

Review

# A Brief Overview on Preparation of Self-Healing Polymers and Coatings via Hydrogen Bonding Interactions

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**Abstract:** Self-healing coatings or materials have received significant importance in paint, coating, and other industries, as well as in academia, because of their capability to extend materials service life, improving protection, and ensuring sustainability. This review article emphasizes significant advances accomplished in the preparation and properties of intrinsic self-healing materials exclusively based on hydrogen bonding interactions, with possible applications in coatings and adhesives. The main topic of discussion in this review article is the preparation, healing conditions, healing efficiency, and mechanical property recovery after healing. The last part of the review discusses the conclusions and outlook of self-healing materials.

**Keywords:** polymers; self-healing; hydrogen bonding; intrinsic; extrinsic

## 1. Introduction

Living organisms play a crucial role in sustaining and prolonging life via self-healing mechanisms [1–4]. For example, the skin of human beings can heal injuries to reduce the risk of death owing to bacterial and fungal infection. Initially, injury triggers the inflammatory response in the skin. Then, with the help of replenishment of materials and energy from the circulatory systems and adjacent tissues, cells around the injury area can proliferate and finally cover the stripped wound surface with newly regenerated skin [2,3]. However, on the other hand, coatings and other synthesized materials are generally susceptible to damage, degradation, and delamination by external factors. This process contributes to limiting its lifetime, therefore, there is a need for continuous monitoring of damage to increase the lifetime of the material by repairing, re-coating, and replacing. This is an expensive process in both cost and time. However, inspired by nature, self-healing materials are at the forefront of recent development [5–12], and a substantial amount of research work has been dedicated to developing self-healing coatings that can restore the fundamental properties of the material [13–17]. By virtue of self-healing abilities, substantial improvements can be brought towards extending the functional lifetime, consistency, efficiency, and safety of coating materials. Moreover, due to the alarming increasing pollution from environmental waste, self-healing coatings play a critical role in addressing these issues.

Self-healing materials are broadly classified into two categories based on the healing mechanism: extrinsic self-healing and intrinsic self-healing materials. For the extrinsic self-healing mechanism, the healing process relies on a combination of two components, i.e., a healing agent (monomer) and a catalyst or healing agent (resin) and hardener. The combination of these two components can be in the form of microcapsules [18], microvascular [19], or hollow fibers [20]. Due to abrupt mechanical damage in the system, microcapsules experience rupture, and a healing agent is released into the cracks due to capillary action. When a healing agent comes in contact with the catalyst or hardener,

a crosslinked polymer is formed, and re-bonding of the crack takes place [21]. The extrinsic self-healing process is close to commercialization; however, this process has a limitation of depleting a healing agent after re-bonding of a crack. As a result, manifold healing is not possible [22]. In order to overcome this drawback, intrinsic self-healing is the most desired process. Intrinsic self-healing materials are attracting much interest among researchers and have been growing, as they require no incorporation of external healing agents, which avoids many of the problems related to healing agents, such as compatibility, intricate pre-embedding processes, and precise and continuous release.

Intrinsic self-healing mechanisms rely on dynamic bonds incorporated into a polymer network. The intrinsic self-healing system can heal multiple times through the inherent dynamic covalent network. Dynamic bonds are also of two types, (a) a dynamic covalent bond, and (b) a dynamic non-covalent bond (referred to as supramolecular interactions) [23]. Dynamic covalent bonds comprehend a vast range of chemistries such as Diels–Alder and retro-Diels–Alder reactions [24], 2 + 2 cycloaddition [25], disulfide bond reshuffling reaction [26], diselenide bond reshuffling [27], trithiocarbonate reshuffling reaction [28], reshuffling of thiuram disulfide [29], acylhydrazone [30], boronic ester, oxime bond, and imine bonds [31–34]. However, the self-healing process using these dynamic bonds requires some external stimulus, such as heat, UV light, pH, or force, to trigger these reversible reactions.

On the other hand, intrinsic self-healing based on supramolecular interactions includes H-bonding interactions [35], ionic interactions [36], metal-ligand coordination [37],  $\pi$ – $\pi$  stacking [38], and host-guest interaction [39]. Upon mechanical damage, these bonds dissociate due to the weak nature of supramolecular interactions. Nonetheless, these bonds re-associate easily after being broken without the intervention of an external trigger.

There are several review articles on self-healing polymers, elastomers, and composites using all kinds of supramolecular chemistry [40]. This review focuses mainly on intrinsic self-healing synthetic polymers and coatings via hydrogen bonding interactions that dissociate and re-associate at moderate to room temperature (RT), leading to self-healing behavior. Self-healing materials based on the extrinsic mechanism do not fall into the scope of this review; interested readers can refer to several review articles about extrinsic self-healing [41–43].

## 2. Hydrogen Bonding

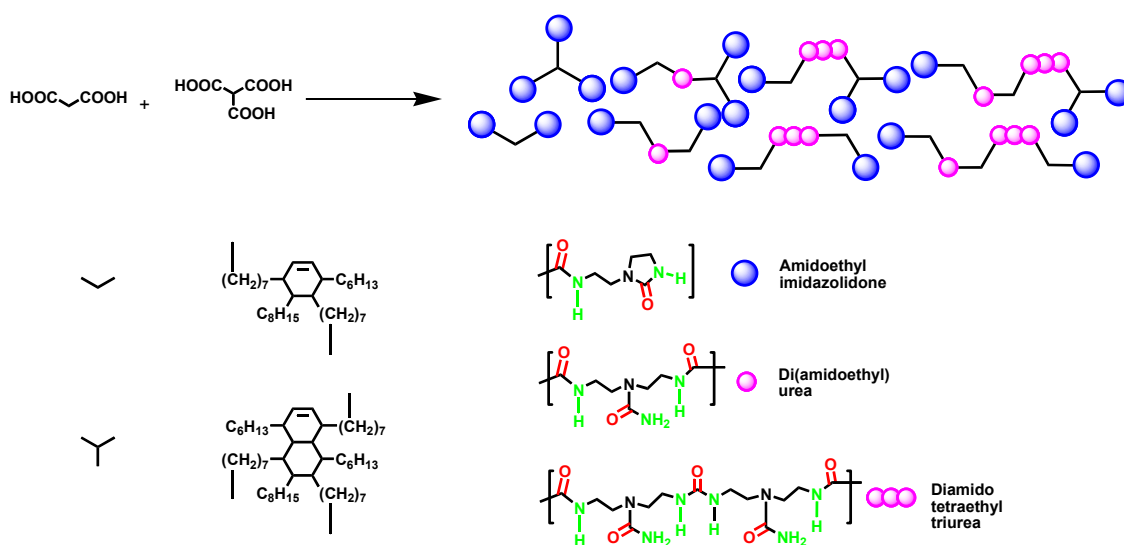
Hydrogen bonds play a crucial role in a living organism by contributing to the stability of proteins and the specificity of protein–protein and protein–ligand interactions. H-bonding is mainly due to electrostatic interaction; the donor atom effectively shares its electrons with the acceptor atom, forming a bond. Because of such an extensive hydrogen bonding, water is a liquid over a far greater range of temperatures than would be expected for a molecule of its size. Typical bonding energy for H-bonding interaction is in the range of 5–30 KJ mol<sup>−1</sup>, which is approximately 10 times lower compared to the covalent bonds (approx. 345 KJ mol<sup>−1</sup> for C–C bond). Even though with lower bonding energy compared to a covalent bond, the H-bond has a great influence on polymer viscoelastic properties, phase separation, and degree of crystallinity [44]. A limited number of H-bonds are not sufficient enough to exhibit a required property. However, desired properties can be achieved by the fine-tuning degree of H-bonding interactions and rigidity in the polymer backbone [45].

