Self-Healing Polymer Nanocomposite Materials: A Review

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Abstract

During the last few years, different kinds of autonomic and non-autonomic self-healing materials have been prepared using diverse techniques for a number of applications. The incorporation of suitable functionalities into these materials facilitates a healing mechanism that is triggered by damage/ rupture as well as various chemistries. This article presents a detailed study of the self-healing properties of different kinds of polymer nanocomposites utilizing a number of healing mechanisms, including the addition of several healing agents. The article will also provide an overview of different chemistries employed in the preparation of self-healing polymer nanocomposites, along with their advantages and disadvantages.

1. Introduction

Synthetic self-healing materials are a class of new emerging smart materials with the ability to spontaneously and autonomously heal, mimicking the self-healing functionality that is observed in many living organisms [1-2]. In fact, spontaneous self-healing is an imperative requirement for sustaining life; it increases the survivability and lifetime of most living organisms [3-5]. Since the publication of our paper on autonomic self-healing of polymer composites in 2001 [6], the Web of Science lists more than 6000 publications covering the field of self-healing materials. These publications reported on self-healing chemistries in different kinds of materials, including thermoplastic polymers, thermoset polymers, elastomers, shape memory polymers, supramolecular polymers, polymer composites, nanocomposites, and coatings [7-12]. Inspired by a variety of natural materials, research in synthetic self-healing materials focuses on the preparation of multifunctional materials that are able to recover their fundamental properties including mechanical strength, conductivity, fracture toughness, and corrosion resistance, after damage has occurred [5]. Self-healing abilities in synthetic materials increase lifetimes and opens a range of promising applications for these materials [7, 13].

During the last few years, several review articles have been published investigating the synthesis and chemistry of self-healing polymers [14-18]. The self-healing properties of polymer composites have also been comprehensively reviewed [4, 19-21]. The concept of self-healing has been successfully applied to a number of materials that also include nanostructured materials [20] [22-24]. On the basis of chemistry of self-healing polymers/ polymer composites, current literature categorizes these materials into two classes: (i) autonomic and (ii) non-

autonomic self-healing materials (Figure 1a-c) [25].

Figure 1 (a). Classification of materials based on their self-healing chemistry. Adapted from [25].

Figure 1 (b). Organization of materials based on autonomic self-healing systems. Adapted from [25].

Figure 1 (c). Organization of materials based on self-healing non-autonomic systems. Adapted from [25].

In autonomic self-healing materials, the harnessed chemical potential is automatically released and facilitates the repair/ healing in response to damage/ rupture. On the other hand non-autonomic self-healing materials need external intervention. Williams *et al.* have reviewed the chemistry of autonomic and non-autonomic healing materials [25]. These materials are also divided into different types depending upon the chemistry and applications [25-27]. Most often these are also divided into intrinsic and extrinsic self-healing system [2-4, 25-26]. These materials have been discussed in detail in the self-healing materials section.

Among different materials, polymer nanocomposites with superior properties in terms of strength, stiffness, cost, thermal stability and lightweight are leading candidates as material components in a number of applications to improve the efficiency and sustainability

[28]. However these also suffer from drawbacks such as mesoscopic damage (e.g., micro-cracks and cavitation), degradation and surface scratches. The implication of self-healing concepts into polymer nanocomposites offers new directions towards sustainable, safer and longer lasting materials for multifunctional applications including, electronics, energy, transportation and coatings to name a few. Indeed, the field of self-healing polymer nanocomposites is rapidly emerging and new chemistries have been reported. The first part of the review will focus on a brief introduction of self-healing concepts and provide a general overview of the different self-healing chemistries employed in polymers and their composites. On the other hand, the latter part signifies the chemistries currently being used in self-healing polymer nanocomposites.

2. Self-Healing: Concept and Materials

In comparison to traditional materials, self-healing materials display the extraordinary ability of self-healing/ self-repair when subjected to failure through fracture/ fatigue. So far most of the research work in self-healing arena is focused on the disciplines of polymers and polymer composites as these materials are used excessively in everyday and industrial applications. Self-healing polymer based materials with imperative self-healing effects are expected to result in the incorporation of a number of merits as well as in resolving the traditional problems of polymers and their respective composite materials. In order to be considered as healing material, it must meet certain set of properties. Table 1 summarizes the characteristics of self- healing materials [8]

Table 1 Different desirable properties of self-healing materials [8]

Self-Healing Materials
Ability to automatically heal the materials
Ability to heal the damage of materials multiple times
Ability to heal the materials with defects of any size
Reduced maintenance cost
Exhibit better or equal performance in comparison to traditional materials
Should be economic than the presently used materials

2.1 Self-Healing Materials: Extrinsic and Intrinsic

Based on the general mechanism of self-healing employed, these materials can be divided into two categories namely extrinsic and intrinsic. The main difference between these two types of self-healing materials lies in their chemistries.

Extrinsic healing systems rely on an external healing agent in the form of capsules or vascular networks [6-7, 29]. In extrinsic self-healing, design of the autonomic materials being developed is based upon the healing agent and a catalyst to be embedded in the matrix [31-37]. The two approaches/ designs frequently used to prepare such materials include the (i) microencapsulation and (ii) microvascular network. In both approaches, the self-healing process is initiated by the external/ internal damage / rupture in the vascular networks as well as the capsules [6, 30]. The capsule shells are typically made of poly (urea-formaldehyde) (PUF); polyurethane; poly (melamine-urea-formaldehyde) (PMUF) and poly (melamine-formaldehyde) (PMF), to name a few [31-36]. Different polymerization techniques have been reported to form these capsules [21]. The microencapsulation approach suffers

from two major drawbacks including (i) high cost of the catalyst (especially Grubbs catalyst) and (ii) the process of self-healing of materials generally can occur only once since the amount of healing agents is depleted in the healed region. However, to overcome these limitations, several other approaches have been investigated during the last few years and are summarized in a number of reviews [14-18].

