

Review Article

Self-Healing Polymers Designed for Underwater Applications

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Polymeric materials have been employed in a wide range of applications in both dry and wet environments. When these materials suffer damage, it becomes crucial to initiate repairs in order to mitigate further losses. The use of self-healing materials emerges as a promising strategy not only to address this issue but also possess the advantage of prolonging the product's lifespan. Nevertheless, the development of self-healing materials tailored for wet environments presents a set of obstacles and complexities. The review examines the current state of research in the field and highlights the challenges associated with developing self-healing materials that can effectively repair damage in such environments. We discuss the self-healing mechanisms and various polymers that are extensively employed in the advancement of self-healing materials. We study the progress made in the research and development of self-healing materials specifically designed for wet environments. Furthermore, it provides a summary of various applications of self-healing materials in wet environments.

1. Introduction

Polymeric materials have been used in various applications in our daily lives, such as coatings [1, 2], adhesives [3, 4], electronic devices [5–8], and matrices in composite materials [9–12]. These applications can be used both in dry and wet environments. Over time, these materials will experience damages, which need to be repaired, so that their function will still be in accordance with product requirements.

The damage that occurs in thermoset polymers is generally challenging to repair. This issue not only causes safety problems but also economic losses [13, 14]. For example, the losses caused by corrosion problems reach around 2%–5% of the world's Gross National Product [15]. Self-healing materials are a promising solution for repairing damage to these materials. These materials can heal themselves after being damaged, which can help prevent further losses from occurring. In 2021, the need for self-healing materials reached USD 2.1 billion. This need is projected to increase to USD

62.66 billion in 2028, mainly used in transportation, which is 56.9%, followed by energy and household appliances [16].

The development of self-healing materials in a wet environment has some challenges. The material might absorb the water molecules and lead to polymer plasticization. The water has a high relative permittivity (or dielectric constant), which can reduce the mechanical properties of polymers [17].

In this paper, the recent research progress of self-healing polymers in wet environments is discussed. This review presents an overview of the self-healing mechanism for polymeric materials. Furthermore, it discusses the development of self-healing materials in wet environments such as freshwater, seawater, and acidic or alkaline liquids. In addition, several applications of self-healing materials for wet environments are presented and discussed.

2. Self-Healing Mechanism

Biological systems, such as human wounds, vascular plants, mussels, and octopuses, have been inspiring scientists to

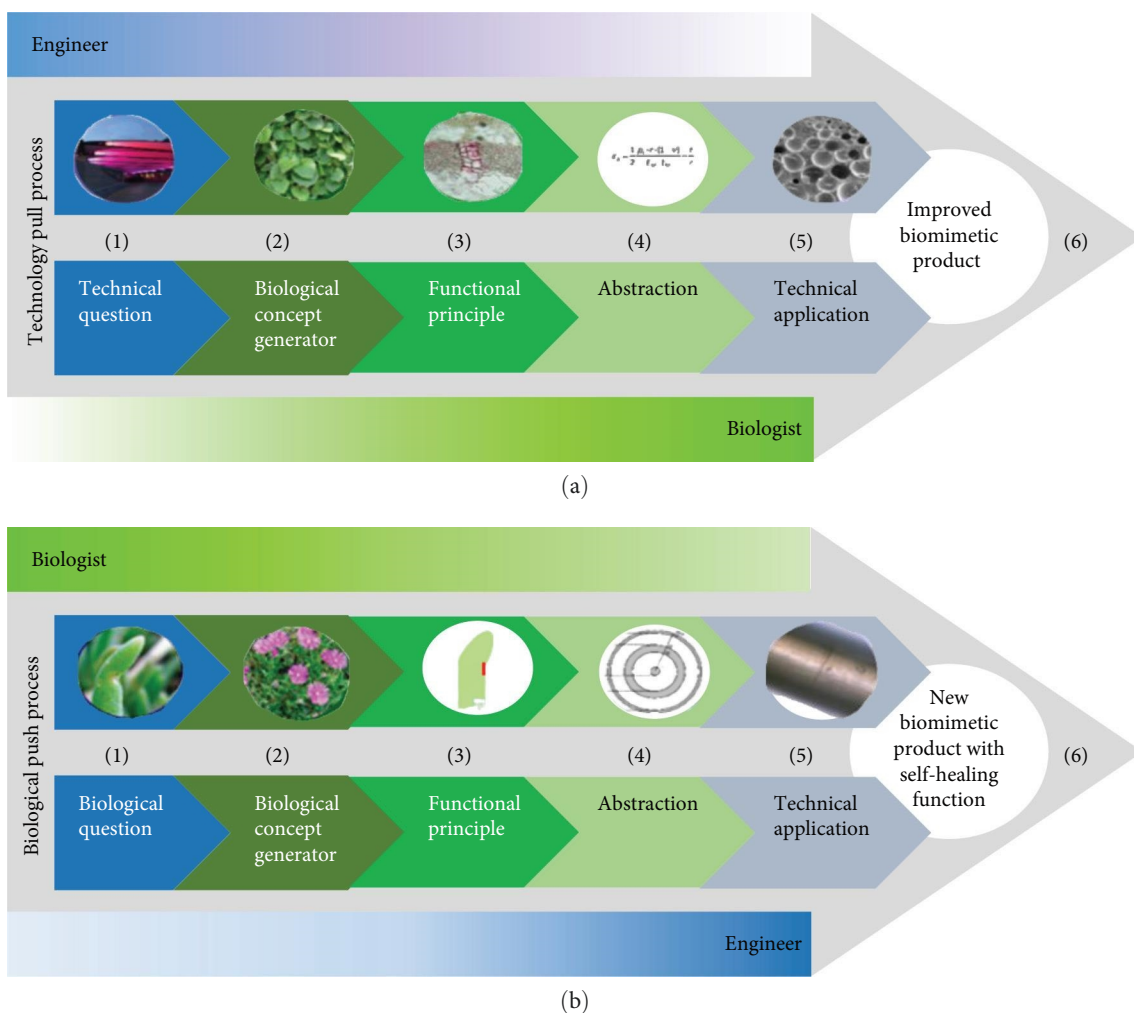


FIGURE 1: Two approaches to develop self-healing materials: (a) top-down and (b) bottom-up approach [19].

develop self-healing materials [18, 19]. There are two approaches to developing self-healing materials. The first is the top-down approach, which starts with technical questions in problem-solving, which is answered by concepts readily available in biological systems. The second is the bottom-up approach, where known biological phenomena are studied, and their concepts are applied in solving technical problems [19]. These two approaches are explained in Figure 1.

There are four key concepts to make the healing process take place properly: localization, temporality, mobility, and mechanism [20]. The first concept, localization, indicates the location and size of the damage. The damage can be located on the surface or in the inner part of a product, and it can be of molecular, micro, or macroscale, leading to different scales of losses. Ideally, one healing protocol can cure damages at any location and scale. The second concept, temporality, refers to the time difference between when the damage occurred and when it has been repaired. One of the challenges in developing materials with self-healing abilities is to achieve a short healing time. This decrease in healing time can occur by increasing mobility, which is the third concept

of the healing material. Mobility of the material will help the healing agent diffuse more easily into the damaged area. Inadequate mobility of the healing agent will lead to a slow healing process or even failure in healing. The mobility of polymer molecules or parts of molecules makes it more superior to self-healing materials compared to metals and ceramics [21]. The last concept is the healing mechanism. This concept classifies materials with self-healing abilities into two groups, namely extrinsic and intrinsic. The concept is based on the presence of healing agents added to the material or already existing within the material itself [22].

2.1. Extrinsic Self-Healing. Materials with extrinsic self-healing capabilities require the addition of healing agents to the polymer system. Healing agents are stored in brittle micro-sized capsules or vascular tubes [23]. In the event of damage, such as scratches or cracks, the microcapsules or microvascular tubes will break and release the healing agents. The healing agents, often in the form of monomers, will flow and fill the gaps, polymerize, and thus repair the damage.

2.1.1. Microcapsule. Self-healing polymeric materials based on microcapsules use controlled release of healing agents to

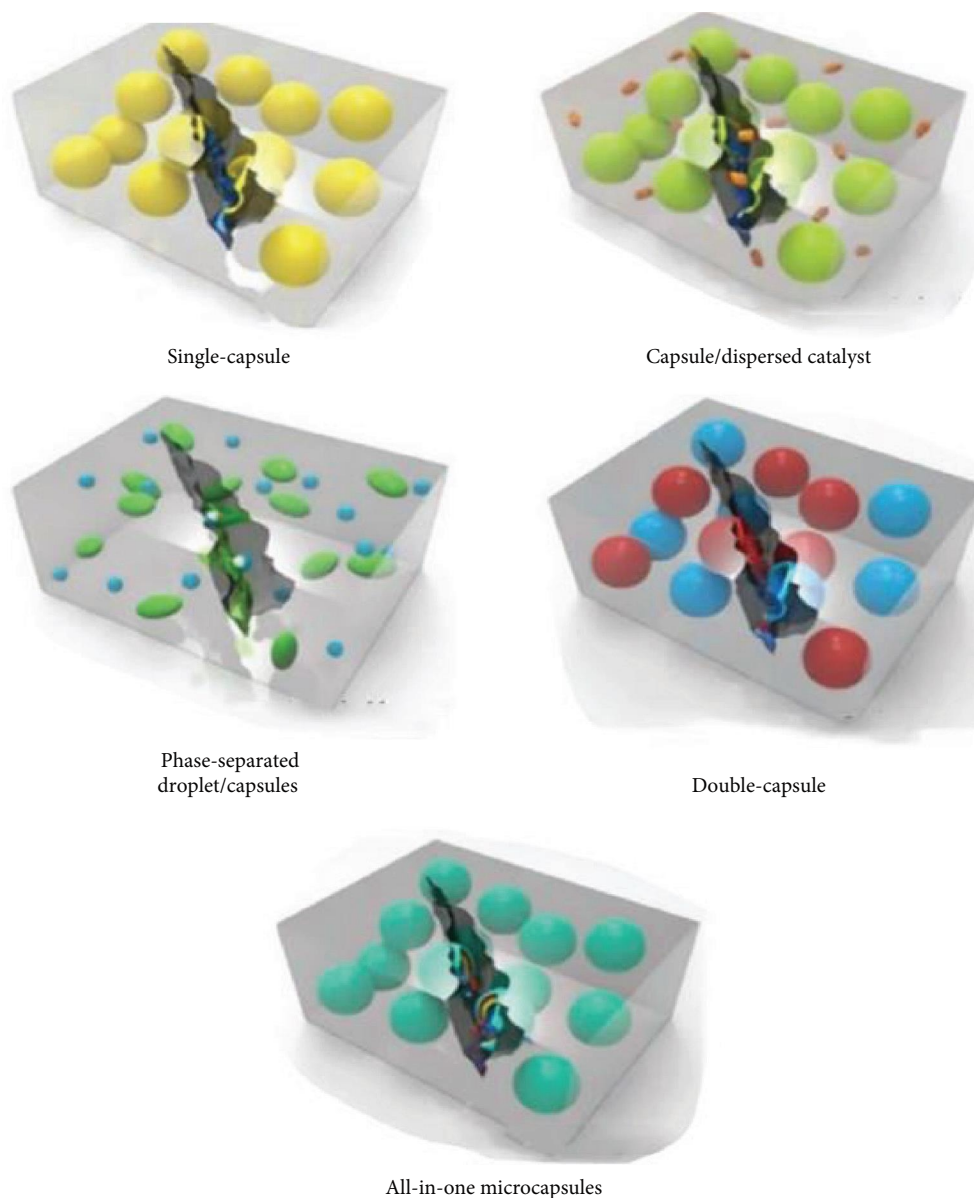


FIGURE 2: Microcapsules-based self-healing systems. Figure reproduced from the study of Ekeocha et al. [24] with permission from John Wiley and Sons.

