Advancements in Marine Antifouling Hydrogels: A Sustainable Approach towards Ocean Conservation

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Keywords: Marine biofouling, antifouling coatings, hydrogels, polymers

Abstract: The unabated growth of marine biofouling on submerged structures has been a subject of concern for the maritime industry, increasing maintenance costs and creating ecological imbalances. Traditional antifouling methods are associated with toxic biocide release into marine life. In response, environmental concerns have spurred a surge in the search for friendly alternatives, where hydrogels have emerged as promising candidates. This review deals with the current status of marine antifouling hydrogels, their harmless nature, and their mechanical properties. The most recent research is discussed in this review, including double-network hydrogels, zwitterionic hydrogels, and self-healing hydrogels. Potential applications in the prevention of marine biofouling are presented. Attention is brought to complex problems of material design and durability that require interdisciplinary research.

1. Introduction

Biofouling can be defined as a natural accumulation of all kinds of organisms on wetted or immersed surfaces in marine environments. It is an important phenomenon that has great economic, ecological, and operational consequences. Biofouling encompasses a complex community of microorganisms comprising bacteria, algae, fungi, and larger organisms such as barnacles, mussels, and seaweeds. Such attachment and growth may result in a number of adverse effects:

1) Increased Hydrodynamic Drag: Biofouling of a marine structure immediately results in increased hydrodynamic drag, which reduces the efficiency of ships and submerged structures. For vessels, increased drag means higher fuel consumption and, consequently, higher operating cost.

2) Material Corrosion and Degradation: Biofilm microorganisms excrete acids and other metabolic products, thereby causing corrosion in metals and organic materials that result in reducing the structural life of marine structures.

3) Impact on Marine Ecosystems: The presence of invasive species changes the balance in marine ecosystems and is often responsible for the decline in native species, along with changes in the food web dynamics.

More traditional antifouling strategies have involved the application of toxic biocides and copper-based paints, approaches which prevent or control biofouling by either killing the organisms outright or inhibiting the growth of others[1]. These, however, have shown to leach harmful substances into the marine environment, posing risks to non-target organisms and contributing to the broader problem of marine pollution. Toxic substances released into the environment from traditional antifouling coatings have been a cause for major environmental concern. These substances may bioaccumulate in the food chain, affecting health problems in the marine life, possibly even entering the human food chain.

With these environmental and economic costs of biofouling, the need for eco-friendly antifouling strategies becomes critical. This has thus enhanced attention to research and development regarding sustainable materials and technologies that can prevent biofouling without harm to the marine environment.

  DOI: 10.25236/iwmecs.2024.003

2. Hydrogel Classification and Properties

2.1. Classification

Hydrogels are the three-dimensional polymeric materials of network structure and capable of absorbing a considerable amount of water without dissolution. According to the different classification basis, there exist several kinds of hydrogels[2].

2.1.1. Classification according to Bonding/Crosslinking Method

1) Physical Hydrogels: They are those that are formed through physical forces such as electrostatic interactions, hydrogen bonds, and chain entanglement. They are nonpermanent and can revert to the solution state when heated, for that reason sometimes they are also called pseudogels or thermoreversible gels. Normally, many of the naturally occurring polymers like k-carrageenan and agar remain in a stable gel state at room temperature; however, in the case of synthetic polymers, the PVA exhibits stable hydrogels below 60° C following freeze-thaw cycling[3].

2) Chemical Hydrogels: They are the result of covalent cross-linking and hence a permanent three-dimensional network was formed; they are also called true gels.

2.1.2. Classification Based on Synthetic Materials

1) Natural Polymer Hydrogels: the name given to naturally occurring viscous materials such as clays and muds. They have excellent biocompatibility and stability in an ecological environment.

2) Synthetic Polymer Hydrogels: polymers produced by chemical synthesis. They offer excellent mechanical performance and stability.

3) Hybrid Hydrogels of Natural and Synthetic Polymers: By using the appropriate crosslinking methods, hybrid hydrogels of natural and synthetic polymers combine all the advantages of natural and synthetic polymers.

