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Review

Carbon-Based Coatings in Medical Textiles Surface Functionalisation: An Overview

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Abstract: The COVID-19 pandemic has further highlighted the need for antimicrobial surfaces, especially those used in a healthcare environment. Textiles are the most difficult surfaces to modify since their typical use is in direct human body contact and, consequently, some aspects need to be improved, such as wear time and filtration efficiency, antibacterial and anti-viral capacity, or hydrophobicity. To this end, several techniques can be used for the surface modification of tissues, being magnetron sputtering (MS) one of [hose that have been growing in the last years to meet the antimicrobial objective. The current state of the art available on textile functionalisation techniques, the improvements obtained by using MS, and the potential of diamond-like-carbon (DLC) coatings on fabrics for medical applications will be discussed in this review in order to contribute to a higher knowledge of functionalized textiles themes.

Keywords: magnetron sputtering; medical textiles; DLC; antimicrobial

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1. Introduction

Infections have been a major source of concern for human health in recent decades, and as the globe becomes increasingly linked, this threat is no longer speculative but very real. Pathogens that may spread from person to person are more likely to produce a global epidemic, and the COVID-19 pandemic is a great illustration of this problem [1]. The best way to prevent an infectious disease spread via respiratory means, when social distancing is not possible, is the use of personal protective equipment (PPE). PPEs, like masks, aprons, gowns, coveralls, goggles, and respirators, are considered critical components that can be used to protect not only healthcare workers but also the general population from droplets infected with a virus/bacteria originating from infected people when sneezing and coughing, besides contaminated surfaces [1,2]. In addition, numerous pathogens, such as fungus, bacteria, and viruses, can be present in hospital facilities. These pathogens can be transported by any person that frequent this kind of facility, being transmitted through three ways: respiratory droplet transmission via the infected person when talking, sneezing, or coughing; indirect or direct contact with an infected person; and airborne transmission [1–3]. It is expected that by 2030 the healthcare industry worldwide will employ around 80 million people, putting a huge amount of healthcare workers at constant exposure to fungi/bacteria/viruses and exposed to infections while treating people with highly infectious diseases [2]. PPEs like surgical masks and medical clothing are crucial to offering a barrier to users and the environment [2,3]. The emergence of drug-resistant microorganisms is another issue that has been seen in hospital settings. Microorganisms, for instance bacteria, play an important role in the global cycling of elements, having a profound impact on the environment in which they live. However, they are also susceptible to the environment, which means that when they come into contact with antimicrobial elements, some microorganisms may develop resistance to them, resulting in the emergence of "multi-drug-resistant" bacteria [4].

When considering masks, several options are available, such as basic cloth face masks (possible to be homemade), surgical face masks, and respirators [4]. A few properties have to be taken in consideration when evaluating masks' performance: comfort, breathability, biocompatibility, fluid resistance, flammability, and filtration efficiency [1,2]. It is with those properties in mind that the masks recommended to use are manufactured. Basic cloth face masks/homemade face masks are the simplest types of masks, with an efficiency highly dependent on the materials used [4–6]. Surgical masks are disposable, and their structure is composed of three layers of non-woven textile, having one specific function [1]. The external layer has hydrophobic characteristics, helping in repelling fluids (for instance, mucosalivary fluid). The intermediate layer acts as a filter with the main purpose of avoiding the penetration of unwanted elements (for instance, dangerous particles or pathogens). The internal layer is produced with an absorbent material to absorb the mucosalivary fluid expelled by the user and moisture of the exhaled air [1]. There are also respirators, which are built with a structure of four layers of filters. Both the external and internal layers (made of non-woven polypropylene (PP)) act as hydrophobic layers, helping to avoid the moisture absorbed by the respirator. The intermediate layers' function, on the one hand, as support to provide thickness and shape (made of modacrylic) to the equipment, and on the other hand, filtering (made of non-woven PP) dangerous particles to the user [3]. When comparing the different kinds of masks mentioned above, some studies indicate that rudimentary cloth face masks/homemade face masks have a low filtration efficiency; however, they are reusable, comfortable, and have a satisfactory breathability. Surgical masks are comfortable, present a satisfactory breathability, and show a higher filtration efficiency than the homemade masks. However, their filtration efficiency for micro and nanoparticles is not excellent. Moreover, surgical masks are not reusable. Respirators are the ones with the better filtration efficiency performance for particles from all sizes, however they are also not reusable and present a low breathability. All in all, respirators have an overall better performance [4,6,7].

The PPEs available, particularly facial masks, have shown a few problems: face masks are more efficient with higher filtration, with the possibility of being reusable, and with antimicrobial capabilities [1,3]. When studying patients infected with the influenza virus, surgical masks were showed to be highly effective in blocking virus-containing particles with bigger sizes ($\geq$5 μm) but less effective for smaller particles [1,2]. Some masks and respirators are made of materials like cotton and synthetic fabric, which have larger pore sizes and, therefore, will not be very effective in filtering tiny virus-laden droplets, pathogens, and nanosized contaminants [1,2]. Another concern is the negative impact that this non-reusable PPE has on the environment. Recent research studies shown that healthcare workers worldwide used more than 44 million non-reusable PPEs every day during the COVID-19 pandemic. The majority of these PPEs are composed of polypropylene, which is a cheap material and has good performance characteristics; however, these kinds of masks are of single-use and are normally incinerated or sent to a landfill aggravating the environmental impact [2,4].