Intrinsic self-healing materials generally are based on either non-covalent chemistries or dynamic covalent chemistries [38]. The non-covalent chemistry approach uses π - π stacking, ligand-metal bonding, hydrogen bonding, or host-guest interaction stacking among other techniques [39- 47], while covalent approaches use Diels-Alder reaction, radical exchange, dynamic urea bond, and trans-esterification, to name a few [48-54]. The chemistry of self-healing polymers based on hydrogen bonding, $\pi - \pi$ interactions, ionomers, and coordinative bonds has been recently reviewed [26]. In this article, the advantages and adaptability of these supramolecular forces for the design and realization of different kinds of self-healing polymers have been discussed. The re-formation of chemical bonds in intrinsic materials is triggered by a number of external stimuli including pH change, light, temperature, pressure, or oxygen to name a few [10, 38-42, 48-55]. Diels-Alder (DA) reactions are most frequently used to create self-healing polymers that utilize reversible bond formation [10] [56]. Bergman and Wudl have reviewed the different Diels-Alder reactions [10].

3. Self-healing of Polymer Nanocomposites: Chemistry and Applications

Different kinds of polymer-based materials have been used for a number of applications due to their inherent characteristics including light weight, copious availability, flexibility, easy processing, lightness, and tailoring ability to name a few [57-60]. However,

compared to metals and ceramics many of these materials exhibit poor mechanical properties, such as lower modulus and strength [58, 61]. Research has shown that incorporation of nanomaterials significantly affects different properties of polymers including mechanical/physical properties [62-64]. Embedding nanomaterials in a host matrix results in material properties that are not achieved by either phase alone [65, 66], typically caused by interactions of the nanomaterials and matrix [67, 68]. In nanocomposite materials, combination of polymer and nanomaterials at the nanoscale results in materials that are highly homogeneous resulting in the development of novel materials with excellent properties. However, crack formation in the synthesized nanocomposites is among very critical problems, comparable to that seen in polymer and polymer composite systems. Indeed it is very difficult to avoid delamination cracks/ micro-cracks in polymer nanocomposites frequently caused even by small impacts during transport and handling for high performance applications such as in armour, aerospace, ballistic protection, etc. To resolve these problems, both theoretical and experimental studies on self-healing of these polymer nanocomposites have been undertaken. In fact, self-healing of polymer nanocomposites has remained largely unexplored and it should provide new opportunities for development of high performance multifunctional materials. In the following section, we will discuss the different theoretical and experimental aspects of self-healing of polymer nanocomposites.

3.1 Theoretical Study of Self-Healing Polymer Nanocomposites

Theoretical modeling and use of computational design tools provides significant information on the self-healing process of polymer and polymer composite materials. However still the use of these techniques in studying the properties of self-healing polymer nanocomposite

materials is limited. Recently some researchers have used these approaches in the self-healing polymer nanocomposites. Computer simulation was used to study the self-healing of composites utilizing nanoparticles [69]. In this work, computer simulations was used in detail to validate that the addition of nanoparticles in the matrix (polymers) results in nanocomposite materials where the particles were found to become localized at nanoscale cracks. Due to the localization, these particles facilitates the repair of damaged regions as a result of formation of “patches”. Different micromechanics simulations were then used to study the properties of the nanocomposites systems in different states. These states primarily include the healed state, undamaged state and damaged, state. From this study, it was concluded that the different mechanical properties of the healed nanocomposites can be restored to 75 – 100 % in comparison to pristine nanocomposite material. Balazs has reviewed the modeling of self-healing materials [70]. She studied different computational approaches to design “artificial leukocytes”. These leukocytes were found to assist the healing of the investigated polymer nanocomposites. The study showed that computational research can provide valuable insight into the emerging field of self-healing polymer nanocomposites [70]. Molecular dynamics was utilized to study the use of CNTs as nano-reservoirs for self-healing applications [71]. From the study it was established that CNTs can acts as both self-healing containers as well as the reinforcement. In this study the dynamic behavior of the organic molecules that were stored in a CNT was studied during its escape from a crack in the CNT wall. The amount of organic molecules escaping through the crack depended on the dimension of crack formed in the wall of CNT.

A new theoretical approach for the development of self-assembling organic–inorganic nanocomposites was also proposed [72]. These nanocomposites exhibit nacre-like hierarchical

structures in which the nanoparticles result in the incorporation of a self-healing ability in the material [72]. “Self-assembly of polymer-grafted nanoparticle/diblock copolymer” blends in this work was explored employing self-consistent field (SCF) theory. This study successfully described the formation of nacre-like nanocomposites. From the study it was established that different components can be assembled into hierarchical structures having nanosized mineral bridges. These bridges connected neighboring platelets and functionally protected the organic macromolecular polymer band resulting in imparting a self-healing function to the material. **Figure 2** is a schematic illustration of the self-healing function of the system. From the figure, it is clearly evident that nanoparticles in certain quantity migrate to the platelet surfaces. These particles were migrated in addition to those involved in the formation of mineral bridges and results in an interphase layer between the organic and inorganic platelets phases. The repulsive enthalpic interaction among nanoparticles/ block copolymers was responsible for the formation of interphase.

Figure 2. Schematic illustration of the self-healing function of the system. When a crack occurs in the organic layer, the dispersed nanoparticles in the soft organic phase (a) will migrate towards the surfaces of cracks and, in turn, repair the damage (b). The blue, pink and yellow colors represent the inorganic aragonite platelets, organic layer, and nanoparticles, respectively. Reprinted with permission from [72]. Copyright 2011 Royal Society of Chemistry.