2.1.3. Classification Based on the Size and Shape of Hydrogels

1) Macrogels: Can vary from cylindrical, spherical, sheet, fiber, sponge-like, etc.

2) Microscopic (Microsphere) Gels: It is named according to the small size of hydrogels in micrometer-sized or nanometer-sized dimensions, which usually finds its application in tissue engineering and drug delivery systems[4].

2.1.4. Classification Based on Degradation Performance

1) Biodegradable Hydrogels: The three-dimensional structure in the natural environment would be degraded with the help of a factor such as microorganisms and enzymes into small molecules. Currently, it finds broad applications in biomedicine and also in tissue engineering.

2) Non-biodegradable Hydrogels: These are insensitive to environmental factors such that for a long period of time, they would maintain their structural and physicochemical stability and hence are used in cosmetic surgery or some special fields in industries.

2.1.5. Classification Based on Response to External Stimuli

1) Ordinary Hydrogels: In different environmental conditions, these are characterized by a stability in structure and physicochemical properties.

2) Environmentally Responsive Hydrogels: Due to external actions or stimuli-transmitted such as temperature, pH, light, electric current, pressure, among others, changes in their physical and chemical properties take place. These hydrogels form part of the sensors and drug delivery systems with great relevance[5].

2.2. Properties

1) Hydrophilicity: There are many hydrophilic groups in hydrogels, such as hydroxyl, carboxyl, and amine groups, which can form hydrogen bonding or other interactive forces with water molecules. Thus, hydrogels are of good water absorption and moisturizing properties. The water content usually varies from 1% to 99%[6].

2) Mechanical Strength: The mechanical properties of hydrogels could be tuned by crosslinking density and chemical nature of polymer chains. Hydrogels with high crosslinking density are normally mechanically stronger, more elastic, and suitable for applications that involve resistance against specific outer forces.

3) Biocompatibility: Most of the hydrogel materials bear good biocompatibility and maintain stability inside the body without harming the surrounding tissues. Thus, they find wide applications in biomedical fields such as drug delivery, tissue engineering, and biosensors.

4) Biodegradability: Some hydrogels degrade through hydrolytic cleavage or enzymatic cleavage inside the body or the environment and have very important biomedical applications. The product of degradation is mostly nontoxic and easily excretable.

5) Stimuli Responsiveness: Hydrogels can respond to external stimuli like pH, temperature, ionic strength, light, and electric fields by changing their volume or shape. Thus, hydrogels seem very promising in sensor, drug delivery system, and smart material applications.

In a word, due to its special classification and various properties, hydrogel has wide application prospects in many aspects. In the meanwhile, with continuous development of science and technology, preparation and application technologies of hydrogels will constantly improve and innovate.

3. Adhesion Strategies for Hydrogel Coatings on Substrates

Adhesion of the hydrogel coating to the substrates is of paramount importance to make sure of the coating's performance and extending its service life. The following are typical strategies for improving adhesion:

3.1. Surface Treatment

·Cleaning: Oil, dust, and other impurities should be removed from the substrate surface in order to enhance the adhesion of the coating.

·Roughening: The roughness of the substrate surface is increased-for example, by sandblast treatment, laser treatment, or chemical etching-which would increase the adhesion area.

·Activation: The second method involves the use of appropriate surface activators like coupling agents or primers that could enhance chemical bonding between hydrogel and substrate.

3.2. Nanocomposite Materials

Nano Fillers: Addition of nano fillers to the hydrogel such as nanoclay or nano-oxides to improve mechanical properties and enhance adhesion of the coating.

3.3. Self-Healing

Self-Healing Mechanism: Leverage the self-healing ability of hydrogels in renewing adhesion automatically upon damage to the coating.

These strategies have been adopted in practice to greatly improve the adhesion performance of hydrogel coatings on various substrates, further expanding their application potentials in such fields as marine antifouling, biomedicine, and industrial protection.

4. Research Progress in Synthetic Hydrogel Coatings

The studies on synthetic hydrogel coatings are aimed at developing eco-friendly materials that can prevent the settlement of marine organisms on submerged structures. Materials have to be developed with no toxicity and long life with efficiency in different sea environments[7].

