Review

Nanostructured surface finishing and coatings: functional properties and applications

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Abstract: This review presents current literature on different nanocomposites coatings and surface finishing for different substrates (such as textiles, concrete, plastics, stones, metals and so on). In particular, this study is focused on smart materials, drug delivery systems, and industrial, antifouling and nano/ultrafiltration membrane coatings. Each of these nanostructured coatings shows interesting properties for different fields of application. In this review, particular attention is paid to the synthesis and the consequent physico-chemical characteristics of each coating and, therefore, to the different parameters that influence the substrate deposition process. Several techniques used in the characterization of these surface finishing coatings are also described. In this review, the sol-gel and polymerization method for preparing stimuli-responsive coatings as smart sensor materials is described; functional polymers and nanoparticles sensitive to pH, temperature, phase, light and biomolecules are also treated. Finally, nanomaterials based on phosphorus, borates, hydroxy carbonates and silicones are used and described as flame retardant coatings; organic/inorganic hybrid sol-gel coatings for industrial applications are illustrated, together with functional nanofiller (carbon nanotubes, metallic oxides, etc.) and polymers employed for nano/ultrafiltration membrane and antifouling coatings. In the last decades, several research institutes and industries have collaborated for the advancement of nanotechnology by optimizing conversion processes of conventional materials into coatings with new functionalities for intelligent, innovative, eco-sustainable and advanced applications.

Keywords: smart materials; drug delivery systems; flame retardant; industrial coatings; filtration membranes; antifouling coatings.

1. Introduction

Different nanostructured coatings and surface finishing, characterized by nanostructure length range (1–200 nm) materials, may be deposited on the external area of a matrix to implement or enhance the materials efficiency for several applications [1]. Most of the atoms are associated with grain boundaries for contributing to improving the physical properties of nanostructured materials. Conventional materials have followed through the evolution of human civilization by defining the historical ages as for stone, iron, bronze ages, up to the most recent cement, and silicon ages. Scientific and technological developments allowed the definition of a "new époque" in which materials acquired a more advanced meaning and specific functionalities. During the last century, the synergism between several scientific disciplines such as chemistry, physics, nanotechnologies, computer science, engineering, electronics, medicine led to innovative composite, nano, and smart materials that represent a step forward respect to conventionally intended ones. This review introduces the study of nanostructured surface finishing and coatings, focusing in particular with smart materials, drug delivery systems, flame retardant, industrial, nano/ultrafiltration and antifouling coatings that are deeply described, through subsections reporting the synthesis, the processing and characterization of nanostructured surface finishing and coatings. The purpose of this review is to give a panoramic view of functional properties and the related applications of all kind of nanostructured coatings.

2. Smart Materials

Smart materials are defined as materials able to respond to physical, chemical, or mechanical external stimuli by producing a quantifiable simple signal and combining the main functions of sensors, actuators, or transductors [2]. They were defined for the first time in 1989 in Japan, although the first examples are coinciding with the discovery of the shape memory materials and intelligent polymeric gels in the 1960s and 1970s, respectively. Besides the sensing properties, the stimuli responses could consist of actuations or corrective functions among which healing or self-mending are of great biomedical applications. The most impressive nanotechnological development provides smart materials including fiber optic sensors, shape-memory materials, electrochromic materials, piezoelectric materials, magneto-rheological and electro-rheological materials. Moreover, fascinating and influential implications are represented by the nanotechnological coating with protective actions in military and civilian fields as well as thermochromic, electrochromic and gasochromic smart materials, controlled drug release membranes, sensors for volatile organic compounds (VOC), contaminants, radiation, chemical warfare gases, land mines and smart coatings for adsorption of proteins [2]. The advance in nanotechnology together with the interdisciplinary activities between research institutes and industries led to the optimization of increasingly technological processes for the conversion of conventional materials to design an ever-growing range of coating with novel functionalities for smart applications. Biosensing materials, pH-sensitive polymers, and thermo-responsive materials are examples of such intelligent materials, which find application in medicine, healthcare, fitness, military, professional workwear, and many other fields.

An important contribution to the advancement of smart materials was provided by an innovative way to consider the textile polymers besides their conventional use. During the last decades, the fascinating and unique properties of textile materials such as flexibility, breathability, mechanical strength, simplicity of processing, biocompatibility (e. g. natural fibers) and washability make they interesting as substrates for the integration of smart functionalities, by paving the way for the research field dealing with the so-called smart textiles. Following the definition of smart materials, they are defined as textiles able to sense external stimuli, react, and adapt to them through specific functionality integrated with the fabric structure [3]. Flexibility, low-weight and comfort are the main challenges of smart textiles, which make them interesting and fascinating toward conventional bulky and rigid sensors although the integration of microelectronics or electronic devices. During the last decades of 1900, sensors and specific functionality started to be integrated with garments by obtaining prototypes of smart textiles for the long-term monitoring of physiological parameters in a non-invasive way and in real-time. With this aim, new processes have been developed to provide strong synergies between textiles and electronics or between different scientific sectors by developing innovative hybrid technologies.

Knitted or woven fabrics with integrated functionalities for sensing, processing, and actuation (e.g. gestures, wearer’s postures, vitals tracking) were integrated with clothes. In this regard, the transfer of specific functionalities by textiles processes (e. g. weaving) or by integration with technological components (e. g. LED) by preserving the main characteristics of textile polymers is possible following "textilification" [4]. Accordingly, a large number of sensors can be integrated with textile fibers, like ECG (electrocardiography), EMG (electromyography) and EEG (electroencephalography) sensors, thermocouples, luminescent elements, but also carbon electrodes, useful for detecting biomedical and environmental components and/or parameters (e.g. oxygen, salinity, moisture or contaminants) [5]. Therefore, iconic smart materials, such as electromyography pants, electroencephalogram caps, and electrocardiography T-shirts have been developed for the detection of different health parameters [6]. An important issue to be addressed in the design of smart textiles is the compliance with the body deformations, of main importance for sensors for the monitoring of body temperature, fluids (sweat, tears or urine), volatile molecules (odors or breath composition) related to body fluids. Such an issue is mainly related to the integration of electronics with textiles, which represent a limiting factor. Indeed, characteristics like flexibility (to accommodate body deformations), miniaturization, biocompatibility (to not affect daily activities) as well as low-consumption work capacity are the most desired in wearable smart sensing. Among many sensors, electronic elements, electroconductive fibers/yarns, miniaturized circuits conventionally integrated with textile fabrics through nanotechnological approaches, the manufacture of miniaturizing silicon sensors thanks to Si technology is of great interest in smart textiles for the detection of contaminants (bacteria, heavy metals, pesticides).

As well as electronic devices, a large number of sensing molecules can be integrated with fabrics allowing the use of such smart fabrics in medicine, health care, fitness, wellness, diagnostic, and environment [7][8]. Such integration can be possible through the development of smart (or active) coatings able to sense and react to specific changes on the environment thanks to reversible or irreversible variations in their physical or chemical properties [9]. Phase-change and memory materials, conductive, antimicrobial and chromic molecules, nanoparticles, are only a small piece of "active" molecules that can be integrated into coatings. Therefore, the designed smart coatings can sense stimuli like humidity, heat, light, chemicals, pressure, and bioactivity changes and react following the intrinsic properties of the active element. Accordingly, the coating responses can be color changes, energy release, shape adaption, drug release, changes in the dimensional structure of the textile fibers, and many others thus providing a wide panorama of wearable sensors as a consequence of their integration with textile structures [10]. As examples, through the combination of conventional and deformation sensitive fibers or the coating of conventional fibers with conductive polymeric composite, it is possible to obtain deformation sensors for respiratory rate monitoring, posture, or body movements. Similarly, carbon nanotubes, conductive polymers or composite can be used to functionalize textiles to obtain moisture wearable sensors based on variation in the electrical resistance as a function of environmental humidity levels [11] or sensors for the heart rate monitoring [12]. The integration of smart functionalities in textile polymers can be achieved by nanotechnological approaches ensuring no interferences with textile engineering processes and the maintenance of the intrinsic textile properties. Such nanotechnological routes for surface modification of fabrics to obtain smart textiles could be represented, among several examples, by electrospinning, grafting polymerization, and sol-gel approaches [13]. An interesting and innovative field in which the so-mentioned nanotechnologies were fully investigated is represented by optical sensors, whose chromic and halochromic smart textiles are the main representatives. In smart textile field, the optical, easily detectable and non-destructive signal provided by chromic materials is strictly related to the nature of the external stimuli and classified as photochromism (color change induced by light), thermochromism (color change induced by heat), ionochromism (color change induced by ions) [14] thus giving a phosphorescence, fluorescence, or visible color changes stimuli-dependent. Stimuli like sorption of chemicals, radiations, temperature changes, presence of heavy metals, redox reactions, as well as pH changes could be easily detectable and monitored by smart materials thanks to the integration of functional molecules such as indicator dyes, pigments or their advanced hybrid systems. Such new materials coated onto textiles can be employed in a large range of wearable biosensing applications thanks to the attractive advantages with respect to conventional sensing systems. Indeed, their selectivity, sensitivity and practicality as well as the low-cost (since no sophisticated or expensive instrumentation for the read-out of the color changes are needed), make such colorimetric sensing systems fascinating by focusing the main challenge in the transformation of the detection events into color change [15]. During the last decades, several smart materials have been studied among which those containing graphene oxide, carbon nanotubes, conjugated polymers, gold, magnetic and cerium nanoparticles [15]. The intriguing potentiality of these materials in colorimetric systems arises from the robust physical and chemical properties. As an example, gold nanoparticles are characterized by different optical properties as a function of size, shape and composition; the color change of the corresponding colloidal solution is dependent on the aggregation or redispersion of nanoparticles. On the other hand, both carbon nanotubes and graphene oxide can catalyze the color reaction thanks to their peroxidase activity. Among conjugated polymers, polythiophene derivatives and polydiacetylene can change their colors upon conformational transitions or aggregation [15][16]. In this wide panorama, smart textiles based on optoelectronic systems for the detection of pH variation are fascinating and innovative over the conventional electrochemical pH electrodes. With respect to the latter, optical pH sensors ensure longer lifetime, low cost, safety, mechanical robustness, fast and reversible response as well as the possibility of miniaturization and high signal to noise ratio (SNR) [17]. On the other hand, ambient light and some sweat components could affect the sensor selectivity, as well as, the long-term stability of the sensor can be influenced by the leaching or photobleaching of the sensing halochromic molecule. The monitoring of the sweat pH is of great interest since the composition of such biological transparent fluid gives useful information concerning human health. Due to the main role of the sweat pH in body hydration and mineralization levels, in skin pathologies, the real-time monitoring of sweat pH provides information dealing with corrective approaches for re-hydration or skin disease with applications in fitness, healthcare, medical diagnostic fields. Moreover, an increase in the sweat pH values are correlated with an increase in the sweat rate, as well as, the concentration of some electrolytes, as for Na^+ can be determined: the highest the sweat concentration, the highest the sweat pH [18][19]. To develop a reversible, robust and optical chemical sensor, the stable immobilization of an indicator dyestuff onto textile surfaces should be ensured in order to avoid the dye leaching. According to the nature of both textile surfaces and chromic smart materials, intermolecular forces, ionic or covalent bonds or weak interactions (e. g. hydrogen bonds, dipole-dipole, or induced dipole-dipole interactions) between textile fibers and smart coatings can be established to ensure the adhesion of the functional materials [20]. As previously mentioned, electrospinning represents an interesting route for the immobilization of halochromic molecules in textile polymers with several advantages with respect to conventional dyeing methods such as low-process time and energy [21]. Conventional methods, mainly represented by exhaustion and direct dyeing processes, are low-cost and facile approaches for the introduction of chromic or halochromic molecules in textile polymers and based on the diffusion of dye molecules into fibers or on weak interaction between the dye and the fiber, respectively. Both of them are characterized by some disadvantages consisting of elevated temperature, low exhaustion, and fixation levels, not sufficient affinity between dye and fibers, long dyeing time, high dye leaching, slow response rate. Conversely, electrospinning approaches represent an efficient alternative to conventional dyeing technique for the incorporation of dyestuff into the textile structure thus ensuring a low dye leaching as a consequence of covalent interactions between dye and fibers [21]. The halochromic functionalities can be introduced during the electrospinning of nanofiber, thus obtaining stable chromic and halochromic functionalities in textiles and combining the intrinsic properties of nanofibers and pH- sensing functionalities [21]. By starting from different polymer solutions or melted forms of polyurethane, nylon, polyacrylonitrile polyvinyl alcohol, or polylactic acid, and applying an electric field it is possible to obtain nanofibers with diameters between 10 and 500 nm [22]. By tailoring ambient and solution parameters interconnected membrane-like network of mat fibers can be achieved. Therefore, via electrospinning of monofilaments, uniform and ultra-thin coating of nanofibers with different properties can be deposited onto textile fibers [22]. In particular, controlling the time processes it is possible to tune the coating thickness in order to ensure the highest sensor sensitivity [23]. Van del Schueren *et al*. [24] provide an interesting example of Nitrazine Yellow pH-sensitive polyamide (6 and 6.6) nanofibrous non-wovens synthesized by electrospinning. In particular, the dye was added directly before the nanofiber formation thus obtaining a highly effective halochromic system with a fast response. Indeed, the performances of the halochromic sensor take advantage by the use of nanofibers since their high porosity and specific surface area enhance the response time and the sensitivity of the halochromic sensor itself. Experimental results demonstrated that the introduction of the NY dyestuff in the electrospinning of PA did not affect: (i) the process; (ii) the morphology and average diameter of the obtained fibers; (iii) the NY halochromism of electrospun PA. Moreover, the typical NY color