It was concluded from the study that polymer nanocomposites with suitable hierarchical architecture can be prepared using the grafted- nanoparticle assembly approach. Urea-formaldehyde polymers (cross-linked) were also studied using molecular dynamics simulation for self-healing nanocomposites [73]. In this study, simulation was used to investigate the structural, thermal and mechanical characteristics of simulated poly (urea- formaldehyde) s (PUFs). From the simulation results it was demonstrated that crosslinking significantly improved the poly (UF) materials properties.

3.2 Self-Healing Polymer Nanocomposite Hydrogels

Hydrogels are water swollen polymer networks having the capability to swell in water/ aqueous solutions from 10-20 % up to thousands of times their initial dry weight. Rising needs in a number of fields such as in biomedical and pharmaceuticals have further led to extensive development in hydrogels and polymer nanocomposite hydrogels. However, self-healing in polymer nanocomposite hydrogels has been recently reported owing to the inherent properties of hydrogels that mostly facilitates the process of self-healing. The development of self-healing in gels/ hydrogels is based on the concept of constitutional dynamic chemistry that comprises of non-covalent chemistry as well as dynamic covalent chemistry. Detailed studies on underlying self-healing mechanisms in different gels, including hydrogels, have been reviewed by Zhao et al. [18]. To avoid the repetition, we will not be discussing the mechanism here. Haraguchi *et al.* studied self-healing in nanocomposite hydrogels [44]. The nanocomposite hydrogels consisted of a unique (poly (N, N-dimethylacrylamide) (PDMAA) and poly (N-isopropylacrylamide) (PNIPA))/clay network structure. These hydrogels exhibited

comprehensive self-healing together with extraordinary mechanical properties. The nanocomposite hydrogels were named as D-NCn or N-NCn gels, contingent on the type of polymer (D- for PDMAA, N- for PNIPA) as well as clay concentration ($C_{\text{clay}} = n \times 10^{-2}$ mol/L- H_2O) used. It was illustrated that self-healing in a D-NC3 gel, in which damaged regions completely healed after 48 h at 37 °C irrespective of their size. The self-healing in all types of gel was attributed to the “autonomic reconstruction of crosslinks across the damaged interface” in the nanocomposites hydrogels. The mechanical damage in nanocomposite hydrogels was also found to autonomically repair. Organoclay was also used as reinforcement in other polymer matrices for self-healing applications. Poly (vinylpyrrolidone) PVP/ organoclay nanocomposite hydrogels with self-healing properties were prepared [74]. **Figure 3** shows images of these nanocomposite polymer hydrogels. In this work the guest-molecule-directed assembly of mesostructured nanocomposite polymer/ organoclay hydrogels was studied at room temperature. The synthesis was carried out in the presence of varying amounts of exfoliated synthetic organoclay (1–5 wt %) at room temperature. These nanocomposites hydrogels could be molded into free-standing objects and were able to self-heal upon damage. They demonstrated stability between pH values of 4 to 11 and also exhibited sustained drug release. These nanocomposite polymer hydrogels were found to be reversibly dried. In addition they could be recharged and reused as well as reconstituted. It was concluded that the strategy employed in this study opens new directions for self-healing nanocomposite hydrogels.

Figure 3 Optical images of nanocomposite polymer hydrogels. a) Nanocomposite PVP/organoclay hydrogel prepared with PVP and organoclay contents of 20 and 5 wt %, respectively; (b) molded into a transparent macroscopic object; scale bar 1 cm; c) nanocomposite PVP/organoclay/ibuprofen hydrogel prepared at PVP, organoclay and ibuprofen contents of 20, 5 and 1 wt %, respectively; d, e) self-adhesion of freshly cut segments of a nanocomposite PVP/organoclay hydrogel; (d) immediately after contact, and (e) after 3 h; scale bars = 1 cm. Dye molecules (methylene blue and orange-2) remain partially localized within the self-healed segments; f–h) time series of images of the same nanocomposite PVP/organoclay hydrogel showing swelling behavior after immersion of a dried sample in water after (f) 0, (g) 24, and (h) 72 h. The gel is dyed with carmine/curcumine to aid visualization. Scale bars = 2 cm. Reprinted with permission from [74]. Copyright 2011 Wiley Interscience.

In addition to organo clay, researchers have also explored the use of gold nanoparticles in hydrogel polymer nanocomposites. Gold nanoparticle (AuNP) reinforced self-healing microgel multilayers polymer nanocomposites were prepared [75]. The average diameter of the nanoparticles used was 13 nm. These hydrogel were prepared using a centrifuge-assisted layer-by-layer technique employing atop elastomeric poly (dimethylsiloxane) substrates. In the swollen hydrogel films, gold nanoparticles were added using immersion method. The amount of AuNP in the multilayer was adjusted by changing the concentration. Optical properties and uniformity of fluorescence quenching confirmed that the NPs were uniformly dispersed within the film. The addition of AuNPs was found to result in a marked difference in strain resistance of the films as well as the original structure after repeated cycles of damage and re-healing. The investigation also showed that there were no alterations in the studied properties irrespective of the applied strains order. The study concluded that Au nanoparticle-doped films exhibit significant reduction in damage compared to hydrogel films without Au reinforcement under identical stretching conditions. In addition on the rehydration, the damage in the film was found to be completely reversible. It confirmed that the film mobility was not reduced due to the addition of AuNP. Along with the nanocomposite hydrogels, supramolecular nanocomposites hydrogels were also prepared for self-healing applications. These bioinspired nanocomposite hydrogels prepared with clay exhibited significant self-healing properties [76]. The swelling-cum-shearing method was used to prepare the exfoliated clays into single layers. Subsequently, *in situ* polymerization of polydopamine (PDOPA) was used to coat the exfoliated clay layers under basic aqueous conditions for preparation of clay hydrogels (**Figure 4**). Self-assembled three-dimensional networks were found to form by the addition of certain amounts of ferric salt into the suspensions (aqueous) of the polydopamine- coated clay as a result of the coordination

bonds formation between D-clay and Fe^{3+} ions. Hydrogels with significant quantity of water were then prepared at room temperature by the formation of coordinate bonds among the D-clay nanosheets and ferric ions. The coordination bonding resulted in a supramolecular network. These hydrogels were found to exhibit significant self-healing properties at room temperature which was attributed to the reformation of damaged catechol- Fe^{3+} complexes in comparison to the covalently bonded hydrogels. These self-healing hydrogels can be used as adsorbents in the removal of Rhodamine 6G (Rh6G) from water.

