

Review Article

Shape Memory Corrosion-Resistant Polymeric Materials

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Shape memory alloys, materials capable of being deformed and maintaining the deformation and additionally capable of returning to the initial position, are valued for a range of applications from actuators to flexible microdevices. Maintaining the properties that make them useful, their ability to deform and reform, requires that shape memory alloys must be protected against corrosion, in which the integration of shape memory polymers can act as a means of protection. Thus, this review is to highlight the utility of self-healing shape memory polymers as a means of corrosion inhibition. Therefore, this review discusses the benefits of utilizing self-healing shape memory polymers for the protection of shape memory, several types of self-healing polymers that could be used, means of improving or tailoring the polymers towards specific usages, and future prospects in designing a shape memory polymer for use in corrosion inhibition.

1. Introduction

Composites, or materials that contain two or more chemically distinct parts that are combined macroscopically to form a new material with compositional properties superior to that of their constituent materials, are a key component of modern everyday life, from the buildings people live in to the vehicles that are used. As such, improving and creating new composites is critical to further advancement into stronger, better, and more environmentally friendly materials. Thus, the development of smart composites or advanced composites that have the capability of “sensing” and responding to some external influence is of express interest in tackling the ever-growing list of demands the materials we use need to undertake [1]. One particularly interesting area of composite development includes composites capable of displaying something called the shape memory effect, in which the material is capable of shifting into and maintaining a temporary position, from a permanent base shape as a result of some external stimuli acting upon it, and then returning to the base shape under its own abilities [2], which can be seen in Figure 1.

As shown by the graph above, stress induced by some stimulus, which, depending upon the material, could be elec-

tromagnetic radiation, water, pH, temperature, or even a magnetic field, causes a physical change of the material into a certain position and can also trigger it to move back into the original position [2, 4]. This application of stress on the material results in the deformation of the material to the point that the material holds a position under constant strain. If the strain continues to increase, it can reach a point in which reversion occurs and the shape memory material moves to its initial permanent form [3]. This ability makes them desirable for machinery and equipment such as actuators, microdevices, and biomedical equipment or in the aerospace industry for lightweight, deployable structures [5] or for other uses in which shape and position control, the control of vibrations and acoustics, or impact resistance may be desirable from the composite [6]. A key concern in the development of shape memory alloys is the effects of corrosion upon the materials as it can lead to the loss of properties and effectiveness in the material.

2. Shape Memory Composites: Alloys

Shape memory alloys are a combination of metals designed to display shape memory effects through a stress-induced martensite transformation where the parent fcc phase

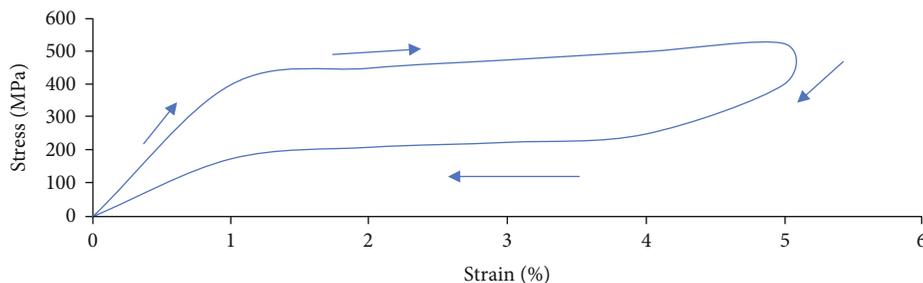


FIGURE 1: A stress-strain curve demonstrating the shape memory effect of a titanium-nickel shape memory alloy [3].

transforms into an hpc phase [7]. Elaborating further, shape memory alloys will exhibit shape memory effects via induced phase transformations, where they move from a high-temperature austenite phase, in which the alloy is more malleable to deformation, but cooling or the application of stress reverts it to a lower-temperature phase, known as the martensite phase [8]. Material property concerns for shape memory alloys focus particularly upon the alloy's abilities to recover from deformations. When determining the rate of recovery for a shape memory alloy, microscopically speaking, it is considered to be a function of grain size in relation to the dimension of the alloy; this implies that grain size is important for a shape memory alloy; if it decreases, strain hardening occurs because of the free space of dislocations that slide prior to interaction with the grain boundaries decreasing and causes plastic deformation and inhibits martensite transformation and strain recovery. Typically, the more impurities there are within a system, the smaller the grain size is, due to dispersed particles causing a grain boundary pinning effect [9]. However, shape recovery for alloys can be more easily tested for and determined via bending tests where the alloy is bent to a certain angle under a certain maximum strain and then recovery may then be induced by heating to a temperature specific to the alloy and subsequently letting cool to room temperature, which allows for the shape memory ratio to be calculated based on the returning angle of the sample [7]. Nickel-titanium, copper, and iron form the basis for some of the more common shape memory alloys [10, 11]; a brief overview can be found in Table 1.

Additionally, the performance of shape memory alloys may be enhanced through the addition of tertiary or quaternary elements [9, 11]. Typically, these shape memory alloys are reinforced with chromium, aluminum, nickel, manganese, copper, silicon, nitrogen, or rhenium, but the addition and quantity of these elements in the alloy may risk sacrificing the superelasticity of the alloy, especially at room temperature conditions [9]. To counter the negative effects that adding these additives may have on the shape memory effect, some manufacturers use certain techniques; aging is a technique used to improve the shape memory ratio of a shape memory alloy, where the metal alloy is treated at a high temperature for an extended period of time; for example, an iron-based shape memory alloy was tested by Yongren et al. to have a base shape memory ratio of 0.2, but after 4 hours of aging, the shape recovery ratio shot up to around 0.6. Unfortunately, the aging process reduces the ability of the alloy to

form a passivating layer, so an aged alloy shows poorer corrosion resistance in comparison to an unaged alloy; there are other developments which would yield good results in terms of corrosion resistance and shape recovery, but these methods tend to be high cost, difficult in terms of "training" the alloy to achieve the desired shapes, result in low recovery stress, and require a high annealing temperature to trigger recovery [7]. Another effect in the addition of other elements to a shape memory alloy is that phase transition temperatures may be increased or decreased, which may also serve to further improve or alter the mechanical properties of the alloy. For instance, the addition of copper can enable nickel-titanium alloys to improve the stability in regard to pseudoelastic behavior, which is good for cyclic mechanical loading. However, the adverse effect of this addition results in the alloy becoming more susceptible to corrosion, as the oxide layer that forms upon the surface is less stable and forms a weaker passivating layer, which enables corrosion attack on the alloy [12], as copper itself provides no additional resistance to the corrosion of the alloy [13]. This brings forth the crux of the issue, in that shape memory alloys have a vulnerability towards corrosion. Corrosion attack on a shape memory alloy focuses on the grain boundaries, in which it may occur on an intergranular level with pitting developing nearby within grains of the shape memory alloy; it is at the grain boundary that precipitates of elements in the alloy, like nickel, form. This intergranular corrosion that occurs at the grain boundary forms zones that reduce corrosion resistance and lead to further degradation of properties [9]. It is possible to help mitigate the corrosion by adding corrosion-preventing elements such as chromium, cobalt, titanium, or even tin in very small amounts to form a quaternary or tertiary shape memory alloy as a means of improving the corrosion resistance [14–16]. However, the addition of these elements may have other, potentially undesirable, effects; for instance, chromium improves the corrosion resistance of the shape memory alloy in exchange for making the alloy more brittle and lowers the transformation temperatures [15], and as Table 2 demonstrates, it is possible to achieve comparable if not greater corrosion resistance without the addition of corrosion-inhibiting elements.

In general, the lower the current density, or I_{corr} value, the better the protection against corrosion; the table above lists several I_{corr} values, three shape memory alloys with corrosion-inhibiting elements, and two polymers. The alloys display good corrosion resistance, whereas the polymers

TABLE 1: Types of common shape memory alloys.

Alloy	Overview
Copper-based	Low cost and highly practical for most applications. Brittle as a result of large grain size, structure, and abnormal anisotropy [10]
Iron-based	Low-cost, good mechanical properties, usable in high-temperature applications, very workable [9]. Low recoverable strains, poor corrosion resistance, requires additions to the alloy matrix [7]
Nickel-titanium	Outperform iron and copper alloys, most commonly used [11]

TABLE 2: Current densities of various alloys and polymers.

Material	$I_{\text{corr}} ((A * \text{cm}^{-2}) * 10^6)$
Cu-Al-Ni [15]	2.56
Ni-Ti-(1.5%)Co [16]	0.62
Graphene/epoxy ester-siloxane-urea [17]	$4.1 * 10^{-3}$
Ti-Ta-0.37Sn [18]	2.615
Blended polycaprolactone with a crosslinked network [19]	2
Polyaniline-epoxy-poly (methylhydrosiloxane)-divinylbenzene blend [20]	$5.1 * 10^{-4}$

perform better, if not superior, to the shape memory alloys in corrosion inhibition. Therefore, applying a polymer coating capable of displaying the shape memory effect to form a shape memory composite would be highly recommended to preserve the mechanical properties of the shape memory alloy.