doi:10.20944/preprints202104.0574.v1

transition from yellow to blue for increasing pH, as well as the fast response (5 min vs 20 min of conventional dyed PA) were provided by the nanofibrous non-wovens. It was also demonstrated that the nature and the structure of polyamide fibers influence the halochromic response thus observing less bluish color for PA 6.6 compared to PA 6 due to different interactions between dye-fibers and fiber accessibility [25]. However, all textile samples revealed reliable color changes as a function of pH variation thus highlighting the potentiality of the electrospinning process and of polyamide as potential parameters for colorimetric textile sensors.

Another interesting chemical approach for the stable immobilization of halochromic molecules in textile structures is represented by the grafting polymerization, which represents a widely investigated route for the surface modification of materials through the introduction of coating with high durability. Such a process forecasts the use of reactive molecules, such as vinyl or acrylate monomers, able to provide, in proper conditions, free radical species for the generation of "active sites" onto textiles surfaces according to initiation and propagation reactions. Such radical species can be activated by several processes like thermal grafting (by radical initiators such as persulfate ions) or high-energy radiations (e.g. UV light) or by high-energy system of ions, radicals and metastable molecules such as in plasma-induced grafting. According to the initiation process, different radical initiators and sources of energy must be properly chosen. Photo-induced grafting represents a valid technique to modify cellulose-based textile polymers [26][27] by grafting functional moieties on the outermost surface of the substrate without affecting the bulky structure due to the depth functionalization of about 200 micron in depth. As an example, according to photo-grafting process, the Nitrazine Yellow (NY) dyestuff was stably immobilized by means of glycidyl methacrylate (GMA) monomers onto cellulose fabrics with the aim to realize a robust and reliable wearable pH-sensor [28]. In a common mechanism, the triplet state species of the photoinitiator (benzophenone) generated by UV light, are able to abstract hydrogen atoms by the OH groups of the cellulose chain by forming cellulose radicals [29]. The latter can attack the double bond of the bifunctional GMA monomer whose epoxy ring group was previously catalytically opened for the covalent functionalization of the NY. Initiation and propagation reactions were established under UV radiation and in the presence of the photoinitiator thus generating the growth of the acrylate-dyestuff chains from the cotton surfaces. A similar approach was performed by Trovato *et al*. [30] with a radical procedure designed to promote the *in situ* thermal-induced grafting of the GMA-functionalized Nitrazine Yellow. In this research, potassium persulfate (KPS) was used as a free-radical initiator able to dissociate giving potassium and persulfate ions under thermal heating [31]. Such a homolytic cleavage produces sulfate radical anions that generate further active sites on the cellulose surface by the abstraction of hydrogen atoms. Similarly to photografting, the dyestuff-acrylate monomers can attack these active sites onto the cotton surface by promoting new covalent bonds between monomers and the textile surface thus resulting in a robust and reliable halochromic wearable sensor.

In the design of stimuli-responsive coatings, the sol-gel technique was widely investigated thanks to the fascinating properties of the derived thin films, among which high chemical stability, optical transparency, flexibility, particular physical properties, high durability, mechanical and chemical protection towards fibers [30]. Not surprisingly, some applications dealing with UV-protection, halochromic, antimicrobial, hydrophilic, self-cleaning, and flame-retardant coatings for textiles [32][33][34][35][36][37][38][39][40][41]. According to subsequent hydrolysis and condensation reactions of metal alkoxides (e. g. Ti, Si, Al, Sn, V or ZR salts), or organometallic substrates in which the metal is bonded to organic functionalities hydrolysable, hybrid organic-inorganic materials with three-dimensional porous structures and highly pure at the atomic scale can be obtained by tailoring the synthetic parameters. Functional organic molecules (e.g. active principles, halochromic molecules, carbon nanotubes, drug molecules) can be stably immobilized in the hybrid network according to weak or covalent interactions by leading to smart coatings with appealing properties for sensing applications. The nature of the so-mentioned interactions affects the sensing properties of the resulting smart materials: non-covalently linked molecules are advantageous for the design of controlled release coatings since the retention of such molecules is stimuli-dependant [42]; conversely, covalently bonded molecules provide robust smart materials for advanced sensing applications (e.g. pH-sensitive coatings). Among several sol-gel precursors, Si-based have aroused much interest in the design of smart coatings thanks to their no cytotoxic effects on human skin cells [43] although their low reactivity with respect to other metal alkoxides. Interestingly, several examples are reported in the literature concerning the use of (3-glycidoxypropyl) trimethoxysilane (GPTMS) due to its bifunctionality: by epoxy ring-opening present in its structure, organic molecules can be covalently linked and, simultaneously, thanks to the hydrolyzed methoxy silane functionalities in the 3D network, the crosslinking toward surface materials can be achieved. The latter can be advantageous in the design of halochromic wearable sensors thus resulting in lowest dye leaching from textiles with respect to conventional dyeing procedures.

Several examples are available in the literature dealing with the covalent immobilization of a halochromic molecule by epoxy ring-opening of the GPTMS that can be performed by acid or base catalyst according to the anion, cation, or covalent nucleophilic mechanism. In this regard, a detailed study was carried out by Guido *et al*. concerning the use of the Lewis acid BF_3OEt_2 as the catalyst in the covalent immobilization of NY by the epoxy ring-opening of GPTMS [44]. The sol-gel reactions were performed using three different concentrations of the Lewis acid (1%, 5%, and 10% w/w GPTMS) to investigate the effect of the acid concentration on both the ring-opening and the formation of the silanol network. The so-obtained solution of NY doped silica matrix was applied onto cotton fabrics and compared to textiles treated with reference GPTMS solutions [45]. It was demonstrated that the concentration of Lewis acid is of great importance to tune both the catalyst and the cross-linker effect: the higher the amount of acid the higher the formation of a more crosslinked inorganic network useful for an efficient hybrid halochromic matrix fixation onto textiles structure. Such experimental findings confirm the increased washing fastness of textile treated with silica matrix obtained by the high concentration of catalyst and the typical pH-response of NY although its covalent immobilization with GPTMS by sulfonic groups and epoxy ring-opening thus demonstrating the effectiveness of the sol-gel techniques in the design of robust and reliable wearable pH sensor [44].

The versatility of nanotechnological processes in the design of halochromic sensors is of great importance to ensure the deposition and the effectiveness of coatings onto textiles with different natures. In this regard, Van der Schueren *et al*. [21] described a sol-gel procedure for Methyl Red (MR) dyestuff stable immobilization by HCl-catalyzed epoxy ring-opening of the GPTMS for polyamide textiles (PA) by demonstrating the feasibility and efficacy of the halochromic hybrid composite respect to conventional dyeing technique [46]. The efficiency of the synthetic procedure for polyamide fabrics was demonstrated in terms of washing fastness of the sol-gel PA treated textiles that showed increased durability to launder cycles (and as a consequence a low leaching of the dye) as well as higher halochromic response compared to PA conventionally dyed with MR. Contrary to potential limiting factors of the sol-gel approach, such as the longer response time due to the diffusion of the molecules into the dried silica network, shorter and easier responses to pH changes were measured for sol-gel treated PA samples than conventionally died (4 min vs 20 min, respectively). Such a finding was proved by morphological images of the sol-gel PA treated cross-sections that reveal the presence of the halochromic molecules only on the surface of the fibers in opposition to the conventional dyed PA textiles in which the MR molecules penetrated inside the singular fibers resulting in longer responses [47]. As reported in the literature, the epoxy ring-opening of the GPTMS can also undergo alcoholysis, hydrolysis, or polyaddition reactions to provide diols and then β-hydroxy ethers or polyethylene oxide (PEO) 3D network. Even if the covalent linkages between a halochromic molecule and the silica matrix ensure stability in terms of low leaching of the dye molecules, it was demonstrated by Rosace *et al*. [48] that also the encapsulation of Resorufin as indicator dyes in the GPTMS-PEO matrix according to weak interactions can provide reliable wearable pH sensor [49]. Notwithstanding the slight influence on the coating durability due to the weak interaction, low leaching of the Resorufin from textiles was observed. Moreover, the efficacy of the non-covalent Resorufin-PEO immobilization onto cotton fabrics and the maintenance of the typical color variation of the pure dyestuff in the pH range between 2 and 8 were demonstrated by UV-Vis spectroscopic measurements.

To provide a reliable wearable pH sensor, the hybrid polymeric network should also ensure the maintenance of the dyestuff photostability in the visible light. Plutino *et al*. [50] provided a detailed study concerning the photostability of the Methyl Red dye covalently functionalized with GPTMS under UV-Vis radiations at pH 2 and 8. Experimental results demonstrated an increase in photostability due to both the electron density of the azo bond and the loosing of the influence relative to the hydrogen bond on the azo group with respect to the unfunctionalized dye. The latter effect seems to significantly affect the reduction rate. Moreover, a substitution in the *ortho* position of the phenyl group relative to the azo bond by GPTMS enhanced the photostability of the functionalized MR dyestuff. As a consequence, the photodecomposition of the hybrid molecules by UV light was prevented since the reduced influence of the so-mentioned hydroxyl following the GPTMS functionalization that acts as a shield towards the hybrid halochromic molecule towards photodecomposition. Experimental results demonstrated both the potentiality of azo dyes and silica hybrid matrix in the development of halochromic materials ensuring the efficiency of the designed systems and the lightfastness [50].

The deprotonation-protonation process of the immobilized dyestuff should be ensured notwithstanding by the silica matrix involved in the dyestuff functionalization but even though by the electronics integrated with for the real-time monitoring of the sweat pH. In this perspective, several studies have been provided by Caldara *et al*. concerning the development of optoelectronic colorimetric pH sensors using Methyl Red or Litmus as dyestuffs covalently linked in GPTMS matrices [51][52][53]. The optoelectronic device for the color sensing variations was realized with a LED and a photodiode to implement the light-to-frequency conversion as the spectral sensitivity curve of the photodiode is monotonic in the smart fabric color variation range. The as-designed optoelectronic system, besides wearability, can take over halochromic reflectance intensity variations and is characterized by low power consumption and easy connection towards a microcontroller for the processing of data. The halochromic system realized through the GPTMS immobilization of Methyl Red coated onto cotton fabrics integrated with electronics (Figure 1) provides, in the pH range 4.0 - 6.0, a resolution greater than 0.05 pH units with a color reproducibility within 2%, a monotonic relation between the frequency output of the color sensor and the pH, and a settling time on H^+ variations of few seconds and few minutes in wet and dried condition, respectively [51].

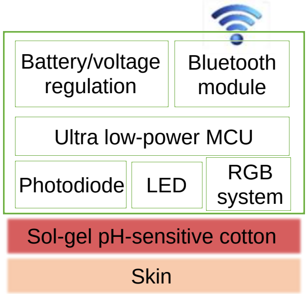

Figure 1. Block diagram of smart halochromic sensor.