Figure 4 Schematic description of the formation mechanism for D-Clay hydrogel. Reprinted with permission from [76]. Copyright 2013 American Chemical Society.

Carbon nanotubes and graphene oxide were also used in the preparation of self-healing nanocomposites hydrogels in addition to clay and gold nanoparticles [77-78]. Graphene oxide (GO) based self-healing nanocomposite hydrogels were prepared for biomedical applications [77]. These gels were prepared at 45°C employing graphene peroxide as polyfunctional initiating as well as cross-linking centers. The self-healing performance was then studied in

detail. The study determined that these hydrogels were able to self-repair when their cut surfaces were in contact **at room temperature and even when they were at lower temperatures (for a short duration)**. At prolonged healing times, extraordinary recovery degrees (up to 88 %) was found to be accomplished. The GO composite hydrogels after healing also exhibited excellent tensile strengths (up to 0.35 MPa) along with the elongations (up to 4900 %). Strong interactions in between GO sheets and polymer chains was found to result in the enhanced strength. **Figure 5** shows the projected self-healing mechanism in hydrogels.

Figure 5. The proposed self-healing mechanism of GO composite hydrogels. Reprinted with permission from [77]. Copyright 2013 Wiley Interscience.

It was concluded that this methodology provides a new approach to prepare smart materials with multifunctional applications. Self-healing nanocomposite gels were prepared employing phenylboronate-diol crosslinked polymers that were incorporated with functionalized single-walled carbon nanotubes (f-SWCNTs) [78]. Crosslinking of the mixture of f-SWCNTs and diol-containing polymer with phenylboronic acid- containing polymers was carried out to synthesize SWCNT/ gel nanocomposites. Rheological analysis and scanning electron

microscopy (SEM) were subsequently employed to characterize these gels and it was confirmed that the f-SWCNTs were homogeneously dispersed in the polymer gel matrices. From the rheological tests it was also confirmed that the hybrid gel demonstrated higher storage moduli in comparison to the pristine gel. Healing efficiencies of all the healed gel samples was found to be higher than 62%. Self-healing tests of the synthesized gels was studied at ambient temperature and showed that they healed autonomously within 30 minutes without any outside stimulus. **Figure 6** shows the self-healing behavior of the nanocomposite gels.

Figure 6 Self-healing properties of the covalent dynamic hybrid gels (a) cracked native gel, (b) cracked hybrid gel (f-SWCNTs = 0.06 wt%); (c) merged bicolor gel by simply putting half (a) and half (b) together in an original container for 30 min without any outside intervention at ambient temperature; (d) merged bicolor gel lifted by tweezers: the gels have merged together

as a whole. Reprinted with permission from [78]. Copyright 2014 Wiley Interscience.

Biorenewable polymers were also used in the preparation of self-healing nanocomposite hydrogels. Healable, stiff nanocomposite hydrogels were prepared using “hard” nanocrystalline cellulose domains and “soft”, supramolecularly cross-linked polymeric domains [79]. Nanocrystalline cellulose was functionalized using surface-initiated atom transfer radical polymerization. These functionalized chain contained methacrylate polymer brushes and bear the naphthyl units. On the other hand, the soft domains utilized cucurbit [8] uril (CB [8])-based ternary complexation. These CB [8] complexation facilitated dynamic host–guest interactions in addition to selective and simultaneous binding of naphthyl and methyl viologen units. **Figure 7** schematically shows the architecture of the nanocomposite hydrogels.

Figure 7 Schematics and architecture for highly specific, dynamic and stiff three-component recognition-driven supramolecular hydrogels based on cellulose nanocrystals (CNC) and CB[8] host-guest chemistry. a) Poly (vinyl alcohol) (PVA) containing the first-guest methyl viologen functionality (PVA-MV). b) CNCs containing copolymer grafts of protonated

dimethylaminoethyl methacrylate (DMAEMA) and second-guest naphthyl methacrylate (NpMA) repeat units (CNC- g -P(DMAEMA- r -NpMA)) with DMAEMA/NpMA ~ 10/1 mol/mol. c) CB[8] as the host motif. d) Selective supramolecular cross-links based on three-component recognition by CB [8] binding together the components into dynamic hydrogels, where the modified PVA bridges the CNC-grafts together. Reprinted with permission from [79]. Copyright 2014 Wiley Interscience.

These nanocomposite hydrogels exhibited high storage modulus ($G' > 10$ kPa) along with rapid sol–gel transition (< 6 s) as well as rapid self-healing. They maintained their healing properties upon aging for several months. The strategy demonstrated that it may open new ways for the preparation of renewable resources based advanced dynamic materials.