3. Shape Memory Composites: Property Considerations

When determining the properties or the overall effectiveness of a shape memory composite, there are many factors to consider; for instance, the shape recovery speed is the ability of the shape memory composite to respond to an external force that has resulted in a deformation of the composite's shape [21], or the plasticity index of the composite, a ratio of the hardness to the elastic modulus, is useful for determining the wear resistance in friction and thereby is useful, along with the functional properties of the memory layer, to help determine the structural state of the shape memory composite under frictional conditions [22]. But when determining the effectiveness of a composite coating in preventing the corrosion of the material underneath, a key factor for consideration would be the hydrophobicity of the surface. The hydrophobicity of a surface is linked to the decreased corrosion rate of a metal through the limitation of interactions with corrosive elements, like water, and with organic coatings; this means limiting the diffusion process of water to the metal underneath [22, 23]. Hydrophobicity is dependent on the coating's chemical properties and the microstructure of the coating's surface, where the surface roughness can

enhance the hydrophobicity of the coating [24] and may be measured by determining the wettability of the surface. Wettability is how spreadable water is across a solid surface, the effectiveness of which is determined by the water contact angle, determined by Young's modulus [23], which can be seen in Figure 2.

Shape memory alloys and polymers have been used extensively, and the individual application of either depends upon the demands of the situation, where polymers are used versus alloys because of their low density, being cheap to afford, being able to control what triggers them to recover, the large degree of recoverable strain in which they have the ability to undergo, and the wide range in which one could tailor their response temperatures to (via manipulation of the glass transition temperature); but they are beaten out by shape memory alloys by orders of magnitude greater when the situation calls for higher recovery stress, shorter recovery time, and a vastly larger amount of cycles they can undergo before failure [1] and have better thermal stability and higher elastic modulus [8]. It is worth noting that circumstances in play may mean that what would normally be negative in whether it should be used or not, like the long recovery times of shape memory polymers, can instead confer an advantage in their use [1].

There are many different models to predict the thermo-mechanical properties of a shape memory material. For example, shape memory polymers act partly springlike, and as per Pan et al., a model for determining the thermomechanical behavior for a particle-reinforced shape memory polymer in 1D may be shown as

$$\sigma(t) + \frac{\eta'(T)}{E(T)} \sigma^*(t) = \frac{\eta'(T)E(T)}{E_1(T)} \varepsilon(t) + \eta'(T) \varepsilon'(t), \quad (1)$$

where

$$\varepsilon(t) = \varepsilon^{\text{Total}}(t) - \alpha \Delta T, \quad (2)$$

$$E(T) = E_1(T) + E_2(T), \quad (3)$$

$$\tau(T) = \frac{\eta'(T)}{E_2(T)}. \quad (4)$$

σ is the total stress, $\varepsilon^{\text{Total}}$ is the total strain, ε is the mechanical strain, α is the thermal expansion, η is the viscosity, t is the time, and T is the temperature [26].

For a shape memory alloy, the model is much different as the formula for a 1D constitutive model is

$$\sigma = D(\xi)(\varepsilon - \varepsilon_1 \xi_S) + \Theta(T - T_0), \quad (5)$$

where

$$\xi = \xi_S + \xi_T, \quad (6)$$

and ξ is the total martensite volume fraction, ξ_S is the stress-induced martensite volume fraction, ξ_T is the temperature-induced martensite volume fraction, σ is the stress, D is Young's modulus of the shape memory alloy that is

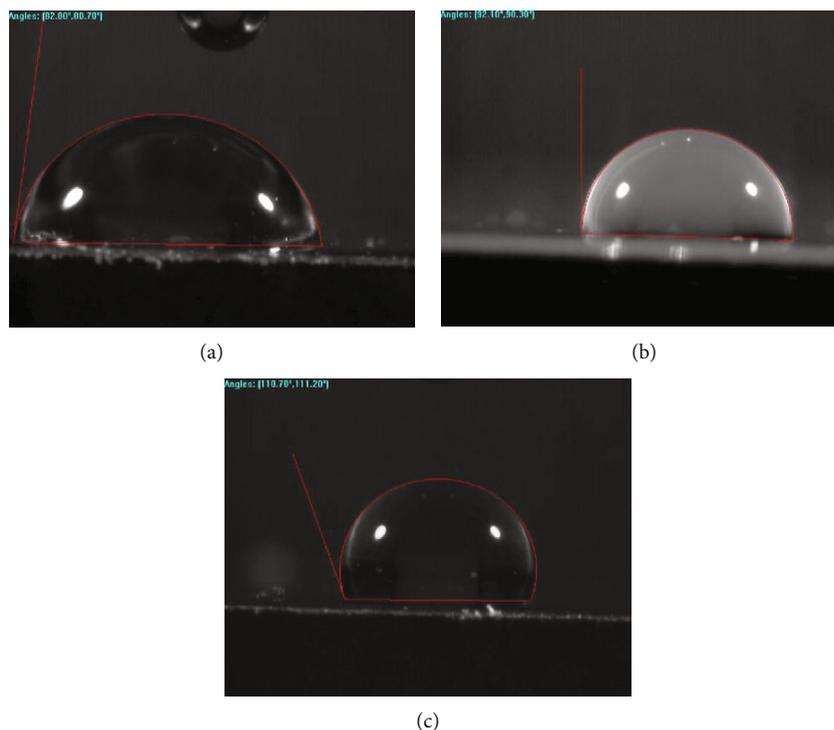


FIGURE 2: Images of water contact angles: (a) neat polyimide, (b) neat polyurea, and (c) poly(urea-imide) (50% polyurea). Courtesy of Feng and Iroh [25].

dependent on ξ , ε is the strain, ε_1 is the maximum recoverable strain, Θ is the thermal coefficient of expansion, T is the current temperature, and T_0 is the reference temperature [27]. These models try to simulate results similar to those shown in Figures 3 and 4.

Polymers function through the potential interactions of thermosets and thermoplastics, where thermosets are defined by their chemical crosslinks that form a three-dimensional network that can extend to an infinite length and thermoplastics lack the interconnected chemical crosslinks and only have a finite length. Processing thermoplastics involves rapid cooling and solidifying viscous polymer melts. Thermoset processing requires the reaction of low-viscosity precursors, and the rate of processing is limited by the rate of the reaction kinetics. Between the two, thermosets tend to have higher dimensional stability and creep resistance, making them preferred for structural composite applications over thermoplastics [28]. By blending these polymers together, one may customize, to a certain extent, the properties of the shape memory polymer, with the base polymer producing the shape memory effect and other polymers for overall cohesion and deformability (for example, after elongation, the crystallinity provided by the other polymers prevents the elastomer from relaxing back into its initial state) [29]. Other advantages for polymers in their usage as materials are their low density, their ease of processability, the ability to withstand strain rates of up to 800%, resistance to corrosion or electricity, how lightweight they are, and the broad range of properties that the building blocks they are composed of [2, 30]. Polymer-based shape memory composites and coatings must also be concerned with the glass transition temperature, or T_g , given that the polymer will be in a

glassy state prior to this point and thereby will affect the shape memory characteristics of said composite; countering this would require that the filler material be capable of inhibiting the thermomechanical effects that the polymer exhibits; these thermomechanical effects are typically demonstrated by friction interactions that resist external loading [21]. For shape memory polymers, this is typically more dependent on the glass transition temperature, also known as the T_g , where phase changes occur above the T_g , where it becomes rubbery, and the position sets once the polymer moves below the T_g as it turns into a glassy state [2]. Given that shape memory composites require the application of external energy to return to their primary form, the composite's thermal absorption and conductivity are necessary factors to consider, as, generally, the greater the ability for a composite to absorb or conduct energy results in better shape recovery times and less energy consumed to exhibit said response times [21]. However, there are demerits in using shape memory polymers, as functionality may be lost over time; thus, a means of countering such loss in effectiveness is important in extending a shape memory polymer's lifespan and its ability to withstand environmental conditions.

4. Shape Memory Composites: Polymers and Polymer Blends

Traditional polymers are fairly inert to the environment, which means a gradual loss of functionality over time [30], especially in the form of microcracks, the most serious challenge that polymers face in long-term applications, as they decrease the lifetime of the material and are much more

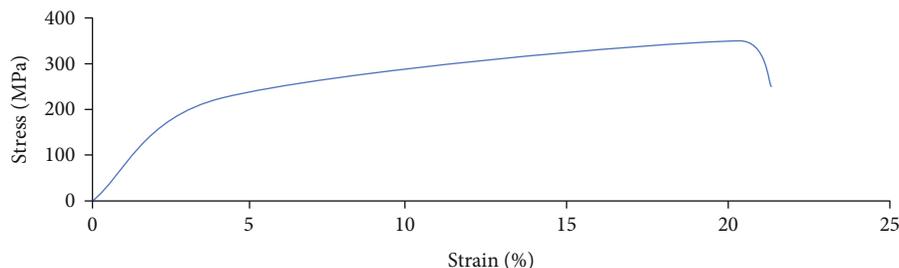


FIGURE 3: Ni-Ti shape memory alloy stress-strain curve (transitions start at 89.11°C and end at 86.33°C for the martensite phase, and the austenite phase begins at -22.73°C and ends at around 91.96°C) [18].

