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Soft Self-Healing Nanocomposites

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This review article provides an overview of the research and applications of soft self-healing polymers and their nanocomposites. A number of concepts based on physical and chemical interactions have been explored to create dynamic and reversible gel and elastomer networks, each strategy presenting its own advantages and drawbacks. Physical interactions include supramolecular interactions, ionic bonding, hydrophobic interactions, and multiple intermolecular interactions. Such networks do not require external stimulus and are capable of multiple self-healing cycles. They are generally characterized by a rapid but limited healing efficiency. The addition of nanofillers enhances the mechanical strength of the soft networks as in conventional gels and elastomers, and do not compromise the network healing dynamics. In certain cases, nanofillers moreover trigger the healing process through e.g., multi-complexation processes between each component. Chemical interactions include Diels-Alder reactions and disulphide, imine, boronate ester, or acylhydrazones bonding, and are usually triggered with an external stimulus. The resulting healing is efficient, leading to good mechanical properties, but is generally slow at ambient temperatures, and dynamic chemical interactions are only reversible at higher temperatures. Conductive nanofillers were reported to speed up the healing process in such systems owing to their energy absorption properties. The challenges with nanofillers remain their functionalization and dispersion within the self-healing formulations. Soft self-healing gels and nanocomposites find applications in engineering such as coatings, sensors, actuators and soft robotics, and in the bio-medical field, including drug delivery, adhesives, tissue engineering and wound healing.

Keywords: nanocomposites, self-healing, elastomers, gels, soft matter, interfacial interactions

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INTRODUCTION

Material's research has traditionally focused on the design of new materials that are intrinsically resistant to chemical and mechanical damage; however, material properties degrade with time, and during service owing to unavoidable impacts and stresses inducing cracks. Since few decades, nature has inspired scientists to develop new chemistries and processes to restore material properties after mechanical and functional damage has occurred. Small wounds can generally be healed in biological systems (Harrington et al., 2016), but large body parts such as limbs can also be regenerated, such as in the axolotl, a type of Mexican salamander (Kragl et al., 2009). This inspiration has led to the development of new materials, in particular polymers having self-healing properties (Binder, 2013; Herbst et al., 2013; Yang and Urban, 2013; Campanella et al., 2018; Dahlke et al., 2018; Diba et al., 2018; Ding F. et al., 2018; Kim et al., 2018; Wang et al., 2018). Compared to conventional polymers, self-healing polymers demonstrate the ability to reform broken bonds via a physical process or a symbiosis of physical and chemical processes. The design of materials having self-healing abilities requires a multidisciplinary process including mechanics, process dynamics, and chemistry. Several realistic strategies have been formulated over the past two decades (Chen et al., 2002; White et al., 2002; Gould, 2003), including elastomers (Sordo et al., 2015), coatings (Samadzadeh et al., 2010; Bailey et al., 2015; Zhang et al., 2018), and composite materials (Cho et al., 2009; Cohades et al., 2018), which not long ago appeared a creation of vivid imagination. A number of review articles comparing different healing concepts in bulk as well as composite materials is available (Caruso et al., 2009; Blaiszik et al., 2010; Binder, 2013; Herbst et al., 2013; Yang and Urban, 2013; Bekas et al., 2016; Cohades et al., 2018).

In practice, two interactive effects are observed in self-healing systems. First, in order to close the damage cavity a certain physical flow of a "mobile phase" has to occur within the network structure (Yang et al., 2015b). Second, in order to ensure the restoration of the functional and mechanical integrity, the polymer network needs to be rebuilt. One of the earliest self-healing techniques relies on an *extrinsic* capsule/vascule based concept, whereby a microencapsuled healing agent is incorporated within the polymer. The stress-induced rupture promotes monomer delivery to the cracks, in turn inducing an appropriate polymerization reaction between the components, often involving a catalyst (White et al., 2002; Brown et al., 2005; Wilson et al., 2008; Guadagno et al., 2010; Coope et al., 2011). However, capsules act as voids in the materials, the encapsulated agent is consumed after a first damage event, thus reducing the ability to heal multiple times, and the stability of catalyst or healing agent is often limited (Brown et al., 2004; Blaiszik et al., 2008; Jin et al., 2013).

The present review focuses on the alternative *intrinsic* self-healing approach, where the polymer itself repairs after damage by the utilization of dynamic/reversible interactions that can be broken and renewed under different physicochemical conditions. Intrinsic self-healing presents several advantages in comparison to extrinsic self-healing due to multiple times of healing at the same location without help of any healing agent and catalyst. Two main strategies, based on physical interactions and chemical interactions have been implemented to create intrinsic self-healing polymers, as sketched in **Figure 1**. Reversible bonding can be either non-covalent, including host-guest interactions, π-π stacking, hydrogen bonds, ionic and hydrophobic interactions, metal coordination, or covalent, such as imine bonds, disulphide and diselenide bridging, Diels-Alder reaction, reversible boronate ester, and acylhydrazones bonds. As detailed in the following, the reversibility of covalent bonds between different functional groups can be induced by external stimuli, and can be influenced by a change in temperature, pH, catalytic activity, irradiation, moisture, etc. (Garcia, 2014).

Focus of the review is more specifically on soft materials (gels, elastomers) and their nanocomposites, that have gained strong interest in recent years. Application examples include actuators, sensors (Wang et al., 2014; Chortos et al., 2017; Han et al., 2017d), flexible conductors (Wu and Chen, 2016b), tissue engineering scaffolds, drug delivery systems (Bowden et al., 1998; Geckil et al., 2010; Vig et al., 2013). Conventional soft materials have low stiffness and ultimate strength of a few MPa or tenths of MPa in the case of tough hydrogels, which greatly limits their application. The addition of nanofillers is thus highly advantageous not only for enhancing their mechanical properties by introducing higher stiffness reinforcement (Tee et al., 2012) but also to improve their functional (for example thermal or electrical conduction) and biological (Annabi et al., 2014; Lau and Kiick, 2015) properties. Traditional nanofillers include carbon nanotubes (CNTs) (Gopal et al., 2010; Qi et al., 2013), graphene (Potts et al., 2011; Huang et al., 2012; Shaygan Nia et al., 2015), ceramic oxides (Mera et al., 2013), nano silica (Engel and Kickelbick, 2013), and nanocellulose (Galland et al., 2014). As an example, the tensile strength of polyvinyl alcohol was increased up to 60 times with the addition of cellulose nano-whiskers (Ding Q. et al., 2018). Nanofillers have also been exploited to promote self-healing properties. For instance, conducting nanofillers with high thermal conductivity (graphene, CNT, metals) are used as nanoscale heaters to accelerate the self-healing mechanisms within the polymer matrix (Bai and Shi, 2017; Dai et al., 2018). In fact, nanocomposite materials feature very large specific interfacial areas, usually above 100 m^2/g. Careful design and control of the polymer-nanofiller interfacial bond dynamics (including through functionalization of the particles and/or the polymer), which remain challenging to optimize nanofiller dispersion and process rheology, represents a further option toward intrinsic self-healing.

Keeping in mind the properties and applications of soft materials, this article reviews the strategies for synthesizing self-healing soft materials based on the concept of constitutional dynamic chemistry (intrinsic self-healing) relying on physical and chemical interactions. For each case, the effect of nanofillers addition as a tool to enhance the self-healing properties of the soft materials is discussed in details. We also illustrate the emerging applications of self-healing soft nanocomposites by highlighting their usage in various fields.