3.3 Self-healing in Composites with Carbon Nanomaterials

Carbon based nanomaterials such as carbon nanotubes, graphene etc. are rapidly emerging as one of the most fascinating component in self-healing polymer nanocomposites. The prime advantages of these nanomaterials include high surface to volume ratio, unique thermal, optical, mechanical and electrical properties to name a few. The characteristic structures of carbon based nanomaterials promote them to interact with polymer matrix materials through covalent and non-covalent bonds. Non-covalent interaction can be named as; hydrogen bonding, π – π stacking and van der Waals forces. Shape memory polymer (SMP) nanocomposites based on graphene were prepared and their self-healing characteristics were studied [80]. In this study, the nano-layered graphene (NLG) was synthesized using a “microwave plasma enhanced chemical vapor deposition method”. Epoxy-based SMP composites were prepared using pristine free standing

nanolayered graphene (NLG) at different loading levels (0.0025% and 0.0125%). The healing efficiency of SMP/ composite samples was studied at room temperature using a CSM scratch tester. Different images such as fractured polymer surfaces; recovered and as scratched were studied. Scratch resistance of the epoxy polymer based SMP was found to enhance as a result of the addition of the NLG whereas the pristine (unfilled) epoxy polymer (G0) exhibited several cracks. Based upon the detailed experimental investigation; the enhancement in scratch resistance of the composites materials was attributed to in-plane fracture strength of graphene sheets particularly the individual sheet. It was concluded that the incorporation of NLG in the SMP resulted in significant enhancement in different properties compared to pristine SMP.

Shape memory polymers were also used to prepare self-healing foams. Self-healing ability of syntactic smart foams subjected to multiple impacts was studied in detail [81]. In this work, syntactic foam based on shape memory polymer (SMP) were prepared using different materials such as shape memory polystyrene, multi-walled carbon nanotubes, glass micro-balloons and then VARIM (vacuum assisted resin infusion molding) technology was employed to fabricate composite sandwich plates with foam-core. In this study, impact-healing cycles in seven rounds were used to study different sandwich panels. Impact damage as well as healing efficiency at room temperature were characterized after each impact and healing cycle using C-scan; scanning electron microscopy (SEM) and compression after impact (CAI) tests. The study indicated that it was possible to heal the impact damage created in foams. The study also confirmed that the carbon nanotubes addition in the polymer enhanced the strength, stiffness, and shape recovery rate.

Different encapsulation techniques were furthermore used to prepare self-healing

nanocomposites. To prepare the nanocomposites, encapsulation of self-healing liquid monomers and carbon nanotubes was done using emulsion electro spinning, emulsion solution blowing, and co-electro spinning techniques [82]. The liquid monomers were incorporated inside polymer fibers [polyacrylonitrile (PAN)] as well as in carbon nanotubes (CNTs) that were amorphous turbostratic in nature. The healing monomers used were dicyclopentadiene (DCPD) and isophorone diisocyanate. Encapsulation of different self-healing monomers was demonstrated through fiber crush tests. The occurrence of self-healing liquid monomers inside the CNTs was analyzed using transmission electron microscopy (**Figure 8**). Figure **8c** and **d** confirm the intercalation of isophorone diisocyanate into the CNTs.

Figure 8 TEM images of the intercalated self-healing materials inside CNTs. DCPD inside

CNTs (a and b); isophorone diisocyanate inside CNTs (c and d). The arrow in (b) indicates the partially broken CNT wall. Reprinted with permission from [82]. Copyright 2012 Royal Society of Chemistry.

Ethylidene norbornene matrix based nanocomposites were prepared using single-walled carbon nanotube for applications in self-healing field [83]. In this study, self-healing nanocomposites were prepared by the reaction of single-walled carbon nanotubes (SWCNTs) and 5-ethylidene-2-norbornene (5E2N) with ruthenium Grubbs catalyst using an ultrasonication method. The ultrasonication was subsequently trailed by three-roll mixing mill process. It was observed that in a huge temperature domain (-15 to up $45\text{ }^{\circ}\text{C}$) the kinetics of the 5E2N ring ROMP reaction was very effective. The kinetics was investigated as a function of SWCNT loading and reaction temperature. Micromechanical characterization of the SWCNT/5E2N nanocomposite was performed using micro-indentation analysis after ROMP reaction. The results showed a significant enhancement in the Young modulus and hardness in comparison to the pristine polymer for CNT loads ranging from only 0.1 to 2 wt %. It was concluded that the results open new avenues for using carbon nanotubes for multifunctional applications including space. The improvement in self-healing efficiency of cross-linked polyethylene (cPE) and carbon black (CB) nanocomposites was also reported [84]. The healing in these nanocomposites was induced by their shape memory effect (SME). The strength of synthesized nanocomposite materials increased significantly as a result of the homogeneous dispersal of CB nanoparticles in the PE matrix. The higher strength at the melting temperature (T_m) of the cPE and the nanocomposites was attributed to the creation of a network between the CB and the cPE matrix, in comparison to the breaking of linear PE (lPE). Nanocomposites based

on the cPE/CB were also found to exhibit a high strain (fixity ratio (Rf) /strain recovery ratio (Rr)).

Thermo-reversible graphene oxide elastomer nanocomposites that exhibited efficient self-healing were also prepared [85]. In this study, the self-healing thermo-reversible elastomer nanocomposites were synthesized by cross-linking a hydrogen bonding polymer network and graphene oxide (GO). **Healing studies in this work were carried out at room temperature.** GO was surface modified in this study using carbonyl chloride (GO-COCl). **Figure 9** schematically illustrates the synthesis of the nanocomposites. The self-healing properties of the nanocomposites were investigated using both optical microscopy and SEM.

Figure 9. a) Synthetic route of HB-NH₂; b) Schematic illustration of the synthesis of the

self-healing nanocomposite (HBN-GO). Reprinted with permission from [85]. Copyright 2013 Wiley Interscience.