## 3. Self-Healing Material via H-Bonding Interactions

### 3.1. Self-Healing Using 2-Aminoethyl-Imidazolidone (UDETA)

The first self-healing phenomenon for network/rubber using H-bonding interactions was reported by Leibler et al. [46,47]. In this work, the authors reported the synthesis of self-healable thermoreversible rubber in two steps, using a fatty diacid and triacid “Empol 1016 and Pripol 1017” (made from renewable sources), diethylenetriamine, and urea. In the first step, acid functionality was condensed with controlled excess of diethylenetriamine. The obtained product was reacted with urea in the second step (Figure 1). The Association of H-bonding in the final product leads to the formation of

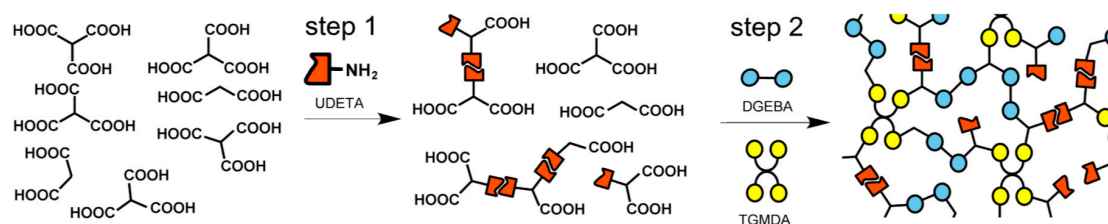
translucent glassy plastic. It behaves like a soft rubber and exhibits strain at breaking of about 350% when heated to 90 °C, and undergoes self-healing under RT.



**Figure 1.** A fatty diacid and triacid mixture is condensed first with diethylenetriamine and followed by a reaction with urea, giving a mixture of oligomers furnished with complementary hydrogen bonding groups: amidoethylimidazolidone, di(amidoethyl) urea, and diamidotetraethyltriurea. The hydrogen bond acceptors are shown in red, and donors in green.

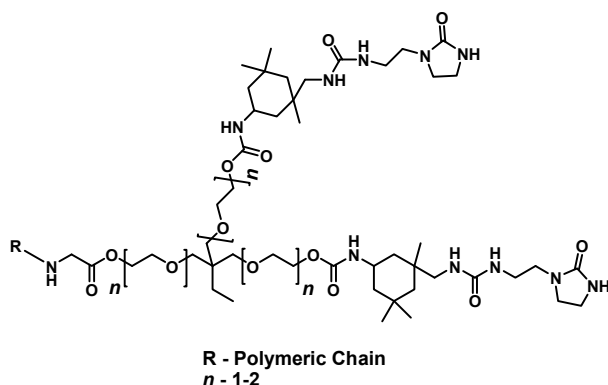
Combining substantial physical crosslinks via complementary hydrogen bonds exhibits significant self-healing properties in a supramolecular system, however, they exhibit inadequate solvent and creep resistance mostly due to the absence of covalent crosslinks [6,48]. To overcome this problem, supramolecular hybrid networks, combining covalent and non-covalent crosslinks, have been developed [49,50]. Montarnal et al. reported a synthesis of such hybrid networks by a combination of supramolecular and epoxide chemistry [49]. The authors reported the preparation of material by condensation reactions using three different monomers, including a mixture of polycarboxylic fatty acids (mainly diacids and triacids), a H-bonding heterocyclic primary amine, 2-aminoethylimidazolidone (UETA), and a diglycidyl ether of bisphenol A (DGEBA). However, the system faced a limitation where an increase in the number of H-bonding groups caused a reduction in the number of crosslinks. They prepared a composition by incorporating 50 mol% of UETA and 6 mol% of 2-methylimidazole as a catalyst (a composition referred to as HN-50-HC). Initially, this composition did not exhibit a gel point and behaved like a liquid at room temperature. Eventually, a successful composition of a network was synthesized, exhibiting a self-healing property, however, all these were achieved at the cost of a rather uncontrolled process and lengthy cure cycles.

In order to address the issue of no gelling of a network, Sordo et al. [51] reported a modified approach using almost similar monomers. Moreover, in this approach, instead of using only one diepoxide, they incorporated a combination of bifunctional diglycidyl ether of bisphenol A (DGEBA) and a tetrafunctional 4,4'-methylenebis(*N,N*-diglycidylaniline) (TGMDA), as shown in (Figure 2). In this method, supramolecular hybrid networks were synthesized through a well-controlled curing cycle in which the number of H-bonding groups was varied at will, and the conversion at the gel point was determined by the number of monomers. In this way, the number of chemical crosslinks was increased in a controlled manner in a catalyzed systems without changing the concentration of H-bonding groups to preserve a high self-healing ability.



**Figure 2.** A synthetic strategy used to generate insoluble hybrid networks containing a fixed amount of terminal H-bonding groups and a tunable amount of chemical crosslinks. Step 1: partial amidation of poly(carboxylic acids) with a fixed amount of the H-bonding molecule UDETA. Step 2: crosslinking with a variable amount of the difunctional DGEBA and tetrafunctional TGMMA epoxy resins. Reprinted with permission from [51] Copyright 2015, American Chemical Society.

Inspired by the aforementioned concept of Leibler et al. [46,47], Wittmer et al. developed a moisture-mediated intrinsic self-healing polyurethane urea polymer using a similar H-bonding monofunctional amine, 2-aminoethylimidazolidone (UDETA) [52]. The self-healing molecule UDETA was covalently fixed onto a polymeric network carrying bonding sites for hydrogen bond formation (Figure 3).



