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SMART COATINGS: A REVIEW OF RECENT ADVANCES

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Abstract:

The present work provides a comprehensive discussion on various factors that need to be considered when utilizing smart polymer coatings. The term "smart coating" refers to coatings that possess the ability to sense their environment and respond accordingly to external stimuli. Significant efforts have been made towards the development of multifunctional coatings capable of detecting corrosion, pressure, and temperature. We explored the application and limitations of self-healing principles in polymer coatings.
Furthermore, this chapter delves into the extensive range of current approaches and technologies encompassing antibacterial polymer coatings and the utilization of low molecular weight antibacterial agents. Additionally, an overview is presented regarding a novel approach that incorporates diverse catalytic mechanisms for decontamination, which are employed in self-cleaning coatings.
Lastly, the concentration and spectral distribution of optical sources can be effectively controlled through the implementation of optical components and filtering optical projection systems, which encompass filters, mirrors, lenses, and optical fibers.

Keywords: smart coating , polymers , nanopartical , optical coating , self-healing, reflectance , filters , anti reflect , self cleaning.

1.INTRODUCTION

Over the past few decades, research on coatings has been increasingly important, encompassing not only the application of paint but also the ability to withstand various weathering effects such as rain and UV light. In recent times, both natural and synthetic materials have been utilized to develop high-performance coatings. The focus has shifted towards the development of smart multi-functional coatings that possess sensitivity to wear, pressure, and temperature.

Smart coatings are essential in the realm of medicine for giving implants and on-demand medication release systems long-lasting antibacterial and anti-inflammatory qualities. Moreover, other types of smart coatings have been developed, such as water-repellent, self-cleaning, fatty acid responsive, and self-wiping coatings. These specialized films possess predetermined characteristics that allow them to sense and react to external stimuli, particularly the surrounding environment. The ability of these coatings to self-heal and self-repair makes them well-suited for surface enhancement, material protection, and corrosion prevention.

Responsive coatings, also known as smart coatings, are materials desirable of dynamically modifying their characteristics in response to outside stimuli. This comprises coatings that are superhydrophobic, stimuli-responsive, antibacterial, antifouling, conductive, and self-healing. In terms of corrosion protection, smart coatings serve multiple functions, including sensing, warning, corrosion inhibition, and repair. The functionality of such coatings relies on the elimination of defects that may arise during service.

Researchers such as Michael W. Keller et al. have explored the development of self-healing coating systems for anti-erosion purposes using microcapsule-based materials in combination with elastomeric and epoxy matrices. Their studies demonstrated successful self-healing in the epoxy coating system based on isocyanate chemistry, resulting in significantly reduced mass loss compared to a non-healing control.

M. Huang and J. Yang focused on creating anticorrosion coatings using polyurethane (PU) microcapsules containing hexamethylenediisocyanate (HDI) as the core material. These microcapsules were synthesized through an interfacial polymerization reaction, and the results showed significant corrosion retardancy in the self-healing coatings when subjected to accelerated corrosion processes. This research highlighted the immense potential of the microencapsulation technique, which is catalyst-free and offers a one-part self-healing coating solution for corrosion control(Figure 2).

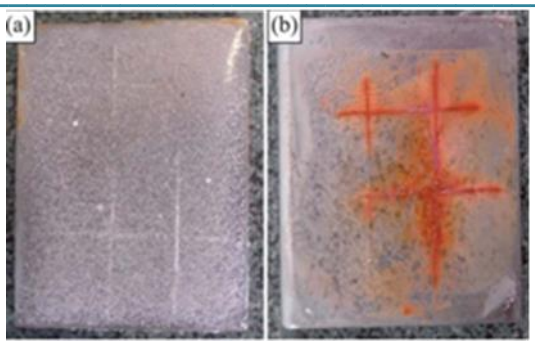

Figure 1: presents fundamental results showcasing the effectiveness of the microencapsulation technique in developing self-healing coatings for corrosion control on steel surfaces [6].

By exploring and advancing the field of smart coatings, researchers aim to enhance the durability, performance, and longevity of coated materials, paving the way for innovative applications and improved protection against corrosion and other environmental factors.

