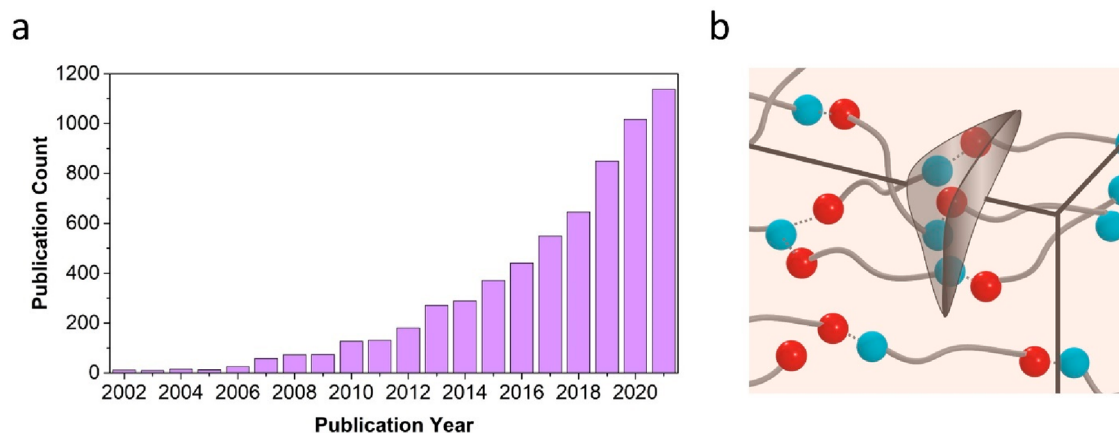


Figure 1. (a) The number of publications per year on topics of self-healing polymers (data from the Web of Science, the search keyword is “self-healing polymer”). (b) Schematic of the material design of intrinsically self-healing polymers with spheres presenting dynamic reversible bonds.¹⁹

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1. INTRODUCTION

Self-healing materials are materials with the capability to repair physical damages and restore functionalities by themselves.^{1–4} The interest to design self-healing materials grew substantially in the recent decade due to an expected increased longevity of materials and devices and hence improved sustainability.^{5–7} Self-healing is an intriguing function in biological systems, while they typically utilize a complex cascade multistep process. The healing mechanisms between plants and animals are different but include the same three general steps: immediate biochemical (e.g., inflammatory) response, wound closure, and then partial or full functionality recovery. Among them, our human skin is a familiar example, which starts with inflammatory response that triggers specific biochemical processes immediately after encountering minor physical damage like a small cut, then merges the gaps within hours, and fully recovers its original function and properties such as sensing capability and high elasticity, after a few days. Self-healing in synthetic systems also includes sealing phase (intermolecular diffusion) and some chemical/physical repair (bond rearrangements), but it differs from the process in biological systems and usually is much simpler with fewer steps to recover the functionality.^{8–10} Yet, the understanding of self-healing mechanisms in synthetic systems remains limited that hinders the further development of facile design principles of materials with desirable self-healing properties.

Polymers, metals, ceramics, and composites with self-healable properties have been developed during the past few decades. Metals are reusable after being melted, while the required energy to achieve melting point is extremely high due to their high melting temperature, T_m . Thus, metals with low T_m such as liquid metal are normally utilized as healable materials,^{11,12} and such examples include a liquid metal-based room-temperature self-healing anode material for lithium-ion batteries¹³ or an autonomously self-healable liquid metal based elastomer.¹⁴ Ceramics can also achieve self-healing by chemical

reactions, e.g., oxidation, of the preincorporated healing agents upon exposure to high temperature or to the atmosphere.¹⁵ For example, locally doped MnO on the fracture path significantly accelerated the healing process, which can be adapted to structural ceramics such as turbine blades in aircraft engines.¹⁶ Polymers exhibit unique advantage among the self-healing materials due to their mechanical flexibility and structural adaptability. The backbone structure, molecular architecture, and functional groups of polymers could be tuned in a broad range to achieve desired self-healability. The self-healing mechanism varies from the recovery of dynamic bonds to the formation of new chemical bonds by different chemical precursors that were initially isolated.¹⁷ Furthermore, the versatility of polymers allows the integration of different functionalities in the same polymer.¹⁸ Currently, polymer-based self-healing systems occupy one of the major research directions in self-healable materials. The number of publications on the topic of self-healing polymers has grown exponentially in the recent decade (Figure 1a), increasing from below 100 per year before 2010 to over 1000 in the year 2021.

The incorporation of self-healing ability significantly prolongs the lifetime of materials against physical damage. It reduces material waste, replacement labor, and life cycle cost, providing a more sustainable path for a lower carbon cycle. For example, the carbon footprint of self-healing geopolymers concrete is estimated to be lower than ordinary Portland cement concrete even under the worst-case assumptions.²⁰ Developing self-healing polymers also addresses another global problem: reduction of the plastic pollution. Annual plastic production reaches 400 million metric tons (Mt),²¹ and combined with manufacturing energy inputs, commodity plastic alone is estimated to account for an annual 104 Mt CO₂ equivalent of greenhouse gas (GHG) emissions just in the U.S.²² With the expected increase of plastic production to 1100 Mt by 2050,²³ extending the longevity of polymer materials is important,²⁴ in addition to developing paths for high recyclability as well as upcycling with closed-loop circularity.²⁵ Developing the intrinsically self-healing polymers provides one of the strategies to improve plastics circularity and reduce overall GHG emissions. The impact of improved longevity extends far beyond the polymer itself because the failure of the polymer often leads to the failure of the entire device or system. Thus, the development of self-healing

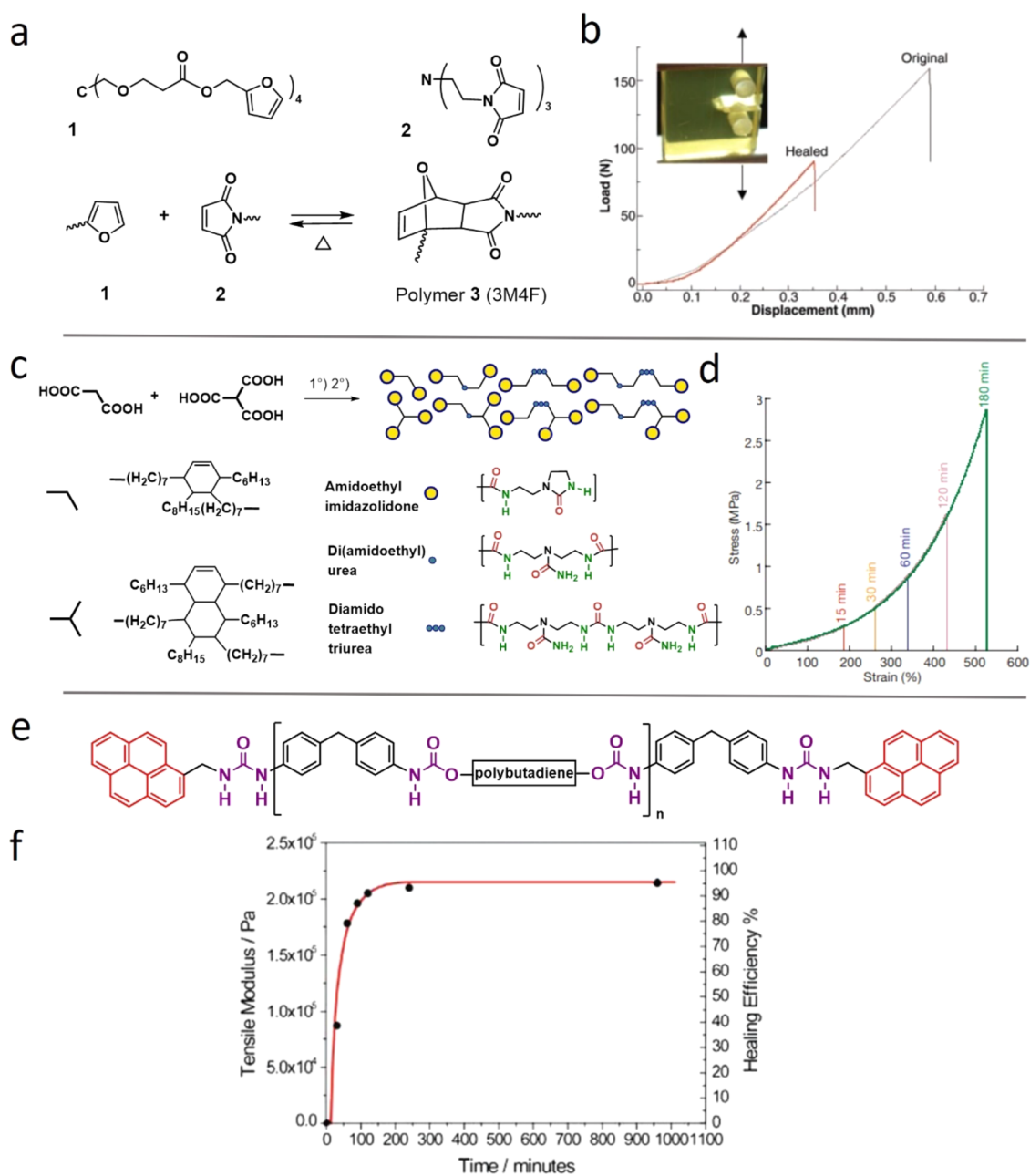


Figure 2. Examples of intrinsically self-healing polymers with different dynamic bonds. (a) Chemical structures of Diels–Alder (DA) reaction moieties. Reproduced with permission from ref 33. Copyright 2002 The American Association for the Advancement of Science. (b) Stress–strain curves including the healed sample and the pristine sample. Adapted with permission from ref 33. Copyright 2002 The American Association for the Advancement of Science. (c) Schematic illustration of the structures of the urea containing self-healable rubber. Reproduced with permission from ref 34. Copyright 2008 Springer Nature. (d) Stress–strain curves of the healed samples at different healing time of the urea containing self-healable rubber. Adapted from ref 34. Copyright 2008 Springer Nature. (e) Chemical structure of the pyrenemethyl end-capped hydrogen-bonding polymer. Reproduced with permission from ref 37. Copyright 2010 American Chemical Society. (f) Healing kinetic of the polyurethane samples. Adapted with permission from ref 37. Copyright 2010 American Chemical Society.

polymers is critical for enhancing sustainability of many technologies. There are two major strategies to achieve self-healing in polymers: the extrinsic and intrinsic approaches. The extrinsic approach typically involves two reactive chemicals under physical confinement, and fast chemical reactions between the two reactants upon physical damage rapidly seal the void.^{19,26} Different from conventional extrinsic approach, some polymer systems can also self-heal or self-repair using the atmospheric CO₂ fixation by mimicking the photosynthesis of plants.^{27,28} On the other hand, the intrinsic approach is

facilitated by the breaking and rebonding of dynamic (reversible) bonds and interdiffusion of polymer chains (Figure 1b).

The first report of self-healing polymer by capsule-based approach was published in 2001,²⁹ where the capsules containing healing agent and catalyst particles were embedded into an epoxy matrix. Such structure achieved 75% recovery of toughness after a razor blade cut. Following those initial reports, the concept of microcapsules in self-healing has been well adopted by researchers for a wide range of applica-

tions.^{30,31} But this approach provides only one time healing and suffers from chemical leaks. Then vascular-based extrinsic self-healing approach was reported in 2007.³² The extrinsic self-healing polymers with a bioinspired microvascular network system significantly improved the repeatability of self-healing and overcame the shortcomings of the first-generation capsule-based materials. Yet, complex structure of the vascular network and the same challenge of potential chemical leaks have prevented broad use of these self-healing systems. A unique strategy based on a polymer gel with embedded chloroplasts that can use the atmospheric CO₂ was developed in 2018.²⁷ This enables the glucose containing poly(methacrylamide) based hydrogel to grow, strengthen, and self-repair. However, the chemical design is limited, the mechanical strength of the obtained hydrogel is relatively weak, and more importantly, the embedded chloroplast loses the bioactivity in a relatively short period, not suitable for long-term self-healability.

In contrast, the intrinsic (autonomous) approach relies on polymer diffusion and reversible bonds within the materials that could rebuild after a physical damage (Figure 1b). The main advantage of the intrinsic self-healing approach is the capability of repeated self-healing process. These polymeric systems could theoretically heal at the same spot repeatedly many times. The concept of intrinsic self-healing of polymer network was introduced in 2002, utilizing thermally reversible Diels–Alder (DA) reaction.³³ The authors developed a remendable polymer with the tensile strength of 68 MPa and elongation before breaks close to 3.2%, and such a polymer could undergo self-healing at a temperature above 120 °C, achieving healing efficiency of 41% at 120 °C and 50% at 150 °C, respectively (Figure 2a,b). A room-temperature self-healable elastomer utilizing hydrogen bonding (H-bonding) was reported in 2008.³⁴ The amidoethyl imidazolidone, di(amidoethyl) urea, and diamido tetraethyl triurea containing rubber exhibited a tensile strength of 3 MPa and extensibility of 600%, and the polymer could fully recover its mechanical properties within 3 h at 20 °C (Figure 2c,d). This discovery inspired the research on room temperature self-healing polymeric materials and many other works have been reported.^{35,36}

A self-healable polymer based on aromatic π – π stacking and hydrogen bonding interactions was reported in 2010.³⁷ The synergistic effect of π – π stacking interactions from chain-folding polyamide and hydrogen bonding interactions from telechelic polyurethane promoted a self-healable polymer capable of recovering 95%, 91%, and 77% of tensile modulus, elongation-at-break, and tensile toughness, respectively, at 100 °C healing (Figure 2e,f). Such a concept of self-healing polymers combining several types of dynamic bonds is widely adopted currently.^{38,39}

Recently, self-healing polymers were categorized into four generations: capsule-based self-healing is the first generation, intrinsic self-healing is the second generation, vascular-based self-healing is named the third generation, while the polymer with combined self-healing mechanisms is the fourth generation.⁴ Because the method of generation assignment is based on the year of the first publication of a particular category, it does not necessarily imply the advancement of the technology. Self-healing materials based on all of the above mechanisms are still in development, and there remain many challenges to be resolved. But in our view, intrinsic self-healing mechanisms based on various types of dynamic reversible bonds present the most promising avenue due to their relative

simplicity and ability of multicycle healing. Even terminology remains not well-defined in this field. General term “dynamic polymers” usually refers to all polymers with dynamic reversible bonds, including covalent and physical (e.g., hydrogen bonding) ones. The “associating polymers” term usually refers to polymers with physical interactions, while the terms “dynamic covalent networks” or “covalent adaptive networks (CANs)” include only polymers with dynamic covalent bonds.

This review focuses on intrinsically self-healing polymers with various dynamic bonds and corresponding self-healing mechanisms. Different from previous reviews focusing on the material design or specific functionalities/application fields,^{6,40,41} the current review presents the underlying physical mechanisms and critical parameters controlling self-healing kinetics in polymers with dynamic bonds. For example, a trade-off exists between the rate of self-healing process and the mechanical strength of the materials, and we discuss potential approaches to overcome this trade-off. We also point out the lack of standardized testing parameters that makes it difficult to compare results from different groups, especially the ones driven by different healing mechanisms. The review summarizes the current state-of-the-art for intrinsically self-healing polymers and formulates suggestions to be implemented for standardized evaluations of self-healing properties. Based on the presented analysis, we would like to emphasize the importance of combining dynamic bonds with different strength (e.g., implementing the idea of sacrificial bonds) and formation of hierarchical structures with hard domains to strongly improve performance of self-healing materials. We also give an overview of applications of intrinsically self-healing polymers in various current and future technologies.

2. DYNAMIC BONDS AND CURRENT UNDERSTANDING OF SELF-HEALING MECHANISMS

2.1. Dynamic Reversible Bonds

The intrinsic self-healing of polymers is generally achieved by (1) a flow of amorphous polymers at temperatures above their glass transition temperature (T_g), i.e., polymer chains interdiffusion, and (2) rearrangements of reversible bonds including dynamic covalent bonds and physical interactions. The polymer flow is usually driven by gains in cohesive energy and removal of surface tensions. Even simple van der Waals interactions will provide gains and drive self-healing process in this way, facilitating the formation of interdigitated structures.⁸ However, van der Waals interactions is similar to a self-healing of any liquid, while requiring a longer time due to very high viscosity of polymer melts. Flow of thermoplastics at temperatures above T_g of the hard blocks can be considered in the same way. If conventional thermoplastics are exposed to temperature significantly higher than their T_g , the viscosity will be lower, and a deformation or welding rather than healing occurs. However, these processes in liquid and thermoplastics are normally not termed as self-healing.

The self-healing polymer networks with dynamic (reversible) bonds provide unique viscoelastic properties, and they can be readily tailored due to the compatibility and adaptability of polymer design, where functional groups could be inserted into the specific location of polymer backbone. There are many classes of dynamic bonds, including hydrogen and ionic bonding, π – π stacking, dynamic covalent bonds, guest–host

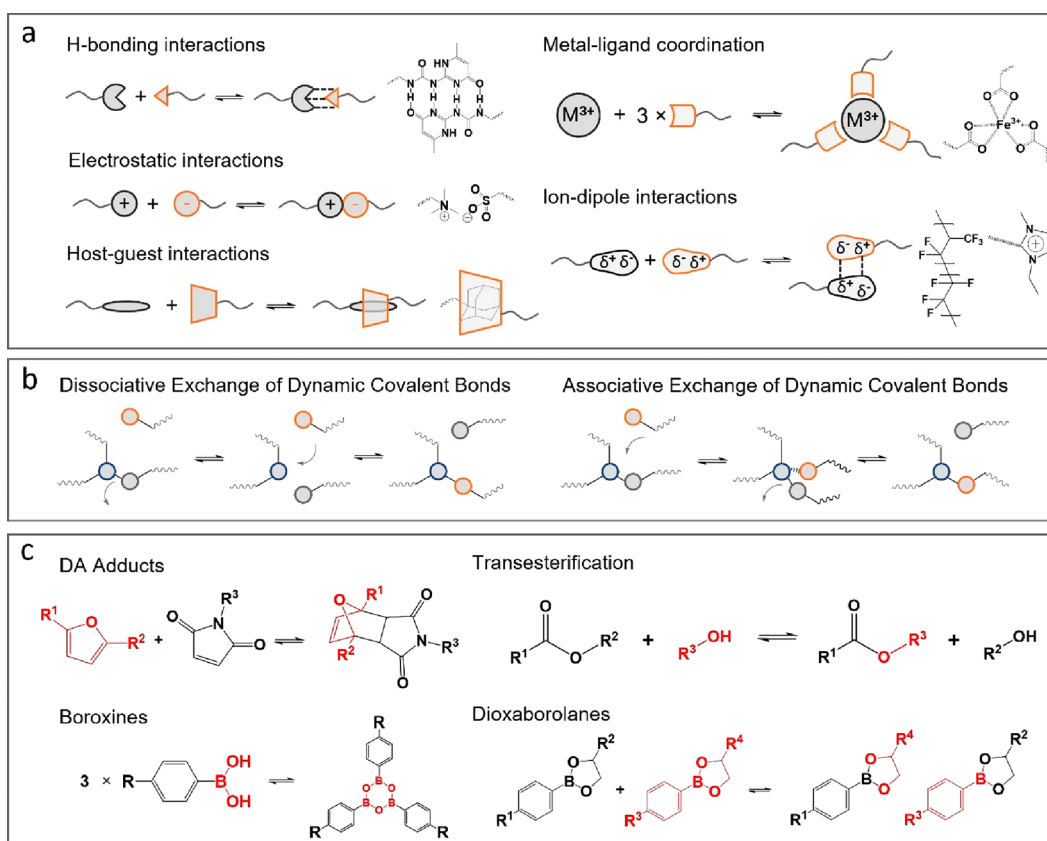


Figure 3. Illustrations of the different dynamic bonds. (a) noncovalent bonds; (b,c) dynamic covalent bonds.⁵ Reproduced with permission from ref 5. Copyright 2022 American Chemical Society.