**Figure 3.** Chemical structure of the self-healing polymer.

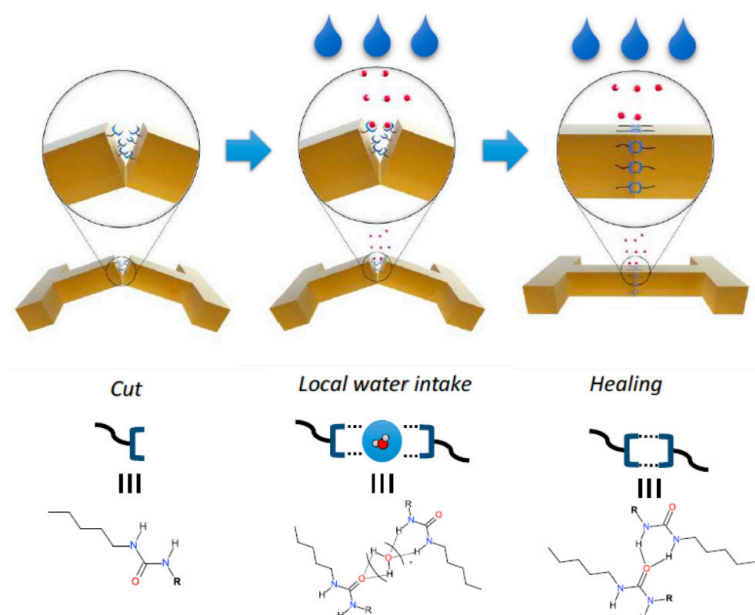
Polymers with varying UDETA content 0–34 mol% were prepared, and self-healing ability was studied. Prepared polymers were applied on aluminum Q-panels with a dry film thickness (DFT) of 60  $\mu$ m. Coated panels were damaged with an Erichsen cupping tester. Damaged samples containing 0, 22, 30, and 34 mol% UDETA were equilibrated for 24 h at 23  $^{\circ}$ C and 50% relative humidity (RH). Only the samples containing 30 and 34 mol% UDETA exhibited self-healing property after 24 h at 23  $^{\circ}$ C and 50% RH.

### 3.2. Moisture-Mediated Self-Healing Coating

In a follow-up study, Wittmer et al. [53] applied similar chemistry of UDETA based polymer to develop and demonstrate moisture and temperature mediated self-healing polyurethane-urea polymer. Additionally, they demonstrated its possible application of self-healing coating in corrosion protection and as a dampening material. Self-healing was studied by measuring gloss at 20 $^{\circ}$  before and after healing. Corrosion protection was evaluated by performing a salt spray test (SST) according to ASTM B117 for a time period of 7 days.

In yet another approach, Willocq et al. reported [54] moisture-driven self-healing urea-based polyurethane (Figure 4). Wherein a robust method was presented on the basis of dynamic urea moieties, and water molecules interchange triggered an autonomous self-healing process. The mechanism described is fairly simple, i.e., when the polymeric material gets damaged by an external factor, it releases free-standing urea functionalities at their surface that quickly interact with water molecules present in the atmosphere. The local plasticization effect occurred at the damaged site and gradually

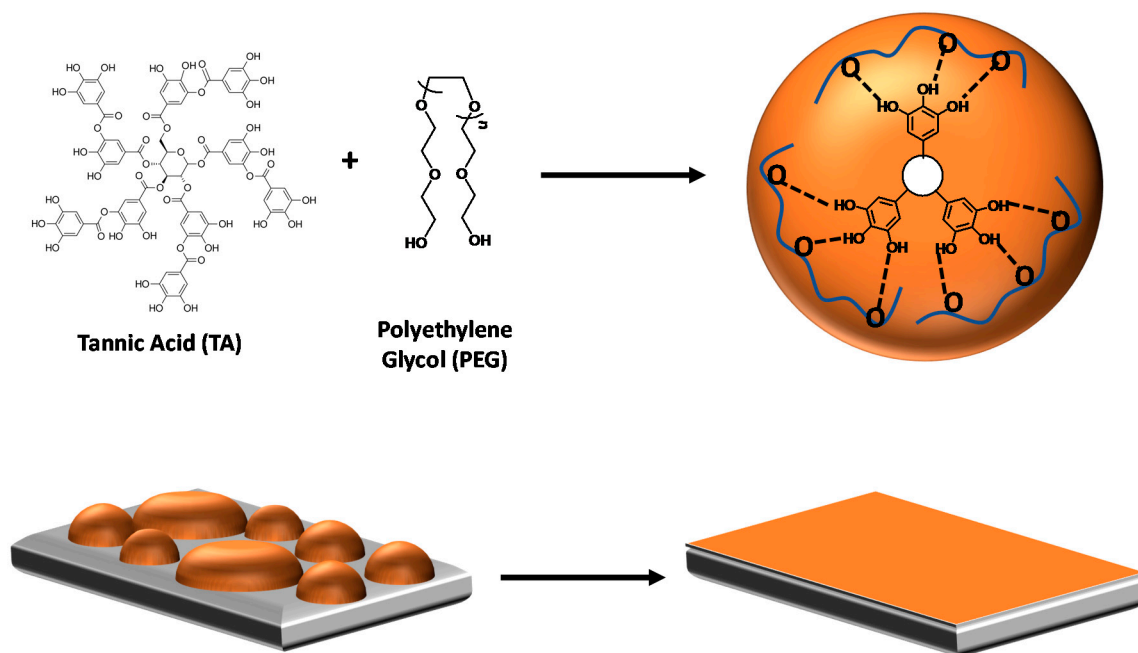
sealed the area upon the reformation of intermolecular clusters between urea-based functionality, consequently favoring the release of water molecules from the surface. The prepared urea-based polyurethane was insoluble in water, however, it retained some water molecules on exposure to ambient humidity. Due to this reason, when the damaged film was introduced to RT and RH of 45%, it exhibited self-healing within 18 h. In the current system, the healing time was reduced to 7 and 4 h when the film was exposed to RH of 69 and 97%, respectively.



**Figure 4.** Schematic illustration of the moisture-driven healing mechanism of the urea-based polyurethane: (i) release of free-standing urea moieties at the damage sites, (ii) establishment of hydrogen bond bridges, as assisted by water, between the free-standing urea moieties, and (iii) reformation of intermolecular clusters between urea-based moieties as water is expelled from the non-hygroscopic polyurethane. Reprinted with permission from [54] Copyright 2019, American Chemical Society.

Moreover, Du et al. [55] reported a facile water triggered self-healing coating on various substrates by coalescing of the precipitated hydrogen-bonded complex of tannic acid (TA) and polyethylene glycol (PEG) in aqueous media (Figure 5). TA being a natural polyphenol, exhibits a high binding affinity to various substrate [56–58] as well as antioxidant properties [59]. Typically, the coating was prepared by mixing TA and PEG aqueous solutions (each one 1.5 mL, 10 mg mL<sup>−1</sup>, containing 0.5 NaCl). TAs associated with PEGs to form stable and insoluble complexes. The formed assemblies quickly precipitated out and coalesced with one other by hydrogen bonding on the bottom substrate to form a soft coating layer. However, after drying, the coating exhibited mechanical robustness and strong adhesion to different substrates due to enhanced hydrogen-bonding interactions. Moreover, again in the presence of water or a moist environment, the coating becomes soft and healable within a short period at RT. The coating is capable of healing micrometer size cracks rapidly and repeatedly. The ideal coating was fabricated with 20 kDa PEG and maintaining a mass ratio (MR) of TA/PEG as 1. The various organic and inorganic substrates can be coated with TA/PEG coating due to high binding affinity to the various substrate [59]. The coating can also serve as an adhesive to two same substrates. The adhesion strengths of the TA-PEG coatings to stainless steel, glass, PS, and PET substrates were found to be 0.76, 0.59, 1.08, and 1.91 MPa, respectively. Besides this, the coating can inhibit the oxidation of the coated substrate before the complete oxidation of TA molecules. Such coatings could find applications in surface modification, material protection, and electronic packaging.