Xiao fan Luo et al. presented a novel shape-memory coating in their research. The coatings were formulated by incorporating electrospun thermoplastic poly (PCL) strands within a shape memory epoxy matrix. When subjected to mechanical damage, the coating exhibited the ability to autonomously repair itself upon heating, triggering two key phenomena. Firstly, the shape memory effect of the matrix facilitated the rejoining of the separated surfaces in close proximity. Secondly, the PCL strands underwent melting and flow, effectively bridging the fracture and restoring the coating's integrity (Figure 2). A lengthy immersion experiment in seawater was used to validate the restored corrosion resistance, and the self-healing coatings showed considerably less corrosion growth in the injured areas [7].

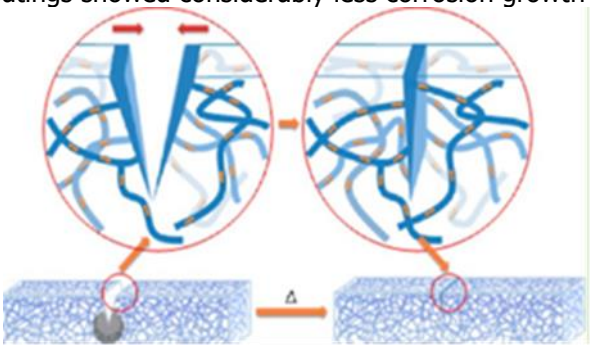

Figure 2 Shape memory assisted self-healing (SMASH) and the coating morphology are shown schematically [7]

In the realm of materials science, smart coatings offer numerous advantages, including enhanced system efficiency by minimizing inspection frequencies, lowering maintenance costs, and reducing equipment downtime. These coatings also contribute to the prolonged lifespan of components and structures made from corrosive materials, thereby reducing the need for replacement in areas affected by corrosion. Moreover, smart coatings have the capability to administer corrosion inhibitors on demand, possess corrosion detection and prevention abilities, and exhibit environmental friendliness. They find wide-ranging applications in various industries, such as healthcare, defense, textiles, transportation, construction, electronics, and more, addressing corrosion, abrasion, and other surface protection requirements. Examples of smart coatings include antimicrobial, antifouling, conductive, self-healing, and superhydrophobic systems [1].

2. Self-healing coating

Elastomers and plastics are commonly employed materials in the field of self-healing materials. However, it is important to note that self-healing properties can be incorporated into various material categories, including metals, ceramics, and cementitious materials. Exposure to harsh environments can lead to degradation of polymeric components, with microcracking being a critical deterioration mode that can result in catastrophic material failure and significantly reduce the lifespan of structures. To address this issue, various healing processes have been developed, involving the introduction of a repair agent contained within microscopic vessels for necessary material repair. A substance must undergo the healing process on its own, without the assistance of outside humans, in order for it to be called completely self-healing. Self-healing polymers can start the healing processes when exposed to outside stimuli like light or temperature changes [2]. Self-healing polymers can be divided into two groups: intrinsic and extrinsic, depending on the healing mechanism [3]. Three steps are normally required for polymers to mend themselves on their own. First, practically immediately after damage is sustained, actuation takes place. Subsequently, materials are transported to the affected region, also happening rapidly. The chemical repair stage, which is the third step, is contingent upon the particular healing mechanism utilized, such as polymerization, entanglement, or reversible cross-linking. The specific approach employed during this stage may differ, depending on the chosen healing mechanism, to facilitate the repair process. Three different categories of self-healing materials can be made: intrinsic, vascular, and capsule-based [8].

2.1 Intrinsic polymer-based systems

The intrinsic approach uses materials with a built-in capacity to independently reestablish their integrity. The healing process in intrinsic healing processes frequently needs an outside stimulus, such as a thermo-mechanical, electrical, or photo-stimulus. There are five basic inherent self-healing methods that can be distinguished. The Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions are the most well-known reversible reactions used in the first technique [9]. Adding moldable thermoplastic additives to thermoset matrices is another approach that promotes healing by allowing the thermoplastic additives to reflow into cracks and provide mechanical interlocking [7]. The third and fourth solutions utilize interlockings of polymers based on ionomers or dynamic supramolecular linkages.