STRATEGIES TO SYNTHESIZE SOFT SELF-HEALING NANOCOMPOSITES

Physical Interactions Based Soft Self-Healing Materials and Their Nanocomposites

This section reviews the strategies for the preparation of physical self-healing gels and elastomers based upon dynamic networks of non-covalent interactions, including supramolecular interactions, ionic bonding, hydrophobic interactions, multiple intermolecular interactions, and nanocomposite interactions. An overview of the reaction types, which are discussed herein, is provided in **Table 1**. Please note that it is difficult to compare the various materials as the methods to assess their mechanical properties and healing efficiency are different. Relying on

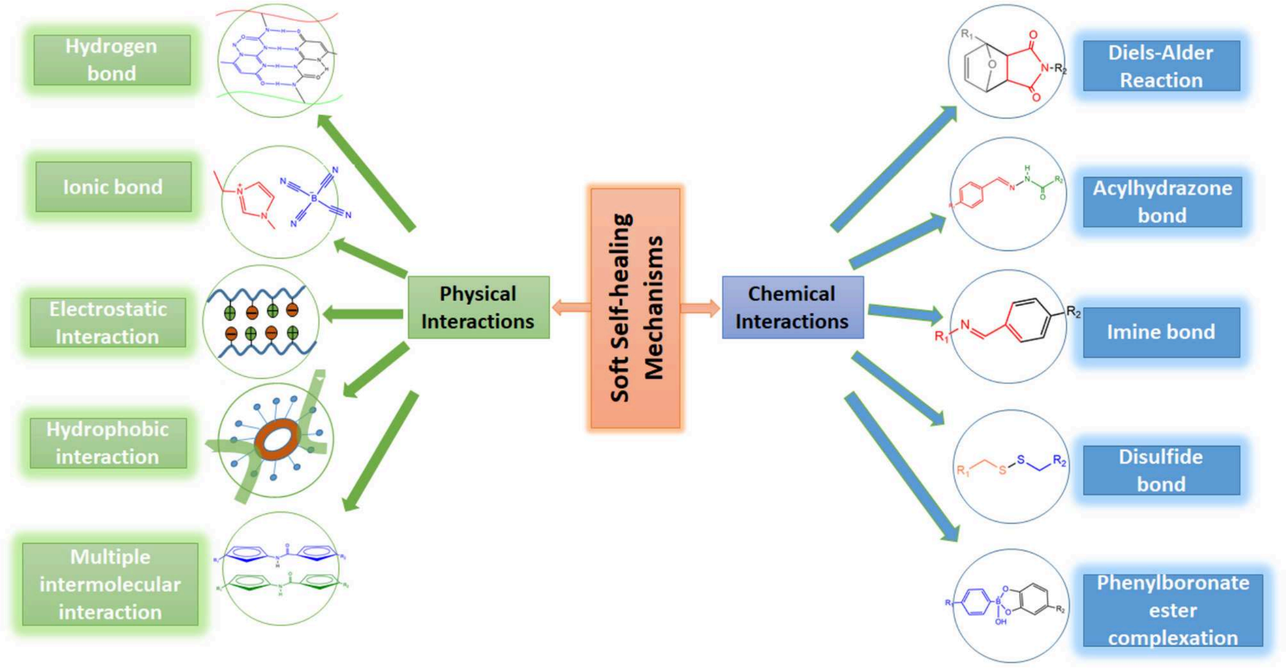

FIGURE 1 | Various strategies used to synthesize physical and chemical interaction based soft self-healing materials.

transient bonds, physical interaction based materials are capable of multiple self-healing cycles, where the mobility of the polymer chains and the density of the network influences the life time of the reversible bonds (Binder and Zirbs, 2007; de Greef and Meijer, 2008). For example, poly(ethylene glycol) based hydrogels were synthesized while functionalizing the prepolymer with quadruple hydrogen bond (UPy groups); due to their hydrophilic nature PEG-moieties can accommodate water, whereas the UPy groups give strength and elasticity while assembling into hydrogen-bonded arrays (Van Gemert et al., 2012). A heart shaped object demonstrated a shape persistent and self-healing behavior when cut into two pieces, which was mended by simply pressing both halves together (**Figure 2**).

In another example, an ionic self-healing mechanism involves charged polymer chains cross-linked with oppositely charged ions or polymer chains. Relative to organogels, ion gels exhibit high chemical stability and ionic conductivity, and are thus advantageous for a wide range of applications from soft actuators (Imaizumi et al., 2012) to electrolytes for lithium ion batteries (Kitazawa et al., 2018). A self-healing and adhesive ionic gel was prepared by the mixing of polycation poly(allylamine hydrochloride) (PAH) with pyrophosphate (PPi) and tripolyphosphate (TPP) (Huang et al., 2014). Due to highly dense ionic crosslinking, a high storage modulus was observed ($G'_\infty \approx 4 \times 10^5$ Pa). Due to stabilization and functional groups rearrangement, the self-healing performance of physically crosslinked hydrogels decreases when increasing the time to place back together the cut surfaces (Herbst et al., 2013). A time independent single-component zwitterionic hydrogel with a capability for spontaneous healing under physiological conditions has been reported (Bai et al., 2014), where carboxylbetaine acrylamide (AAZ) was physically crosslinked *via* electrostatic interactions among zwitterionic moieties, resulting in a time-independent healing behavior. In addition, their self-healing process does not require any external stimulus; however, a decrease in self-healing was observed with increase in crosslinking density (Bai et al., 2014).

Electrostatic interaction based physically cross-linked zwitterionic hydrogels were developed using carboxybetaine acrylamide, 7-acrylamidoheptanoate acid and hydroxyhexylacrylamide (Bai et al., 2014). Interestingly the reported hydrogel demonstrates a time-independent healing behavior, in that the separation time of cut fragments does not compromise healing efficiency. Wei et al. reported electrostatic interactions based self-healable supramolecular luminescent hydrogels from ABA triblock copolymers [Poly(2-(2-guanidinoethoxy) ethyl methacrylate)-*b*-poly(ethylene oxide)-*b*-poly(2-(2-guanidinoethoxy) ethyl methacrylate)] and polyoxometalates (Wei et al., 2014), where the mechanical strength of the hydrogel can be simply tuned by altering the ionic strength, concentrations, and copolymer composition. A reversible electrostatic interaction promoted ionic self-healing mechanism was emphasized by Varghese et al., where a charged polymer chain crosslinks with an oppositely charged polymer chain or with oppositely charged ions. However, based on experimental conditions the materials also illustrate the hindrance in self-healing due to electrostatic repulsion when the polymeric ions were deprotonated (Phadke et al., 2012). Recent years have observed a growing attention in the development of nature inspired dopa-modified polymeric

TABLE 1 | Summary of physical interactions based soft self-healing materials.

Classification	Substances	Healing conditions	Healing efficiency	Mechanical properties	Rheological properties	References
Supramolecular interactions	PA6ACA	RT, pH ≤3, 24 h	66 ± 7%[a]	*52 KPa	–	Phadke et al., 2012
	PDMAEM/SCMHBMA	20°C, pH= 7–8, 2 min	100%[b]	–	–	Cui and del Campo, 2012
	Ureidopyrimidinone terminated PEG	RT	100%[c]	–	#24 KPa	Bastings et al., 2014
	Dimeracids, Diethylene triamine with urea	RT	100%[d]	–	#30 KPa	Cordier et al., 2008
	Barbutric acid functionalized PIB	RT, 24 h	100%[d]	–	#10^5 KPa	Herbst et al., 2012
	DNA-grafted polypeptide and "X"-shaped DNA linker	RT	100%, 5 min[e]	–	#275 Pa	Li et al., 2015
	β-cyclodextrin-functionalized poly(acrylamide) and *N*-adamantane-1-yl-acrylamide copolymer or α-cyclodextrin-functionalized poly(acrylamide) *n*-butyl acrylate copolymer	RT 24 h	74–99%[d]	–	#330 Pa	Kakuta et al., 2013
Ionic bonding	PFMA-b- PDMAPM	UV light, 120 min	15–88%[b]	–	–	Banerjee et al., 2018
	Alginate-boronic acid	RT, 5 min	44–98%[f]	–	#314 Pa	Hong et al., 2018
	P4VP/Br-PS-Br	UV light, 1 h	100%[d]	–	–	Dong et al., 2018
	PAH/PPi and PAH/TPP	24 kPa, 3 h	30–50%[d]	*350–450 KPa	–	Huang et al., 2014
	NR/ZDMA	RT,30 s- 5 min	50–95%[d]	*4 × 10^3 MPa	–	Xu et al., 2016
	1-butyl-3-methylimidazolium hydrogen sulfate (BmimHSO$_4$)	RT, 24 h	93.8%[a]	*15.8 KPa	–	Zhu et al., 2018
Hydrophobic interactions	Micelle-based	RT, 10–130 min	98–100%[d]	*75 KPa	–	Tuncaboylu et al., 2011
	Liposome	RT	100%[e]	–	#210Pa	Rao et al., 2011
	N- acryloyl 11-aminoundecanoic acid (A11AUA)	60°C, 2 h	64–94%[g]	*1,016 KPa	–	Wei et al., 2018
	poly(styrene-acrylonitrile)	RT, 24 h	68%[d]	*62 KPa	–	Chen et al., 2018a
	UPyHCBA	30 s	100%[d]	&5 KPa	–	Jeon et al., 2016
	OP-4-AC or OP-10-AC	RT, 6 days	100%[d]	*210 KPa	–	Jiang et al., 2009
	sodium dodecyl sulfate	24°C, 10–130 min	100%[d]	*13 KPa	–	Tuncaboylu et al., 2012
Electrostatic interactions	carboxybetaine acrylamide, 7-acrylamidoheptanoate acid and hydroxyhexylacrylamide	RT	90%	*250 kPa	–	Bai et al., 2014
	ABA triblock copolymers	RT	100%	–	#320 kPa	Wei et al., 2014
	acryloyl-6-aminocaproic acid (A6ACA)	Low pH	90%	*66 kPa	–	Phadke et al., 2012
	poly(acrylic acid)	pH-9	100%	$1.5 MPa	–	Wang et al., 2015
Multiple Intermolecular Interactions	Tetra-acylhydrazine-terminated PDMS	catalytic acetic acid, 24 h at 25°C or annealing at 120°C for 2 h	60–120%[d]	*2 MPa	#0.98 KPa	Zhang et al., 2017