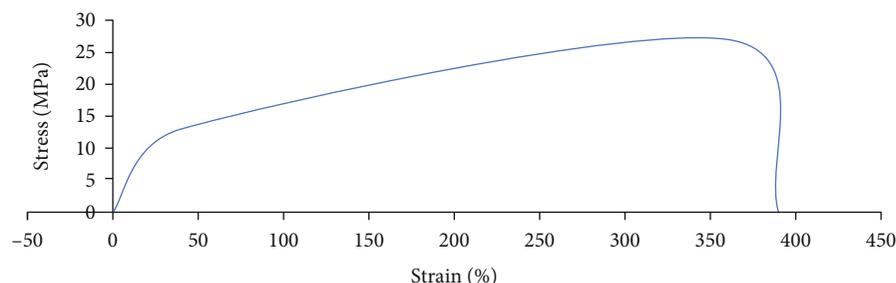


FIGURE 4: Polycaprolactone polymer (T_m of 51.7°C) stress-strain curve [19].

difficult to detect or repair [31]. Hence, polymers require some means of maintaining and repairing their functionality, either by means of some external application or, more optimally, by a trait inherent to the polymer or polymer blend; in other words, the polymer must have the inherent capability to heal itself. As the polymer is a shape memory material, stress resulting from a variety of triggers, such as chemical, mechanical, or thermal, can result in mechanical deformation in the material and additionally may activate a healing response towards physical damage that has been generated [32]. Commonly, crack healing occurs because of thermal effects and is initiated at or above T_g . As such, developments have typically focused on adjusting the effective T_g to the desired temperature, which is typically lower than a polymer's normal T_g [31]. Accomplishing self-healing for polymers includes two different approaches that rely upon different chemical interactions to achieve the objective: one is through supramolecular forces, and the other is by dynamic covalent bonds formed within the polymer blend. First, though, is the primary means by which the polymer adheres to the surface. Interfacial adhesion between the polymer matrix and the 2D filler is an important part of property enhancement and being able to reproduce the desired results. Strong interfacial bonding between the polymer matrix and the 2D filler gives the polymer coating a high modulus and tensile strength, improves hardness, and increases coating resistance to tear, fatigue, and corrosion [17]. Thusly, the formation of a shape memory composite between a polymer and an alloy necessitates the use of coupling agents, like trimethoxysilylpropyl methacrylate, to form the connection between the organic and inorganic phases of the coating, as the lack of such connection compromises the overall

mechanical properties because organic materials do not adhere well to inorganic materials [33]. One of the most effective choices for corrosion inhibition and recommended options for coupling agents includes polysiloxanes. Polysiloxanes are hydrophobic polymers capable of improving the corrosion resistance of a polymer blend by limiting water's ability to access the metal/hybrid polymer coating interface [17]. Characterized by a Si-O-Si group, which has a bond angle between 104 and 180 degrees attached to the polymer chain, the degree range of the bond angle affects the flexibility chain and improves the bond energy, forming the basis for the notable durability and resistance to heat that polysiloxanes have [34].

4.1. Polydimethylsiloxane. One of the most commonly used polysiloxanes is polydimethylsiloxane, abbreviated to PDMS. PDMS elastomers are typically formed from crosslinking linear polymers that have been entangled and are stiffer than the threshold value for the dense entanglements that act effectively as crosslinks [35]; the structure may be found in Figure 5. One method in which PDMS could be improved for usage is reducing the stiffness of PDMS elastomers that would reduce the energy necessary for deformation. This is critical for improved adherence to an object that would otherwise be difficult to apply a coating to, and accomplishing this would mean an overall reduction in the density of the crosslinks. Applying a solvent can accomplish the reduction in the density, but the solvent can leach out and potentially harm the surrounding environment. PDMS cannot have a shear modulus lower than 200 kPa. By forming a crosslinking bottlebrush matrix as opposed to a linear polymer, it is possible to inhibit entanglement formation and form a

controllable elastic modulus that can range from 1 to 100kPa, where the modulus corresponds linearly to the density of the crosslinking chains. Additionally, there can be independent control over the loss modulus; it reduces adhesiveness, can be relatively simple to produce, and may be furthered tuned via the backbone/side chain/crosslinking chain ratio to further tailor the mechanical properties [35].

4.2. Polymethylhydrosiloxane. Of the polysiloxanes available, polymethylhydrosiloxane, or PMHS for short, is a particular siloxane of choice as it is nontoxic, is stable in air, is resistant to high temperatures, and can be used as a reducing agent for the conversion of carbonyls to alcohols [17, 33]; the structure may be found in Figure 6. PMHS has low surface energy and good innate hydrophobicity and, thanks to its inorganic and organic molecular parts, acts as a good coupling agent between polymers and metal surfaces. PMHS is useful as no organic solvent is necessary to prepare the coating, which is important given the restrictions in volatile organic compounds that can be considered hazardous to the environment. Despite this, the application of PMHS as an anticorrosion measure is relatively rare. The effectiveness in the addition of PMHS may be demonstrated by an experiment performed by Sun et al. where PMHS was added to a polyaniline-epoxy coating. This successfully reduced the overall surface energy of the coating, improving the wettability, and formed small protuberances on the surface, which allowed for a layer of air to form and inhibit contact by a corrosive solution and the adsorption of the solution's corrosive ions, resulting in an increase in the effectiveness of the coating to 70 days, whereas the coating without PMHS had only lasted 34 days [20].

4.3. Supramolecular Polymers. Supramolecular bond-based self-healing material has polymer bonds that are connected by sticker-like behavior, in that they can connect and reconnect, and it is this stickiness that gives the material strength; it is important to note that this does not come from covalent bonds or chain entanglements. These bonds affect the polymer blend's strength, viscosity, flow, and ordering of its polymer chains within and therefore have a relationship with the dynamic behavior the polymer exhibits. Once the damage has occurred to the structure, the interface of the damaged surfaces will then have unbound supramolecular bonds that remain "sticky" and are capable of being recombined and reformed to close the damage and revert to the previous undamaged state of being. In using supramolecular bonds, the central concerns are the time it takes for recovery to occur, the strength of the material, and the material's ability to recover properties after damage [32]. Some examples of polymers to use in a blend that relies upon supramolecular forces to accomplish self-healing are as follows.

4.3.1. Epoxy Ester. Epoxy ester resins are known to have good corrosion-inhibiting properties and adhesion to surfaces but are restricted in use because of their poor chemical resistance and weak mechanical properties; as such, it is recommended to improve them through the use of blending or copolymerization with other polymers that are capable of resisting high

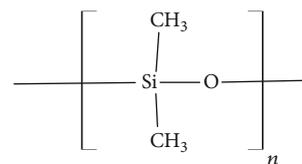


FIGURE 5: Polydimethylsiloxane.

temperatures like polyurea or polysiloxane [17, 33]; the representation of the structure may be found in Figure 7. Polyurea is typically used for laminates in buildings and the automotive industry, where it can improve the impact and blast resistance of the epoxy ester [17]. Epoxy esters are also limited by their highly reactive rings, which inhibits processability for polymer blends and thereby makes them more expensive to produce. Generally, when reacting epoxy esters to produce certain polymers, the epoxy functional groups are opened through the esterification of unsaturated fatty acids to then form alkyd-modified epoxy esters, with properties controlled by means like the level of unsaturation or the chain length. The produced epoxy ester emulsion is then dehydrated through the evaporation of water to coalesce and form a film, which is cured through autoxidation, or oxygen reaction to cause a free radical chain mechanism. The outcome of the properties depends upon the oil chain length. For instance, long oil chains in epoxy esters mean lower chemical resistance, longer drying times, and enhanced ability to penetrate and seal poorly cleaned surfaces, whereas short oil chains are hard and brittle and have good chemical and moisture resistance [36].

4.3.2. Polyimide. In general, polyimides are favored in engineering applications as they possess outstanding mechanical properties, great thermal stability, a high glass transition temperature, and a low dielectric constant [36]; a representation of the structure may be found in Figure 8. Most studies that focus on self-healing polymers are ones that operate under low or medium T_g , whereas high T_g polymers, which would be suited for self-deployable aerospace or jet propulsion applications, are not as well studied. A shape memory variant of polyimide would be one such polymer, as it is capable of high T_g , with temperatures around 218°C, and self-healing (which occurs at 243°C) at the cost of lowered mechanical properties and a lower T_g (235°C) for the non-self-healing variant than the non-self-healing variant, but that may well be due to the polystyrene, and another material may be better suited [37]. Polyimides are defined by a rigid heterocyclic imide functional group and are noted for the interaction of their electron-rich nitrogen atom and their electron-deficient carbonyl group located in the backbone of the polyimide [38]. However, polyimides tend to be limited for their use due to poor moisture absorption and adhesion, which can lead to interfacial failure and limits them to a more moderate coating lifespan as compared to other coatings, as well as their high surface energy and dielectric constant [36, 38]. Overcoming these limitations typically means inserting hydrophobic polymer blocks into the backbone of the

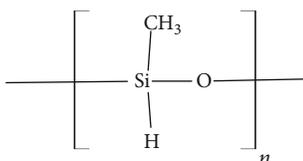


FIGURE 6: Polymethylhydrosiloxane.

