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Basic physicochemical processes governing self-healable polymers†

Siyang Wang and Marek W. Urban*

Abstract

This short review outlines basic chemical and physical principles that can be utilized in the development of self-healing polymers. Physical processes include the interdiffusion of polymer chains, the introduction of phase-separated morphologies, shape memory effects or incorporating active nanoparticles into a polymer matrix. Dynamic covalent, free radical or supramolecular bonds are predominantly chemical processes. However, self-healing will also involve a combination of physical and chemical events, such as taking advantage of enhanced van der Waals forces resulting in inter-digitated copolymer morphologies or embedded reactive encapsulated fluids that burst open upon damage to fill up a wound. Sufficient molecular mobility for autonomous self-healing under ambient conditions can also be achieved while maintaining high strength and stiffness in precisely designed commodity polymers. The efficient storage and recovery of conformational entropic energy stored during damage or excess of surface energy resulting from damage will drive the reduction of newly generated interfaces created upon damage by shallowing and widening wounds until healed.

Keywords: physicochemical self-healing mechanisms; autonomous self-healing; role of enthropic recovery on self-healing; self-healable polymers

Self-healing is the ability of materials to autonomously recover from physical damage. The general approaches to self-healing can be classified as physical (Fig. 1(a)) and chemical events (Fig. 1(b)), but there is a significant degree of overlap between the two approaches (Fig. 1(c)). A goal of these chemical and physical events[1–3] is to create self-healing materials that will last and function longer. Physical self-healing includes processes such as interchain diffusion,[4] restructuring in phase-separated morphologies,[5,6] shape memory effects (SMEs)[7] or embedding superparamagnetic nanoparticles.[8] Introductions of dynamic covalent,[9–13] free radical[9,10] or supramolecular[6,14–20] bonds are predominantly chemical processes. However, self-healing will also involve a combination of physical and chemical events, such as taking advantage of enhanced van der Waals (vdW) forces[21] resulting in inter-digitated copolymer morphologies (Fig. 1(c1)), embedded reactive encapsulated fluids that burst open upon damage to fill up a wound (Fig. 1(c2))[22] or using the same concept in cardiovascular networks (Fig. 1(c3)).[23]

Historically, crack healing in thermoplastic polymers (Fig. 1(a1)) was considered as a five-stage process: segmental surface rearrangements, surfaces approaching each other, wetting, diffusion and randomization.[4,24] Although the importance of vdW interchain forces in thermoplastics has been recognized for a long time, only recently were they recognized as a driving force in self-healing polymers.[21] This concept formulated the strategy for the use of these ubiquitous vdW dipolar interactions to obtain self-healable properties in thermoplastic acrylic-based copolymers. Relying on non-covalent dipolar interactions present in all macromolecules, novel self-healable fluorine-containing copolymers were developed; they are shown in Fig. 2(a).[25] Fluorine atoms serving as a protective sheath surrounding the C—C copolymer backbone resulting in the nonpolar nature of fluorinated polymers is responsible for many properties ranging from chemical inertness to thermal stability, or low coefficients of friction and others. Taking advantage of dipolar interactions between neighboring chains a new family of fluorinated acrylic-based copolymers was copolymerized by reacting 2,2,2-trifluoroethyl methacrylate (TFEMA) and *n*-butyl acrylate (nBA) monomers using free radical polymerization.[25] As shown in Figs 2(b) and 2(c), these repeating units containing side groups terminating with CH_2/CH_3 and/or CF_3 moieties exhibit H···H, F···F and H···F through space interchain and intrachain interactions, which are sensitive to the reorientation energy barrier during the damage-repair cycle.

The acceleration of self-healing in alternating/random hydrophobic acrylic-based copolymers in the presence of confined water molecules occurs because vdW interactions do not allow H_2O-diester hydrogen bonding, thus forcing nBA side groups to adapt L-shaped conformations, generating stronger dipole–dipole interactions resulting in shorter interchain distances compared to 'key-and-lock' associations without water.[26] Because no covalent rebonding takes place, damage recovery relies on the return of energetically unfavorable vdW forces for preferentially alternating/random copolymer compositions to energetically

* *Correspondence to: MW Urban, Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA. E-mail: mareku@clemson.edu*

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Department of Materials Science and Engineering, Clemson University, Clemson, SC, USA

more favorable states resulting in self-healing. Although the process may be viewed as an SME, its autonomous nature does not require external input.