(Continued)

TABLE 1 | Continued

Classification	Substances	Healing conditions	Healing efficiency	Mechanical properties	Rheological properties	References
	low-molecular-weight organogels (LMOGs)	6–40 h, RT	70–79%^{b}	–	$^{\#}$9 Pa	Mukhopadhyay et al., 2010
	P(NAGA-*co*-NBAA)	90°C, 10 min	95%^{d}	*1.1 MPa	–	Feng et al., 2018
	PM1-b-PM(NCP)A	50°C, 30 min	100%^{d}	–	$^{\#}$50 KPa	Yan et al., 2015
	7-nitrobenzo-2-oxa-1,3-diazol-4-yl-cholesteryl	UV	100%^{d}	–	$^{\#}3.29 \times 10^4$ Pa	Xu et al., 2013

Types of self-healing:

[a] *Healing of ruptured surfaces of the specimen.*

[b] *Microscopy observation of cracks/scratches on the specimen surface.*

[c] *Storage modulus via rheology.*

[d] *Pieces of cut hydrogel rejoined.*

[e] *Hydrogel injected after gelation.*

[f] *Partial cut the specimen,*

[g] *Alternative step strain deformation.*

*#storage modulus, *tensile strength; $adhesive strength; &nominal stress.*

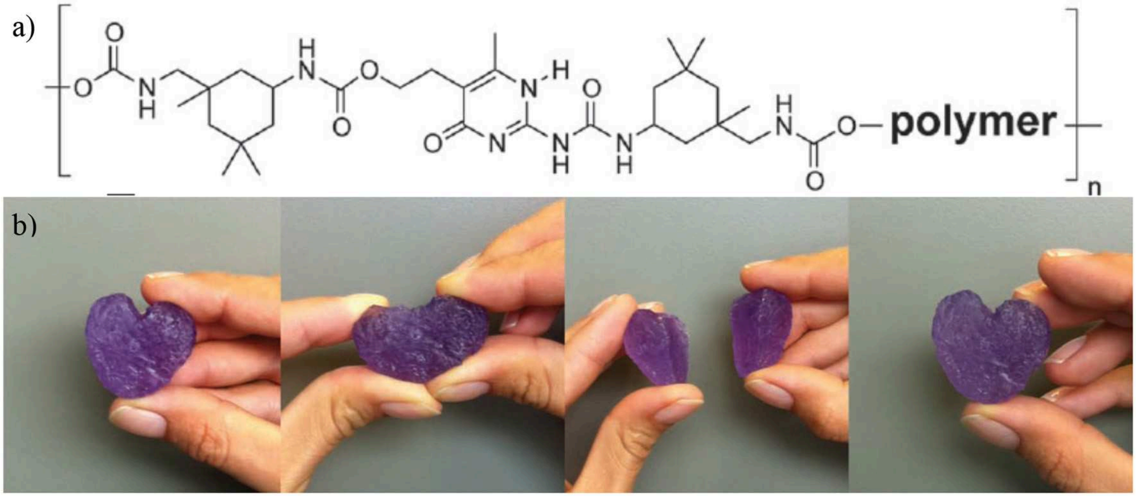

FIGURE 2 | (a) UPy-containing polymer. **(b)** Supramolecular hydrogel made of PEG-UPy polymer 15 wt% in water (Van Gemert et al., 2012). Reproduced with the permission of 2012 WILEY-VCH Verlag GmbH & Co. KGaA Weinheim, SupraPolix BV, 2010.

structures, in particular to explore the biomimetic adhesives for tissue engineering (Barrett et al., 2013; Kim et al., 2014). Catechol induced polyelectrolyte coacervate bioadhesive has been developed using a poly(acrylic acid) backbone decorated with catechol appendants in presence of weak divalent cross-linker Zn^{2+} (Wang et al., 2015), where negative charged carboxylic groups from poly(acrylic acid) electrostatically interact with zinc chelated mono-catechol group, thus leading to a quick generation of the dense coacervates.

A double-network (DN) based self-healing material with improved mechanical properties has been reported, where a symbiosis of covalent and non-covalent crosslinking network had been employed (Gong, 2010). However, as the chemically covalent-cross-linked network cannot reversibly recover to its original state, the DN soft materials exhibit poor self-healing efficiency (Chen et al., 2015, 2016). Thus, a multiple non-covalent cross-linked network could be more advantageous for designing self-healing materials with high mechanical properties. A double network based poly(N-acryloyl glycinamide-*co*-N-benzyl acrylamide) containing a triple amide in one side group was reported by Feng et al. The triple amide based soft material demonstrated a good shape memory ability, high mechanical strength (1.1 MPa) and about 95% self-healing efficiency at room temperature (Feng et al., 2018).

Most of the widely explored soft materials are also now often combined with nanosized inorganic components to form nanocomposites, as summarized in **Table 2**. The addition of stiff nanofillers is strategic not only for enhancing the mechanical properties of the soft matrix (Tee et al., 2012) but also to improve their self-healing properties (Bai and Shi, 2017; Dai et al., 2018).

TABLE 2 | Physical interaction based self-healing mechanism, healing efficiency, recovery, mechanical/electrical properties of soft nanocomposites.