recover the cracks. Upon a crack formation, the healing agents will flow to fill the cracks and react or polymerize to repair the damage. Typical self-healing systems based on microcapsules are illustrated in Figure 2 [24]. In the single capsule system, there is only one type of reactive chemical embedded in the microcapsules, which will react with latent functional groups of the matrix to repair the damage. Liu et al. [25] prepared epoxy resin microcapsules with a diameter of $100\ \mu\text{m}$ via interfacial polymerization of epoxy resin droplets with ethylenediamine. When the capsules were ruptured due to an external stimulant, the encapsulated resin flowed out of the capsules and reached with polyamine hardener existing in the matrix. The optimum concentration of microcapsules was 20%. The epoxy coating applied on carbon steel was almost restored in 4 hr after the cracks were generated.

The double capsule system is made of two different healing agents encapsulated in different capsules. Epoxy resin and amine-based curing agents with a dual capsule self-healing system were developed by Safdari et al. [26]. Each capsule stores the epoxy resin and curing agent separately, so if the capsules are broken, the system can self-heal. The healing efficiency of up to 99% could be reached by 1% of microcapsules addition according to the electrochemical impedance spectroscopy (EIS) results.

Three other microcapsule-based healing mechanisms were developed based on the previously mentioned systems. The capsule/dispersed catalyst system contains encapsulated monomer and catalyst dispersed in the matrix. In the phase-separated droplets/capsules, there are droplets of one healing agent and encapsulated another healing agent dispersed in the matrix. The all-in-one microcapsules contain all of its

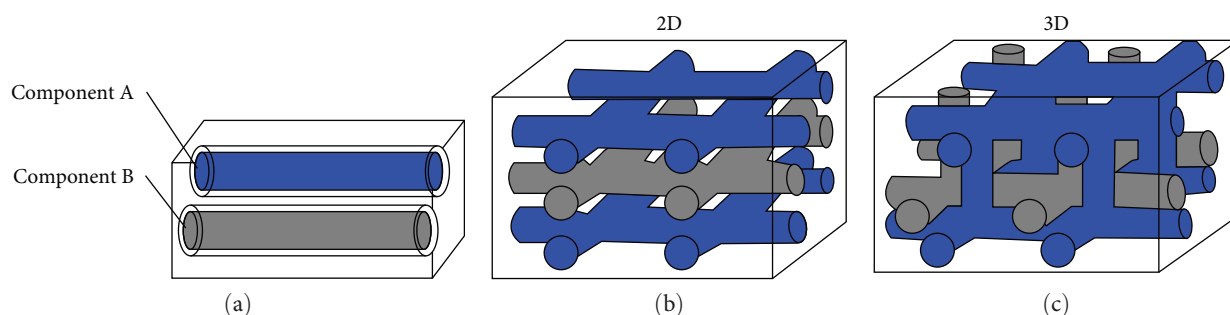


FIGURE 3: 1D (a), 2D (b), and 3D (c) microvascular self-healing system [30].

healing agents separately, either in core-and-shell or capsule-in-capsule configuration [27].

Healing with a microcapsule mechanism is by far the simplest method, because it does not need any changes in the chemical structure of commercially available polymers, and encapsulation is a matured technology [27]. Even though healing with a microcapsule mechanism can recover 80%–85% of mechanical properties, the integration of microcapsules within the matrix acts as induced damage and then decreases the mechanical properties of the samples. This is mostly owing to the microcapsule size and volume used and the fact that after breakage, the microcapsule shells stay within the material, functioning as a stress concentrator for other mechanical stresses that the structure may be subjected to the study of Vintila et al. [28]. Another problem is this method cannot fix recurring damage occurring in the exact same location where all of the healing agents are already used [24].

2.1.2. Microvascular. The microvascular healing method is inspired by nature, where damages in living organisms can be self-repaired by using liquids in hollow fibers [19]. The use of microvascular overcomes the limitations of the microcapsules in recurrent self-healing. The amount of healing agents stored in a microvascular network is more abundant than those in microcapsules due to its larger storage volume [29]. The utilization of microvascular self-healing systems can be greatly useful in fabricating thermosetting polymeric composite materials [28]. Microvascular-based self-healing systems can be categorized into 1D, 2D, and 3D (Figure 3) [30]. Microvascular systems may include more than one healing agent, i.e., polymer resin and hardener. In a 1D system, the resin and hardener are stored in different vessels assembled in a 1D configuration. In a 2D network, the vessels are criss-crossing with one another, while in a 3D system, the vessels containing the same healing agents are interconnected. The 2D and 3D systems ensure recurring healing ability, since the healing agents are constantly available [30].

Kato et al. [31] developed a self-healing system using multiple through-thickness microvascular channels, a system similar to the 3D microvascular system. An epoxy-glass fiber composite was modified so that it contains microvascular channels. Cyanoacrylate glue was injected into the channels. Delamination was simulated by introducing an indentation to the material. The material was left for 30 min at room temperature for healing. The compression strength of healed

material with sealing up to 57.3 kN is about 96% compared to the virgin material.

In addition to the microvessels, catalysts can be dispersed in the polymer matrix. Toohey et al. [32] developed self-healing coatings via a 3D microvascular network embedded in epoxy-based coatings. Liquid phase dicyclopentadiene (DCPD) was injected into the vessels, while solid phase Grubb's catalyst was dispersed in the matrix. Healing tests revealed that the microvascular substrate specimens had an average healing efficiency of 38% for all catalyst concentrations. The number of healing cycles of this microvascular mechanism depends on the variation of size and distribution of the catalyst particles. The microvascular healing system can heal a brittle epoxy coating up to seven times, whereas microcapsule-based healing occurs for only one cycle. Although this system was proven to be capable of recurrent healing, in this example, the strength recovery was poor. Moreover, the system was rigorous to build.

2.2. Intrinsic Self-Healing. In contrast to extrinsic self-healing, intrinsic self-healing involves a reversible reaction or movement of polymer molecular chains triggered by external stimuli such as heat, ultraviolet light, humidity, and pressure to reorganize its microstructure [33–39]. The interaction between atoms and molecules results in stronger molecules as compared to a single atom. As illustrated in Figure 4, this interaction is classified into two categories: intramolecular force (covalent interaction) and intermolecular force (noncovalent interaction) [40].

2.2.1. Diels–Alder (DA). DA chemistry has been successfully used to create polymeric materials with self-healing capabilities, providing a wide variety of options for designing new products [41]. The DA reaction occurs between a diene and dienophile at a relatively low temperature. The retro-DA reaction breaks the adduct into its precursors at an elevated temperature, enabling local molecular mobility, which subsequently leads to healing [42]. Thus, this healing mechanism requires external stimulus in the form of heating.

Thermo-reversible cross-linked epoxy for composites application was developed by Turkenburg et al. [43] with a two-step process. The first step was the functionalization of diglycidyl ether of bisphenol A (DGEBA) with furan, a type of diene, by reacting DGEBA with furfuryl amine. The second step was cross-linking of the oligomer with bismaleimide (a dienophile) via the DA reaction by using batch

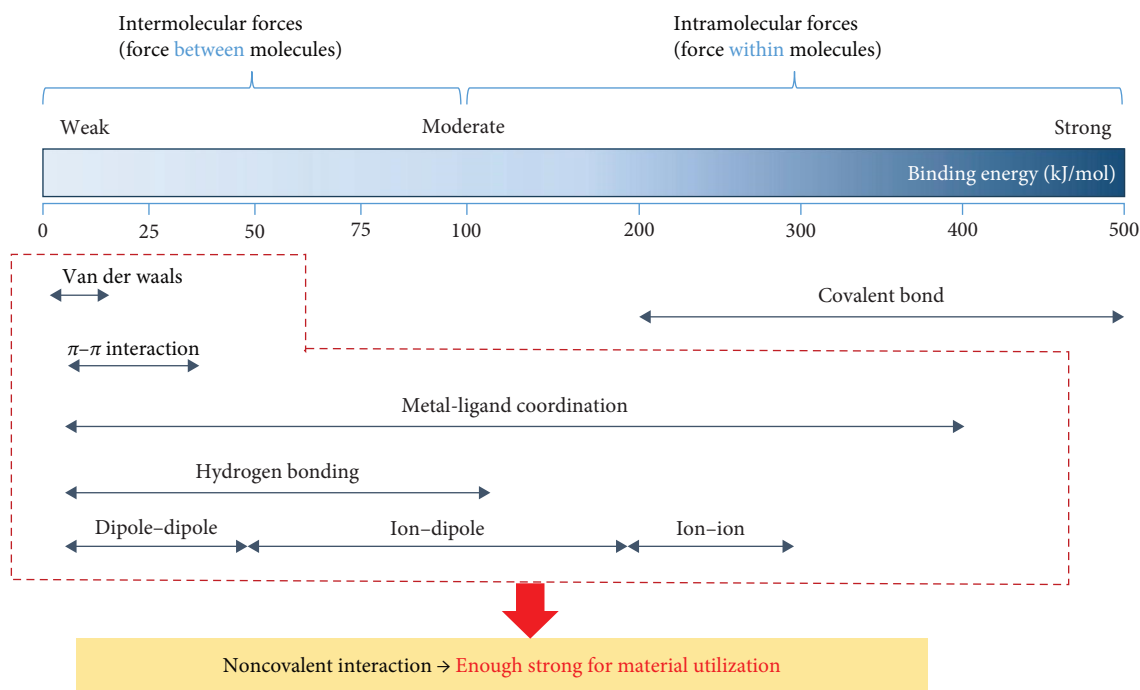


FIGURE 4: Binding energy of some molecular interaction [40].

extrusion [41]. The product can be de-cross-linked by introducing heat to promote the retro-DA reaction.