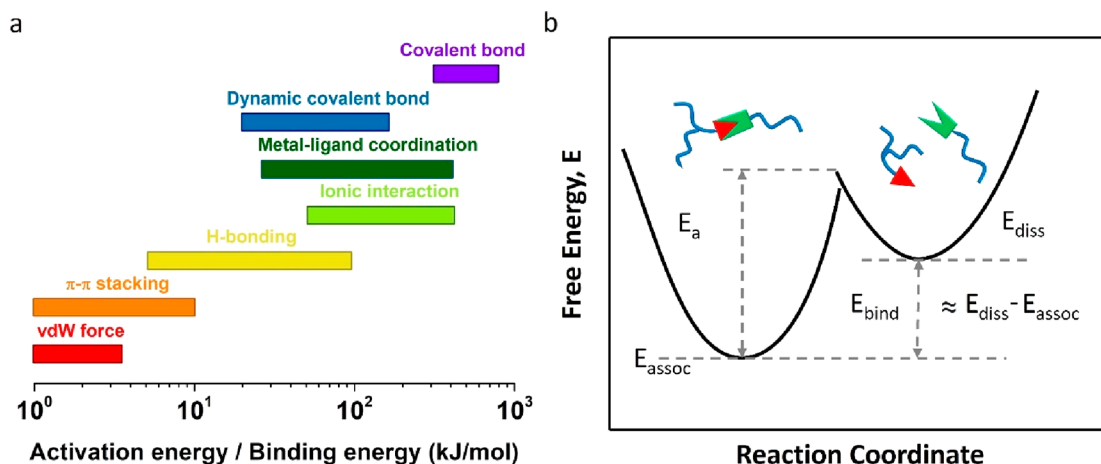


Figure 4. (a) Characteristic dissociation energy for different types of dynamic reversible bonds.⁴⁹ Reproduced with permission from ref 49. Copyright 2021 American Chemical Society. (b) Illustration of the critical energy parameters of bond rearrangement.⁴⁹ Reproduced with permission from ref 49. Copyright 2021 American Chemical Society.

interactions, and metal–ligand coordination (Figure 3).^{39,42,43} All of these bonds can be switched multiple times, enabling multiple healing processes. They differ by the energy of dissociations (Figure 4a) that controls the characteristic time of the bond rearrangements. In many cases, the bond rearrangement time is the longest relaxation time in the dynamic network and defines the terminal relaxation time that marks the beginning of the flow process.^{44–48} Recent nonlinear rheological studies revealed that the kinetics of self-healing process correlates well with the terminal relaxation time defined by dynamic bonds rearrangements.⁴⁵ Thus, the

rearrangement time of dynamic bonds is a critical parameter for the self-healing rate, and before discussing self-healing mechanisms, we need to consider the mechanisms of bond rearrangements in typical dynamic polymers.

2.2. Mechanisms Controlling Dynamic Bonds Rearrangements

The critical parameters for dynamic bond rearrangements are the binding energy, E_{bind} , defined as the difference in Gibbs free energy between associated (E_{assoc}) and dissociated (E_{diss}) states, and the energy barrier for bond dissociation E_{a} (Figure

4b).⁴⁹ The two key parameters E_{bind} and E_a are often confused in literature. Although they might be connected (in the sense that high E_{bind} also means high E_a), these parameters have very different physical meaning. E_{bind} defines the population of dissociated bonds at equilibrium and will influence whether bond rearrangement at a given temperature will undergo a dissociative (relatively low $E_{\text{bind}}/RT \sim 1-3$) or associative mechanism ($E_{\text{bind}}/RT \gg 1-3$). Polymers with associative dynamic bonds are typically categorized as vitrimers, although some polymers with dissociative dynamic bonds show similar rheological behavior. In contrast, E_a defines the rate of bond dissociation at specific condition, i.e., viscoelastic properties of the material. In fact, the E_a can be high even if E_{bind} is relatively low. These energies can be strongly affected by presence of catalysts or in the vicinity of other dynamic bonds.

Very often, E_a is calculated from the temperature dependence of viscoelastic properties (e.g., terminal relaxation obtained from rheology or stress relaxation from DMA).⁵⁰⁻⁵³ This is inaccurate by two reasons.⁴⁹ First of all, temperature dependence of the bond dissociation is controlled not only by the energy barrier E_a but also by segmental mobility/dynamic of the polymer chain. If segments in the polymer are not moving (e.g., the sample is at temperatures much below T_g), no bond dissociation is possible. Thus, the characteristic bond dissociation time is also controlled by the segmental relaxation time $\tau_\alpha(T)$ following the equation:^{49,54-57}

$$\tau_{\text{dis}}(T) = \tau_\alpha(T) \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Second, the viscoelastic properties are defined by bond rearrangements and not by the bond dissociations.^{46,58,59} If the dissociated sticker (bond) reassociates back with the same partner, no changes are detected in mechanical or viscoelastic properties. Only when the stickers change partners, stress relaxation can occur. At the same time, bond dissociation can be measured by other experimental techniques, e.g., dielectric spectroscopy if the dipole moment is changing with actual bond dissociation.^{46,47} Direct comparison of bond dissociation time from dielectric spectroscopy to the bond rearrangement times measured by rheology revealed that in some cases they can differ by thousands of times,^{46,47,60} and such difference can be explained by the bond lifetime renormalization model⁵⁸ that will be discussed below.

Yet, most of the literature use the apparent activation energy estimated from mechanical properties as the energy of bond dissociations. As a result, there is a large difference of the dissociation energy estimates in literature for the same type of the bond. For example, as one of the mostly utilized associative dynamic covalent bond, the activation energy (E_a) of bond exchange/dissociation for vinylogous urethane is normally calculated to be in the range from 55 to 65 kJ/mol.⁶¹⁻⁶³ However, based on the slope of the fitted Arrhenius curve, the activation energy of vinylogous urethane is calculated as 42 kJ/mol for a soft PDMS based elastic network,⁶⁴ while 102 kJ/mol is obtained for a rigid PMMA based vitrimer with the same vinylogous urethane bond.⁶⁵ Analysis of literature presented in ref 50 demonstrates the estimates of the activation energy of imine exchange reaction bond vary from ~ 48 kJ/mol to ~ 157 kJ/mol.⁵⁵ The activation energy for disulfide based vitrimers was estimated to vary between 99 and 357 kJ/mol.⁶⁶ The role of segmental relaxation of a specific polymer backbone in the activation energy estimated from stress relaxation was revealed

in the model analysis presented in recent research.⁵⁷ All of these data clearly demonstrate that the apparent activation energy does not provide reliable estimates of the energy barrier for the bond dissociation.

2.3. Models Describing Dynamic Bonds and Self-Healing Processes

Existence of dynamic (reversible) bonds significantly affects the viscoelastic properties of polymers. These changes in chain dynamics have been described using sticky Rouse (for unentangled polymers) and sticky reptation (for entangled polymers) models.⁶⁷⁻⁶⁹ According to these models, stickers along the chain slow down only chain modes that involve part of the chain longer than the average distance between the stickers, and the characteristic relaxation time of these modes will be controlled by the stickers' dissociation time. At the same time, the chain dynamics for the shorter part of the chain should remain unaffected by stickers. These models provide specific predictions for viscoelastic properties of chains with stickers.⁶⁷⁻⁶⁹ A good summary of the sticky Rouse and reptation models, as well as some other gelation models, was presented in the recent perspective article by Wu and Chen.⁷⁰ Recent studies revealed that stickers also slow down segmental dynamics and increase T_g of the polymers,^{56,71} and these changes can be described using statistical mechanical theory developed by Schweizer and co-workers.⁷² These models and theory, however, do not address the self-healing mechanism in polymers.

The bond lifetime renormalization model developed by Rubinstein and co-workers⁵⁸ provides one of the most comprehensive analyses and description of the self-healing process in polymers with dynamic bonds (stickers). The model considers a branched chain with multiple stickers and analyzes three regimes of bond dissociation energy E_a (the model implicitly assumes $E_a \approx E_{\text{bind}}$): (i) weak association $E_a < RT \ln(N)$ (N is the number of segments between stickers), where stickers essentially play no significant role in viscoelastic properties. (ii) Intermediated regime $RT \ln(N) < E_a < 2RT \ln(N)$. (iii) Strong association regime $E_a > 2RT \ln(N)$. In the case of the intermediate regime, there are many open stickers, and the rate of bond rearrangements is controlled by a diffusion of a sticker to find another partner. In most cases, the dissociated sticker will reassociate with the same initial partner and no stress relaxation occurs. Then the bond rearrangement time, τ_r , is defined by the bond dissociation time, τ_{dis} , multiplied by the number of returns to the initial partner J plus the time of diffusion to the new partner τ_{open} :⁵⁸ $\tau_r = J^* \tau_{\text{dis}} + \tau_{\text{open}}$. This equation explains well why the bond rearrangement time estimated in rheology was found in many cases to be much longer than the bond dissociation time estimated from dielectric spectroscopy data.^{46,47,59} In the strong association regime, most of the stickers are associated, and the bond rearrangement happens by bond hopping (associative dynamic exchange), and it is defined by the bond dissociation time and $\tau_r \approx \tau_{\text{dis}}$.⁵⁸ Detailed test of the model revealed that it indeed describes experimental data well even on a quantitative level.^{46,47,59}

To describe the self-healing process, another important parameter was introduced: the waiting time from the moment of physical damage until the beginning of the healing process, τ_w .⁵⁸ Sample damage (e.g., rupture or cut) creates a nonequilibrium state with many open stickers and deformed polymer chains. If the self-healing is initiated immediately after

the damage, self-healing occurs in relatively fast time because most of the stickers in the interfacial region remain open/active, and they might not need to diffuse far to find another open sticker as a partner. The number of open stickers will decrease significantly with waiting time approaching a new equilibrium state. If the waiting time is longer than the equilibration time of the damaged surface, the healing process will be equal to a simple adhesion process (Figure 5).⁵⁸ The theory predicts various regimes of the self-healing process as a function of waiting time and the bond dissociation energy E_a (Figure 5).

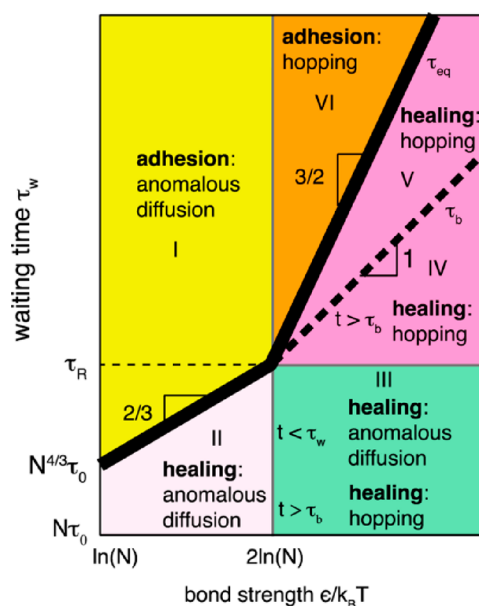


Figure 5. Different regimes of the self-healing process from anomalous diffusion (very fast) to hopping (relatively fast) and to adhesion (relatively slow) as the function of the dynamic bond strength $\epsilon = E_{\text{dis}} = E_a$.⁵⁸ There are several important time scales, including segmental relaxation time τ_0 , rouse time τ_R , and bond dissociation time τ_b . The equilibration time τ_{eq} (thick black line) marks the crossover from healing to adhesion behavior. Adapted with permission from ref 58. Copyright 2013 American Chemical Society.

Normally, before reaching the equilibrium state, the longer the waiting time is, the slower the self-healing process will be, and the black line in Figure 5 marks the bulk equilibration time. This time depends on bond dissociation energy (bond strength) and the length of the chain between stickers, denoted as N . Above this waiting time, the damaged parts reach new equilibrium state that does not change with longer waiting time. In this case, the healing process of two equilibrated surfaces becomes an adhesion process, and this process does not depend on the waiting time (assuming no dust will interfere during the waiting time).⁵⁸ Thus, overall, the self-healing kinetics in systems with dynamic bonds depends on the bond-rearrangement time and waiting time after the cut and before the start of healing. The former depends on the energy barrier for the bond dissociation (the strength of the dynamic bond), segmental relaxation time, and the length of the polymer chain between the dynamic bonds. Unfortunately, most of the papers do not report the waiting time between the sample cut or damage and the beginning of the self-healing process, which complicates the direct comparison of data obtained in different groups.

There are additional details that also affect the self-healing process efficiency and its rate. They include the roughness of the damaged surface, equilibrium concentration of stickers at the surface, and the effect of relatively faster segmental dynamics in the interfacial layer of the open surface in comparison with those inside of the bulk polymer (effect well-known for thin polymer films).^{73,74} If stickers prefer an open surface, they will have higher concentration at the interface, and this scenario should accelerate the self-healing process. In the opposite situation, when stickers prefer to stay in the bulk, concentration of stickers at the damaged surface will be lower and the self-healing process should be slower. Another interesting example is the shape-memory assisted self-healing mechanism.^{75,76} For example, cross-linked elastomer after local rupture will return to its initial equilibrium shape and close the damaged spot. With dynamic bonds, these materials will possess self-healing ability, which will be accelerated by this shape memory effect.

The model discussed above considers dynamics of the networks with binary interacting stickers (dimers). However, many dynamic bonds (e.g., ionic or hydrogen bonds) form microphase separated clusters (Figure 6a), which alter viscoelastic properties of the polymer drastically. The microphase separation of stickers happens due to their limited miscibility with the polymer matrix, which leads to a coexistence of binary stickers and their clusters (Figure 6a).⁷¹ These systems have unique viscoelastic properties with relatively high modulus and extensibility, leading to exceptional toughness.^{71,77} Specific design of the elastic networks with microphase separated clusters even with the same concentration of dynamic bonds can further improve their modulus and toughness (Figure 6b).⁷⁷ In some sense, they are analogous to spider silk, where partially crystalline structures and strong hydrogen bonding also lead to extreme toughness.^{78,79}

At temperatures below T_g of the clusters, the systems with phase separating stickers will behave as a cross-linked rubber. In the case of crystalline clusters, melting temperature of the clusters T_m will be the critical parameter. However, at higher temperatures, once dynamic bonds in the clusters start dissociating and moving, rearrangements of the polymer networks are possible.^{48,60,71} It has been clearly demonstrated that structural relaxation in these clusters rather than the polymer segmental relaxation plays a critical role in viscosity and terminal relaxation of these systems.^{47,48} The detailed quantitative description of the mechanism of bond rearrangements in systems with phase separating stickers has not been developed yet. Computational studies suggested that bond exchange should happen through fusion and separation of different clusters.⁸⁰ However, more recent experimental studies by NMR and rheological measurements questioned this mechanism.^{60,81} The recently developed model⁴⁸ proposed a very different qualitative scenario of mechanism controlling bond rearrangements in systems with clusters of stickers. According to this model, the bond rearrangement time is controlled by the time of pulling a sticker from a cluster. The time of pulling a sticker should follow eq 1, with structural relaxation time in the clusters instead of segmental relaxation time and with the energy barrier controlled by Flory–Huggins interaction parameter χ defined by miscibility of the functional group (sticker) and polymer matrix. This model was able to describe well rheological data in systems with phase separated

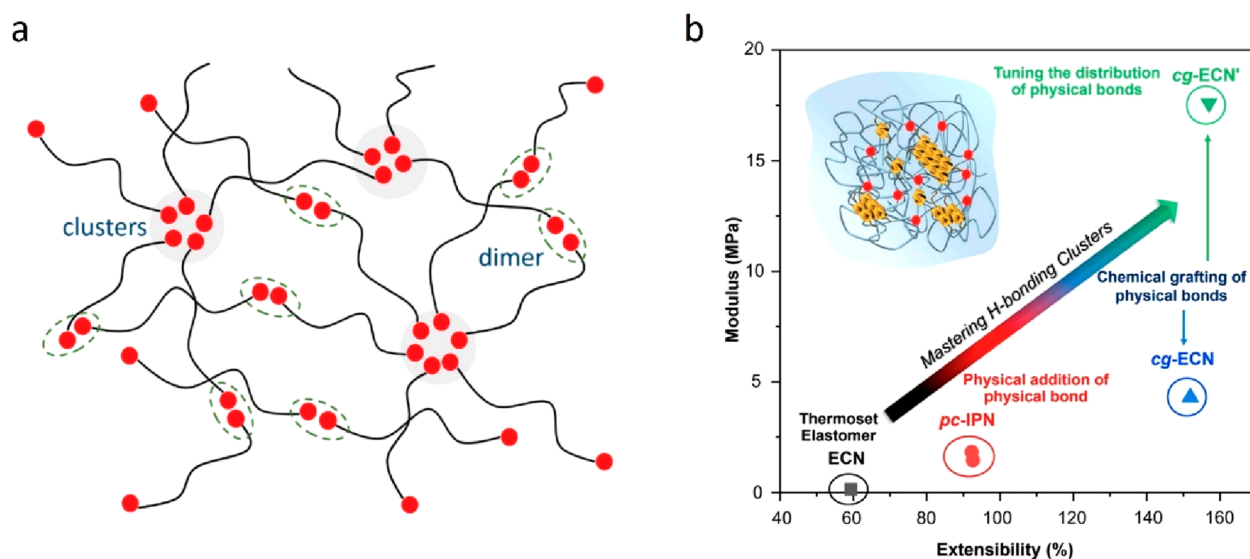


Figure 6. (a) Schematic illustration of polymer structure with stickers forming individual pairs (dimers) or microphase separated clusters. Adapted with permission from ref 71. Copyright 2018 Royal Society of Chemistry. (b) Demonstration of two potential pathways toward simultaneously enhancing the modulus and extensibility of polymers: incorporating hydrogen bonding networks (physical bonds) and introducing rationally designed clusters of hydrogen-bonding units.⁷⁷ Adapted with permission from ref 77. Copyright 2022 Elsevier Ltd.

stickers using structural relaxation time of clusters estimated from dielectric spectroscopy data.⁴⁸

Detailed rheological studies for systems with phase separated dynamic bonds revealed that self-healing time measured immediately after sample rupture correlates well with the bond rearrangement time of the samples (Figure 7). It is

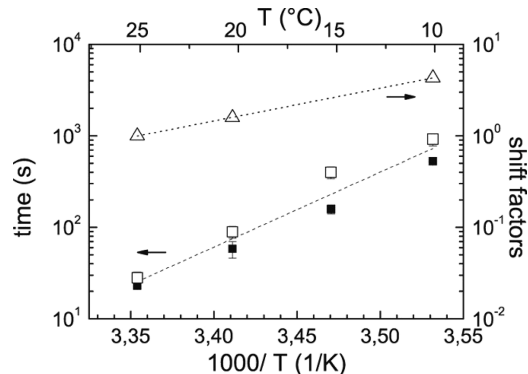


Figure 7. Detailed analysis using rheology revealed that self-healing time is comparable to the terminal relaxation time of the polymer with dynamic bonds. The latter in this specific case is controlled by bond rearrangements between clusters of dynamic (hydrogen) bonds.⁴⁵ Adapted with permission from ref 45. Copyright 2016 Springer Nature.

important to emphasize that the estimated self-healing time not only follows the temperature dependence of bond rearrangements time but also has very similar values (Figure 7). Thus, even in the systems with phase separated stickers, bond rearrangement time remains the most critical parameter controlling the self-healing kinetics.^{45,48} But in this case, the bond rearrangement time is not controlled by the segmental dynamics of the polymer backbone. It is defined by the characteristic time of structural relaxation in these clusters and by miscibility of stickers in the polymer matrix.⁴⁸

Another important observation in systems with phase separated dynamic bonds is unusually high elastic mod-

ulus.^{48,82–84} Already in 1990, it was proposed that an interfacial polymer layer with restricted segmental mobility and higher modulus can be formed around clusters of dynamic bonds.⁸² It is analogous to the interfacial polymer layer formed around nanofillers in polymer nanocomposites.⁸⁵ This idea was developed and successfully applied to describe mechanical reinforcement in poly(dimethylsiloxane) (PDMS) with phase separated hydrogen bonding stickers.^{48,84} Thus, phase separation of dynamic bonds not only provides additional parameter controlling their viscosity and terminal relaxation but also enables mechanical reinforcement analogous to the one observed in polymer nanocomposites.