In the context of the intrinsic approach, materials possess an inherent capability to autonomously restore their structural integrity. However, intrinsic healing methods often require an external stimulus, such as thermal, mechanical, electrical, or photo-induced stimulation, to initiate the healing process. Five fundamental intrinsic self-healing techniques can be identified. Among these, the widely employed Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions serve as the predominant reaction scheme for the first strategy, which relies on reversible chemical reactions [9]. Adding moldable thermoplastic additives to thermoset matrices is another strategy that promotes healing by allowing the thermoplastic additives to reflow into cracks and provide mechanical interlocking. Temperature variations start this process, making it easier for the thermoplastic additives to flow again and for interlocks to develop [10,11]. The third and fourth techniques make use of dynamic supramolecular bond-based polymer interlockings [12].

Erika D. Rodriguez et al. introduced a novel self-healing polymeric system that can simultaneously close and reconnect cracks using a simple thermal trigger. This system involves a blend of cross-linked poly(ε-caprolactone) network (n-PCL) with linear poly(ε-caprolactone) (l-PCL) [13]. They achieved remarkable healing performance in films through the SMASH (Simultaneous Mechanical Activation and Self-Healing) mechanism, with nearly complete healing observed for l-PCL contents exceeding 25 wt% [14].

2.2 Extrinsic polymer-based systems

In external systems, two common approaches are utilized: capsule-based polymers and vascular networks. In capsule-based polymers (Figure 3a), healing agents are encapsulated within microcapsules that are separate from the surrounding polymer. These capsules rupture upon damage, releasing the healing agents, which then interact and restore the material's functionality. However, since the local healing agent is depleted after release, only a single local healing event can occur [15].

In vascular self-healing systems (Figure 3b), the healing agent is contained within capillaries or hollow channels within the polymer matrix. These channels can be in one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) forms. When damage occurs, the initial delivery of the healing agent takes place, and the network can be refilled either from an external source or from an undamaged but connected region of the vasculature [16,17,18].

However, these complex interconnected networks have their drawbacks. For instance, when a slowly reacting healing agent is used, a single event of damage with a crack opening to the outside environment can result in excessive bleeding and the consumption of a large quantity of healing agents. Additionally, an early reaction may lead to irreversible blockage of the supply channels, rendering the concept ineffective. In both capsule-based and vascular systems, if a second damage event occurs in a location not close to the initial damage site, it cannot be repaired as the healing agent is no longer present. To overcome these challenges, inspiration can be drawn from the non-continuous tubular compartments found in plant structures, which allow for local healing events [18].

B. Soo et al. A chemically stable self-healing material system was developed by utilizing tin-catalyzed polycondensation of phase-separated droplets comprising hydroxy end-functionalized polydimethylsiloxane (HOPDMS) and poly diethoxysiloxane (PDEs). Within this system, di-n-dibutyltindilaurate (DBTL) served as the catalyst and was encapsulated in polyurethane microcapsules dispersed within a vinyl ester matrix [19]. Rongguo Wang et al. conducted an investigation on the synthesis of microcapsules through in-situ polymerization. They observed that the distribution of microcapsules and the presence of a latent curing agent significantly influenced the healing efficiency. Through optimization, it was determined that the optimal weight ratio of microcapsules to curing agent 2MZ-AZINE was 15 wt.% and 2 wt.%, respectively, resulting in an approximate healing efficiency of 83% [20].

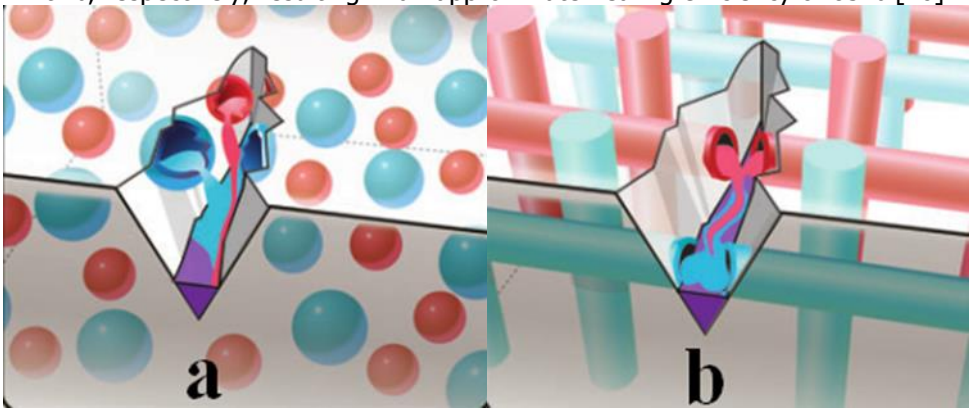

Figure 3 Extrinsic approaches to self-healing (a) capsule-based, (b) vascular [17].