Some works also studied self-healing material from renewable resources. Viela et al. [44] reported the synthesis of branched or cross-linked polymer from di- and trifunctional furan and maleimide, made of biobased undecenoic acid and undecen-1-ol. Turkenburg et al. [43] reported the synthesis of thermo-reversible crosslinked polymer networks consisting predominantly of bio-based diethyl itaconate in a simple two-step process. The first step in this polymerization was the reaction of diethyl itaconate and furfuryl methacrylate. The next step was the cross-linking reaction between bismaleimide and furfuryl groups through the DA reaction. Both reports demonstrated that the obtained polymers showed thermo-reversibility as a result of the DA chemistry.

2.2.2. Trans-Esterification. Many researchers have reported the application of trans-esterification reactions involving polyesters in self-healing polymers. There are three primary mechanisms by which dynamic polyester bonding occurs, namely (1) intermolecular alcoholysis, (2) intermolecular acidolysis, and (3) trans-esterification, as illustrated in Figure 5 [45]. In intermolecular alcoholysis, the acyl oxygen debonding occurs with the alkoxy group being unbroken. In intermolecular acidolysis, either the acyl or alkyl oxygen can be cleft. Cleavage of the acyl oxygen results in an anhydride intermediate, which will react with an alcohol to form an ester [46].

Self-healing materials with a trans-esterification mechanism usually use a catalyst to decrease the bond exchange reaction temperature. Some of the catalysts that can be used for this mechanism are zinc acetate, zinc acetylacetonate, and tertiary amine [47–49]. Lu et al. [50] synthesized a thermoset

epoxy using phthalic anhydride as the curing agent and zinc acetylacetonate hydrate as a catalyst. The cross-linked material was ground into powder and remolded to simulate healing. A healing efficiency as high as 88.1% can be reached at a healing temperature of 150°C for 10 hr. They found that the efficiency is affected by molding time, temperature, pressure, particle size, and particle size distribution.

Some issues about the usage of catalysts are the incompatibility of the catalyst while mixing, which can reduce the mechanical properties of the polymeric materials, and the potential toxicity of catalysis [51]. In order to overcome these problems, some researchers developed catalyst-free self-healing materials [52, 53].

Zhang and Xu [54] improved the trans-esterification rates of a non-catalytically cross-linked epoxy by adding conductive polymer-wrapped carbon nanotubes. They successfully cured the epoxy with citric acid, incorporating polypyrrole-wrapped carbon nanotubes (CNT/PPy) as a dopant. This technique lowers the trans-esterification temperature and improves its conductivity.

2.2.3. Metal-Ligand Coordination. Metal-ligand coordination refers to the organic-inorganic bonding of metals and ligand atoms associated with the Lewis acid-base. The Lewis base is an electron donor known as a ligand, whereas the Lewis acid is an electron acceptor known as a central metal ion. This system is inspired by the ability of mussels to attach to various surfaces, utilizing catechol groups as ligands [40]. There are various combinations of metals and ligands that can be used for this mechanism, with a binding energy ranging from 100 to 300 kJ mol⁻¹ [55].

Some advantages of metal-ligand coordination in self-healing: (1) metal-ligand coordination offers comparable

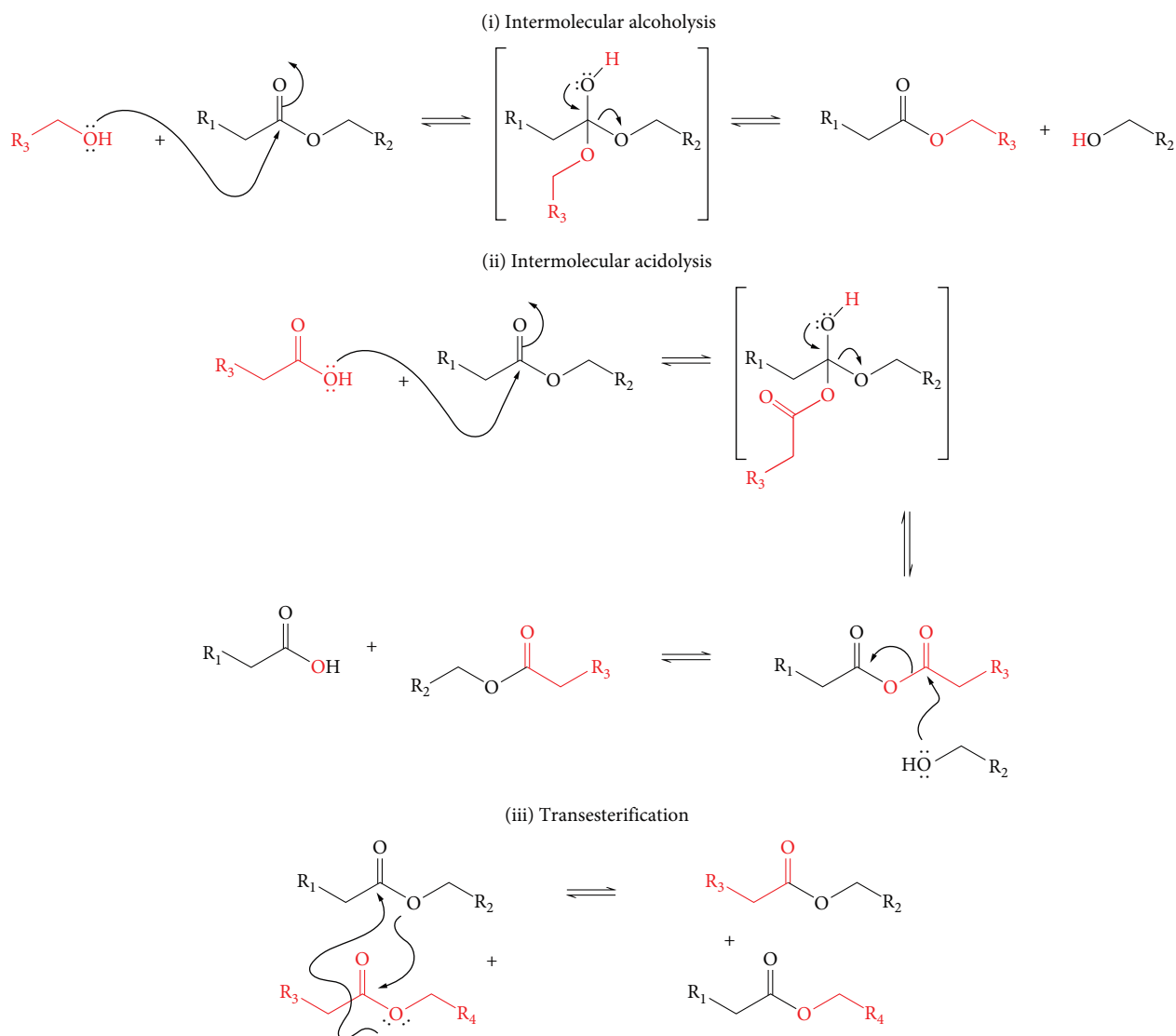


FIGURE 5: Mechanism of trans-esterification reactions involved in polyesters [45].

strength with covalent cross-linking material. (2) Multiple metal–ligand complexes provide near-covalent stabilities with noncovalent reversible rates and a variety of cross-link modes ranging from zero to three per metal ion. (3) Metal–ligand complex can be used to tailor the degree of cross-linking in polymers dissolved in organic solvents by adjusting the pH of the solution. (4) The pH-adjustable cross-link kinetics allow easy control of viscoelastic properties [56].

Interaction between ion metals with ligands can be detected using spectroscopy techniques such as Fourier transform infrared (FTIR), Raman, and UV–Vis spectroscopy. Zhang et al. [57] studied the complexes of Zn^{2+} with $-CN$ in the nitrile butadiene rubber using FTIR. They found that the peak at $2,280\text{ cm}^{-1}$ indicates Zn^{2+} – CN complexes. This peak gradually increases when the Zn^{2+} content increases. Raman analysis shows that the coordination bond of Fe^{3+} with catechol has a peak in the range of $500\text{--}600\text{ cm}^{-1}$ [5, 56, 58]. On the other hand, UV–Vis analysis shows the absorption peak at 340 nm , which indicates the

formation of the complexes of the ion metals with terpyridine ligand [59]. A summary of these characterizations is shown in Table 1.

2.2.4. Hydrogen Bonding. Electrostatic interaction is primarily responsible for hydrogen bonding. The donor atom creates a bond by effectively sharing its electrons with the acceptor atom. Water is a liquid over a much wider temperature range than expected for a molecule of its size because of the substantial hydrogen bonding. H-bonding interactions typically have bonding energies between 5 and 30 kJ mol^{-1} , which is around 10 times less than the binding energies of covalent bonds. A small number of H-bonds is insufficient to demonstrate a necessary characteristic. However, the degree of H-bonding interactions and rigidity in the polymer backbone can be fine-tuned in order to produce the desired qualities [2]. One of the most often employed methods for creating supramolecular healable polyurethanes is hydrogen bonding interactions [62].

TABLE 1: Metal–ligand coordination characterization methods.