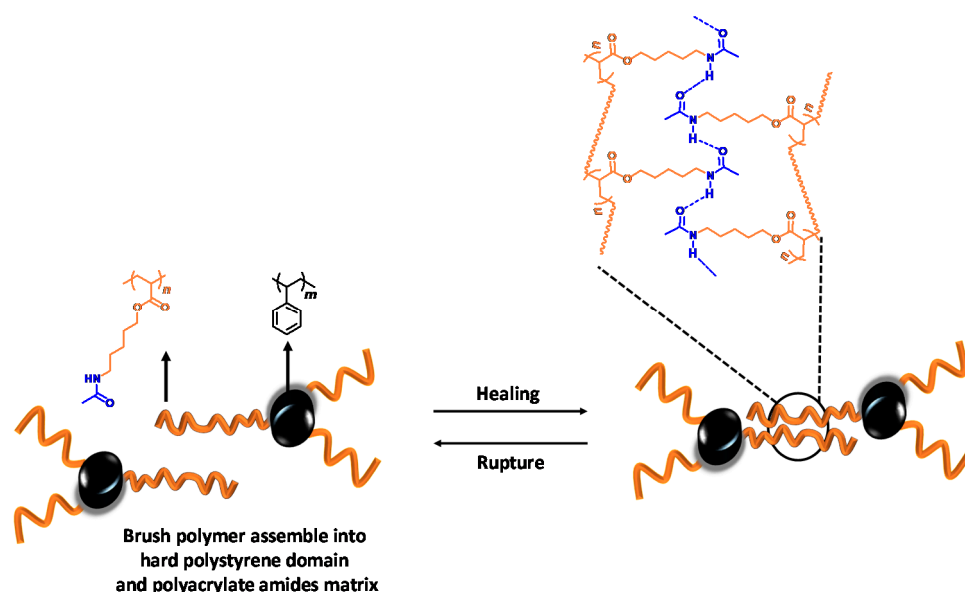
**Figure 5.** Schematic representation of the formation of TA-PEG hydrogen-bonded complexes and the fabrication of the coating.

### 3.3. Trigger Free Self-Healable Brush Polymer

Brush polymers are another type of interesting macromolecule that shows a wide range of applications as an antibiofilm forming, antifouling, and antibacterial in coatings [60]. Chen et al. demonstrated and developed RT self-healing hydrogen-bonded brush polymer (HBP) without the need of any plasticizer, solvent, external stimulus, or healing agent [61]. This brush polymer consists of the same combined unique properties (stiffness and toughness) as those of hybrid polymers with a self-healing capability of supramolecular assemblies. HBP consists of polystyrene (hard backbone) with higher ( $T_g$ ) and polyacrylate amides (soft brush), with lower ( $T_g$ ) as hydrogen bonding motifs for dynamic supramolecular assembly. The dangling secondary amide functional group was synthesized easily and able to form a dynamic network, possessing both hydrogen bond donor and acceptor motifs. The HBP collapsed into a core-shell nanostructure with a hard-polystyrene core and a soft polyacrylate amide (PA-amide) shell when processed from a polar solvent. The hydrogen-bonding directed supramolecular assembly of the PA-amide brushes leads to the formation of a microphase-separated nanostructure having dynamic characteristics that can be broken and reformed, affording a spontaneous self-healing behavior (Figure 6). The authors designed three HBPs. The most balanced HBP exhibited the tensile strength of 1.92 MPa, strain-at-break at 780%, and self-healing efficiency of greater than 90%.

### 3.4. Ureidopyrimidone (UPy) Based Self-Healing Coating

UV radiation has been widely used to cure coating for many years. The UV-curing process exhibits several distinguished advantages, including a rapid curing rate, low volatile organic compound (VOC) emission, high efficiency (energy, labor, and space), the possibility of curing heat-sensitive substrates, and so on, along with providing protective, durable, and attractive finishes. In recent years, UV-curing has developed rapidly in many applications. The technology is now widely used in coating [62–66], electronic engineering [67], and printing industries [68].



**Figure 6.** Schematic representation of self-assembled HBP into core-shell morphology and supramolecular connections between soft brushes via hydrogen bonding interactions and its rupture under stress.

Hydrogen bonded dimerization of ureidopyrimidone (UPy) monomer was first reported by Meijer [69,70] and has been used in numerous supramolecular polymers with distinct properties and applications. UPy motifs that dimerize strongly via quadruple hydrogen bonds have been demonstrated to synthesize self-healing materials [71–75]. Ren Liu et al. [76] introduced a combined system where curing was achieved through UV irradiation and self-healing through UPy based dynamic quadrupolar hydrogen bonds. Self-healable oligomers were prepared by reacting Tri-HDI as a core with PCDL500 as a chain extender. THPU<sub>x</sub>C<sub>y</sub> was fabricated by grafting THP with varying content of UPY-NCO and IPDI-HEA (Figure 7). The authors prepared five self-healing compositions of coating; out of these THPU<sub>20</sub>C<sub>80</sub> exhibited enhanced healing performance. The coating exhibited an ability to repair in a short period using a hot air gun. The coating remarkably self-healed scratches with a depth from 3–4 mm. Healing efficiency varied depending upon the thickness of the coating. The coating with 81 mm, 110 mm, and 207 mm revealed healing efficiency of 80%, 92%, and 96%, respectively.

In a follow-up publication, Gao et al. [77] reported a similar kind of self-healing polyurethane coating based on UPy motifs. In this work, they have prepared UPy and methacrylic terminated polyurethane (PU) based on polycarbonate diol with varying molecular weight. The coating was cured in the presence of various acrylic reactive diluents using UV irradiation. It was investigated whether a coating comprising of PCDL2000-PU-UPy exhibited the highest healing efficiency. This was attributed to increased hydrogen bond content in longer PU chains [78]. Furthermore, outstanding mechanical and self-healing properties were obtained when 20 wt.% of triethoxylated trimethylolpropane triacrylate was used as a reactive diluent. The self-healing efficiency of PCDL-PU-UPy-TMP3EOTA-10, PCDL-PU-UPy-TMP3EOTA-20, and PCDL-PU-UPy-TMP3EOTA-30 coatings was calculated to be 98.1%, 95%, and 70% respectively, as quantified using the scratch depth that was healed.

Recently, J. Liu et al. [79] developed a stiff self-healing coating based on UV-curable polyurethane (PU) having a hard core and flexible arm. Isocyanate terminated prepolymers were synthesized using 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or polycarbonate diol (PCDL) of varying molecular weight (500, 1000, and 2000 Da). Isocyanate and acrylic terminated polymer was grafted on chemically modified cyclotriphosphazene as a core. The oligomer prepared consists of a rigid aromatic ring as hard core and long chains as a flexible arm.