3. Bioactive Coatings

Smart polymer synthesis improvements have created new potential for their successful use in medicine, notably in the area of drug administration. The potential for many synthetic polymers to act as smart carriers and provide controlled therapeutic release is high [2]. Within the medical field, smart coatings have emerged as crucial components, offering long-lasting antimicrobial and anti-inflammatory properties to medical devices like implants and drug delivery systems. These coatings contribute to the prevention of infections and the reduction of inflammation in medical settings. The applications of antimicrobial and anti-inflammatory coatings extend to diverse areas, including drug-eluting medical devices, military garments, household appliances, and hospital equipment. By integrating these specialized coatings, medical advancements and improved patient outcomes can be achieved. Antimicrobial coatings are commonly developed by integrating biocidal agents into the formulation or polymer structure. This integration leads to the inhibition of microbial activity, effectively deactivating microorganisms and preventing their normal functioning. Silver and its derivatives are widely used in applications such as drug-eluting medical tools, military attire, and hospital equipment [1].

Antibacterial effects can be categorized into five technical terms. The first term refers to microbiocidal effects, where bacteria are effectively killed. However, this concept does not specify a clear target or limited range. In the realm of materials science, the term "sterilization" holds substantial importance as it encompasses not only the eradication but also the removal of bacteria or viruses from a given target. This process is applicable irrespective of the level of harm caused by the microorganisms. While achieving a completely bacteria-free environment may be challenging, the Sterility Assurance Level (SAL) is commonly employed to assess the extent of sterilization. Sterilization is universally defined as a state where the SAL is less than 10-6, indicating an extremely low probability of viable microorganisms remaining. On the other hand, the term "disinfection" refers to a process that aims to reduce the number of pathogenic bacteria to a harmless level, without necessarily achieving complete sterilization. This can be accomplished through microbiocidal effects, similar to the first concept. However, disinfection can also be achieved by eliminating pathogenicity without necessarily killing the bacteria. The fourth technical term involves reducing the bacterial count without specifying the targets or extent. The objective is to determine how many bacteria can be eliminated. The fifth term refers to an action that inhibits bacterial growth on the target object. Typically, reduction of bacteria on the order of 102 is required [21].

In the case of antibacterial coatings, long-term effectiveness is a critical requirement for practical applications where these coatings are applied to contact surfaces. These materials can incorporate specific drugs for therapeutic purposes and release the treatment in response to stimuli. Smart polymeric materials with this stimulus-responsive capability can respond to external and/or endogenous stimuli like pH, chemical triggers, temperature, ultrasonic power, light, magnetic fields, redox gradients, and a wide range of other potential stimuli to release pharmaceuticals [2].

Yanan Wang et al. presented a viable approach for fabricating natural polymer-based nanocomposite antibacterial coatings using in-situ polymerization of flexible hybrid caprolactam-casein/ZnO nanocomposite (CCZ). The resulting films exhibited satisfactory mechanical properties and excellent antibacterial activity against Staphylococcus aureus and Escherichia coli, making them suitable for various applications in industries such as textiles, leather, packaging, and paper [22].

Mitra S. Ganewatta et al. Surface immobilization was accomplished through the utilization of two robust and efficient chemical processes: surface-initiated atom transfer radical polymerization and azide-alkyne 1,3-dipolar cycloaddition click reaction. These techniques proved effective in combating both Gram-positive Staphylococcus aureus and Gram-negative Escherichia coli, demonstrating potent antibacterial and antibiofilm properties. Biocompatibility assessment involved hemolysis tests and the growth of human skin fibroblasts on the modified surfaces, allowing for the evaluation of the materials' compatibility with biological systems. The researchers came to the conclusion that sustainable biomass integration can be successfully accomplished to prevent bacterial infections and biofilm development in biomedical applications by grafting quaternary ammonium-decorated abietic acid complexes and polymers onto surfaces [23].