On the other hand, shape memory assisted self-healing (Fig. 1 (a3)) in synthetic polymers relies on two approaches. The first is based on the classical definition of the SME. When pre-tensioned shape memory alloy wires[27] or fibers[28] are placed in a polymer matrix, upon activation by elevated temperature, self-healing occurs due to contractual forces pulling crack surfaces towards each other. Thus, polymers are able to 'remember' a permanent shape that can be altered to create a temporary form and, triggered by external or internal stimuli (heat, light, deformation), can recover back to the remembered permanent shape. The second approach takes advantage of the SME resulting from phase-separated components of a composite polymer (Fig. 1(a2)),[5,29,30] in which rigid and tough components are combined with softer dynamic macromolecular assemblies.[6] Phase-separated morphologies will facilitate mobility and rigidity, thus inducing SMEs.[31,32] It is anticipated that entropic and interfacial energies stored during damage may play an important role in the recovery of mechanical properties.

While the early 1980s sparked initial interests in self-healing polymers via interchain diffusion, it was not until later that embedding reactive encapsulated fluids that burst open upon damage to fill and repair damaged areas (Fig. 1(c2)) were conceptualized and experimentally demonstrated.[22] This engineering concept found limited practical applications, though, but it certainly inspired other developments.[33–35] Instead of embedding reactive microcapsules, incorporating superparamagnetic γ-Fe_2O_3 nanoparticles into a polymer matrix facilitates repair by applying an oscillating magnetic field. As depicted in Fig. 1(a4), when an oscillating magnetic field is applied,[8] γ-Fe_2O_3 nanoparticles oscillate at the frequency of the magnetic field. As a result, polymer matrix–nanoparticle interfacial regions melt, facilitating

Siyang Wang received her B.S. degree in chemical engineering from Lanzhou University in China followed by a M.S. degree in polymer engineering from The University of Akron. Siyang joined the Urban Research Group, and her PhD studies involve the development of novel autonomous self-healing copolymers, molecular processes responsible for self-healing, and other stimuli-responsive polymeric materials.

Marek W. Urban is the J.E. Sirrine Foundation Endowed Chair and Professor of Materials Science and Engineering and Chemistry (courtesy) Departments at Clemson University. He is the Fellow of American Chemical Society (ACS) PMSE Division, the Royal Society of Chemistry (RSC), American Institute of Chemists (AIC), and the American Association for Advancement of Science (AAAS). His research group current research efforts focus on the development of polymeric materials and interfaces with "living-like" functions.

