Functional Protective Sustainable Coatings

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To meet modern society's requirements for sustainability and environmental protection, innovative and smart surface coatings are continually being developed to improve or impart surface functional qualities and protective features. These needs regard numerous different sectors, such as cultural heritage, building, naval, automotive, environmental remediation and textiles. In this regard, researchers and nanotechnology are therefore mostly devoted to the development of new and smart nanostructured finishings and coatings featuring different implemented properties, such as anti-vegetative or antibacterial, hydrophobic, anti-stain, fire retardant, controlled release of drugs, detection of molecules and mechanical resistance.

Keywords: eco-friendly finishings ; sustainability ; antifouling ; protective ; coatings

1. Anticorrosive Hybrid Nanostructured Coatings Doped with Green Corrosion Inhibitors

Every structure that is subjected to corrosion agents must be protected in order to withstand corrosive forces for the duration of the structure's required life. Corrosion can be decreased or prevented by using specialized procedures that delay or inhibit anodic or cathodic reactions, or by eliminating conductivity between anodic and cathodic sites. Corrosion is the collective term for all chemical and electrochemical processes that return metals to their lower Gibbs free energy states. This phenomenon is largely caused by electrochemical processes, in which electrons move between two half-cell reactions [1][2][3].

Anodic or metal oxidation processes are one of the half-cell reactions that generate electrons, as shown in Equation (1), in which M represents the metal.

$$M^0 \rightarrow M^{n+} + ne^- \quad (1)$$

The produced electrons are involved in the cathodic or reduction reaction, which is the other half of the cell reaction. The pH and the accessibility of different components affect cathodic reactions. Under acidic circumstances, hydrogen and oxygen reduction are the most frequent cathodic reactions, as shown in subsequent Equations (2) and (3):

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (3)$$

Additionally, water or oxygen reduction processes occur in neutral or alkaline conditions, as shown in the following Equations (4) and (5).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (5)$$

The procedure for protecting the metal surface often involves two (pre)treatments that are performed in sequence, namely the preparation pretreatment of the target surface, which removes any impurities or remnants of earlier corrosive processes from the metal or substrate to be protected, and the final application of the protective top-coat [4][5]. Actual anticorrosive protective solutions require the employment of hazardous phosphating and chromating procedures, which, despite their efficacy, have considerable and negative environmental and energy consequences [6]. In particular, toxic phosphates and chromium compounds, in fact, lead to the production of large amounts of hazardous sludge that must be disposed. In this regard, new developments in the field of environmentally friendly polymer-based anticorrosive coatings of parts or specific objects/substrates have been studied and described in several research products.

These cutting-edge and environmentally friendly materials/technologies, can be divided into five groups: hyperbranched/hybrid polymer technologies, bio-based materials, green corrosion inhibitors, and (super)hydrophobic coatings.

The use of natural additives to enhance the properties of an anticorrosive coating is a new finding that has fascinated researchers as well as product end-users [7].

Carbon-based nanomaterials, such as graphene or graphene oxide, are of great interest due to their powerful anticorrosion feature and barrier properties, which prevent corrosive substances from entering and supplying an electron flow channel between the sacrificial anode and the substrate [8][9].

Moreover, hyperbranched polymers have most recently drawn a lot of interest in the field of polymer research due to their remarkable qualities, including high cross-linking density, superior solubility and high reactivity, thus leading to the further production of low solvent chemical-resistant and long-life coatings [10][11][12].

The application of plant extracts as environmentally benign corrosion inhibitors, such as polyphenols, has also attracted the scientific community's interest [13]. Its inhibitory impact is due to a unique antioxidant property that causes complexes to form on the metal surface, promoting the formation of a strong barrier that protects the surface from external agents. Various studies have proved the use of pure tannins and other polyphenols as corrosion inhibitors [14][15][16].