2.4. Other Stimulus-Accelerated Self-Healing Kinetics

We considered thermal stimulations of the self-healing process in the discussion above. When the increase in temperature enables bond rearrangements, the higher the temperature is, the faster the self-healing process will be. This acceleration of self-healing kinetics is caused by two reasons (eq 1): faster segmental mobility $\tau_{\alpha}(T)$, and faster over barrier process due to lower value of E_a/RT . Aside from heat, there are also other methods to enable or accelerate the self-healing process, including solvent, gas, and UV light. One approach is a use of specific solvents. First, a solvent can work as a plasticizer and speed up the segmental relaxation process of the polymer. This will also speed up the bond rearrangements and shorten self-healing time. Some solvents can also affect the bond rearrangement process directly. For example, water accelerates bond rearrangements for boronic ester and imine bonds, leading to accelerated dissociation and rearrangements.⁸⁶ The facile dynamic exchange by the presence of water opens interesting opportunities where hydration of the surface speeds up the self-healing process, and the physical properties, like mechanical modulus, can be recovered upon further drying of the sample. Several examples of accelerated self-healing process for dynamic B–O bonds were reported in the presence of water or even at higher humidity.⁸⁷ Despite the sensitivity of these dynamic bonds to water, the samples remained intact even when they were immersed in water for several days.⁸⁸

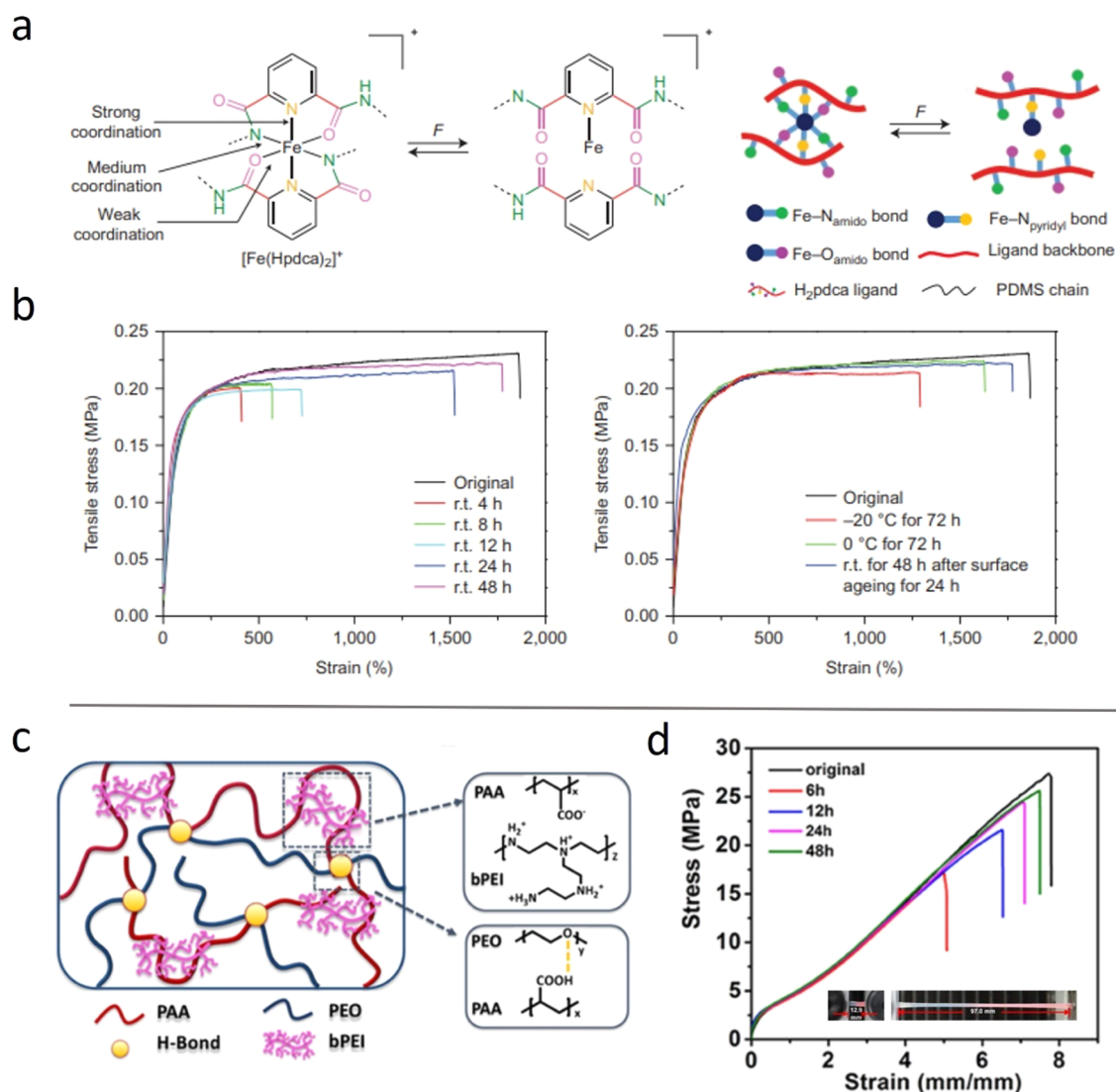


Figure 8. (a) Schematic illustration of the chemical structures of $[\text{Fe}(\text{Hpdca})_2]^+$. Adapted with permission from ref 35. Copyright 2016 Springer Nature. (b) Stress–strain curves including the healed sample of the $[\text{Fe}(\text{Hpdca})_2]^+$. Adapted with permission from ref 35. Copyright 2016 Springer Nature. (c) Schematic illustration of the structures of the bPEIx/PAA/PEO complex. Adapted with permission from ref 97. Copyright 2019 American Chemical Society. (d) Stress–strain curves of the healed samples at different healing time of the bPEIx/PAA/PEO complex. Adapted with permission from ref 97. Copyright 2019 American Chemical Society.

This stability was ascribed to the hydrophobic nature of the polymer backbone that limited the water access to the dynamic bonds. Strong acceleration of self-healing process was further demonstrated by addition of methanol to polymers with ionic bonds.⁸⁹ Another interesting strategy is the utilization of CO_2 gas to accelerate self-healing process in elastomers.⁹⁰ In PDMS based elastomer containing ionic functional groups, the self-healing process occurs with the rearrangement of the ionic clusters. At ambient condition exposed to atmosphere, the rearrangement of ionic clusters renders slow self-healing process. Replacing air with CO_2 atmosphere enables an accelerated (~ 10 times) self-healing process at ambient pressure and temperature. The authors ascribed faster self-healing to softening (or plasticization) of the ionic clusters by CO_2 .⁹⁰ Acceleration of the self-healing process can be also achieved by adjusting the pH (mostly for H-bonding systems) or addition of special ions (mostly for ionic and metal coordinated systems).⁹¹ Thus, adding small molecules whether

in liquid or gas phase can significantly accelerate the self-healing kinetics.

Another promising way of accelerating self-healing process can be application of UV or visible light for polymer networks containing a light-sensitive dynamic bond. A variety of self-healing mechanisms were adopted in this approach, such as photo-cross-linking reaction, photo-triggered metathesis reaction, and photothermal effect triggered self-healing. Photo-triggered cross-linking reaction could be triggered by UV or visible light. For example, coumarin, a class of benzopyrone compound commonly discovered in natural materials, can undergo $[2\pi + 2\pi]$ cycloaddition reaction to form a cyclobutane ring when exposed to light with a wavelength greater than 300 nm. The reaction could be reversed when the irradiation wavelength is below 260 nm. Therefore, utilizing coumarin-containing cross-linker, a series of light-responsive cross-linked polymers were synthesized from a range of acrylate monomers: butyl methacrylate (BMA), methyl acrylate (MA), hexyl methacrylate (HMA), and ethyl acrylate

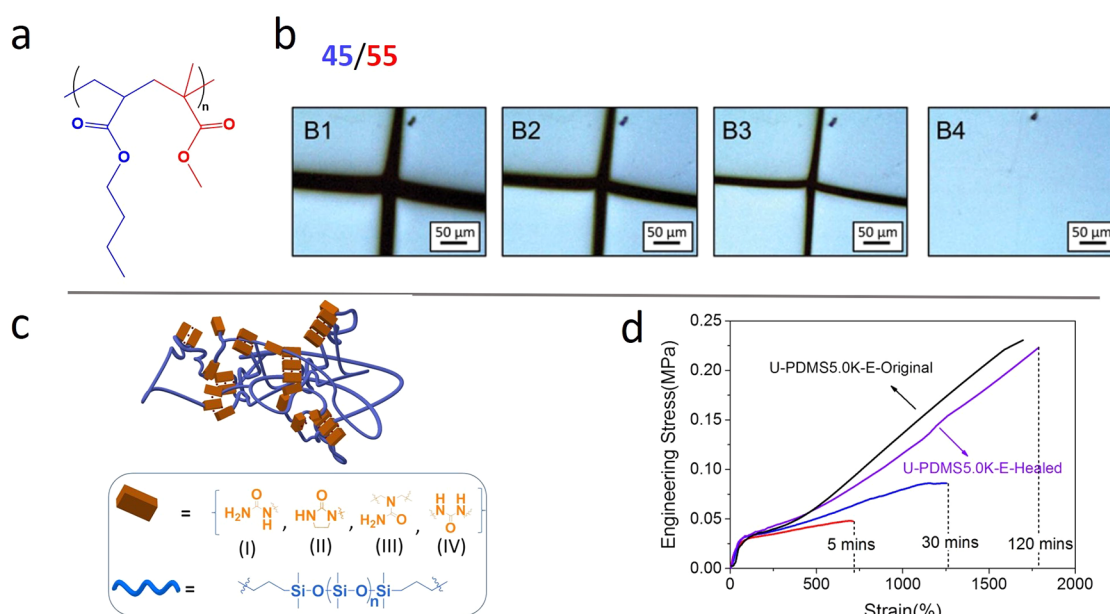


Figure 9. (a) Chemical structure of the PMMA-*r*-PnBA copolymers. Reproduced with permission from ref 8. Copyright 2018 American Association for the Advancement of Science. (b) Healing kinetics observed by optical microscope of the PMMA-*r*-PnBA, MMA/nBA is 45/55. Adapted with permission from ref 8. Copyright 2018 American Association for the Advancement of Science. (c) Schematic illustration of the structures of the urea rich PDMS elastomer. Adapted with permission from ref 36. Copyright 2018 Wiley-VCH. (d) Stress–strain curves of the healed samples at different healing time of U-PDMS-5.0K-E. Adapted with permission from ref 36. Copyright 2018 Wiley-VCH.

(EA).⁹² When it is exposed to a razor blade cut (width: 40 μm), the healing process could be triggered by 254 nm UV light with an energy flux of 11.66 J cm^{-2} to activate the photo cleavage process. Then visible light could trigger the cross-linking reaction that almost fully heals the crack without heating. Photoinduced metathesis reactions are also utilized for light-triggered self-healing polymers. Utilizing Zn^{2+} as an ion source and 2,6-bis(19-methylbenzimidazolyl)pyridine as ligand, self-healable supramolecular polymers under light were created.⁹³ After being exposed to UV radiation with a wavelength of 320–390 nm and an intensity of 950 mW cm^{-2} , the damaged $3[\text{Zn}(\text{NTf}_2)_2]_{0.7}$ sample recovered completely after 30 s. The UV light can also induce disulfide metathesis to allow dynamic rearrangement of polymers, which can be used in intrinsically self-healing polymers.⁹⁴ Another example, a cross-linked poly(*n*-butyl acrylate) with trithiocarbonate as chemical cross-linker was reported, in which the UV light triggered the breakage of trithiocarbonate bonds for self-healing process.⁹⁵ One drawback of such a process is normally requiring the inert atmosphere because the intermediate of carbon radical is reactive with oxygen or other gases. The light triggered self-healing process has the advantages of easily achieving remote activation, spatially controlled activation, and on-demand control by turning off or on the light triggers.⁹⁶

3. REPRESENTATIVE INTRINSIC SELF-HEALING POLYMERS

3.1. Self-Healing Materials with Noncovalent Dynamic Bonds

Noncovalent bonds based on physical interactions are important pathways to achieve intrinsic self-healing. Metal–ligand coordination, ionic interaction, and hydrogen bonding (H-bonding) are the most common physical interactions used in intrinsically self-healing polymers. Metal–ligand coordination bond describes the interaction between a metallic core

with one or multiple π -donor ligand(s). The presence of an equilibrium state between the association and dissociation processes could be tuned to favor one process by changing the environment such as temperature and other stimuli and enables the utilization of metal–ligand coordination bonds for self-healing materials. For example, the ionic-based metal–ligand coordination was incorporated into elastic polymers as self-healing chemistry, in which a telechelic low molecular weight PDMS ($M_n = 5000\text{--}7000$ g/mol) functionalized with 2,6-pyridinedicarboxamide (H_2pdca) ligand was physically cross-linked with the Fe(III) (Figure 8a).³⁵ The H_2pdca ligands coordinate with Fe(III) through two different interactions: a strong pyridyl–iron, and two weaker carboxamido–iron with the nitrogen and oxygen atoms of the carboxamide groups. The $[\text{Fe}(\text{Hpdc})_2]^+$ can readily dissociate to $[\text{Fe}(\text{Hpdc})]^{2+}$, where the iron centers remain attached to the ligands through the stronger interaction with the pyridyl ring. The Fe(III) coordination can break and reform, allowing reversible unfolding and refolding of the chains. The reversible iron-coordination in a very soft PDMS matrix allows the polymer to possess a very high stretchability (10000% with lower amount of Fe-Hpdc, H_2pdca : PDMS = 1:6) and self-healing capability (complete recovery of original extensibility and tensile stress after 48 h) (Figure 8b).

Ionic (or electrostatic) interactions are physical bonds where two oppositely charged ionic species electrostatically attract each other, and the reversible nature of such ionic bond formation could also promote self-healing with high healing efficiency. For example, utilizing the ionic interactions between $-\text{COO}^-$ and $-\text{NH}^+$ groups as well as hydrogen bonding, the branched poly(ethylenimine) (bPEI)/poly(acrylic acid) (PAA)/poly(ethylene oxide) (named as bPEI/PAA/PEO) complex reached a tensile strength of 27.5 MPa and an extensibility of 770% and exhibited room temperature self-healability. After healing at 90% relative humidity (RH) for 48 h, the recovered maximum stress and elongation-at-break of

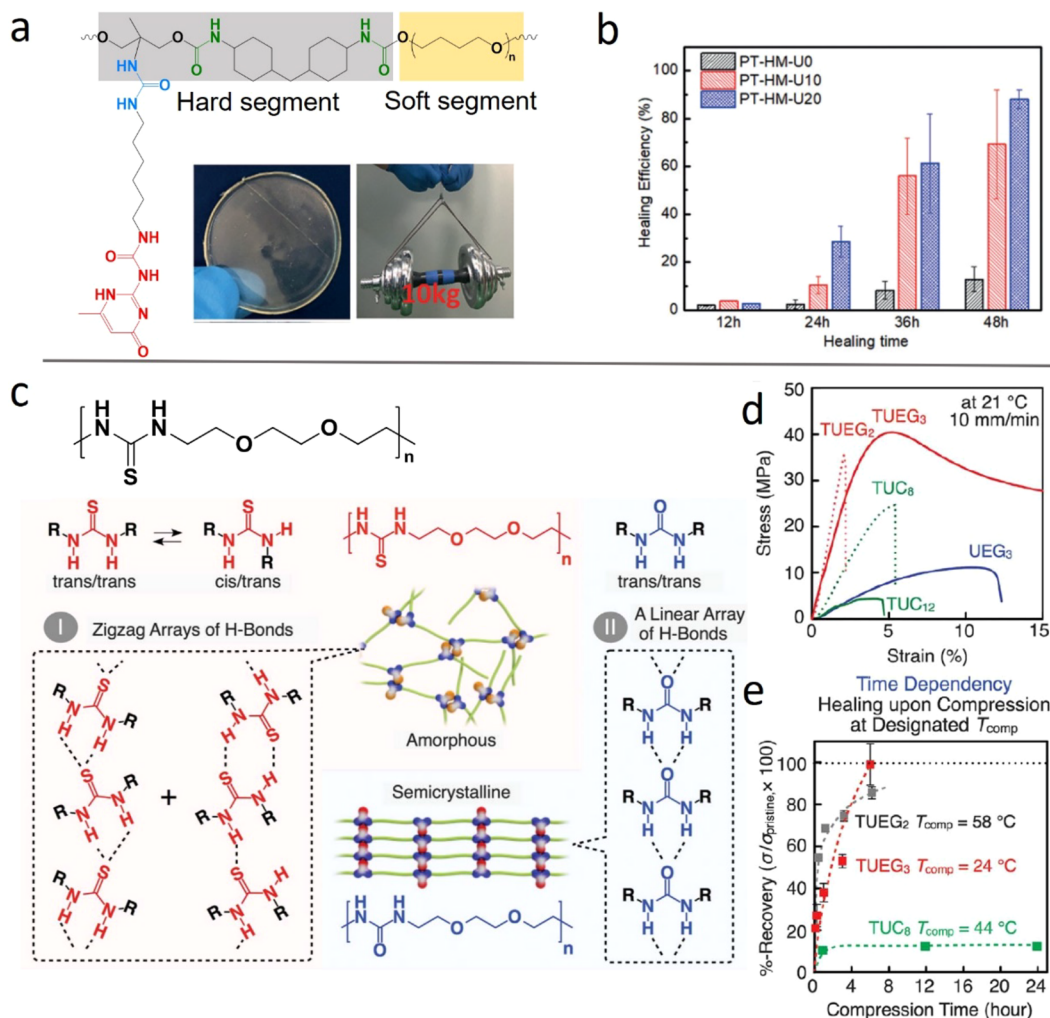


Figure 10. (a) Chemical structure and photo of the dynamic polyurethane sample. Reproduced with permission from ref 102. Copyright 2018 Wiley-VCH. (b) Healing efficiency at different healing time of the damaged PT-HM-U films. Adapted with permission from ref 102. Copyright 2018 Wiley-VCH. (c) Chemical structure and illustration of the assembly of poly(ether-thiourea) TUEG₃. Reproduced with permission from ref 100. Copyright 2017 The American Association for the Advancement of Science. (d) Tensile properties of poly(ether-thiourea) TUEG₃ and its reference polymers. Adapted with permission from ref 100. Copyright 2017 American Association for the Advancement of Science. (e) Percentage of mechanical properties recovery of TUEG₃ and other polymers at different healing temperatures and time lengths. Adapted with permission from ref 100. Copyright 2017 American Association for the Advancement of Science.

the polymer reached 25.7 MPa and 750%, respectively (Figure 8c,d).⁹⁷

Self-healing even by van der Waals interactions was recently demonstrated.⁹⁸ The random copolymers of poly(methyl methacrylate)-*r*-poly(*n*-butyl acrylate) (PMMA-*r*-PnBA) achieved self-healing behavior in a narrow window of the copolymer composition from MMA/*n*BA = 45/55 to 50/50. PMMA-*r*-PnBA with MMA/*n*BA = 45/55 to 50/50 exhibited the tensile strength up to 10 MPa and 650% elongation at break, and 90–100% recovery of the tensile property after 14 h of healing at room temperature (Figure 9a,b).⁸

Hydrogen bonding (H-bond) is one of the most studied pathways for design of intrinsically self-healing polymers. Dominated by the electrostatic force, hydrogen (H) atom could be attracted by a nearby atom or group with higher electronegativity, such as atoms of nitrogen (N), oxygen (O), or fluorine (F). An H-bond will form between these two atoms or groups once the pairing between the donor and acceptor occurs. The strength of H-bond (for example, N–H···O ~ 8 kJ/mol) is much lower than that of covalent bond. Lower bond

strength results in faster bond breakage and formation, and this character of H-bond could help create a polymer system with fast molecular rearrangements.³⁴ Such fast molecular rearrangements of H-bonds were utilized to design a series of self-healing elastomers with capabilities for extreme stretchability, excellent energy damping, and intrinsic self-healing (Figure 9c,d).³⁶ Synthesized by urea functionalization of PDMS, the polymeric elastomer showed high elongation-at-break (from 984% to 5,600%). Adjusting the length of the PDMS chain enabled elastomers with desired mechanical strength, elasticity, and extensibility. The mechanical strength and gas-separation performance of the designed network were completely recovered within 2 h at ambient temperature, or 20 min at 40 °C after being cut by a razor blade.