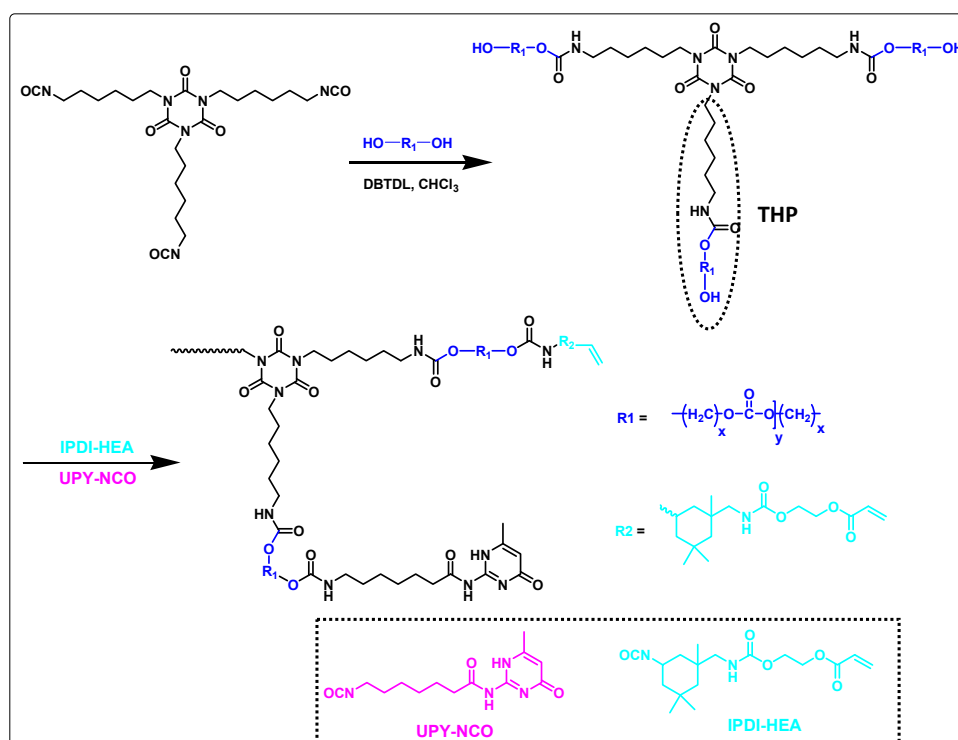
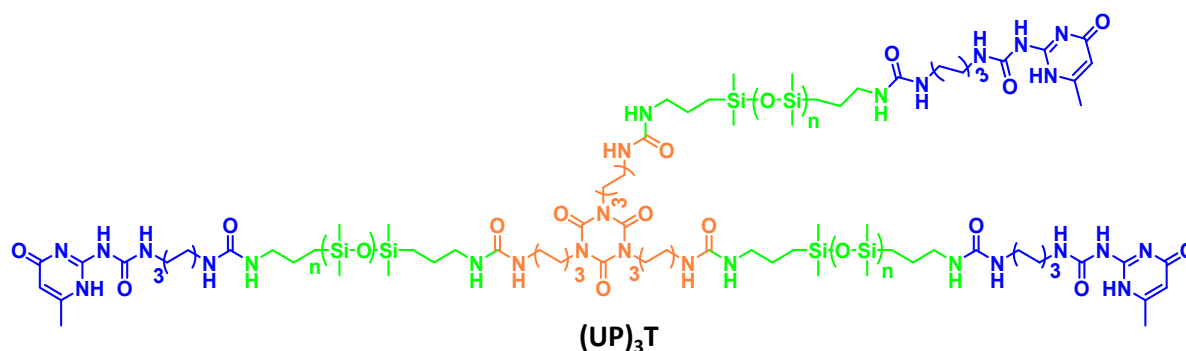


Figure 7. Synthetic scheme of THPU<sub>x</sub>C<sub>y</sub>.

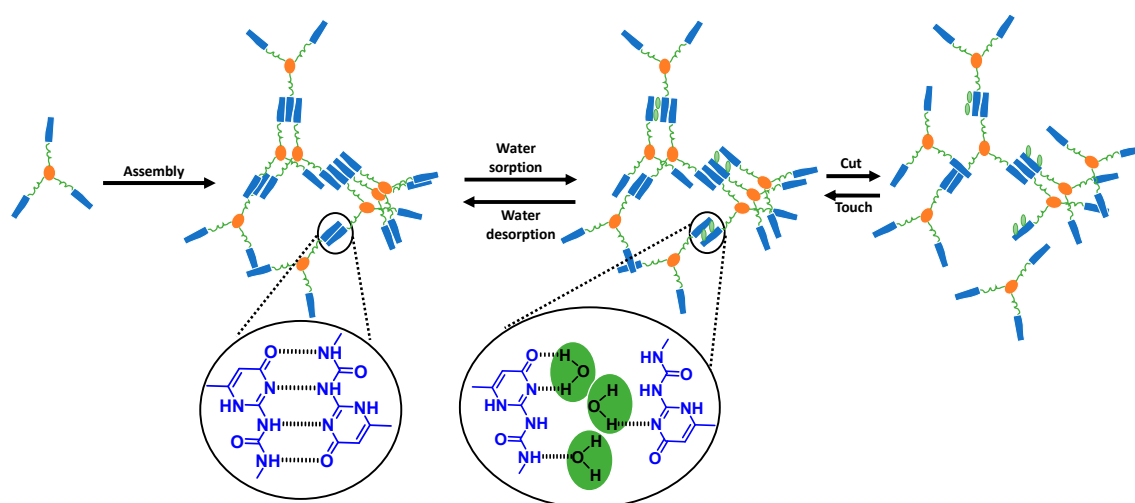
Polydimethylsiloxane (PDMS) containing polymers and elastomers demonstrate outstanding properties such as waterproofing, chemical resistance, and biocompatibility. Due to these reasons, they are widely used in varied fields such as coating, electronics, automobiles, food industry, and biomedical [80–84]. In this context, M. Liu et al. [85] demonstrated the synthesis of healable silicone material (Figure 8) via a hydrogen bonding assembly mechanism with improved mechanical properties. The unique feature of this design was that presence of water enhanced the healing process due to the dissociation/association of H-bonding interactions (Figure 9). Again ureidopyrimidinone (UPy) was used as a H-bonding motif. These units formed a dimer via complementary quadruple hydrogen bonding [86,87], and the presence of UPy on trifunctional oligomer undergoes network formation with a high crosslinking density. The resulting (UP)<sub>3</sub>T films exhibited a high Young's modulus  $\sim 47.39 \pm 1.03$  MPa and storage modulus  $\sim 151.4 \pm 10.7$  MPa. It was discovered that healing efficiency increased with an increase in relative humidity, higher temperature, and longer healing time. When the healing process was carried out in the air (RH  $\sim 35\%$ ), the healed samples exhibited strength recovery to 5.46 MPa over 12 h at 70 °C, whereas, the sample could simply bind to each other when they were put in humid air (RH  $\sim 90\%$ ). When the healing process was carried out underwater, the healing process was enhanced significantly. It was observed that to heal a sample at 86% recovery required 4 days at 20 °C, whereas underwater, it only required 5 min for the healed sample to reach the same quality as pristine at 70 °C. To date, this is the fastest reported silicon healing material with a healing efficiency of above 90%.

