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Sol-Gel Finishing for Protective Fabrics

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Abstract: Sol-gel method has been used since the early 1960s in various applications. There has been a growing interest in this method in recent decades, its materials, and its functionality. The sol-gel reaction consists of a series of simple hydrolysis and condensation reactions, and they are easy to perform and do not require special conditions or high temperatures. This reaction can be influenced by several factors: water-to-precursor molar ratio, types of catalyst, pH, modifier, reaction, aging temperature, and varying solvent. Scientific databases, namely Scopus and ScienceDirect, mainly address the organic solvent-based sol-gel method. Since 1996, the water-based sol-gel method has attracted much attention to simplify the procedure further and reduce cost and environmental damages. This is a review of water-based and typical solvent-based sol-gel methods, focusing on protective fabric coatings. It discusses the most relevant and recent findings related to the sol-gel method, including its applications, advantages and limitation, and future potential. It describes the effects of using water to replace organic solvents that can influence the characteristics and properties of sol-gel materials. Water-based sol-gel preparation methods are relatively advanced, and some products are currently on the market. However, many difficulties related to their water-precursor compatibility prevail. Therefore, chemistry and physics are areas that need to be exploited to create new materials that meet the protective fabric criteria.

Keywords: sol-gel method; materials and functionality; protective fabrics; review; water and solvent-based sol-gel.

1. Introduction

Protective fabrics are highly desirable due to their utility in a wide variety of applications, such as protecting an individual and products from interacting with an unfavorable environment. These environmental factors can be divided into physical factors (high temperature, low temperature, wind, rain, water, fire, dust, static electricity, radioactive sources, etc.), chemical factors (poison, oil, acid, alkali, etc.), and biological factors (insects, bacteria, viruses, etc.) [1, 2]. The global protective fabrics market is expected to benefit tremendously from end-use industries due to increased consumer demand. The protective fabric market industry is also driven by rising concern for industrial workers' safety.

Protective fabrics have the following features: fire-retardant, chemical insulation, radiation protection, heat technology, ultraviolet (UV) protection, anti-static, waterproof and breathable, anti-mosquito, antibacterial, odor-resistant, and antifouling [3-20]. Recent studies also remarked on using protective fabrics for wearable electronic textiles in which the finished fabric's electromechanical properties are sought [21]. The demands of different applications mean different methods have been used, employing chemical, physical and biological techniques to manufacture protective fabrics.

The sol-gel method has become a fast-expanding area of research in the field of materials science due to its simple methodology, cost-effectiveness, and environmental-friendly. Thus, it does not require complicated technological installation, which is a plus point for small and medium-size industries [22, 23]. A collection of materials produced through the sol-gel method have demonstrated exceptional properties and characteristics that are challenging to achieve via conventional methods [24–26]. A popular method to modify fabrics is dipping or spraying sol-gel recipes onto the fabric substrates [27-30]. In most cases, the sol acts as a carrier or binder layer to bond a second functional component, transferring the properties to the fabric substrate. Common sol-gel coating applications involve using harsh, environmentally damaging organic solvents, especially in large-scale industrial processes [31-33]. The solvents can emit volatile organic compounds (VOCs) [34], but their emissions are regulated by limiting the amount in a given period. The EPA sets national rules for OCs, but some states have tightened restrictions even further, necessitating concerted efforts to limit their emission.

Water-based dispersions do not have much impact on environmental concerns and, therefore, are of greater technological interest [35]. The water-based sol-gel method uses water as a solvent, but they do not necessarily contain zero organic solvents. Many contain lower concentrations of co-solvents and are used for the hydrolysis of sol-gel precursors. Since water-based dispersions use zero or significantly fewer organic solvents, they are a great way for companies with VOC output to cut their spending on environmental compliance advising or to prevent them from paying penalties for exceeding VOC emission limits [36].

This review focuses on the water-based sol-gel process and its use in developing various protective finishes for fabrics that will have the following novel and useful features: water repellent, self-cleaning, UV protection, antibacterial, and flame retardant. Limitations and future trends of the water-based sol-gel method are also discussed.

2. Sol-Gel Coatings for Fabrics

The sol-gel method has become very popular in providing functional fabric surfaces in recent decades. It involves depositing functional silica coatings on textile materials creating new properties and applications. The method also ensures good ceramic purity and hybrid coatings on different substrates. Their unique structure and reduced thicknesses would ensure the sol-gel coatings adhere to and stay transparent even on flexible substrates, like textiles. Their versatile chemistry, in short, provides a variety of properties to fabrics in addition to providing functional inorganic, composite, and hybrid coatings on many different types of materials. This chemical versatility enables various functionalities in a single coating, such as water- and oil-repellence, UV resistance, bacteriostatic activity, the release of active molecules, and abrasion resistance [37, 38].