While most of the reported intrinsic self-healable polymers have soft rubbery polymer components,^{6,34–36} there are several reports on more mechanically robust self-healing polymers.^{99,100} Such example includes the incorporation of 2-ureido-4[1H]-pyrimidinone (UPy) groups onto poly-(norbornene) to form ABA-triblock copolymer ($M_n =$

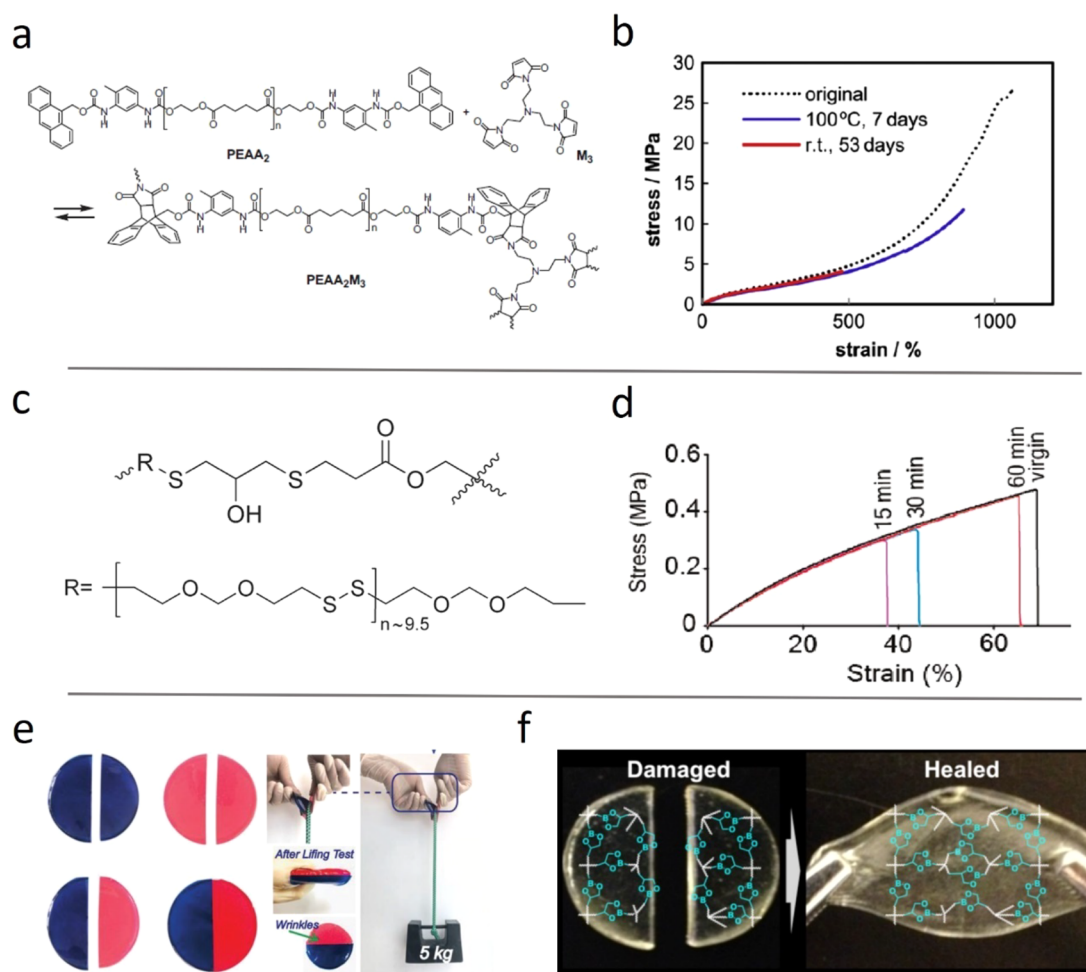


Figure 11. (a) Schematic illustration of the chemical structures of PEEA₂M₃. Adapted with permission from ref 105. Copyright 2011 Elsevier Ltd. (b) Strain–stress curves including the healed sample of PEEA₂M₃. Adapted with permission from ref 105. Copyright 2011 Elsevier Ltd. (c) Chemical structure of the thiol cross-linked epoxy resin. Reproduced with permission from ref 110. Copyright 2011 American Chemical Society. (d) Stress–strain curves of the healed samples at different healing time of the thiol cross-linked epoxy resin. Adapted with permission from ref 110. Copyright 2011 American Chemical Society. (e) Photo illustration of dynamic disulfide bond containing polyurethane during the healing test. Adapted with permission from ref 115. Copyright 2018 Wiley-VCH. (f) Chemical structure and photo demonstration of the dynamic-covalent boronic esters. Adapted with permission from ref 124. Copyright 2015 American Chemical Society.

100000–150000 g/mol) that consists of A block of UPy-functionalized norbornene and B block of a long random copolymer consisting of UPy-functionalized norbornene and flexible dodecanyl norbornene.¹⁰¹ The UPy-rich A blocks form hard domains driven by very strong hydrogen bonding that prevents macroscopic deformation, and the B blocks form a more flexible segment with sparse UPy interaction serving as sacrificial bonds. Their ABA-triblock copolymer exhibited high toughness of 62 MJ m⁻³, tensile stress of 17 MPa with a dissipated energy >27 MJ m⁻³ at room temperature. The scratch on the ABA-triblock copolymer film was healed after 3 h at 50 °C. Furthermore, the utilization of urethane, urea, and UPy groups allowed preparation of hydrogen bonding facilitated tough self-healing polymers with a highest toughness of 345 MJ m⁻³ and a high tensile strength of 44 MPa.¹⁰² A polyurethane-like prepolymer was prepared by the reaction between poly(tetramethylene ether glycol) (PTMEG) as soft segment and dicyclohexylmethane-4,4'-diisocyanate (HMDI) as the hard segment, and the polymers were obtained after the introduction of 1,4-butanediol and UPy modified diol (U₂-diol). The high UPy loading sample PT-HM-U20 exhibited the highest healing efficiency of 90% after 48 h of

healing at 80 °C or 24 h at 100 °C (Figure 10a,b). Combining covalent cross-links and reversible hydrogen-bonding networks also produced tough self-healing elastomers.⁹⁹ The elastomer exhibited high fracture energy of 13.5 kJ/m² and high tensile strength of 10–20 MPa. After 12 h of healing at room temperature, the elastomer exhibited a tensile strength close to 4 MPa, which is 30% of its original value. Furthermore, low molecular weight polymers with dense thiourea groups exhibited mechanical robustness with good reparability.¹⁰⁰ The tensile strength was as high as 40 MPa and their Young's modulus was 1.0–1.9 GPa (Figure 10c-e). While these polymers did not exhibit autonomous self-healing, the compression allows repairing of the fractured surfaces. The thiourea polymers exhibited mostly recovered tensile strength and Young's modulus after 1 h compression at temperature slightly above room temperature. The formation of zigzag hydrogen-bonded array by the presence of thiourea group in each repeat unit activates the exchange of hydrogen-bonded pairs and enables the healing by compression on the fracture.

3.2. Self-Healing Materials with Covalent Dynamic Bonds

Dynamic covalent bonds, including Diels–Alder (DA) reaction, reversible disulfide bond, boronic esters, and many others are widely explored and utilized for developing self-healing materials. Diels–Alder reaction is a type of thermally reversible covalent bond with dissociative mechanism in which a conjugated diene reacts with a dienophile. Hence upon application of physical damage, heat could be introduced to trigger the reverse Diels–Alder reaction to regenerate dienes and dienophiles, and these reactants could further react to reform chemical bonds to heal the damage. For example, thermally remendable epoxy resin having furan–maleimide adducts was reported.¹⁰³ The cured epoxy exhibited tensile strength of 53 MPa and self-healing of cracks at 100–125 °C for 20 min, followed by 80 °C for 0–72 h treatment. While healing efficiency was limited, Diels–Alder reaction was used to provide the remendability of cross-linked rigid epoxy network. Polyurethane-urea based Diels–Alder adduct was synthesized from carbon dioxide and furfuryl amine.¹⁰⁴ Furfuryl amine was converted to diglycidyl furfurylamine, followed by the conversion to difunctional cyclic carbonate by reacting with CO₂. The dicyclic carbonates were reacted with diamine to form nonisocyanate polyurethane-urea, and then furan in the structure was reacted with 4,4-bismaleimidodiphenylmethane to produce the polyurethane-urea Diels–Alder adducts. It exhibited 15–18 MPa tensile strength and almost full recovery of the mechanical properties after healing at 120 °C for 10 min, followed by healing at 60 °C for 24 h. The Diels–Alder cycloaddition between anthryl-telechelic poly(ethylene adipate) (PEAA₂) and tris-maleimide (M₃) enabled self-healing property of the PEAFA₂M₃ polymer, which was able to restore 55% of the original tensile strength and 90% of the elongation-at-break after a 7-day healing process at 100 °C (Figure 11a,b).¹⁰⁵ The use of cyanodithioester (CDTE) compound and cyclopentadiene as DA reagents demonstrated that the healing condition of DA reaction could be less critical.¹⁰⁶ The polymer reached a maximum tensile stress of 1 MPa with 40% elongation-at-break, upon 10 min of heating at 120 °C under pressure of 1kN, the sample fully recovered its tensile properties.

Reversible disulfide bonds are also utilized for the design of self-healing materials due to the exchange reaction of S–S linkages, in which the bond exchange could occur and self-healing could be achieved when heated at elevated temperature.^{107–109} Autonomous healing after a cut of a covalently cross-linked rubber with disulfide takes place at 60 °C and leads to full recovery of mechanical properties over 60 min (Figure 11c,d).¹¹⁰ Furthermore, a cross-linked polymer utilizing thiuram disulfide (TDS) as the main component achieved high-efficiency self-healing. The reshuffling reaction of TDS can be accelerated by the visible light. The healing process occurred at room temperature under visible light, and 88% of the original toughness was recovered after 24 h of healing.¹¹¹ As a very stable sulfur radical, bis(hindered amino)disulfide-based thermally healable cross-linked polymer network was developed in refs 112 and 113. Its incorporation into a polymer backbone such as polyurethane or polymethacrylate enables self-healing with over 85% efficiency at elevated temperature ~120 °C for 24 h. Cross-linked polyurea elastomers based on aromatic disulfide metathesis exhibited room-temperature self-healing,¹¹⁴ where the original material exhibited a tensile strength of 0.81 MPa and an elongation at break of 3100%. The mechanical properties were restored by

80% after 2 h healing at room temperature, while longer healing did not improve healing efficiency.

When dynamic disulfide bonds are embedded in the hard phase of polyurethane elastomers,¹¹⁵ the self-healing elastomer exhibits a maximum tensile stress of 25 MPa and a fracture strain of over 1600%. Over 85% self-healing efficiency was achieved at 6–24 h healing at 70 °C (Figure 11e). A series of thermoplastic polyurethane containing aromatic disulfide was also investigated.¹¹⁶ The poly(tetramethylene ether glycol) was used as a soft segment and bis(4-hydroxyphenyl) disulfide (SS) was used as the aromatic disulfide component embedded in the hard segments. Four diisocyanates were incorporated, including isophorone diisocyanate (IP), 4,4'-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(phenyl isocyanate), and hexamethylene diisocyanate. IP-SS thermoplastic polyurethane exhibited the highest mechanical properties among them, exhibiting tensile strength and toughness of 6.8 MPa and 26.9 MJ m⁻³, respectively. Furthermore, IP-SS polyurethane also provided the best self-healing efficiency. The healing of IP-SS for 2 h at room temperature resulted in 88.2%, 99.6%, and 76.6% recovery of the tensile strength, elongation at break, and toughness values of the virgin IP-SS, respectively. More recently, self-healing polymers combining the disulfide bonds with other interactions, such as hydrogen bonding, have been developed.^{107–109,117} Compared with previous self-healing polymers with only disulfide bonds, the polymers from the hybrid approach exhibited multiple advantages. The synergistic effect of the disulfide bond and hydrogen bond enabled a mechanically strong copolymer (tensile strength = 20 MPa, strain = 1800%), yet self-healable at ambient temperature, with 92.76% stress recovery and full strain recovery after 48 h of healing at room temperature.¹⁰⁸ The incorporation of disulfide linkage in polyurethane elastomer also facilitated healable polymers with high stretchability, reaching a strain of 14000%,¹⁰⁷ that is highly suitable for applications such as ionic skins or conducting devices.¹⁰⁹

While various self-healing polyurethane and polyurea systems with disulfide bonds are reported, another mechanism to construct self-healable dynamic polymers is the incorporation of dynamic urea into the polymer. Hindered urea bonds can be utilized as dynamic bonds due to their dynamic exchange mechanism of reversible formation of linkages and isocyanate/hindered amine.⁸⁰ Diethylurea-based polyurethane exhibited a tensile strength of 0.6 MPa with 243% elongation at break and provided the best healing efficiency among them. The 12 h of self-healing at 37 °C of the polymer recovered 87% of strain, while healing at room temperature for 12 h was limited to 29% strain recovery.¹¹⁸ Dynamic urea without hindered amine was also utilized as a dynamic bond with the presence of Zn based catalyst.¹¹⁹ The urea-linked PDMS–Zn(OAc)₂ materials exhibited a tensile strength of 7.0 MPa and elongation-at-break over 600%, and the tensile stress and elongation at break can recover to about 90% after healing at 110 °C for 16 h.

The formation of boroxines from the dehydration of boronic acids is reversible upon hydrolysis (Figure 3c), which provides reversibility and enables a dynamic mechanism for self-healing applications.¹²⁰ Boronic acid was incorporated into PDMS by end group functionalization, and subsequent dehydration fabricated a stiff but self-healable PDMS-boroxine network. The network exhibits tensile strength of 9.46 MPa, and its mechanical properties were completely recovered when healed at 70 °C for 12 h.¹²¹ It is also reported that combining

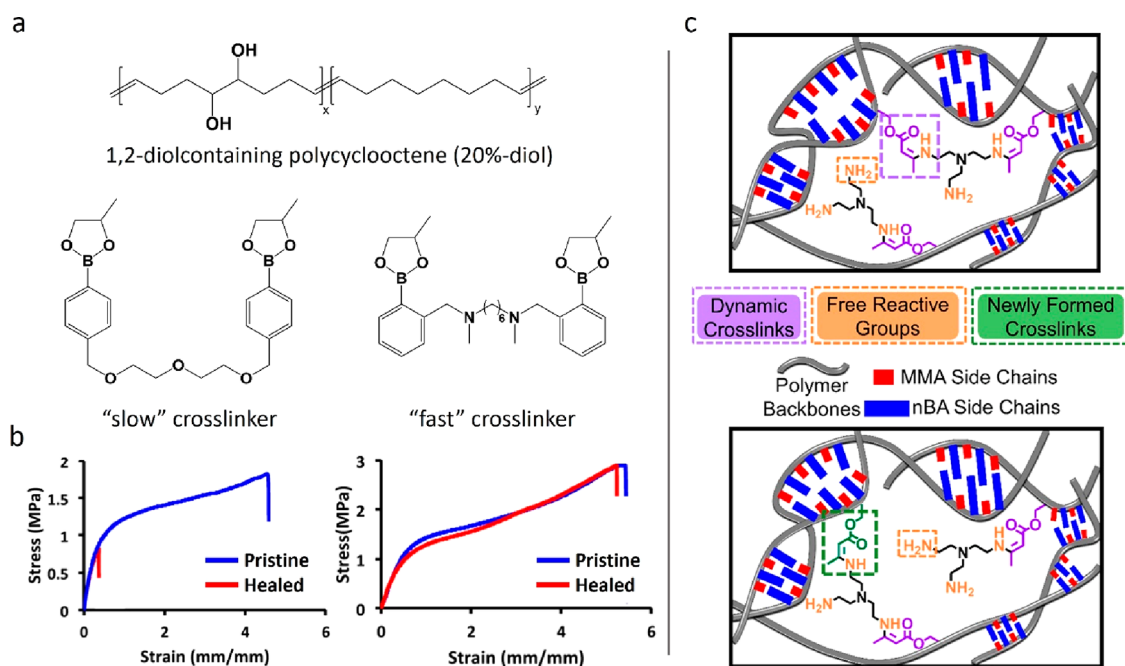


Figure 12. (a) Chemical structure of the cross-linker and 1,2-diol-containing polycyclooctene. Reproduced with permission from ref 126. Copyright 2015 American Chemical Society. (b) Tensile data of pristine and healed polymers prepared by different cross-linkers. Reproduced with permission from ref 126. Copyright 2015 American Chemical Society. (c) Schematic illustration of p(AAEMA/MMA/nBA) covalently adaptive networks containing dynamic cross-links with MMA and nBA repeating units facilitated transamination exchange reactions. Reproduced with permission from ref 131. Copyright 2022 American Chemical Society.

boroxine with hydrogen bonding groups formed iminoboroxane/boroxine-based polyurethane network¹²² with tensile strength of 11 MPa and elongation-at-break of 3%. The polymer could fully recover its mechanical properties after healing for 12 h at 70 °C, or healing at room temperature with 70% RH for 12 h. In another study, the elongation of boroxine system was tuned by the incorporation of PDMS and dynamic imine bond.¹²³ The combination of boroxine and imine bonds with flexible PDMS backbone achieved elongation at break of 4200% and tensile strength of 0.25 MPa, as well as self-healing at room temperature in 20 min. Similarly, self-healing polymers based on dynamic-covalent boronic esters exhibited facile reversibility of the networks and allowed intrinsic self-healing under ambient conditions.¹²⁴ Highly efficient self-healing of these bulk materials was confirmed, where over 80% of original toughness was recovered after 3 days of healing at 85% RH (Figure 11f). High healing efficiency was reported in nitrogen-coordinated boroxines cross-linked 3D polymer networks containing poly(propylene glycol) (PPG) and poly(acrylic acid) (PAA), and the *N*-boroxine-PPG/PAA polymer samples with different PAA loading from 6% to 40%. *N*-Boroxine-PPG/PAA_{10%} showed a healing efficiency close to 100% after 6 h at room temperature. The tensile strength of these materials can be tuned in the range from 1.7 to 12.7 MPa with elongation-at-break from 659% to 182%.¹²⁵

1,2-Diol containing poly(cyclooctene) (20%-diol) cross-linked with telechelic diboronic ester cross-linkers demonstrated efficient self-healing properties (Figure 12a).¹²⁶ Two kinetic variant diboronic esters were used as dynamic cross-linkers for self-healing, where the boronic ester design controls the rate of boronic ester transesterification. The cross-linker provided distinctively different self-healing. The faster exchanging linker showed nearly complete recovery of the mechanical property in 16 h healing at 50 °C, while the slower

exchanging linker exhibited minimal healing in the same condition (Figure 12b).

Boronic ester-containing dithiol was also utilized as a cross-linker in styrene-butadiene rubber (SBR)¹²⁷ or epoxidized natural rubber (ENR).¹²⁸ The mechanical property of the cross-linked SBR was ~90% restored after 24 h healing at 80 °C, while the healing at room temperature reached ~60% recovery. In the ENR with the boronic-ester dithiol cross-linker, the amount of cross-linker (1–10 wt %) significantly impacted the mechanical properties. Upon increase of the cross-linker from 1 wt % to 10 wt %, the tensile strength increased from 1.6 to 14.6 MPa, and the elongation at break decreased from 811 to 475%. The self-healing properties were optimum at 3–5 wt % boronic ester cross-linking that achieved nearly complete recovery of the mechanical properties upon healing at 80 °C for 24 h.

Vinylogous urethane is another associative dynamic bond, which is commonly incorporated into polymeric systems. There are several reports of intrinsic self-healing polymers with vinylogous urethane bonds.^{129–131} Among them, poly((2-acetoacetoxy)ethyl methacrylate/methyl methacrylate/*n*-butyl acrylate) P(AAEMA/MMA/nBA) copolymer networks show significant advancement (Figure 12c).¹³¹ These networks are processable by compression molding at 120 °C and exhibit room temperature self-healing. P(AAEMA/MMA/nBA) copolymer exhibits the tensile strength of 25.7 MPa with the elongation-at-break of ~215%. Upon self-healing at 22 °C, RH ~ 34% after 24 h, the mechanical properties were recovered to 83% (tensile strength) and 91% (strain), respectively.