Polymer	Metal	Ligand	Characterization methods			Ref
			FTIR	Raman	UV–Vis	
Poly(ethylene glycol) diglycidyl ether (PEG-DE)	Fe ³⁺	Catechol	—	512–627 cm ⁻¹ (catechol–Fe ³⁺ bond vibrations)	—	[58]
Polyethylene glycol (PEG)	Fe ³⁺	Dopa	—	500–650 cm ⁻¹ (chelation of the Fe ³⁺ by catechol)	—	[56]
Methyl vinyl silicone rubber	Fe ³⁺	Dopa	—	500–600 cm ⁻¹ (coordination between DOPA and Fe ³⁺)	500–600 nm (coordination between Fe ³⁺ and catechol groups)	[5]
Nitrile butadiene rubber (NBR)	Zn ²⁺	Acrylonitrile	2,280 cm ⁻¹ (restricted –CN in Zn ²⁺ –CN coordination) –	—	—	[57]
–	Zn ²⁺	Terpyridine	—	—	392 nm (Zn ²⁺ –terpyridine complex)	[59]
Hexamethylene diisocyanate (HDI) and polydimethylsiloxane (PDMS)	Ln ³⁺	Terpyridine	1,587, 1,571, and 1,562 cm ⁻¹ (terpyridine C=N, linked to terpyridine and Ln ³⁺ complexation)	—	292 nm (π – π^* pyridine ring transition) and red-shifted to 324 nm	[60]
Polyethylene glycol (PEG)	Ni ²⁺	Histidine	—	1,596 cm ⁻¹ (coordination between Histidine and Ni ²⁺)	—	[61]

3. Self-Healing Material

3.1. Polyurethane. A family of materials called polyurethanes has a lot of potential for usage in a variety of applications. They have a wide range of density, hardness, and stiffness, which makes it possible to create many kinds of polyurethane stretchable fibers, stiff elastomers, flexible and rigid lightweight foams, and other materials. Polyurethane materials are widely used in furniture, textile fibers, coatings, adhesives, artificial leather, and other products [63, 64].

Polyurethane is a type of polymer that is created from the reaction of alcohol and isocyanate. There are various sources from which polyurethane can be synthesized, and the polymers are categorized based on the desired properties. Some polyurethanes are rigid, while others are flexible. Some are thermoplastic, meaning they can be heated and molded into different shapes, and some are thermosets. Some are organic-solvent-based and others are waterborne, meaning they can be spread on surfaces and absorbed into the material. The wide range of polyurethane characteristics enables them to be used as binders, coatings, adhesives, sealants, and elastomers.

Various researchers have reported studies to make self-healing polyurethane through the extrinsic mechanism [65–68]. Recently, Xiang et al. [69] reported the manufacturing of polyurethane microcapsules with isocyanate prepolymer as a core material through the interfacial polymerization of a commercial polyurethane curing agent (Bayer L-75) and 1,4-butanediol (BDO) as a chain extender in an emulsion solution. The self-healing property of this material enables healing of cracks within 24 hr.

Polyurethane is also quite popular in the field of intrinsic self-healing polymer research, as many works have already been reported [70–72]. An interesting example was reported by Wang and Urban [22], who developed self-healing polyurethanes using multiple metal–ligand bonds. They used diamidepyridine as a ligand and for the metal ions, they used ferric chloride, terbium trifluoromethanesulfonate ($\text{Tb}(\text{OTf})_3$), and zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$). The superior self-healing ability for this material was attained in polymers cross-linked by Fe^{3+} and Tb^{3+} ions, providing the polymer with both labile and strong bonds at the same time, enabling a complete healing [73].

3.2. Epoxy. Epoxy resins are a type of thermoset polymer that is widely used as adhesives, coatings, and composites. Most epoxy resins are produced by the reaction of a compound that contains at least two active hydrogen atoms and epichlorohydrin. After a dehydrohalogenation process, epoxy resin is created (Figure 6). One type of epoxy resin is DGEBA. The DGEBA contains two oxirane function groups that allow the construction of an epoxy with a 3D structure. The maximum cross-linked level of DGEBA epoxy resin is obtained by adding aliphatic or aromatic diamines since oxirane is extremely reactive to nucleophilic substances like amines [74]. Like almost all thermosets, this material cannot be reprocessed and recycled. Difficulty in repairing the damaged epoxy is also a problem in actual application.

To solve this problem, some researchers have developed epoxy that can heal itself automatically with or without

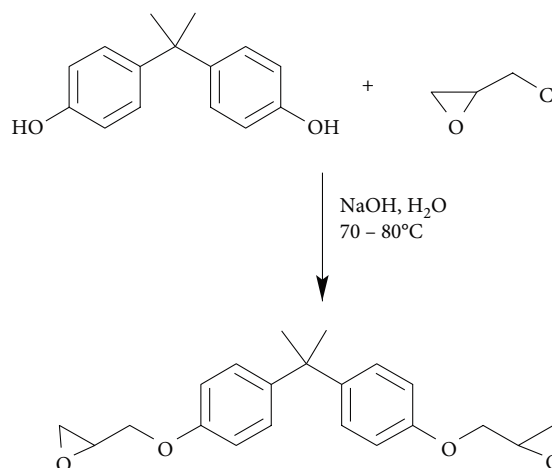


FIGURE 6: Synthesis of DGEBA from bisphenol A and epichlorohydrin [74].

external stimulus. Both extrinsic and intrinsic mechanisms can be used to develop self-healing epoxy. Some researchers employed extrinsic mechanisms using microcapsules and microvascular networks to develop self-healing epoxy. Jialan et al. [75] synthesized self-healing microcapsules by in situ polymerization with urea formaldehyde and epoxy resins as the wall and core materials consecutively. This technique is capable of repairing the materials after being damaged.

Altuna et al. [49] developed self-healing epoxy by transesterification mechanism. They used a blend of citric (CA) and sebacic (SA) acids as a cross-linker. Self-healing epoxy with Diels Alder mechanism was developed by Turkenburg and Fischer [41] with a two-step process.

Other researchers try to develop epoxy from renewable resources. Yang et al. [76] develop self-healing epoxy from epoxidized soybean oil. Yuliati et al. [77] also develop epoxy from jatropha and sunflower oils. Merighi et al. [78] developed a bio-based amino cross-linker for epoxy, and other cross-linkers based on vanillin and furfural were developed by Fache et al. [79]. The curing agent with a rigid structure can improve the mechanical and thermal stability of reprocessable epoxy from vegetable oils [80].

3.3. Acrylic. Acrylic polymers are a group of polymers synthesized from esters of acrylic and methacrylic acid monomers. The structure contains a vinyl group next to an ester. There is a vast variation of the type of the monomers; thus, the produced polymers possess different characteristics, suitable for different applications. These polymers are known for their clarity, stability against aging, elasticity, easy functionalization, good biocompatibility, and low cost [81, 82].

It is interesting that an acrylic-based polymer has the ability to heal autonomously without any modification. Fan and Szpunar [83] studied a commercially available acrylic-based elastomer (VHB 4910) that had an autonomous self-healing ability by using a hydrogen bonding mechanism. When a stripe of the elastomer was cut and put together with a little pressure. They discovered that at the cut interfaces, there was an increase in the intensity ratio of hydrogen-bonded

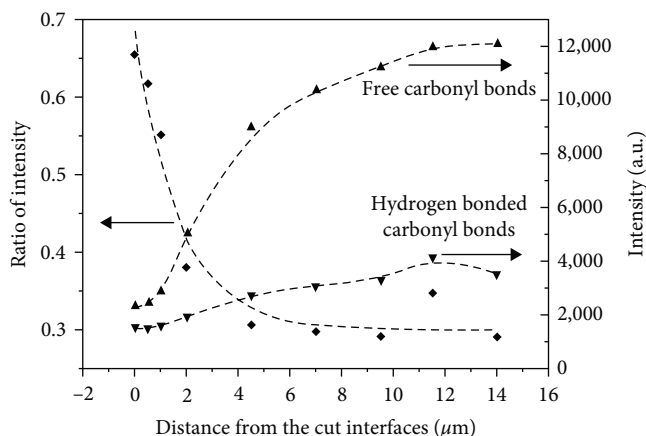


FIGURE 7: The Raman intensity ratio of the hydrogen-bonded carbonyl bonds to the free carbonyl bonds changes as the distance from the cut interface increases. Figure reproduced from the study of Fan and Szpunar [83] with permission from John Wiley and Sons.

carbonyl bonds to free carbonyl bonds (Figure 7). This rising ratio proves that some free carbonyl bonds at the cut interfaces converted to hydrogen-bonded carbonyl bonds. The toughness of the healed sample reached about 70% of its original after being kept at ambient conditions for 960 min.

Other studies on self-healing acrylic-based copolymers employing different healing mechanisms have been studied. Lessard et al. [53] reported self-healing materials from methacrylic monomers and a trifunctional amine, showing repeated healing and recycling abilities from dynamic covalent bonds between primary amines and β -ketoesters. Urban and Wang [84] found that poly(methyl methacrylate/*n*-butyl acrylate) [*p*(MMA/*n*BA)] copolymer healed itself by employing dynamic cross-links via the Van Der Waals interaction. Davydovich and Urban [85] reported that the same copolymer, although it was hydrophobic, underwent accelerated healing when water molecules were confined in the polymer. The same group continued the research by adding a type of co-monomer and found that the new copolymer was also reprocessable. Wang et al. [86] developed a poly((2-acetoacetoxy)ethyl methacrylate/methyl methacrylate/*n*-butyl acrylate) [*p*(AAEMA/MMA/*n*BA)] network that can heal itself without any external intervention. These materials were reprocessable by compression molding at 120°C and exhibited several self-healing cycles in ambient conditions.

4. Self-Healing Materials in Underwater Environment

Compared to the dry condition, self-healing materials in underwater environments are still limited [17, 87]. Both extrinsic and intrinsic mechanisms can be used to develop self-healing materials for wet environments. Self-healing materials based on extrinsic mechanisms for this application usually use epoxy with microcapsules or microvascular networks that contain an amine-based curing agent as the healing agent (Table 2). Commonly, a conventional amine-based curing agent will get deactivated in the presence of water. In

order to solve this problem, a modified curing agent was developed by using a fluorescent latent curing agent (FLCA). In the water, FLCA will decompose into a fluorescent dye and a curing agent, as shown in Figure 8. Furthermore, the epoxy resin released from microcapsules will fill the crack and solidify after reacting with this curing agent. Self-healing material with FLCA can be healed underwater at a temperature of 60°C for 4 hr, and its healing efficiency reached 85.6%. Additionally, the fluorescent dyes can change its color after the crack is repaired [88].

Ye et al. [89] reported a combination of two kinds of the microcapsule and a zwitterionic copolymer to make a dual-functional coating with underwater self-healing and anti-fouling properties. They prepared the microcapsules based on polyurea formaldehyde and polymethyl methacrylate as the shell materials. These microcapsules had excellent thermal stability and were resistant to acid, alkali, and salt solutions. A modified-amine underwater epoxy hardener was used as an epoxy resin hardener due to its excellent characteristics of underwater quick solidification at low temperatures and good compatibility.

