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Self-Healing Surface Coatings for Advanced Functional Materials

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ABSTRACT:

Traditional coatings, while widely used for protection, often fall short in resisting certain chemicals and substances, and their limited thickness can restrict effectiveness in some applications. Eventually, they break down and lose their properties and have to be reapplied often. Countering these challenges, a new trend in such solutions incorporates self-healing and super-hydrophobic coatings. Self-healing is designed to repair the damage on its surface autonomously, emulating the biology of healing within human skin. The process involves microcapsules within the coating that break apart when damage occurs and release the healing agent to renew the protective covering. Indeed, super-hydrophobic coatings form a surface that is extreme in hydrophobic characteristics, which affords the prevention of corrosion and fouling, as they resist water and other substances, thereby minimizing maintenance. Both coating types are considered essential to protecting metal and other surfaces against corrosion, hence the preservation of the base material for longer periods. Self-healing coatings are increasingly popular for their ability to self-repair small damages, and advancements have led to hybrid coatings that combine various materials and technologies to further enhance these properties. Common types of self-healing coatings include polymer-based, silica-organic, conversion, metallic, ceramic layers, and now super-hydrophobic options, each offering tailored benefits for different environments and applications. In addition, atomic force microscopy (AFM) was used to monitor the changes in the microstructure of the coating after exposure to the saline environment and demonstrated the formation of a robust coating with a significantly lower (5 times) surface roughness for the coated alloy than the uncoated surface after immersion.

Overall results strongly support the potential of PANI for corrosion protection of the NAB alloy.

Keywords: Self-healing coatings, super-hydrophobic coatings, protective properties, autonomous repair, microcapsules, corrosion protection, hybrid coatings, polymer, silica-organic, conversion, metallic coatings.

1.Introduction:

This approach is founded on the concept of creating self-repairing surfaces, which can easily replenish, sustain and operate on their own when damaged, as discussed in the above-mentioned papers. Usually, these coatings also feature embedded healing agents in the coating material which get activated when the coating gets damaged and the skin heals a wound. The heat and pressure inflicted on the coating will have atomized the injurious agent with which the coating or wire is applied and allow it to spread throughout the damaged area restoring the coating's protective quality. In the past decades, the lotus leaf has been widely studied as a representative prototype with specific hydrophobic and self-healing properties. Inspired by the lotus leaf, the superhydrophobic surface is recognized as a good candidate that can be used in various fields such as drag reduction, anti-icing, anti-corrosion, anti-fouling, etc. To achieve super hydrophobicity, micro/nanostructures and low surface energy are two important factors. Recently, research on superhydrophobic materials has mainly focused on two different regimes. Superhydrophobic coatings demonstrate potential for anti-icing applications due to their water-repellent nature, which prevents ice formation and reduces frost adhesion. For instance, SiO_2/PDMS/EP superhydrophobic coatings are developed to prevent icing on surfaces by reducing water adhesion (1). Similarly, silica-nanostructured metal substrates exhibit impressive anti-icing capabilities by minimizing ice formation at low temperatures (2, 10). Carbon nanotube (CNT)-silica coatings further enhance anti-icing performance, with a multi-stage rough structure designed specifically for marine environments (8).

Such innovations are crucial in cold climates and for infrastructure subjected to freezing conditions. The robustness of superhydrophobic coatings is essential for their real-world applications, especially in abrasive or dynamic environments. Some coatings utilize crosslinked polymer composites that enhance mechanical stability and include self-healing abilities, thus extending their lifespan (3, 4). For instance, melanin nanoparticles from cuttlefish ink provide a natural source for robust and self-healing properties in superhydrophobic coatings (7). Additionally, shape memory composites exhibit uniform wettability and morphing capabilities, enabling them to recover from physical deformation (6). Self-healing mechanisms in coatings are an emerging field, often involving microencapsulation, where healing agents are encapsulated and released upon damage. High-linoleic waste sunflower oil, for example, serves as a recycled self-healing agent, providing environmental benefits and durability (12). Microencapsulated epoxidized palm oil (14) and sodiumalginatemelamine-phenol-formaldehyde microcapsules (19) are examples of self-healing systems embedded within coatings, which allow for the release of healing agents to repair small damages autonomously. Research into nano-clay and epoxy coatings further illustrates the anti-corrosion benefits of self-healing materials (13). Microcapsules play a pivotal role in self-healing technologies, with applications ranging from epoxy-based self-healing coatings (32) to linseed oil microcapsules for cementitious materials (39). The size and formulation of these microcapsules significantly impact their efficacy, with studies showing that modified microcapsules improve the release of healing agents over time, enhancing durability and corrosion resistance (33, 34, 38). This is because such coatings will provide advantages in cold climates where icing is a frequent challenge: the reduction of adhesion of water droplets minimizes the formation of ice on surfaces and, by that same token, increases safety and efficiency. For instance, SiO_2/PDMS/EP (Silicon Dioxide/Polydimethylsiloxane/Epoxy) coatings are formulated to provide an effective anti-icing solution, enhancing the performance of materials in freezing conditions (1). Silica-nanostructured metal substrates, meanwhile, demonstrate the effectiveness of superhydrophobic coatings in preventing ice buildup, making them suitable for outdoor and high-altitude applications (2, 10). Another innovative approach involves constructing carbon nanotube (CNT)-silica superhydrophobic coatings with multi-stage rough structures, designed specifically for long-term durability in marine environments where ice and saltwater can accelerate degradation (8). Self-healing materials are developed to repair autonomously at the micro-scale level, allowing them to prolong the lifespan