To combine the protective feature of graphene oxide and reduce its agglomeration due to π–π stacking, which makes it hard to disperse uniformly in a polymer matrix, different covalent and/or noncovalent functionalization approaches can be employed. In fact, thanks to its organic functionalities (i.e., hydroxyl, carboxyl, epoxy groups), it can react easily to form stable dispersions. An example is represented by the functionalization of graphene oxide with phytic acid. This latter is a naturally abundant organic coordination molecule with the chemical structure of $C_6H_{18}O_{24}P_6$ in which each phosphate group, characterizing the molecule, is connected to a carbon atom of the cyclo-hexamehexol ring [17]. Thanks to its non-toxicity, biocompatibility and environmental friendliness, it has been widely employed in a variety of applications, i.e., food and cosmetic additives, cleaning agents, and complexation of pollutants [18][19][20]. An embedding waterborne host sol–gel matrix can be easily obtained by the use of proper silane precursors and cross-linkers, in order to produce a uniform, homogeneous, durable, stable and functional coating for metal substrates.

The results of polarization measurements and a neutral salt spray test confirmed the anticorrosive behavior on steel and aluminum substrates of the final obtained sol–gel based nanostructured hybrid coating doped with phytic acid intercalated graphene oxide [21].

Electrochemical coatings are a popular method for protecting metallic surfaces. These coatings can be made of simple metals as well as binary and ternary alloys, which improve corrosion, oxidation, and wear resistance. An electrochemical deposition is a low-cost option for thin-film synthesis since it does not require complicated or expensive equipment and employs common raw materials. By altering deposition settings, electrodeposition enables the simple control of the coating's chemical composition, shape, and thickness [22].

Because of its recognized anticorrosion potential and environmental friendliness, the electrodeposition of polyaniline (PANI) coatings onto metal surfaces has gained attention. The anticorrosion effect of such PANI coatings is thought to be accomplished through a variety of mechanisms, including barrier protection, corrosion inhibition, anodic protection, a shift of electrochemical reactions from the metal/coating interface to the coating/electrolyte interface, passivation, and so on. By using a potentiostatic technique, a polyaniline-reduced graphene oxide composite (PANI-rGO) film was electrochemically deposited on 5083 Al alloy. The results revealed that the presence of rGO promoted PANI electropolymerization and improved Al alloy passivation [23].

As mentioned before, tannins are well-known polyphenols coming mainly from pine bark and acacia, featuring anticorrosion inhibition properties. The presence of OH groups in the ortho position of the aromatic ring of tannins leads to their reaction with iron, iron salts and oxidized steel substrates, promoting the formation of mono- and bi-ferric tannate species (tannin-Fe complexes), inhibiting the activity of the corrosion agents. In this regard, a hybrid self-healing coating, containing silane and tannins functionalized zinc oxide nanoparticles, was produced to protect steel substrates. In particular, ZnO nanoparticles, obtained by the method of arc discharge in a controlled atmosphere, were functionalized with APTES, mixed with *Pinus radiata*-derived tannin and an epoxy resin to obtain the functional hybrid epoxy. Subsequently, the obtained formulation was deposited on ASTM A36 steel plates through a spray coating approach. The anticorrosive properties of the functionalized nanoparticles were demonstrated using electrochemical analysis. Moreover, the contact angle and Kelvin probe delamination studies showed the self-healing capabilities of the film with the substrate [24].

Corrosion is a more aggressive-related phenomenon affecting all the surfaces exposed in a marine environment. In this case, the proposed corrosion mechanism for steel surfaces, for example, is as follows (Equations (6)–(9)) [25]:

$$Fe \rightarrow Fe^{2+/3+} + 2e^{-}/3e^{-} \text{ (anode)} \quad (6)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \text{ (cathode)} \quad (7)$$

$$Fe^{2+}/Fe^{3+} + 2Cl^{-}/3Cl^{-} \rightarrow FeCl_2/FeCl_3 \quad (8)$$

$$FeCl_2/FeCl_3 + 2H_2O/3H_2O \rightarrow Fe(OH)_2/Fe(OH)_3 + 2HCl/3HCl \text{ (unstable)} \quad (9)$$

For these purposes, natural inhibitors for corrosion were also evaluated. An extract of tropical plant *Mangifera indica* L. leaf (MIL), containing a high quantity of polyphenols, was used to obtain an amorphous silica-based hybrid material, subsequently incorporated in an epoxy coating. In detail, a precipitated amorphous silica functionalized with MIL was dispersed in an epoxy resin and its polyamide curing agent with a ratio of 2:1. Finally, by a dip-coating approach, the dispersion was employed for the treatment of commercial steel substrates.