To improve the efficiency of facial masks and other medical textiles, several studies have been performed, like employing modified filter layers, for instance, nanofibers, or by modifying the filter surfaces by adding materials with antimicrobial capabilities to improve their efficiency [3]. It has been proven that adding antimicrobial agents to these products is a highly effective way to prevent infections caused by various pathogens through the inhibition of viruses, fungi, and bacteria [2].

There are different chemical and physical methods to promote superficial changes in fabrics. Although the most used ones are solution-based processing, other methods have attracted a lot of attention in the last few years for fabric surface modification, such as spray coating, sol-gel processing, direct chemical grafting, dip-coating, or physical vapor deposition (PVD) methods [7–10]. The sputtering process (PVD technique) is a coating method performed in a vacuum atmosphere. The coating material (target) is sputtered with a noble gas (typically Ar). Then, in a vapor phase, it is transported until it reaches and condenses at the substrate, forming a coating. It is even possible to introduce a reactive gas that will interact with the growing film forming a compound coating [10]. This technology has been implemented to modify various material surfaces, with particular attention to textiles. Several kinds of coating can be obtained to modify the textile surface, but to introduce the hydrophobic character without toxicity, diamond-like carbon (DLC) is the most appropriate [11]. The antimicrobial feature is gained with this coating, but if the DLC is doped with silver nanoparticles (AgNPs) in a non-toxic amount, the fabric becomes efficient against microbial colonization [12,13].

In this review, it is intended to show the most relevant improvements in the surface treatment of textiles by several techniques, mainly in medical fabrics. It will also be shown how such techniques can be an efficient approach to transform simple textiles, giving them the properties that the population needs to be able to live a healthier life, especially during a pandemic period. In addition, the advantages of using a new type of functionalization, the doped-DLC coating, will be discussed, since it is already used as a surface modifier but mostly on metal surfaces to improve various properties, such as antimicrobial property.

2. Technical Textiles

A technical textile can be defined as a textile material and product manufactured mainly for its technical and performance characteristics rather than its artistic or ornamental features [14]. According to application and final properties, technical textiles can be classified into Mobiltech, Indutech, Medtech, Hometech, Clothtech, Agrotech, Buildtech, Sportech, Packtech, Geotech, Protech, and Oekotech. While such a classification is not static, because some areas may overlap, it is useful to gain an idea of the world of products that can be included in surface modification [15].

Textile materials are composed of different types of fibers, filaments, yarns, and different fabric structures are made of natural or synthetic fibrous substances. The development of new fibers and manufacturing technologies for yarns and fabrics have been the main contributions to the improvement of textiles, adapting them according to needs. There is a huge variety of fibers used for technical textiles, depending on the end-product: natural fibers that are characterized by high modulus/strength, moisture intake, low elasticity and elongation; regenerated cellulosic fibers that possess low modulus/strength and elasticity as well as high elongation and moisture intake; and synthetic fibers, for instance, nylon, polyester, and PP, which possess high modulus/strength and elongation with an acceptable elasticity and comparatively low moisture intake [14]. The combination of all these different fibers with functional finishing processes allows the creation of tailor-made textiles that have an improved performance when compared to conventional textiles.

When referring to the textile industry, medical textiles have attracted the most attention in the last few years and are those making the fastest progress in the textile field [16]. The recent pandemic situation has further increased interest in these textiles due to concerns about their effectiveness in protecting healthcare personnel and the general population.

Textiles have characteristics such as, among others, strength, extensibility, flexibility, air permeability, various fiber lengths, different thicknesses, absorbency. These characteristics allow their use in the medical field. However, in specific cases where a combination of these or other characteristics is required, it is necessary to modify or improve the characteristics of the textiles according to their function. This is the case for medical textiles that need high surface areas, absorption properties (water and blood) and that are antimicrobial, or even promote blood clotting and wound healing [17].

Within medical textiles, these can be divided into in-body (tissue engineering) and out-body (dressings, hospital garments, sutures, or hygiene and personal care products) applications. In this review, the focus will be on surface modification techniques on textiles for use outside the human body [17].

The variety of textiles available for use in biomedical applications is vast, and various textiles are chosen based on the purpose. Natural wool, for example, may provide great thermal insulation and physical protection to the user in many situations (dry and wet conditions) due to its outstanding characteristics (hydrophobicity, etc.) [18].

However, there are a few concerns regarding the application of textiles in medical products. Because of their capacity to retain humidity and large surface area, numerous textiles are prone to facilitate the growth of microorganisms, for instance fungi and bacteria, and their quick multiplication under ideal circumstances [1,4]. This causes several negative effects such as diminished mechanical strength, production of unpleasant odors and discoloration of the textiles, and, more importantly, increased chance of user contamination [4]. With the intention of find solutions to these problems and improve or give certain properties to some textiles, several superficial modifications are being studied. For example, with plasma treatments is possible to confer to the surface of the textiles very low surface energy, giving to these textiles hydrophobic capabilities, which make them water-repellent with a bonus of not affecting the original characteristics of the textiles, for instance, the feel as well as the breathability [9]. Moreover, depending on the used finishing agent, plasma treatments can also provide other functional properties to textiles: UV protection, flame-retardant, antimicrobial, and cosmetic properties [19].