3.3. Combining Different Dynamic Bonds and Employing Sacrificial Bonds

An emerging strategy for design of intrinsically self-healing polymers during the past decade is a combination of different types of dynamic bonds in a single system. Different

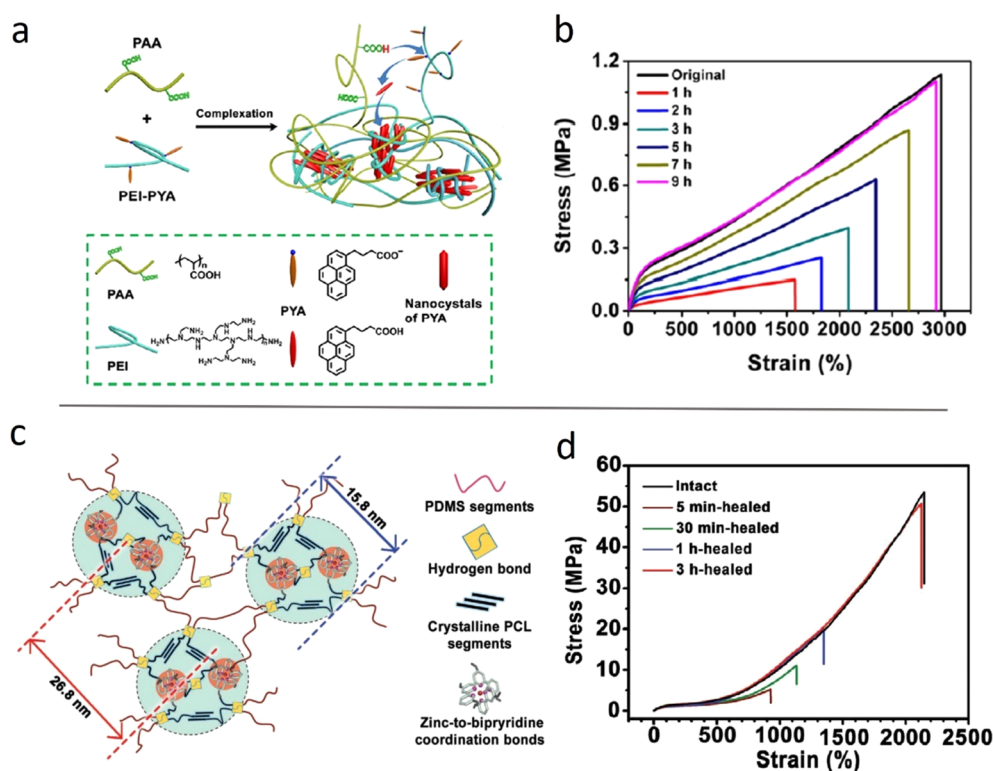


Figure 13. (a) Schematic illustration of the structures of PAA/PEI–PYA complexes. Adapted with permission from ref 138. Copyright 2019 American Chemical Society. (b) Strain–stress curves of the original and healed samples of PAA/PEI–PYA complexes at different healing time. Adapted with permission from ref 138. Copyright 2019 American Chemical Society. (c) Illustration of the structures of the PU-BPY_{0.5}-Zn elastomer. Adapted with permission from ref 133. Copyright 2020 Wiley-VCH. (d) Stress–strain curves of the intact and healed samples at different healing time of the PU-BPY_{0.5}-Zn elastomer. Adapted with permission from ref 133. Copyright 2020 Wiley-VCH.

characteristics of dynamic bonds could be utilized synergistically through rational molecular design. Since the past decade, multiple studies adopted the strategy based on the combination of H-bonds with coordination bonds,^{35,38,132–134} H-bonds with electrostatic (or ionic) interactions,^{97,135–140} boronic esters with coordination bonds,¹²⁸ etc. For example, a room temperature self-healable hydrogel was fabricated by combination of ionic and hydrogen bonding (Figure 13a,b).¹³⁸ Poly(acrylic acid) (PAA) and prefabricated complex PEI–PYA derived from mixing of branched poly(ethylenimine) (PEI) and 1-pyrenybutyric acid (PYA) were further mixed to generate PAA/PEI–PYA complexes, and the ionic and hydrogen bonding by the PYA moiety provided significantly enhanced mechanical properties of the PAA/PEI–PYA complexes, compared with the control sample PAA/PEI (tensile toughness 18.17 vs 3.77 MJ/m³). Meanwhile, the self-healing property was not compromised despite significant increase in the mechanical strength. The sample PAA/PEI–PYA_{2.1%} exhibited complete recovery of its mechanical properties after healing for 9 h at room temperature (Figure 13b). In addition, the noncovalent nature of these interactions enabled great recyclability of PAA/PEI–PYAs, where the hydrogel was ground and then healed to 87% of the original toughness. Utilizing similar electrostatic and hydrogen bonding interactions. A tough, self-healable hydrogel was synthesized by utilizing PAA and poly(ethylene glycol) (PEG) methacrylate as the main building block and PEI as the electrostatic interaction provider.¹⁴¹ The hydrogel reached the highest toughness value of 32.6 MJ/m³ with 57.8 wt % water content, while maintaining good tensile recovery and shape

memory properties. Hydrogen bonds were also combined with coordination bonds to obtain a series of tough self-healable polyurethane elastomers.¹³³ Those elastomers exhibited exceptional tensile strength of 52.4 MPa and a toughness of 363.8 MJ m⁻³; the PU-BPY_{0.5}-Zn elastomer recovered nearly all of the original mechanical properties after being healed at 100 °C for 3 h (Figure 13c,d).

The combination of boronic ester cross-links with sacrificial weak Zn²⁺-O coordination interactions in a polymer network achieved significant improvement in mechanical properties without any loss in self-healing ability.¹²⁸ The highly healable sample reached an elongation-at-break of 650% and tensile strength of 9 MPa, along with nearly fully recovered mechanical properties within 24 h at 80 °C.

A few other notable strategies include the combination of multiple linkages in the intrinsically self-healing polymers, where permanent cross-links are combined with dynamic covalent and noncovalent bonds. Utilizing secondary amide side chains, dynamic energy dissipative hydrogen bonds were incorporated as sacrificial bonds into a self-healable network (Figure 14a),¹⁴² and a significant improvement in the overall mechanical properties was achieved. Compared with the hydrogen-bond-blocked control network (BACON), the amide-containing network (ACON) with sacrificial bonds exhibited significantly increased mechanical properties in all aspects, e.g., the toughness increased from 1.51 MJ/m³ to 11.13 MJ/m³, and the elongation-at-break increased from 167% to 938%. The ACON recovered nearly 30% of toughness after 1 h healing and 90% of toughness after 3 h of healing at 50 °C (Figure 14b,c). A conductive 3D network hydrogel with

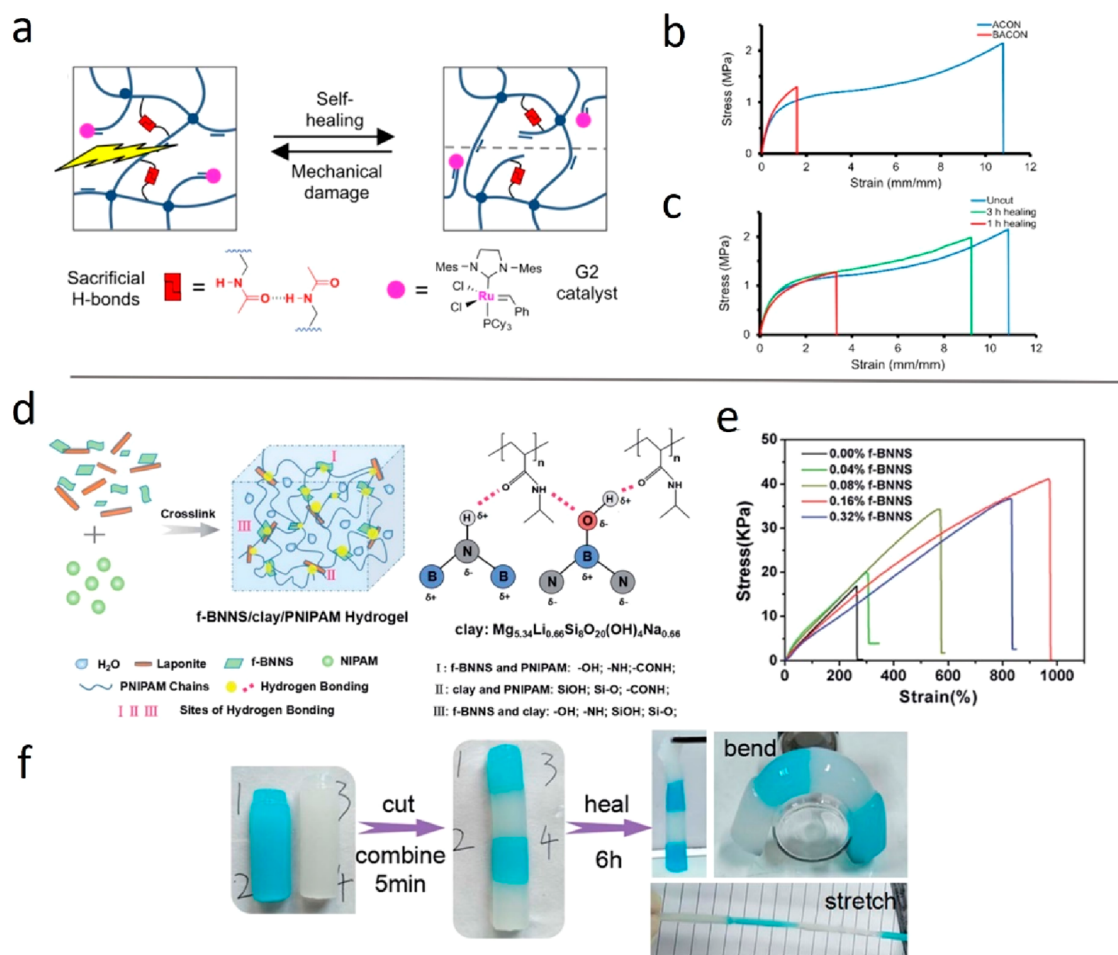


Figure 14. (a) Schematic illustration of the structures of ACON. Adapted with permission from ref 142. Copyright 2015 American Chemical Society. (b) Stress–strain curves of ACON and control BACON. Adapted with permission from ref 142. Copyright 2015 American Chemical Society. (c) Stress–strain curves of ACON at different healing time. Adapted with permission from ref 142. Copyright 2015 American Chemical Society. (d) Schematic illustration of the structures of f-BNNS/clay/PNIPAM. Adapted with permission from ref 143. Copyright 2018 Royal Society of Chemistry. (e) Stress–strain curves of the composite hydrogels with increasing f-BNNS content. Adapted with permission from ref 143. Copyright 2018 Royal Society of Chemistry. (f) Demonstration of the self-healing property of f-BNNS/clay/PNIPAM. Adapted with permission from ref 143. Copyright 2018 Royal Society of Chemistry.

sacrificial H-bonding groups was also reported. In this functionalized 2D boron nitride nanosheets/clay/poly(*N*-isopropylacrylamide) composite, the incorporation of H-bonding between the polymer and clay significantly enhanced its mechanical properties (Figure 14e) while maintaining good self-healing capability (Figure 14f).¹⁴³

The concept of sacrificial bonds could also be utilized in systems with a single type of dynamic bonds by employing bonds with different strength.¹⁴⁴ In this work, the supramolecular network consisted of strong and weak H-bonds, where the weak H-bonds act as sacrificial bonds that could absorb more energy during deformation and extend the elongation. The sample PDMS–MPU_{0.4}–IU_{0.6} (MPU stands for 4,4'-methylenebis(phenyl urea), IU stands for isophorone bisurea, and 0.4/0.6 represents their molar ratio) exhibited the highest tensile strength (1.5 MPa) with an elongation-at-break of 1670% and recovered 78% of its original toughness after 48 h of room temperature healing. High stretchability and toughness of PDMS–MPU_{0.4}–IU_{0.6} was utilized to prepare a capacitive strain-sensing e-skin, which shows high toughness and mechanical robustness against physical damage.

4. QUANTIFYING SELF-HEALING PERFORMANCE

4.1. Characterizing Kinetics of the Self-Healing Process, Healing Efficiency

Traditionally, the healing rate (i.e., some characteristic time) and the degree of a property recovery are the two major characteristics of the self-healing process. Both parameters depend strongly on the temperature used for self-healing and to a smaller degree on the pressure applied to the healing region. To quantitatively track the kinetics of self-healing process, multiple definitions of healing efficiency have been proposed by researchers.¹⁹ The most accepted definition of the healing efficiency (η) is the ratio of recovery in material properties:^{102,145,146}

$$\eta = \frac{f_{\text{Healed}}}{f_{\text{Pristine}}} \quad (2)$$

where f is the physical property of interest (e.g., modulus, toughness).

Majority of the studies in intrinsically self-healing polymers analyze a recovery of mechanical properties. However, because mechanical properties include different parameters such as

Young's modulus, elongation-at-break, toughness, tensile strength etc., the choice of f varies among different papers, strongly limiting comprehensive comparisons among the data from different groups. For example, Burattini and co-workers selected 3 different properties as f , tensile modulus, elongation-at-break, and tensile toughness, and then the corresponding healing efficiency resulted in 95%, 91%, and 77%, respectively.³⁷ Thus, it is of great importance to clarify which particular property is being evaluated during the experiment. Another important parameter is the temperature at which the self-healing process is performed, and in literature it varies from room temperatures to temperatures well above 100 °C. As we discussed in section 2, the waiting time between the physical damage and the beginning of self-healing process also plays a role in self-healing rate, but it is not reported in majority of papers. All of these parameters complicate a direct comparison of self-healing properties of different materials, especially the data obtained in different groups.

4.2. Experimental Methods to Study Self-Healing

Tensile properties are commonly reported in the study of self-healing polymers. ASTM standards such as ASTM D638 and ASTM D1708 methods are typically utilized to examine the tensile properties of polymers before and after self-healing, where the specimens are stretched in a single axial until break. It is worth noting that those ASTM standards have different testing rates available, and the rate of 1 mm/s is the most often used. Different tensile behaviors can be expected at different elongation rates. The tensile properties of pristine self-healable polymers are generally tested first, and then the healed samples are tested under the same testing conditions after several healing times. By comparing the tensile properties of the pristine and healed samples such as Young's modulus, tensile strength, elongation-at-break, and tensile toughness, the healing efficiency of a healable polymer is determined. The most common practice is (1) Analysis of the tensile properties of self-healing materials at different healing times and a kinetic diagram can be expected.^{117,135,138} (2) The tensile studies at different healing conditions (e.g., temperature or pressure) are conducted.^{100,147}

Bending and compression loading have also been used to analyze the healing efficiency of self-healing carbon fiber/epoxy composites.¹⁴⁸ Using eq 2, they introduce stiffness recovery ratio where the flexural stiffness defined as the property of 3-point bending was employed to evaluate self-healing behavior of modified Bisphenol A diglycidyl ether epoxy resin.¹⁴⁹ The healing efficiency was determined by analysis of fracture toughness.⁷ Also, the tapered double cantilever beam geometry can be used for healing performance evaluation through analysis of the fracture toughness.¹⁵⁰ Several other examples of mechanical analysis of self-healing process have also been described in the recent review.⁷

One of the most interesting studies on the evaluation of self-healing kinetics is application of nonlinear rheology, where initial strong strain breaks the sample, and then recovery of the shear modulus can be monitored in situ as a function of time (Figure 15).⁴⁵ This approach provides detailed quantitative analysis of mechanical strength recovery with time and can be used in a broad temperature range accessible for rheology. The authors chose 90% recovery of the shear modulus as the characteristic time of self-healing. The estimated self-healing time in this way appears to be close to the terminal relaxation time defined by the bond rearrangements time in this system

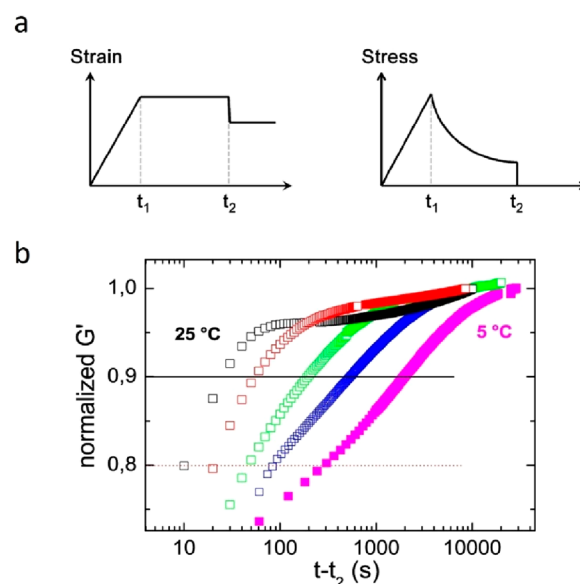


Figure 15. (a) Schematic representation of the time dependence of strain and stress during the self-healing experiment. Adapted with permission from ref 45. Copyright 2016 Springer Nature. (b) Resulting normalized storage modulus during recovery for sample of telechelic polyisobutylene with barbituric acid functionalized chain ends at different temperatures (25 °C, 20 °C, 15 °C, 10 °C, 5 °C) as a function of time $t - t_2$.⁴⁵ Adapted with permission from ref 45. Copyright 2016 Springer Nature.

(Figure 7).⁴⁵ These studies revealed that there is an initial recovery of the shear modulus up to $\sim 95\%$ level and then much slower recovery process at longer times (Figure 15). One potential problem of this approach is the degree to which the sample is really broken in the initial strain. Nevertheless, this approach provides in situ measure of self-healing process kinetics.

Optical microscopy is utilized to obtain visual information on their self-healing behavior, where visually tracing the healing process is a direct, but qualitative approach.⁸ The relationships between the area of damage and healing time or healing temperature are commonly studied, and qualitative analysis could be derived from these results.¹⁵¹ Two good examples from refs 8 and 152 are shown in Figure 16, where the optimum healing sample composition, temperature, or the healing time were determined. Also, electron microscopy and atomic force microscopy imaging were employed to follow the self-healing kinetics.^{153–156} Recently, the diffusion process of polymer chain in self-healing hydrogel network with attached fluorescent molecules was visualized by fluorescence microscopy.¹⁵⁷ Although the images are illustrative, the lack of quantitative data analysis to correlate their physical properties prevents further utilization of this method for self-healing kinetic studies.

The energy-dispersive X-ray (EDX) spectrum imaging in scanning transmission electron microscopy (STEM) has also been utilized to study the kinetics of self-healing process in a quantitative manner.¹⁵⁸ After mending the two metallopolymer films containing different elements, i.e., europium-based and terbium-based, the authors were able to track the interdiffusion of both elements on a time scale comparable to the self-healing time estimated using traditional tensile tests. The width of mixed interphase achieved surprisingly large size of 104 ± 35 nm at the time of full tensile property recovery.¹⁵⁸ The authors

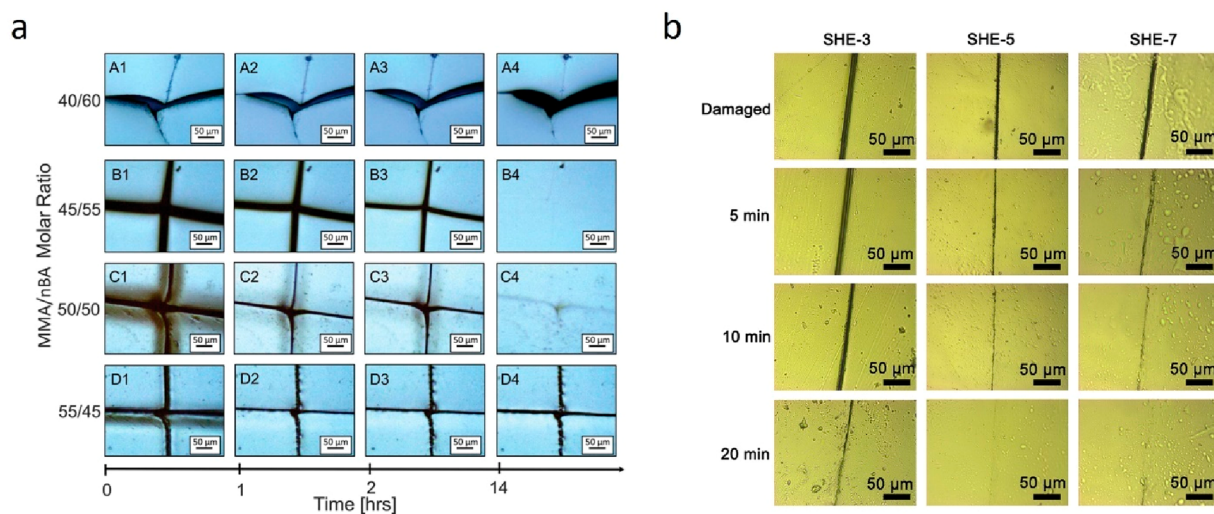


Figure 16. (a) Optical microscope images of self-healing materials from ref 8 Adapted with permission from ref 8. Copyright 2018 American Association for the Advancement of Science. (b) Optical microscope images of self-healing materials from ref 152 Adapted with permission from ref 152. Copyright 2019 Elsevier Ltd.

noted that such large length scale can be in part related to the roughness of the surfaces. In any case, this result indicates that complete self-healing requires rather substantial interdiffusion of chains.

Several other properties and spectroscopy can be employed to monitor self-healing kinetics. For example, electrical conductivity measurements have been used to analyze self-healing properties of electrically conductive polymers.^{7,159,160} Essentially, the change of the sample resistivity during the healing process can be monitored. Several spectroscopies such as infrared (IR), Raman, or nuclear magnetic resonance (NMR) spectroscopy have been also utilized to characterize the intrinsic self-healing of polymers. Once the characteristic peaks of functional groups in a polymer are identified in the IR spectrum, IR could be utilized to continuously monitor the changes in the bonds of interest. For example, a series of strong and tough self-healing elastomers consisting of Diels–Alder cross-links was developed,¹⁵¹ and IR was utilized to monitor the changes of the absorption peaks corresponding to Diels–Alder reaction and confirmed the formation of Diels–Alder cross-links. Similarly, the use of Raman spectroscopy in analysis of various self-healing materials was also presented.¹⁶¹ Most of the Raman studies were focused on the systems with microcapsules and 3D vascular systems to monitor release of chemicals and to follow the chemical reactions (see, e.g., refs 162 and 163). NMR was also employed to reveal the detail of molecular evolution during the self-healing process. For example, NMR was utilized to confirm the reaction between the modified epoxy and bismaleimide in a Diels–Alder reaction facilitated self-healing system.¹⁶⁴ Another example presented tracing the formation of a supramolecular self-healable hydrogel by monitoring the molar ratio between the host and guest moieties using NMR, and thus the optimum component ratio for the host–guest interaction induced self-healable hydrogels was directly determined.¹⁶⁵ NMR was also utilized to confirm the interaction between different moieties that facilitate self-healing process.^{166,167}

4.3. Developing a General Approach to Study Self-Healing

To advance the field of self-healing materials and enable better comparison of data obtained by different groups, a general

approach for analysis of self-healing efficiency and kinetics should be developed. Below, we formulate our suggestion for this general approach with the focus on four major parameters.