4.1. Double Network Hydrogels

Otherwise known as DN gels, double network hydrogels are a special class of hydrogel material that shows outstanding mechanical strength and toughness. The two crosslinked polymer networks in such gels serve their functions cooperatively: one provides a kind of rigidity, while the other

imparts flexibility.

1) Structure and Formation: DN gels are typically prepared by simultaneous or sequential cross-linking of two different polymer networks. Usually, the first network provides a strong, brittle structure, while the second network gives rise to a tough, energy dissipative one. The two networks can be based on distinct monomers, which can be both chemically and/or physically crosslinked.

2) Mechanical Properties: Due to the strong synergistic interaction between the two networks, DN gels with high tensile strength and fracture resistance were obtained. They have good energy dissipation and can bear considerable stress without breaking. Because the gels can recover after big deformation, there is a property called excellent elasticity.

3) Self-Healing Ability: As touched on briefly in the introductory remarks, one intriguing property of DN gels is the ability of self-healing after destruction. This normally involves the breakage and formation of bonds within the network in order for these to regain their strength. The self-healing property emerges due to the reversibility from some of the crosslinks or even the presence of dynamic covalent bonds.

4.2. Zwitterionic Hydrogels

Zwitterionic hydrogels present a special class of polymeric networks that bear both cationic and anionic groups within their structure. These hydrogels have been at the focus of much attention because they are highly biocompatible and exhibit antifouling properties. In this paper, the in-depth look into zwitterionic hydrogels is going to be based on:

1) Structure and Properties: Zwitterionic hydrogels are composed of zwitterionic monomers, which, upon polymerization, form a neutrally charged and quite stable polymer network. The nature of the zwitterions imparts a more hydrophilic surface when compared to conventional neutral or charged polymers. These hydrogels have the main characteristics of high water content, good swelling behavior, and excellent biocompatibility.

2) Antifouling Mechanism: The zwitterionic character reduces the nonspecific protein adsorption and cell adhesion, which is the primary cause for biofouling. Hydrophilic surface provided by these hydrogels reduced interaction with the hydrophobic fouling organisms. They maintain their antifouling properties over an extended period without the need of leaching biocides.

4.3. Self-Healing Hydrogels

Self-healing hydrogels are a class of smart material that can self-repair in case of damage. Features such as these make self-healing hydrogels very useful in many applications where longevity and durability are of essence. Following is a general overview of the self-healing hydrogels:

1) Structure and Properties: Self-healing hydrogels are those that have a polymer network which, once broken under specific conditions of pH, temperature, or other stimuli, can reform. Many of them include reversible linkages within their network, such as hydrogen bonds, ionic bonds, or covalent bonds like the disulfide linkages that enable the network to break and reform. These hydrogels have tunable mechanical properties with very high water content and excellent biocompatibility[8].

2) Self-Healing Mechanism: The rebonding of dynamic bonds within the polymer matrix generally characterizes self-healing upon material failure. While a number of hydrogels rely on a stimulus-responsive mechanism for healing-perhaps due to some external action such as light, heat, or chemical stimulation-others could intrinsically be self-healing because of the nature of the polymer network that can reform bonds with no external action whatsoever[9].

Hydrogels with self-healing ability offer a promising avenue toward sustainable and durable materials. Recoverability from damage to health care in engineering, without human involvement, might seriously revolutionize many of their applications. Further research into self-healing materials will be the means to develop more sophistication and versatility of these smart materials, pushing forward their scope of service and benefits[10].

4.4. PEG-based Hydrogels

Further research into self-healing materials will be the means to develop more sophistication and versatility of these smart materials, pushing forward their scope of service and benefits. As a kind of anti-protein material, PEG and its oligomers have been developed in many products. In the main chain structure, there is a high polarity of oxygen atoms, hence it endows PEG with high hydrophilicity. Nowadays, the major steps in the preparation of hydrogels are basically modifications of the PEG hydroxyl terminal and the introduction of some controllable chemical crosslinking functional groups [11].