polyimide or incorporating nanoparticles into the matrix as a means of reducing diffusivity and relative permittivity of the polyimide coating [38]. Including nanoparticles has the drawback of increasing the surface energy for the polyimide, which in turn reduces its adhesion, whereas the inclusion of polymer blocks into the backbone can reduce the decomposition temperature and thereby the service temperature and mechanical properties [38]. Durability relates to the retention of the barrier properties held by the polymer coating and is, for polymers, controlled by the crystallinity within the coating. A decrease in the surface energy of the coating is related to an increase in coating resistance [25]. Polysiloxanes can be utilized for improved energy dissipation, flexibility, and surface adhesion, but as a trade-off, they reduce the ultimate strength and Young's modulus; therefore, mitigating these detractions primarily requires manipulation of the molecular weight percent of polysiloxane. For Young's modulus to remain close to that of plain polyimide, the polysiloxane weight percent must be between 10 and 20%; it is worth noting that ductility significantly improves for the copolymer if polysiloxane is within 10 to 40 wt%. Overall, attaching a polysiloxane to the backbone of the polyimide chain improves the overall processability of the polymer, inhibits the absorption of water, makes the polymer more capable of adhering to a wide range of surfaces, improves the thermal stability, and decreases the decomposition temperature in relation to an increase in the wt% of polysiloxane in the polymer (this appears to be more related to the reduction in polyimide). The drawbacks of the polyimide-polysiloxane chains could be overcome through the addition of other copolymers, like polyphenylsilsesquioxane, which is a suggested polymer that could also further improve the decomposition temperature of the polymer blend. Introducing an ester group to the imide backbone produces the effect of increased flexibility of the polymer but reduces the glass transition temperature, where the combined poly(ester-imide) molecule has a glass transition temperature of 185°C and further analysis has shown that it loses 10 wt% of its mass in air at 300°C [33]. Because the T_g of a polymer blend is not the actual average of the T_g of the polymers that make up the blend, in fact, it appears to act more like a range that varies depending upon the composition of the bulk, the architecture of the blend, the molecular weight of the polymers, and other factors. At the lower end of this range, thermal activation occurs but is hindered by steric constraints, the severity of which may be determined by the relative rate of component dynamics [36].

4.3.3. Polyurea. Polyurea is a semicrystalline polymer prized for its piezoelectric abilities, often used as an insulator, and can exhibit high-temperature stability with a piezoelectric e

constant of 15 mC/m² that remains so until it reaches temperatures of 200°C [38]; a representation of the structure may be found in Figure 9. If blended with polyimide, the hydrogen bond donors and acceptors within the blend enable self-assembly in addition to an ultralow dielectric constant, a value between 1.56 and 1.94 with any decrease corresponding to an increase in the concentration of polyurea, which would be immensely beneficial in the inhibition of corrosion [25, 38]; a representation of the polyimide-polyurea blend may be seen in Figure 10.

Additionally, for the created poly(urea-imide) blend, two rubbery plateau regions occur exponentially as a result of two T_g regions caused by the mole fraction content of polyurea in the polyimide block chain, which in turn increases the storage modulus of the polymer. The T_g of copolymers increases with an increase of concentration of a high- T_g component, where a sharper effect occurs with the addition of a slightly higher amount of polyurea to the polyimide (it is worth noting that the degree of imidization has little bearing on this behavior as it decreases as the polyurea mole fraction increases) as a result of the self-supporting, complementary hydrogen bonding [38]. As a result, polyimide-b-polyurea forms a coating with an expected lifetime of 8 years, higher than that of polyimide, providing superior corrosion resistance [25], which can be seen in Figures 11(a) and 11(b).

4.4. Dynamic Covalent Bonds. Briefly stated, dynamic covalent bonds are the classic covalent bonds that form up traditional polymers but have the additional capability of being reversible under equilibrium conditions, like noncovalent bonds, where the reformation of bonds occurs within seconds or minutes [30]. Networks formed by these dynamic covalent bonds have the benefits of thermoset polymers and act as thermosets under certain conditions but have the reprocessability that thermoplastics are known for. The main drawback that can occur is that dynamic covalent bonds may sacrifice the creep resistance of the material as they may be activated when not needed and therefore cause creep within the material; this may be controlled using thermal phase transition temperatures to lock in the polymer until sufficient energy can unlock and trigger shape memory or self-healing effects [28].

4.4.1. Siloxane-Poly(methyl methacrylate). Siloxane-poly(methyl methacrylate), also known as siloxane-PMMA, has excellent corrosion-resistant and adhesive properties for less environmental impact than coatings such as chromate-based coatings. These silica-PMMA films are noted not only in their low preparation temperature, cheap processing cost, and ability to remain homogeneous as applied across large-area substrates but also in their vulnerability to brittleness from chemicals like water, methanol, and ethanol, especially after thermal treatment [33]; a representation of the structure may be found in Figure 12. Preparation typically can involve the usage of water acidified with chemicals such as nitric or hydrochloric acids as a means of enhancing corrosion resistance, but this treatment process risks the formation of Cl⁻ ions that may form corrosive agents, and the high acidity of the hybrid may instead act to compromise the substrate

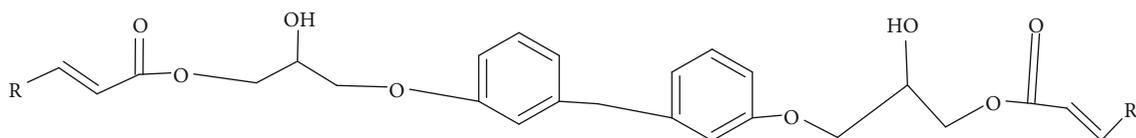


FIGURE 7: Epoxy ester.

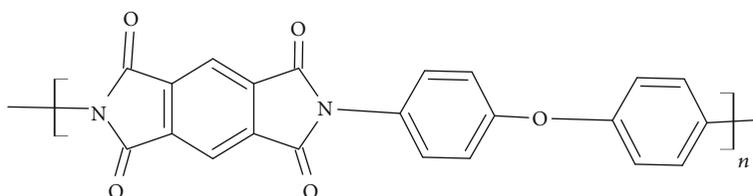


FIGURE 8: Polyimide polymer.

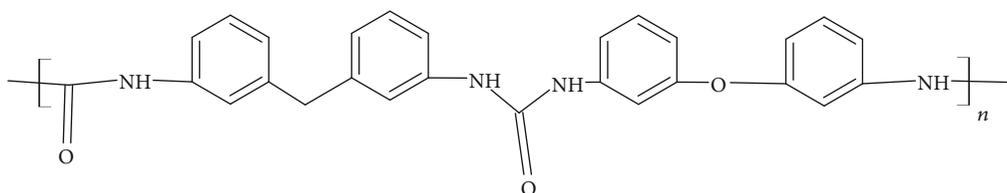


FIGURE 9: Polyurea.

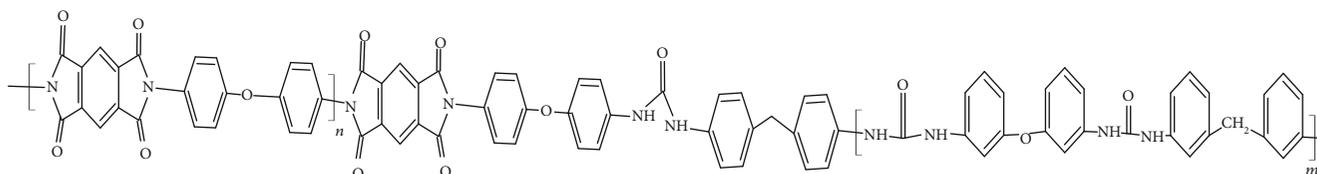
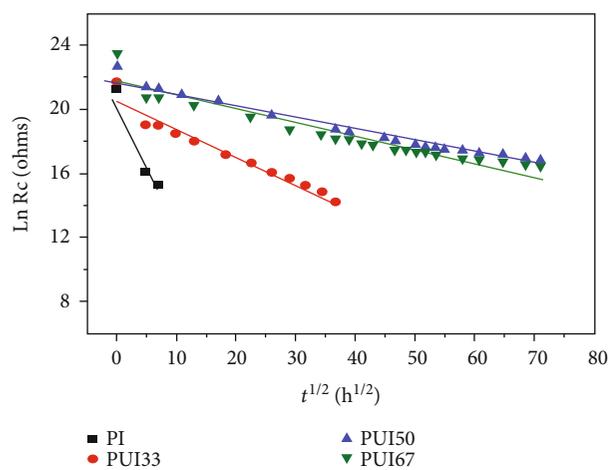
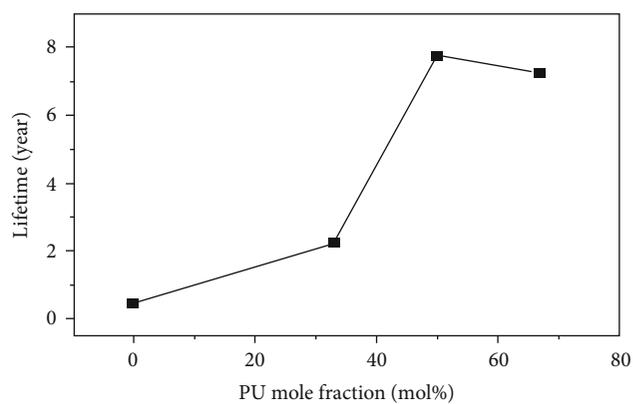


FIGURE 10: Polyimide-b-polyurea supramacromolecule.