In another study, the designed sol-gel smart composite was employed in the real-time monitoring of both sweat pH and skin temperature [52]. In this regard, the wearable sensor platform was developed by using Litmus, a non-toxic dyestuff, in a GPTMS functionalization of textile, and a silicon-based thermometer. Besides the latter, the electronic device includes an RGB color sensor, a low-power microcontroller, a nonvolatile memory, a power supply and a Bluetooth miniaturized module. The smart textile was designed with the aim of minimizing the power consumption and performing high resolutions and accuracies thus measuring greater than 0.01 °C and ± 0.4-pH temperature resolution and accuracy, respectively. To evaluate the reliability of the designed smart platforms, the described system was tested on-body during a bike exercise by measuring the sweat simultaneously through the miniaturized electronic device integrated with the treated textile and a reference electrochemical pH meter for five times (Figure 2). The high sensitivity and the embedded processing allow to obtain a resolution of 0.2 pH units and accordance equal to 0.5 pH unit respect to the reference pH-meter [53]. Moreover, the wearable platform reveals a settling time of 8 min due to the poor sweat rate at the beginning of the perspiration [53].

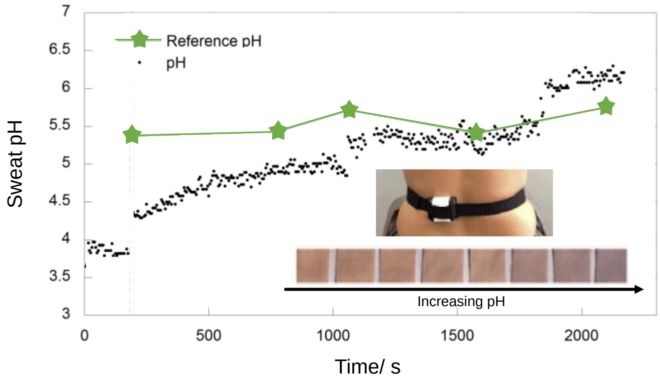

Figure 2. Sweat pH measurement and images of color textiles variations during physical activities performed on-body and compared with a reference pH meter.

The so-obtained non-invasive wearable pH sensor, thanks to the on-body experiments performed [53] reveals fascinating potentiality in the monitoring of athletes' parameters for the evaluation of body hydration level or other health parameters [52] with application in sport, fitness and medicine fields.

In this panorama, "Health Belt" (Figure 3) is proposed as a prototype of halochromic smart textiles for sweat pH real-time monitoring. It consists of an elastic strip with embedded a cotton fabric treated by the sol-gel technique as the sweat pH-sensing element and a miniaturized electronic device. As already stated, the involvement of the sol-gel technology ensures the adhesion of the halochromic film onto textiles thus providing an environmentally friendly and healthy human safe application. The miniaturized electronic device trough the LED/photodiode system is able to detect the pH-dependent colorimetric variation of the textile and, after the removal of interferences, to transmit the data remotely by a Bluetooth Serial Portal Profile easily readable through a specific App for mobile phone.

Figure 3. Prototype "Health Belt" for the real-time monitoring of sweat pH.

The described nanotechnological processes highlighted the potentiality of smart materials in the development of advanced, reliable and robust wearable pH sensors. Even more innovative applications would be provided as results of the combination of smart coatings, textile fabrics and microelectronics.

3.0 Drug release/delivery systems

Active pharmaceuticals are allowed, under specific conditions, to reach the target site and improve its effectiveness, through the use of controlled drug release nanosystems [54]. Drug delivery systems contribute to implementing specific properties of 'free' drugs by improving biodistribution, solubility in biological media and their *in vivo* permanence. By employing a nanosystem which incorporates or encapsulates drugs and release them, under external stimulation, such as pH or temperature, controlled release can be achieved [55]. Controlled-release drug delivery systems are employed to obtain:

i. constant release into the blood of quantities of therapeutic compounds, avoiding drug waste;
ii. repeatable and scheduled long-term release rates;
iii. reduction of side effects;
iv. personalized therapy;
v. drug stabilization [56]

A proper excipient helps keep drugs intact until delivery and facilitates their release at desired sites with maximum efficiency, while an appropriate processing method avoids unwanted degradation and waste of nanosystems [57]. These systems also change disadvantageous pharmacokinetics of some 'free' drugs. In addition, extensive loading of pharmaceuticals' administration on drug delivery systems can distribute 'drug reservoirs', for controlled and continuous release, to provide the drug level within the therapeutic window. Currently, many delivery nanocarriers based on nanometric size compounds as micelles, dendrimers, nanotube and metallic nanoparticles have been designed. Many researches are focused on these delivery systems to support and provide a promising alternative to chemotherapy. Pharmaceutical research is attracted to planning advanced antineoplastic drugs with specific selectivity on cancer cells. In recent years, chemotherapy is principally focused on destroying all rapidly proliferating cells. The disadvantage of this therapy is that the body's other rapidly dividing cells, such as in the hair follicles and intestinal epithelium are also killed off, leaving the patient to deal with harmful side effects. These new drugs should be able to exceed any resistance of the tumoral cells and they should provoke bland side effects. Chemotherapy drugs, used in current therapies, are often lipophilic molecules so, micelles are also excellent systems to make insoluble drugs soluble due to their hydrophobic core and hydrophilic shell [58]. The further functionalization of the micelle's surface with PEG, increases the ability of the nanocarriers to pass through tumoral tissue as a result of passive transport, therefore resulting in higher drug concentration in cancer cells. Numerous polymeric micelles, incorporating anticancer drugs, are under clinical trials [59] and others are already approved for breast cancer patients. Dendrimers are repetitively branched macromolecules with lots of functional groups available for the connection of drugs, which are used as targeting and imaging agents and their absorption, distribution, metabolism and elimination profile is correlated to diversified structural characteristics. Nanoparticle therapeutics based on dendrimers can improve the therapeutic index of cytotoxic drugs by using biocompatible segments, such as PEG, acetyl, glicosane and various amino acids, linked on the surface area [60]. There are several other models of nanoparticles which show promising results in cancer treatment, a today used system contemplates carbon nanotubes. This carbon nanosystem is an allotropic form of carbon with a cylindrical structure extending on a number of sheets in concentric cylinders (single-walled carbon nanotubes and multiwalled carbon nanotubes) [61]. Water-insoluble drugs can easily be loaded on the hydrophobic hollow interior of carbon nanotubes. The large surface area consents a specific outer surface functionalization for defined cancer receptors as well as contrast agents [62]. A spherical molecule as Fullerene (C_{60}) and its derivatives are evaluated for the treatment of cancer [63] thanks to its ability to enhance the cytotoxicity of chemotherapeutic agents [64]. A study conducted using Doxorubicin uploaded on the complex of Fullerene C_{60} demonstrated that tumor volumes of treated rats were 1.4 times lower compared to the untreated rats [65]. These results are probably due to the direct action of C_{60} + Doxorubicin complex on tumor cells as well as immunomodulating effect. The development of nanoparticles has contributed to a new route for chemotherapy. With the design of smart nanoparticles, targeted drug delivery at the tumor site or a specific group of cells widely prevent the toxic and unwanted effects on other healthy tissues and organs [66]. Gold nanoparticles take advantage of their unique chemical and physical properties to carry and release drugs; they are able to deliver different size of drug molecules from little one to large biomolecules such as peptides, proteins or nucleic acids like DNA or RNA. This nanosystems recognize the surface of anionic protein as a result of interdependent electrostatic interaction and inhibit its activity [67]. Gold nanoparticles could be functionalized with lots of molecules with appropriate functional groups, in the monolayer [67]. Carbazoles, for example, were widely investigated for all their properties, which can be improved by changing functionalized groups or by introducing suitable substituents on carbazole core, with the intent to purchase new and unique properties as antioxidant or antimicrobial [68]. These compounds promote antiproliferative activity and considerable apoptotic response approaching cancer cells selectively. An approach to release pharmaceuticals, as carbazoles, involves the use of gold nanoparticles [69]. These nanocarriers are suitable to deliver different payloads into target cells. In addition to the surface chemistry of gold nanoparticles, a promising perspective, in cancer therapy, is the photothermal damage [70] to cancer cells, which is an additional technique for enhancing the selective damage of unhealthy cells, based on the irradiation of nanoparticles, with 20 ns laser pulses (λ= 532 nm), to produce local heating. A circumstance for an effective drug release therapy can be improved thanks to external stimuli such as light or from the inside, through variations in the pH levels [71]. Tunable size and functionality make them a suitable scaffold for efficient delivery of biomolecules. It has also been demonstrated that functionalized gold nanoparticles can act as carriers of insulin [72] and chitosan, a green biopolymer stabilized them. Gold chitosan-coated nanoparticles strongly adsorb insulin on their surface and are efficient for transmucosal delivery of insulin. For *in vivo* applications, the target of nanocarriers is the diseased tissue after the release into the circulatory system. There are two methods to deliver nanocarriers, 'passive' targeting and 'active' targeting [73]. The first one depends on vectors' release in unhealthy cell tissues due to extravasation through a cracked blood vessel. Thanks to the nanometric diameter, the nanocarrier systems take advantage of the enhanced permeation and retention (EPR) effect [74]. On the other hand, 'active' targeting holds ligands on the carrier surface, for distinct recognition by cell surface receptors. Combination of both types of targeting will distribute an ideal carrier for *in vivo* delivery. Nanocarriers experience a non-specific uptake and possible degradation in macrophages. Therefore, targeting is essential for maximizing drug efficiency as long as minimizing side effects. Different physicochemical properties, such as size, PEGylation, or the ligand choice, coordinate non-specific versus target-specific uptake [75]. Gold nanoparticles with or without PEGylation of varying sizes (50, 80, 100, or 150 nm) are used for active targeting of cancer cells. Generally, PEGylation increases blood circulation life-time and a specific ligand should facilitate filtration of nanocarriers into target cells. Two targeting molecules, folic acid (FA) and methotrexate (MTX) are specifically recognized by folate receptors that are overexpressed on the surfaces of many tumor cells [76]. Gold nanoparticles are not only convenient for cell-specific targeting, but also for localization into desired organelles. Recent research [77] proved that PEGylated gold colloids, functionalized with adsorbed protein, better detect a nuclear localization signal, for delivering drugs into nucleus' cells. Nanoparticles have been developed as a promising scaffold for implementing drug delivery release compared to traditional delivery vehicles. They combine low toxicity, high surface area and tunable stability provides them with unique properties such as bioavailability and nonimmunogenicity.

Drug delivery systems are obtained with biocompatible materials, sensitive to particular external physiochemical stimuli, able to release an active biomolecule in the target site and at an adequate rate in response to specific functions [78]. New smart polymers for the controlled delivery of therapeutic drugs have been developed in the field of polymer engineering. Their physical, chemical, and biological signals can be supported by external sources, employed as triggering stimuli, and they can be promoted by internal environment conditions [79]. Smart polymeric systems may be dissolved in aqueous solutions or maybe chemically grafted onto aqueous-solid interfaces, chemically bonded through hydrogen-bond systems, or by hydrogel formulations [80]. The desired pharmacological action is not achieved with the rapid release dosage forms, it is, therefore, very important to control the timing of drug release. The release times are established based on the nature of the drug: water-soluble drugs require a slower release and a longer duration of action; those lipophilic require an increase in solubility to have an adequate therapeutic level, those with a short half-life require repeated administration and, finally, those with indefinite action require delivery to the target sites. To receive the drug level required for treatment, the drug delivery system should deliver exact amounts of a particular drug at a planned rate. To design and implement this system, several factors must be considered, such as the physico-chemical properties of the drug, its route of administration and its pharmacological and biological effects [81]. Some advantages of controlled release systems are (i) the maintenance of drug levels within the desired range, (ii) the reduction of side effects, such as toxicity and frequency of administration, (iii) the improved efficacy [82]. The problems encountered in the use of these systems are due to the possible toxicity of the materials used, the need to operate through surgical procedures to insert or remove the system, possible poor availability of the system and high production costs [81]. New polymeric materials are currently being formulated, which respond to specific environmental changes in biological systems [83]. Stimulus reactive polymers mimic the behavior of biological molecules, thanks to external stimuli or changes in the local environment that can trigger a change in properties, such as solubility, shape, conformation, charge and size. Drug release could be regulated in spatial conformation by targeting and in time as a function of external stimuli [84]. The smart polymers,

doi:10.20944/preprints202104.0574.v1

currently under study, are classified into the following categories: pH and temperature-sensitive, dual stimulus reactivity, phase, light and biomolecule sensitive.