4.3.1. Mechanical Properties. Mechanical properties, including tensile strength and extensibility, provide the best way to characterize integrity of the healed materials, and thus they are the most used to evaluate intrinsic self-healability.^{10,34,100,115,145} While tensile modulus, tensile strength, elongation-at-break, and tensile toughness are all important, the toughness value represents better an integrated healing efficiency of a typical polymer sample. Toughness characterizes the total energy required to deform and break a polymer sample, and higher toughness indicates a stronger resistance to mechanical failure of a sample. While only some of the reported studies evaluated self-healing efficiency by toughness, the percentage of recovered toughness upon self-healing reveals the efficacy of overall mechanical property recovery, rather than the stress or strain recovery alone. For example, one study of polyurethane/urea-based self-healable polymer reported self-healing efficiency by toughness,¹⁴⁴ while another study of a similar polymer structure only reported tensile strength and elongation at break upon self-healing.¹⁶⁸ Due to lack of available data on toughness recovery upon self-healing, we could not compare all the references by toughness. Therefore, the researchers should be mindful of reporting toughness when evaluating self-healing efficacy by mechanical properties. While ASTM-type of standard does not exist for self-healing materials analysis, we propose that each paper should report tensile modulus, tensile strength, elongation-at-break, and tensile toughness when intrinsic self-healing polymers are evaluated as a function of time or temperature.

4.3.2. Self-Healing Time. The healing time of self-healing polymers will significantly affect their performance, and in general, a fast healable material is preferred. The faster the material could restore functionality, the less service interruption would occur. However, this does not mean that materials with slow recovery are not suitable for specific application. For example, a self-healable isolation membrane or anticorrosion coating (see section 5.2) with a fast response to physical damage but slow tensile recovery is still considered adequate because the tensile property recovery does not serve

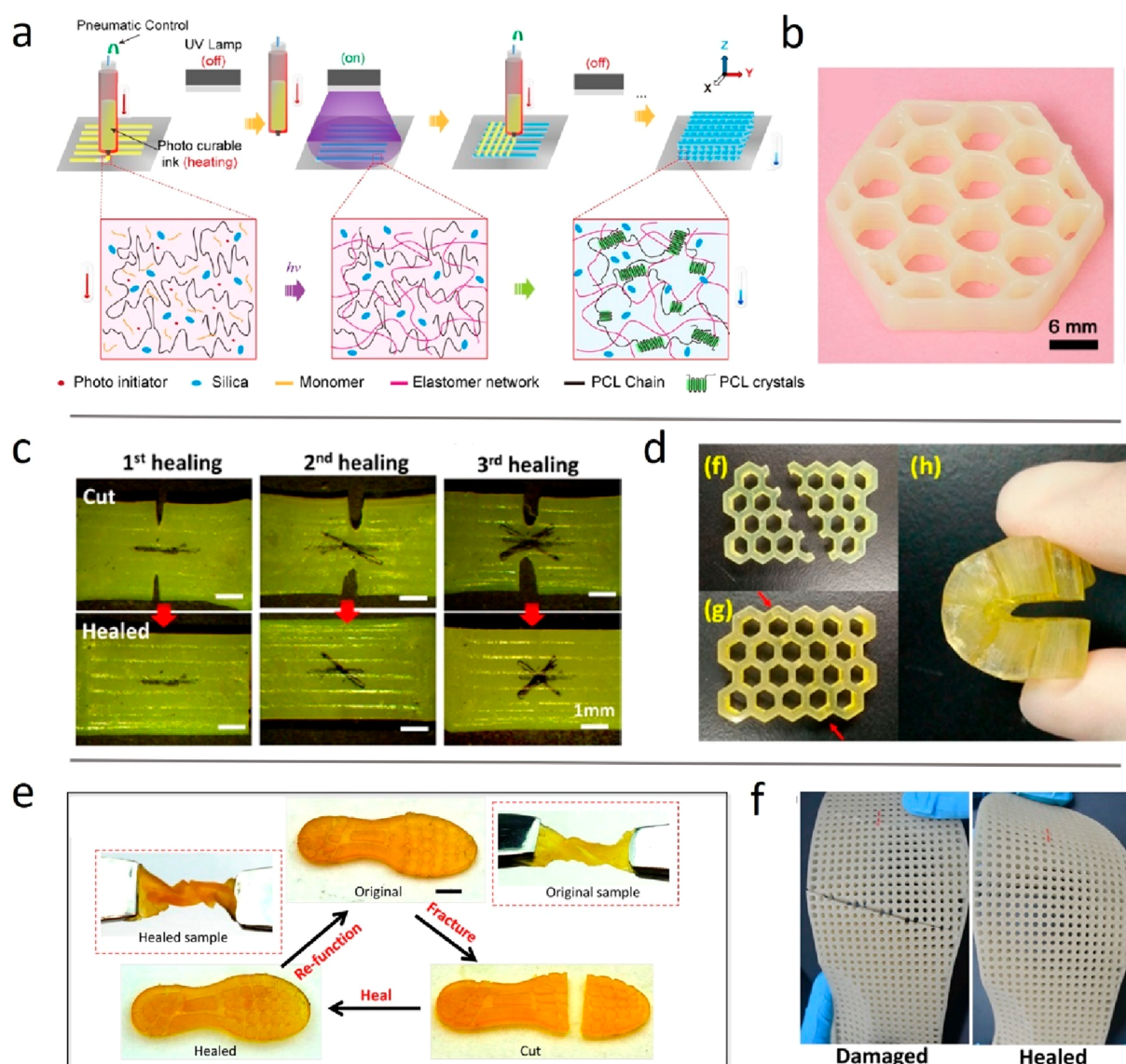


Figure 17. (a) Schematic illustration of the UW-assisted DIW technique and chemical illustration of the semi-IPN elastomer. Adapted with permission from ref 169. Copyright 2018 American Chemical Society. (b) As-printed honeycomb shape polymeric structure. Adapted with permission from ref 169. Copyright 2018 American Chemical Society. (c) Demonstration of the healing properties at 80 °C. Adapted with permission from ref 169. Copyright 2018 American Chemical Society. (d) Pictures of self-healable polyurethane elastomers prepared by DLP 3D printing. Adapted with permission from ref 173. Copyright 2019 American Chemical Society. (e) Picture demonstrating the self-healing of a shoe pad sample. Adapted with permission from ref 172. Copyright 2019 Springer Nature. (f) Photos of 3D-printed damaged and healed orthotic insole. Adapted with permission from ref 174. Copyright 2021 Elsevier Ltd.

the main purpose of these materials. One of the critical characteristics of the self-healing process can be the time to recover 80–90% of the initial property, e.g., 80–90% of the toughness. When self-healing time is evaluated, the surrounding condition including temperature, humidity, and gas atmosphere need to be carefully chosen. Some of intrinsic self-healing polymers exhibit accelerated healing upon exposure to humidity⁹⁷ or certain gas, such as CO₂,⁹⁰ as discussed in the section 2.4. Thus, we recommend all the paper should report not only temperature of self-healing process but also atmospheric condition (air, average RH) as one data series as well as healing time with more specific conditions.

4.3.3. Self-Healing Temperature. The healing temperature plays a pivotal role during the self-healing process. Because segmental and chain dynamics are faster and dynamic bond rearrangement time is shorter at elevated temperatures,

the self-healing process can be dramatically accelerated upon increasing the temperature. Self-healing is usually not achievable at temperatures below T_g of the polymer. To facilitate self-healing process, some materials with dynamic covalent bonds need a high temperature above 100 °C, which introduces extra complexity to achieve self-healing. In general, many applications prefer self-healable polymers with low healing temperatures, for example, room-temperature (20–25 °C) autonomous self-healing without extra heat. To achieve that, the polymer matrix should have T_g significantly below the room temperature. To provide a general approach for analysis of different self-healing polymers at temperatures above ambient, we suggest using temperature 10% or 20% above the matrix's T_g . Several works reported healing efficiency at multiple temperatures, which enables more precise comparison and is highly encouraged.^{35,100,132,147} In the case of the systems

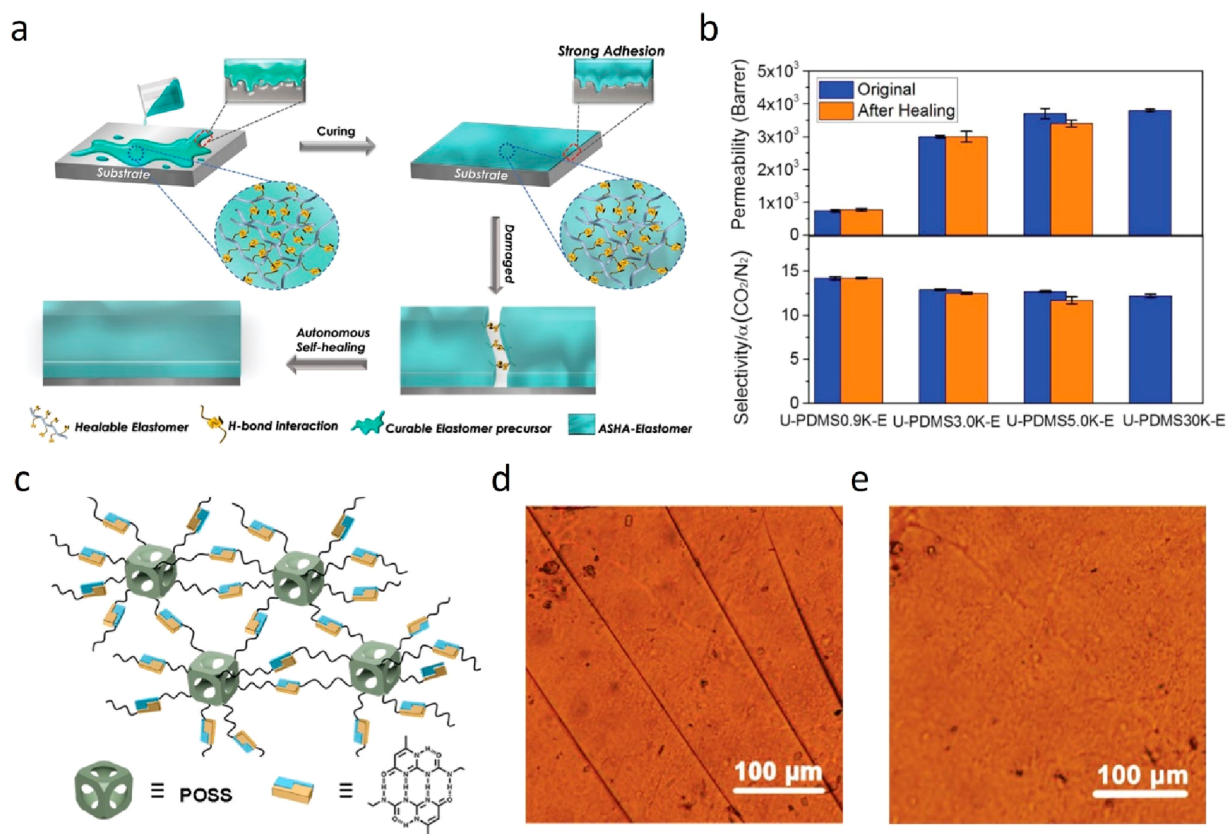


Figure 18. (a) Schematic illustration of the preparation method and mechanism of poly(BCOE)-sealant blends (ASHA elastomer). Adapted with permission from ref 9. Copyright 2021 Wiley-VCH. (b) Gas separation performance of PDMS-based intrinsic self-healable polymers before and after healing. Adapted with permission from ref 36. Copyright 2018 Wiley-VCH. (c) Schematic illustration of the hydrogen-bonded UPy-POSS supramolecular polymer coatings. Adapted with permission from ref 177. Copyright 2018 Wiley-VCH. (d) Optical microscope image of the coating with cracks that expose the underlying Kapton sheet. Adapted with permission from ref 177. Copyright 2018 Wiley-VCH. (e) Optical microscope image of the coating after being healed at 80 °C for 2 min. Adapted with permission from ref 177. Copyright 2018 Wiley-VCH.

with phase separated dynamic bonds, it can be T_g of the dynamic bonds clusters instead of the polymer matrix T_g . Ideally, a temperature dependence of self-healing kinetics should be studied.

4.3.4. Waiting Time. Another important parameter that is usually not reported in publications is the waiting time between the sample damage and starting point of the self-healing process. As was discussed in section 2.3, the waiting time can strongly affect the rate of self-healing. Leibler and co-workers provided a good illustration of this effect on an example of a system with strong hydrogen bonding cross-links.³⁴ In comparison to the self-healing process that starts immediately after physical damage (zero waiting time), waiting for 6 h decreased self-healing efficiency at the same healing time (e.g., 3 h) by ~50%, and waiting for 18 h decreased the self-healing efficiency at the same healing time by ~75%. Of course, if the sample was damaged and kept at temperatures below T_g of the matrix, the waiting time at this temperature does not play an important role, because the chains cannot rearrange and reach new equilibrium. Thus, we suggest that only the waiting time at temperatures above T_g should be reported.

5. APPLICATIONS OF INTRINSICALLY SELF-HEALING POLYMERS

Intrinsically self-healing polymers have great potential for use in diverse applications, improving longevity and efficiency of

many systems. In this section, we provide an overview of their use in additive manufacturing, envelope, energy storage, and stretchable electronic applications. Their use in other applications such as biomedical applications are excluded from this discussion.

5.1. Intrinsic Self-Healing Polymers for Additive Manufacturing

Intrinsically self-healing polymers exhibit unique viscoelastic properties, and thus, a specific type of self-healing materials needs to be tailored toward requirements of each application. For example, there are several reports on additive manufacturing (AM) of intrinsically self-healing polymers that require careful control of viscoelasticity during the process. AM provides the advantages of geometrical freedom, customized design, less waste, shorter time, and reduced energy from design to finish. AM of intrinsically self-healing polymers combines the advantages of efficient manufacturing and extended longevity of products. Manufacturing highly stretchable self-healable elastomer objects utilizing 3D printing has been achieved recently, where the direct-ink-write (DIW) approach was utilized to create the semi-interpenetrating polymer network (semi-IPN) elastomer (Figure 17a–c).¹⁶⁹ The 3D printed elastomers exhibited tensile strength of 5 MPa and extensibility of 600% with good self-healing capability. The use of digital light projection (DLP) technique created self-healable and shape memory poly(caprolactone)-based polymers.¹⁷⁰ The photo cross-linking of poly(caprolactone)

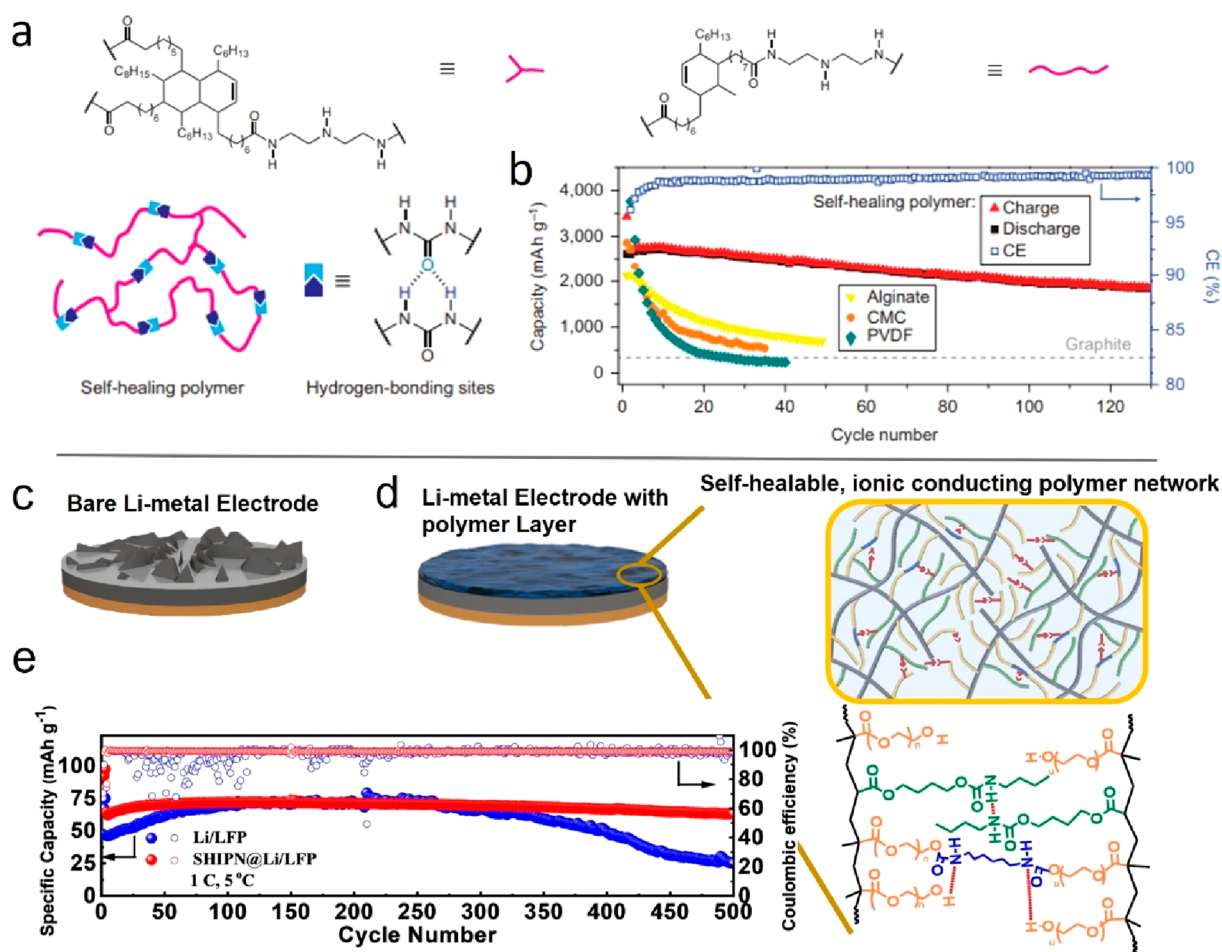


Figure 19. Self-healing polymer for energy applications. (a) Chemical structure of the self-healable polymer as binder for Si anode. Adapted with permission from ref 184. Copyright 2013 Springer Nature. (b) Capacity retention of self-healing polymer coated electrodes compared with other polymer additives. Adapted with permission from ref 184. Copyright 2013 Springer Nature. (c) Schematic illustration of the intrinsic SEI layer of the lithium–metal electrode. Adapted with permission from ref 192. Copyright 2022 American Chemical Society. (d) Schematic illustration of the protective SEI layer and its chemical structures of lithium–metal electrode. Adapted with permission from ref 192. Copyright 2022 American Chemical Society. (e) Cycling performance of Li/LiFePO₄ cells using the self-healable and ionic-conducting polymer network protected Li metal or bare Li metal as the anode at 1C and temperature 5 °C. Adapted with permission from ref 192. Copyright 2022 American Chemical Society.

dimethacrylate) (PCLDMA) macromonomers with methacrylates bearing 2-ureido-4[1H]-pyrimidinone motifs (UPyMA) was successfully conducted after printing. The UPy moiety enabled the polymer with self-healing capability and shape memory characteristics. The important balance of self-healing and shape stability in 3D printed self-healable polymers based on dynamic covalent bonds was discussed in ref 171. AM of disulfide based self-healing elastomers was reported using a photopolymerization-based printing method,¹⁷² similar to stereolithography. The PDMS-based resin containing thiols groups were used for thiol–ene reaction upon printing and the residual thiol groups formed disulfide linkages. The printed soft elastomers have both thiol–ene linkage and disulfide linkages, and the presence of disulfide linkage enabled successful self-healing at 60 °C (Figure 17e). Similarly, DLP was utilized on self-healing polyurethane elastomers containing disulfide bonds (Figure 17d).¹⁷³ Disulfide containing elastic polyurethane diacrylate macromonomer is first synthesized and used for DLP. The tensile strength reached 3.4 MPa with 400% elongation and repeated 95% healing efficiency were achieved with healing at 80 °C for 12 h. Selective laser sintering (SLS) was utilized to print PDMS elastomer

containing hindered pyrazole urea dynamic bonds.¹⁷⁴ SLS of PDMS elastomers successfully produced various 3D objects including orthotic insoles (Figure 17f). The presence of hindered pyrazole urea dynamic bonds enabled self-healing at elevated temperature such as 110–120 °C to exhibit close to 100% healing efficiency. Furthermore, fused filament fabrication (FFF) of upcycled ABS vitrimer with dynamic imine linkage has been reported with closed-loop circularity.¹⁷⁵ While the focus of the study was not self-healability, the scratch was healed at 150 °C. Due to the required viscoelasticity before and during printing, many of the self-healable polymers, especially elastomers, cannot be printed by FFF. But this study sheds light on the use of dynamic polymers for FFF, which is the most accessible and user-friendly AM technology. These various examples of additively manufactured self-healable 3D objects can be utilized for various applications including soft robotics.¹⁷⁶

5.2. Intrinsic Self-Healing Polymers for Envelope Applications

Other practical applications of intrinsic self-healing polymers have been reported, including envelope applications such as sealants, coating, and gas separation membranes. For example,

intrinsic self-healable sealants for building envelope applications have been recently developed.⁹ The self-healable low T_g ($-3\text{ }^\circ\text{C}$) poly(2-[[[butylamino]carbonyl]oxy]ethyl acrylate) (poly(BCOE)) and a commercial sealant were mixed prior to cure in a varied ratio. The blend can be readily cured, triggered by moisture, and it can readily self-heal at room temperature (Figure 18a). Compared to unhealable commercial sealants, poly(BCOE)-sealant blends (ASHA elastomer) showed superior adhesion force, especially on dusty surfaces due to its self-healing ability. The formulation requires no change of conventional manufacturing or application process, which shows an example of new self-healing materials with facile adaptability to a current industrial process. Another application of intrinsic self-healing polymers includes gas separation membranes. PDMS-based intrinsic self-healable polymers with multiple hydrogen bonding can readily self-heal the damage and exhibit the same gas separation performance on CO_2 and N_2 separation (Figure 18b).³⁶ Considering the kinetic diameter of gas molecule is $\sim 3\text{ \AA}$, intrinsic self-healing is effective to seal the damage to only allow gas permeation through the solution-diffusion mechanism. We note that the density of hydrogen bonding in these systems was important because the sample with lower content of hydrogen bonding and longer PDMS segment in the network could not effectively heal to exhibit the same gas separation performance as the original sample despite being visibly healed. Furthermore, intrinsic self-healing polymers were utilized as oxygen-resistant coatings. The use of UPy-functionalized polyhedral oligomeric silsesquioxane (POSS) that contained hydrogen bonding enabled self-healable atomic oxygen (AO)-resistant coating on Kapton film (Figure 18c).¹⁷⁷ The obtained film surface maintained its smoothness after AO exposure of 1.96×10^{20} atoms cm^{-2} , and the cracks on the film can be fully healed in 2 min at $80\text{ }^\circ\text{C}$ (Figure 18d,e).