(a)



(b)

FIGURE 11: (a) The projected lifetimes of poly(urea-imide) coatings with varying concentrations of polyurea applied to aluminum. (b) The coating lifetime compared to the % mole fraction of polyurea. Courtesy of Feng and Iroh [25].

rather than protect it. A change in the formulation of the coating will result in a change of the film's formation characteristics, and thus, an environmentally friendly coating must be prepared through an environmentally friendly precursor solution. Porous films promote crack and discontinuity formations that cause the barrier to fail and reduce the overall corrosion resistance to decrease. Silane films that are more hydrophobic are better at protecting metals as barrier and adhesion properties are dependent on the time of exposure to either air or water as Si-O-Si bonds are vulnerable to hydrolysis reactions provided by exposure [34].

4.4.2. Hydrazones: Self-Healing and Shape Memory Materials. Acylhydrazones are formed from the condensation of hydrazine and carbonyl compounds and may be catalyzed in the presence of acid to make their C=N bonds more pH-responsive [30]; the structure may be found in Figure 13. Acylhydrazones are more resistant to water than amines and, under mild conditions, may be considered a dynamic molecule capable of reshuffling with other hydrazones or in the presence of differing hydrazines. Most importantly, however, they are responsive to the pH of the surrounding environment, where their formation is catalyzed in the presence of acids and the formation is reduced in more basic environments. Alternating copolymers can, with hydrazones, access different polymer compositions and functions through the exchange of monomers, allowing for tunable mechanical properties. Siloxanes can be used as a spacer to form a stretchy, soft hydrazone film, and if reacted in acid with a harder, more rigid hydrazone, monomers are exchanged between the two to form a new copolymer whose properties are determined by the monomer exchange rate and how the monomers are exchanged. Additionally, a polyacylhydrazone may achieve self-healing through the addition of a polysiloxane unit and allows for deformation recovery to occur over the course of several hours without the need for heating [30].

4.4.3. Diels-Alder Reactions. A Diels-Alder reaction occurs through a cycloaddition reaction in which a conjugated diene and a double-bond dienophile form a six-membered cyclohexane ring; most applications make a reactant electron-rich, otherwise known as the diene, and another reactant electron-poor, which is known as the dienophile. The result is an exothermic reaction; therefore, the inverse reaction, or retro-Diels-Alder reaction, is an endothermic process and thusly requires heat to proceed. Diels-Alder reactions are self-contained and do not require a catalyst nor the addition of any other materials; as such, most Diels-Alder-based dynamic covalent polymers are network polymers [30]; a representation of the general reaction may be found in Figure 14. Diels-Alder cycloadducts or other molecules that form dynamic covalent bonds or have supramolecular interactions have been used to achieve intrinsic self-healing in thermoset polymers through reversible/dynamic interactions. These chemistries enable for fabrication of crosslinked networks capable of healing and improve mechanical properties and thermal and chemical stabilities of the polymer being enhanced. DA adducts form at low temperatures (90°C) and

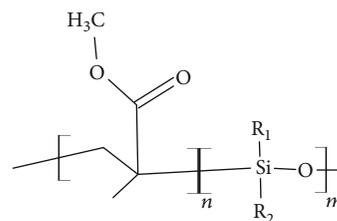


FIGURE 12: Siloxane-poly(methyl methacrylate) copolymer.

can store shape memory in the polymer structure by way of crystallization and vitrification, which are capable of triggering physical phase transitions through thermal means, which has the added bonus of closing cracks and thereby assists in the coating's healing process. Dense crosslinking promotes mechanical properties of a polymer but risks reducing polymer flexibility and healing ability. Thus, healing a polymer with DA reaction means undergoing a retreatment process at a retro-DA temperature of 120 to 150°C, as it causes partial debonding that enhances molecular mobility; unfortunately, this process may result in the loss of the polymer's reversibility and continued healing in addition to the inefficient curing of DA. It has been suggested that the copolymerization of a siloxane, such as polydimethylsiloxane (PDMS) with polyurethane to assist in the closure of cracks, the flexibility of the polymer, and the reconstruction of DA bonds improve mechanical properties, as PDMS can hinder the crystallization of the urethane to preserve mobility [39]. Improving the properties of a polysiloxane polymer may be achieved through the incorporation of inorganic nanoparticles and may utilize the nanoparticles as crosslinkers to further improve self-healing. The molecular structure of the coupling agent, the spacer length, helps to determine the healing properties for Diels-Alder self-healing polymers, as long spacer groups appear to promote the transition state of the Diels-Alder reaction better [40]. As far as shape memory goes, DA bonds are preserved below the T_g but can be activated above the T_g to initiate the healing and reconstruction of broken bonds. The healing efficiency of a DA-PDMS-PU copolymer was improved over the DA polymer as the flexible PDMS segments enhanced the overall flexibility of reversible units and the reaction kinetics of the healing process at a mild temperature [39].

5. Shape Memory Composites: Coating Additives

Another factor of consideration is that the grain size of the surface layer of composite materials can affect the properties of the composite, ranging from elasticity to strain resistance; as such, choosing the correct material for the composite application is a key component in designing a new shape memory composite [22]. Thus, the addition of fillers may serve as a means to further enhance the polymer composite; some types of fillers may be seen in Table 3.

Conductive fillers are especially important to shape memory polymers, as polymers suffer from a very low

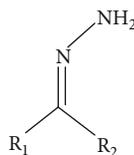


FIGURE 13: Hydrazone.

thermal conductivity on the order of somewhere between 0.15 and 0.3 W/m * K, which make for better insulators; thus, conductive fillers are added with greater conductive effect proportional to their weight percent within the polymer composite. There is a drawback to such fillers though, as they can inhibit shape deformation and recovery versus that of a purer shape memory polymer; this effect is more pronounced with larger particles [21]. For example, the addition of silicon-carbon and silicon-oxide fillers to around 40 wt% inhibits the shape memory composite's ability to recover completely from deformation [5]. Carbon fillers form a number of possible nanoparticles capable of being used as fillers within the matrix, with several notable carbon fillers being carbon black, nanotubes, or graphene [2, 4, 5]; a figure of a graphene-polymer composite is shown in Figure 15.

Graphene is a useful polymer coating filler thanks in part to its low mass density, high modulus, and high strength and can also work to improve the corrosion resistance of the coating as it is impermeable to gases or liquids that might act to corrode the metal beneath the coating; ultrathin nanosheets have even been tested successfully as a protective film. Graphene is very transparent, so coatings preserve the optical properties of the metal; they also have a high surface area and promote great adhesion between the nanofiller and the matrix [17]. Graphene is capable of improving the rubbery plateau modulus by up to 400,000 vol% when added to form a polyimide composite and can improve Young's modulus, ultimate strength, and glass transition temperature when used to form other polymer composites. If there is an area of concern, it is that the surface properties need to be tailored to suit the desired application, as surface charge, hydrophilicity, and wettability that are changed by the inclusion of graphene will affect cell attachment and polymer performance regarding the applied surface [41]. Carbon nanotubes, on the other hand, can reinforce and enhance shape memory effects, can improve electric-based shape memory recovery, and can be used for the creation of complex composite systems capable of being tuned for specific purposes and the enhancement of the shape memory polymer's ability to respond [4]. Metals and their oxide forms are often chosen in the fabrication of electronic devices [5], and because of their conductivity, some, like ferrite, can even be affected by magnets. This enables shape memory transformation as the metallic particles can generate heat when exposed to a very strong magnetic field. If there is a major drawback, it is that polymers and metals have differing interfacial properties that make them somewhat incompatible to use as a filler. Additionally, it is worth noting that the alignment of the filler can affect the polymer as well. As an example, with the addition of carbon nanotubes to a thermoplastic shape memory polymer, the carbon nanotubes aligned with the direction

of the force applied to the polymer. This resulted in a change to the overall shape stability, affected how the polymer recovered to a permanent shape, and changed the crystalline distribution within the polymer matrix [42].

Shape memory effects on self-healing are insufficient enough when applied to deep cuts and as such require the utilization of other methods of corrosion prevention [43]. One of the more common approaches of enhancing corrosion prevention is to embed corrosion inhibitors into the matrix; these can act as healing agents and thereby leach into any defects, allowing for the suppression of corrosion. For coatings that include inhibitors, healing is determined by inhibition of corrosion versus the coating's ability to repair the matrix barrier properties and is therefore irreversible in terms of reaction, and the amount of inhibitors located in the matrix is limited, as large quantities will lead to loss of desired matrix properties. Coating matrix mobility provides for the restoration of corrosion protection of the coating and is usually initiated through the usage of heat or light. Heating above T_g allows for physical closure as the coating would soften and trigger shape memory effects and thereby partly restore barrier properties; this process may be further enhanced by a corrosion sensing component capable of locating damage and healing it or at least preventing further possible damage [44]. Some corrosion inhibitors include benzotriazole, 8-hydroxyquinoline, or inhibitors that are cerium-based. Corrosion inhibitors leach out after damage has occurred to form a barrier film onto the exposed surface. High concentrations of corrosion inhibitors promote greater corrosion resistance but may cause a reduction in mechanical properties. Corrosion inhibitors appear to not affect the rate at which water penetrates the matrix; as such, damage that has been healed may still allow for corrosion to occur, especially in areas where damage once took place [24]. Inhibitors are typically designed to last around 6 to 8 years, in other words, at least until the next maintenance period. Organic coatings typically absorb water via defects into pores within the coating whereby inhibitor pigments may then dissociate and dissolve [45]. Triazole and thiazole are generally used as corrosion inhibitors for aluminum, especially in lieu of toxic chromium-based anticorrosive agents. 2-Mercaptobenzothiazole (MBT) is favored as it adsorbs to aluminum alloy surfaces to form a thin, protective film; however, MBT and other corrosion inhibitors do not work well with a polymer coating as they can deactivate and do not provide the desired corrosion protection [46]. Chromate coatings are the baseline corrosion inhibitor, and high levels can slow the crack growth rate but can be considered environmentally harmful [45]. Adding micro- or nanocapsules has the possibility of reducing the barrier properties depending upon the size of the container or if the container is incompatible with the matrix. The desired trigger mechanism plays a strong role in determining how to encapsulate the inhibitor, alongside the type of matrix and inhibitor that will be used. Common methods of activation are local changes in pH, mechanical rupture, and ion exchange. Ion exchange occurs by containers containing corrosion-inhibiting anions that are released, which allow for more aggressive anions, like chloride, to replace them [46]. If the inhibitor is mixed with the coating,