3.1 pH-sensitive smart polymers

The response to the pH changes of a polymer occurs through the protonation and deprotonation cycle of a polyprotic weak base and / or acid in block copolymers at different pH or by conformation changes [85]. Ionizable polymers with a pKa value between 3 and 10 are suitable for use in pH-sensitive systems. For this reason, groups such as carboxylic acids, phosphoric acid and amines, induce a change in the conformation of the soluble polymers and a swelling of the hydrogels. It is necessary to know the molecular mechanism of the translocation process in various pH environments, to overcome the barriers to the administration of drugs for the tumor and to increase the efficiency *in vitro* and *in vivo* [86]. Poly(ethylene imine) (PEI) is one of the best standards against which new polymers are tested, some other polymers include PAMAM dendrimers, poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMEMA), poly(L-lysine) (PLL), and modified chitosan. Polyacrylamide-g-polyethylene glycol (poly (AA) -g-PEG) nanoparticles have been used for the administration of oral insulin, acrylamide (AA) at a pH higher than its pKa value (4.5), ionizes becoming hydrophilic [79]. Chitosan is a biocompatible, pH-dependent cationic polymer that is soluble in water up to pH 6.2 [87].

3.2 Temperature-sensitive smart polymers

Temperature is an easily controllable condition, so temperature-sensitive smart polymers have practical advantages *in vitro* and *in vivo* [88]. Polymers with a low to medium critical solution temperature (T = 30/40 ° C) commonly dissolve in aqueous solvents, while polymers with a higher critical solution temperature (T> 50 ° C) better dissolve in organic solvents [89]. The drug may be released as a result of changes in body temperature following a fever or local infections. The sensitivity to temperature, in polymers, depends on the equilibrium between hydrophilic and hydrophobic portions, these intermolecular and intramolecular interactions lead to aggregation of the polymer chain [79]. Poly (*N*-isopropyl acrylamide) (PNIPAAm), is the most studied intelligent temperature-sensitive polymeric system. The solubility in water decreases drastically when heated to approx. 32 °C in pure water and a few less in physiological saline solution [80]. Gelatin and carrageenan are natural polymers that show a sol-gel transition and adopt an amorphous spatial conformation in solution at high temperatures, while during cooling, a continuous and homogeneous network is formed. The solubility of a polymer in water depends on factors such as temperature, molecular weight or the addition of an additive or co-solvent. The variation of the balance between the intermolecular forces causes the disassembly of the micelles, thus freeing the encapsulated host. This response can be induced from within, by exploiting the tendency of tumor tissues to have a slightly higher temperature, or by applying heat externally. Poly (*N*-isopropylacrylamide) (PNIPAAM) undergoes an abrupt phase transition at 32 °C and separates from the aqueous phase. PNIPAAM is non-toxic, and can be chemically adapted by changing the alkyl part or by copolymerizing it with other more hydrophilic monomers but it is not biodegradable. There are natural temperature-sensitive systems and they are suitable carriers. For example, collagen with glycineproline- (hydroxyl) proline (Gly-Pro-Pro (Hyp)) forms a triple helix. The Thermo-sensitive polymers can be classified according to the mechanism and the chemistry of the inner groups. These polymers solubilize many hydrophobic drugs such as paclitaxel and have an excellent formulation for poorly water-soluble drugs [79]. Micelles are formed when the concentration of the polymer is increased above the critical micellar concentration (CMC), then below the low critical solution temperature (LCST) the heat-sensitive polymer is hydrated and hydrophilic (Figure 4)

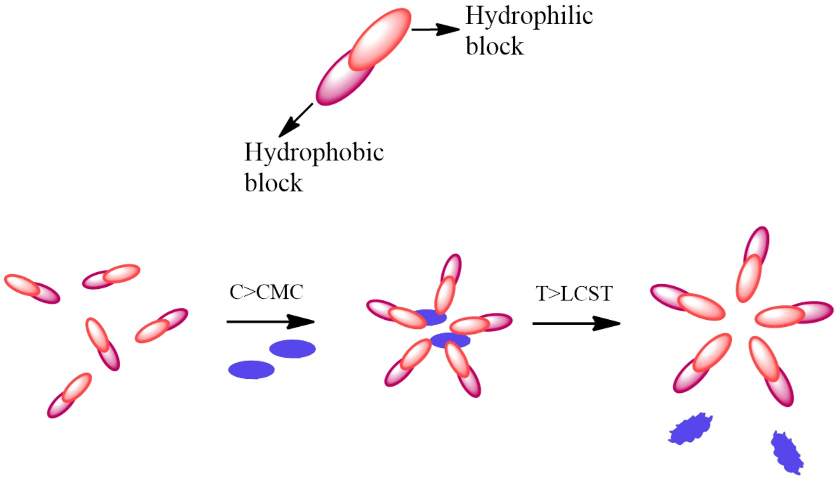

Figure 4. Scheme of behavior of thermo-responsive amphiphilic polymers

3.3 Phase-sensitive smart polymers

Release systems for biomolecules should preserve their biological activity and conformational stability. Intelligent polymer systems were tested that form *in situ*, injectable, phase-sensitive gels, potentially usable for drug delivery control. These injectable formulations allow single injections of high doses with small volumes and small needles and improve the stability of biomolecules. An instant gel forms *in situ* after these formulations are injected. The hydrophilic solvent causes the formation of a shell on the outside, while the hydrophobic solvent slows the penetration of water in order to decrease the hydrolysis of the polymer and potentially increase the stability of the biomolecules [90]. In these systems, drug release rates can be controlled by optimizing factors such as drug loading and solvent composition [91]. In drug delivery systems, the response to light can be introduced through a linker that can be cleaved by irradiation with electromagnetic radiation having a certain wavelength. Encapsulated hosts are activated or released after being irradiated with a radiant source from outside the body, resulting in a spatial and temporal release [92]. These polymers are designed for use in microsystems, medical imaging and tissue engineering. Photo-refractive polymers with near-infrared (NIR) sensitivity have also been reported, such as a matrix of poly (*N*-vinyl carbazole), *N*-ethylcarbazole as plasticizer and 2,4,7-trinitro-9-fluorenone (TNF) as a sensitizer [93]. These NIR-sensitive materials could be used to visualize tumors thanks to the different refractive index of tumors compared to that of normal tissues [82].

3.4 Light-sensitive smart polymers

Materials sensitive to harmless electromagnetic radiation (mainly UV, visible and near infrared radiation), could be used as drug delivery systems. Such materials, sensitive to light, trigger an irreversible change that causes the release of the entire drug dose, others are able to undergo reversible structural changes and behave as multi-switchable carriers, releasing the drug in a pulsating manner [78].

3.5 Biomolecule-sensitive smart polymers

Polymers that respond to biomolecules can provide high specificity, higher than those that respond to physical or chemical stimuli, therefore they are being studied in the context of Drug Delivery Systems. An example is glucose sensitive polymers, which use phenylboronic acid, glucose oxides or concanavaline A for the treatment of diabetes by administering insulin, which is regulated by a closed-loop feedback system, but the use of proteins such as glucose oxides or concanavaline has limitations. These proteins are difficult to immobilize, so they cause an uncontrolled release of host proteins. Furthermore, several monosaccharides could compete for glucose binding sites. Glutathione is another polypeptide that regulates cellular redox state [79]. For example, a hybrid hydrogel has been designed, integrating genetically modified calmodulin, which is capable of changing swelling based on the response of calcium ions and phenothianzines. These systems have the potential to be used in microfluidics and miniaturized drug delivery systems [94].

4. Flame retardant coatings

Among the various textile finishing, flame-retardant treatment is crucial as it directly relates to human health and hazards. At the beginning of the 21st century, the Earth's population annually experience a reported 7,000,000–8,000,000 fires with 500,000–800,000 fire injuries and 70,000–80,000 fire deaths [95]. Although sometimes it is not easy to discriminate whether a fire is the consequence of technical failure or human behaviour, statistics demonstrate that the presence of upholstered furniture and textiles is common in a domestic fire. According to the U.S. Consumer Product Safety Commission [95], fires involving residential upholstered furniture are the main reason for fire deaths in U.S. households, claiming 300 lives each year, causing 500 serious burn injuries and resulting in 1.6 billion dollars damages. For all the above reasons, most scientific community efforts have been addressed to investigate the flammability of textiles, fibres and fabrics [96].

Wool and silk as well as cotton and flax, as protein- and cellulose- based natural fibres respectively, are mostly used in apparels and home furnishings, due to their unique advantages, including biocompatibility, biodegradability, and hydrophilicity [97]. With the increasing demand for high-performance materials, to be used besides apparel and home-furnishing applications, also for the technical textiles market [98][99][100], thermoplastic synthetic fibres are also extensively used. Polyester, polyamide, acrylic, and even to some extent polypropylene, have dominated the fibre market since the mid-1990s when they overtook cotton volumes [43]. Among other criteria, a specific classification for textile materials distinguishes them according to their fire behaviour as melting or non-melting. For natural or artificial fibres, the heated material does not melt, but the breaking of a number of covalent bonds, with subsequent destruction of the structure and the formation of volatile products and carbonaceous residues occur. Even if the Limiting oxygen index (LOI) test does not provide a reliable indication of material performance in real fires, obtained values appear to be very sensitive to the composition of the material and therefore can be used to show the fire behaviour of polymers. LOI represents the minimum oxygen concentration that supports combustion of a material (ASTM D2863 and ISO 4589). Since air consists of about 21% oxygen by volume, any material with an LOI less than 21% can burn easily in air. As a consequence, a material with an LOI greater than 21% can reduce the flame after removal of igniting source. A number of research has shown that materials burning in the region between 21% and 28% can be referred as slow-burning materials, while materials with an LOI > 28% are generally flame retardant [101]. As the majority of the natural and man-made fibres has LOI values <25, there is a need for imparting flame-retardant finishes to make them suitable for various end applications requiring fire resistance.

Since their high flammability, if exposed to an irradiative heat flux or a flame without adequate protection, textile materials burn very easily, significantly limiting their use in those sectors where fireproofing is mandatory. In addition, during the combustion there is the generation of smoke that can further cause severe issues and restrictions in the use because of its toxicity.

In order to overcome this issue, in the last 100 years, different flame retardant finishes (FRs) have been developed with the aim of inhibiting or at least slowing down the propagation of a flame, were proposed [102][103]. Nowadays, some of these products are on the market with a high effectiveness according to the specific chemical and/or physical mechanisms that take place when FRs activate [104].

The key role in determining the way through which the FRs can be active in the gas or condensed phase is played by the chemical composition and the relative thermal and fire behaviour of the flame retardant molecules [104]. A fire-retardant product can contrast the combustion process, possibly stopping it, through mechanisms carried out in:

(a) Condensed phase, able to influence the substrate pyrolysis by the development of non-combustible gases and the formation of intumescent, which reduce the contact with the oxygen;

(b) Gas phase, working on the volatile fuel products and their interaction with oxygen, by introducing inhibiting factors (free radicals).

To make a compound resistant to flame it is necessary to well understand the mechanism of combustion, which occurs when, by supplying heat to a substance (solid or liquid), the energy required for evaporation or pyrolysis is reached and this, in the gas phase, combining with oxygen, it creates exothermic reactions that allow the maintenance of combustion itself [105]. There are essentially three ways to avoid this [106]:

i. use of additives that release radicals; [107]
ii. use of substances which give such endothermic reactions as to subtract all the heat necessary for the propagation of the reaction [108][109];
iii. intumescent substances (i.e. substances which after combustion form a protective solid layer, mostly carbonaceous, which prevents the exchange of energy and matter between the condensed phase and the gas phase) [110][111].