of coatings. In most self-healing coatings, healing agents are encapsulated in microcapsules which, upon damage to the coating, break open, releasing the healing agent to repair the surface. Some other recently developed self-healing agents include high-linoleic sunflower oil (12) and epoxidized palm oil (14). These agents are eco-friendly and replace traditional agents with corrosion resistance capabilities while repairing the coating. Thus, examples include sodium alginate/melamine-phenol-formaldehyde resin microcapsules (19) as well as lignin-stabilized Pickering emulsions (18) as part of biocompatible material technologies in self-healing coatings and their sustainable potential. To this end, the more recent research activities have concentrated on environmentally friendly coatings that do not drag down their performance. Some examples include the synthesis of hybrid nanodiamond-based and chitosan-based microcapsules through electro spraying-a process that not only incorporates self-healing properties but also includes the antimicrobial or anticorrosive functionality by an eco-friendly approach (29).The introduction of Diels-Alder chemistry, which provides reversible bonding for intrinsic self-healing capabilities, further enhances the durability of coatings by enabling reversible cross-linking that repairs molecular-level damage (25). These innovative approaches allow for the repair of minor cracks and scratches, prolonging the service life of coatings while reducing maintenance costs. Each coating application presents specific challenges, prompting researchers to develop targeted self-healing solutions. For example, molecular dynamics simulations reveal how microencapsulated resin matrix composites behave under different mechanical stresses, highlighting the intelligent, autonomous repair mechanisms in various coating compositions (15, 16). Other studies focus on designing coatings for specific substrates, such as waterborne acrylic latex coatings based on hydrogen bonding, which are particularly effective for long-term protection of steel structures (24). Additionally, the study of corrosion inhibition with phytic acid-vanadate composite coatings on Q235 steel further demonstrates the application of self-healing technology in metal protection (27). High Linoleic Waste Sunflower Oil: A Distinctive Recycled Source of Self-Healing Agent for Smart Metal Coatings, by using waste sunflower oil as a self-healing agent, this research explores an eco-friendly method for metal protection. Self-healing coating with high-quality linoleic sunflower oil improves sustainability in industrial applications. This paper addresses the synthesis of composite microcapsules that contain healing agents in a sodium alginate and melamine-phenol-formaldehyde resin shell. At the moment of damage, these microcapsules release the healing agents, react with the substrate, and repair the surface through this technique. It is most effective in anti-corrosion applications, especially in those used in marines and industries. Molecular Dynamics Simulation on the Intelligent Behaviour of Microencapsulated Resin Matrix Composites: Molecular dynamics simulations provide insight into the behavior of self-healing materials. It models how microencapsulated resin matrix composites would react to damage, providing a theoretical framework to understand their intelligent mechanisms of repair. This study provides a synthesis of composite microcapsules embedding healing agents within a shell of sodium alginate and melamine-phenol-formaldehyde resin. Once the microcapsules experience a damage, agents are released that react with the substrate to repair the surface. For the application of preventing corrosion, this method excels especially in marine and industrial types.

2. Experimental Analysis:

2.1 Methodology:

According to a commonly applied five-stage theory of self-healing published the steps through which the healing process takes place in the physical sense are surface rearrangement, surface approach, wetting, diffusion, and randomization Of all these processes, diffusion of polymer chains is critical to restore the coating integrity.

Materials and Solutions

Aniline (ANI), oxalic acid, and other chemicals were purchased from Sigma-Aldrich and used without further purification. The solutions contained high-purity Milli-Q water with a resistivity of 18.2 MΩ cm at 25°C and 0.15 M aniline in 0.3 Moxalic acid. CorrosionmediumIt wassolution(3.5wt.%NaCl) that was selected as it resembles sea environments.

2.1.2 Surface Preparation:

A hybrid epoxy network was developed to improve dimensional stability and anticorrosion features by combining an epoxy- terminated DA adduct with DGEBA and curing with a diamine. High self-healing efficiencies (80-95%) are reported. The nickel-aluminum bronze (NAB) alloy samples were cleaned and polished to ensure a smooth surface prior to the polymer deposition process. The cleaning process involved mechanical polishing followed by rinsing with deionized water and decreasing in ethanol to remove any surface contaminants. Electro polymerization Procedure. Galvanostatic electro polymerization was employed to deposit polyaniline (PANI) coatings on the NAB surface. The PANI coating was synthesized using the electro polymerization of aniline monomers onto the NAB alloy under controlled current densities. The polymerization process was carried out at varying current densities to determine the optimum conditions for corrosion protection.