2. Eco-Friendly Approaches for Flame-Retardant Coatings Preparation

The majority of polymeric materials are characterized by highly combustible chemical and organic components. However, the polymers' inherent flammability, resulting from their chemical structures and organic components, limits their practical usage. The most common flame-retardants employed in various industries are mainly based on inorganic, halogenated species and phosphorus-based agents together with nitrogenous compounds (due to their synergistic effect) [26].

Flame retardants are essentially based on the trapping of free radical species involved in ($H^{\bullet}$ and $OH^{\bullet}$) oxidation reactions (gas phase) to inhibit them. Even though there are many radical reactions occurring during gas phase combustion, only the following two steps, as shown in Equations (11) and (12), are accountable for the rapid process and the energy released [27]:

$$H^{\bullet} + O_2 \rightarrow OH^{\bullet} + O^{\bullet} \text{ (propagation stage)} \quad (11)$$

$$OH^{\bullet} + CO \rightarrow CO_2 + H^{\bullet} \text{ (exothermic reaction)} \quad (12)$$

In this regard, researchers are working on the development of new flame-retardant agents and nanocomposites, employing different nanomaterials and compounds. The addition of a relatively modest loading level of around 5 wt% of nanomaterials to the final polymeric nanocomposites can reduce their flammability, resulting in a decrease in the heat release rate (HRR) and mass loss rate (MLR) [28]. Despite nanocomposites, naturally derived compounds can also be employed for the development of sustainable flame retardants.

As a result, it is important to properly rationalize a flame-retardant finishing and consider both its physical and chemical methods of action [28][29]. Several of them, which will be further reviewed, deal with:

- Encouraging endothermic processes;
- Creating inert gases that reduce/dilute the air oxygen's content;
- Producing an impermeable layer of protection;
- Introducing flame retardants that can scavenge and eliminate active radicals in the gas and condensed phases;
- Dehydrating, cyclizing, and cross-linking flame retardants and/or the polymer matrix to create a carbonaceous protective layer.

Besides the sol–gel synthetic method [30][31], a better eco-friendly approach is represented by the use of natural or waste materials, such as coffee biowastes, as sustainable flame retardants. In particular, spent coffee grounds were chemically modified with phosphorus (dimethyl phosphite) in different ratios to obtain the P-coffee derivative. An epoxy resin containing 30 wt% P-coffee demonstrated a considerable reduction in the pHRR (40%) value by flammability analysis in pyrolysis combustion and flow calorimeter analysis. The presence of a carbon source, coffee biowaste, and phosphorus in the epoxy resin aided and sped up the production of a carbonaceous residue (char layer) that served as a barrier against heat and mass diffusion of gases into the gas phase. In the interim, the released phosphorus compounds stopped the spread of the flame by capturing free radicals in the gas phase [32].

Through the in-situ synthesis of hydroxyapatite (a bio-derived polycrystalline calcium phosphate ceramic with a hexagonal structure) in the presence of lignocellulose, a novel bio-based flame retardant for poly(lactic acid) (PLA) was developed. In particular, the hydroxyapatite-modified lignocellulose was produced from a milled bagasse-derived lignocellulosic biomass and perylene dianhydride as the grafting agent. The resulting hybrid material incorporates phosphorus, hydroxyl, and aromatic functionalities to work as a long-lasting flame-retardant system. Finally, it was combined with ammonium polyphosphate and integrated into a PLA matrix to achieve higher flame retardancy than pristine PLA [33].