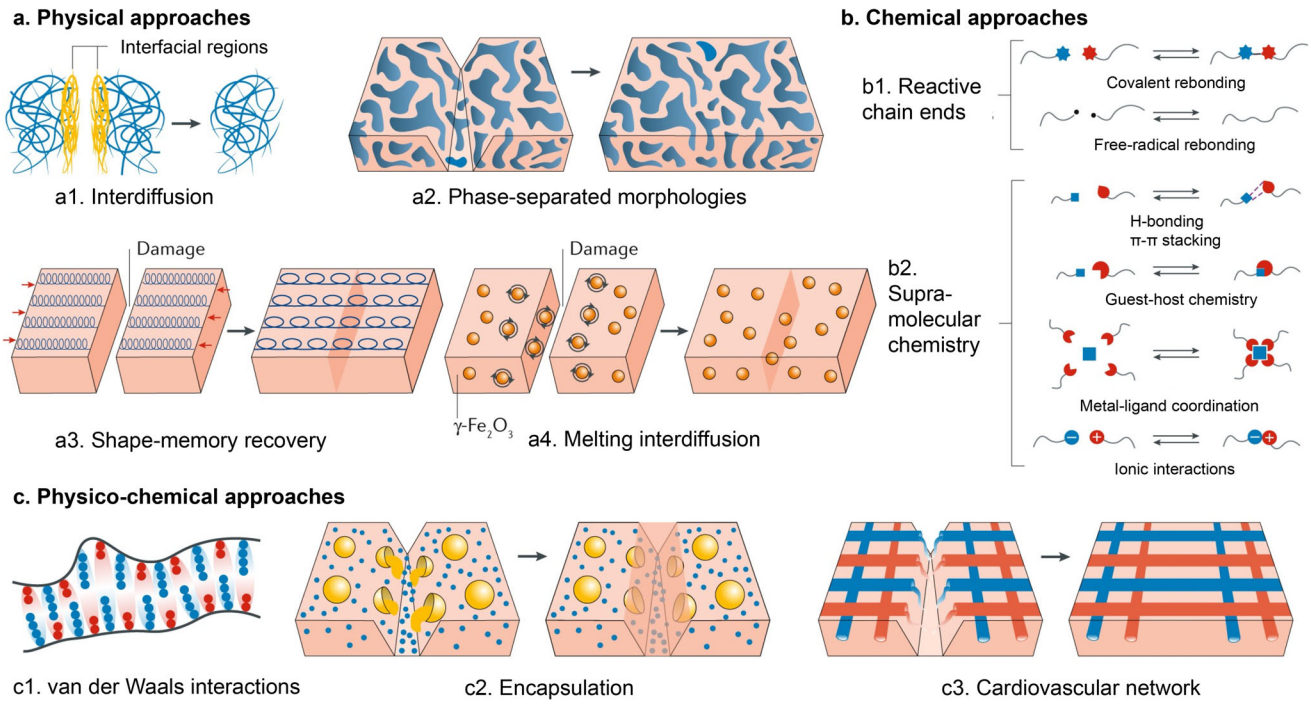

Figure 1. Self-healing mechanisms: (a) physical processes to realize self-healing include interdiffusion of polymer chains, the introduction of phase-separated morphologies, shape memory effects and the introduction of active nanoparticles into a polymer matrix; (b) chemical processes to facilitate self-healing involve introducing either reactive chain ends or supramolecular chemistries; (c) physical and chemical processes can be combined to realize self-healing. Self-healing is achieved by incorporating enhanced van der Waals interactions, or encapsulating nanocapsules or microcapsules containing healing agents to close a wound, or by mimicking cardiovascular architectures composed of hollow fibers filled with reactive chemicals to heal a polymer matrix. (Reproduced with permission from ref. 1.)