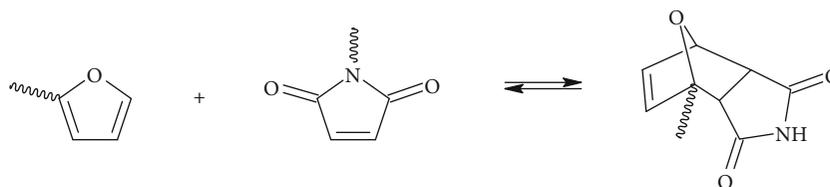


FIGURE 14: Representation of a general Diels-Alder reaction.

TABLE 3: Types of fillers and their roles within the polymer matrix.

Filler type	Filler role
Fiber or fiber particulates	Increase mechanical properties but at the expense of shape memory abilities [21]
Silicon-carbon or silicon-oxide	Improve mechanical responsiveness, properties, and recovery times. Are most typically used due to their prevalence [5]
Carbon-based fillers	Enhances mechanical properties and converts energy, such as heat or electricity, to trigger shape memory effect [2, 4, 5]
Metals/metal oxides	Good mechanical properties, more conductive than carbon fillers, can achieve good biocompatibility in the nanoparticle form [5]
Cellulose	Biodegradable, can easily generate and break hydrogen bonds, allows for water-triggered shape memory responses [5]

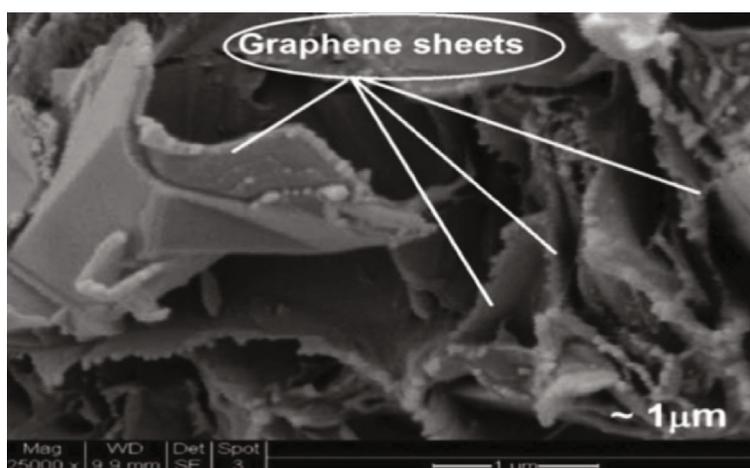


FIGURE 15: SEM micrograph that shows the cross-sectional morphology of a nanographene sheet-clay composite, coated with polyimide. Courtesy of Longun et al. [41].

the inhibitor gets dissolved in the solution and creates micropores when the solution is applied as a coating. Metal-organic frameworks are a type of encapsulating method where metal ions are connected by organic linkers; they operate by releasing the inhibitor to form an adsorption layer on the exposed surface, and then the metal-organic framework itself impedes any penetration by electrolytes or further corrosion around the afflicted area. A key desired ability of any capsule is the controlled release of inhibitors, to not prematurely expend the limited agent within, thereby giving the coating more longevity in application [47]. Proper storage of corrosion inhibitors reduces leaks, prevents the inhibitors from interacting with the matrix, and can improve the amount of inhibitors stored within. Generally, the preferred containers for corrosion inhibitors are nanoparticles that have large nanocavities,

have large surface areas, are very stable, and have low density. Hollow containers are far more capable of storing great amounts of inhibitors than other carriers. Typical container materials are calcium carbonate, titanium oxide, halloysite nanotubes, mesoporous silica, and cerium oxide. Most release methods are typically triggered because of chemical damage or pH changes, as they are common causes of damage to the metal. Inorganic containers have the benefit of being able to be more easily dispersed throughout the polymer matrix and may have additional anticorrosion properties themselves [48].

Capsules that contain a healing agent could be dispersed throughout a polymer matrix, whereupon damage to the matrix may act to trigger the self-healing by causing polymerization to occur from the agents within the capsule. Desirable properties for such a capsule are long shelf life,

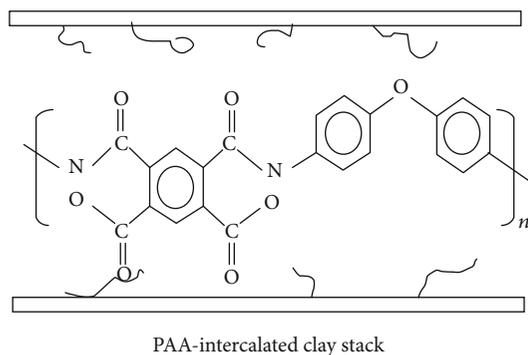


FIGURE 16: Representation of intercalation of the montmorillonite clay stack. Courtesy of Wang et al. [53].

the strength to maintain structural stability until self-healing needs to occur, and being able to demonstrate excellent bonding to the host matrix. The development of submicrons and nanocapsules could allow for smaller interstitial spacing. Particulate fillers significantly influence the mechanical properties of a material, and depending on the filler, they may sometimes affect the polymer beneficially, like increasing the fracture toughness; at other times, they may act negatively like decreasing the elastic modulus or ultimate tensile strength (these negative effects have been noted to occur with increasing capsule concentration of large capsules) [49]. Key advantages to the inclusion of microcapsules or tubes that contain healing agents are the ability to close a cut with minimal material; the fibers can perform at the same level even after repeated usage thanks to the constrained recovery resulting in renewed tension programming. By using stress recovery, it is possible to force the closure of a crack or cut within the matrix [50]. Microcapsules are preferred for short-term corrosion protection. When damage occurs, the microcapsule breaks down, which allows for the healing agent to react with the metal substrate to form a passivating conversion layer; this provides time for healing to take place and prevents further corrosion. This basically means that healing is a two-step process in which the microcapsules disperse to form a passivating layer that improves the adhesion strength and corrosion resistance of the substrate, and from there, the matrix may then be heated to initiate the shape memory effect to close the damaged area [51]. Encapsulating a catalyst, where there exists an initiator pellet and a resin pellet, can act to induce self-healing in a polymer composite; this has been tested in polydimethylsiloxane successfully. Hollow glass fibers made up of borosilicate can act as capsules for the containment of liquid healing agents, are capable of restoring up to 97% of the original flexural strength, are more capable per volume of storing healing agents, and could be used as a means of visual detection for damage, but such fibers are limited in that they must first be broken in order to distribute the agents, and the fibers could possibly expand under heat which may lead to damage of the matrix [52].

Another suggested anticorrosion coating material would be high-aspect ratio fillers, like clay additives. One specific clay of interest would be montmorillonite clay, a sodium clay that has been organically modified resulting in better com-

patibility and higher reinforcement to polymer matrices; it has a 2D crystal structure hydrated with an alumina octahedral sheet in between two silica tetrahedral sheets; these stacking layers result in van der Waals gaps [53].

Montmorillonite clay (shown in Figure 16) is positively charged, which, when added to a polymer coating, compensates for the excess negative charge by adsorbing alkali metal ions onto the clay platelets which creates a hydrophilic form of clay that has stable suspensions in water. At a certain point of concentration, these clay suspensions form a highly viscous gel in water where the volume filling is jammed or has a percolated network of clay particles that can be observed by the pseudosolid behavior the gel exhibits; it is worth noting that polymer-clay nanocomposites are also capable of exhibiting gelation after a critical concentration of clay has been achieved. When added to the polymer coating, montmorillonite clay must be made more organophilic through the replacement of alkali metals with cationic surfactants typically of primary, secondary, tertiary, and quaternary alkylammonium ions as reinforcing nonpolar polymers necessitates the addition of compatibilizers. Mechanical, physical, and thermal properties of polymer-clay nanocomposites are capable of being improved through the dispersion and exfoliation of the clay platelets throughout the matrix [54]. Specifically, the fillers allow for the polymer to achieve a higher modulus, an increase in thermal stability and conductivity, better solvent resistance and ionic conductivity, and improved self-passivation and barrier properties [53]. Inclusion of clay into the polymer matrix appears to have a bell curve in effectiveness, as the corrosion current density for a polymer of 1 wt% of clay is an order of magnitude lower than that for a polymer without clay, but it reaches the same value as the wt% of clay reaches 10%. Coatings with low values (between 0 and 2 wt% clay) demonstrate an increase in impedance in comparison to the plain polymer coating, but it drops significantly as the weight percent of clay reaches 2 wt% or greater, due to clay aggregating and agglomerating within the matrix [54]. Additionally, the inclusion of clay in the polymer improves the rate of polymerization as well as the degree of polymerization, while also improving the processability as the condensation polymerization reduces the reaction solution viscosity [53]. Polymer chain movement gets impeded by the clay within the matrix, and the clay also imbues lower porosity and greater stiffness as the polymer chains are physically entangled [54]. The performance of polymer composites depends upon the filler dispersed throughout the matrix; as such, one of the main focuses when it comes to adding fillers is the dispersion of the material in a manner that prevents agglomeration [53].