In a follow-up study, M. Liu et al. [88] developed damage-healable, oil-repellent supramolecular silicone (DOSS) coatings by molecular engineering siloxane oligomers to self-assemble onto coated substrates via multivalent hydrogen bonding. Besides the healing property, the coating exhibited robust repellency to organic liquids, along with strong interaction with various substrates that include metals, plastics, and even Teflon due to the unique molecular configuration of the siloxane oligomers.





**Figure 8.** Molecular structure of siloxane oligomer (UP)<sub>3</sub>T.

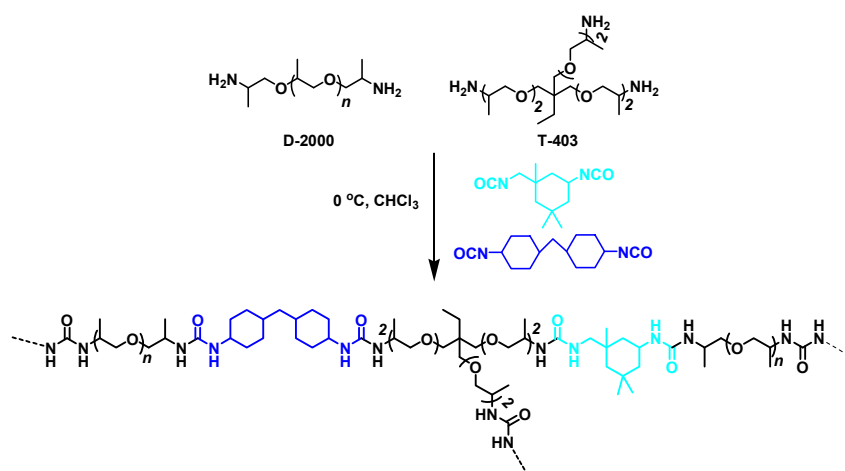


**Figure 9.** Representing self-assembly of (UP)<sub>3</sub>T units into a network via the dimerization of UPy and the assembly of UPy stacks (blue). UPy dimers and stacks dissociate and undergo an exchange with water molecules (green dots) upon water sorption to release free UPy motifs. UPy dimers and stacks reform and finally heal by water desorption.

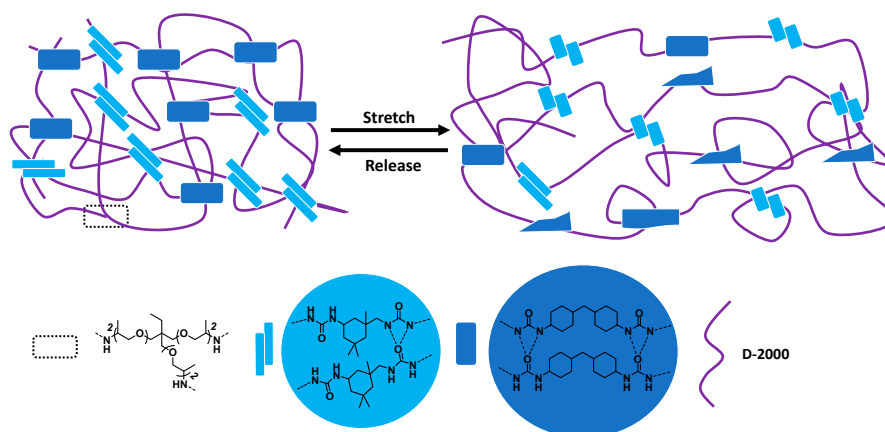
### 3.5. Self-Healing Transparent Coating

A self-healing coating for an optical and electronic device is of great interest among industries and academics. However, designing such a self-healing optical material is a highly ambitious goal, because the coating should satisfy at least some of the following essential criteria: (a) be able to heal multiple events of damage repeatedly, (b) able to recover all the physical and mechanical properties of the material after damage recovery, (c) enhance the sustainability of material, (d) able to recover the damage at low to high levels of severity, (e) have position-specific activation only when and where necessary, and (f) should be economical and suitable for mass production [89]. Inspired by such challenges, one such approach was recently demonstrated by Zhang et al. [90]. They designed and synthesized transparent supramolecular polyurea elastomers in a facile one-pot polycondensation fashion (Figure 10). The prepared elastomers combined covalent crosslinks and multi-strength hydrogen bonds with varying ratios. Mechanical and self-healing properties of elastomers were optimized by adequately controlling the ratio of weak and strong hydrogen bonding interactions (Figure 11). By virtue of this, self-healing can be achieved at RT within 6 h, without loss of mechanical strength and any manual intervention. The authors reported the synthesis of four different polyurea elastomers with varying compositions of IPDI and HMDI. Out of these, DT-IPDI<sub>2</sub>-HMDI<sub>1</sub> exhibited the highest self-healing efficiency (>98%) and elongation at break (2000%). The outstanding healing ability was attributed to the substantial difference between weak and strong dynamic hydrogen bonds in the

elastomers. The authors also demonstrated the self-healing property of a coating by painting the DT-IPDI<sub>2</sub>-HMDI<sub>1</sub> on the optic lens. The coating revealed a superior transparency of 93%.



**Figure 10.** Synthetic scheme of the self-healing polyurea elastomer.



**Figure 11.** A schematic representation of DT-IPDI<sub>x</sub>-HMDI<sub>y</sub> elastomer, highlighting the covalent links and the strong and weak reversible hydrogen bond derived from the urea groups.

In yet another approach, Jucius et al. [91] developed a hydrogen-bonding-assisted scratch-healing transparent coating based on partially crosslinked poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA), that could have a potential application as a high-performance transparent material in the field of optoelectronic applications. The colorless viscous coating was simply prepared by mixing PVA and PAA with a molar ratio of hydroxyl groups to carboxyl groups in the range of 3:1–1.5:1. The coating was applied via the Meyer rod coating method [92] on a pretreated glass slide and kept in the oven for 30 min at 35 °C followed by thermal crosslinking at 150–170 °C for 5 min. The initial experiment revealed that the best result was obtained for PVA–PAA polymer coatings fabricated with a molar ratio between hydroxyl and carboxyl groups of 1.5:1. The coating was cured at 150 °C for 5 min exhibited a damage healing at 20 °C for 24 h (@ RH-40%), a scratch-healing ratio of 96.3–99.2% was achieved for a scratch constant loading of 1.2 N, 1.5 N, 1.8 N, and 2.7 N. Healing time was drastically diminished to 30 min when RH was increased from 40 to 99%. This is due to the hydrophilic and hygroscopic nature of PVA–PAA coatings. More water molecules from the surroundings get attracted at a higher RH of 99%; as a consequence, more rapid chain diffusion occurs across the scratch interfaces and association of the hydroxyl groups to reform multiple hydrogen bonds, thus resulting in the more rapid scratch recovery process. Table 1 highlights the polymeric backbone used, their physical properties, healing conditions, and healing efficiencies.

**Table 1.** Self-healing system based on hydrogen bonding interactions: physical property, healing condition, healing efficiency, and appearance (NA—not available).