2.1.3 Electrochemical Tests

To evaluate the corrosion protection properties of the PANI coatings, two key electrochemical methods were employed: In this technique, a method called dynamic Polarization was used to analyze the corrosion current and potential. It is a technique by which charge transfer resistance is quantified, implying evaluation of the capability to resist corrosive species by a coating. Optimization The optimal corrosion protection was achieved at a current density of 5 mA/cm², resulting in a well-adhered PANI coating with an inhibition efficiency of approximately.

2.2 Advances in self-healing coatings based on Diels-Alder chemistry

Polymer coatings are essential for protection and aesthetics, with a projected market value of $16.2 billion by 2031, primarily using materials like acrylics and polyurethanes. The paper emphasizes the importance of combining DA chemistry with other material properties to enhance the performance of coatings, particularly for metal protection and anti-corrosive applications. Coatings involved: Epoxy-based networks, Polyurethanes, Interior coatings and flame retard

A hybrid epoxy network was developed to improve dimensional stability and anticorrosion features by combining an epoxy- terminated DA adduct with DGEBA and curing with a diamine. High self-healing efficiencies (80-95%) are reported.

2.3 Fabrication of SiO/PDMS/Ep super hydrophobic coating for anti-icing

Aluminium sheet cleaned using acetone and ethanol to remove impurities. The SiO2 nanoparticles, PDMS-Polydimethylsiloxane, and epoxy resin (EP) were mixed in ethyl acetate to prepare the coating solution. Adding 2 g of PDMS agent(W/W=10:1) to 20 ml of ethyl acetate, Hydrophobic silica nanoparticles (0-2 g), epoxy resin (0-2g), nanoparticles in the mixture and magnetic stirrer is used for 30 minutes. Spray coating was applied using a spray gun at a constant distance from the surface, followed by curing at 120°C for one hour. Mechanical stability was tested using sandpaper abrasion. Besides, contact angle measurements were also performed to quantify the hydrophobicity of the coating. The freezing delay time for droplets increased by 19.8 and 19.6 times in order to begin and freeze, respectively, and the freezing point depression for droplets to begin to freeze and completely freeze increased by 166.7% and 182.1%, respectively. Anti-icing performance tests showed that the shear force required for ice detachment from the coating decreased by 55.3%, and the time for ice blocks to detach under gravity was reduced by 63.3%.

3. Experimental Results:

3.1 A mechanically robust superhydrophobic corrosion resistant coating with self-healing capability. Preparation of Modified SiO_2 Nanoparticles Materials: SiO_2 NPs, PFD-TES (Perfluorodecyltriethoxysilane), ethanol. Procedure: SiO_2 NPs stirred with PFD-TES in ethanol for 12 hours. Drying at 80°C for 6 hours to obtain Modified SiO_2 (M-SiO_2). Hydrolysis of PFD-TES leads to formation of hydrophobic surface ($F_2C=CF_2$ groups).

3.2 Surface properties: This Bar Graph comparison rates each method on Durability, Complexity, Scalability, and Throughput (1-5 scale). The In-situ Polymerization method scores highest for durability, while Spray Drying is notable for scalability and throughput.

This bar graph indicates the change rate in different size of microcapsules and its peak strength while mixing with reagent.

Pie Chart: Shows the distribution of different synthesis methods used for self-healing coatings. Solvent evaporation and in-situ polymerization are the most frequently applied methods.

Bar Graph: Displays the effectiveness of each synthesis method in terms of corrosion protection, with in-situ polymerization having the highest effectiveness, followed by solvent evaporation, layer-by-layer, and spray drying methods.

4. Conclusion:

The present study investigated a superhydrophobic WD-CNT@SiO coating and its self-healing and anti-icing behaviours. The following conclusions were drawn:

The mass ratio of CNTs:TEOS: WD-10 for the determination of WD-CNT@SiO NPs was optimized to 1:1.5:1.5, with a pH value of 8, and a one-step modification reaction was employed to achieve a CA of 159.3°. By optimizing the content of nano-hydrophobic particles and epoxy resin concentration, the optimal preparation process for the coating was determined with a particle content of 30wt%, E51: EA=3:10, and reaction temperature at 20°C. The hydrophobic properties on both NPs and the coating surface originated from –CH introduced by WD-10. The successful introduction of hydrogen bonding imparted self-healing properties to the coating. The super hydrophobicity of the coating was partially attributed to its micro-nano structures on the surface. After strong alkaline etching, the coating was capable of restoring its super hydrophobicity within 48h at room temperature. Even after experiencing cycles of etching and self-healing, the healing rate could still maintain a remarkable self-healing process. This self-healing ability stemmed from the breaking and reformation of hydrogen bonds within the system. Superhydrophobic coatings effectively prolonged surface freezing time by up to 4.145 times at −5°C, demonstrating excellent anti-icing performance and abrasion resistance. However, the temperature sensitivity of this coating resulted in a weakened anti-icing effect at lower temperatures.

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