5.3. Intrinsic Self-Healing Polymers for Energy Storage

The self-healing feature of polymeric materials is particularly desirable for energy storage devices because the long-term electrochemical stability of electrodes is always limited by mechanical fractures during the cycling process. In past decades, self-healing polymers are widely used in battery applications, including binders for silicon (Si) electrode in lithium-ion batteries, polymer electrolytes, and artificial solid electrolyte interphase (SEI) layer in lithium-metal batteries.^{39,178} The self-healing polymer can spontaneously repair the mechanical damage of electrolyte, protective layer of electrode, or electrode itself, thus prolonging the cycling lifetime of batteries.

Silicon is one of the most promising anode materials for next-generation high-energy density batteries.¹⁷⁹ The major problem faced by Si is the excessive volume expansion during the lithiation/delithiation process, which damages the integrity of electron transport pathways to the current collector.^{39,180} Conventional binders, such as poly(vinylidene difluoride) (PVDF), carboxymethyl cellulose, and alginate, have been the dominant binders in battery industry in the past decades.¹⁸¹ But these binders show limited binding strength for Si electrodes due to the lack of efficient binding groups on Si surfaces. Self-healing polymers can spontaneously repair the mechanical damage and recover the electronic conducting network of the Si electrode, prolonging the cycling lifetime. For example, after hydrolysis, the Meldrum's acid based polymers can bind Si and show some self-healing property

which can improve the cycling performance of Si electrodes.¹⁸² A self-healing polymer binder with a three-dimensional (3D) network consisting of poly(vinyl alcohol) and lithium metaborate achieved significantly improved cycling stability.¹⁸³ But these reports are all based on the nano-Si, while the Si particles with larger size normally show more industrial potentials. Therefore, a self-healing polymer that can be used as an efficient binder for relatively low-cost Si microparticles was reported.¹⁸⁴ The low T_g ($\sim 0\text{ }^\circ\text{C}$) and abundant dynamic groups, i.e., hydrogen-bonding units, of the polymer enable the repeating healability for cracks and damages of the electronic conducting channels (Figure 19a,b). Furthermore, Si electrode with 3D spatial distribution of self-healing polymer in Si microparticles was developed to achieve high mass loading. Due to the enhanced self-healing kinetics, the assembled cell with high areal capacity and low-cost large Si particles also exhibits excellent electrochemical performance.¹⁸⁵ By incorporating the poly(ethylene glycol) groups into the self-healing polymer, a self-healing polymeric binder with enhanced Li ion conducting channels has been fabricated and enhanced electrochemical performance was achieved.¹⁸⁶

Lithium metal is considered as an ideal anode material for high energy density rechargeable batteries due to the ultrahigh theoretical specific capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (-3.04 V vs standard hydrogen electrode).¹⁸⁷ The practical application of Li metal electrodes is impeded by unstable SEI and Li dendrite growth, which may even penetrate separator/electrolyte for a microshort circuit.¹⁸⁸ It has been demonstrated that with self-healing polymer as an artificial SEI layer, enhanced electrochemical performance can be achieved. Different from the intrinsic SEI layer, which is mechanically brittle and cannot accommodate the significant volume variation during the repeated Li plating/stripping process, the self-healing artificial SEI layer possess good shape-adaptive capability that can effectively buffer the volume changes and regulate Li deposition and growth. For example, a self-healing and single-ion conductive artificial SEI was reported by using cross-linked PDMS filled with 7 wt % SiO_2 nanoparticles.¹⁸⁹ A highly viscous and self-healable polymer as an artificial SEI layer also achieved uniform lithium deposition.¹⁹⁰ The introduction of dynamic imine bond based PEI interlayer on a Li metal surface demonstrated a self-healing protective layer. The distribution of Li^+ at the electrode/electrolyte interface can be better adjusted, and self-healing ability achieves recovery of interlayer even after being damaged by a Li dendrite.¹⁹¹ Recently, a readily synthesized copolymer network endowed with simultaneously high ionic conductivity and good self-healability at relatively low temperature is fabricated based on the weak but abundant hydrogen-bonding units (Figure 19c,d).¹⁹² The assembled Li-metal battery with such a protective layer shows superior electrochemical performance than that with bare a Li-metal electrode, even at relatively low temperature of $5\text{ }^\circ\text{C}$, as shown in Figure 19e.

Apart from the polymer binder and artificial SEI layer for the electrode, the self-healing polymers have also been utilized as a solid electrolyte. Compared with the conventional polymer electrolytes, the self-healability can effectively heal the crack and avoid battery failure during cycling. For example, a highly stretchable (extensibility $>4000\%$ and stress $>130\text{ kPa}$), nonflammable, and notch-insensitive intrinsic self-healing polymer electrolyte was prepared.¹⁹³ A solid polymeric electrolyte with fast self-healing, rigid-soft coexisting stability, and high ion conductivity is also designed, and the resulting all-

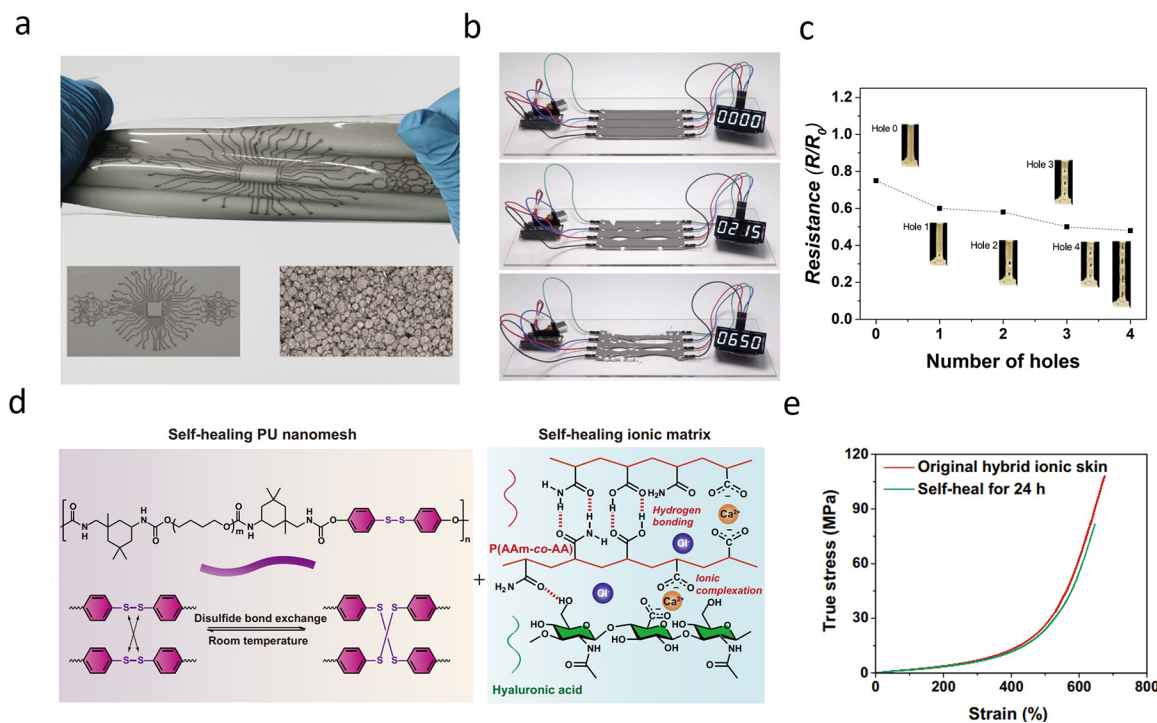


Figure 20. Self-healing polymer for stretchable electronics applications. (a) Liquid metal elastomer composite being stretched and twisted with an intricate design of electrically conductive traces. Adapted with permission from ref 14. Copyright 2018 Springer Nature. (b) Example of the reconfigurable material ($\phi = 50\%$) transmitting dc power after severe damage was induced. Adapted with permission from ref 14. Copyright 2018 Springer Nature. (c) Photos of hole-punch test during tension; no loss in electrical conductivity was observed after stretch. Reproduced with permission from ref 197. Copyright 2021 Springer Nature. (d) Schematic illustrations of the hybrid structure and respective self-healing mechanisms of PU nanomesh scaffold and ionic matrix. Adapted with permission from ref 109. Copyright 2022 Springer Nature. (e) True stress–strain curves of the original and self-healed hybrid ionic skins. Adapted with permission from ref 109. Copyright 2022 Springer Nature.

solid state batteries show superior cycling stability and good bending flexibility.¹⁹⁴ With UPy as hydrogen bonding units, a dual-network self-healing polymer electrolyte was prepared, and the assembled cells showed good reversible specific capacity and considerable rate capability.¹⁹⁵

Rational design of self-healing polymers has been demonstrated to be a viable approach for improving the electrochemical performance of electrodes, yet challenges still exist. Toward practical applications of these polymers in batteries, more efforts should be devoted to solving the following problems:

- (1) Surpassing the self-healing rate and mechanical strength trade-off (see section 6). Higher temperatures could facilitate the self-healing process but reduce the mechanical strength and vice versa. Considering the practical application conditions of batteries, the as-prepared polymers should possess fast self-healing ability under ambient or even lower temperature and sufficient mechanical strength to suppress the mechanical crack/failure.
- (2) Improving the electrochemical stability of self-healing polymers. Until now, most of the self-healing polymers are used for the modification of anode materials. These polymers should have good reduction stability, especially in contact with Li metal. On the other hand, used as a cathode binder, cathode electrode interphase, or even solid electrolyte, high voltage stability is required, and most of these polymers do not possess high voltage stability.

- (3) Modified self-healing polymers with functional lithophilic groups. The polymers with lithophilic functional groups, i.e., polar groups, nonpolar groups, charged groups, and multifunctional groups, can effectively regulate Li⁺ flux, lead to a uniform Li⁺ deposition, and improve the electrolyte wettability.

5.4. Intrinsic Self-Healing Polymers for Stretchable Electronics

Self-healing characteristics have been incorporated in materials for applications such as stretchable conductors and electronic/ionic skins. For example, embedding liquid metal alloy (typically gallium–indium, EGaln) in polymers has produced multiple self-healable composites functioning as flexible electronics.^{14,196–198} Large-area stretchable electronics were fabricated by utilizing this liquid metal composite approach (Figure 20a). Embedding EGaln in silicon elastomer produced composite for a stretchable circuit that is electrically stable and achieved instantaneous electrical self-healing after multiple external damages (Figure 20b).¹⁴ Similar approach in the other report also demonstrated the good electrical self-healing of such composite design (Figure 20c).¹⁹⁷

Intrinsic self-healing technique actively evolves with the development of artificial skin. The complexity of artificial skin involves multiple key features: good self-healability, strain-adaptive stiffening response, good stretchability, and sensing capability. During the past decade, those features are achieved and integrated through rational material design.^{109,144,199} Parts d and e of Figure 20 present the latest design toward high-performance artificial skin. Mimicking skin's nanofibrous structure, a hybrid design which embeds a high-energy self-

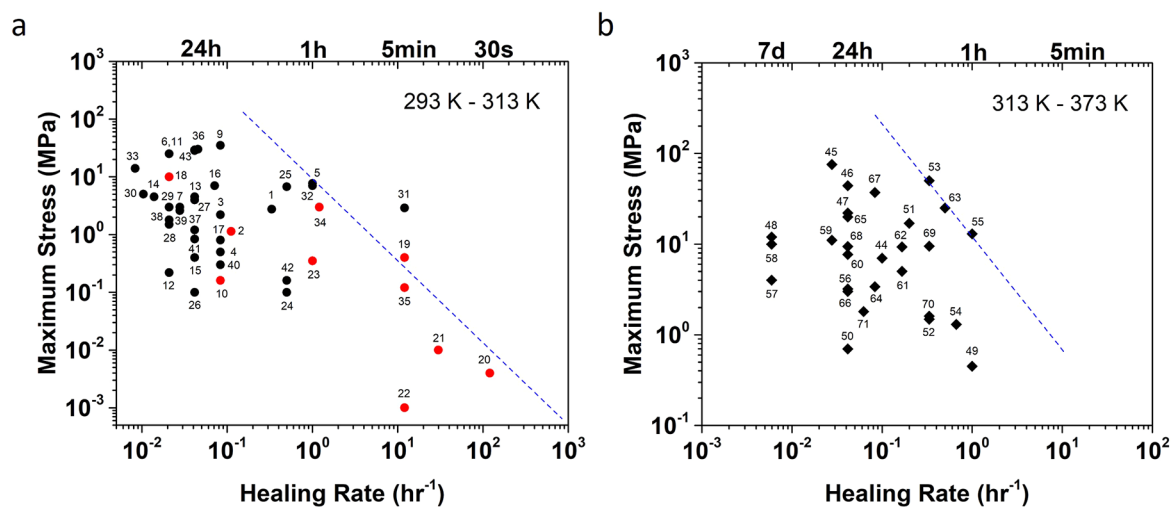


Figure 21. Diagram of the maximum tensile stress vs healing rate for intrinsically self-healing polymers. (a) Data for polymers healable at between 20 and 40 °C (red dots indicate gel samples). (b) polymers healable between 40 and 100 °C. The healing rate was chosen as an inverse time to reach at least 90% healing efficiency. Specific polymers, dynamic bonds, and references to each presented data point are given in Table 1. Dashed lines present upper bound for the tensile strength self-healing rate trade-off.

healable elastic nanomesh scaffold into another self-healable soft ionic matrix was implemented (Figure 20d).¹⁰⁹ A polyurethane with disulfide bond moiety was fabricated as PU nanomesh, and poly(acrylamide-*co*-acrylic acid)-based cross-linked gel containing hyaluronic acid and CaCl₂ served as the ionic matrix to provide conductivity. Such design delivered exceptional fracture energy (16.3 kJ m⁻²), high fatigue threshold (2950 J m⁻²), good stretchability (680%), and strain-stiffening response (stiffened to 67.5 MPa) while maintaining skin-like self-healability with sensing capability (Figure 20e). Another example includes water-insensitive healable skin with stretchability up to 1200% and high toughness of 12,000 J m⁻², that could undergo autonomous self-healing even in artificial sweat.¹⁴⁴ As many new intrinsic self-healing polymers are developed,^{18,135} one needs to develop a deeper understanding of mechanisms controlling viscoelastic properties, their manufacturing process, as well as adaptability to existing industrial processes and applications.

Several intrinsically self-healing polymers with dynamic bonds have already moved from academic studies to real industrial applications. For example, Suprapolix BV produces self-healable polymers based on multiple hydrogen bonding for various applications, from biomedical to adhesive and coatings. Malinda Inc. has developed resin impregnated carbon fiber mats based on imine cross-linked technology that enable closed-loop recyclability and damage repair using reversible imine bonds. NEI Corporation offers self-healing protective coatings based on thermoset/thermoplastic polymer matrix that is capable of heat assisted self-healing. Industrial use of self-healing materials will grow tremendously in the near future. Most of these materials are easily recyclable, which provides additional incentives for their broad industrial use.

6. CURRENT CHALLENGES AND FUTURE PERSPECTIVES

6.1. Trade-off between Self-Healing Kinetics and Mechanical Strength

One of the major challenges in intrinsically self-healing polymers is a trade-off between mechanical strength and self-healing kinetics. For example, a material with high mechanical

strength rarely has high healing efficiency at moderate temperature. This phenomenon could be explained by the facts that the high healing efficiency requires (1) fast segmental dynamics and (2) readily breakable/exchangeable dynamic bond, which normally comes at the price of soft polymer chains with low modulus and weak dynamic bonds. For example, with T_g around -123 °C, PDMS possesses the fastest segmental dynamics at ambient conditions that facilitate the fast self-healing kinetics but also results in relatively low modulus for those PDMS based elastomers.^{36,64}

To explore the trade-off relationship, we analyzed the data accumulated during the recent decade^{107,168,200–229} and summarized them in Figure 21. The *x*-axis is the healing rate (1/healing time in hours) to achieve the healing efficiency of 90% or higher, and the *y*-axis is the maximum tensile stress of the materials. All tensile tests data were measured at room temperature, while the healing time was measured at different temperatures that strongly affect the healing rate. To overcome this problem, we split the data in two groups: Figure 21a presents the results of healing at temperatures close to ambient (20–40 °C), while Figure 21b presents the results obtained at elevated temperatures (40–100 °C). These plots demonstrate the known trend for self-healing polymers:²³⁰ the healing time increases with increase in tensile strength of the material. Specific information about the samples and the references for the data collected in Figure 21 are given in Table 1. We note that many important parameters affecting the healing rate (e.g., the waiting time, humidity, pressure used, etc.) are usually not reported in literature. This complicates detailed quantitative analysis and comparison of different systems. Nevertheless, the data presented in Figures 21 revealed some guidance for design of materials with fast self-healing rate and relatively high mechanical strength.