Polymer	Tg °C	Healing Condition	Healing Efficiency (%)	Appearance	Ref.
Polyurethane Urea	5–25	24 h, RH 50%, RT	NA	Transparent	[52]
Polyurethane Urea	−1 and 69	6 days, RH 90%, RT, and 24 h, 80 °C	NA	Transparent	[53]
Urea based polyurethane	12	4 h, RH 97%, RT	NA	Transparent	[54]
Tannic acid (TA)-polyethylene glycol (PEG)	NA	5 min, water, RT, and 30 min, RH 100%, RT	NA	Transparent	[55]
Polystyrene and polyacrylate amide-based brush polymer	2–5	24 h, Ambient conditions	92	Non-transparent	[61]
UV curved polyurethane	15–25	Healed using heat gun for 1 min with temperature set of 170 °C at a 10 cm distance to surface	96	NA	[76]
UV curved polyurethane	NA	1–2 min, 70 °C	98	NA	[77]
UV-curable polyurethane	15.5	5–10 min, 100 °C	NA	NA	[89]
Silicone based	34	5 min, water, 70 °C 12 h, RH 90%, 70 °C	>90	Transparent	[85]
Polyurea elastomer	−57	6 h, 25 °C	>99	Transparent	[90]
poly(vinyl alcohol) and poly(acrylic acid) complex	NA	24 h, RH 40%, RT and 30 min, RH 90%, RT	>95	Transparent	[91]
Polyethylenimine /poly(acrylic acid) complex	NA	30 min, water, RT	NA	Transparent	[93]
poly(acrylic acid) and poly(ethylene oxide) solution complex	NA	30 min, pH 2.5, RT	NA	Transparent	[94]
poly(acrylic acid) and poly(ethylene oxide) bulk complex	20.5	24 h, RH 90%, RT	>95	Transparent	[95]
(PDMS-COOH) and (PEGDGE) complex	0.5	6 h, RT	>97	Transparent	[96]

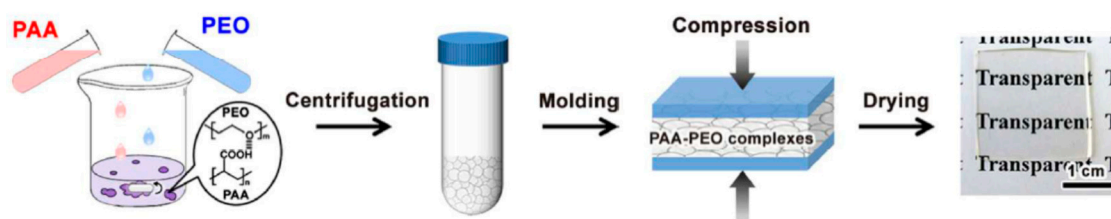
#### 4. Self-Healing via Carboxylated-Bonded Supramolecular Interactions

Carboxyl groups have been utilized to form supramolecular motifs to induce self-healing properties. One such role of carboxylic acid groups in preparing transparent, self-healing, antibacterial film was demonstrated by Wang et al. [93], by fabricating a layer-by-layer assembly of branched polyethylenimine (bPEI)/poly(acrylic acid) (PAA) on a glass surface. The antibacterial property was achieved by loading encapsulated triclosan on the coating. The main driving force for film formation was by electrostatic interaction and hydrogen bonding between the amine and carboxylic acid groups. The film was able to heal the scratches completely after immersing triclosan-(bPEI/PAA)\*30.5 coated glass underwater for 30 min. Alternatively, scratches on the film could be healed by spraying water on the damaged film. The film had the ability to heal multiple times on repeated damage at the same location. The incorporation of triclosan-loaded cetyltrimethylammonium bromide (CTAB) surfactant micelles did not alter the self-healing ability of the LbL-assembled bPEI/PAA films, which was attributed to the high ability of bPEI and PAA to flow and recombine in water.

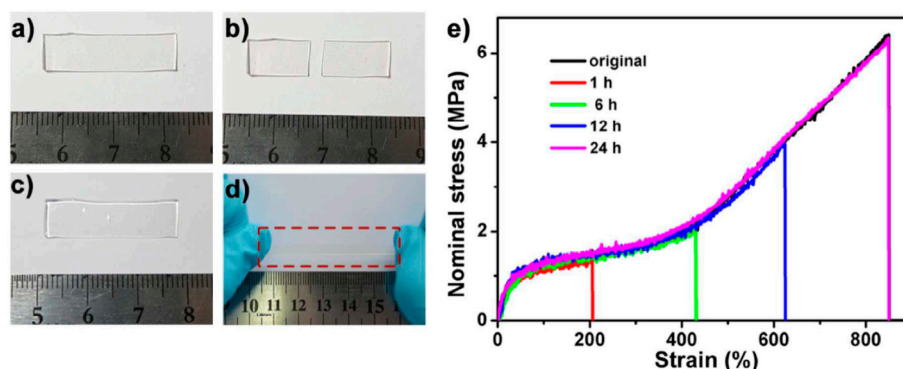
In follow-up research work, Wang et al. [94] demonstrated a proof-of-concept that layer-by-layer assembly of poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) produces hydrogen-bonded transparent PAA/PEO films. Scratches on film were healed after immersing the film in acidic water for 30 min, and more importantly, when the scratch surpassed the capability to repair, the damaged film could be erased off from the substrate. The easy decomposition of film from substrate means the film can be easily replaced with a new one when the damage is beyond repair. The advantage of PAA/PEO film above reported PAA/PEA film is that the PAA/PEO films have a stronger ability to heal broader and deeper cuts made by a scalpel.

Polymer complexes are formed at the interfaces of solid substrates and polymer solutions when polymer film is fabricated by layer-by-layer assembly [97–102]. It was envisioned that when polymer complexation was carried out in bulk via non-covalent interactions, can lead to polymer composites with healing characteristics [103,104]. Compared to a solid film formed at the interfaces of solid substrates and polymer solutions, polymer complexation made-up in bulk will favor a high degree of chain entanglements in the resultant composite materials, especially when polymers with high molecular weights are used. This composite material exhibits enhanced mechanical strength, owing to the entanglement of polymer chains in a cross-linked polymer network [105,106]. Additionally, the presence of reversible non-covalent bonds in the composite materials leads to dynamic break and reform upon external stress, thereby facilitating the unfolding and sliding of the polymer chains during deformation and thus endowing the composite materials with good elasticity [107]. Inspired by the above-described concept, Wang et al. [95] demonstrated the creation of transparent, healable elastomers with high mechanical strength and elasticity by simply complexing high-molecular-weight poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) (Figure 12). The elastomer fabricated from the hydrogen-bonded PAA-PEO complexes exhibited high transparency, water-triggered healability, and a high mechanical strength (true strength at break) and toughness (fracture energy) of 61 MPa and 22.9 kJ/m<sup>2</sup>, respectively. Elastomer PAA1.4/450k-PEO1.0/600k was cut into two pieces and brought back in contact, and healing was carried out at RT and RH of 90%. The sample was healed completely and restored mechanical performance equivalent to a pristine sample after 24 h of healing (Figure 13). Damaged composite materials were also self-healed under ambient RH (30–50%). However, a longer healing time (over 7 days) was required as compared to an elevated RH condition.