Zhang et al. [12] prepared core-shell polystyrene microspheres by the styrene soap-free emulsion polymerization using styrene, hydroxyethyl methacrylate, and polyethylene glycol methyl ether methacrylate as the monomers and then prepared PEG composite hydrogels with PEG hydrogels used as the matrix. Accordingly, adding an appropriate amount of polystyrene microspheres can improve the mechanical properties of PEG composite hydrogel. While the mass fraction of polystyrene microspheres was 14.2%, the maximum compressive stress of composite hydrogel reached 5.83 MPa, and the relative compression ratio was up to 161.96% and the compression elastic modulus as high as 73.7 kPa.

Park et al. [13] prepared a PEG hydrogel using polyethylene glycol dimethacrylate as a crosslinking agent, glycidyl methacrylate as a monomer and 2, 2-dimethoxy-2-phenylacetophenone as a photoinitiator. Then, the authors modified commercial silica nanoparticles (G-SiNPs) with 3-glycidoxypropyl trimethoxysilane containing epoxy groups. Modified G-SiNPs were incorporated into the PEG hydrogel. The modified silicon nanoparticles improved the surface mechanical properties of the hydrogel coating through the reduction in its weakness regarding low hardness and vulnerability to destruction.

5. Research Progress in Natural Hydrogel Coatings

5.1. Cellulose-based Hydrogel

Cellulose is an abundant, green, and biodegradable polymer. All these features make cellulose an ideal raw material for the synthesis of biohydrogels or soft materials. Cellulose is highly enriched with hydroxyl groups and has to be chemically modified to obtain cellulose hydrogel [14].

Palantöken et al. [15] synthesized, by using glycine, a new type of natural hydrogel coating that exhibited high efficiency and stability showing good performance in an alkaline medium. The following is the synthesis: The cellulose was first dissolved in a NaOH solution using an ice bath at temperatures of 0-4°C; then, an alkaline glycine solution was added, mixed well until viscous. The solution with viscous properties was then poured into the mold, kept for 12 h, and neutralized afterward with acetic acid. Finally, freezing at a temperature of -23°C takes place to obtain a stable cellulose hydrogel coating.

5.2. Alginate Hydrogel

Polysaccharides are one class of polymers with different biological functions and have a high affinity for water. Among all the naturally occurring polysaccharides, one is alginate, whereas sodium alginate is a by-product extracted after extracting iodine and mannitol from brown sea weed like kelp or sargassum. When sodium alginate meets calcium ions, instantaneous ion exchange takes place. Then, with much potential, it forms a hydrogel in marine anti-fouling applications .

Bauer et al. [16] modified the covalently coupled alginate and hyaluronic acid with hydrophobic fluorinated amine to obtain an amphiphilic alginate hydrogel coating. In general, chelation of divalentions reduces their anti-fouling effect in seawater. In comparison, the absorption of Ca2+ ions was much lower for the fluorinated alginate hydrogel coating. Tests conducted verified that this coating exhibited good stability in seawater. The single-species settlement tests using bacteria, diatoms, and larval barnacles were performed; results showed that the modified alginate hydrogel coating was capable of reducing both settlement density and adhesive strength of the test species.

Liu et al. [17] added cellulose fibers to a calcium alginate hydrogel and then encapsulated Irgarol, a hydrophobic and phytotoxic anti-fouling agent that inhibits the function of photosystem II in algae and prevents the growth of aquatic plant species. The experimental results showed that cellulose fibers improve the mechanical strength of hydrophilic calcium alginate hydrogel and the hydrogel beads release the biocide, showing good anti-fouling effects.

6. Conclusion

Thus, the search for sustainable solutions in marine antifouling strategies is emphasized. Considerable progress has been made recently in developing marine antifouling hydrogels, and the resulting materials have emerged as a nontoxic and environmentally friendly alternative method of preventing marine biofouling. This review focused on the ability of hydrogels-most specifically, double-network hydrogels, zwitterionic hydrogels, and self-healing hydrogels-to offer new opportunities in changing marine antifouling practices. In their continuous research and development phases, these materials can revolutionize marine industries towards healthy environments and economic efficiency. The way forward now is further innovation, thorough testing, and an unswerving commitment to sustainability.

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