The transfer of sol-gel technology from the laboratory to large-scale industrial applications is potentially easier than other techniques. Table 1 compiles the most recent coating deposition techniques for cotton and polyester fabrics. It was found that the dip-pad-cure process is the most commonly used as it is straightforward and economically feasible [39].

This method involves immersing or dipping the fabric into a solution of coating material at a constant speed using a padder, followed by drying and curing. During drying and curing, a film with a thickness of about 100 nm is formed onto the fabric's surface. The functional groups of precursors then react with the surfaces of the textile to form hydrogen or covalent bonds, which strongly increases the hybrid film's adhesion to the textile [40].

3. Water-Based Sol-Gel Finishing

In the mid-1960s, industries began research to produce zero-waste volatile organic components using the sol-gel process. However, in the 1970s, findings pointed to its unsuitability for commercialization, and these experiments came to a halt. The first trial was reported in 1976 for coating in paint application [55, 56]. In the 1990s, the water-based sol-gel process attracted much attention in efforts to produce environmentally safe coating materials. Additionally, concerns over health and overall production cost led to efforts to develop a water-based sol-gel process. The latter method was first applied to produce a clear coat for application in the automotive industry at an Opel plant in Germany [55]. Nowadays, the water-based sol-gel process is classified as the main class of coatings used globally and is not limited to the paint and automotive industry only. It has been applied in fabric, militaries, biomedical, furnishing, and many more industries due to its low production cost, low toxicity and flammability, better coverage, good abrasion, and heat resistance.

The water-based sol-gel method differs from common sol-gel in terms of the solvents used. In the former, water is used as a medium reaction to supply oxygen for the formation of metal oxide. Meanwhile, in the common sol-gel process, organics solvents, such as alcohols, aldehydes, and ketones, are used as reaction mediums [57]. These solvents supply the oxygen required for forming metal oxide in this route [58]. These organic solvents also serve to modify components, such as particle size, morphology, composition, and surface properties of the metal oxide NPs [57]. Metal alkoxides are widely used as precursors in the water-based sol-gel process due to their high reaction affinity toward the water. Other metal precursors used in water-based sol-gel are metal acetates, sulfates, nitrates, and chlorides [59]. In the common sol-gel process, the precursors include inorganic metal salts, alkoxides, metal acetates, acetylacetonates, and organometallic.

3.1. Applications for Protective Fabrics.

Zelca *et al*. (2017) studied dipping time and sol-gel compositions' influence on coating morphology to ensure long-lasting and smooth coatings for fibers [60]. The results suggested that the use of sols with increasing concentration leads to an increase in the thickness of the coatings and bridging of nearby fibers, resulting in reduced flexibility in the treated fabric.

Camlibel and Arik (2017) studied sol-gel technology using metal alkoxides and metallic salts as precursors to analyze the catalytic effect of an acid or alkali, hydrolysis, and condensation reactions [27]. As a result, sol-gel technology contributes to an increase in the following properties in the fabric: resistance to flame, repellence to water/oil, antibacterial, anti-wrinkle, anti-crease, durable press or easy-care effect, ultraviolet (UV) protection, self-cleaning or soil repellence, photocatalytic activity, development in fastness behavior, resistance to abrasion, and tensile and thermal properties.

Table 1. Most recent coating developments for cotton and polyester fabrics.