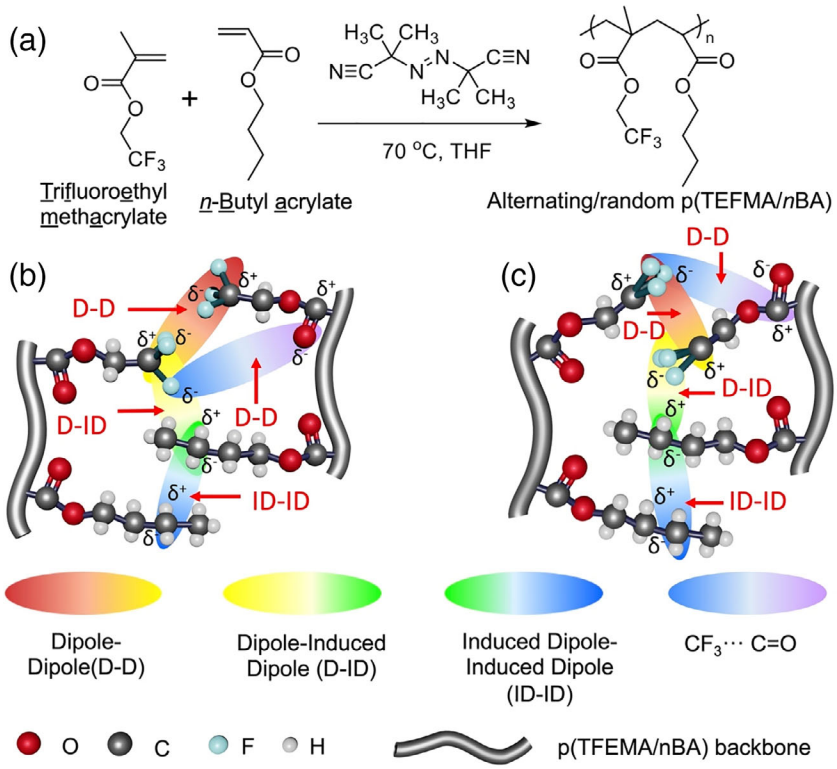

Figure 2. (a) Synthesis of poly(2,2,2 trifluoroethyl methacrylate/*n*-butyl acrylate) (p(TFEMA/nBA)) by copolymerizing 2,2,2-trifluoroethyl methacrylate (TFEMA) and *n*-butyl acrylate (nBA) via conventional free radical polymerization. (b)–(c) Dipole–dipole (D–D), dipole–induced dipole (D–ID) and induced dipole–induced dipole (ID–ID) forces between (b) neighboring chains in equilibrium and (c) non-equilibrium damaged states. (Adapted from ref. 25.)

polymer flow and a repair of physically separated polymer surfaces.

Incorporating covalent[9–13] (Fig. 1(b1)) or supramolecular dynamic bonds (Fig. 1(b2)),[6,14–20] self-assemblies[36] or living organisms[37] that are capable of chemical repairs at molecular level, extended to nano- and micro-scale repairs, have also been exploited to achieve self-healing. An attractive feature of covalent rebonding in self-healing polymers is the ability to regain original properties by recoupling free radicals or other reactive groups generated during damage. If carbon dioxide is consumed during the self-healing of synthetic materials, it will certainly have a positive environmental effect. This concept was utilized for the first time in reactions of methyl-α-D-glucopyranoside (MGP) molecules with hexamethylene diisocyanate trimer and polyethylene glycol to form crosslinked MGP-PUR networks.[11] These materials are capable of self-repairing in the presence of atmospheric carbon dioxide and water by regenerating reactive amine functionalities that react to re-form urethane and carbonate linkages. In a similar manner, sacrificial hydrogen bonding was introduced by the incorporation of secondary amide side chains that enhance mechanical properties.[38] Retro Diels–Alder reactions offer a disconnection between diene and dienophile, but elevated temperatures reconstruct the covalent bonds to repair the crack.[13] One example is the photochemical [2 + 2] cycloaddition of a 1,1,1-tris(cinnamoyloxymethyl)ethane (TCE) monomer utilized for self-healing reactions to form cyclobutane structures via the reversibility of cyclobutane to C=C bond conversion.[39] Cycloaddition reactions[40] capitalize on the C–C bond cleavage of cyclobutane rings between TCE monomers induced by mechanical damage, resulting in the formation of original cinnamoyl groups, but healing occurs due to reversibility of cyclobutane crosslinks of TCE via [2 + 2] photocycloaddition upon UV (> 280 nm) exposure. Reversible reshuffling reactions of S–H and S–S bonds were also utilized in trithiocarbonates in which copolymerization of nBA and a trithiocarbonate crosslinker resulted in a high mobility of polymer segments, triggering homolysis of C–S bonds.[41] Owing to the reversible nature of S–S bonds resulting in two thiol (S–H) groups and reversable oxidation to restore the disulfide linkage, self-healing has also been achieved.[42] Introducing disulfide (S–S) crosslinks into covalently crosslinked networks resulted in poly(*n*-butyl acrylate)-grafted (pBA) star polymers. Reversible thiol-ene click reactions can also be utilized in the Michael addition reactions in which trithiol reacts with a bisbenzylcyanoacetamide derivative to generate self-healable dynamic polymer networks above 60 °C.[43] Condensation polymerization can be applied to form imine crosslinks in poly(ethylene glycol) bis(3-aminopropyl) and 1,3,5-triformylbenzene that showed malleability and self-healing.[44] Tetramethylammonium silanolate-initiated ring-opening co-polymerization of octamethylcyclotetrasiloxane and bis(heptamethylcyclotetrasiloxanyl)ethane showed that these crosslinked polymers containing ethylene bridges along with active silanolate end groups exhibit remodeling attributes.[45]