Among the class of cellulosic-derived products, ammonium starch phosphate carbamates (mixed starch esters primarily composed of covalently bound ammonium phosphate groups with trace quantities of carbamate groups) can be applied as new and sustainable coatings with flame-retardancy features. They are produced significantly more easily than cellulose phosphates by adopting a solvent-free eco-friendly method to combine starch with urea (as an “esterification promoter”) and phosphoric acid. Ammonia was found to be a result of ammonium starch phosphate carbamates decomposition and, as inert gas, aids in flame extinguishment [34].

Moreover, other natural derivatives and bio-macromolecules, such as proteins and casein, a phosphorylated protein derived from renewable precursors, find application as green potential flame inhibitors for textile materials due to their capacity to induce the dehydration process of cellulose chains creating a char layer rather than the depolymerization process and their ability to achieve outstanding flame retardancy action through the heat consumption process [35][36]. Additionally, precious inorganic clay compounds, such as halloysite nanotubes (HNTs) characterized by hollow nanotubular structures, are still currently used as a useful synthon for creating polymeric nanocomposite materials with implemented features due to their large surface area and low cost [37][38][39]. Different techniques have been utilized to obtain HNT nanocomposites, among which the melt mixing process seems to be the most popular. To obtain the good dispersion of HNTs into polymeric blends, the HNTs must be functionalized. The inclusion of HNTs enhanced the mechanical, thermal, and flammability qualities of the functionalized surfaces and materials [40][41].

To combine the features of casein and HNTs, a new one-dimensional nanocomposite coating was developed for different textile supports. In particular, a different number of mass loadings of HNTs (10, 30 and 50 wt%) was uniformly dispersed in a rennet casein (RC) solution prepared from renewable skim milk with the help of ultrasonication. The created bio-inspired nanocomposite was then employed to cover various textiles (cotton, polyester and blend of cotton and polyester) with the dry-pad-cure process. The coated textile fabrics’ flammability, toxic gas suppressing, reinforcing, antibacterial, and antiviral characteristics were all greatly improved. In a horizontal test, treated textile fabrics’ flame retardancy reached a rate of burning of zero, compared to 119 mm/min for untreated cotton fabrics. Further, a high LOI value of 35%, as opposed to 18.5% for a blank sample, supports the flame retardancy properties of the green coating developed [42].

3. Hydrophobic and Water-Repellent Sustainable Coatings

The use of hydrophobic surfaces in both everyday life and some industrial processes has generated a lot of interest in recent years [43].

Surface composition, as well as its texturing and roughness, have been shown to have a significant impact on its hydrophobicity. In this regard, numerous techniques, such as the deposition of layers made of nonrenewable materials (such as fluorine or hydrocarbon compounds, some wax or organic and inorganic materials), have been opportunely formulated to lower the surface energy and, therefore, improve the water contact angle (WCA) of surfaces [44][45]. In the same way, surfaces with a hierarchical structure consisting of nanostructured texturing were successful in achieving high levels of hydrophobicity and superhydrophobicity [46].

Recent attention has been focused on the design of bio-inspired surfaces by the superhydrophobicity natural model, i.e., the lotus leaf [47]. The majority of hydrophobic surfaces are produced by treatments with fluorine compounds, which have negative environmental effects due to their bioaccumulation [48]. However, the majority of the approaches that have been documented up to this point involve high costs, difficult processes, and the use of hazardous chemicals and solvents. To increase the range of industrial applications for hydrophobic surfaces with controllable morphology, it is still difficult to develop straightforward, quick, inexpensive, and environmentally responsible methods [49].

In the next paragraphs, an overview of the recent advancements in organic–inorganic hybrid and sustainable coatings is reported for the development of nanostructured finishings for cultural heritages and textile surfaces to achieve different improved features.

3.1. Cultural Heritages Stones Protection

The development of protective coatings for both transportable and immovable cultural heritage items has drawn increasingly more attention in recent years [50]. In particular, it has mostly been caused by an increased awareness of the need to preserve cultural artifacts and monuments affected by weathering exposure and the existence of reactive airborne chemicals that may interact with the materials and compromise them [51]. Several research studies have advanced significantly from the end-of-the-last-century acrylic resins to the modern biomaterials and nanoparticles used today [52][53].