For medical textiles, there are many textiles materials used depending on their functionality. They can be used as implantable materials (sutures, vascular grafts), as non-implantable materials (pressure garments, secondary dressings), in healthcare/hygiene (clothing, masks, wipes), or intelligent medical and healthcare textiles (chromic materials, phase changing materials) [20]. In the example of the PPEs, non-woven fabrics (TNTs), cloth, and jersey format fabrics are the most commonly used.

TNT is created by connecting a mass of fibers using heat, chemical, or mechanical methods, rather than intertwining fibers as in traditional textiles. TNTs are the most commonly utilized material for medical clothing, despite being mechanically weaker than their counterparts. This is owing to its comparatively low cost and speed of production, as well as their excellent levels of sterility and infection control, which are critical in applications such as medical clothing. For these reasons, TNTs are frequently used in the production of disposable medical clothing, such as surgical masks, surgical caps, and surgical gowns [1,2]. Regarding surgical masks, they are typically produced with non-woven fibers, for instance, glass papers, PP, and woolen felt [3].

Alternatively, homemade masks are typically produced by woven textiles made from pure cotton or polyester-cotton blends, such as jersey textiles [2]. The downside of using woven fabrics in protective clothing when compared with TNTs are their worse barrier properties against liquids and bacteria; however, they normally provide a better wearer comfort to the user and are able to sustain several washing/cleaning processes, giving them a reusability property that TNTs usually fail to have [2]. Furthermore, while selecting materials for medical textiles, sustainability and environmental factors must be considered [14]. As a result of the rising limits on the use of synthetic fabrics (such as TNTs), eco-friendly alternatives, such as natural fibers, are being used to manufacture these items. Cotton is an excellent example of natural fibers that may be utilized to make medical clothing, not only because it is a sustainable material, but also because it is inexpensive, biodegradable, renewable, and lightweight [14,21].

3. Surface Modification of Textiles

3.1. Current Research in the Textile Surface Modification

Nowadays, in textile manufacturing, surface treatments are of the most importance to give the desirable properties for its application. Surface treatments, including printing, dyeing, and other chemical or physical treatments, can improve the appearance or feel of textiles and add to textiles' unique functions, such as control of surface wetting or UV protection, among other functions. Most of these surface treatments rely on heavy use of heating sources during the process to dry the textiles, and consequently, are energyintensive processes and expensive. Thus, the textile sector is seeking new methods to improve existing product characteristics while minimizing environmental impact and energy use. Some surface modification methods are described as follows.

The atomic layer deposition (ALD) is a surface modification method that can coat substrates with excellent uniformity across large areas with complex topographies. Due to these characteristics, ALD has been studied as a possibility to coat textiles give them new capabilities [18].

It is known that when textiles are exposed to ultraviolet rays, the fiber mechanical performance degrades and also leads to visible color changes. The ALD technique by coating textiles and fibers increases physical stability and ultraviolet protection [18]. The desire for high-performance and self-cleaning fabrics has prompted researchers to investigate how ALD might manipulate fiber surface wetting characteristics. Increased surface energy, which may be obtained by the deposition of polar metal oxide nanocoatings using ALD, is one approach to improve fiber wetting capacities. Inorganic ALD layers on polymer films have been shown in certain experiments to considerably decrease the passage of water and other vapors into and through the polymer. ALD has also been investigated by various research groups for biocompatible and bio-adhesive surface treatments, and to alter and regulate nanomaterial toxicity. All of these characteristics might be useful in biomedical applications such as face masks and medical gowns [18].

The high temperatures involved in the process, which some fabrics may not tolerate without damage, and the fact that traditional batch processing is too slow and expensive for most applications, are the most difficult hurdles for ALD use in textiles. This final point might indicate that ALD will be used first in high-value items such as specialty medicinal materials [18].

The sol-gel technique is a low-temperature approach for synthesizing materials that are either completely inorganic or partially inorganic and organic and is based on the hydrolysis and condensation reactions of organometallic compounds [22]. Sol-gel chemistry has been used to treat textiles with modified inorganic sols in recent years, offering a slew of new options for fiber surface functionalization [22,23]. The use of sol-gel technology in textiles offers several advantages, including reduced chemical use, less water use, low-temperature treatment, ease of application, and the ability to provide textile materials several functional characteristics in one step by combining suitable inorganic precursors (multifunctional finishing). The sol-gel technique, on the other hand, has drawbacks such as high precursor material prices, the potential to limit the elasticity of textile materials, and limited washing durability [22,23].