A razor blade was used to cut the nanocomposite material into two separate pieces and then gently brought back into contact to heal. Both SEM and optical microscope images confirmed the physical healing of the damaged surfaces. In addition, it was demonstrated that the healed sample could be subjected to high strain (100 %) after the two pieces were brought together for 1 minute, and the healed sample after stretching were also able to revert to the initial dimension. Here, the healing mechanism did not require external stimuli such as heating, light exposure, healing agents, plasticizers, or solvents. The authors also proposed that the combination of these elastomer nanocomposites with electrical fillers should result in elastomer composites with electrical conductivities.

Near IR induced self-healable graphene/ polyurethane (PU) polymer nanocomposites were produced using poly (tetramethylene glycol) (PTMG) and 4, 4'-methylene diphenyl diisocyanate (MDI) with varying small amounts (0–1 wt %) of modified graphene (MG) [86]. The goal was to strengthen and supplement the near infrared (NIR) absorption characteristics of pristine polyurethane (MG000). The glass transition temperature (T_g) as well as the modulus (initial) of the PU was found to increase with the incorporation of modified graphene. On the other hand, elongation at break as well as break strength of the polymer nanocomposites increased only at small loading (MG050) and at high loading levels (MG075, MG100) these properties were found to decrease. This effect was attributed to the fact that GO may interrupt the chain orientations at high loadings/ elongations. The NIR absorbance of the self-healable PU/MG nano-composite was found to enhance with the modified graphene and the effect was utmost prominent at the MG 075 loading. At this loading, the nanocomposites demonstrated higher

elastic strain energy than the pristine material up to ca 200 % strain. The self-healing characteristics of the nanocomposites were investigated using intermolecular diffusion of polymer chains. The thermal energy produced as a result of NIR absorption augmented the diffusion. Table 2 shows the healing efficiency and temperature rises of MG series with NIR irradiation for 2 h.

Table 2 Healing efficiency and temperature rises of MG series with NIR irradiation for 2 h.

Series	Irradiation time (h)	Sample temperature (°C)	Healing efficiency (%)
MG000	2	30	17.02
MG050		30–33	13.42
MG075		30–33	39.12
MG100		30–33	15.86

The effect incorporation of nanoparticles on self-healing poly (urea-formaldehyde) composite microcapsules was also studied [87]. *In situ* polymerization was used to prepare poly (urea–formaldehyde) (PUF) microcapsules. These capsules contained dicyclopentadiene (DCPD) as a self-healing component. Subsequently, single-walled carbon nanotubes (SWCNT) and nanoalumina were incorporated into the PUF shell wall to study different properties including mechanical as well as surface roughness of the microcapsule for self-healing applications. Nanoindentation was used to study these properties while the surface morphology, topography, and roughness was studied using scanning electron microscopy (SEM), optical microscopy (OM), and atomic force microscopy (AFM). The incorporation of nanotubes and nanoalumina into the PUF shell walls was found to result in the increment in the elastic modulus from 2.78 GPa for pristine microcapsules to 3.17 and 4.07 GPa, respectively. In addition, the nanoalumina/ PUF nanocomposite microcapsules exhibited

increased hardness compared to traditional and nanotube/ PUF nanocomposite microcapsules. AFM was employed to analyze the surface roughness of the microcapsules and it was observed that the pristine microcapsules were rougher compared to the nanocomposite microcapsules. The higher surface roughness in pristine microcapsules decreased the mechanical properties of the microcapsules and its performance in self-healing applications.

3.4 Miscellaneous Self-Healing Polymer Nanocomposites

In addition to the self-healing of composites with carbon nanomaterials, self-healing of nanocomposites based on other nanomaterials such as silica nanoparticles [88], halloysite nanotubes (HNT) [89-92], gold nanoparticles [93], silver nanoparticles [94-95], and nanocellulose [40-43] have been also studied. Silica-polymers and core-shell nanoparticles based self-healing nanocomposites were prepared and studied in detail [88]. These nanocomposites were synthesized using Diels-Alder (DA) and reversible Diels-Alder (rDA) reactions. Rheological measurement was used to analyze the increase in storage modulus of the nanocomposites during the DA reaction at 80 °C. The crosslinking between different components in the nanocomposite resulted in the increment in storage modulus. Self-healing properties of the nanocomposites were then studied using optical microscopy and scratch-healing tests on glass surfaces. Halloysite nanotubes (HNT) reinforced self-healing epoxy nanocomposites were prepared for structural applications [89]. Dimethyl sulfoxide (DMSO) and nitrobenzene were used as healing agents and were encapsulated in the nanotubes. The encapsulation was confirmed by Fourier transform infrared analysis, specific surface area (BET), scanning electron microscopy, X-ray diffraction and thermogravimetry. The autonomic healing was triggered by release of the liquid solvent into the crack plane as a result of the embedded nanotubes in the polymer. Halloysite clay polymer nanocomposites

based self-healing coatings for protecting the copper alloys from corrosion were also prepared [90]. In this study, nanotubes from natural halloysite clay were used as nanocontainers to entrap benzotriazole (BTA), 2-mercaptobenzimidazole (MBI), and 2-mercaptobenzothiazole (MBT) which are frequently employed as corrosion inhibitors. These containers containing the inhibitors were subsequently incorporated into self-healing composite coatings as additives for copper. These inhibitors were found to reduce corrosion as a result of formation of protective films on the metallic copper strips. The mechanisms involved in the formation of the film was studied using UV-vis spectrometry, optical and electron microscopy, and adhesivity tests. Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor were also developed [91]. In this study silica–zirconia hybrid sol–gel films were used for anticorrosive applications. These films were doped with nanocontainers of benzotriazole inhibitor and these nanocontainers in response to pH changes (frequently caused by corrosion) released the entrapped corrosion inhibitor. The nanocontainers in this study were synthesized using silica nanoparticles coated layer-by-layer (LbL) with polyelectrolyte molecules. It was concluded from the study that nanocontainers approach increases the long-term corrosion protection performance of metallic substrates. Monodisperse, mesoporous silica nanoparticles loaded with corrosion inhibitor (1H-benzotriazole (BTA)) were also used as nanocontainers for the corrosion protection of aluminum alloy [92]. These nanocontainers were embedded in hybrid SiO_x/ZrO_x sol–gel films and were homogeneously distributed with the uniform coating thickness. The scanning vibrating electrode technique (SVET) was then used to study the corrosion process and confirmed that the silica nanocontainers improves the performance of active anticorrosive coatings. Conducting polymer (CP) based nanocapsules system were developed for redox-responsive self-healing [93]. In this