Textile substrate	Fabrication method	Deposition technique	Additional functionality	References
Cotton	*In situ* thiol-ene click reaction of Octavinyl-polyhedral oligomeric silsesquioxane and Pentaerythritol tetrakis (3-mercaptopropionate)	Chemical vapor deposition	Resistance to acid, alkali, organic solvents, and UV irradiation	[41]
	Solvent extraction of betulin from bark birch to form betulin-terephthaloyl chloride copolymer	Impregnation and compression molding	Not specified	[42]
	Fly ash (FA) coated with a TiO_2 shell layer via charge adsorption. FA-TiO2 is then grafted with Polydimethylsiloxane (PDMS) molecules to form FA-TiO2-PDMS particles.	Chemical vapor deposition	Self-cleaning and photocatalysis	[43]
	Ultrasonication of commercial hydrophobic silica nanoparticles (NPs) in Hexane	Spray coating	Self-cleaning	[44]
	Simple synthesis method using Hydroxyl-terminated polydimethylsiloxane, Isophorone diisocyanate, and Pentaerythritol triacrylate as precursors	Dip coating	Oleophobicity	[45]
	Acid-base catalyzed SiO_2 aerogel dissolves in isopropyl alcohol, PDMS, and curing agent to obtain PDMS/SiO_2 coating solution.	Dip-pad-cure	Superamphiphobic Self-cleaning	[46]
	Synthesizing glycidyloxypropyl trimethoxysilane (GPTMS) and titanium isopropoxide (TIPT) nanosols containing coffee-scented microcapsules.	Pad-dry-cure	Fragrance release Antibacterial Wrinkle resistance Abrasion resistance	[47]
	Sol-gel technique used to produce a silane-based coating containing Alizarin covalently bonded.	Pad-cure	Halochromic properties	[48]
Polyester	Eco-friendly method using Polydopamine and stearic acid emulsion	Dip coating	Biodegradable, UV shielding, solar-induced self-healing, and oil-water separation properties	[49]
	One-step process using Methyltrimethoxysilane	Dip coating	Not specified	[50]
	One-step chemical reaction between cellulose nanofibers and Octadecylamine through glutaraldehyde-assisted coupling process	Spray coating	Self-cleaning and healing abilities	[51]
	Customized foam-coating emulsions were synthesized by mixing commercial fluorinated foam and cross-linking agent	Single-sided blade coating	Asymmetric wetting properties	[52]
	Solvent-induced crystallization process using Hexafluoroisopropanol and Carbon black	Dip coating	Conductivity, breathability	[53]
	Superhydrophobic precipitated calcium carbonate (SHPCC) sol-gel from dolomite as a precursor and stearic acid as a surface modifier and binder for calcium carbonate.	Dip-coating	Sel-cleaning Mechanical abrasion Washing	[54]

Bentis *et al*. (2020) studied Titanium (IV) butoxide (TBT) and boric acid as a functional additive applied to cotton fabric via the pad-dry-cure process [61]. The results showed that coated cotton fabric possessed high thermal stability and flame retardancy. At the same time, water-repellent properties were strengthened while drop time and water uptake improved. Recently, boron has gained much attention in the textile field due to its ecological benefits, such as conservation efficiency, neutral pH, and reduced influence on mechanical properties compared with other flame-retardant products. TiO_2 is a flame retardant agent as it has the properties to boost the production of dense protective physical barriers against heat, mass transfer, and oxygen. Using the sol-gel method based on Titanium sol and boric acid as functional additives, the treatment of cotton fabrics leads to flame retardancy and water repellence of cotton fabric for end users.

Lavinia *et al*. (2016) studied sol-gel coating to functionalize Tetra-ethyl-ortho-silicate based (TEOS) hybrid coatings; these are prepared by utilizing various Si-alkoxides functionalized with other alkyl chains or fluorinated groups. The authors also examined the treated fabrics' resistance to abrasion, oil and water contact angle, mechanical properties, and water vapor permeability. The study showed hybrid sol-gel silica coatings synthesized by utilizing Si-alkoxides functionalized with hydrocarbon or fluorinated chains improve wear resistance and anti-stain properties in silk fabrics [37].

Textor (2009) studied the modification of inorganic metal oxide on textile surfaces using the sol-gel technique [62]. The metal oxide embedded into the fabric tends to form chemical bonds during the formation of the xerogel. The general process entailed three steps: hydrolyzation, application, and curing. The first involved hydrolyzation of precursors using tetraethoxysilane (TEOS). In this study, modifying textiles improved the repellence of ultraviolet absorption and wear resistance. The results also showed a simple silica coating leads to higher surface energy than untreated fiber and improves the retardancy of fabric.

Onar and Mete (2016) studied the flame retardant and water and oil repellent properties in cotton fabric using the sol-gel method. They used alkyl-modified silanes or alkoxyl silanes modified with hydrophobic organic materials, commercial fluorochemical agents and flame retardant textiles using phosphorous, and nitrogen-doped silanes modified with organic materials [63]. The water and oil repellent properties of treated cotton fabric using the sol-gel process were retained for up to five washes, and after that, the treated fabrics lost their flame retardancy. In order to regain their flame-retardant properties, cross-linking agents were added to the solution.