Water or oil repellency, dyeing, antimicrobial properties, self-cleaning properties, bioactivity, thermal and tensile properties, UV protection, and reduced flammability are just a few of the functional properties that can be given to textile materials using sol-gel technology, many of which are of interest for biomedical applications [22,23]. A hydrophobic effect can be achieved by lowering the surface tension of textile materials against liquids. A sol-gel technique and a mixture of nano-sol containing silica nanoparticles, triethoxysilane, and hexadecyltrimethoxysilane, certain experiments in cotton, cotton/polyester, and polyester textiles were able to give those materials superhydrophobic characteristics [23]. Furthermore, functions such as ultraviolet protection may be achieved via the sol-gel technique, for example, by incorporating TiO_2 and ZnO nanoparticles into textile materials. Through a photocatalytic reaction, TiO_2 nanoparticles provide ultraviolet protection as well as self-cleaning, a process that can also lead to the breakdown of organic and inorganic contaminants. This indicates that the photocatalytic reaction provides antibacterial characteristics in addition to ultraviolet protection and self-cleaning [23]. When considering giving antimicrobial properties to textiles using sol-gel technology, there are plenty of antimicrobial substances that can be applied through this technique. For example, silver chloride (AgCl) is usually used in cotton fabrics against fungi, ZnO is applied in cellulosic fibers, and chitosan is applied in wool to give it antimicrobial activity [23].

With the introduction of polymer nanocomposites, a new class of nano finishing materials for textiles may be developed, each with its own set of structure-property relationships that are only tangentially connected to their components and their micron and macro-scale composite counterparts. Although polymer nanocomposites with inorganic fillers of various dimensionality and chemistry are feasible, research into the immense potential of these novel materials has only just begun [24]. Significant research activities have been directed towards developing antimicrobial coatings to protect high-touch surfaces in healthcare institutions to minimize the financial burden and avoidable fatalities caused by healthcare-associated infections (HAIs). Surface hydrophilization has been widely used as a new paradigm to minimize microorganism colonization in recent years. Surface hydration layers induced by hydrophilic polymers could give anti-biofouling properties to surfaces because a layer of tightly bound water acts as an energetic and physical barrier to biofouling processes such as protein attachment, initial bacterial attachment, and subsequent biofilm formation [25].

Electrospinning is a simple but powerful technique for producing a continuous stream of nano- and microfibers from natural and man-made polymers, as well as inorganic oxide materials. The following are the fundamental ideas of a typical electrospinning process: To produce the fiber, a high voltage is utilized to create an electrically-charged jet of polymer solution or melt, which dries or hardens on extrusion [26].

Conventional fiber spinning processes typically generate polymer fibers with diameters in the micrometer range, but when the fiber diameter is lowered to nanometers, the surface area to volume ratio increases dramatically. High specific surface area, nanoscale interstitial space, heat insulating capabilities, electromagnetic shielding, biocompatibility, adjustable porosity, and mechanical resistance are all structural characteristics of electrospun nanofibers and non-woven textiles. Electrospun fibers have a large specific surface area, which allows them to have a high capacity and a large amount of adsorption sites for the effective absorption or release of molecules, particles, and functional groups [26–29]. Because the porosity may be adjusted in the electrospinning process, it is feasible to produce a high porosity, which allows for the development of extra channels for air to move through the fabric while preventing the passage of undesirable particles. Consequently, by providing selective permeability for water droplets or vapor, the high porosity and well-designed pores provide the feasibility of waterproof and moisture permeable fabrics [28,29].

Different functions can also be produced depending on the materials utilized in the electrospinning method. Electrospun textiles made of natural polymers, for example, nucleic acids, proteins, and polysaccharides, have inherent biocompatibility. Additionally, introducing different antibiotics and antimicrobials such as ZnO and AgNPs has shown an increase in the antimicrobial effectiveness of electrospun textiles [26]. To give this antimicrobial ability, there are two different methods. The first technique involves electrospinning precursor liquids or suspensions containing polymers and antimicrobial chemicals in one step to produce antimicrobial nanofibers. The second technique consists of two steps: electrospun polymeric nanofiber production and antimicrobial nanofiber post-functionalization [26]. These characteristics make electrospun textiles promising scaffolds for various applications.

Electrospun materials have attracted attention in recent years, not only in traditional textile sectors, but also in cutting-edge research disciplines such as fundamental and applied biomedical research. The COVID-19 pandemic, for example, has generated a surge in demand for PPE, underlining the relevance of electrospun fabrics, such as those used in mask filters, in effectively preventing nanoscale contaminants like viruses [26].

Nanotechnology applied to textile materials might result in the addition of a variety of functional characteristics to the underlying substrate. These functional qualities are crucial since they provide substantial benefits in wear comfort and maintenance. The implementation of nanotechnology in textiles might result in introducing or improving various functional properties, such as antimicrobial ability, flame-retardant, UV protection, and easy-care finishes, in particular with the application of metal oxide and metal nanoparticles.

Novel uses of textile materials utilizing nanotechnology in biological detection, hazardous gas breakdown, and self-decontamination are also being researched and investigated [30].

Plasma is an ensemble of charged, excited, and neutral species that includes any or all of the following: electrons, positive and negative ions, atoms, molecules, radicals, and photons. It is frequently referred to as the fourth state of matter [22,31]. These particles, which are formed by the electrical dissociation of inert gases, receive their own energy from the applied electric field and lose it when they collide with the material surface. Chemical bonds in the material surface are disrupted during surface collisions, resulting in the formation of free radical groups on the surface. These particles are chemically active and can add new functional groups to the material's surface, which can then be employed as polymerization precursors [31]. Because plasma surface modification does not need the use of wet-chemical compounds, it is considered a low-cost and ecologically friendly method [22,31]. One of the primary benefits of plasma treatment is that it only affects the surface characteristics of substrates, not the bulk qualities [32].