As previously described, intrinsic self-healing involves a reversible reaction or movement of polymer molecular chains. The structure enabling self-healing capabilities for underwater applications are the reversible and dynamic bonds such as hydrogen bond, boronic-ester bond, metal-ligand interaction, and imine bond. In order to get these bonds, the polymer backbone should be modified with some molecules of functional groups, such as ligands, that can interact with metal ions or molecules of water via the dynamic bonds. In the metal-ligand coordination mechanism, the ligands usually consist of catechol, imidazole, pyridine, or carboxylate groups. Furthermore, these ligands will bind with the ion metals with metal-ligand coordination bonds. Mechanical properties of self-healing materials with metal-ligand coordination depends on the ligand content and pH of the system [40].

The underwater intrinsic self-healing materials are usually based on noncovalent bonds such as metal-ligand interaction, hydrogen bonds, and Van Der Waals forces. The ligands that are grafted on the polymeric structure will interact with metal ions to get self-healing polymers. These ligands usually consist of catechol, imidazole, pyridine, or carboxylate groups. Furthermore, these ligands will bind with the ion metals via the metal-ligand coordination bonds. The level of mechanical properties of self-healing materials with metal-ligand coordination depends on the amount of ligand and pH of the solution [40]. The presence of hydroxyl groups in the polymeric structure is also used to develop self-healing materials with hydrogen bond mechanisms. In another research, Yuan et al. [90] developed self-healing materials from tannic acid (TA) and polyethylene glycol that can heal in an aqueous solution. Another approach to develop self-healing materials for underwater applications is by using Van Der Waals forces, with the advantage of not being affected by water molecules. Niu et al. [38] developed self-healing materials from 2-methoxyethyl acrylate and ethyl methacrylate through the Van Der Waals forces. These

TABLE 2: Extrinsic self-healing materials for underwater environment.

Mechanism	Polymer	Healing condition	Healing efficiency (%)	Mechanical properties	Ref.
Microcapsule	Diglycidyl ether of bisphenol-A (DGEBA) polyurea formaldehyde (PUF) microcapsule	60°C; 4 hr	83.5	Lap shear = 70 N	[88]
Microcapsule	Epoxy Polyurea formaldehyde (PUF) and polymethyl methacrylate microcapsule	RT; 48 hr			[89]

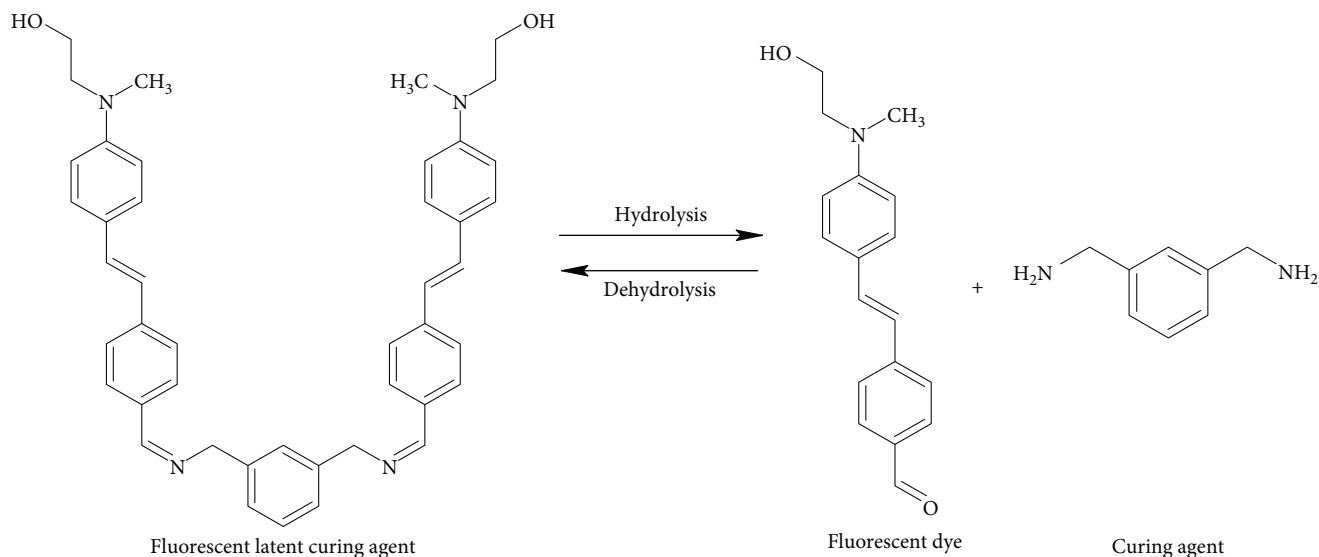


FIGURE 8: Structure and reversible reaction of the FLCA in the presence of water [88].

materials can be healed after being immersed in the water for 24 hr [91].

Table 3 summarizes some reports on underwater self-healing materials. The table shows that, generally, self-healing materials for underwater applications have a tensile strength of less than 3 MPa. Although the self-healing material that uses epoxy with a boronic-ester mechanism has a tensile strength of 37.5 MPa, its healing temperature is relatively high (80°C) [90]. In intrinsic self-healing, the mobility of the molecular chains is one of the factors that support the occurrence of self-healing. The easier the molecular chain moves, the easier the healing process can occur. Likewise, when a polymer that has hygroscopic parts is exposed to water, the mobility of the polymer chains will increase and result in a decrease in the mechanical strength of the material [91]. However, the presence of new cross-link bonds that are formed when the polymer is in water can prevent the decrease in mechanical strength. An example of a new cross-link bond that can be formed is a coordination bond between metal ions in water and catechol [94].

Figure 9 describes reversible imine bonds and hydrogen bonds involved in the self-healing mechanism in polydimethyl siloxane (PDMS) system. PDMS is functionalized with methylene diphenyl diisocyanate (MDI) and triformaldehyde benzene (TFB). The healing ability of this material is strengthened by TFB soft phase moieties. The reversible imine bonds formed via Schiff base reaction because TFB

acts as a chain extender for PDMS. The TFB-based imine bonds are stable and weak. These bonds also show the reversible potentiality in a soft environment. On the other hand, the transamination reaction between primary amine and sterically unhindered imines enables fast healing of cleaved imine. Hence, a combination of stronger hydrogen bonds and weaker imine bonds is the basic principle of PDMS-MDI_x-TFB_{1-x} dynamic bond network [98].

Xia et al. [95] developed the lipophilic hyperbranched polymer, which is functionalized by dopamine and hydrophilic carbonyl groups and then crosslinked by catechol-Fe³⁺ complexation. The hydrophilicity of the damaged surface of this material would be slightly improved because of more carbonyl groups under the inducement of water. Moreover, the permeation of water into the subsurface is facilitated by carbonyl groups. When the polymer is damaged, the spontaneous dynamic complexation between catechol and Fe³⁺ will be occurred and starts to reconnect the cracked in water. Figure 10 shows the dynamic rearrangement of the damaged network during healing with the catechol-Fe³⁺ coordination bonds.

Kang et al. [96] reacted bis(3-aminopropyl)-terminated poly(dimethylsiloxane) (H₂N-PDMS-NH) and a mixture of 4,4'-methylenebis(phenyl isocyanate) and isophorone diisocyanate to get elastomeric materials. These polymers had a healing efficiency up to 78% in the water via the mixture of strong and weak crosslinking hydrogen bonds. Other researchers

TABLE 3: Intrinsic self-healing materials for underwater environment.

Mechanism	Polymer	Healing condition	Healing efficiency (%)	Mechanical properties	Ref.
Metal–ligand	Poly(dopamine acrylamide- <i>co-n</i> -butyl acrylate) (P(DA- <i>co</i> -BA))	RT, 72 hr	91	Tensile strength = 2.8 MPa	[92]
Metal–ligand	Poly(dopamineacrylamide- <i>co-n</i> -butyl acrylate) (P(DA- <i>co</i> -BA))	25°C; 72 hr	—	—	[93]
Metal–ligand	Methyl vinyl silicone rubber–2-isocyanatoethyl acrylate	RT, 84 hr	91	Tensile strength = 0.075 MPa	[5]
Metal–ligand	Polyurethane	RT, 24 hr	84.36	Tensile strength = 1.34 MPa	[39]
Metal–ligand	Poly(dopamine acrylamide- <i>co-n</i> -butyl acrylate)	RT, 24 hr	78	Tensile strength = 2 MPa	[94]
Metal–ligand	Hyperbranched polyurethane (HBPU)–dimethylol propionic acid (DMIPA)	25°C; 72 hr	87.2	Tensile strength = 1.9 MPa	[95]
Van Der Waals	Poly(2-methoxyethyl acrylate- <i>co</i> -ethyl methacrylate)	RT, 360 hr	53	Tensile strength = 1.3 MPa	[38]
Van Der Waals	Poly(methyl methacrylate/ <i>n</i> -butyl acrylate) Acrylate-based butyl methacrylate (BMA), butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA)	150 hr	92.8	Tensile strength = 2.6 MPa	[85]
Hydrogen bond	PDMS–MPU _x –IU _{1–x}	80°C; 30 min	100	Modulus = 1.03 GPa	[91]
Hydrogen bond	PDMS–MPU _x –IU _{1–x}	RT; 48 hr	78	Tensile strength = 1.3 MPa	[96]
Disulfide	Polyurea-urethane	60°C; 2 hr 25°C; 6 hr	98.182.1	Tensile strength = 0.185 MPa	[97]
Boronic ester	Epoxy-boroxine	80°C; 12 hr	79.46	Tensile strength = 37.23 MPa	[90]
Imine bond	PDMS–MDI–TFB	RT; 1 hr	95	Tensile strength = 0.75 MPa	[98]