Kappes *et al*. (2016) studied flame retardant properties in fabrics adopting the sol-gel method [64] using amino silanes and phenyl phosphoric acid. The results showed that sol-gel-based composite using phosphorus and nitrogen modification cure is promising in developing effective, easy-to-apply flame-retardant coatings.

In conclusion, the versatile chemistry of sol-gel technology can be exploited to impart various protective properties to fabrics. Therefore, sol-gel technology has the potential for the functionalization of fabrics. They have the following features: improved abrasion resistance, water-repellent, flame retardant, easy to care, anti-stain, and wear resistance.

3.1.1. Water repellence.

Recently, protective clothing with water repellent properties has been the industry's focus. Water repellent textile is different from waterproof textile as the former does not block the air from passing through the fabric; it only blocks water. Waterproof textile is impermeable to air and water because of the interstices between warp and weft yarn which are completely blocked by the continuous hydrophobic film of the substances [65]. The water repellence feature may help remove bio-settlement from the surface and avoid textile deterioration. It directly helps to prevent biofouling and bacterial colonization primarily as a result of the characteristic of biomaterials [66]. This feature can be introduced through mechanical, chemical, and coating methods [67]. In order to achieve the desired repellence effect, the water repellence chemicals are introduced to the textile fiber with minimal effect on other functional properties, such as flexibility, strength, and others. Water repellent finishes are designed for general wear, such as expensive silk clothing, uniform, protective clothing filter fleece, carpet, and table cloths.

Mohd Za'im *et al*. (2021) successfully developed a hydrophobic coating for polyester fabric using a simple water-based sol-gel process. Hexyltrimethoxysilane (HTMS) was used as a precursor and diluted in a mixture of water, ethanol, and sulfuric acid (2.31:1:2.28). The solution was stirred vigorously on a magnetic stirrer at 30 °C until a clear solution was obtained and coated onto the fabric using the dip-pad-cure process. The water contact angle obtained for the coated polyester fabric was 136.2° with a particle size of 115.3 µm. The HTMS sol-gel coating produced a good surface morphology with invisible cracks, and it is able to create surface roughness on the coated polyester fabric. Thus, these characteristics help give it the hydrophobic property without changing the nature of the fabric, especially its softness and smoothness [68].

Simoncˇicˇ *et al*. (2012) developed a method involving the use of commercial aqueous organic-inorganic hybrid precursors fluoroalkyl-functional siloxane (FAS) and 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (SiQAC) as finishing agents [40]. Both products were dissolved in water at the desired concentration. The hybrid sols were applied onto the cotton fabric employing the dip-coating and pad-dry-cure methods. Sols were applied to the fabric samples using two application procedures: a one-step treatment and a two-step treatment. A one-step treatment used a sol mixture consisting of both precursors (coating FAS-SiQAC), while a two-step treatment used SiQAC sol and FAS sol (coating SiQAC + FAS). A one-step treatment was found to be more effective compared with a two-step treatment. However, both treatments exhibited superhydrophobic, oleophobic, and antibacterial properties in cotton fabrics.

Xu *et al*. (2012) used modified silica hydrosols to develop superhydrophobic cotton fabric. Methyl trimethoxy silane (MTMS) sodium dodecyl benzenesulfonate (SDBS) were diluted in 100 mL of water and stirred vigorously until a homogeneous emulsion was formed. NH3.H2O was added to the aqueous solution as a catalyst. Then, hexadecyltrimethoxysilane (HDTMS) was added to the solution and continuously stirred. The modified SiO_2 hydrosols were coated onto the cotton fabric samples using the dip-pad-cure process. It was applied to the cotton fabric using a one-step coating process. The modified SiO_2 NPs with a diameter of 110 nm to 140 nm were observed, and the diameter size can be controlled by adjusting ammonia hydroxide and surfactant concentrations. The coated cotton fabrics exhibited excellent superhydrophobicity due to the synergistic effect of its surface roughness provided by the SiO_2 nanoparticles and the low surface energy created by HDTMS modification [30].