study raspberry-shaped redox-responsive capsules which comprises a redox-sensitive polyaniline (PANI) shell along with self-healing agent encapsulated in the core were synthesized by the miniemulsion technique. To investigate the healing potential of the capsules, these were used as a part of a composite coating on zinc. These capsules were also decorated with gold nanoparticles (AuNPs) in order to avoid direct contact between the metal and CP during cyclic voltammetry (CV) study. These nanoparticles ensured a stable electronic contact during the measurement. This study demonstrated that PANI capsules exhibit remarkable switchable permeability for the stored agents encapsulated into these capsules. The composite coating of these capsules was found to be capable of corrosion-triggered release of active agents ensuring the stoppage of the corrosion and related delamination.

Self-healing

polystyrene sulfonate/ silver nanocomposite were prepared to use them for biomedical applications [94]. The sizes of the nanoparticles used was found to be around 25 nm. The formation of nanoparticles was confirmed through different characterization techniques including scanning electron microscopy (SEM). Supramolecular nanocomposite polymer system capable of self-healing was designed and synthesized by Vaiyapuri *et al.* [95]. The nanocomposite polymer system was prepared employing pyrene-functionalized gold nanoparticles (P-AuNPs), pyrene-functionalized polyamide and polydiimide. In this system, pyrenyl-encapped polyamide interacts with a chain- folding polydiimide through π - π stacking interactions. A healable polymer-nanocomposite system was then obtained by the incorporation of pyrenyl functionalized AuNPs into the polymer system. Complexation studies carried out in mixture of solvents such as chloroform- hexafluoroisopropanol successfully demonstrated that the incorporation of P-AuNPs leads to the formation of supramolecular network (insoluble) at a more rapid rate in comparison to control samples (without P-

AuNPs). The self-supporting robust nanocomposite films were tough and flexible. From the EDX mapping and DSC analysis, it was confirmed that the nanocomposites contain a uniform dispersal of P-AuNPs. Nanocomposites films containing P-AuNPs exhibited higher mechanical properties and were stiffer in comparison to the films without P-AuNPs as well as films that contained AuNPs and were lacking in the pyrenyl motif. The self-healing properties of the films were studied employing a classic break/ heal test protocols. It was observed that the films containing up to 10 wt % P-AuNPs exhibited healing efficiencies reaching 108 %. The tensile properties of the films were also studied and these films exhibited linear increment in strength (tensile moduli/ ultimate tensile strength) with the increase in loading of P-AuNP.

Hybrid organic–inorganic copolymer nanocomposites based on nano-building blocks (NBB) also exhibited self-healing properties [96]. Self-healing nanocomposite materials were prepared by hybridization of polymers (poly (n-butyl acrylate) (pBuA)) with nanobuilding units of butyltin oxo-cluster macrocation, $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$. 2-acrylamido-2-methyl-1-propanesulfonate anions (AMPS) was then used to functionalize these chains. The self-healing chemistry in these nanocomposites was attributed to the incorporation of sacrificial as well as reversible cross-linking in the polymers. When pieces of monolithic hybrid samples were brought into contact at room temperature, they healed. After healing the mechanical properties (recovery of aspect, tensile strength/ elongation at break) of the studied samples were found to be enhanced and the healing efficiency depended upon the period duration as well as temperature. The study showed that this approach has the potential to be generalized and extended to numerous polymerization schemes along with the NBBs in order to increase the long-term life of plastics and rubbers.

Nanoparticle-containing microcapsules were used to repair the damage of a cracked substrate [97]. A “repair-and-go” concept was used on a cracked polymer substrate (polydimethylsiloxane (PDMS)) employing CdSe nanoparticles. These nanoparticles were captured in oil droplets that were stabilized by polymer surfactant. **Figure 10** shows the repair-and go-approach. These microcapsules were found to selectively deliver the nanoparticles into the cracks formed on the surface. The release of these nanocapsules was attributed to the thin microcapsule walls along with the hydrophobic–hydrophobic interactions among the cracked surface and nanoparticles. Microcapsules based self-healing polymer composites have been extensively studied and reported [98-102]. However limited information is available on nanocapsules based self-healing composites. Nanocapsules-based self-healing polymer nanocomposites were recently prepared [103]. The nanocapsules were prepared by an *in situ* encapsulation method using a sonication technique. Urea–formaldehyde (UF) was used as the shell material and dicyclopentadiene (DCPD) was employed as the healing material.

Figure 10 (a) Optical micrograph of a cracked substrate (surface-oxidized PDMS) used for repair-and-go experiments. Scale bar, 500 μm . (b) PCOE-graft-PC polymer used for droplet stabilization and nanoparticle (NP) encapsulation. (c) Frame from a simulation that depicts nanoparticle deposition (blue particles) into a crack, followed by rolling of the capsule to the next crack (red arrow) (d) Fluorescence micrograph of a substrate following nanoparticle deposition into the cracks. Scale bar, 100 μm . Reprinted with permission from [97]. Copyright 2012 Nature Publishing Group.