Healing mechanism	Materials	Self-healing conditions	Self-healing efficiency (recovery %, obtained from tensile strength)	Mechanical properties (Tensile strength)	Electrical conductivity/ resistance	References
Hydrogen bonding	AgNWs/branched polyethylenimine/poly(acrylic acid)-hyaluronic acid	RT, with a drop of water	100%	–	0.38 Ω sq^{-1}	Li et al., 2012
	Nanofibrillated cellulose (NFC), poly(vinyl alcohol) (PVA), and borax	RT (20°C)	98%	74.0 kPa modulus, and 29.0 kPa max. stress	–	Spoljaric et al., 2014
	Montmorillonite nanoplates/PDMAA	48 h, RT	100%	140 kPA	–	Zhong et al., 2015b
	Montmorillonite nanoplates/poly(acrylamide)	7 days, RT	100%	100–180 KPa	–	Gao et al., 2015
	Organoclay/poly(vinylpyrrolidone)	RT, 3 h; pH 4–11	100%	210 Pa	-	Gao et al., 2015
	Zirconium hydroxide/Poly(acrylamide)	RT, 24 h	86%	404 KPa	–	Jiang et al., 2017
	Graphene oxie/Polyacrymide	RT, 1 day	98%	180 KPa	0.1 S cm^{-1}	Han et al., 2017b
	Graphite/polyethylenimine	RT, 10 s	98%	0.2 ± 0.04 MPa	1.98 S cm^{-1}	Wu and Chen, 2016a
Hydrophobic interactions	Graphene oxide/poly(acrylamide)	3 days	53%	243 kPa	–	Cui et al., 2015
	Graphene peroxide/poly(acrylamide)	24 h, 30°C	88%	0.35 MPa	–	Liu et al., 2013
Supramolecular interactions	Cellulose nanocrystals/PVA	10–30 s, RT	100%	14.3 kPa	–	McKee et al., 2014
	SWCNT (10–20 wt.%)/poly(2-hydroxyethyl methacrylate)	RT	100%	0.6 MPa	7.76 S m^{-1}	Guo et al., 2015
Ionic interaction	Fe^{3+}/ graphene oxide/ poly(acrylic acid)	48 h, 45°C	80%	860 kPa	–	Zhong et al., 2015b
	Ferric ions/silica nanoplates/poly(acrylic acid)	70°C	30%	1.0 MPa	–	Zhong et al., 2015a
	Fe_3O_4 NP (2.5 Vol.%) /PEG (metal-ion coordination)	RT	100%	10^4 Pa (Modulus)	–	Li et al., 2016b
	Ferric ions/Silica/poly(acrylic acid)	50°C, 24 h	70%	860 kPa	–	Zhong et al., 2015a
	Fe ions/PDMS/2,6-pyridinedicarboxamide	RT, −20°C	90% at RT; (68% at −20°C)	0.22 MPa	6.4 (Dielectric constant)	Li et al., 2016a
Multiple interactions	MWNT/Polyethylene polyamine (MWNT-0.5 wt%)	RT, 90 sec	100%	2 N/cm^2	–	Du et al., 2014b
	Cellulose/polyvinyl alcohol (PVA)-borax (PB)	RT,	100%	∼22 MPa	3.65 S m^{-1}	Ding Q. et al., 2018

Zhong et al. (2015a) proposed a tough and highly stretchable self-healing hydrogel based on silica nanoparticles, ferric ions and poly(acrylic acid) (PAA). The hydrogel demonstrated excellent toughness (tensile strength 860 kPa, elongation at break ∼2,300%). It was suggested that the stretchability and toughness arose from the reversible cross-linking interactions between polymer chains, helpful for energy dissipation through stress triggered dynamic process. Exfoliated sodium montmorillonite based self-healing hydrogel was formed by *in situ* polymerization of acrylamide monomers (Gao et al., 2015). These hydrogels demonstrated good stretchability with a high fracture toughness (10.1 MJ m^{-3}) and fracture strain up to 11,800%, however, exhibited slow recovery of mechanical properties (RT, 5 days) and required multiple dry/re-swell handlings.

A host-guest interaction based healable, stable, and recoverable nanocomposite hydrogel was developed using a three-component architecture consisting of poly(vinyl alcohol) (PVA), cucurbit[8]uril (CB) and cellulose nanocrystals (McKee et al., 2014). These nanocomposite hydrogels exhibit significant mechanical strength and stiffness with a storage modulus of 10 MPa. Immediate self-recovery was shown *via* step-strain measurements at RT and rapid self-healing abilities were

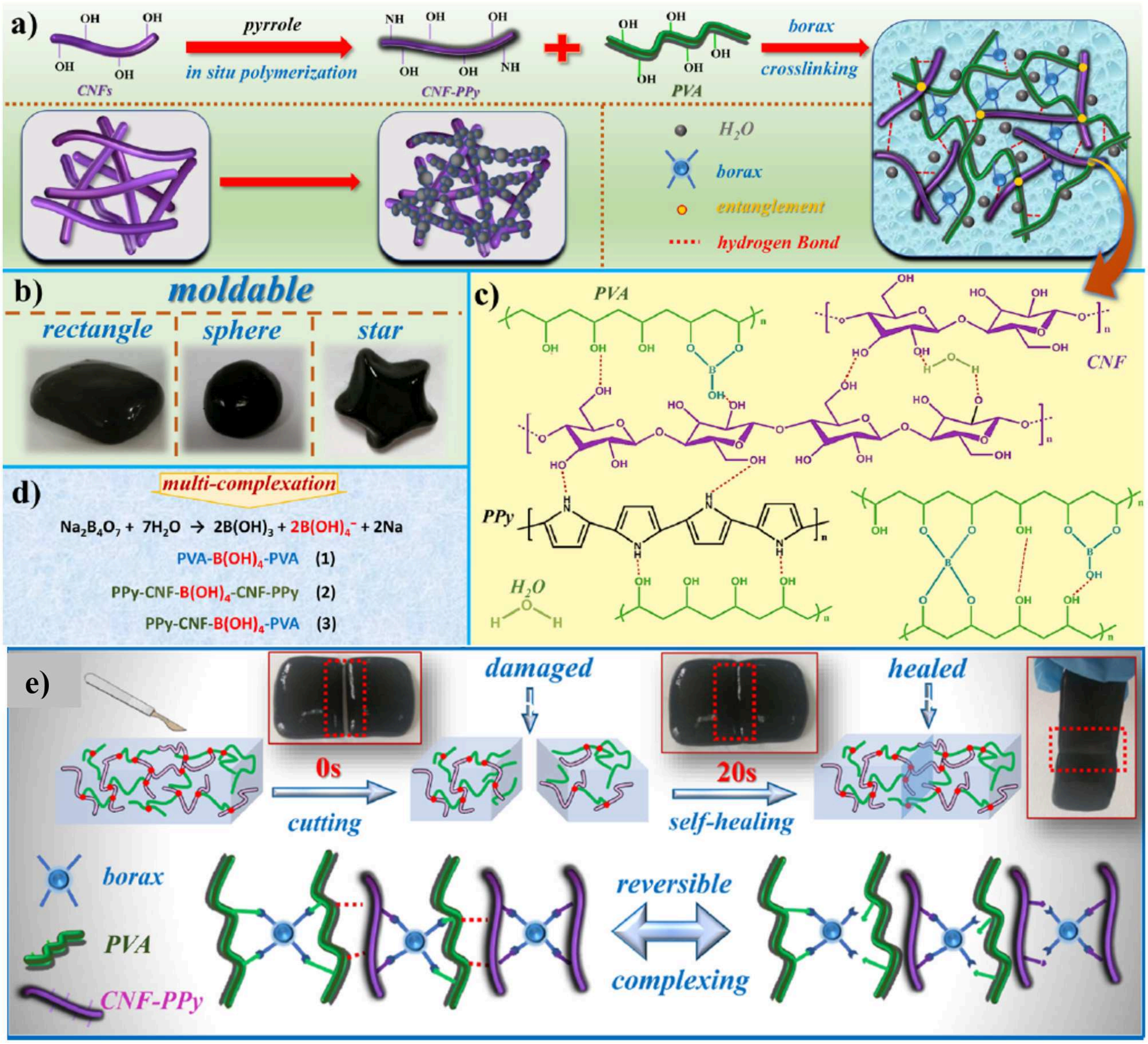

FIGURE 3 | (a) Schematic illustration of preparation and synthesis process of CNF–PPy/PB hydrogels. **(b)** CNF–PPy/PB hydrogels molded into various shapes. **(c)** Formation mechanism of the integrated 3D network within CNF–PPy/PB hydrogels. **(d)** Multi-complexation between PVA, CNF–PPy, and borax. **(e)** Schematic illustration of *in situ* self-healing and dynamic reversible cross-links of hydrogels (Ding Q. et al., 2018). Reproduced with the permission of 2018 American Chemical Society.

observed (within 30 s, RT). Also the hydrogel was able to rapidly self-heal (within 10 s) once re-joined even after 4 months.