As seen in Figure 21a, achieving fast healing in mechanically strong material at moderate temperature is challenging. We found a few papers reporting almost full recovery of mechanical properties at room temperature for materials with tensile strength above 20 MPa (Figure 21a),^{43,89,97,229,231,232} and we found none with the tensile strength above 40 MPa. For materials that exhibit high tensile strength up to 30 MPa,

Table 1. List of the Self-Healing Polymers Presented in Figure 21 with Their Parameters and References; Numbers in Figure 21 Correspond to the Line Numbers in the Table

	backbone material	type of dynamic bonds	maximum stress (MPa)	healing time (h)	healing rate (h ⁻¹)	healing temp (K)
1	polyurea ³⁴	hydrogen bond	2.75	3	0.333	293
2	poly(acrylic acid) ¹³⁸	hydrogen bond and ionic bond	1.13	9	0.111	298
3	poly(urea-urethane) ²⁰⁰	dynamic exchange reactions	2.2	12	0.083	313
4	poly(acrylamide) ²⁰¹	host–guest interactions	0.5	12	0.083	298
5	polyurethane ²⁰²	hydrogen bond	7.7	1	1.000	298
6	polyurethane ²³²	hydrogen bond	25	48	0.021	298
7	PDMS ²⁰³	hydrogen bond and imine	3	36	0.028	298
8	PDMS ²⁰⁴	hydrogen bond and imine	0.4	24	0.042	298
9	polyurethane ²³¹	hydrogen bond	35	12	0.083	298
10	poly(thioctic acid) ¹³⁵	hydrogen bond and ionic bond	0.16	12	0.083	298
11	poly(acrylic acid) ⁹⁷	hydrogen bond and ionic bond	25	48	0.021	298
12	PDMS ³⁵	metal–ligand coordination	0.22	48	0.021	298
13	poly(butyl acrylate) ¹³⁴	hydrogen bond and metal–ligand coordination	4.5	24	0.042	298
14	boronic ester network ¹²⁴	boronic ester	4.5	72	0.014	298
15	polyurethane ¹¹¹	disulfide links	0.4	24	0.042	298
16	PMMA/P(<i>n</i> -butylacrylate) ⁸	van der waals force	7	14	0.071	269
17	tetra(ethylene glycol) ¹¹⁸	hydrogen bond	0.8	12	0.083	310
18	PEI ¹⁴⁶	hydrogen bond	10	48	0.021	298
19	poly(α -lipoic acid) ¹³²	hydrogen bond and metal–ligand coordination	0.4	0.0833	12.005	293
20	poly(butyl acrylate) ²⁰⁵	hydrogen bond	0.004	0.00833	120.005	298
21	poly(acrylic acid) ¹⁴⁰	hydrogen bond and metal–ligand coordination	0.01	0.0333	30.030	298
22	poly(carboxymethyl chitosan) ²⁰⁶	hydrogen bond	0.001	0.0833	12.005	298
23	poly(acrylic acid) ²⁰⁷	hydrogen bond	0.35	1	1.000	298
24	PDMS ¹⁰⁷	hydrogen bond and disulfide links	0.1	2	0.500	298
25	thermoplastic polyurethane ¹¹⁶	disulfide links	6.76	2	0.500	298
26	poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene) ²⁰⁸	hydrogen bond and coordination	0.1	24	0.042	298
27	PDMS ²⁰⁹	metal–ligand coordination	4	24	0.042	298
28	PDMS ¹⁴⁴	hydrogen bond	1.5	48	0.021	298
29	TEG ¹⁰	hydrogen bond	3	48	0.021	298
30	PDMS ²¹⁰	hydrogen bond	5	96	0.010	293
31	polyethylene- <i>co</i> -polypropylene ²³³	van der Waals force	2.9	0.0833	12.005	298
32	polyethylene- <i>co</i> -polypropylene ²³³	van der Waals force	7	1	1.000	298
33	polyethylene- <i>co</i> -polypropylene ²³³	van der Waals force	14	120	0.008	298
34	poly(methacrylic acid) ¹⁴⁵	hydrogen bond and imine	3	0.8333	1.200	298
35	poly(vinyl alcohol) ²¹¹	boronic ester and hydrogen bond	0.12	0.0833	12.005	298
36	polyacrylate ⁸⁹	ionic bond	30	22	0.045	298
37	styrene butadiene rubber ²¹²	hydrogen bond and ionic bond	1.2	24	0.042	298
38	curcumin polymer block ²¹³	hydrogen bond and metal–ligand coordination	1.8	48	0.021	298
39	PDMS ³⁸	hydrogen bond and metal–ligand coordination	2.6	36	0.028	298
40	PDMS ²¹⁴	metal–ligand coordination and π – π stacking	0.3	12	0.083	298
41	poly(urea-urethane) ¹¹⁴	hydrogen bond and disulfide links	0.84	24	0.042	298
42	PDMS ²¹⁵	hydrogen bond and imine	0.16	2	0.500	298
43	polyurethane ²²⁹	hydrogen bond	29	24	0.042	298
44	poly(tetramethylene glycol) ²¹⁶	hydrogen bond	7	10	0.100	363
45	polytetramethylene ¹⁴⁷	hydrogen bond	75.6	36	0.028	373
46	poly(urea-urethane) ¹⁰²	hydrogen bond	44	24	0.042	373
47	PPG ¹¹⁵	hydrogen bond	22	24	0.042	373
48	anthryl-telechelicpoly(ethylene adipate) ¹⁰⁵	disulfide links and hydrogen bond	12	168	0.006	343
49	epoxy resins ¹¹⁰	disulfide links	0.45	1	1.000	373
50	polyurethane ²¹⁷	bond exchange and hydrogen bond	0.7	24	0.042	333
51	poly(vinyl alcohol)/Nafion ¹³⁹	hydrogen bond	17	5	0.200	323
52	poly(urea-urethane) ¹³⁷	hydrogen bond and ionic	1.48	3	0.333	353
53	PEG ¹³³	hydrogen bond and ionic bond	50	3	0.333	338
54	PDMS ¹⁴⁴	hydrogen bond and metal–ligand coordination	1.6	1.5	0.667	333

Table 1. continued

	backbone material	type of dynamic bonds	maximum stress (MPa)	healing time (h)	healing rate (h ⁻¹)	healing temp (K)
55	PDMS ¹⁶⁸	hydrogen bond	13	1	1.000	333
56	poly(3-caprolactone) ²¹⁸	hydrogen bond	3.2	24	0.042	348
57	polyacrylates ¹⁵¹	Diels–Alder reaction and ionic bond	4	168	0.006	333
58	polyacrylates ¹⁵¹	Diels–Alder reaction and ionic bond	10	168	0.006	333
59	polyurethane ²¹⁹	hydrogen bond and host–guest interaction	11.07	36	0.028	373
60	poly(urea-urethane) ²²⁰	hydrogen bond and disulfide links	7.7	24	0.042	333
61	polyurethane ²²¹	hydrogen bond and disulfide links	5	6	0.167	333
62	ENR ²²²	hydrogen bond and disulfide links	9.3	6	0.167	393
63	polyurethane ²²³	hydrogen bond and disulfide links	25	2	0.500	373
64	polyurethane ¹⁷³	hydrogen bond and disulfide links	3.39	12	0.083	353
65	polyurethane ²²⁴	hydrogen bond and disulfide links	20	24	0.042	363
66	PDMS/polyurethane ²²⁵	hydrogen bond and Diels–Alder reaction	3	24	0.042	353
67	polyurethane ²²⁶	hydrogen bond and Diels–Alder reaction	37.11	12	0.083	333
68	poly(urea-urethane) ²²⁷	metal–ligand coordination and Diels–Alder reaction	9.4	24	0.042	353
69	polyurethane ²²⁸	metal–ligand coordination and Diels–Alder reaction	9.5	3	0.333	338
70	polycyclooctene ¹⁴²	hydrogen bond	1.6	3	0.333	323
71	polycyclooctene ¹²⁶	boronic ester	1.8	16	0.063	323

the shortest time for full recovery is 12 h.²³¹ These polymers have backbones with T_g slightly below room temperature that provides relatively high tensile strength, and hydrogen or ionic bonds that enable a reasonable healing rate at ambient temperature. Moreover, the system with the highest tensile strength (no. 9 in Figure 21a) presents a composite material reinforced with layered WS₂ structures.²³¹ Tannic acid (TA) was added to construct the interface between WS₂ nanosheets and the polyurethane (PU) matrix. Meanwhile, TA could also regulate and control the aggregation density of hydrogen bonds. Strong hydrogen bonding in the TA-WS₂/PU systems delivered composites with high toughness, mechanical strength, and outstanding self-healing capabilities. Mechanical reinforcement in another system (no. 36 in Figure 21a) was achieved through the formation of ionic clusters that also provide self-healing ability.⁸⁹ However, to achieve a good healing performance at room temperature, ethanol was used to wet the damaged surfaces, which strongly speeds up the process of bond rearrangements in ionic clusters. Almost all other data for self-healing around room temperature exhibit tensile strength below 10 MPa (Figure 21a). The fastest healing rate (healing time below 1 h) is achieved on polymer gel samples (red symbols), and most of them have tensile strength below 1 MPa (Figure 21a). An interesting example of very fast healing (~5 min) and decent tensile strength ~3 MPa is demonstrated using block copolymer structure (no. 31 in Figure 21a).²³³ This unique combination of self-healing rate and mechanical strength was achieved by combining soft and hard segments in addition to crystalline nanodomains.

The same trade-off is observed for healing at higher temperatures (Figure 21b). In this case, the tensile strength measured at room temperatures can reach much higher values (close to 100 MPa) for materials with high temperature healing time of the order of hours or days. The best combination of the tensile strength and rate of self-healing (no. 53 in Figure 21b) is again demonstrated by a complex polymer structure combining hydrogen bonding and phase

separated ionic clusters complemented by crystalline nanodomains.¹³³

The trade-off relationship (Figure 21) is similar to the well-known Robeson plot (a trade-off between permeability and selectivity) for gas separation membranes.^{234–236} The Robeson plot traditionally presents a straight line touching the best performing data, the so-called “upper bound” line that indicates the limit of current technology. Utilizing this analogy, we also propose introduction of the “upper bound” line for these self-healing polymer data (dashed lines in Figure 21). This upper bound line provides some guidance on the expected fastest healing rate for a material with the given tensile strength. Alternatively, it might suggest the maximum tensile strength achievable at the required healing rate. However, we want to emphasize that further understanding of the design principles for intrinsically self-healing polymers will enable surpassing the current upper bound line in the future works.

The trade-off relationship here signifies the major current challenge of intrinsically self-healing polymers. Faster healing for any system is desirable, but it usually can be achieved only in soft polymers and gels with relatively weak dynamic bonds. These fast self-healing polymers can satisfy the requirements for some sealants and stretchable substrates but are too weak for the majority of applications.⁹ When mechanically robust polymers have dynamic bonds, their bond strength and T_g are typically too high to have efficient self-healing at the operating condition. To accelerate the self-healing process, applying heat on demand could provide the required healing rate. However, active heating to trigger the healing process is not preferred or even not possible in many applications. Use of specific solvents can also speed up the self-healing process of some materials at ambient conditions. Although this might be a bit simpler than applying heat, it is still not desirable for many applications. Thus, designing mechanically strong materials with sufficiently fast healing will be beneficial for many technologies. Below we formulate some potential approaches that might surpass the trade-off between the rate of self-healing and mechanical strength of the polymer materials.

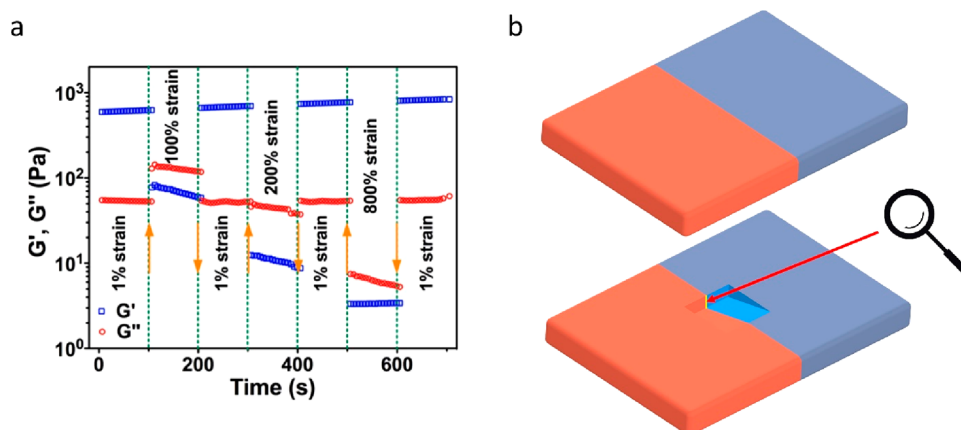


Figure 22. (a) Example of rheology test at alternate small oscillation strain and large strain. Adapted with permission from ref 206. Copyright 2018 American Chemical Society. (b) Illustration of the proposed in situ observation approach for self-healing.

6.2. Employing Complex Architectures and Combination of Dynamic Bonds to Surpass the Modulus–Self-Healing Rate Trade-off

The presented analysis (Figure 21) demonstrates that breaking through the modulus–self-healing rate trade-off requires a complex molecular design combining different dynamic bonds as well as polymer architecture to provide specific morphology. It is obvious that fast self-healing requires polymer with T_g below the targeted healing temperature and dynamic bonds with a relatively low energy barrier for dissociation (e.g., hydrogen bonds). However, T_g of the polymer should not be very low to have a reasonable modulus, and the presence of hard domain (analogue to spider silk) will provide additional reinforcement. These hard domains can be nanofillers used in polymer nanocomposites with surface functionalized with dynamic bonds.¹⁴⁷ They also could be crystalline domains or phase separated hard domains of the self-healing polymers.¹⁰² It is well-known that nanoparticles in a polymer matrix create nanoscale interfacial polymer layer with strongly enhanced mechanical properties, providing additional reinforcement in polymeric nanocomposites.^{85,237} A similar effect with interfacial shear modulus reaching ~ 100 MPa at temperatures much above the matrix's T_g has been reported recently for polymers with hard clusters formed by phase separating hydrogen-bonding groups.^{48,84} Thus, the incorporation of hard domains (or nanofillers) could provide a substantial increase in the tensile strength without significant sacrifice in the rate of self-healing. These hard domains provide not only mechanical reinforcement that increases with their volume fraction but also enhances mechanical properties of the interfacial layer surrounding them. The latter increases with the surface area of the hard domains and appears very efficient when domains have a size of a few nanometers.^{48,84}

Also, the combination of different types of dynamic bonds in a single polymer network show very promising results.^{35,38,97,138} The dynamic bonds with lower bond strength (sacrificial bonds) provide fast self-healing especially when combined with the backbone having faster segmental dynamics. The presence of stronger dynamic bonds such as ionic bonds or quadruple hydrogen bonds provide mechanical robustness while keeping self-healing ability. The strategy to combine several different dynamic bonds, such as the combination of weak and strong dynamic bonds and inclusion of hard domains could lead to intrinsically self-healing

polymers with superior toughness, high tensile strength, and fast self-healing.

6.3. Needs for in Situ Analysis of Self-Healing

As discussed in section 4, another major challenge in the field is the absence of a standard in experimental studies of self-healing kinetics. The standard would enable direct quantitative comparison of results obtained in different groups. Establishing the standardized method for evaluation of self-healing properties is critical for the field. An even more important task would be the development of an experimental method that provides in situ characterization of the healing process kinetics. Example of these kinds of techniques is the nonlinear rheology used in ref 45 (Figure 15). Direct monitoring of recovery of mechanical properties without sample destruction by the nonlinear rheology will be instrumental in understanding the self-healing process, especially in systems with multiple types of dynamic bonds and hierarchical structures with hard and soft domains. These systems should exhibit multistep healing processes due to several characteristic time scales of bond rearrangements. Several works utilized another nonlinear rheology approach: continuous strain sweep with alternate low (1%) and high (100–500%) amplitude of strain oscillations to mimic the damage-healing process (Figure 22a).^{140,206} Tests at each strain were conducted for 30 s or 100 s. By monitoring the change in storage modulus (G') and loss modulus (G'') of the sample, the repeatability and efficiency of the sample's self-healing property could be quantified.

As it was discussed in section 4.2, the optical or similar microscopy will provide images of in situ healing. The traditional microscope could inspect samples at the top-down view; however, it lacks tracking of the healing process in depth. To obtain an image of the healing process, focused ion beam scanning electron microscope (FIB-SEM) can be utilized (Figure 22b). The starting stage of healing and the cross-section will be exposed to the camera directly after the removal of materials by the ion beam. Such observation window enabled by material removal could provide direct, continuous monitoring of the self-healing process in depth of the sample. While these imaging techniques exhibit in situ information, the obtained data may only represent visual kinetics. To comprehend a self-healing system and correlate it quantifiably to self-healing kinetics, one needs to complement it with the other techniques, such as nonlinear rheology, or ex situ tests, such as tensile tests, to determine toughness.

It will also be beneficial if tensile strength and self-healing kinetics will be measured at the same temperature. For example, the data presented in Figure 21 can be easily shifted along the X -axis (healing rate) by changing the healing temperature, while the tensile strength of the sample measured at ambient conditions (Y -axis) will remain the same. For better comparison of different samples, the temperature range of self-healing studies should be scaled with T_g of the polymer matrix (or T_g of clusters of dynamic bonds). An even more definitive method will be analysis of the temperature dependence of the self-healing kinetics, although such process will be significantly more time-consuming unless some direct in situ measurements are developed.

6.4. Theoretical and Modeling Challenges

The current model of self-healing polymers developed by Rubinstein and co-workers⁵⁸ considers a branched homopolymers with a single type of dynamic bonds. As we have seen from the data analyses, the best performing self-healing materials present complex copolymers with a combination of various dynamic bonds, including some sacrificial bonds, and even phase separated clusters of units containing dynamic bonds.^{89,97,133,231,232} Thus, rational design of efficient self-healing polymers requires more complex models considering a combination of the dynamic bonds with different dissociation energy, bond rearrangements between clusters of dynamic bonds, and potential combination of backbones with various flexibility and molecular weight between the functional groups. The number of tunable parameters in design of self-healing polymers is extremely broad, and this complexity hinders theoretical ability to provide any quantitative predictions for design of self-healing materials with desired properties. Computational studies with involvement of machine learning (ML) and artificial intelligence (AI) approaches might be also instrumental in design of these complex molecular structures.

7. CONCLUSIONS AND OUTLOOK

Intrinsically self-healing polymers provide a unique and important function to soft materials with prolonged service lifetime. While self-healing is a regular process in biological systems, the development of synthetic intrinsically self-healing polymers receives significant attention only during the last two decades. There are many recent exciting achievements in the field, including employment of more types of dynamic bonds that demonstrate great potential of self-healing polymers for various current and future technologies. For most of these applications, the rate of self-healing is one of the most important parameters. It is well understood now that this rate in polymers with dynamic bonds is controlled by the rate of bond rearrangements. The latter depends on segmental mobility (softness of the materials) and the strength of the dynamic bond. This explains why healing is only possible at temperatures above T_g of the polymer matrix (or T_g in clusters of dynamic bonds in systems with phase separated stickers), and the healing rate increases significantly with temperature. Also, the waiting time between the physical damage and start of the self-healing process plays a role in self-healing kinetics, and after a long waiting time, the self-healing process becomes a normal adhesion. However, this waiting time dependence is rarely analyzed. The kinetics of self-healing can be accelerated not only by raising temperature but also by using specific solvent (including water or high humidity atmosphere), pH,

light, and other triggers that can accelerate the bond rearrangement.

The review of the current literature shows many examples of relatively fast self-healing materials even at ambient conditions. But all of these materials are very soft and have rather low tensile strength. These results emphasize an important challenge in the field: the trade-off between the rate of self-healing and the mechanical strength of the material (Figure 21). Although this trade-off seems to be natural because softness of the material is usually coming with fast molecular rearrangements, smart design of materials with multiple types of dynamic bonds, and hierarchical structures with hard and soft domains can potentially break through this trade-off. Additionally, a phase separation of dynamic bonds and multiarm (or grafts) architectures may provide a promising approach to developing intrinsic self-healing polymers with desired mechanical properties and short healing time. We also want to emphasize that using the upper bound line in the tensile strength vs healing rate plot (Figure 21) provides a guidance for expectations of the fastest self-healing rate at the given mechanical modulus and can be instrumental in design of self-healing materials.

As demonstrated in this review, the number of parameters that can be tuned to control the self-healing materials' properties is extremely broad. It includes among others different types of dynamic bonds and their combinations (e.g., sacrificial bonds), chemical structure of the polymer backbone and its architecture, molecular weight between stickers, and their microphase separation. This complexity creates a significant challenge for a predictive design of intrinsically self-healing polymers and requires development of more sophisticated models and theory. Moreover, development of predictive models by computation, especially utilizing AI and ML, will also provide a critical guidance for the new design of intrinsically self-healing polymers.

Additional challenges in this field are also caused by the absence of a standard evaluation of self-healing efficiency and rate (such as, e.g., ASTM standard) and rather limited study of in situ kinetics of self-healing process. In most cases, it is almost impossible to provide accurate quantitative comparison of the results of studies performed by different research groups. We propose measuring self-healing efficacy by standardizing healing temperature, use of toughness recovery vs healing time as the major parameter, and other evaluation criteria. Moreover, further progress in the field requires more advanced characterization methods, especially the techniques able to quantitatively analyze the kinetics of the healing process.

Despite all of these challenges, significant current advances in precision polymer synthesis and the great variety of dynamic bonds open tremendous opportunities for design of functional self-healing polymeric materials with many unique properties. They usually exhibit extreme toughness and exceptional adhesive properties, and most of these materials are easily recyclable. The latter helps to address the current need for establishing polymer circularity. We discussed here several important applications where intrinsically self-healing polymers are expected to play a vital role. But the potential of these materials is far beyond the discussed list of applications, and they should penetrate many other technologies.

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Notes

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