As happens in most cases, we try to make products in which the "active substances against fire" (flame retardants) are inserted directly into the polymers in the preparation phase, otherwise subsequently as coatings or fillers that possibly also possess more than one of the previously mentioned qualities: there are substances that release radicals by preventing the propagation of reactions and at the same time form a carbonaceous barrier that protects the underlying material by preventing its combustion. For example, during combustion, polymers binding pendants can also act as flame-retardants (FR) because of the energy needed for pendant removing and cross-linking hinder combustion. In fact, the fragmentation of polymer leads, starting from cross-linking, to the charring in four stages: i) cross-linking, ii) aromatization, iii) condensation of aromatics and iv) graphitization. In this way is built a barrier that prevents mass and energy exchange between the polymer surface and the gas phase in which radical reaction spreads up. This char wall avoids the pyrolysis of the combustible not only creating a physical medium that can't be passed through from the fragments of polymer but isolate the matter from the heat generated reflecting it outwards.

FR are more useful when directly mixed in the polymerization phase (covalently linked to the polymer) compared to additives one (fillers) that need higher concentrations to obtain same results; moreover, in this way, mechanical properties of the polymer are better maintained. Despite that, additives are more generally used because of their wider applicability and lower costs.

It is very important to optimally design an FR and consider his mechanism of action both from physical and chemical point of view. Regarding FRs physical mechanisms we can consider the following:

i. promote endothermic reactions;
ii. generate inert gases that dilute the concentration of the atmospheric oxygen;
iii. form a protecting impermeable coating.

Chemical mechanisms are mostly based on the inhibition of the oxidation reactions (gas phase) through trapping the free radical species involved in ($H^\bullet$ and $OH^\bullet$). Despite the great number of radical reactions involved in the gas phase combustion, it's important to focus our attention only on two of these reactions that are responsible one of the high speed of the process and the other of the energy released:

- $H^\bullet + O_2 \rightarrow OH^\bullet + O^\bullet$ (propagation stage)
- $OH^\bullet + CO \rightarrow CO_2 + H^\bullet$ (exothermic reaction)

There are three main families of flame-retardant chemicals [96]:

1. Inorganic flame retardants;
2. Halogenated flame retardants;
3. Phosphorus-based flame retardants, along with nitrogenous compounds due to their synergistic effect.

Several inorganic compounds are employed as flame retardants in fire retardant systems. Due to their characteristics, these chemicals have to be used in large concentrations or combined with other types of flame retardants to achieve desired results. For example, when applied alone, antimony oxide does not show specific flame retardant properties. Nonetheless, when combined with halogen-based flame retardants, it acts as a catalyst causing the bromine or chlorine to break down even faster. The result of this synergistic action involves the faster release of active halogen atoms able to remove the high energy radicals that feed the gas phase of the fire. Other inorganic flame retardants can be used independently, including aluminium and magnesium hydroxides. Both through the release of inert gasses (like water vapour) and energy absorption mechanisms, these compounds interfere with the burning process creating a protective char layer or reducing the fire's energy, respectively. In the past, halogens based polymers were a good choice because maintained, and in some case improved, mechanical properties of the treated materials, optimally performing this task (radical trapping). In fact, halogen-based polymers, in the flame, provide radicals that are less reactive than $H^\bullet$ and $OH^\bullet$ hampering flame propagation. Halogens have a great heat capacity and work as "heat sink" avoiding to provide the amount of energy necessary to the pyrolysis of the polymer and excluding oxygen from the surface of the polymer.

Although the halogen-based compounds, from a technical point of view, are the most efficient FRs, some of these chemicals (namely pentabromodiphenyl ether, polychlorinated biphenyls, and decabromodiphenyl ether) were banned since they have been proven to be persistent, bioaccumulative, and environmentally toxic for humans and animals [112].

Researchers have so moved towards other classes of compounds non-containing halogens. Phosphorus is an excellent candidate to substitute halogen-based polymers [113]. Phosphorus, as an FR, is highly versatile and covers a wide range of uses. Depending on its oxidation state and structure, it can be added as a filler or directly incorporated into polymer chains through homopolymerization or copolymerization [114]. Phosphorus exhibits (in the gas phase) free-radical trapping properties and act as heat sink inhibiting complete oxidation of C to CO_2 decreasing the energy released by combustion. Heat capacity, heat of vaporization and endothermic dissociation of P-based compounds occurring in the gas phase concur to the flame retardancy [115][116][117][118]. The most commercially used inorganic P-based compounds as FRs fillers are ammonium polyphosphate, phosphinates, phosphonates and phosphate esters; they act as intumescent forming a barrier between condensed phase and gas phase, protecting the former. Another class of P-based, phosphazenes, compounds has recently attracted researcher interest; they are synthetized as linear or aromatic derivatives, and shows interesting properties as FRs because synergistically combine the properties already mentioned of the P-based compounds with those of the N-based compounds which are described below [119][120][121][122][123].

FR treatments containing nitrogen arouse great interest because, unlike phosphorus, nitrogen is not an element among those considered to be depleted and makes the material more suitable for recycling. Among the FRs, N-based compounds are ones of the more environmentally friendly. N-containing FRs are very useful mainly in addition of polyamides and lesser extent with polyolefins (polyurethanes), but usually they are not much effective with another polymer alone [124][125][126][127]. One of the most used N-based compounds is melamine [128]: it is a very stable crystalline product (mp= 343 °C, 67% of N m/m) obtained from urea. Melamine sublimates at around 350 °C absorbing a great amount of heat and decreasing temperature of the surface of the matter exposed to fire. Under heating between 250 and 400°C, melamine decomposes in ammonia and forms cyclic compounds called melem, melam or melon, which constitute the surface layer of char [96].

In the condensed phase, nitrogen-based compounds promote the char formation. These are relatively stable at high temperatures and physically inhibit the decomposition of materials in flammable gas. Moreover, in the gas phase the nitrogen obtained by ammonia released at the pyrolysis temperature, dilute oxidizing and flammable gases. Although numerous studies referring to the synergism between nitrogen (N) and phosphorous (P) for flame retardant cotton treatments have been published so far, only a qualitative observation of this phenomenon has been argued. Indeed, some studies [129][130] have demonstrated that it is possible to identify a real synergism between two species only through the calculation of a synergism effectiveness parameter P-N. In some cases, the two species' effect can be merely additive or even antagonist [131].

Another class of FRs are intumescent products. Applied to materials, they are able to expand upon heating, forming an insulating fire-resistant layer at the treated surface, which protects it from further pyrolysis and burning. The result is a char residue with a characteristic foamy appearance [132][133]. Usually, intumescent systems consist of three components: i) an acid source (e.g. ammonium polyphosphate, melamine polyphosphate), ii) carbonization compounds (e.g. pentaerythrithol, phenol-formaldehyde resins, starch) and iii) blowing agents (e.g. melamine, guanidine, urea, chlorinated paraffin) [134]. During combustion, first (at lower temperature), acid sources decompose providing acids (inorganic acids overall) that react with carbonization compounds (generally polyols) dehydrating them and, rising up the temperature, blowing agents allow growing of char. The final volume of the char depends basically on the amount of developing gas and on the rheological properties of the forming char. In fact, more the char shows plastic characteristics more will have a considerable volume, hindering much better heat and mass transfer between condensed and gas phases. Intumescent system result to have an efficient fire protection, but their efficiency is related to their thermal stability and amount. To increase the performances of intumescent is possible to use synergists, both organics and inorganics [135].

In the field of nanotechnology applied to improve flame retardancy of materials, three approaches have exhibited the most interesting results [136][137]: a) the addition of nanosized particles in traditional back-coatings, b) the nanostructuring of the synthetic fibres, and c) the deposition of nanosized films.

For example, clays are utilized as nanofillers, enhancing chemical (forming aluminophosphate ceramic structures) and physical (superior char strength, better thermophysical characteristics) properties.

Also minerals can be used as FRs, overall metal hydroxides, borates and hydroxycarbonates [138][139]. During combustion, the metal hydroxides act as a heat sink by releasing H_2O, by evaporation, in the same temperature range as the polymer pyrolysis. Moreover, water vapors dilute combustible gases caused by polymer decomposition, leaving on the surface a nonflammable inorganic layer. Most used mineral FRs are $Al(OH)_3$ (hereafter ATH) and $Mg(OH)_2$ (hereafter MDH); endothermic decomposition of i) $Al(OH)_3$ occurs at 180-200 °C absorbing ± 1 kJg^{-1} of heat energy and of ii) $Mg(OH)_2$ occurs at 360 °C absorbing ± 1,3 Kjg^{-1} of heat energy. For a good FR behavior, ATH and MDH must be at least 60% of the total mass, but this negatively effects the polymer's mechanical properties. Better performances as FR have been reached from MDH when used as nanoparticles. Zinc borates in addition with inorganic additives, are used in combustion hindering; so $(x)ZnO \bullet (y)B_2O_3 \bullet (z)H_2O$ acts as: intumescents; heat-sink absorbing, 0,5 kJg^{-1} for its endothermic decomposition developing water and boric acid; forming a boron oxide layer that protects and isolates the surface of the matter [119]. Hydroxycarbonates are a family of inorganic FRs, specifically magnesium hydroxycarbonate known as hydroximagnesite ($3MgCO_3 \bullet 3Mg(OH)_2 \bullet 3H_2O$). This mixture of carbonate and hydroxide of Mg absorbs heat developing CO_2 and H_2O in a wide range of temperatures. In nature it can be found in mixed deposits with huntite ($Mg_3Ca(CO_3)_4$) [139] that shows higher thermal stability then the hydroxides, it is often used with the latter especially when the processing temperature of the polymer could decompose metal hydroxides.

Silicon-based compounds substantially reduce the flammability of polymers. They are employed as co- and stand-alone additives, also in a nanoscaled arrangement. When exposed to heat, silicon-based compounds decomposes leaving an inorganic silica residue on the surface of polymer, forming a barrier against mass and heat passages [140]. The most commonly used silicon-based FRs are polyorganosiloxanes, specifically polydimethylsiloxanes (PDMS). The choice falls on this category of compounds because of the Si-O-Si ether bonds; they are in fact enough strong and thermally resistant, but also flexibles, assuring good FR behavior and maintaining good mechanical properties too [141][142]. Often silicon-based polymers are not able to reach good performances to satisfy sufficient FR qualities, so they can be used in addition to other substances as kaolin, montmorillonite, talc, silica, mica, and other inorganic fillers that are added with. A better approach is to use polyborosiloxanes that provide a more cohesive ceramic layer to the surface, thus offering better protection against fire [143].

These act overall as physical barrier avoiding heat transfer to the surface of polymer and hence preventing pyrolysis. Si-based nanomaterials (clays), besides providing a protective layer, act as catalysts promoting char formation. The graphite char forming during combustion, and his effectiveness as FR, oriented researcher on testing carbon nanotubes on this application. Indeed, it appears that carbon nanotubes act as a mirror that reflects much of the electromagnetic radiation that accompanies combustion, protecting the underlying layers.

Due to the electrostatic attraction between positively and negatively charged layers on the surface's substrate in layer by layer (LbL) assemblies, [144] the resulting interactions are robust and independent from the substrate size and topology. Among several investigations reported in literature, Carosio et al. [145] exploited the LbL technique to improve the flame resistance and to solve the dripping of polyethylene terephthalate fabric. Tests, carried out according to ASTM D6413 standard, showed that the treatment reduced the burning time by 95 % and eliminated melt dripping phenomena.

Furthermore, in the last years, the sol-gel technique has been exploited in order to protect polymer surfaces with nanosized films exerting a thermal shielding effect, thus improving the flame retardancy of the treated materials [56, 57]. Generally speaking, the investigated coatings can be divided into two groups, namely: fully inorganic, and hybrid organic-inorganic systems. Concerning the sol-gel based fully inorganic coatings on cotton, the effect of the type of hydrolysable groups on the overall flame retardant features of cotton samples was investigated [146].

In particular, tetramethyl orthosilicate (TMOS), Tetraethyl orthosilicate (TEOS) and tetrabutylorthosilicate (TBOS) were utilized to develop silica coatings on cotton samples [147]. The findings observed by flame spread tests, realized in vertical configuration, confirmed a well-defined effect of the type and chain length of the alkoxy group in the precursor on the residue at the end of the tests. The longer the chain length of the precursor, the worse the overall fire performance.