In another example, self-recovering hydrogels have been formed based on a viscoelastic polyvinyl alcohol (PVA)-borax (PB) gel matrix and nanostructured CNFs–PPy (cellulose nanofibrils-polypyrrole) complexes that synergizes the bio-template role of CNFs and the conductive nature of PPy. The CNF-PPy complexes not only tangle with PVA chains though hydrogen bonds, but also form reversibly cross-linked complexes with borate ions (Ding Q. et al., 2018). The multi-complexation between each component leads to the formation of a hierarchical three-dimensional network (**Figure 3**). Owing to a combined reinforcing and conductive network inside the hydrogel (2 wt.% CNFs-PPy), it demonstrated high storage modulus (~0.1 MPa) and nominal compression stress (~22 MPa), about 60 and 2,240 times higher than those of pure PVA hydrogel, respectively.

Mussel inspired, metal coordination bonds based on reversible dynamics have been demonstrated to function as dynamic cohesive cross-linkers in bulk polymer materials (Amstad et al., 2009). Niels-Andersen et al. incorporated iron oxide nanoparticles (Fe_3O_4 NP) in catechol modified polymer networks to obtain hydrogel cross-linked via reversible metal-coordination bonds at Fe_3O_4 NP surface (Li et al., 2016b). The structure provides solid-like yet reversible hydrogel mechanics. Zirconium hydroxide has been utilized as nanofiller in a poly(acrylamide) to produce hydrogen bonding interaction based self-healing gel. The gels exhibited good mechanical properties with 114 KPa-404 KPa tensile strength and 284–723% elongation at break (Jiang et al., 2017). A metal-ligand network based highly stretchable self-healing elastomer was developed consisting of 2,6-pyridinedicarboxamide ligands that coordinate to Fe(III) centers through weak carboxamido-iron ones, a strong iron-pyridyl one. The material demonstrated self-healing at a temperature as low as −20 °C (**Figure 4**) (Li et al., 2016a).

Carbon nanomaterials (CNT, graphene), which show good compatibility with polymers due to their large π-conjugated system, have been widely used to produce mechanically enhanced composite materials. Such nanofillers moreover improve the chemical stability, the electrical and thermal conductivity (Balandin et al., 2008), and the microwave and infrared (IR) absorbing capacity of polymers (Sui et al., 2011). CNT based supramolecular hydrogels directed by hierarchical hydrogen bond (a mixture of strong and weak bond) interaction has been reported (Du et al., 2014b), where the gel was obtained by mixing multiwall carbon nanotubes (MWCNT) with polyethylene polyamine (PAA). The

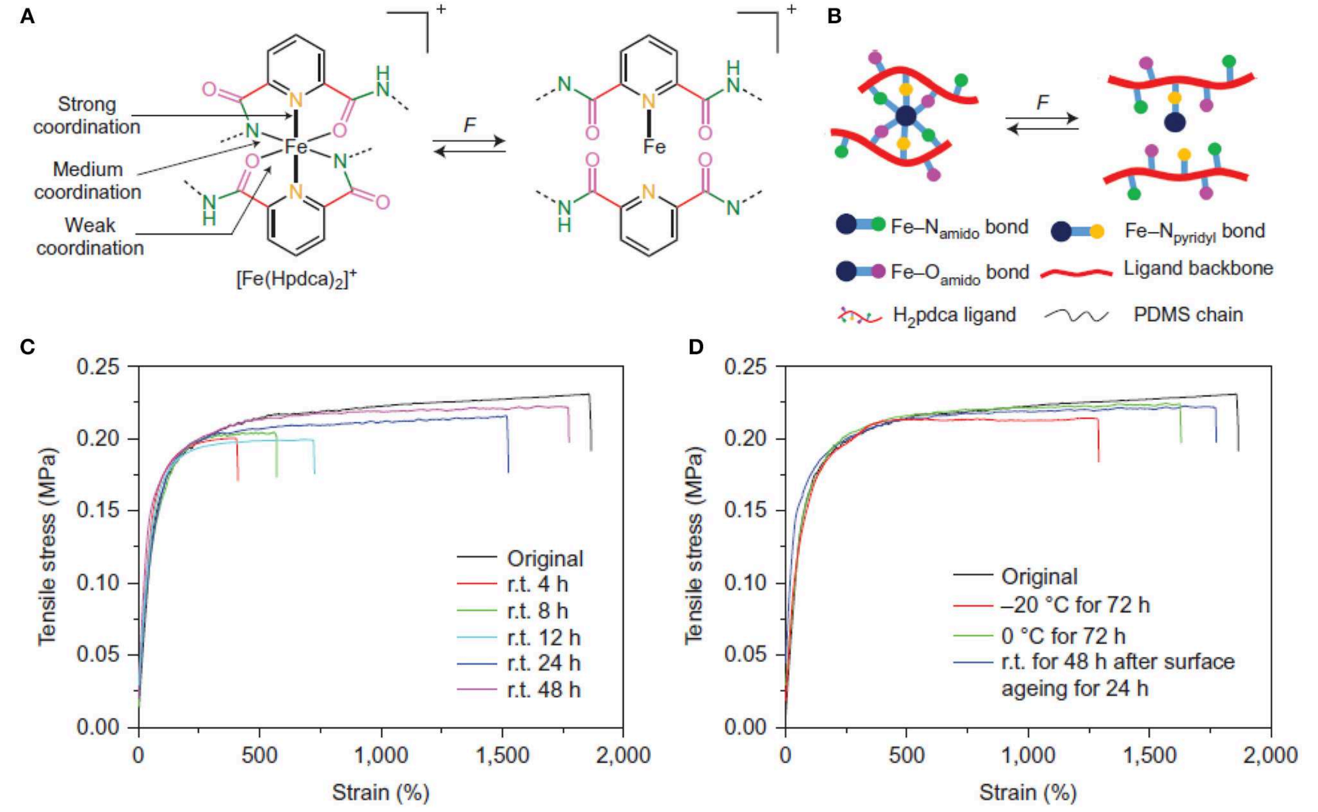

FIGURE 4 | (A,B) Schematic structure of material design and single-molecule force spectroscopy characterization. **(C)** Stress–strain curves of a film healed at room temperature (r.t.) for different lengths of time show an increase of the stretching ability when the film is allowed to heal for longer. **(D)** The stress–strain curves of the film healed at −20 and 0°C for 72 h, and the stress–strain curves of the film healed at room temperature for 48 h after surface aging for 24 h (Li et al., 2016a). Reproduced with the permission of 2016 American Chemical Society.

TABLE 3 | Examples of chemical interactions based soft self-healing materials.