The widely accepted standards of cultural heritage restoration and preservation should offer the qualities of the ideal protective coatings (including transparency, reversibility, compatibility with the surface, long lifetime, ease of synthesis, low-cost maintenance and non-toxicity) and must be typically designed for cultural objects [52].

Synthetic polymers such poly acrylates, siloxanes, and fluorinated polymers have been widely used as protective coatings for stone surfaces in cultural heritages leading to different implemented and protective features.

Despite their excellent water repellent and optical clarity properties, the continuous exposure to UV light, humidity, high-temperature changes, etc., can result in their degradation, unintended cross-linking and/or chain scission reactions that diminish protection, cause yellowing, or cause the polymeric layers to separate. To improve the coating qualities and durability, silicon-based and silane-based polymers were also evaluated with and without the addition of inorganic silica (SiO_2) and titanium dioxide (TiO_2) nanoparticles [12][54].

A hybrid coating, made of acrylate monomers (as binding agent) and chemical compounds such as organosilanes, fluorinated silanes and titania nanoparticles, has the necessary qualities, such as thermal resistance, mechanical resistance, weathering resistance, hydrophobicity and self-cleaning, to be used as a protective coating for cultural treasures made of precious stones. In this regard, methyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate were employed for the preparation of a functional acrylate-based coating. In order to increase the coating's thermal resistance, tetraethyl orthosilicate (TEOS, an organosilane) was added to the polymeric blend. Moreover, to achieve better hydrophobicity and resilience to weathering, perfluorooctyl-trichlorosilane is further added to the mixture. Additionally, the formulation was completed by adding titanium dioxide employed to enhance the coating's thermal resistance and photocatalytic properties. The as-obtained multifunctional organic–inorganic hybrid nanocomposite was finally employed to coat a little area of historical monuments of Persepolis in Fars province (Iran) via impregnation. Cracking resistance, hydrophobicity, water absorption resistance, weathering durability, and color durability are only a few of the qualities that have been significantly improved by the presence of opportunely added functional compounds. The hydrophobicity of the coating is improved thanks to the achievement of a rough surface obtained by the employment of the organofluorine–titania hybrid nanocomposite. Additionally, titanium dioxide enhances thermal resistance and hardness and trigger photocatalytic activity, which results in the surface's ability to self-clean [55].

To replace fossil-derived polymers and fluorine-compounds, some other more sustainable approaches and formulations can be evaluated. An example is represented by a silane/siloxane emulsion employed as a water repellent agent coupled with chitosan and silver nitrate as biocides to create an eco-friendly finishing with both hydrophobic and biocide qualities. Chitosan is a naturally occurring amino-polysaccharide obtained from the deacetylation reaction of chitin coming from the shells of crustaceans, and it is the second-most common biopolymer in nature after cellulose. It is distinguished by a high concentration of amine and hydroxyl functionalities and has attracted growing interest in several fields [56][57][58]. The formulation Tegosivin® HE 328 serves as the foundation for the protective coatings described in the example. It is an emulsion concentration built on alkoxy-functional silanes and organo-modified siloxanes. Chitosan was first added to the water repellent sol–gel formulation in various quantities as well as low concentrations of silver nitrate. A limestone called the Dom stone was finally spray-coated with the functional biocide and hydrophobic formulation achieving from 122.8° to 129.4° of WCA and a significant Chlorella vulgaris biocide impact [59].