Wan *et al*. (2021) successfully fabricated water-based SiO_2-TiO_2 aerogels with the help of surfactant by incorporating TiO_2 into MTMS-based SiO_2 sol. MTMS was used as the precursor, and the intermediary surfactant cetyltrimethylammonium bromide (CTAB) was used as a catalyst to homogenize water and organic components. The solution was stirred and mixed with a proper amount of TiO_2 to form SiO_2-TiO_2 alcogels and soaked in distilled water at 60°C for 12 hours. It was then dried at ambient pressure at multiple temperatures for 2 hours to produce the final SiO_2-TiO_2 aerogels. The dip-coating solution was prepared by mixing SiO_2–TiO_2 aerogel powder, PDMS, and its curing agent in 20 mL of ethanol. The sol was then coated onto cotton fabric using the dip-coating method. The coated cotton fabric exhibited good superhydrophobic properties with a water contact angle of 152°. It also exhibits antifouling, self-cleaning, and liquid repellent properties and performs photocatalytic activity [69].

3.1.2. Self-cleaning.

The development of self-cleaning textiles through nanotechnology has been extremely helpful to many, especially busy people. Self-cleaning fabric can prevent dirt and oil and act as a disinfectant [70]. This type of fabric could be used to manufacture medical and sports attire, uniform, and other domestic applications such as curtains. Self-cleaning fabric is useful for military personnel who survive in harsh conditions. The textiles also have a long shelf life and would always look new [71], as well as being environmental and cost-friendly [72]. The aging of the fabric is also improved by extending its surface purity effect [73].

Ahmad *et al*. (2019) modified the surface of cotton fabric to create self-cleaning and enhance its UV protection properties. Titanium oxide (TiO_2) sol consisting of tetraisopropoxide (TTIP), water, absolute ethanol (EtOH), glacial acetic acid, and hydrochloric acid (5:70:20:4:1) were prepared. The TTIP was dissolved separately in EtOH before mixing it with a solvent medium and heated at 70 °C. The Reactive Blue 21 (RB 21) solution, which acts as the reactive dye, was added into TiO_2 sol and mixed thoroughly before the coating process. The RB21/TiO_2 sol was applied to the cotton fabric using the pad-dry-cure method. In order to test the self-cleaning property, the coated cotton fabric was dipped into a staining solution, Rhodamine B (RhB), and dried in the dark. The coated cotton fabric showed excellent self-cleaning property; all the stains from the fabric surface were removed by degrading Rhodamine B (RhB) and exposing it to light. The coated cotton fabric also exhibited excellent UV protection with ultraviolet protection factor (UPF) values ranging between 112.631 and 162.841, which makes the fabric suitable for outdoor activities [74].

Vasiljevic *et al*. (2013) modified the surface of cotton fabric to create superhydrophobic, oleophobic, and self-cleaning properties of the fabric. It involved the application of low-pressure water vapor plasma followed by a pad-dry-cure sol-gel coating with water and oil repellent organic-inorganic hybrid precursor fluoroalkyl-functional siloxane (FAS). The plasma was created with low pressure, and the water vapor from the fabric was used as gas. A FAS sol was dissolved in distilled water and applied to the pre-treated fabric samples using the pad-dry-cure method. The samples were left for 14 days under standard atmospheric conditions (65 ± 2% relative humidity and 20 ± 1 °C) to allow complete network formation of the coated fabrics; the FAS coating after plasma pre-treatment resulted in both a small increase in surface roughness and increased effective concentration of the FAS coating on the fabric by enhancing its repellence before and after repetitive washing [75].

Galkina *et al*. (2012) modified cotton fiber using nanocrystalline titanium dioxide (TiO_2) sol. The low temperature of the sol-gel method was used for synthesizing TiO_2 NPs. Titanium (IV) tetraisopropoxide was dissolved in an aqueous medium consisting of isopropyl alcohol and water (3.5:90) at a temperature of 80 °C. Nitric acid was used as a peptizing agent, and the synthesizing process was completed once the transparent sol was formed. 1,2,3,4-Butane tetracarboxylic acid was used as a spacer leading to a strong fixation of NPs on the surface of cotton fiber. As a result of low-temperature sol-gel synthesis, photoactive NPs were formed, which led to the formation of titanium dioxide of anatase-brookite modification. The addition of BTCA cross-linking agent and sodium hypophosphite as a cross-linking catalyst for TiO_2 sol resulted in the displacement of the absorption band from 1642 to 1660 cm^{-1} - indicating high self-cleaning properties of the fabric [76].