Non-covalent bonding represented by hydrogen bonding, metal–ligand coordination, $\pi-\pi$, ionic, guest–host, vdW interactions and self-assemblies has been utilized in self-healing polymers.[46,47] Although these interactions are weaker than covalent bonding, collectively they result in mechanically strong and dynamic systems. Classical examples are represented by Fe^{3+} and catechol groups,[48] dynamic ionic interactions between the carboxylic group of polyacrylic acid and ferric ions as well as polyelectrolytes[50] and self-healable hydrogels.[51,52] Hydrogen

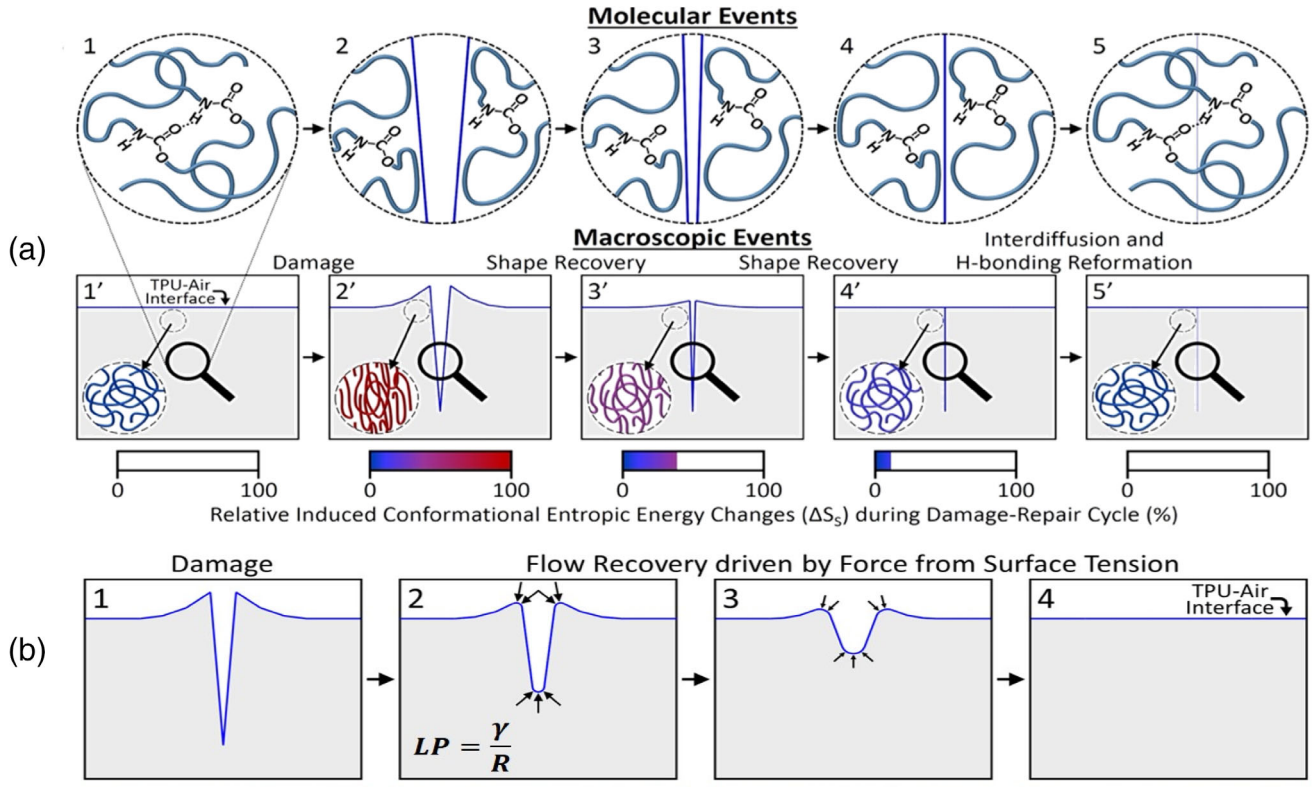

Figure 3. (a) Pictorial representation of molecular level (1–5) and macroscopic (1′–5′) events during entropy driven self-repair of thermoplastic polyurethane (TPU), illustrating chain conformational changes around the damage, breakage and formation of hydrogen bonds, and disentanglement and re-entanglement of chains during the process; (b) schematic illustration of surface energy driven self-healing (adapted from ref. 66).