4. Self-Cleaning Coatings

Nonstick and self-cleaning surface coatings have gained significant interest in various application areas due to their ability to enhance the resistance of coated substrates against water and particulate dust. Dust contaminants can have severe health impacts on humans and other mammals [25]. Minimizing dust accumulation is crucial for the proper functioning of tools used in both manned and unmanned missions, as dust accumulation on vehicles and sensors can impede movement and data collection [26]. To address this challenge, superhydrophobic coating substrates have emerged as promising candidates for self-cleaning coatings, owing to their nonstick properties and ease of dust removal [27]. Various commercial products, including protective gloves, masks, and lenses, are utilized to safeguard health against harmful environmental toxins originating from dust particles [25, 2]. Numerous studies have focused on the development of superhydrophobic surfaces, drawing inspiration from the behavior of lotus leaves. The excessive superhydrophobicity is achieved through hierarchical micro/nanostructures and the use of low surface-energy wax materials, where both surface roughness and low surface energy play crucial roles (Figure 4).

Figure 4 Water droplets following a rain shower on the surface of a cabbage (Brassica oleracea) leaf as an illustration of how water droplets moisten superhydrophobic surfaces. The droplets fled once the leaf slightly tipped[28].

Due to their outstanding qualities, superhydrophobic surfaces have attracted a lot of attention in a variety of industries, including optics, metals, electronics, and automotive applications. By forming stable air pockets within their uneven interstices and having a low surface energy structure, these surfaces reach a non-wetting condition. In order to avoid soaking and to increase water-repellency, this mixture creates a barrier between a water droplet and the solid surface. These superhydrophobic surfaces are highly sought-after for a variety of industrial applications because to their abundance of benefits, including greater optical clarity, increased corrosion resistance, less ice formation, and self-cleaning characteristics [29, 28, 30].Nakajima et al. and Yamauchi et al. demonstrated that the addition of a small percentage of TiO2 photocatalyst effectively imparts self-cleaning properties to superhydrophobic films, allowing them to maintain high contact angles even after prolonged exposure to outdoor environments [31].

S. A. Brewer and C. Willis DERA On non-porous and extended polytetrafluoroethylene (PTFE) substrates, oxygen plasma was used to induce micro-roughening to increase water repellency. Decane, on the other hand, tends to wick into the substrate when it comes into contact with porous PTFE due to capillary action. This was avoided by adding a low surface energy plasma polymer layer to the top of the micro-roughened PTFE surface, which increased its ability to resist liquids. Due to the higher contact angle at the liquid-solid interface, decane was no longer able to penetrate into the enlarged PTFE substrate's subsurface [32].

Hyun Yoon et al. an alumina precursor that had been coated with organosilane was successfully electrosprayed to create a highly transparent self-cleaning superhydrophobic surface. The resulting coating exhibited both superhydrophobic properties and good transparency in the visible range. The researchers observed that increasing the spraying time led to an increase in the contact angle of water, indicating enhanced water repellency. However, they also noted that longer spraying times resulted in reduced transparency of the coatings. A water droplet on the coated surface exhibited an ideal spherical shape with a contact angle of 162° and easily rolled off at an extremely low sliding angle of less than 3°. These transparent, superhydrophobic, self-cleaning coatings have potential uses in the optical sector [29].

Panagiotis N. Manoudis et al. proposed a cost-effective method for creating superhydrophobic surfaces using composite films composed of poly(methyl methacrylate) (PMMA) and Rhodorsil (a commercial siloxane) mixed with SiO2 nanoparticles. The resulting hierarchical structure displayed water-repellent properties when applied to a glass substrate. The researchers demonstrated that the concentration of nanoparticles played a significant role in the hydrophobic behavior of the PMMA-SiO2 and siloxane-SiO2 surfaces. They concluded that the static contact angles (θs) rapidly increased with increasing particle concentration, reaching maximum values. This highlights the influence of particle concentration on the hydrophobic characteristics of the composite films [33].

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