Among the nanostructured hybrid coatings approach, some natural derivatives such as Zein can be employed to achieve hydrophobic protective coatings for cultural heritages. It is an amphiphilic prolamine obtained from corn endosperm and is characteristic of about 80% of corn proteins. Its hydrophilic behavior is determined by the relatively high content of glutamine (21–26%). A 5% (*w*/*v*) solution of zein in DMSO was therefore prepared to obtain a protective hydrophobic coating of a Serena stone (a fine-medium grain sandstone) with the spray coating technique. A WCA of about 120° was achieved. In particular, using spray coating, the solution was released as tiny droplets in the air, causing the solvent to quickly evaporate from the surface of the droplets. Before the solvent completely evaporated, a radial zein concentration gradient formed within each droplet in a very short amount of time. Zein began to harden, in particular, from the exterior of the droplet at the air–liquid interface toward the interior. The hydrophilic polar side of zein remains in contact with the solvent since there is still DMSO inside the droplet, forcing the non-polar hydrophobic side to face the outer portion of the droplets. As the drying process progresses, the solvent completely evaporates from the inside of the droplets as well. Atmospheric pressure placed on the partially solidified zein particles and the force of the droplets colliding with the stone surface cause the droplets to collapse on top of each other, creating the hydrophobic coating [60].

3.2. Functionalization Approaches for Textiles Surface Modification

To give or enhance functional qualities of common polymer fabrics, two main approaches could be employed. The first is centered on the creation of novel fibers, which is still an expensive strategy that frequently necessitates learning new techniques for producing products and acquiring new machinery for various materials. The second strategy is based on the more useful functionalization of the surface of traditional fibers or fabrics while making minimal changes to the manufacturing methods [61]. This latter strategy is the most intriguing in the field of functional and engineered textiles. In addition to functional hi-tech fabrics, the development of more sophisticated coatings has produced engineered textiles able to interact with and react to their surroundings for applications in different innovative and nanotechnological sectors.

The preparation of active coatings for smart and functional textiles can be achieved using a variety of methods, most of which are traditional, while others are more modern and cutting-edge, including nanotechnologies [62][63][64]. While all of these processes are based on the attachment of certain chemical moieties to textile surfaces, they differ in terms of the modifying substance, substrate to be changed, kind of modification, and other aspects. The fabric's wettability and the coating's adherence to the fabric sample are both important aspects of the coating process. While the adherence of the coating is necessary for stable contact with fabric surfaces, the wettability of the textiles by the coating has a specific impact on the wicking of the treated fabrics. Intermolecular forces, ionic or covalent bonds, or weak interactions (dipole–dipole, hydrogen bond, induced dipole–dipole interactions, or dispersive) may all play a role in coating adhesion to textiles [65].

The coating process optimization must be considered since it can affect a variety of important textile qualities, such as comfort, breathability, and the hand of the coated fabric. Furthermore, the surface of the fabric and the presence of impurities can both affect the coating adhesion [66]. To achieve both functional and smart textiles with outstanding performance, uniformity and good coating distribution on the fabric surface are crucial components.

After preparing the substrate, the next step is the designed synthesis of the coating, which can be represented by a combination of functional substances in solvents or emulsions. Stabilizing additives are frequently used in this step to keep the coating solution stable for the duration of the application process. A post-processing phase may be necessary after the coating application, such as curing (cross-linking) using thermal treatment or various energy sources, including gas, an infrared oven, or UV radiation [67][68].

The sol–gel reaction, fabric impregnation process, chemical grafting, layer-by-layer (LBL) assembly, and other surface modification technologies are examples [69][70][71]. Among the aforementioned fabric finishing techniques, sol–gel technology has been widely used and adopted in a variety of industries due to its gentle reaction conditions, high efficiency, cheap cost, and environmental friendliness [72]. As a matter of fact, the sol–gel technique represents an eco-friendly method of functionalizing fabric surfaces by depositing a thin layer with specific physical properties, chemical stability and optical transparency, thus representing an advantageous technology over the ones currently available for the introduction of specific functionality onto textile fabrics. In fact, the sol–gel method makes it feasible to create textile coatings with different implemented properties [21][73][74][75][76][77][78].

The widely used sol–gel coating application procedures are based on dip-coating, padding, or spraying, producing smart or functional textiles with precisely designed properties. The dip-pad-cure method was shown to be the most popular due to its simplicity and viability from an economic standpoint. Using a padder, the fabric is immersed or dipped into a coating material solution while moving at a constant speed. After drying and curing, the process is repeated.