The plasma treatment technique in textiles can bring characteristics to fabrics such as antibacterial activity, hydrophobicity, flame retardancy, and ultraviolet protection, depending on the materials employed in the procedure. Many researchers have demonstrated that water-repellent characteristics may be bestowed on many fabrics, such as cotton, polyester, and silk, utilizing plasma treatments. Also, with the introduction of metallic particles like Ag or Cu, it is possible to give antimicrobial properties to some textiles' surfaces [22,33].

3.2. Magnetron Sputtering (MS) in Medical Textile Functionalization

Physical vapor deposition (PVD) is defined as the formation of a condensable vapor by physical mechanisms and subsequent deposition of this material onto a substrate as a thin film or coating. This can be achieved by a wide range of thin film deposition techniques, where atoms are removed from a surface by physical means. One such technique is sputter deposition where the atoms are released from a source solid or liquid by momentum exchange and which is usually performed under high vacuum conditions to achieve the desired levels of purity of the thin film deposited [34]. Metals and non-metals can both be deposited in general [10]. To satisfy this requirement, a variety of deposition methods are used. These approaches use a vacuum to reduce undesired interactions with the environment and make it easier to shape the coating composition.

PVD stands for physical vapor deposition and encompasses a wide range of vacuum deposition techniques. PVD is typically split into two processes: evaporation and sputtering. To create vapor in the form of atoms, molecules, or ions supplied from a target, physical techniques such as sputtering and evaporation are utilized. The particles are subsequently transported and deposited on the substrate surface, resulting in the development of a film.

The evaporation technique requires high temperatures during the process, which limits the use of this technique to coat textiles.

Sputtering, on the other hand, uses a substrate temperature that is far lower than the target material's melting point, making it a viable option for coating temperature-sensitive materials like textiles. This leads to the sputtering technique becoming more relevant among physical vapor deposition techniques to meet the constant increase in market demand.

The most prominent sputtering processes are the cathodic arc physical vapor deposition (CAPVD) and the magnetron sputtering (MS). The MS process is accomplished, during PVD deposition, by adding a closed magnetic field parallel to the target surface where the secondary electron is attached to a specific area of the target surface to increase the ionization efficiency through the orthogonal electromagnetic field formed on the target surface. With this additional element it is possible to increase the ion density and energy, and increase the deposition rate [35].

The CAPVD is a technique that includes passing a low-voltage high-density electric current across two electrodes. Due to the simultaneous vaporization and ionization of the cathodic substance, this action is carried out under a vacuum, culminating in the creation of plasma. Unlike other PVD processes, the coatings produced are intermixed layers with improved adherence, which is owing to the high kinetic energy [36].

The MS process involves energetic ions colliding with a target surface, which usually results in the ejection of target atoms. The MS method confines the plasma to an area near the target using strong magnets, which dramatically enhances the deposition rate by maintaining a greater ion density, making the electron/gas molecule collision process much more efficient. Alloys, elements, and compounds may all be sputtered and deposited using the MS method. The sputtering target also provides a steady and long-lasting material supply. Reactive deposition may be accomplished in a variety of conditions by utilizing reactive gaseous species activated in plasma. The cathode and substrates can be positioned close together in this technique, resulting in a compact system chamber. Another benefit of magnetron sputtering is the reduced electron bombardment of the substrate, which is beneficial for temperature-sensitive substrates like textiles. As a result of these advantages, the MS technique is of great interest among the scientific community since the obtained coatings allow a much larger surface area with improved durability and functionality without any adverse effect on the textile feel. Furthermore, because of the nano-scaled alteration on textiles, it is an environmentally benign technique that provides an appealing alternative for adding new functions such as water repellency, mechanical and antibacterial characteristics, and biocompatibility [37]. Consequently, it can be applied in a large number of industrial applications, with a particular focus on surgical/medical applications such as face masks.

There are opportunities for improvements using the versatile MS technique for high-quality coatings on temperature-sensitive substrates like textiles. Sputter films offer new ways to functionalize textiles by combining oxide, metallic, and composite films to obtain various characteristics. The most significant benefit of sputtering deposition is that even the highest melting point materials may be sputtered on textile substrates at low temperatures. Nanocomposite films can also be made by co-sputtering different materials. The sputtering approach for functionalizing textiles is usually applied only on the side facing the target due to the technology's directed deposition [38].