Classification	Substances	Healing conditions	Healing efficiency	Mechanical properties	Rheological properties	References
Diels-Alder reactions	PFMA–BM	120°C,4 h	100%[f]	–	–	Kavitha and Singha, 2009
	Dex-L-PEG	37°C,7 h	98%[a]	–	[#]5,000 Pa	Wei et al., 2013b
	PB-3F-M	60°C	100%[g]	[*]6 MPa	[#]17,000 Pa	Bai et al., 2015
	octakis(furan-2-ylmethyl)-functionalized poly- hedral oligomeric silsesquioxane	187°C, 5 min	100%[d]	–	–	Nasresfahani and Zelisko, 2017
	PFMA-co-PBMA	130°C, 4 h	90–100%[a]	^0.268 GPa; contact depth 66 nm	–	Pramanik et al., 2014
	C60 and SBS-Fu	180°C, 10 min	100%[a]	[*]19.84 MPa	[#]78.25MPa	Bai et al., 2017
	CNC-PEG	90°C	78%[h]	[*]160 KPa	–	Shao et al., 2017
	C-PMPU–DA	120°C and 50°C	64–92%[a]	[*]46.5 MPa	–	Du et al., 2014a
	C-PEMIPU–DA	130°C	80–95%[a]	[*]19–32 MPa	–	Zhong et al., 2015c
	APDMS-FDB	130°C, 45 min then 80°C, 48 h	93%[a]	[*]0.80 MPa	–	Wang et al., 2018
Acylhydrazone bonds	PEO–aldehyde	RT,7 h	100%[h]	–	[#]6.4 MPa	Deng et al., 2010
	HG1G2	RT, pH = 6–9, 24–48 h	∼50%[b]	–	–	Gaulding et al., 2013
	BODIPY	RT, 2 h	100%[d]	–	[#]1,700 Pa	Ozdemir and Sozmen, 2016; Darabi et al., 2017
	Diacetone acrylamide	25°C, 12 h with slight pressure	92%[h]	[@]11 KPa	–	Guo et al., 2017
	arboxyethyl cellulose-*graft*-dithiodipropi- onate dihydrazide and dibenzaldehyde-terminated poly(ethylene glycol)	25°C, 4–36 h	96%[h]	[!]50 KPa	–	Yang et al., 2017)
	Calix[4]arene	RT, 96 h	100%[d]	[*]0.19 MPa	–	Yang et al., 2018
	P(NIPAM-co-FPA)	72 h	100%[d]	–	[#]1,100 Pa	Chang et al., 2017
	tetra-acylhydrazine-terminated PDMS	120°C, 24 h	90%[d]	[*]2.2 MPa	–	Zhang et al., 2017
	poly(N-iso-propylacrylamide) (PNIPAM)	24 h	100%[h]	–	[#]2,000 Pa	Sun et al., 2019
Imine bonds	Chitosan–PEG	RT,2 h	100%[h]	–	[#]1,050 Pa	Zhang et al., 2011
	dialdehyde-functionalized polyethylene glycol (DF-PEG) and β-glycerophosphate (GP)	37°C, 5 min pH 6.5 and 7.4	100%[h]	–	–	Han et al., 2018
	oligoethylene glycol	6 h	90%[h]	–	[#]2300 Pa	Liu et al., 2018a
	P(H2N-Leu-HEMA)-b-PIB	RT	100%[e]	–	[#]30.4 KPa	Haldar et al., 2015
	PDMS	4 h	95%[d]	[*]0.14 MPa	–	Lv et al., 2018
	PEO-diamine	RT, 24 h	100%[h]	[@]0.14 MPa	–	Chao et al., 2016
Disulfide bonds	SS-LCE	UV (or) 130°C, 3 h	24–80%[a]	[*]0.8 MPa	–	Wang et al., 2017c
	Poly(arylether sulfone)–Poly (alkylthioether)	UV, 5 h	51%[a]	[*]2.95 MPa	–	Akiyama et al., 2017
	PDMS-PU	120°C, 3 h	97%[d]	[*]3.31 MPa	–	Wu et al., 2018
	poly(urea–urethane)	RT, 2 h	80%[d]	[*]0.8 MPa	–	Rekondo et al., 2014
	NR	70°C, 7 h	90%[a]	[*]753 MPa	–	Hernández et al., 2016

(Continued)

TABLE 3 | Continued

Classification	**Substances**	**Healing conditions**	**Healing efficiency**	**Mechanical properties**	**Rheological properties**	**References**
	PUU	150°C, 30 bar, 20 min	90%[d]	*0.8 MPa	–	Martin et al., 2014
	HS–F127–SH and DT–PEG–DT	37°C or body temperature	100%[d]	–	#1,900 Pa	Yu et al., 2017
	CNC-containing gel	Visible light	100%[d]	–	#6,865 KPa	Li et al., 2018b
Phenylboronate ester complexations	cPEG–BDBA	RT, pH = 9.0 (d)	100%[d]	–	#1,500 Pa	He et al., 2011
	PVA with phenylboronic acid functionalised PPO–PEO–PPO	pH 3–9, 25°C	>95%[d]	–	#3,000 Pa	Piest et al., 2011
	Phenyl Boronic Acid- and Maltose- Modified Anionic Polysaccharides	pH ≥ 7.4	>90%[d]	–	#1,000 Pa	Tarus et al., 2014
	phenylboronic acid-diol ester	RT, 30 min	>95%[d]	*11 KPa	–	Xu et al., 2011

Types of self-healing:

[a] *Healing of ruptured surfaces of the specimen.*

[b] *Microscopy observation of cracks/scratches on the specimen surface.*

[c] *Storage modulus via rheology.*

[d] *Pieces of cut hydrogel rejoined.*

[e] *Hydrogel injected after gelation.*

[f] *Partial cut the specimen.*

[g] *Alternative step strain deformation.*

[h] *Pieces of separately prepared hydrogels joined.*

*#storage modulus, *tensile strength; ‘plateau modulus; ^hardness; @compressive stress; !fracture strength.*

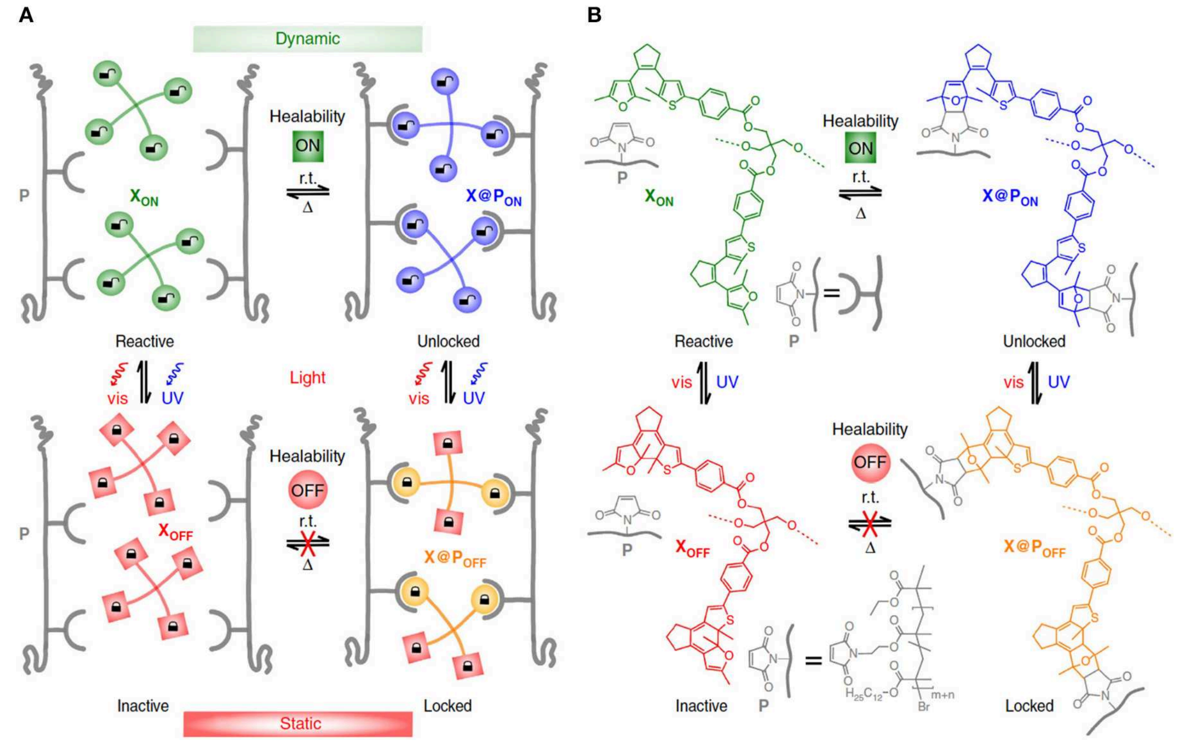

FIGURE 5 | Schematic representation of **(A)** photo-switchable, dynamically crosslinked polymer network and **(B)** the chemical structures of the crosslinkers, indicating the switchable reactivity for the reversible DA reaction and healability of the network (Fuhrmann et al., 2016). Reproduced with the permission of 2016 Springer Nature, United Kingdom.

properties of the gel can be easily tailored by controlling the ratio of strong and weak hydrogen bonds. The autonomous healing gel demonstrated a multiple responsiveness (NIR light, pH, and thermal) including temperature dependent reversible adhesion behavior. A host-guest interaction based self-healable conducting elastomer consisting of singe-walled carbon nanotubes (SWCNT) and poly(2-hydroxyethyl methacrylate) (PHEMA) was reported (Guo et al., 2015). The elastomers sustain a high conductivity up to 180% stretching, however, under large strain the conductivity decreases. This might be due to partial breakdown the SWCNT network that leads to a decrease in the total number of conduction paths. Wang et al. have developed a rapid room temperature self-healing elastic nanocomposite material by combining the hydrogen-bonded polymer and graphene oxide as a cross-linker (Wang et al., 2013), where hydrogen bonding network in polymer

TABLE 4 | Chemical interaction based self-healing mechanism, healing efficiency, recovery, mechanical/electrical properties of soft nanocomposites.