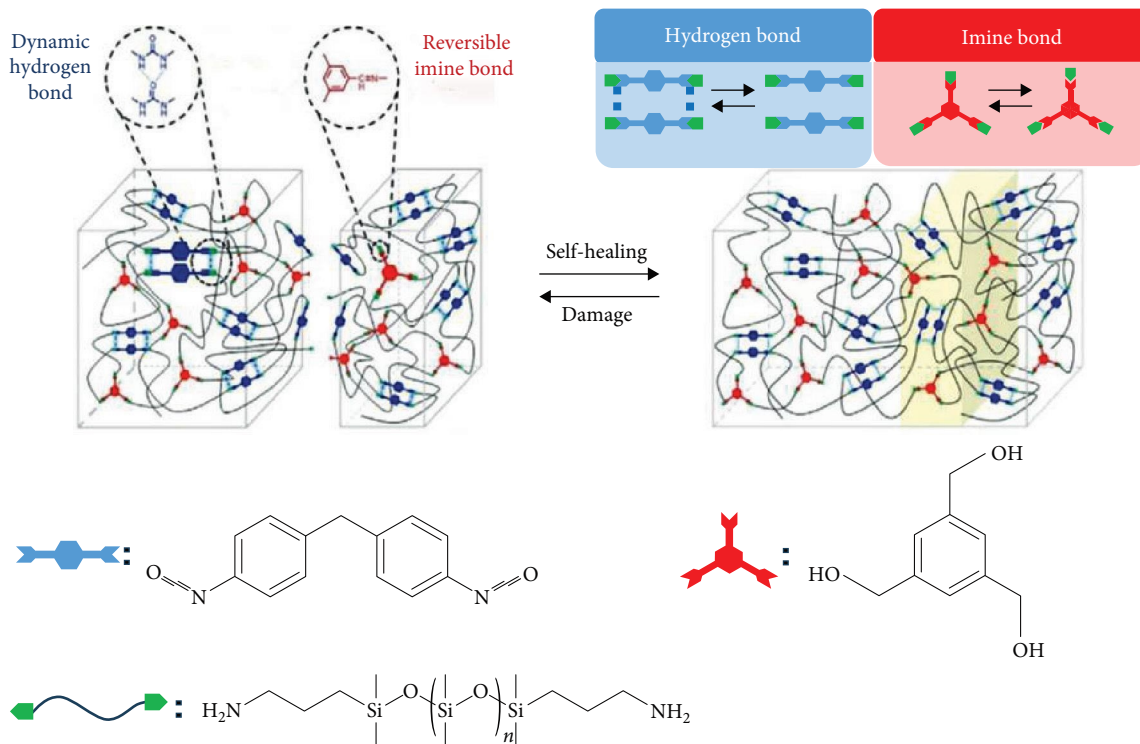


FIGURE 9: Structure illustration of PDMS-MDI_x-TFB_{1-x} based on reversible imine bonds and hydrogen bonds [98].

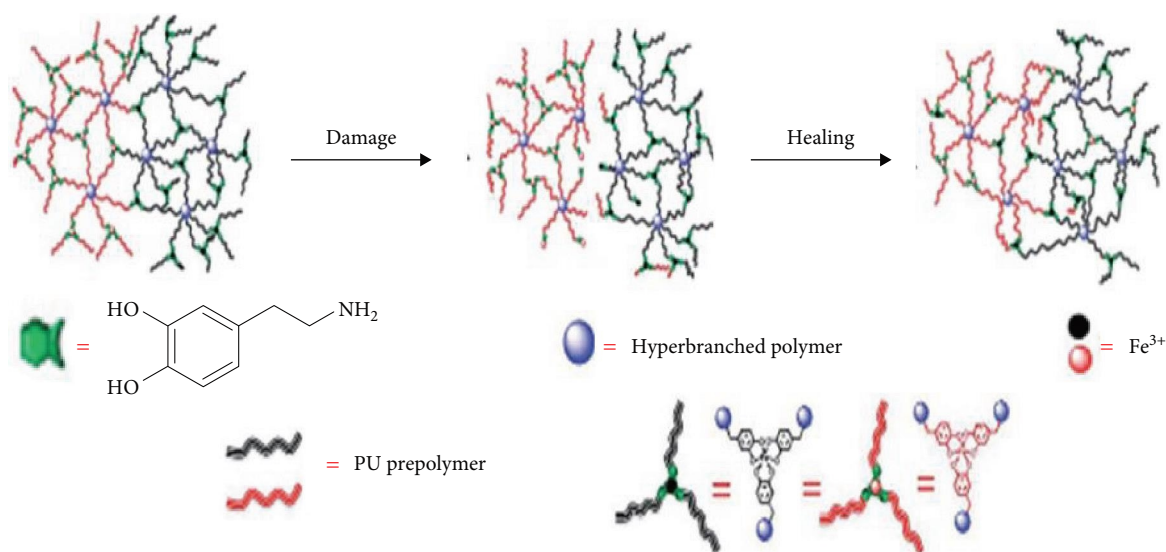


FIGURE 10: Restoration of harmed HBPU-DMPA-(Fe(DOPA)₃) in seawater with metal-ligand coordination [95].

used the metal-ligand coordination mechanism to develop self-healing materials. Li et al. [94] developed self-healing material from poly(dopamine acrylamide-*co*-*n*-butyl acrylate) with dopamine as a ligand and Ca²⁺ ion. When placed in seawater, this material was more capable of healing than when placed in air, with healing efficiency reaching up to 78% in 24 hr. They also found that the swelling on this material is higher in freshwater than in seawater. Kim et al. [92, 93] reported the synthesis of poly(dopamine acrylamide-*co*-*n*-butyl acrylate) (P(DA-*co*-BA)) that was cross-linked

network polymers with *p*-phenyldiboric acids (PDBA) (P-PDBA) and CaCl₂ (P-Ca²⁺). They found that the boron-containing catechol polymer was more stable, transparent, and highly capable of self-healing in seawater. Additionally, they discovered that the P-PDBA had superior underwater self-healing abilities and less water uptake than P-Ca²⁺. Furthermore, P-PDBA had swollen up to 2 wt% while P-Ca²⁺ 100% was swollen up to 20 wt%. Xu et al. [39] reported a self-healing polyurethane from 4,4'-diphenylmethane diisocyanate (MDI) and polytetrahydrofuran (PTMG) with

dopamine as a ligand and Ca^{2+} as a metallic ion. The healing efficiency of this material in artificial seawater is 84% [39]. Self-healing material from methyl vinyl silicone rubber was developed by Li et al. [5]. They also used dopamine as a ligand for this self-healing material. This rubber had healing ability in a pH 9 solution with the healing efficiency up to 91% in 84 hr [5].

Although these dynamic or reversible chains were designed to be applied in harsh underwater conditions, none has been reported to use these materials in the depth of actual sea, lake, or river. Some self-healing polymers using metal–ligand coordination bonds are highly pH dependent. At low pH, mono complexes are formed, and the stable bis and tris complexes will appear with the increase of pH. These studies have shown that the polymers are stable on the high pH ($=9$) [17, 95]. Another study used dynamic Debye forces to develop self-healing materials for underwater applications on the poly(benzyl methacrylate)–poly(ethyl acrylate) (PEMA–PEA) elastomer, yielding a material that can heal in acids, bases, and salts water. This study also found that the self-healing properties of PEMA–PAE only occurred on the freshly fractured interfaces [99].

There are some limiting conditions of the environment to utilize the self-healing materials for underwater applications, such as pH, type and concentration of metal ions, temperature, and aquatic microorganisms. For metal–ligand mechanism, the stronger interaction between metal ions with ligands will occur at higher pH due to the bis- and tris-complexes formation [95, 100]. At the low pH, the complex between metal ions with ligands is relatively unstable. In contrast with metal–ligand interaction, the hydrogen bond will be formed at acidic pH [17]. The difference in ionic solution also affected the adhesion strength of wet adhesive coatings. Zhao et al. [101] found that there was no wet adhesion when the adhesive was immersed in Fe^{3+} solution due to the chemical binding of Fe^{3+} with 3,4-dihydroxy-L-phenylalanine (DOPA). On the other hand, the adhesive coatings that were immersed in NaCl, KCl, MgCl_2 , and ZnCl_2 had adhesion strengths of approximately 4 kPa.

Besides pH, other factors, such as temperature, have to be taken into account. Most of the studies about self-healing materials for underwater application were performed at room temperature. Thus, we do not know yet whether these systems can be applied at low temperatures. The effect of microorganisms, water current, and other significant factors present in the actual environment is yet unknown. Therefore, we suggest that the self-healing materials proven to work in the laboratory to be tested in real environments.

Self-healing processes occurring in the materials can be evaluated and characterized by physical, mechanical, and chemical analysis techniques. The physical technique can be done by visual observation using an optical microscope or scanning electron microscope. The healing efficiency is analyzed by comparing the width of scratch or crack before and after the healing process; unfortunately, these techniques do not reveal the healing mechanism [102, 103]. Xu et al. [39] used a polarized microscope to observe the self-healing abilities of metal–catechol polymers. They made a cut of about $50\ \mu\text{m}$ by a clean razor blade, and the cut location

was wetted by artificial seawater. Then, the samples were allowed to heal at room temperature for 30 min. The cuts on the samples had disappeared within this period.

The mechanical techniques to evaluate the self-healing process such as tensile test and lap shear test. A tensile test is a standard technique to determine the mechanical properties of materials. This test also can be used to measure the self-healing efficiency of materials [102]. Xia et al. [95] measured the healing efficiency using tensile test. Several dumbbell specimens were cut in artificial seawater. Afterward, the broken surfaces were brought into contact for 24 hr in the artificial seawater at 25°C . Then, the tensile testing was applied to the healed samples in a chamber full of artificial seawater. Self-healing efficiency was calculated by comparing the tensile strength of the healed sample and the original one [95]. A lap shear test can be used to study the adhesion properties of adhesives. A thin slice of self-healing adhesive is placed between two plates, and then the sample is tested under tension until the lap joint breaks. The measured shear strength can be used to calculate self-healing efficiency. The advantage of this test is that the fracture surfaces may be placed into contact in a more controlled manner than the tensile test [104]. Xia et al. [95] also used a lap shear test to evaluate the healing efficiency of hyperbranched polyurethane (HBPU) with functional catechol. Two iron plates were bonded with this polymer and tested in the seawater. After the first failure, the iron plates were rebonded and tested again in the seawater. These cyclic experiments indicate that the polymer has the capability to repeatedly self-heal in seawater. In order to achieve effective healing, a close contact between the damaged surfaces must be present.