Sivakumar *et al*. (2013) developed a self-cleaning fabric using ZnO NPs based on a water-based sol-gel method. Zinc acetate used as a precursor was diluted in deionized water, and the pH of the solution was adjusted to 10 by diluted ammonia and later heated at 100 °C for 12 hours. The ZnO sol was coated on the fabric using the pad-dry-cure method. The small NPs with 9nm were obtained and dispersed uniformly, and they adhered strongly to the fabric matrix. The self-cleaning property of the treated fabric was investigated based on the degradation of the coffee stain on the fabric. The degradation rate was between 58.4% and 63.4% during 12 hours of exposure to sunlight. The treated cotton fabric also had UV protection property (UP) values between 30.62% and 35.2%. The ZnO NPs finishing on cotton fabric resulted in self-cleaning and high UV protection, but it was also antimicrobial and possessed soil release action [77].

Yuzer *et al*. (2022) used sol-gel-based Copper (II) sulfate pentahydrate ($CuSO_4$) doped by TiO_2 to develop the self-cleaning fabric. The Cu-doped TiO_2 sol was prepared by adding titanium tetraisopropoxide (TTIP) solution and acetic acid into 500 mL of distilled water. Nitric acid (HNO_3) was added to the solution as a catalyst. It was then heated at 80 °C and stirred vigorously for 2 hours. The $CuSO_4$ was added dropwise into the sol-gel solution and mixed properly before being coated on the cotton fabric using the dip-coating-cure method. The coffee stain was used to determine the self-cleaning performance. The degradation was 78% in 1 hour, and it was completed in 2 hours under UV illumination. The coated cotton fabric also had antibacterial properties under low and higher illumination intensities [78].

3.1.3. UV protection.

Exposure to the sun's UV radiation can cause skin cancer, accelerate skin aging, and cause cataracts and other eye diseases. About 60,000 people die every year from skin cancer due to their long-term exposure to UV radiation [79] which also adversely affects one's immune system [80]. Minimizing exposure to sunlight, applying sunscreens, and wearing protective attire may reduce the deleterious effect of UV radiation. Wearing UV protection textiles, such as shoes, hats, apparel, and baby carrier covers, is the easiest way to protect against UV radiation. The chemical structure of the fibers is directly responsible for protecting the wearer against UV rays and UV transparency [81]. Natural fibers, such as cotton, wool, and silk, have a reduced UV radiation absorption rate compared with synthetic fibers, such as polyethylene terephthalate (PET). Bleached fiber has a high UV transparency because of the reduction of natural pigments, pectin, and waxes, which act as UV absorbers during the bleaching process.

Arik and Katmaka (2020) used zinc salts and zinc oxide nanopowders to improve the performance of linen fabric. They prepared 10 sol-gel coatings with zinc salts (zinc acetate, zinc nitrate, and zinc sulfate) and zinc oxide nanopowders. Zinc salts were dissolved in pure water, while zinc oxide nanopowders were dissolved in acetic acid and pure water with a ratio of 30:170. The pad-dry-cure method was used to apply the sols to linen fabrics. The particle size sequence was found to be zinc nitrate > zinc acetate > zinc sulfate > ZnO nanopowder. The zinc salts particles were micro (µm) size while ZnO nanopowder particles were nano (nm) size [82]. The ZnO nanopowders were in spherical shapes with a uniform dispersion of the particles [83–86], and they were better than micro-sized zinc salts in terms of efficiency. Improvements were seen in the linen samples in terms of having greater protection against UV rays and bacteria; they were also smoother.

Wang *et al*. (2019) developed a multifunctional textile using an aluminum-doped zinc oxide (AZO)-embedded lemon microcapsule and SiO_2 dual-layer coating. The fabric showed greater ultraviolet protection, thermal insulation, and superhydrophobic and aromatic performance. The synthesizing of AZO involved the use of the water-based sol-gel method. The nano AZO was obtained through the precipitation and calcination process, and it was deagglomerated using dispersant 5040 to get a homogeneous dispersion. The AZO-embedded lemon microcapsule was prepared using interfacial polymerization technology, and the cotton fabrics were immersed in them and padded before they were washed and dried. To give a superhydrophobic property, the treated fabrics were immersed in silica sol, followed by the padding process. The spherical shape AZO-loaded lemon microcapsules had an average diameter of 1.5 mm, and they were obtained through interfacial polymerization. The treated cotton fabric showed outstanding thermal insulation with very low light transmittance in the ultraviolet waveband. Additionally, it showed an excellent waterproof property with a contact angle of 153.35 [4].