Healing mechanism	Materials	Self-healing conditions	Healing efficiency (recovery % obtained from tensile strength)	Mechanical properties (tensile strength)	Electrical conductivity	References
Diels-Alder Reactions	C_{60}/Poly(styrene-b-butadiene-b-styrene)	80°C (DA); 180°C (rDA)	100%	19.8 MPa; 7.7 MPa (3rd cycle)	–	Bai et al., 2017
	POSS/siloxane	50°C (DA); 110°C (rDA)	100%	0.75 MPa	–	Nasresfahani and Zelisko, 2017
	Cellulose nanocrystal/Poly (ethylene glycol)	50°C (DA); 90°C (rDA)	78%	160 KPa	–	Shao et al., 2017
	Graphene oxide nanosheets/Polyurethane	65°C, 5 h (DA); 120°C, 30 min (rDA)	100%	76 MPa	64 kΩ	Li et al., 2018a
	CNT/ Poly(styrene-b-butadiene-b-styrene)	80°C, 6 h; 80 laser (10 s, rDA)	100%	18.5 MPa	-	Bai and Shi, 2017
Boronate ester linkage	Cellulose-Polyvinyl alcohol	RT, pH	100%	–	–	Lu et al., 2017
	Au particles/poly(vinyl pyrrolidone)	39°C, 15 min	90%	550 Pa	–	Amaral et al., 2018
	MWNT-PDMS	Water vapor	90%	1.81 MPa	1.21 S/cm	Wu and Chen, 2016b
Didulfide bonds	Au particles/PEG/Bioactive glass	RT, 12 h	100%	35 KPa	–	Gantar et al., 2016
Transesterification	Bentonite/Natural Rubber	150°C, 3 h	96%	4.5 MPa	–	Xu et al., 2018
Diselenide bonds	Graphene oxide/polyurethane	NIR light (5 min)	90%	6 MPa	–	Xu et al., 2018

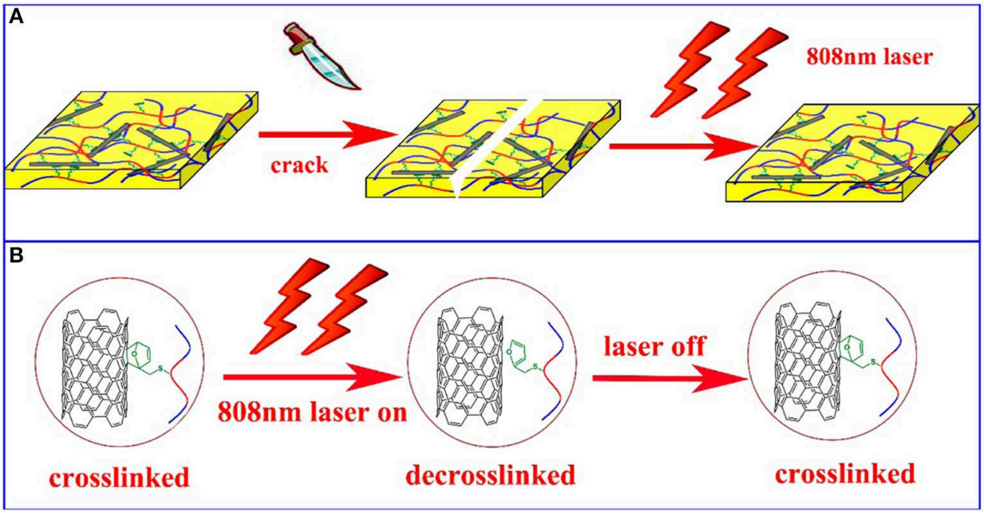

FIGURE 6 | (A) Healing Process of the Sample; **(B)** Reaction Occurring during the Healing Process (Bai and Shi, 2017). Reproduced with the permission of 2017 American Chemical Society.

TABLE 5 | Demonstrated applications for soft self-healing nanocomposites and associated healing features.

Materials	Self-healing mechanism	Self-healing conditions	Self-healing efficiency (recovery %)	Applications	References
PAA/CNS NC	Hydrogen bonding	RT	91%(tensile strain) 98% (toughness)	Soft robotics	Hu et al., 2018
tannic acid-coated cellulose nanocrystals (TA@CNC)	Coordination bonding	RT	92.5% fatigue and resilience 70% adhesive strength 97.1% electrical resistancejbh	Wearable sensors	Shao et al., 2018
Tio$_2$/BMIMBF$_4$ ionogel	Supramolecular interactions	100 to −10°C	98% (compression strength)	Electro-chemical actuators	Liu et al., 2014
PVAc/Graphene	Diffusion of polymer Chains	60°C	89% (mechanical properties)	Actuators and sensors	Sabzi et al., 2017
PAA-GO-Fe^{3+}	Ionic interactions	RT	100% (tensile strength)	Soft actuators	Zhao et al., 2017a
PPy/G-Zn-tpy	Metal-ligand supramolecular interactions	RT	100% conductivity	Electronics, biosensors, artificial skins	Shi et al., 2015
Li$_2$SO$_4$/CMC	Supramolecular	RT	94% (tensile strength) 88% (current density)	Lithium ion battery	Zhao et al., 2016
GO/PAAM derivatives	Hydrophobic interactions	RT	66%	Waste water treatments, adsorbents	Cui et al., 2015
Graphene/SWCNT	Hydrogen bonding	Ambient temperature	98% (conductivity)	piezoresistive strain sensor	Cai et al., 2017
RFGO/PU	Diels-Alder	Microwave	93% (youngs modulus)	Strains sensors, flexible conductors	Li et al., 2017
rGO/SAP	Hydrogen bonding	RT	100% (resistance)	sensors	Rengui et al., 2014
CNCs-Fe^{3+}	Ionic interactions	RT	98% (elastic modulus)	Soft strain sensor	Liu et al., 2017
PPy/PAC/Fe^{3+}	Ionic interactions	RT	100% (tensile) 90% (conductance)	Soft sensor	Darabi et al., 2017
PU/GO	Diels-alder	Ambient conditions	96% (break strength) 97% (elongation) 100% (young's modulus)	Flexible electronics	Wu et al., 2017
rGO/polyacrylamide(PAM)	Mussel-inspired chemistry (non-covalent)	Ambient environment	95% (conductivity) 60% (tensile strength) 80% (Extension ratio)	Bioelectronics	Han et al., 2017b
11-(4-(pyrene-1-yl) butanamido) undecanoic Acid/CNT/rGO	π-π stacking and Hydrogen bonding	RT pH = 13.4	93% (strain)	Biomedical	Roy et al., 2013
GO/PAA	Diffusion of polymer chain Hydrogen bonding	RT	88% (tensile strength)	Biomedical	Liu et al., 2013
PDA/Nanoclay/PAM	Mussel-inspired chemistry (non-covalent)	Ambient environment	100% (compression strain for 20 cycles)	Wound healing	Han et al., 2017a
graphene oxide (GO)-hectorite clay-poly(N,N-dimethylacrylamide) (PDMAA)	Hydrogen bonding	Near-infrared (NIR) irradiation	96% (tensile strength)	Wound dressing	Zhang et al., 2014
pDMAA/β-CDrGO	Hydrogen bonding	37°C	80%	Drug delivery	Chen et al., 2014
Graphene oxide(GO)/poly(acryloyl-6-aminocaproic acid) (PAACA)	double-network mechanism	RT pH<3	86%	Drug release	Cong et al., 2013

(Continued)