6. Designs

Shape memory effects may help self-healing via pulling crack surfaces closer together; this may be achieved by embedding or combining a shape memory system into the polymer. An example would be wires encased in a polymer, where if a crack forms in the polymer, the shape memory effect produced by the wire forces the crack to close, and capsules located throughout the polymer may

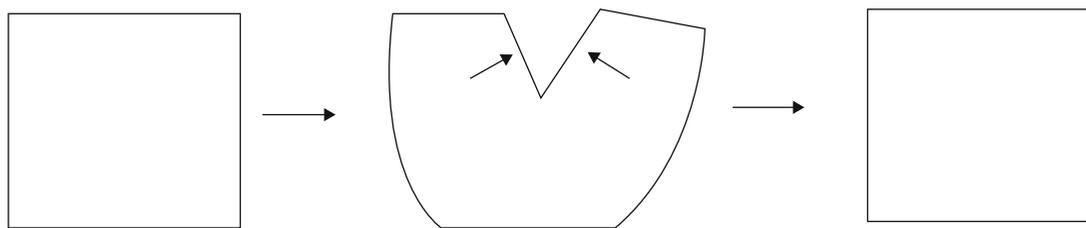


FIGURE 17: When a crack or similar damage occurs to a shape memory polymer capable of self-healing through physical means, if the polymer can be made to physically close the crack by means of a wire or the surface bending the polymer shut, and heat is applied, the polymer can then self-heal and repair the damage, resuming its former shape with minimal loss of properties.

then release the polymeric self-healing chemicals to seal the crack, so long as the crack is in an area where the wire can exert the shape memory effect [55]; an example is shown in Figure 17.

Self-healing is generally induced by heat, meaning that a frictional process that can generate sufficient heat to bring the polymer to a viscoelastic melt state would enable the polymer to rebond and repair. Heating-induced healing of thermosets relies upon the crosslinking of unreacted polymer groups, where heating is applied until the molecules within can interdiffuse with each other and thereby allow for any residual groups to react. Requirements for thermoset healing agents are that they should be reversibly bonded to the cross-linked network while below the healing temperature (to minimize the effects they may have upon the mechanical properties), but once above the healing temperature, they become mobile to enable diffusion across the crack, and the addition of linear chain molecules will not interfere with the mechanical properties of the matrix. If cracks and loss of strength are the result of broken molecules or other changes at the atomic level, then repair must occur through the reaction to recombine said molecules, or in other words, an inverse reaction must occur. Deterioration of the polymer is minimized if the recovery rate occurs at the same pace as deterioration, but high temperatures are required for self-healing to occur by reversible chemical interactions. In applying self-healing by external means, it is not the matrix that acts to heal itself but the encapsulated healing agents, which are stored in the form of either a “pipeline” or a microcapsule that is destroyed, and said agents are released to heal the crack [31]. It should be noted that if temperatures exceed what the polymer is capable of healing, it will cause the polymer to deteriorate and no longer function properly. Additionally, a defect in a polymer coating that would allow corrosion to occur at the metal underneath can result in loss of coating adhesion and a reduction in the integrity of the metal. Self-healing by the chemical reaction process is susceptible to side reactions that may reduce healing or shape memory properties. Physiochemical mechanisms in shape memory polymers can reverse mechanical deformation that was induced by stress or strain by several methods, the most popular and easiest being heating the material, without the need for a chemical reaction to take place. This process takes advantage of the multiple glass transition temperatures (T_g) or melting temperatures (T_m) found within the polymer, as the polymer partially melts and can solidify later, but a differ-

ent part of the block keeps a solid form, enabling both strain recovery and shape retention [19].

As mentioned previously, transformations are induced in a shape memory alloy through heating; this is a cause for concern for the application of shape memory polymers as a means of corrosion protection as they may have differing temperatures to induce transformation. This concern may be alleviated by the limitation that most current shape memory alloys have transition temperatures below 100°C; thus, it is possible for polymers to act as a means of corrosion inhibition [11]. For instance, most DA adducts form at temperatures of around or below 90°C and dissociate at temperatures ranging from 110 to 130°C. The healing process of DA copolymers that contain furan/maleimide occurs at a temperature range of 120 to 150°C as this triggers partial debonding and therefore enhances molecular mobility [39]. Therefore, it is possible for polymers to match the range of temperatures of shape memory alloys and induce healing within that range; the problem then is fine-tuning to match the temperatures that the shape memory effect takes place for both the polymer and the alloy. There are several methods by which to induce this process, one of the easiest being blending polymers as, generally, increasing the T_g of a polymer blend follows the increase in the concentration of the higher- T_g copolymer [38]. Alternatively, the inclusion of spacers into a polymer can affect the T_g as, for example, a polycaprolactone-based polymer material has a melting temperature or T_m of 51.7°C, but the addition of spacers reduces it to 49.6°C. Additionally, the spacer units can act to delay the recrystallization of the polymer or enhance crystallization if in the presence of polymers capable of forming hydrogen-bonded crystalline segments, such as polyurea [19]. Other materials, like carbon nanotubes or graphene nanofillers, can also influence the T_g of a polymer blend as, for example, the addition of 1 wt% graphene to an epoxy ester-siloxane-urea polymer blend can increase the T_g from 95 to 115°C, as shown in the graph in Figures 18(a)–18(c) [17].

When the maxima of the loss tangent, $\tan \delta$, occur for the α transition across a range of temperatures, it can be considered the T_g of the polymeric material, as it relates to the thermal energy needed for changes to occur with the molecules at the microscopic level [56]. Therefore, the addition of graphene may increase the T_g of the material, but it is not entirely straightforward as it appears that the wt% added can affect polymers differently, as may be shown in the

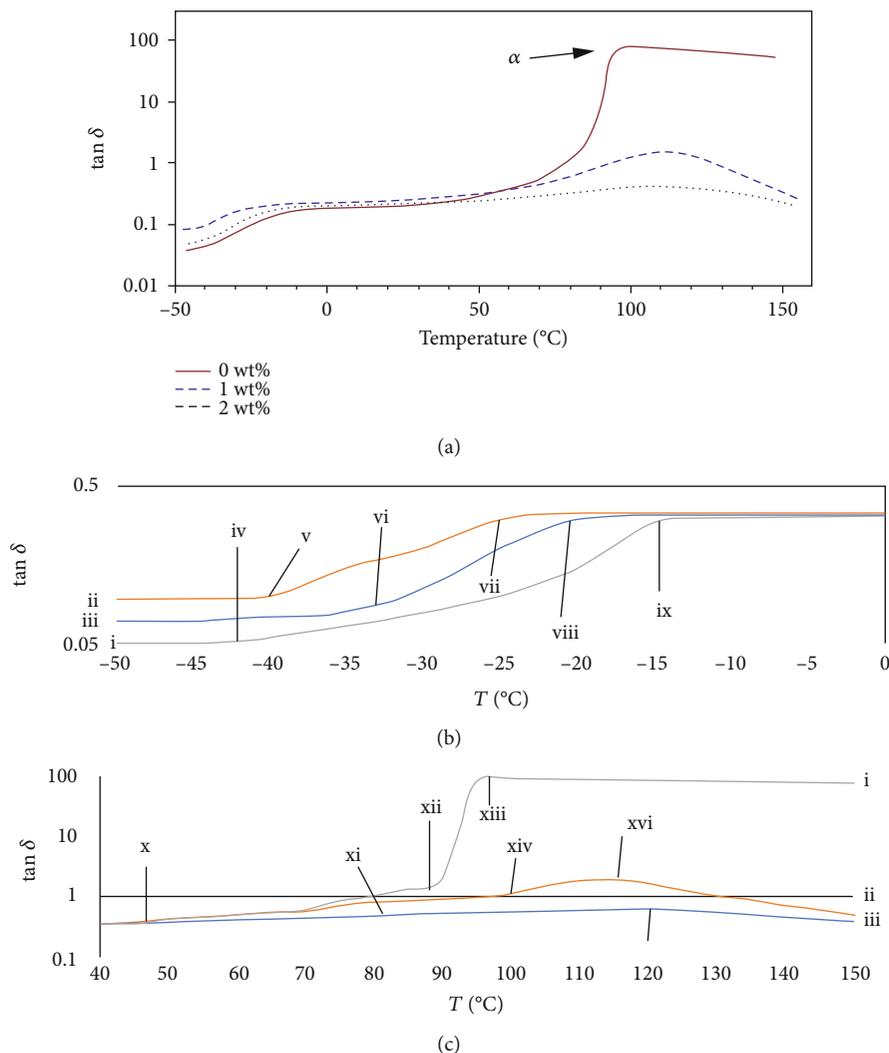


FIGURE 18: (a) The effect the introduction of graphene has upon an epoxy ester-siloxane-urea polymer system. (b) A closer view of the first T_g curve. (c) A closer view of the second T_g curve. For (b) and (c), (i) is 0 wt% graphene added to the polymer system, (ii) is the effect when 1 wt% graphene is added to the polymer system, and (iii) is the effect of 2 wt% graphene being added to the polymer system. (iv), (x), and (xii) are possible T_g points for the polymer system with no graphene added. (x), (v), and (xiv) are possible T_g points for the polymer system with 1 wt% graphene added. (x) and (vi) are possible T_g points for the polymer system with 2 wt% graphene added. (ix) and (xii) are local $\tan \delta$ maxima for the polymer system with no graphene added. (vi) and (xvi) are local $\tan \delta$ maxima for the polymer system with 1 wt% graphene added. (viii) and (xv) are local $\tan \delta$ maxima for the polymer system with 2 wt% graphene added [17].

graphs above. There are major $\tan \delta$ maxima shown; graph (c) shows the secondary $\tan \delta$ maxima and is the one of primary consideration and is relatively straightforward in that an increase in wt% graphene from 0 to 2 wt% results in an increase of T_g from 95 to around 120°C. In contrast, graph (b) shows the first $\tan \delta$ maxima, where it appears that the addition of graphene overall works to also lower the T_g , demonstrated by both 1 and 2 wt% having a lower T_g value; it is also worth noting that increasing the wt% brings the T_g closer to that of the neat polymer [17]; this can be more easily shown in Table 4.