The adherence of MS-deposited films to textiles is superior to that of other coating methods. Despite this, due to sputtering techniques and varied textile substrates, adhesion between films and textiles was inconsistent. HiPIMS, for example, enhanced adhesion between films and textile substrates by operating at higher energies and with a greater density of electron/metal ion pairs than DCMS [39]. Aside from the fabric structure differences such as knitted textiles, woven textiles, and non-woven textiles, a variety of other factors may influence the adhesion between the sputter film and textile substrates, such as surface morphology different surface chemical properties, and porosity size of the fiber materials. When adhesion was lacking, it was feasible to significantly improve adhesion by correctly correcting inadequate fiber surface activation, thermal expansion coefficient discrepancies, and internal stress [40]. The adherence of coatings and fabrics can be improved by plasma pretreatment of the fabric substrates. The effect on adhesion was universally positive. Chen et al. [41], for example, utilized oxygen plasma to pretreat polyester cloth for one minute before applying a brass coating by HIPIMS. The brass coating's adherence to the cloth was significantly enhanced. Because it produces activation and the required material surface functionalization, the coating adherence is improved by pretreatment with oxygen plasma. In addition to physically cleaning the textile surface, the chemical significance conferred by the oxygen plasma pretreatment is critical. Before applying a TiO_2 coating to a polylactic acid textile, Saffari et al. [42] employed low temperature plasma to pretreat it. The TiO_2 particles on the polylactic acid fibers' surface grew more compact as the plasma treatment time and sputtering time were increased. The initial TiO_2 coating and the chemical change caused by the oxygen plasma pretreatment significantly improved film adherence and resistance to washing. Al_2O_3 coatings on the surface of polyester woven and nonwoven fabrics were applied by Depla et al. [43]. Plasma pretreatment significantly improved the adhesion, continuity, and compactness of the films in all samples. Hegemann et al. [37] have demonstrated an alternate approach for depositing Ag on textiles, plasma sputtering, which combines cleaning and deposition in a single step. With smooth films, they were able to obtain excellent adherence to polyester fibers.

The application of MS for the deposition of metallic and oxide films on textiles has grown in popularity in recent years for functional purposes in several applications, specially, the medical ones.

Recently, polyester fabrics were coated with Ag/TiO_2 composite films by magnetron sputtering. These textiles not only were able to realize the structural coloration of the surface, but also have good photocatalytic, conductive, anti-ultraviolet and other properties, so they have a good application prospect [44]. On the other hand, UV resistance was improved by depositing Ag/Cu nanocomposite film on non-woven fabric [45].

Fireproof fabrics play a vital role in the life of fireguards; therefore, the search for a better high temperature barrier is routine. Ti–Si–N nanocomposite reflective coating was deposited by using magnetron sputtering improving the heat resistance in the NATAN® fabric [46]. Also, aluminum and zirconium (IV) oxides were deposited on the Nomex® fabric, basalt fabric, and cotton fabric with flame-retardant finishing using the magnetron sputtering method, in order to improve the thermal properties of textiles [47].

Fabric coloration can be fine-tuned by deposition of metallic thin films using magnetron sputtering. Due to the optical absorption edges of CuO and Cu_2O, these thin films have proven useful for having a fabric set with a color palette [48,49].

UV resistance and antibacterial characteristics were found in textiles coated with Cu films [50]. MS-coated Cu film textiles exhibited good antibacterial activities against *Escherichia coli* (*E. coli*). The bacteriostatic rates against *E. coli* of the Cu film produced by HiPIMS were more than three times greater than those deposited by DCMS under the same sputtering circumstances [39]. Cu and Ag were sputtered on textiles by Scholz et al. [51]. Cu's antibacterial capabilities outperformed Ag only on a few types of bacteria, such as *Staphylococcus aureus* (*S. aureus*) and *E. coli*, when compared Cu and Ag coated textiles. Several other publications reported the antimicrobial properties of Cu and Cu/Ag thin films deposited on polyester knitwear fibers [52], poly(lactide) non-woven fabrics [53] and polypropylene fiber [54].

Rtimi et al. [55] coated polyester textiles with TiON and TiON-Ag coatings to improve the antibacterial action. *E. coli* was completely killed in 120 min when the TiON coating thickness was 70 nm. On the TiON-Ag coating, *E. coli* was killed much quicker (within 55 min) when Ag was added to the coating. Rtimi et al. [56] also used polyester textiles to deposit TiN and TiN-Ag coatings. They discovered that when Ag-doped (TiN-Ag) coatings were compared to TiN coatings, the rate of bacteria deactivation increased.

The sputtering deposition of TiO_2 coating on textiles improves their UV resistance and antimicrobial properties [57,58]. In another work, Rtimi et al. also deposited Cu, TiO_2 film, and TiO_2/Cu coatings [59]. They discovered that TiO_2/Cu coating had a considerably greater antibacterial impact than the others. TiO_2 was said to have a synergistic impact on Cu [50]. Also, the neodymium-doped TiO2 film coated on polypropylene non-woven fabric via a sputtering method showed antibacterial and ultraviolet protective properties [60].