Furthermore, when an organic component is combined into a sol-gel solution, or incorporated in hydrolyzed metal alkoxide precursors, the obtained finishes convey new fire-retardant properties to treated polymer surfaces. Indeed, in this composition, the hybrid organic-inorganic coatings show the properties of both phases or even new [148]. Therefore, the thermal stability at high temperatures proper of inorganic constituents can be combined, for instance, with the flame retardancy of organic phosphorus-based compounds. The concurrent presence of P and Si elements can be exploited for preparing hybrid organic-inorganic coatings that behave, at the same time, like char promoters (because of the phosphoric-acid source) and thermal shields (due to the inorganic component).

Among the most recent results obtained [104][148], some papers showed high flame retardant properties in treated cellulosic-based materials.

The combination of TEOS, sodium alginate and phytic acid resulted in a coating able to enhance the thermal stability of cotton, also suppressing smoke emissions [149]. Moreover, self-extinguishing cotton fabrics thanks to the deposition of a sol-gel precursor containing 3-glycidyloxypropyl trimethoxysilane modified with *N*-(phosphonomethyl) iminodiacetic acid, hydrolyzed and condensed in the presence of TEOS, were obtained [150]. The coating decreased the heat release rate, the peak of heat release rate, and total heat release values. At the same time, findings showed an increased time to ignition and a residue higher than 26% at the end of the combustion tests. Furthermore, flammability tests performed on fabric samples finished with 2,2-dimethyl-1,3-propanediol-(3'-triethoxysilanepropyl)phosphoramidite, a P-containing siloxane product, showed a considerable increase of LOI (30%) [151]. Treated fabrics exhibited high char-forming character, achieving self-extinction without afterflame or afterglow.

5.0 Industrial coatings

Industrial coatings play a key role in modern society, contributing significantly to our care, health and wellbeing. The protection provides by sealants, paints and other coatings preserves and extends the lifetime of buildings, transportation vehicles, industrial equipment and other infrastructure [152]. Many of the actual coatings for corrosion protection represent a threat to the environment. Therefore, the main strategy is the development of innovative materials with better performances and eco-friendly at the same time.

In recent years, the world of materials engineering was involved in developing new functional coatings to modify surfaces' properties through the sol–gel process. Silica – based nanostructured coatings are, indeed, one of the most advanced techniques employed in nanotechnologies [153]. This type of method, which leads to the formation of organic – inorganic hybrid coatings with a nanocomposite structure, can modify some properties of the materials under study, such as the resistance to abrasion, wettability, impart antibacterial characteristics and resistance features to UV radiation, in order to release bioactive substances [154]. Over time, the advantages of organic-inorganic hybrid materials were proved by several researchers, which established that these compounds are

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obtained from the structural incorporation of organic groups, such as, vinyl, acrylic, epoxy, amine etc., in the sol–gel precursors through Si - C bonds [154][155]. More in detail, the inorganic part is formed by alkoxides of silicon or other transition metals through a hydrolysis reaction, whilst the organic one is constituted by molecules, which can differ in their structure from the length and branching of the alkyl chains [156][157].

The inorganic moiety gives to the hybrid material some properties among which, hardness, chemical resistance and adhesion to the substrate, whilst the organic one provides elasticity, toughness and low curing temperatures [155][158]. Curing time and temperature, pH, aging concentration, molar ratio and nature of the precursors are all factors that contribute to the final chemical structure of the silane produced [155][157][159][160].

In literature, there are several works which explain different types of coatings and their applications as anticorrosion, anti-scratch, antiadhesive, antimicrobial, antifouling and self-cleaning coatings [161][162][163][164]. However, one of the most important research fields for these hybrid materials is the application of sol-gel coatings on metal surfaces or composite with the aim to work as a protective barrier against corrosive species or as a decorative agent, instead of chromates protective pretreatments, considered toxic and carcinogenic [165][166]. Moreover, the treatment of sol–gel hybrid coatings by doping with environmentally friendly inhibitory materials is a promising approach that prevents the corrosion of the substrate by improving its mechanical properties [167][168][169]. The hybrid material used as a coating for corrosion mitigation need to show resistance to the abrasion processes and good adhesion to the substrate surface, including copper [170], magnesium [163][171] and aluminium based alloys [172][173], stainless [174], galvanized [175] and carbon steel [176]. Generally, the organic-inorganic hybrid compounds, which are featured by covalent bonds between the organic and inorganic components (class II), show properties that are well suited to an anticorrosive product, such as good corrosion protection, good scratch resistance, good corrosion protection, high hydrophobicity and low dielectric constants [157][177]. In this paper, recent studies were reviewed to show how sol–gel surface functionalization with silica-based nanosols represents an important technology for a variety of applications in industrial coatings [153]. Table 1 summarized composite coatings features used to prevent corrosion in steel and metallic materials reported in the literature of the last 10 years.

Table 1. Different compositions fabricated on different metallic substrates by sol-gel method in corrosive NaCl media

Sol – gel coating	Additive agent	Substrate	Average Thickness	Ref.
GPTMS/TEOS	none	Carbon Steel	47.6 – 92.8 μm	[155]
GPTMS/TEOS/TETA	TETA	Mild steel	8 – 10 μm	[178]
TEOS/APTES	Caffeine	Mild steel	5 μm	[179]
Zeolite	X-type zeolite/polyaniline	Carbon Steel	Not reported	[180]
TEOS/TEMS	MMT + Basil extract	Mild steel	40 μm	[181]
GPTMS/TEOS	Silica NPs	Mild steel	20 - 40 μm	[182]
GPTMS/TEOS	AP / BPA + TPOZ (Zr^{4+})	Hot dip galvanised steel (HDG)	0.8 – 2.4 μm	[183]
GPTMS/TEOS	SiO_2 $Ce(NO_3)_3$	Aluminum Alloy AA7075	4.2 – 8.6 μm	[184]

DMDES/MTES	Not reported	Stainless steel AISI 304	580 – 760 μm	[185]
GPTMS/MTEOS	TiO_2 NPs	Aluminum alloy AA6061 –T6	2 μm	[172]
Zeolite / DMDMS/PTMS	None	Aluminum alloy AA6061	15.0 μm	[186]
GPTMS/MTEOS	Graphene Oxide	Aluminum alloy AA6061 – T6	200 – 300 nm	[187]
GPTMS/TEOS + Nanotubes Halloysite	Ce^{3+}/Zr^{4+}	Magnesium alloys AZ91D	3 - 3.5 μm	[163]
TEOS/VTMS	EDTPO	Aluminum alloy AA2024 – T3	145 – 200 nm	[188]
GLYMO/AMEO	Not reported	Mild steel	1.8 – 2 μm	[189]
GPTMS/TEOS	Silica/alumina NPs	Carbon steel	Not reported	[176]
TEOS/ MTES	ZrO_2 TiO_2	Stainless steel AISI 304	115 – 545 μm	[184]

[1] GPTMS = (3-glycidyloxypropyl)trimethoxysilane; TEOS = tetraethylorthosilane; TETA = triethylenetetramine; APTES = (3-Aminopropyl)triethoxysilane; TEMS = teriethoxymethylsilane; TMS = *N*-propyl-trimethoxy-silane; MTES = methyltriethoxysilane; GLYMO = Glycidoxypropyltrimethoxysilane; DMDES = dimethyldiethoxysilane; DMDMS = dimethyl-dimethoxy-silane; 1H,1H,2H,2H-Perfluorooctyltriethoxysilane; VTMS = vinyltrimethoxysilane; AMEO = Aminopropylethoxysilane; MMT = Montmorillonite; AP = mono-phenol; BPA = bi-phenol; TPOZ = Zirconium (IV) n-propoxide; EDTPO = ethylenediamine tetra(methylene phosphonic acid).

Figuera *et al.*, show the application of siloxane functionalized coatings on different metallic substrates and assert that most of them were used on aluminium and iron-based alloys [156][175][190]. The influence of the molar ratio of two compounds, generally (3-glycidyloxypropyl)trimethoxysilane (GPTMS) and tetraethylorthosilane (TEOS), on the structure of the molecular net produced by sol-gel technology for the protection corrosion coating were the main objectives of study by several researchers, as reported Alcantara *et al* [155]. Kirtaky *et al.* and Aparacio *et al.*, show a similar study employing Glycidoxypropyltrimethoxysilane (GLYMO) and Aminopropylethoxysilane (AMEO) for the first one and a mono-substituted methyltriethoxysilane (MTES) with dimethyldiethoxysilane (DMDES) for the second one as precursor materials [189][185]. Over time, the sol – gel coating techniques have evolved with the implementation of synthetic or natural inhibiting agents into the hybrid matrix [191]. In this regard, Balan *et al.* claimed that nanoparticles added in the silane sol – gel networks can improve corrosion resistance [192]. They evaluated the electrochemical corrosion resistance of low carbon steel coated with hybrid organic-inorganic sol-gel film, made by 3-glycidoxy-propyl-trimethoxy-silane (GPTMS) and tetra-ethyl-ortho-silicate (TEOS) precursors and filled with silica or alumina nanoparticles [176]. A similar study was performed by Vivar Mora *et al.*, which assessed the impact of silica nanoparticles on the morphology and mechanical properties of a GPTMS/TEOS sol – gel coating [182]. The authors observed that features, such as hardness, elastic modulus, brittleness and fracture toughness, were improved when the mild steel surface was treated with silica NPs, leading to a more durable and corrosion resistant coating. The influence of nanoparticles in the synthesis of industrial coating was also evaluated by Rivero *et al.*, which doped layers of a sol – gel hybrid matrix (GPTMS/ MTES) with TiO_2 NPs deposited on flat samples of aluminium alloy [172]. Hybrid silica sol – gel coatings (GPTMS/TEOS) doped with cerium nitrate were synthetized and characterized by Tringer *et al.*[184]. The authors revealed that $Ce(NO_3)_3{\cdot}6H_2O$ encapsulated into the sol – gel matrix together with silica particles affect the corrosion properties of the coating improving the material resistance (Aluminium alloy). The enhancement of this feature was attributed to the combination of the silica matrix hindering properties with the active protection of $Ce(NO_3)_3$. In order to obtain coatings with better anticorrosive properties, Adsul *et al*., investigated the effect of Ce^{3+}/Zr^{4+} corrosion inhibitors loaded into halloysite nanotubes dispersed in a GPTMS/TEOS sol – gel matrix on the corrosion resistance. The studies were conducted on magnesium alloy substrates and demonstrated how these cationic inhibitors prolonged corrosion protection [163].

The evaluation of anticorrosive properties of hybrid sol – gel coatings hosting graphene oxide as corrosion inhibitor was presented by Maetzu *et al*., which demonstrated the protective power enhancement when these formulations are applied to aluminium alloys [187]. The use of graphene oxide can be exploited for the design and the application of novel multi-layered coatings in the engineering fields. However, silica or aluminium nanoparticles, as well as the other doping agents mentioned above, are not the only inhibitor agents that contribute to favouring the protective action of sol – gel matrix.

Dalmoro *et al.* examined the effects of the ethylenediamine tetra(methylene phosphonic acid) (EDTPO) addition to a hybrid sol–gel matrix prepared with vinyltrimethoxysilane (VTMS) and tetraethylorthosilicate (TEOS) [188], whilst Peerin *et al*., studied the influence of triethylenetetramine (TETA) in GPTMS/TEOS sol – gel formulations [178]. In the first case, the results evidenced the formation of Si-O-Al and P-O-Al bonds in VTMS/TEOS/EDTPO system, which were considered responsible for the good anticorrosive behaviour. In the second case, the presence of TETA in the sol – gel matrix led to the formation of interconnected epoxy-amine and silica networks, acting as a catalyst for the condensation of GPTMS and TEOS, as well as an improver of barrier proprieties. Moreover, considering the research works in which organic compound was employed for the preparation of industrial anticorrosive coatings, Agustín-Sáenz *et al.* proposed the incorporation of mono-phenol (AP) and bi-phenol (BPA) organic precursors in an epoxide functionalised-silica-zirconia matrix, in order to obtain a sol – gel coating material with higher corrosion protection for zinc-coated steel [183]. In this work, sol – gel matrix containing AP and BPA showed improved corrosion protection properties owing to the formation of a highly cross-linked network due to the organic compounds, which act as a bridge between the epoxide functions of two GPTMS molecules.