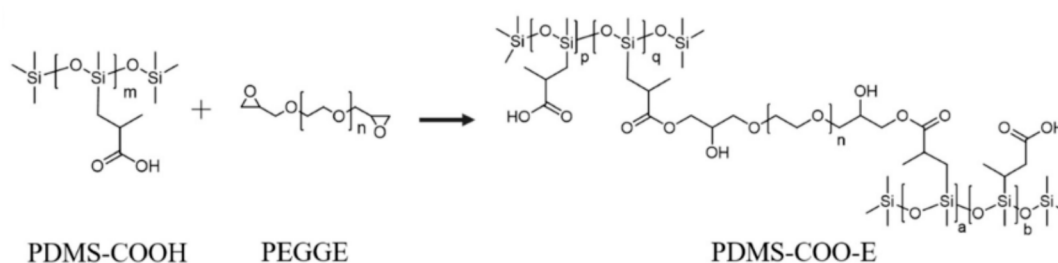
Polymeric materials possessing shape memory along with self-healing properties (dual-functional) has attracted increasing interests of researchers [12,108,109]. Lai et al. [96] demonstrated the effect of carboxylated hydrogen bonding and shape memory of the polymeric system to exhibit self-healing phenomena at body temperature. A three-dimensional crosslinked network was simply prepared by reacting PDMS-COOH linear chains with poly(ethylene glycol) diglycidyl ether (PEGDGE) in a stoichiometric ratio of 1:0.015, respectively (Figure 14). The obtained polymer film has ample hydrogen bonds and was transparent in nature, showing a transmittance of greater than 85% in the visible range. The network exhibited outstanding mechanical properties in addition to excellent self-healing properties, mainly due to the presence of abundant hydrogen bonding interactions. The sample can be healed with the healing efficiency of close to 100% in 6 h at 25 °C. Mended material exhibited properties equivalent to an undamaged sample (Figure 15).



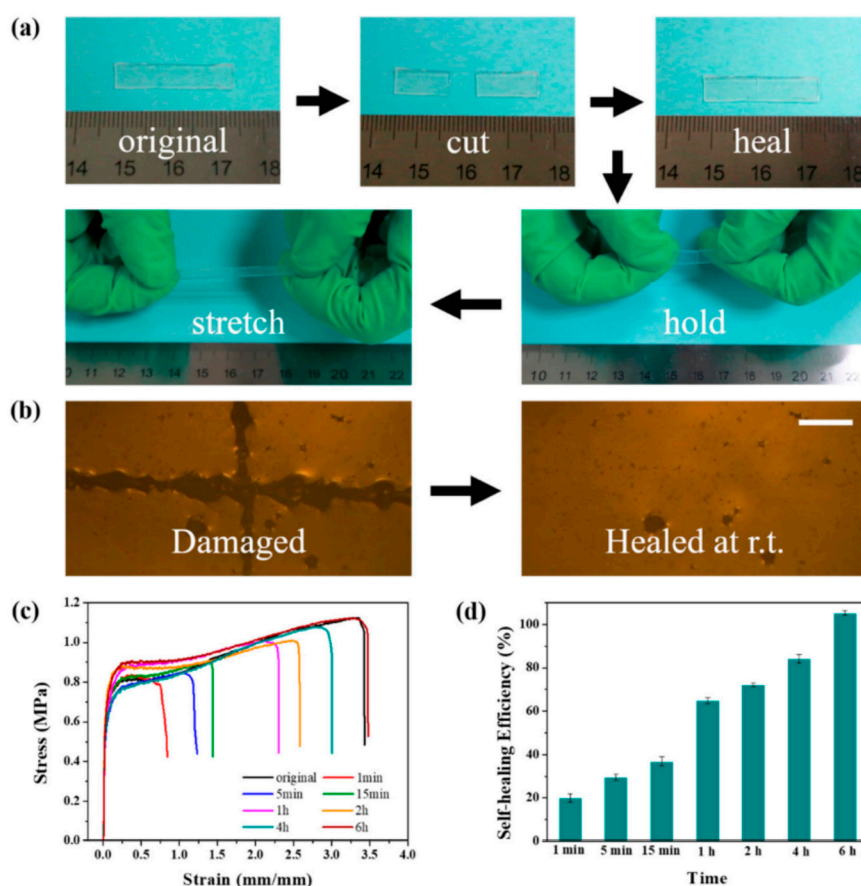
**Figure 12.** Schematic illustration of the preparation process of the PAA-PEO elastomers based on the hydrogen-bonding complexation between PAA and PEO. Reprinted with permission from [95] Copyright 2017, American Chemical Society.



**Figure 13.** Photos of the PAA1.4/450k-PEO1.0/600k composite sheet before (a) and after (b) being cut into two pieces. Photos of the 1 h healed PAA1.4/450k-PEO1.0/600k sample before (c) and after (d) being stretched to a 175% strain. (e) Stress-strain curves of the pristine and 1 h, 6 h, 12 h, and 24 h healed samples. Reprinted with permission from [95] Copyright 2017, American Chemical Society.



**Figure 14.** Synthetic scheme for PDMS-COO-E polymer [96].



**Figure 15.** (a) Digital images of cutting-healing-stretching procedure of PDMS-COO-E films at 25 °C. (b) Microscopic images of a film before (left) and after (right) healing at 25 °C for 6 h. Scale bars, 100 mm. (c) Uniaxial tensile tests of PDMS-COO-E before and after healing at RT for a different time. (d) Self-healing efficiencies of PDMS-COO-E samples self-healed for varying times at 25 °C [96].

## 5. Conclusions and Outlook

This review emphasized and covered the recent trends in self-healing polymers and coatings exclusively via dissociation and re-association of hydrogen bonding interactions. It can be concluded from the examples discussed in this review is that water and heat play a crucial role in softening and mobility of polymeric chains; as a consequence, dissociation and re-association of hydrogen bonding interactions take place, leading to a healing mechanism. It has been demonstrated that this interaction is highly versatile and advantageous for the fabrication of transparent self-healing coatings capable of undergoing multiple healing cycles at a relatively moderate temperature range. However, there needs to achieve a profound understanding of the self-healing mechanism, enhancement in the self-healing efficiency, duration of mending, a dimension of crack, and recovery of mechanical properties after damage to address the issues relating to real-world applications.

Developing and embracing hydrogen-bonded intrinsic self-healing material in a feasible way is difficult, challenging, and far from the reality due to obvious reasons. Future work on self-healing polymers should focus on (a) improving mechanical properties of the material, (b) envisioned self-healing properties within an hour or even quicker at relatively moderate temperature, (c) accomplishing macro-damage repair and capability to heal under extreme weathering conditions, (d) incorporating self-healing properties into multifunctional materials such as antibacterial, antifouling, anticorrosion, anti-icing, antifogging, and transparent coating for optoelectronics and other applications. Therefore, we foresee that the constant improvement of the chemistries involved and the advances of rational



solutions to the above-mentioned challenges may drive the field towards practical applications in the longer term.

Nonetheless, we can expect that in the near future, currently developed materials may find applications as self-repairing materials and serve the purpose for the micro or milli-scale damages or as a repairable material for shorter-lived applications.

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