Because of its antibacterial characteristics, Ag has been widely utilized in the functionalization of textiles. Hegemann et al. [37] deposited Ag on fabrics by magnetron sputtering process. They were able to achieve good antibacterial activity with modest quantities of deposited Ag while maintaining the fabric's characteristics. The antibacterial efficacy of platinum, silver, copper, gold, and platinum/rhodium layers was determined. Copper was presented to be the more efficient against fungus and bacteria. Silver was also efficient against bacteria, although its activity against fungus was found to be limited. The efficacy of the other metals tested was not achieved [51,61]. Shahidi's objective was to improve the fastness and antibacterial characteristics of colored cotton samples. Cotton textiles were dyed using a variety of dyes, and the dyed samples were then sputtered with Ag and Co for 15 s using a plasma sputtering apparatus. For the production of a metal nano-layer on the surface of samples, he employed a DCMS method. He noticed that the differences in characteristics caused by sputtering might improve the performance of some textiles. As a result, the sputtering approach might be a unique way to improve the washability and lightfastness of colored cotton samples. The textiles' antimicrobial activity lasted for at least 30 cycles after laundering [62,63]. Using HiPIMS, Chen et al. deposited Ag on poly(ethylene terephthalate) fabric. Antimicrobial activity against *Staphylococcus aureus* and *E. coli* was discovered in the samples. Rtimi et al. [64] deposited ZrNO and Ag on PET textiles to create antimicrobial textiles with ZrNO-Ag composite coatings. The antimicrobial effect of the composite coating on *E. coli* was significantly improved when compared to the single-layer coating. On the other hand, Subramanian et al. deposited CuO coatings on polyester non-woven textiles. The coated textiles revealed a strong antibiotic effect on *S. aureus* and *E. coli* [65]. Furthermore, the antibacterial effectiveness of the Cu/CuO coating deposited on polyester textile against *E. coli* was more than three times that of the deposited Cu coating [66]. When deposited ZnO coatings on textiles, the coated textiles could also get favorable anti-ultraviolet and antimicrobial properties [67,68].

3.3. Diamond-like Carbon in Medical Textile Functionalization

The hydrophobicity, high hardness, transparency, excellent thermal conductivity, chemical stability, and biocompatibility of diamond-like carbon (DLC) coatings are well-known.

Deposition techniques for DLC coatings include radio frequency, plasma-enhanced chemical vapor deposition, ion beam deposition, ion plating, plasma immersion ion implantation and deposition, filtered cathodic vacuum arc, pulsed laser deposition, ion beam sputtering, and mass-selected ion beam deposition [69–74].

The magnetron sputtering process, in particular, is a very promising and versatile technique for performing DLC coatings because it allows carbon coating growth even at low substrate temperatures and delivers ion bombardment of the surface, which has the benefit of increasing coating adhesion to the substrate and thus improving coating quality.

For their role as outstanding protective coatings in bio-applications, DLC characteristics have been widely investigated. In vitro, diamond-like carbon coatings have antibacterial and anti-biofouling properties against bacteria such as *S. aureus*, *Staphylococcus epidermidis* (*S. epidermidis*), and *Pseudomonas aeruginosa* [75,76]. Bacterial adherence to the diamond-like carbon film is linked to their sp^2 and sp^3 hybridization, and lowering the sp^3/sp^2 ratio improves antimicrobial efficacy significantly [77]. Because of their strong interaction with human cells and improved corrosion resistance and wear, DLC coatings having a large proportion (>80%) of sp^3 bonds are often used for biomaterial films [78]. Some methods have been proposed in order to better understand the bactericidal efficacy of DLC films. One mechanism is the direct physical damage to microorganisms caused by interaction with pure diamond-like carbon films, which results in severe membrane degradation and the release of microbial internal compounds [79]. Other researchers hypothesized that diamond-like carbon films' antibacterial action stems from their chemical inertness as a result of the weakening of the chemical contact during the bacterial adhesion process [80]. The mechanism of DLC coatings can be altered depending on the microbiological species in a variety of circumstances. DLC and DLC doped with germanium, for example, had a significant anti-biofouling impact against Gram-negative bacteria but did not inhibit gram-positive bacteria [81]. It is worth noting that there is some evidence that DLC films have extremely poor or non-existent antibacterial action against *S. epidermidis* and *S. aureus* [81–83]. DLC coatings' bactericidal activity is closely connected to their surface profile, which includes a strong dispersive component of surface energy, hydrophobicity, and smoothness [84].

The high hydrophobicity of DLC coatings, in particular, can induce changes in bacterial cell membranes, leading to biological death [85]. Furthermore, the surface free energy is a key factor influencing DLC antibacterial efficacy. The surface energy value of DLC coatings is frequently carefully chosen for specific purposes. Many elements can be added to DLC coatings with the goal of changing the value of surface energy. The addition of fluorine groups, for example, causes bonding changes in DLC coatings by lowering C–CF bonds and increasing CF and CF_2 bonds, enhancing antibacterial effectiveness by raising the work of adhesion of the coatings for bacteria [86]. Fluorine has the capacity to change the wettability of diamond-like carbon coatings by lowering the surface free energy and increasing the contact angle [87]. The initial attachment of microorganisms is known to be significantly connected to the total surface energy of the coatings, as the number of adherent cells decreases as the total surface energy of the coatings decreases [88]. As a result, considering the surface characteristics of DLC films will aid in the design of bactericidal films by optimizing the surface energy.