The chemical techniques to characterize self-healing processes are FTIR, Raman spectroscopy, and EIS. FTIR is a commonly used technique to verify the healing function by comparing the pristine and healed materials [104]. Kim et al. [92] analyzed the dynamic crosslinking of catechol-functionalized polymers with PDBA using FTIR spectroscopy. They found that two peaks at $1,243$ and $1,254\ \text{cm}^{-1}$ from phenolic groups of catechol were merged into a single peak at $1,248\ \text{cm}^{-1}$ as a result of esterification of catechol and boronic acid groups. The coordination between catechol and PDBA acted as a dynamic crosslinker in this catechol-based polymer [92]. Raman spectroscopy is another method to detecting and monitoring chemical reactions. The analysis of chemical shifts in self-healing polymers synthesized through the crosslinking of terpyridine- Fe^{2+} metal complexes can be performed using this technique [102]. Fan and Szpunar [83] analyzed the hydrogen bonding between carbonyl and hydroxyl groups on acrylic elastomer using Raman spectroscopy. They found that the peak intensity ratio of the hydrogen-bonded carbonyl groups to the free carbonyl groups increased with a closer distance between the cut interfaces. This increasing ratio proves that some free carbonyl groups were converted at the cut interfaces to hydrogen-bonded carbonyl groups. Another researcher studied the self-healing mechanism of waterborne polyurethane with tunable disulfide bonds. In this study, the peak intensity of the disulfide bonds of 2-hydroxyethyl disulfide in waterborne

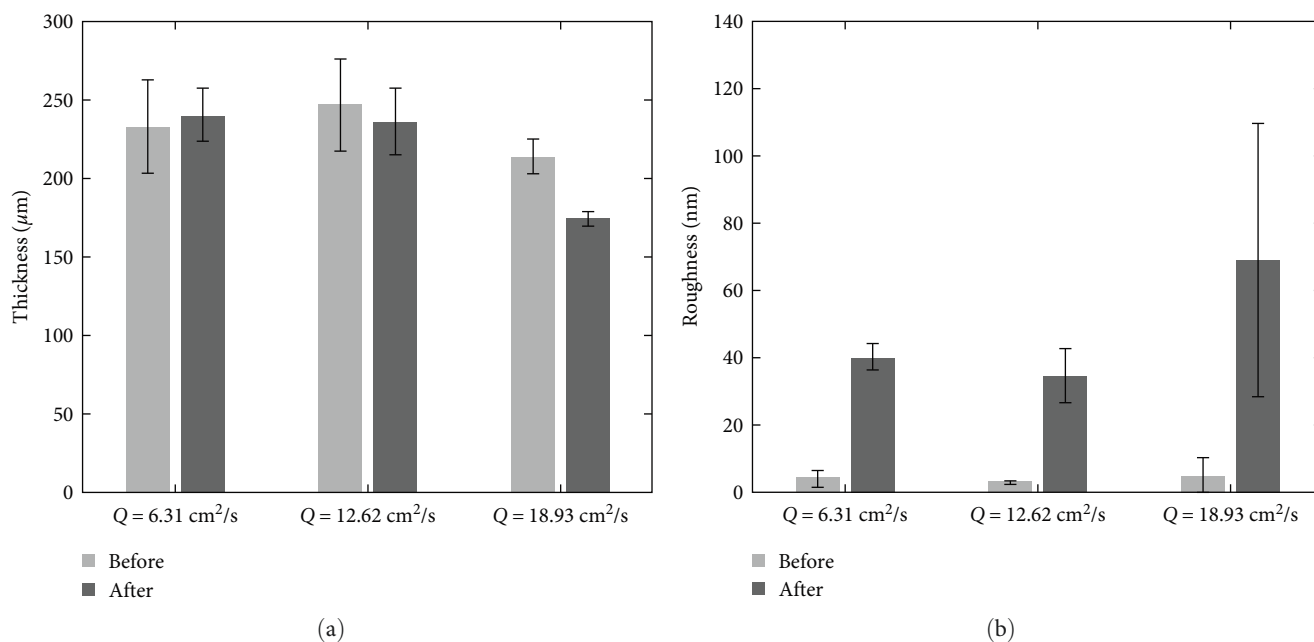


FIGURE 11: Thickness (a) and roughness (b) of the coating before and after the immersion in the impingement flow. Figure reproduced from the study of Vedadi et al. [108] with permission from Springer Nature.

polyurethane cannot be detected in FTIR spectra. Therefore, they used Raman spectra to observe stretching vibration peaks of disulfide bonds at 510 cm^{-1} [105]. EIS is an analysis technique that is used to assess the performance of the self-healing process of underwater scratched coatings. Koochaki et al. [106] chose EIS as a noninvasive probe technique because it can indirectly monitor the formation of the polyurea inside the crack on the polymer coatings. Hao et al. [107] conducted an EIS test to evaluate the self-healing performance of the acrylic coating that contains corrosion inhibitor loaded into metal-organic framework-199 (MOF-199). A scratch with a length of 2 mm was applied on the sample prior to the self-healing test. EIS test was conducted by immersion of the damaged coating in 3.5 wt% NaCl with an amplitude of 20 mV at the frequency range from 10^5 to 10^{-2} Hz.

5. Self-Healing Polymer Application in Underwater Condition

5.1. Coating. One of the purposes of coating is to protect the substrate from corrosion. However, the coating can be damaged during long-term exposure to the environment. This damage can be caused by heat, chemicals, mechanical loads, UV light radiation, microorganisms, and fluid flow [1, 108–111]. In the marine environment, fluid flow has a significant impact on the thickness and surface roughness of the coating (Figure 11) and results in the deterioration of the barrier properties of the coatings [108]. Degradation of epoxy coating in the deep-sea environment was simulated by Meng et al. [112]. They found that the synergistic effects of fluid flow and hydrostatic pressure can accelerate the coating failure. Therefore, the damage that occurs to the coating needs to be repaired.

There are several techniques to protect metals from corrosion, such as environmental modification, design improvement, potential change, coating, and plating. Among these techniques, coating is the most widely used because it is effective, simple to use, and cost-efficient [113, 114]. Conventional coatings have low adhesion strengths in the water, so they cannot resist the erosion from the water [115]. Based on this problem, researchers develop coating specifically tailored for underwater applications.

In addition, the aqueous environment may affect the reactivity of the healing agent or active site [14]. Coating thickness for marine applications is usually around $250 \mu\text{m}$, which is thicker than conventional coating [116]. The need for coatings for these marine applications reach around USD 4 billion by 2020 and will continue to increase as trade and marine activities grow [117].

Several strategies have been developed to make healable underwater coating materials. Shen et al. [14] developed an anticorrosion coating based on infiltrating paraffin wax within a micro-sized polypropylene network. This coating can be healed by NIR laser irradiation underwater once damaged.

Some researchers developed a self-healing coating for underwater environments. Wang et al. [118] synthesized graphene oxide-mesoporous silicon dioxide layer-nanosphere structure loaded with TA (GSLNTA) as a self-healing coating additive. The GSLNTA showed a self-healing capability in an alternating hydrostatic pressure environment. Zhang et al. [119] developed a novel healing agent from fatty acid-based epoxy ester in microcapsules. They found that the fatty acid-based epoxy ester is applicable for anticorrosive smart self-healing coating. Ghomi et al. [120] added titanium dioxide (TiO_2) functionalized with 3-(triethoxysilyl) propyl methacrylate and absorbent acrylamide/acrylic acid (AA) copolymer

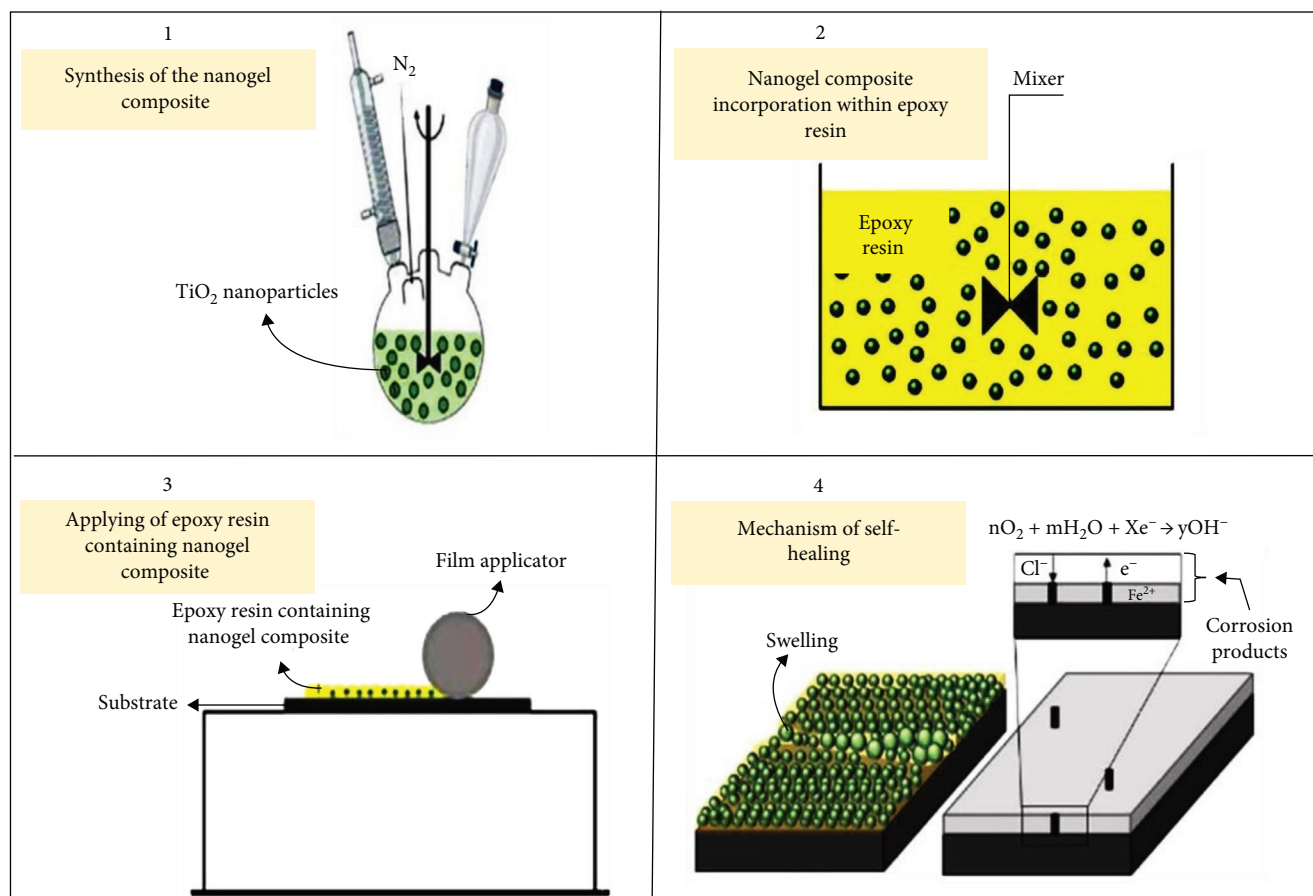


FIGURE 12: Coating preparation and self-healing mechanism illustration. Figure reproduced from the study of Ghomi et al. [120] with permission from Elsevier.

into epoxy resin to develop a self-healing epoxy coating. This approach can generate a healing efficiency up to 94% [120]. The coating preparation and self-healing mechanism of this coating are illustrated in Figure 12.