Pan *et al*. (2012) used nano alumina sol to ensure the cotton fabric has superhydrophobic and high UV protection properties. Aluminum nitrate nonahydrate (Al $(NO_3)_3 \cdot 9H_2O$) was used as a precursor, distilled water as a solvent, and concentrated ammonia ($NH_3 \cdot H_2O$) to adjust the pH. The nano-Al sol was obtained by precipitation and peptization. It was first precipitated by ammonium and converted into AlOOH after vigorous stirring. The slurry condition of AlOOH was peptized using nitric acid after the filtration and washing process. The mixture was kept in a microwave reactor to form a homogeneous transparent nano-Al sol. The cotton fabrics were coated with nano-Al sol using the pad-dried method before they were immersed in an ethanol solution of fatty acid and later pad-dried and cured. The NPs with a constant size of ~65 nm were observed, and the coated fabric showed good UV protection capability and excellent hydrophobic properties. The water contact angle can reach up to 146.27°, and its UPF value was 164.06 (UPF rating 50+) [87].

3.1.4. Antibacterial activity.

Antibacterial textile has become very popular recently due to increased public health awareness. It has the potential to minimize the transmission of bacterial and fungal infections. Therefore, antimicrobial textile has been used widely to make hospital gowns, bed covers, and curtains [88]. The demand for antimicrobial textiles for manufacturing sports clothing, home furnishing, air filters, and water purification systems, among others, has also increased [89, 90]. An antibacterial textile can also reduce odor caused by bacteria when it comes in direct contact with the NPs attached to the fabric. The NPs disrupt the biological process, namely the cell functions of the bacteria [91, 92]. The antibacterial agents can be applied to the fabric through various finishing methods, such as pad-dry-cure, exhaustion, spraying, and foaming.

Sun *et al*. (2016) developed a method that deposits nanostructured ZnO on cotton fabric to provoke antibacterial functionality. This involved in-situ synthesizing of nanoparticles using ultrasonic irradiation. The sol was prepared by dissolving amino-terminated silicon (AEAPTS) in a mixture of ethanol, water, and HCl with a ratio of (8:50:0.008). Ultrasonic irradiation was used to promote the growth of ZnO on the cotton fabric surface. The morphology of spindle-like ZnO NPs with a width of 150–200 nm and length of 250–300 nm was observed. The ZnO-loaded cotton was found to possess better antibacterial performance against *S. Aureus* and *E. Coli* and moderate cytotoxicity against L929 fibroblasts. The ZnO-loaded fabric additionally has excellent UV protection with ultraviolet A (UVA) and ultraviolet B (UVB) values of 5.21 and 1.37 %, respectively [88].

Mahltig *et al*. (2010) examined the antibacterial finishing of polyamide textile to test the efficiency of silver-containing silica sols against E. Coli with high wash fastness up to 40 cycles. The silica/$AgNO_3$ sols were prepared by mixing 10 mL of TEOS and GLYEO (7:3) with 60 mL of water; 30 mL of 0.01 molar HCl was added into the solution to form a turbid mixture, and the solution was stirred until a clear solution was formed. The sols were applied onto polyamide fabric in a continuous pad-dry-cure process. The dot-like structure with sizes below 100 nm was observed on the fiber surface, indicating the presence of silver NPs [93].

Vigneshwaran *et al*. (2006) used zinc oxide-soluble starch nanocomposites (nano-ZnO) to coat cotton fabric to enhance their antibacterial property and protection against UV radiation. Zinc nitrate hexahydrate $Zn(NO_3)_2$ was used as a precursor, water as a solvent, and soluble starch as a stabilizer. Nano-ZnO was synthesized by reacting $Zn(NO_3)_2$ with sodium hydroxide (NaOH) in the presence of soluble starch, and the former was coated on the fabric using the pad-dry-cure method. The morphology of granules-like NPs with an average particle size of 38± 3 nm was observed. The nano-ZnO coated cotton fabric proved excellent antibacterial efficiency against *Staphylococcus aureus* and *Klebsiella pneumoniae*. Treated cotton fabric offered better protection against UV radiation [94].

3.1.5. Flame -retardant textile.

Flame-retardant textile protects workers from thermal and fire exposure. It is self-extinguishable and prevents the flame from spreading to reduce the risk of injury. It also protects the wearer from electrical short circuits, arc flames, and flash fire. Due to its unique properties, the textile has broad applications in military, civil, and industrial sectors. Flame-retardant textiles are produced by modifying their fibers using chemicals that inhibit flame ignition and spread [95]. Textiles, such as nylon, polyester, polypropylene, cotton, and wool, are made of highly ignitable materials. However, the development of nanotechnology that uses inorganic materials, chemically treated textile (that has flame retardant properties), and polymer modification has led to the production of textiles with reduced ignitability [96]. For example, silica sol-gel has been proven to avoid melt-dripping, a major fire hazard when coated with synthetic materials. It also improves the durability of other flame-retardant surface treatments [97].