Nanoparticles are commonly added to DLC coatings in order to activate or enhance their antibacterial characteristics. Incorporating a metal particle into the DLC structure can function as a catalyst for the formation of sp^2-rich boundary sites [89,90]. It has been discovered that a low silver concentration can reduce the number of carbon atoms bound in sp^2 configuration, which promotes sp^3 bonding, but a greater Ag content raises the sp^2/sp^3 ratio [91]. Cu nanoparticles, on the other hand, are well recognized for improving the bactericidal activity of DLC coatings. Experiments revealed that adding Cu to a-C:H enhanced its antibacterial activity by up to 99.9% (>58.76 wt.%) [89]. Furthermore, Cu has the ability to alter the wetting characteristics of DLC coatings, affecting bacterial adhesion considerably [92,93]. Metallic nanoparticles may have disadvantages for the DLC matrix in a variety of scenarios. For example, adding Ag to a-C:H coatings improved their antibacterial and hydrophobic properties, but it came at the cost of decreased hardness. Additional increases in Ag content did not help to improve antibacterial ability, but they did result in a significant loss in surface flatness and hardness [94]. Whether the mechanism of nanoparticles embedded in DLC films is identical to that of free particles or whether these particles function differently is unknown [81]. Nonetheless, due to their ability to control the release of antimicrobial nanoparticles, DLC/composite coatings are used effectively as tailored antimicrobial films [95].

Because of their small sizes, unique chemical and physical properties, and high specific surface, materials for instance metal nanoparticles, metal oxide nanoparticles, carbon nanomaterials, and their composites have been extensively used as new antimicrobial agents. This enables them to dissolve more quickly in a given solution than bigger particles, releasing more metal ions [4,96]. Furthermore, these compounds are readily incorporated into the polymeric matrix of fibers, making them excellent for use in textiles [4].

Consequently, the incorporation of Au, CuO, ZnO, TiO_2, or Ag Nanoparticles to DLCs, with Ag being the element most likely used to obtain antimicrobial properties, could allow fabrics, including those used in masks, to have the two properties that are crucial in this study: antimicrobial and hydrophobic [97].

AgNPs are the most widely used antimicrobial nano agent because of their broad-spectrum antimicrobial properties and strong antimicrobial effectiveness against a large number of bacteria, viruses, and fungi, which is also higher when compared to particles made from other heavy metals such as Au and Zn [96]. The antimicrobial mode of action of metals, which may be triggered by the metal reduction potential, metal donor atom selectivity, and/or speciation, can trigger the biocidal effect of metals [4]. This mode of action may cause a variety of processes, such as the formation of reactive oxygen species, that have a significant impact on the integrity and functionality of bacteria and viruses, including cell wall synthesis damage or inhibition, cell membrane function inhibition, protein synthesis inhibition, nucleic acid synthesis inhibition, and inhibition of other metabolic processes [4]. The antibacterial activity of Ag, particularly, has been recognized as an oligodynamic effect, and in compounds exhibiting this oligodynamic effect, only very tiny amounts of the active substance are required for substantial antimicrobial activity, further supporting Ag's high efficiency [98].

In relation to the combination of DLC and Ag, there are several studies that show that silver-doped DLC (AgDLC) coatings have an excellent antimicrobial effect [13,79,97,99–104].

The biocidal action of AgDLC thin films is longer than other substrates with metallic NPs, as the film surface is continuously renewed with Ag due to its segregation through the carbon matrix. Concentration gradients attract Ag ions to the top layer of the surface, where most of the moisture and less Ag ions are present. The bacteria are also contained in this higher layer, allowing the silver ions to reach their target locations and impact microbial viability [98]. As bacteria only interact with surface materials, AgDLC films exhibit improved and extended antimicrobial activity compared to films without silver segregation. This phenomenon shows the advantage of AgDLC films over AgNPs, as the Ag content can be reduced while maintaining a high antimicrobial activity [97], creating the possibility of controlling the antimicrobial action of this type of coating. Therefore, a successful deposition of AgDLC coating in textiles may provide a wide range of possibilities in the biomedical sector, depending on the desired application.

4. Conclusions and Perspectives

The textile industry is not indifferent to nanotechnology advancements and, therefore, all these new surface functionalization approaches are being increasingly studied in order to improve the effectiveness and performance of textiles in several areas.

The pandemic that the world is living through has again highlighted medical textiles, because of the fundamental importance in the antiviral protection of health professionals and the population in general. New antibiotic-resistant pathogens and the high impact of unknown strains such as SARS-CoV-2 boost research attention to more efficient and durable textile products based on antimicrobial activity.

The medical textiles available throughout healthcare environments all over the world are far from ideal, however the technology required to enhance some of those textiles' performance is already available. Some of the methods that raise more interest are surface modification methods. Nowadays, there are a few surface modification methods, such as polymer coatings, that allow the implementation of finishing treatments in textiles in a way that is far more appealing to the textile industry sector, as they have the potential to reduce energy use and environmental impact while giving the desired finishing properties.

Despite these available technologies, surface modification textiles still fall short of hospital needs. Of all the modification techniques, PVD has grown in use because of its efficiency in transforming textile surfaces into antimicrobial and hydrophobic textiles, which are among the characteristics needed to isolate the patient and health care worker.

Already with recognized antimicrobial and hydrophobic capacity, the AgDLC coatings, produced by PVD are still at an exploratory stage in the area of surface modification of technical textiles. This type of coating will certainly be a kick-start for the use of C-based thin films doped with metallic elements to enhance the properties of textiles.

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