bonding is typically among the strongest of non-covalent interactions and its directionality as well as high per-volume concentration levels result in acceptable mechanical strength offered by thermoplastic polymers and self-healing characteristics.[53,54] For example, high segmental mobility polyisobutylenes (PIBs) functionalized with thymine and 2,6-diaminotriaine end groups assemble into strong rubber-like materials by the formation of triple hydrogen bonds. When supramolecular PIB networks are equipped with directional associative end groups, tunable dynamic behavior including self-healing can be achieved.[55] Combining four hydrogen bonds offers high association constants[56,57] which enable the formation of urea isopyrimidone with enhanced association strengths between the units when incorporated in polysiloxanes, polyethers and polyesters.[58–60] Fatty diacids and triacids have also been utilized to form self-healing networks.[14] Using condensation polymerization of acid groups with an excess of diethylenetriamine and subsequent reactions with urea involving amidoethyl imidazolidone, diamidoethyl urea and diamido tetraethyltriurea groups resulted in an oligomer mixture with excessive hydrogen bonding. Through the combination of hydrogen bonding and dispersive interactions in piezoelectric bipyrazole crystals, opposite electrical charges on fractured surfaces can be induced by large stress, resulting in electrostatically driven self-healing.[61] Metal–ligand complexes offer many advantages that are primarily associated with the ability of coordinating different metal ions and ligand substitutes, thus leading to different association strengths. When mechanical forces are applied, such complexes dissociate, and their re-formation will result in self-healing. Reversibility upon mechanical damage can be obtained by metal ion–ligand dissociations. Heating at 200 °C without solvent or at 150 °C in the presence of dimethyl sulfoxide vapors repairs a wound due to dynamic metal–polymer equilibrium. When hydroxyl ethylene diamine triacetic acid is utilized as a molecular weight and crosslinker density controller in the presence of terpyridine-Ru, temperature changes decouple Ru metal from the ligand, thus facilitating bonding and debonding.[62] Taking advantage of the coordination between Fe^{3+} and catechol ligands, pH-induced crosslinked self-healing polymers with near-covalent elastic moduli were developed.[63] Metal ion coordination between multivalent Ni^{2+} and dynamic N-donor ligand containing diarylethene facilitate the development of light-switchable and self-healable polymer electrolytes.[64] Hydrophobic cavities of cyclodextrins can also be used to bind and trap other molecules inside them. If one surface contains a cyclodextrin host and the other guest molecules, host–guest interactions will result in bonding.[17] These polymers are equipped with multipoint molecular recognition sites achieved by various water-soluble polymer backbones modified with β-cyclodextrin as host and hydrophobic adamantine as guest at the side chain. A transparent, flexible and tough hydrogel can be formed with self-healing in wet and dry states.[65] In summary, significant advances have been made in dynamic reversible covalent and non-covalent bonding chemistries for self-healing polymers, but an ultimate goal is to create high strength and stiffness commodity materials capable of repair without intervention under ambient conditions.

Taking advantage of the continuous viscoelastic nature of the glass transition, sufficient molecular mobility for autonomous self-healing under ambient conditions can be achieved while maintaining high strength and stiffness in precisely designed

commodity polymers through efficient storage and recovery of conformational entropic energy using viscoelastic shape memory (VESM).[66] Furthermore, excess surface energy resulting from damage can drive self-healing without intervention in low molecular weight polymers lacking sufficient junction density (ν_j) for entropic memory of the undamaged geometry. Two mechanisms of self-healing depicted in Fig. 3 have been identified: VESM driven by conformational entropic energy stored during mechanical damage, and surface energy/tension that drives the reduction of newly generated surface areas created upon damage by shallowing and widening wounds until healed. Owing to significant advances in polymer chemistry and materials science over the last decades, numerous self-healing polymers have been developed that utilize physicochemical processes or the combination of the above. Nevertheless, there is a myriad of opportunities for creating new polymers with more tunable, time-sensitive self-healability that exhibit thermomechanical properties suitable for applications under mechanical stresses, elevated temperatures or in harsh environments.

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