TABLE 5 | Continued

Materials	Self-healing mechanism	Self-healing conditions	Self-healing efficiency (recovery %)	Applications	References
PDA/ Fe_3O_4/ Carbon black/PAM	π-π stacking and Hydrogen bonding	RT	100% Tensile, conductivity and magnetic properties	Drug delivery and tissue engineering	Han et al., 2017c
Chitosan/Go	π-π stacking	RT	91% (compressive stress)	Tissue engineering	Jing et al., 2017
GO-UPy-PNIPAM	Supramolecular	RT	100% (elastic modulus)	Drug delivery	Chen et al., 2018b
GO/DNA/SH	π-π stacking and Hydrophobic interaction	90^0C for 3min	100% (adsorption)	Drug delivery	Xu et al., 2010
PDMAA-PVA/rGO	Hydrogen bonding	RT	100% (ultimate tensile strength and conductivity)	Artificial skin	Hou et al., 2013
p(HEMA-co-BA)-Fe_3O_4	Host-guest interactions	RT	94.98% (electromagnetic absorption bandwidth) 40% (tensile)	Coating	Wang et al., 2017b
lignin-modified graphene (LMG) and waterborne polyurethane (WPU)	Polymer diffusion	Infrared	171% (elastic modulus)	Anticorrosion coatings	Seyed Shahabadi et al., 2017
PAA-MBAA-$FeCl_3$	Covalent bond and ionic interaction	RT	99% (elastic modulus)	Coating	Wei et al., 2013a
CNT/PU/Ze^{2+}	Supramolecular	Near infrared (NIR) light (4.2 mW/mm^2)	93% (toughness)	Coating	Zheng et al., 2016

chain provides self-healing capability, while GO enabled good mechanical properties.

A symbiosis of shape memory and self-healing was also achieved for graphene oxide based polyurethane (GO-PU) nanocomposites (Thakur et al., 2015), where fracture of the composite was effectively healed by exposure to direct sunlight and MW. The nanocomposites were effectively healed within 30–50 s under low MW power (360 W) and within 5–7 min under direct sunlight. During the healing process, GO absorbed energy from the stimulus, and then transferred this energy to the HPU matrix, where the soft segment of the HPU melted (low T_m $\sim 50^\circ C$). Thus, the crack could repair with a higher mobility of the soft segment of HPU. To achieve combined attributes of shape memory, self-healing and self-cleaning properties, hyperbranched polyurethane (HPU)-TiO_2/reduced graphene oxide (TiO_2/RGO) nanocomposites were reported (Thakur and Karak, 2015), where the fabricated nanocomposite exhibited composition and dose-dependent mechanical properties with excellent shape recovery ratio (91–95%) as well as shape recovery rate (1–3 min) under exposure to sunlight. The presence of a high amount of RGO (0.5–1 wt.%) in the nanocomposite helps in rapid and efficient healing, whereas a high amount of TiO_2 nanoparticles (5–10 wt.%) aids in achieving good self-cleaning properties.

Chemical Interactions Based Self-Healing Soft Materials and Their Nanocomposites

This section covers the strategies for the preparation of chemical self-healing soft materials based upon dynamic networks of covalent interactions, including Diels-Alder reactions, disulphide, imine bond, boronate ester bond, acylhydrazones, and nanocomposite interactions. An overview of the reaction types, which are discussed herein, is provided in **Table 3**. Depending on the conditions, dynamic permanent covalent bonds can break and reform. For instance, a disulfide and acylhrazone bonds based self-healing network was developed, where in PEO based hydrogel, disulfide exchange reaction occurs at basic pH, whereas acidic pH is helpful for acylhydrazone exchange reactions (Deng et al., 2012). The material did not show self-healing at neutral pH as the covalent bonds were not dynamic. In general, the broadly investigated temperature triggered reversible diene and dienophile based [4+2] cycloaddition and retro Diels-Alder (DA) mechanism make good candidates for healing networks.

A comprehensive study by Garcia et al. demonstrated the effect of reversible DA bonds in covalently cross-linked networks (Garcia et al., 2014). The study shows that due to retro-DA reaction at high temperature, an increased mobility in the network leads to the self-healing of the system. However, the required high temperature for DA/retro DA damages the properties of the parent material. A switchable "on" and "off" based photo-switchable DA dynamic network was developed by Hecht et al., where the incorporation of furan crosslinker allows reversible (de- and re-crosslinking) in short and mobile maleimide-substituted poly(lauryl methacrylate) chains (**Figure 5**) (Fuhrmann et al., 2016). In general, the common dynamic chemical interactions based self-healing are reversible upon temperature usage, thus limiting their application areas.

The incorporation of nanofillers with this type of self-healing mechanism is also widely described, as highlighted in **Table 4**. In particular conductive nanofillers are used to trigger and catalyze the self-repair performance, owing to their superior heat absorption properties and resulting local heating under sunlight and microwave radiation. Indeed, due to their high photo-thermal conversion, conductive nanofillers enable to increase the temperature up to 200°C in a very short time (Kohlmeyer et al., 2012). Shi et al. developed a dynamic reversible cross-linked organic-inorganic network via DA reaction between poly(styrene-butadiene-styrene) and CNT. The material demonstrated DA based self-healing with complete recovery of the mechanical properties in a time as short as 10 s due to the photo-thermal effect of CNT under laser irradiation (**Figure 6**) (Bai and Shi, 2017) whereas no self-healing occurred in absence of CNT.

APPLICATIONS

Self-healing soft materials find applications in engineering and bio-medical fields. The major uses of self-healing materials so far are in surface coating (Canadell et al., 2011; Yoon et al., 2012; Yang et al., 2015a), drug delivery (Huebsch et al., 2014; Liu et al., 2016; Wang et al., 2016, 2017a; Xing et al., 2016; Xia et al., 2017; Yavvari et al., 2017; Hong et al., 2018), tissue engineering (Dankers et al., 2012; Bastings et al., 2014; Gaffey et al., 2015; Rodell et al., 2015; Loebel et al., 2017), wound healing (Gaharwar et al., 2014; Han et al., 2016; Zhao et al., 2017b; Zhu et al., 2017; Li et al., 2018c), and soft robotics (Shi et al., 2015; Darabi et al., 2017; Han et al., 2017b; Liu et al., 2018b). Herein, some applications of soft self-healing nanocomposites in biomedical fields including drug delivery tissue adhesive, as well as in industrial fields including actuators, sensors, and coatings are gathered (**Table 5**).

CONCLUSIONS AND OUTLOOK

A large variety of concepts based on physical and chemical interactions have been explored to design soft self-healing materials, each strategy presenting its own advantages and drawbacks. In general, materials based on chemical interactions require an *ad-hoc* external stimulus to trigger the healing reactions, whereas those based on physical interactions enjoy an autonomous and fast repair. As a matter of fact and as highlighted in many reviews, no standard measurement technique is available to quantify self-healing, so it is difficult to compare the merits of each material in terms of healing efficiency as easily as it is for their strength or toughness. According to the summarized data, soft self-healing materials based on ionic bonding and hydrogen interactions demonstrate a fast but moderate healing efficiency, whereas a slow but high healing efficiency is observed in case of supramolecular bonding. When considering applications, it is important to keep in mind that mechanical robustness and self-healing properties are often opposite, except in some cases where chemical interactions triggered with external stimulus can be relied upon. However, even if there is no straightforward technique to compare the mechanical properties of soft materials, generally, the modulus followed the usual trend, with covalent bonding > ionic bonding > hydrophobic bonding > supramolecular interactions. The addition of nanofillers enables enhancing the mechanical and other physical properties such as thermal and electrical conductivity (Ding Q. et al., 2018). The addition of conducting nanofiller was found more effective for not only enhancing the conductivity but also mechanical properties of the soft materials. As for self-healing, conducting nanofillers are used as triggers/catalysts for photo-thermal activation and resulting enhanced self-repair performance. Laser-induced photo-thermal activation was for instance found to speed up the healing process, but this also led to the partial breakdown of the conductive network, thereby preventing multiple healing. Efficient healing combined with desirable mechanical properties seems at this stage to be reached using a chemical interaction-based concept. Certainly, the selective functionalization and dispersion of nanofillers is quite challenging, and perhaps that is the reason why most of the soft self-healing nanocomposites are nowadays based on physical interactions, rather than on chemical interactions.

AUTHOR CONTRIBUTIONS

RS and BK performed the literature search and tables as well as first drafts. YL, SR, and VM organized the outline and wrote the text. All authors have contributed to the review article.

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