Duran *et al*., reported a review in which structure, properties and features of coatings produced in the first decade of the 2000s were discussed. They assert that good oxidation resistance was achieved using mixed or hybrid organic - inorganic SiO_2 layers. In particular, the authors referred to alkylalkoxysilanes linked to polymerisable groups for the coating synthesis and the alternative use of a doping agent, such as an environmentally friendly inhibitors, to improve the corrosion resistance [167]. In this regards, a novel practice to replace high volatile organic content coatings consisting of toxic agents, such as hexavalent chromium compounds, was the use of water-based coatings modified with green active agents. Izardi *et al*., as well as Hamidon *et al*., proposed sol – sol gel formulations treated with aqueous – based basil extract and caffeine, respectively [181][179]. The results obtained by Izardi *et al*., confirmed the precipitation of basil-containing thin film on the mild steel specimens, which led to an improvement towards corrosion processes. In addition, Hamidon *et al*., asserted that caffeine – doped silane coating offered a high corrosion resistance for mild steel samples.

Finally, some researcher, such as Abdelaziz *et al*. and Calabrese *et al*., studied new anticorrosion coatings, exploiting the high chemical affinity of a zeolite filler with the silane matrix [180][186]. Nowadays, the research on innovative materials has also focused on developing sol – gel based coatings for the construction, finishing and decoration of structural materials different from the steel, such as Portland concrete.

In this regard, sol – gel technique represents a possible method to improve the high- temperature resistance on cement composite. As it is well known, cement is an inorganic binder, which is featured by high strength and fast hardening, but if it is subjected to high temperatures or some of other external agents, such as an acid attack, its structure undergoes several cracks and even burst in extreme conditions, losing its structural role quickly. The most commonly reinforced material is steel fibre, but it easily undergoes deterioration over time [193]. In the light of these considerations, Xu *et al.*, show an improvement of the resistance to high temperatures when Portland cement is filled with a carbon fibre felt and treated with an Al_2O_3 sol – gel coating [194]. Moreover, it is possible to treat cementitious material with functional TiO_2 coatings, as reported by Costantino *et al*. [195]. The authors evaluated the photo-activity the hydrophilic properties of the material under study, before and after the TiO_2 thin film deposition.

Further investigations on new corrosion inhibitors encapsulated in a sol – gel matrix should be performed. Smart coatings with self-healing properties are the possible materials of the future in this field. The self-heling properties of an organic – inorganic hybrid coating achieved with the incorporation of additive agents, lead to the reinstatement of the material structure and restore the protective coating wholeness, due to external factors (e.g., pH, UV, the presence of Cl), by avoiding the initiation of the corrosive process.

6. Nano/Ultrafiltration Membrane Coatings

Membranes for Nanofiltration (NF) and ultrafiltration (UF) processes in the water treatment field are employed to remove the most common organic and inorganic contaminants (e.g. natural organic matter, pharmaceuticals, inorganic salts, organic dyes) with high efficiencies, through different removal mechanism like electrostatic repulsion, size/steric exclusion, hydrophobic adsorption etc. [196][197][198][199].

The major problem of this technology, mostly in low-pressure processes, is the membrane fouling that negatively affects membrane performance. In recent years, a proposed solution to reduce the membrane fouling, improve their durability, selectivity, retention, and permeate flux, consists in the surface modification of membranes. This can be easily done using coatings that represent the most efficient approach, because of its easy processability, which involves chemical modifications to change surface properties of membranes. In particular, membranes coatings based on nano-sized materials like graphene oxides (GOs), carbon nanotubes (MWCNT), and titanium dioxide (TiO_2), thanks to their higher hydrophilicity and the capacity of reduce pore size and increase charge effects of membranes, represents a technology of growing interest in the water treatment field.

GO nanosheets coatings for membranes have good chemical stability, exceptional transport properties, and excellent mechanical stiffness and strength; in particular, the nanochannels of GO sheets 1-nm wide, by a sieving mechanism, can reject larger molecules when the water passes through the membrane filter [200][201][202].

Some studies have reported the removal of several contaminants by GO membrane in combination with polymeric membranes like polyvinylidene fluoride (PVDF), polysulfone (PS), polyamide (PA), or poly(ether sulfone) (PES), fabricated with various methods in which GO layers are bonded or unbonded together (Figure 5).

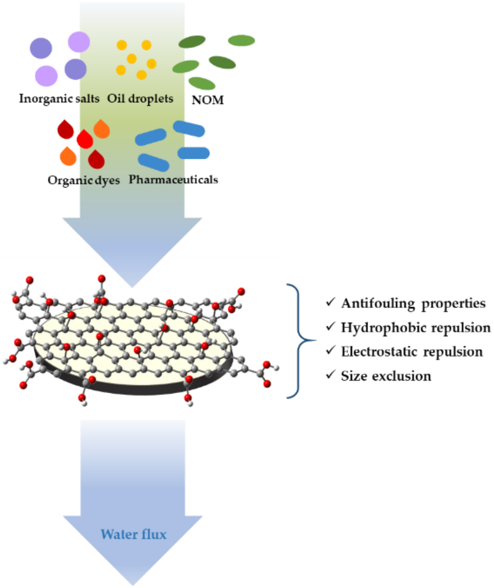

Figure 5. Schematic representation of water contaminants retention of GO coated UF membrane.

GO membrane supported on microporous substrates of PVDF exhibit high rates of rejection for organic dyes methylene blue and Rhodamin WT, under a transmembrane pressure of 50 psi (0.34 MPa), in a range of 46–66% and 93–95%, respectively and NaCl and Na_2SO_4 in a range of 6–19% and 26–46% respectively, depending on the specific number of GO layers deposited [203]. Also ceramic membrane coated with GO, at the expense of a low water permeability compared with the pristine membrane, show retention efficiencies of NOM (natural organic matter, humic acid and tannic acid), pharmaceuticals (ibuprofen and sulfamethoxazole), and inorganic salts (NaCl, Na_2SO_4, $CaCl_2$, and $CaSO_4$), in the order of 93.5%, 51.0%, and 31.4% respectively, much higher than the pristine membrane [204]. Moreover, the abundant oxygen-containing functional groups feature of GO (carboxyl, carbonyl, hydroxyl and epoxy, distributed at edges and structural defects of GO flakes), which causes a high negative charge on the surface of the membrane, enhance the hydrophilicity, retention, and antifouling properties. Multiple layers of graphene oxide (GO) coated on PES ultrafiltration membrane obtained via vacuum filtration of a GO suspension, exhibit a NOM rejection in the order of 31-67%, based on the number of GO layers coated, and a water flux change of the permeate less than ±10% [205]. GO coated UF membranes, thanks to their underwater superoleophobicity and low oil-adhesion, are very effective in oil-in-water emulsion separation and the removing of oil droplets with sizes in the micrometer range, to obtain water with low oil/grease concentration. Porous polyamide (PA), with 200-nm 3D pores, coated with GO by vacuum filtration for antifouling oil/water separation, show an excellent antifouling performance thanks to the low oil adhesion on the membrane surface, resulting from the optimized micro-/ nano-hierarchical roughness of the GO in particular with a 10 nm thickness and exhibit a 100% recovery by surface water flushing [206]. The underwater oleophobicity of GO sheets can be tuned by oxidative etching with ultraviolet (UV) light, to create or enlarge structural defects and introducing oxygen groups around them, to improve potential applications of GO coatings in oil/water separation, oil-repellent materials, microfluidic devices, anti-bioadhesion materials, and robust antifouling materials [207].

The most common fouling agents in water, present a negative charge, so they are sensitive to a negatively charged membrane surface due the electrostatic repulsion, as we have seen in the case of a GO coated membrane. Are developed several methods to enhance the surface charge of membranes, one of them is the fabrication of electrically conducting membranes (ECM) to perform electrofiltration processes by the application of an electrical field. This type of membranes can be produced by coating UF membranes with conductive inorganic materials like carbon nanotubes (CNTs) or multiwalled carbon nanotubes (MWCNTs), that can also be used as inorganic fillers to fabricate nanocomposite membrane, to improve their performance also for desalination of water [208]. CNTs and MWCNTs before their use in the fabrication of nanocomposites or coatings for their application in membranes, are treated by acid treatment, that however can lead structural damage of MWCNTs, or by coatings with some molecules like poly(vinyl alcohol), polyaniline or polydopamine, to enhance their hydrophilicy [209]. An example is represented by a thin film made by cross-linked poly(vinyl alcohol) and carboxylated MWCNTs, deposited by pressure on a PS membrane. This system, used in an electrofiltration cell, in which a cell potential of 3–5 V and fields of 9–15 V/cm are applied, demonstrates the inhibition of a negatively charged fouling agent, represented by alginic acid, and the potential of CNT based coatings on the reduction fouling rates [210]. Also composite membranes based on CNT-conjugated polymers (i.e., PANI, polypyrrole), fabricated through a process of electropolymerization of aniline on a CNT substrate under acidic conditions, the latter obtained by a coating of a PS membrane with a CNTs suspension performed by pressure deposition, demonstrate that the application of an anodic potential to the ECM surface, is able to degrade a model organic contaminant (methylene blue) through an Electro-Oxidation process, also showing an electrochemical *in situ* membrane cleaning capacity [211]. To reduce membrane fouling by photo-oxidation, there is another solution that can be represented by the use of Titanium dioxide coatings. Photoactivity properties of the semiconductor Titanium dioxide, exhibiting under UV irradiation, can be exploited for the photodegradation of smaller organic molecules entrapped in UF membranes. In particular, photoactive anatase membranes on asymmetric ceramic supports, prepared by slip-casting on asymmetric tubular supports in alumina, subsequently immersed in nanocrystalline anatase sols, shows a high retention capacity of colloids and macromolecules, ensured by the separative top layer and the photodegradation of smaller organic molecules performed by UV irradiation of the opposite side of membrane [212].

Manganese oxide and iron oxide coatings for catalytic membranes are also evaluated for the retention and removal of total organic carbon (TOC) in ultrafiltration processes, that is proven to depend from the number of times the membrane was coated with the metal oxide nanoparticles. This type of membranes is produced by coating, using a layer-by-layer self-assembly technique, of commercial UF ceramic membranes, that can also be cleaned from fouling with DDI water using an ozonation-filtration. Hybrid ozonation-ceramic membrane filtration performed with Mn oxide-coated membranes, have given the best results in comparison with other metal oxide coatings (titanium oxide and iron oxide), thanks to the excellent catalytic properties of manganese in the oxidation of organic material and then in the reduction of TOC in the permeate [213].

Another application of metal coatings in filtration techniques, is their use as metal mesh coatings for application in oil/water filtration. An example is an eco-friendly iron-based, with a micro/nano-structure, metal mesh coating, produced by immersion of a stainless steel mesh in a solution in which is performed the reduction of $FeCl_2$ with $NaBH_4$, resulting in a membrane with underwater superoleophobicity, with oil contact angle as major of 152°, that can separate oil/hot corrosive water mixed liquid efficiently, with a separation efficiency > 96.2 % [214].

A further approach of water filtration in water treatment processes, consists in the use of other types of membranes like chemically-functionalized membranes (CFMs), in which are incorporated selective ligands or ion-exchangers for the extraction specifically chemical species, bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs), supported liquid membranes (SLMs) in which two aqueous phases (feed and stripping) are separated by an organic liquid as interphase and polymer inclusion membranes (PIMs). PIMs, more stable than SLMs, have acquired significant importance in recent years in the field of separations and extraction of organic molecules and metal ions (Au(III), As(V), Cd(II), Co(II)) from water [215]. This type of membranes also has an important relevance in the preconcentration of antibiotics (sulfonamides and tetracyclines), which is highly influenced by sample pH, in environmental water samples [216]. PIMs are thin, flexible and stable films made by casting a solution containing an extractant (or carrier), usually an ionic liquid for the selective extraction of the target chemical species, a plasticizer to improve the elasticity of the membrane or modify the solubility of the extracted species and a base polymer such as cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) [217]. The extractant agent in PIMs can also be represented by inorganic species that have a high capability of ion exchange and cation fixation like clays, in particular montmorillonite clay [218]. A PIM membrane based on PVC, whit montmorillonite and ionic liquids (Aliquat 336, Alicy and thiomalic acid) like extractant and plasticising agents, for the absorption and preconcentration in particular of Sn^{2+} from water samples, can be produced in two different methods: casting the clay modified with organosilanes (by a sol-gel method with Dynasylan and APTES) in the solution of membrane (*one pot* method) or by coating the PIM membrane with the organoclay (*layer by layer* method).