Waitinen (2015) examined the coating of linen fabric with silica sols for its flame retardancy properties. The research used TEOS as a precursor, distilled water as a solvent, and HCl as a catalyst. The sol was coated on the linen using two different methods: bath exhaustion and ultrasonication and dry and cure. The coating methods influenced nanoparticle distribution; in the bath exhaustion method, the NPs were not homogenously distributed using the ultrasonication method. The fabric was washed in both coating methods three times to examine its flame-retardancy property [98].

Alongi *et al*. (2013) examined optimization of the multistep sol-gel process, which involved a pre-hydrolysis followed by deposition of hybrid phosphorus-doped silica layers to cotton fabrics. The aim was to examine their flame retardancy properties. The hydrolysis step is fundamental in ensuring the success of the overall process of optimization by the precursor [99]. Diethylphosphatoethyltriethoxysilane (DPTS) was pre-hydrolyzed for 24 hours using hydrochloric acid (HCl), and water was subsequently added to obtain the sol solution. The fabrics were impregnated with sols using the pad-dry method before they were thermally treated in a gravity convection oven. The findings showed fine and homogenous coverage of NPs. The flame retardancy of the fabrics was enhanced, and the treated fabrics were washed five times [100].

Alongi *et al*. (2012) examined the use of hybrid phosphorus-doped silica films on cotton fabric to gauge their thermal and fire stability. They did this using the sol-gel method. 3-aminopropyltriethoxysilane (APTES) and diethylphosphatoethyltriethoxysilane (DEPTES) were hydrolyzed separately in deionized water to obtain silica sols. N,N,N',N',N",N"-hexakis-methoxymethyl-[1,3,5] triazine-2,4,6-triamine (MF), which acted as the cross-linker was prepared with dimethylbenzene sulphonic acid in deionized water. The APTES and MF solutions were added and reacted with DEPTES solution. The sols were applied on the surface of cotton fabric using the pad-dry-cure method. Results showed the distribution of the particles was homogenous and compact at the warp and weft of the fibers. The hybrid phosphorus-doped silica sols coated on the cotton fabric could also reduce the total burning time and burning rate of cotton in addition to protecting it from flame [101].

Zhao *et al*. (2021) synthesized a simple and halogen-free flame retardant for cotton formed by a spontaneous Mannich-type reaction between branched polyethylenimine (PEI) and tetrakis(hydroxymethyl)phosphonium chloride (THPC), which consist of 80% of an aqueous solution. A polymer network applied with 5 wt% THPC and 10 wt% PEI provides self-extinguishing behavior to the cotton fabric in vertical flame tests. The treated cotton retains its high flame retardancy even after simulated washing. This coating promotes the formation of a continuous, intumescent char layer that effectively protects the cellulose matrix from fire and prevents the production of flammable volatiles during pyrolysis and combustion [102].

4. Future Trends and Challenges of Water-Based Sol-Gel Finishing

A wide variety of protective fabrics is currently being successfully developed using nanotechnology. However, there are rising concerns that this technology may threaten consumers' health and safety. The nanoparticles are extremely small and can be readily absorbed by the body compared with larger-sized particles, causing health complications. The government is providing incentives to enhance business competition to produce eco-friendly products in line with consumer and industry trends. Despite this, significant improvements are needed to the ecological features of the nanocoating process. Therefore, the water-based sol-gel method is gaining attention and popularity to address the ecological deficits of the current products.

Additionally, improving the water-based sol-gel process also reduces reliance on chemicals, namely solvents such as ethanol and isopropanol, to be replaced with water for synthesizing. This also reduces operational and environmental costs. In the long run, using water-based sol-gel finishing would benefit investors as it reduces the overall cost of production. However, challenges prevail in ensuring the stability of the sols in water due to precursor-solvent compatibility. Lack of human expertise and slow progress in research and development (R&D) in this area have affected the industry. The water-based sol-gel method is still evolving, and the focus is on developing novel and sustainable products. Research must now target ways to develop innovative ways to widen the application of protective fabric that has good functionality as well in line with consumer and environmental needs. In short, the new methods must meet health, safety, comfort, and environmental demands. The water-based sol-gel method would play a key role in the nanocoating finishing of fabrics primarily due to environmental concerns associated with other methods.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

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