The capsules filled with healing agent were thermally stable until 150 $^{\circ}\text{C}$ and revealed mean diameters of $1.56 \pm 0.5 \mu\text{m}$. On the other hand, in this study the smallest measured diameter was $220 \pm 113 \text{ nm}$ with uniform urea formaldehyde shell walls (77nm mean thickness). The

volume of healing agent in these capsules was found to be almost 94 %. These capsules were magnificently dispersed up to a capsule volume fraction of 0.02 in the polymer (epoxy) matrix. Authors have concluded from the study that the synthesized nanocapsules exhibit the potential to make the material responsive to damage. This responsiveness can be extended to smaller scale for a number of applications.

High-strength, healable polymer nanocomposites reinforced with cellulose nanocrystals (CNCs) were prepared employing a supramolecular polymer blend as the self-healing matrix material [41]. The π - π interactions between a π -electron-rich pyrenyl end-capped oligomer and a chain-folding oligomer resulted in the formation of supramolecular polymer blend. **Figure 11** shows the structure of the self-healing blend.

Figure 11. Molecular structure of healing polymer blend 1·2 (1:3 w/w ratio). Reprinted with permission from [41]. Copyright 2012 American Chemical Society.

Nanocomposites with CNC loading levels ranging from 1.25 to 20.0 wt % were prepared by utilizing a solvent-based dispersion technique and compression molding. The tensile strength of the nanocomposites increased with increasing CNC filler levels (>30-fold for 10 wt % CNC based nanocomposites). These nanocomposites were able to heal after exposure to elevated temperatures and the healing rate was found to depend upon the dispersed CNCs content. At 7.5 wt % loading of CNC in the polymer blend, the

nanocomposites demonstrated the highest healing efficiency and best mechanical properties.

Light-healable metallosupramolecular (MSP) polymer nanocomposites were also synthesized employing cellulose nanocrystals (CNCs) as the reinforcement with the aim to enhance the mechanical and stiffness of the resulting nanocomposites [40]. **Figure 12** schematically shows the metallosupramolecular nanocomposites.

Figure 12. Chemical structure of the metallopolymer $[Zn_xBKB](NTf_2)_{2x}$ and the CNCs and a schematic representation of the metallosupramolecular nanocomposites. Reprinted with permission from [40]. Copyright 2014 American Chemical Society.

Metallosupramolecular polymers were synthesized using telechelic poly (ethylene-co-butylene). 2, 6-bis (1'-methylbenzimidazolyl) pyridine (MeBip) ligands and $Zn (NTf_2)_2$ were then used to end-functionalized the poly (ethylene-co-butylene). The CNCs were found

to bind with the Zn^{2+} ions without any significant effect on its morphology. These nanocomposites were optically healable because the polymer absorbed the ultraviolet light and converted it into heat. The generated heat then results in the dissociation of the metal–ligand motifs as well as the metal-CNC complexes. This dissociation process results in liquefaction of the material and fills small defects present in the polymer nanocomposite material. Subsequently, the removal of UV irradiation resulted in the reassembly of the metallopolymer (MSP), thus leading to the efficient healing of such materials. From the mechanical characterization test it was confirmed that the metallopolymer along with CNCs flows back into the healed zone and restores the pristine nanocomposite.

Same research group also prepared light-healable supramolecular nanocomposites employing the same principle discussed above using modified cellulose nanocrystals [43]. Ureidopyrimidone (UPy) in this study was used to modify cellulose nanocrystals (CNCs) through hydrogen-bonding and the telechelic poly (ethylene-co-butylene) was also modified with hydrogen-bonding ureidopyrimidone (UPy). The synthesized nanocomposites were found to exhibit considerable increment in their mechanical properties compared to the parent supramolecular polymer, poly (ethylene-co-butylene). Even at 20 % loading of modified nanocellulose, the nanocomposites healed quickly and efficiently.

From the above discussion it is clear that self-healing polymer nanocomposites exhibit huge potentials for a number of applications. Different potential applications of self-healing polymer nanocomposites require the scientific community to address several issues such as designing advanced nanocomposites with high mechanical performance; multi-functionalities as well as development of assessment systems for evaluation of self-healing performance. In addition, considerable attention should be given to understand the mechanism of self-healing in

nanocomposites by theoretical studies along with the experimental investigation.

Conclusions

Recently, significant developments have been made in the field of polymer nanocomposites, their processing and design. However, the inherent problems of their damage repair are still limiting their use in diverse applications. The self-healing chemistries in the polymers and composites field have opened the way for applying these systems in polymer nanocomposites. Different self-healing approaches have been primarily applied to polymers/composites, however little attention has been paid to nanocomposite systems. We reviewed the chemistries of self-healing polymer nanocomposites and introduces examples of self-healing polymer nanocomposites. The research in the self-healing of nanocomposites is still in its early development stage. The self-healing mechanisms in polymer nanocomposites rely on different polymerization mechanism as discussed in this article. In the field of polymer nanocomposites, there is immense opportunity for further progress and development of new self-healing polymer nanocomposites. Although different chemistries have been reported for a number of materials, still limited information is available on the self-healing polymer nanocomposites. Several barriers needs to overcome in the self-healing nanocomposites to integrate these materials for different applications. Effective strategies are highly desired to optimize the design and enable the proficient synthesis and applications of polymer nanocomposite materials. Especially there should be repeated self-healing of these nanocomposite materials that would make them materials ideal for multifunctional applications. It would also allow the production of nanocomposites with enhanced sustainability. Innovative researches in the self-healing of polymer nanocomposites would benefit the new advanced high-strength polymer

nanocomposite. The future progress in self-healing polymer nanocomposites will depend upon the discovery and applications of advanced chemistries offering facile, rapid and controlled formation of advanced materials.

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