The research of new technologies for the improvement of retention and regeneration properties of membranes in the waste water treatment, is constantly expanding, but strong evidence, as reported above, shows that the simplest and most efficient methodology for changing the surface properties of membranes, is represented by the use of membrane coatings based on various nanomaterials, which in particular allow easy cleaning, through simple washing or electrochemical methods, from fouling or oil residues for their reuse, in a circular economy perspective.

7. Antifouling coatings

Preventing the growth of microorganism on several surfaces, namely known as biofouling, is one of the crucial application of nanocoatings. Over the years, it has been a significant challenge in the design of antifouling coatings owns to the diversity of fouling organism and their adhesion mechanism [219]. The term fouling generally refers to an undesirable process in which a surface becomes encrusted with material from the surrounding environment. In the case of biofouling, that material consists of organism and their by-products. The marine biofouling process starts from the moment the surface is immersed in water and takes place in distinct steps of growth [220] as follows:

i. Adsorption of organic molecules such as proteins, polysaccharides and glycoproteins that form a conditioning film.
ii. Primary colonization with a settlement of microorganisms such as bacteria and diatoms, by creating a biofilm matrix.
iii. Secondary colonization consisting mainly of a biofilm of multicellular species (e.g., visible algae and invertebrates) generally called microfouling.
iv. Tertiary colonization including macrofoulants, which consists of, shelled invertebrates like barnacles, mollusks and sponges.

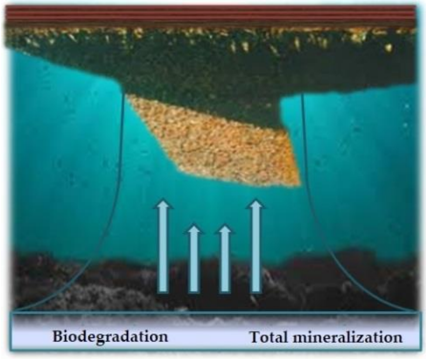

Figure 6. Illustration of undesirable accumulation of marine biofouling on artificial surface immersed in seawater.

The unwanted adhesion of microorganism (Figure 6) may affect the performance of devices, causing several problems for marine industries due to corrosion and hydrodynamic drag, which leads to elevated fuel consumption and, consequently, to higher maintenance costs. In view of the variety of problems biofouling poses, altering the surface properties of substrate via molecular engineering is essential. In addition, this biofilm can lead to microbially induced corrosion (MIC) due to H_2S formed by the bacteria, especially sulfate-reducing bacteria, creating surface cracks and leading to stress corrosion and potential release of products into the seawater. The search for solutions to these problems stimulated extensive research on coatings, which prevent and control biofouling known as biocidal and non-biocidal coatings. In the middle 19th century, most of the control procedures involve paints with dispersed chemical biocides, i.e., toxic compounds for the marine biological organisms. Biocide-based antifouling coatings function by slow leaching of the incorporated biocides into the coating. It is important that the biocide does not have any adverse effects on marine life while carrying out its antifouling activity. For example, historically, tributyltin

(TBT) represents the easiest and cheapest biocidal agent to prevent the growth of biofilms because of its excellent antifouling efficiency and its wide-range activity, but it is no longer used due to its toxicity. Basically, the use of triorganotin derivatives seemed to be the answer to the several problems of the biofouling effects until environmental concerns with TBT started to be raised. For this reason, TBT-based AF coatings were banned worldwide in 2008 as a follow up from an International Convention [221]. After the ban of tributyltin due to the harmful effects on the marine organisms, copper-based paints were applied in marine antifouling applications. However, the short-time activity of the coatings and the risk of heavy metal ions leaching and bacteria resistance directed the researchers to look for alternative approaches; In this scenario, intense research started to be aimed toward the development of environmentally benign and economically AF alternatives systems able to inhibit bacterial settlement like biocides used to [43][44][46][30]. In view of the time-being societal expectation of using new clean, flexible and effective products respect to the above-mentioned unhealthy ones, the sol – gel coating technology is probably one of the most important platforms for the development of eco-friendly antifouling and fouling release formulations [222]. By the way, silane-based coatings have been widely used in biofouling mitigation treatment of different surfaces, providing a non-toxic alternative to biocidal-based AF coatings [223]. Depending on the appropriate choice of the silica precursor and its related characteristics, the sol – gel technique offers the possibility to create hybrid nanocoatings within which it is possible to include substances that are able to introduce specific potentialities such as antibacterial, self-cleaning or water repellency activity [43]. In this context, the sol – gel nanotechnology can be an excellent tool to convey new properties to surfaces and to combine different functionalities in a single material, contributing for example to obtainment of low fouling surfaces thanks to the unique structure and properties of hybrid inorganic-organic silica-based coatings. Application of nanotechnology has been proven to effectively improve the anti-bacterial properties and the high durability performance of the doped-silane coatings, thanks to the nanomorphology of the filler used. According to literature, in fact, a number of antifouling products have been developed by using micro-encapsulation of inorganic biocides such as a silver oxide (AgO), zinc oxide (ZnO), copper oxide (CuO), titanium dioxide (TiO_2) and selenium. Based on different analysis, the AF effects of the metal oxide can be attributed to the reactive oxygen species (ROS) produced by photocatalysis and to the slow release of toxic metal ions when the metal oxide nanomaterials are exposed to visible light irradiation [224]. Among these, ZnO has largely been used as an antimicrobial agent since it showed the strongest and the most versatile antimicrobial activity against several marine fouling bacteria. The AF mechanism is still not very clear, but three different mechanisms of the action of ZnO are proposed: (1) the micro/nano-topography of the coatings; (2) the toxicity of Zn^{2+} ions released from the coating, which binds with the bacteria, affecting the bacterial growth cycle and (3) the above-mentioned production of reactive oxygen species (ROS) under an appropriate environment. ZnO nanoparticles and nanorods coatings are attractive due to an easy and controlled sol-gel process of fabrication and because of their increased stability and lower toxicity [225]. In fact, due to the slow release rate of zinc ions, no harmful effect was detected on the non-target organism. In addition, zinc is an important constituent of DNA and RNA polymerase enzymes which is essential for fish growth [226]. Titanium dioxide nanoparticles represent another common antifouling agent, which is not only cost-effective, but also non-toxic to the marine organisms. Bactericidal nanocoatings can also be included light-activated photocatalysts such as TiO_2 or other photosensitizers activated by light irradiation with appropriate wavelength to kill the bacteria. The main mechanism is the production of reactive oxygen species (ROS) such as superoxide anion (O_2^-), hydroxyl radical (OH•), and phototoxic singlet oxygen ($^1O_2^-$) under light irradiation providing antibacterial properties [227]. Due to the limitations involved in the use of biocides in antifouling marine systems, several technologies have been developed to produce new coatings aimed to interfere directly with the adhesion of microorganism as a result of topography or surface chemistry. Many attempts have been made by reducing the critical surface tension using fluoropolymers combined with silicones. Moreover, deepen research has also been made on the development of hydrophobic surface able to inhibits the initial step of microfouling settlements [228]. Fluoropolymers can be successfully used to form anti-adhesion surfaces by virtues of exposed CF_2 and CF_3 groups at the interface that can reduce the attachment of fouling, depending also on the degree of mobility of the fluorine atoms [229][230]. These fluorinated coatings, in addition to having low adhesive properties, show a good antimicrobial activity towards different kind of bacteria. Moreover, the eventual biocide effect due to the product release in the liquid medium evaluated by microbial cell experiments showed no biocidal effects [223]. However, besides the high cost of fluoropolymer-modified silicons, this non biocidal approach is only effective for vessels cruising at relatively high speeds and that are not inactive for a prolonged period. Of course, the low efficacy of these coatings has limited their use on a larger scale. In the last few years, researchers have been trying to produce new nanostructured surface simply taking inspiration by the natural antifouling behavior of some marine organisms. The surface roughness of sharks, for example, allows them to remain free from fouling and the antifouling mechanism is based on the reduced number of available attachment sites by weakening attachment strength when the surface is subjected to hydrodynamic forces [231]. Despite designing/reproducing the marine antifouling systems based on surface texture has been successful, it still needs more careful experiments to investigate. Based on all these considerations, it seems that a one-dimensional approach could not be enough for inhibiting the attachment and growth of all the organisms implicated in marine biofouling. In this regard, the best way to develop more promising antibacterial nanocoatings with a higher performance consists of combining different approaches in order to achieve synergistic effects, for example combining nano surface roughness together with amphiphilic or zwitterionic surface chemistry to act on the bioadhesives.

5. Conclusions

This review describes the synthesis of different type of nanostructured coatings and surface finishing, the related properties and the most important applications. The published results show that the potentiality of smart materials in the development of advanced, reliable and robust wearable sensors and several innovative applications would be the result of the combination of smart coatings, textile fabrics and microelectronics.

The use of polymers or nanomaterials in drug delivery systems finds the main application in the medical sector, in particular in cancer diagnostics and therapy and in traditional oral delivery systems. The combination of different nanocarriers, which exhibit different responses to external stimuli, can, in some cases, enhance the desired effect or influence each other in the desired way. Nanomaterials are the most promising materials also regarding flame retardancy. Despite of their nano dimensions, nanoparticles have a great superficial development, providing high results with a low amount of matter.

The recently described literature highlights also the characteristic proprieties of sol – gel materials and their possible employment in coatings for corrosion mitigation on different metallic surfaces or structural consolidation.

The simplest and most efficient methodology to modify the surface properties of membranes and thus improve the retention and regeneration properties of membranes in wastewater treatment, involves the use of membrane coatings based on nanomaterials.

The availability of prototypes as concrete results of the multidisciplinarity in nanotechnological sectors highlights the innovation of such advanced materials in daily life, the effects on modern society in terms of costs and quality of public health, as well as the importance of even more advanced research activity in this research field. In this panorama, even if significant improvement has been provided by the more recent smart textiles, several challenges should still be addressed. Besides the fabrication cost and the lack of standards, a relevant challenge could be represented by the total integration of electronics in textile polymers for application fields like wound monitoring and healing, and surgery.

There are different scientific and technological questions, which have not been figured out yet, such as coatings nanostructure and their thermal stability conditions. Although these questions, experiments indicate that nanostructured coatings present powerful technological potential and important industrial progress.

Author Contributions: Conceptualization, I.I, V.T., S.S., GI.R., F.G., G.R., M.R.P.; methodology, M.G.; software, I.I, V.T., S.S., GI.R., F.G.; validation, M.G., I.I, V.T., S.S., GI.R., F.G.; resources, G.R. M.R.P.; data curation, I.I., GI.R., S.S., F.G., V.T.; writing—original draft preparation, I.I, V.T., S.S., GI.R., F.G., G.R., M.R.P.; writing—review and editing, G.R. and M.R.P.; supervision, G.R., M.R.P.

Funding: This research received no external funding.

Acknowledgments: MURST, CNR and MUR are gratefully acknowledged for financial support. The authors are grateful to the projects "AGM for CuHe: Advanced Green Materials for Cultural Heritage (grant number: ARS01_00697)" and "Thalassa -TecHnology and materials for safe Low consumption and low life cycle cost veSSels and crafts (grant number ARS01_00293)" within Programma Operativo Nazionale "Ricerca e Innovazione" 2014-2020 (PON R&I 2014-2020), and to the P.O. FESR SICILIA 2014/2020 projects n. 08CL4120000131 - SETI (Sicilia Eco Tecnologie Innovative) and n. 08ME7219090182 "SI-MARE - Soluzioni Innovative per Mezzi navali ad Alto Risparmio Energetico – CUP G48I18001090007. S. Sfameni and G. Rando are grateful to CNR and Noxorsokem Group S.r.l., and to PON-MIUR 2014-2020 - "RESTART" project, respectively, for their Industrial PhD funding.

Conflicts of Interest: The authors declare no conflict of interest.

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