The types of chemical bonds, involving the adhesion of a coating to a surface, include covalent bonds (such as those between a silane end and an OH-group belonging to a cotton cellulose molecule), molecular attractions (such as Van der Waals forces, hydrogen bonds, dipole–dipole interactions) and, finally, the retention of the molecule by the substrate through adhesive and cohesive forces between the molecule and the substrate, as well as the molecule to itself [27][79].

Recent years have seen the application of hydrophobic treatment to textile surfaces for antifouling, self-cleaning, anti-ice, and oil–water separation purposes [80][81]. Additionally, due to their low surface energy and oil/water repellent qualities, stain-resistant surfaces and anti-stain coatings have important applications in a variety of industries, including textiles, construction, cars, and electronics [82]. Unfortunately, fluoroalkyl silanes and fluorine compounds were frequently used to further increase the surface water repellency of textile fabrics [83][84]. The ECHA committees most recently proposed restricting the use of particular perfluoroalkyl compounds (PFAS) in certain application sectors [85]. As a result, examples of environmentally friendly, fluorine-free textile finishings with stain- and water-repellent properties are also documented [86][87][88].

For example, some TEOS and citric acid superhydrophobic coatings were developed using a sol–gel approach and a spray coating/dry-curing technique to achieve fabrics (90% cotton and 10% polyester) with a WCA above 150°. The strength of adhesion between the silica and the cotton was improved by the use of citric acid [89].

Moreover, functional alkyl(trialkoxy)silane-modified hybrid nanostructured materials were successfully produced and used as hydrophobic and water-based strain resistance coatings for cotton fabrics, via the sol–gel process and pad-dry-cure technique.

The specific objective of the reported example was to investigate different functional alkyl(trialkoxy)silanes (Hexadecyltrimethoxysilane, Triethoxy(octyl)silane and Triethoxy(ethyl)silane: C_x and C_y) as precursors to synthesize efficient and stable hybrid sol–gel GPTMS-based coatings and further reduce cotton surface energy to enhance textile hydrophobicity and water-based stain resistance. By pad-dry-cure deposition of the produced nano-hybrid coatings, the double coating synthetic approach was successfully applied to increase the cotton surface's hydrophobicity.

The hydrophobicity of the fabrics was evaluated by WCA measurements, which showed that the treated fabrics have high static contact angle values (up to roughly 150°). The resistance of the treated fabric to water-based stains against several tested liquids, solutions, and soil was also proved. The moisture adsorption analysis and the air permeability test were also used to assess the fabric quality, and the results of these tests revealed that coated cotton fabrics had better overall breathability compared to pristine cotton ones.

4. Anti-Fouling and Fouling-Release Sustainable Coatings

The phenomenon of fouling occurs when macromolecules, bacteria or suspended particles stick to the surface of different materials. The construction industry, cultural heritage, marine industry and industrial sectors are all interested in this problem [90][91]. In this regard, one critical use of nanostructured coatings might result in the inhibition of microbial proliferation on various surfaces. Due to the variety of fouling organisms and their adhesion processes, designing antifouling (AF) coatings has proven to be a considerable challenge over time. Significant research on biocidal and non-biocidal coatings that prevent and decrease biofouling was sparked by the need to find answers to these problems [92][93]. Most control measures in the middle of the 19th century employed paints that included biocides. However, the biocide is a highly harmful agent (similar to the now-banned tributyltin) that is put into paints as an additive and, when exposed to seawater, is gradually released into the marine environment as a result of chemical and physical phenomena [94].

Fouling is influenced by surface characteristics, such as surface energy and wettability. As a result, altering the surface morphology and functionalities offers a key method for providing antifouling features on different surfaces [95]. One efficient way to do this is to treat the substrate with a formulation made of antifouling and antibacterial polymers. These coatings and paints can prevent biofouling and biocorrosion because they incorporate functional anti-adhesion, antimicrobial and anticorrosion chains rather than releasing biocides.

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