Although the development of self-healing materials experimentally shows a positive trend, computational research is also done to gain a better understanding on the experimental observations. Javierre reviewed different modeling frameworks that focus on the healing mechanisms of polymeric materials. One example is the dynamic adaptation of the network of molecules, the degradation and restoration of the material's mechanical properties, and the movement and reaction of various species within the matrix. Computational simulation based on these models is a complementary tool in materials development [121].

Coatings with macroscale damages are easy to be visually observed. However, the nano- or microscale damages on coatings are difficult to observe manually without specialized instruments. Therefore, some researchers develop techniques to detect the damage or crack location by using fluorescent or color indicators [122, 123]. Thus, the damage that occurs on the coating can be easily to be detected.

5.2. Adhesives. Adhesives are nonmetallic substances applied to the surfaces of two separated objects to prevent further

separation [124]. Most adhesives are liquid and have good wettability and weak cohesive strength before application. Once applied, the liquid dries to form a solid with good cohesive strength [125]. Some industries use adhesives because they are strong and flexible, which makes them suitable for many purposes [126].

In the dry condition, the adhesive can employ the Van Der Waals forces, static electricity, and hydrogen bonds. Unfortunately, these mechanisms are less effective for wet or underwater applications [18]. Reversible adhesion in the wet conditions is challenging to achieve due to the complex interfacial interaction [101]. In water, the adhesion between substrates is more difficult to achieve because water can prevent and deteriorate adhesion [125]. To solve these problems, the interfacial interaction of adhesives has to be improved to accomplish a perfect underwater bonding [127].

Zhao et al. [101] reported reversible bio-inspired adhesive for the underwater environment by host-guest interaction mechanism. They polymerized dopamine, adamantine, and methoxyethyl acrylate monomer to form a guest copolymer and poly(*N*-isopropylacrylamide) and β -cyclodextrin to form a host copolymer. This adhesive had an adhesion strength of $4,370 \text{ mJ m}^{-2}$ at a temperature of 40°C and also had a good performance in the acid solution.

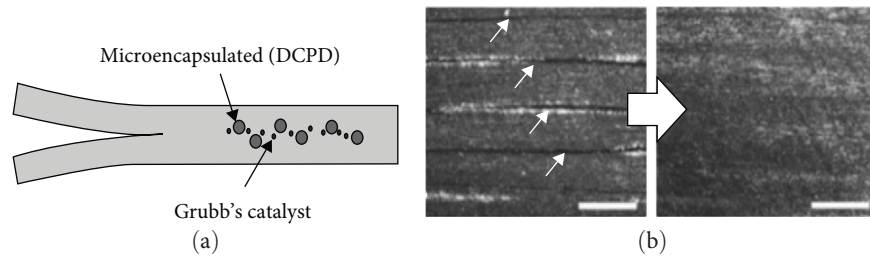


FIGURE 13: (a) Self-healing composites in which the healing agent and the catalyst are encapsulated in microcapsules and the healing process is autonomic [132]. (b) Before and after optical microscope photographs of a composite laminate [133].

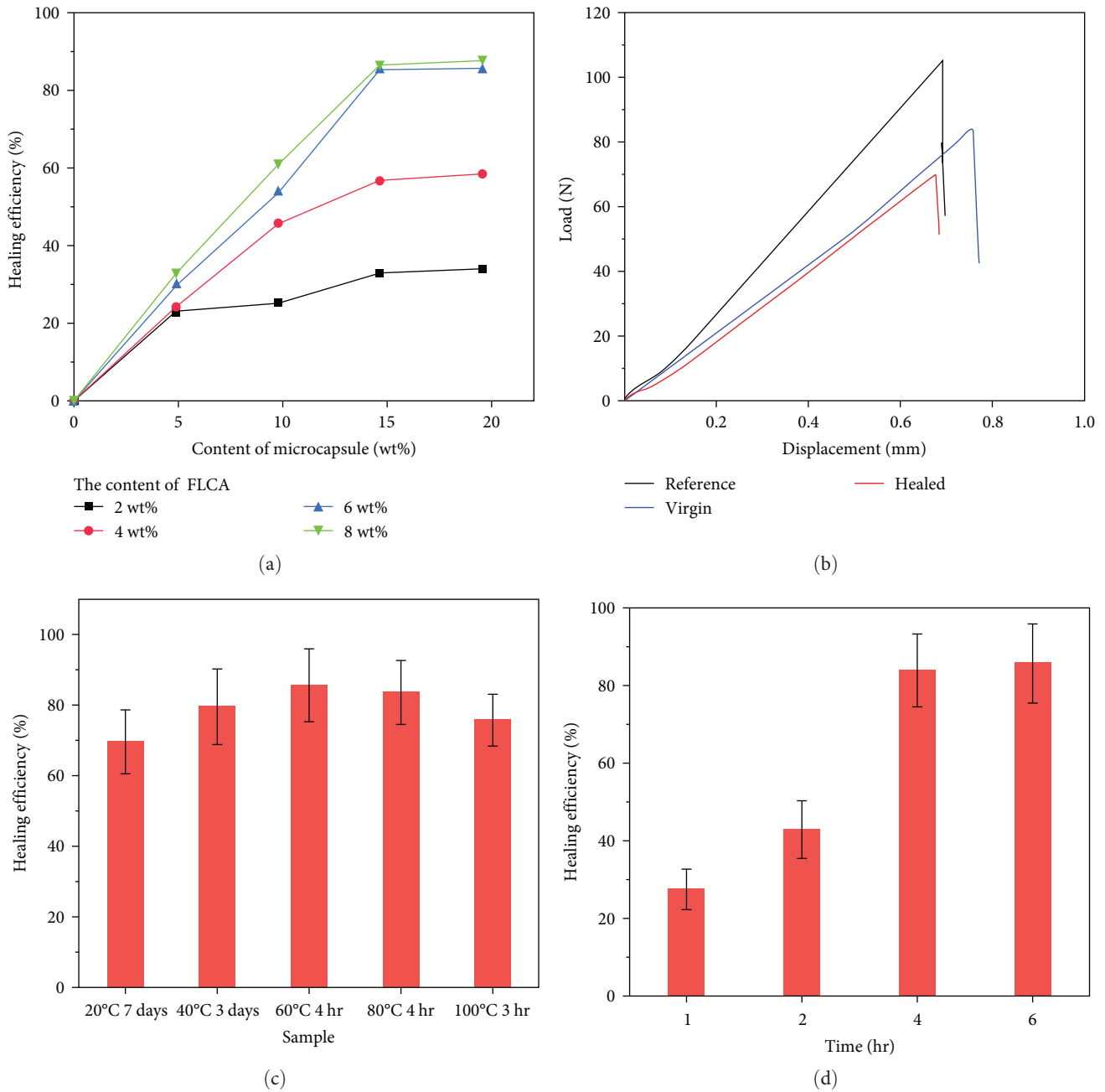


FIGURE 14: (a) The impact of FLCA content on the healing efficiency at various FLCA contents. (b) Load-displacement curves of the specimen that contain 15 wt% epoxy resin microcapsules and 6 wt% FLCAs. (c) Healing efficiency of samples at various temperatures. (d) Healing efficiency of samples that were healed in water at 60°C for various amounts of time. Figure reproduced from the study of Feng et al. [88] with permission from RSC Publishing.

Cheng et al. developed a hydrogel made from ionic liquid (1-butyl-3-methylimidazolium chloride), AA, and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ through one-pot method. The self-healing efficiency of this material reached 80.5% at room temperature. This hydrogel also showed a good underwater adhesion for wood, rubber, and glass [128]. The other self-healing hydrogel adhesives for wet environments were developed by Luo et al. [129]. These adhesives are derived from silk fibroin and TA. Das et al. [130] developed a repeatable adhesive based on a copolymer with cation-catechol and aromatic functional. This adhesive showed a stronger adhesion in seawater than deionized water

5.3. Composites. The use of polymer composite materials has increased yearly and is predicted to reach \$113.6 billion by 2024. Carbon fiber-reinforced plastic (CFRP) composites are attracting attention because of the increasing demand for lightweight structures, particularly in the construction of buildings and other large structures [33, 131]. Kessler et al. [132] reported the use of a DCPD healing agent encapsulated in microcapsules in order to prevent delamination failure of CFRP composites (Figure 13(a)). Another CFRP was developed using thermal responsive healable polyurethanes with DA cycloaddition adducts (Figure 13(b)) [133]. These composites can repeatedly be healed, with the first healing cycle efficiency averaging around 85% and the second healing cycle around 73%.

Feng et al. [88] reported a fabrication of composites with underwater self-healing ability using microcapsules. They used FLCAs that were stored in the microcapsules. These fluorescent dyes could indicate the scratches and healing area visually. The optimum microcapsules and FLCAs content for these composites was 15 and 6 wt%, respectively. Meanwhile, the optimal healing condition can be reached at a temperature of 60°C for 4 hr in the water (Figure 14).

6. Conclusions

Self-healing materials have been widely used for various applications. The development of self-healing materials has been carried out by many researchers using extrinsic and intrinsic mechanisms. However, the use of these materials for wet environments still has challenges. This is due to the presence of water molecules, which will encourage plasticization of the polymer and reduce its mechanical properties. Although there are various self-healing mechanisms, only a few are used in wet environments, namely microcapsules, metal–ligand coordination, Van Der Waals bonds, hydrogen bonds, disulfide bonds, boronic esters, and imine bonds. Self-healing materials in wet environments are used for industrial purposes such as coatings, adhesives, and as a matrix in composites. Self-healing materials for underwater, which can heal at room temperature, mostly have a tensile strength of less than 3 MPa. The ones with higher tensile strength require high temperature to heal. The low tensile strength problem can be solved by using a combination of different healing mechanisms. Although these materials were designed to be applied in harsh underwater conditions, none has been reported to use these materials in the depth of actual sea, lake, or river. The effect of microorganisms,

water current, and other significant factors present in the actual environment is yet unknown. Further studies are needed to answer these challenges. Solving the problems could give benefits to the underwater equipment and have a great impact on science, technology, and economy.

Data Availability

The data that support this study are openly available at <https://doi.org/10.1002/app.42135>, <https://doi.org/10.1007/s11998-021-00472-2>, and <https://doi.org/10.1039/d0ra03197f>.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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