Markets are pushing towards developing high-temperature shape memory alloys capable of transformation temperatures much higher than 100°C. However, any attempts at forming stable materials higher than 100°C are

frustrated by the issue that exposure to large amounts of thermal energy affects the rate-dependent processes that occur within the material and therefore affects the microstructural stability, its resistance to deformation, the recovery, and the environmental resistance [11]. Matching the developments has been the development of high-temperature shape memory polymers; one such example would be that of a self-healing high-temperature polyimide which has an operational temperature of 243°C if polystyrene is incorporated into the polymer [37].

Naturally, there are more novel approaches being developed that could further improve the possible applications for shape memory polymers. It is worth noting that in environments where the material may experience low-temperature conditions, self-healing may not occur or be inadequate

TABLE 4: $\tan \delta$ peak temperature [17].

wt%	0 wt%	1 wt%	2 wt%
Temperature where $\tan \delta$ initiates change for graph (b) in $^{\circ}\text{C}$	-45	-40	-35
Temperature where $\tan \delta$ reaches the peak for graph (b) in $^{\circ}\text{C}$	-15	-25	-20
Temperature where $\tan \delta$ initiates change for graph (c) in $^{\circ}\text{C}$	45	45	45
Temperature where $\tan \delta$ initiates second change for graph (c) in $^{\circ}\text{C}$	90	100	80
Temperature where $\tan \delta$ reaches the peak for graph (c) in $^{\circ}\text{C}$	95	115	120

towards the damage received; thus, in such environments where it may be applied, it would necessitate the use of agents capable of self-heating the material to achieve the desired effects. Therefore, another means of initiating self-healing must be devised; an easy method to accomplish this is with infrared radiation, microwave radiation, or other forms of radiation, depending upon the material chosen, though this may even occur at room temperature [52]. Beneficially, using microwave or infrared radiation to activate the self-healing mechanism can be done remotely and over only a specific area without affecting the surrounding surface, acting almost instantaneously, from the second the light is turned on to the moment it is turned off [57]. Though not quite related to shape memory alloys, microwave or infrared radiation can also serve as a trigger mechanism for shape memory polymer recovery behavior, and because they are energy-efficient, low cost, and quick to trigger recovery behavior, they have immense appeal for other shape memory applications [58]. Shape memory polymers that use infrared or microwave radiation as a means of activation generally include photosensitive fillers, like metal nanoparticles or conjugated polymers, and conductive fillers like graphene or carbon nanotubes into thermally activated shape memory polymers to induce the desired recovery behaviors from the material [2, 52, 57, 58]. For example, multiwalled carbon nanotubes were distributed in a polyurethane matrix which resulted in improving the maximum stretch stress by 120%, the recovery force by 100%, the tensile strength by 24%, and the loss modulus by a third in comparison to plain polyurethane; additionally, it enabled microwaves to activate the shape memory effect in polyurethane [2]. These polymers that activate their self-healing mechanisms via microwave or infrared radiation have uses such as surface coatings, electronic devices, or other biological uses and are particularly noteworthy for potential uses in aerospace applications [2, 52]. Another factor of consideration would be the toughness of typical self-healing polymers, which are worse than covalent polymer networks because they can reversibly form bonds or, in other words, break and reform their polymer networks to achieve their healing ability. If a permanent, covalent network could be introduced to a reversible network, then the mechanical properties could be improved. Typically, doing so forms a hydrogel, but they contain an immense amount of water within that makes them unsuitable as a coating material as they can leach or corrode the material and affect its overall properties. Reversible crosslinking between the covalent and reversible polymer networks is difficult, as the crosslinked materials are immiscible and would normally require cosolvents to mix; attempting to form a “dry” polymer network often results in viscoelastic phase separation. One

notable attempt at forming a “dry” network is a fabrication of randomly branched crosslinked polymers capable of supporting reversible hydrogen bonding in addition to permanent covalent crosslinks, which forces mixing at the molecular level without viscoelastic phase separation or the need for cosolvents. This was formed from a combination of diamines and acrylic acid that form a supramolecular network with either amide-amide connections or amide-carboxyl connections. Small deformations of the hybrid elastomer material only result in the breakage and reformation of hydrogen bonds, and larger deformations result in macrocrazing on a scale of 1 to 1000 μm that preserves the material’s integrity and has a fracture energy of 13,500 J/m^2 , which is comparable to natural rubber. Self-healing can occur at room temperature and, post-recovery, can have a tensile strength comparable to most other elastomers at 4 MPa. Unfortunately, applications that may consider corrosion inhibition for shape memory materials would be limited as the polymer network has a T_g of 4-14 $^{\circ}\text{C}$ and acts as a rubbery elastomer at room temperature and thus would require the modification and the sacrifice of some of its properties to act as a coating [59].

Another development for shape memory composites would be triple-shape memory composites. These polymer composites can change into two other temporary shapes prior to recovering into the primary, permanent shape when their recovery behavior is triggered, thus performing complex recovery motions much better than more traditional shape memory composites. These transition stages can be accomplished through either a series of temperatures in which it will switch forms or a singular temperature value in which the changes shall occur [60]. The step transition behavior within the polymer is what affects the number of temporary positions that the polymer may assume within its shape memory cycle, meaning that the number of transition temperatures within a polymer blend affects the number of shapes it can assume and therefore implies that quadruple-shape or greater shape memory composites could be feasible. The basic approach to accomplishing this is through a polymer with a singular, broad phase of polymer chain transition as the increase of monomer diversity requires even more precise synthesis of the desired polymer material [42]. By combining the shape memory alloys and shape memory polymers to form a shape memory composite, one can form a shape memory composite with three-way motions by 3D printing a shape memory polymer around a shape memory alloy [3]. Notably though, studies about the material indicate that deformation is generally restricted to a range around the linear elastic region and that the stiffness above the transition temperatures is low enough to promote creep under external

loading; also, for certain triple-shape memory polymers, thermal expansion of the composite leads into far higher values of deformation than normal at high temperatures. Developments in correcting the issues of triple-shape memory polymer composites focus on the polymers used in producing the materials, as most triple-shape memory composites are created via polymer blending. Polymer blending is the most critical step as the goal is to create a composite from polymers that are thermally miscible with each other; otherwise, weak or separated interfaces form at the boundaries, thereby weakening the overall properties of the potential composite, and given that, unfortunately, most resins and plastics are incapable of blending with each other thermally, a necessary factor in the development of better triple-shape memory polymer composites will be determining the materials capable of blending with each other effectively [60].

7. Conclusion

Polymers present a potential opportunity in corrosion inhibition, as they are capable of matching or surpassing the more traditional method of including elements such as the hazardous chromium to inhibit corrosion. But as polymers are inherently inert to the environment, they risk a gradual loss of functionality due to microcracking, and therefore, it is desirable to use polymers capable of self-healing such as a polyimide-b-polyurea blend. Additionally, self-healing polymers may be enhanced further by means of nanomaterials or other filler materials, as they can improve the conductivity of the polymer blend or work to improve the response times of shape memory polymers. Future developments regarding shape memory polymers will likely focus on tailoring the polymer blend towards a preferred goal through the addition of certain fillers, such as microcapsules, or selectively initiating the self-healing process or shape memory effect, such as the application of infrared or microwave radiation across a specific area through the inclusion of, for example, carbon nanotubes. These developments should allow for a coating tailored to possible aerospace, particularly deployable structures, or robotics and other applications, such as actuators. In general, areas where a shape memory polymer alone would have insufficient strength or other material properties that a shape memory alloy has while maintaining a cheaper and less toxic corrosion-preventative coating would make the most effective use for a shape memory polymer coating.

Data Availability

The data supporting this Literature Review are available from their corresponding author cited from the journals found in the references section of the review. They are cited at relevant places within the text as references [1–60]. For the figures and tables, the references may be found within the table or below the figure in the text describing the figure. Figures 2, 11, 15, 16, and 18 are used with the permission of the Author.

Conflicts of Interest

The authors declare no conflict of interest that would influence the paper.

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