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Review

Revolutionizing textile manufacturing: Recent advances in the synthesis of chitin derivatives and their application in sustainable processing and multifunctionalization of textiles

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ABSTRACT

The textile industry is recognized as a significant environmental polluter due to its reliance on numerous non-biodegradable and toxic petroleum-derived chemicals and polymers for textile processing. A considerable portion of these substances is discharged into the environment as effluent, resulting in significant pollution. To mitigate this reliance on petroleum-based chemicals and reduce environmental harm, a comprehensive approach is necessary, emphasizing the use of alternative feedstocks, enhancing energy efficiency, and implementing principles of a circular economy. In this context, chitin derivatives show great promise as substitutes for many of the chemicals and polymers currently utilized in textile processing. Recent advances in chitin derivatization have allowed for its derivatives to be employed in various applications: as a sizing agent for cotton warp yarns, a shrink-resist agent for wool fabrics, a mordant for dyeing textiles with natural dyes, a modifier for cellulosic fibbers for salt-free dyeing, and a finishing agent that imparts antibacterial, UV-protective, wrinkle-resistant, antioxidant, and fire-retardant properties to textiles. Chitin offers several advantages, including being renewable, non-toxic, biocompatible, and extractable from biomass. Nevertheless, challenges remain, such as high costs, scalability issues, and performance limitations, which hinder its broader application in textile manufacturing. Addressing these challenges will not only enhance the use of chitin in textiles but may also extend its impact across other sectors, such as medical textiles and biomedical materials. The integration of chitin and its derivatives in textile manufacturing has the potential to foster greener and more sustainable textiles by providing renewable, high-performance, and biodegradable auxiliaries and finishing agents. Successfully overcoming obstacles related to cost and performance will assist the fashion industry in achieving sustainability goals.

1. Introduction

The textile industry is a significant industrial sector that manufactures not only fibers and fabrics for garments but also medical textiles, protective textiles, conveyor belts, geotextiles, and wound care materials, generating substantial revenue and employment. Clothing plays a crucial role in human life, providing not only coverage for the human body but also protecting it from harmful environmental factors, such as dust, dirt, microbes, heat, cold, and light. In the manufacturing of textiles, a range of organic compounds and polymers is used as sizing agents, shrink-resist agents, fiber modifiers, and finishing agents that not only enhance functional properties of fabrics but also make them suitable for the desired end uses. However, most of these chemicals and polymers are petroleum-derived, non-biodegradable, toxic, and potentially pollute the environment when they are discharged as effluent. They are not only released as effluent during the manufacturing of textiles, potentially polluting water and soil environments [1], but when post-consumer textiles are disposed of at the end of life, these toxic chemicals are released into the environment. The application of such types of petroleum-derived fiber modifiers and finishing agents can affect the biodegradability of textiles, even made from biodegradable fibers [2]. When incinerated, these textiles contribute to air pollution, releasing toxic gases and airborne particulates that can harm respiratory health and produce substantial amounts of greenhouse gases. The disposal of pre- and post-consumer textile waste in landfills is a concern as it releases significant amounts of methane, a potent greenhouse gas,

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and toxic liquids, and can also lead to microplastic pollution [3]. Overall, the textile industry, particularly the chemical processing sector, poses significant environmental risks due to the release of toxic chemicals into the ecosystem. To align with the United Nations' targets for reducing annual greenhouse gas emissions, a transition from petroleum-based textile auxiliaries, fiber modifiers, and finishing agents to renewable alternatives is crucial to decarbonize textile manufacturing [4]. Many of these harmful petroleum-derived textile auxiliaries, fiber modifiers, and finishing agents can be easily replaced with bio-derived alternatives that are non-toxic, cost-effective, and can contribute to enhancing the sustainability of textile products. There is an urgent need to transform future textile manufacturing from petroleum-derived materials and chemicals to biobased ones, enhancing their sustainability.

In this context, chitin has been studied as a viable and sustainable feedstock for sizing and shrink-resist agents, fiber modifiers for salt-free and mordant dyeing, and finishing agents. Chitin, an *N*-acetylated amino polysaccharide, is the most abundant natural polymer after cellulose, and its global production is estimated to be 1000 billion tons/annum [5]. Chitin is a naturally derived polysaccharide with the advantages of being bio-renewable, environmentally friendly, biocompatible, biodegradable, and bio-functional. Fig. 1 shows the applications of chitin derivatives studied in textile manufacturing. Some of these applications may include coating wool fibers with or without chlorination to provide shrink resistance [6], sizing cellulosic and other warp yarns [7], as a fiber modifier to enhance dye absorption and salt-free dyeing [8], and as an antimicrobial agent to make textiles antimicrobial [9], and dye-adsorbent for dyehouse effluent treatment [1].

In this comprehensive review article, we discussed the extraction of chitosan (CS) from various biomass sources and the synthesis of different CS derivatives for textile applications. We also explored the application of CS as a sizing agent for cotton yarns, a shrink-resisting agent for wool fibers, a modifier for cotton fibers to improve dye absorption, and a bio-mordanting agent. We compiled and compared the performance of CS and its derivatives in terms of antibacterial activity, shrinkage resistance, antioxidant properties, UV protection, and flame retardancy. The mechanisms by which CS and its derivatives exhibit antibacterial, shrink-resistant, antioxidant, UV-protective, and flame-retarding properties are also discussed. We outlined the remaining challenges for CS as a feedstock for fiber-forming polymer to textile finishing agents, and future research needs to solve them. To the best of our knowledge, no other review articles have reported a comprehensive review of the application of CS to textiles, covering fiber production to textile finishing.

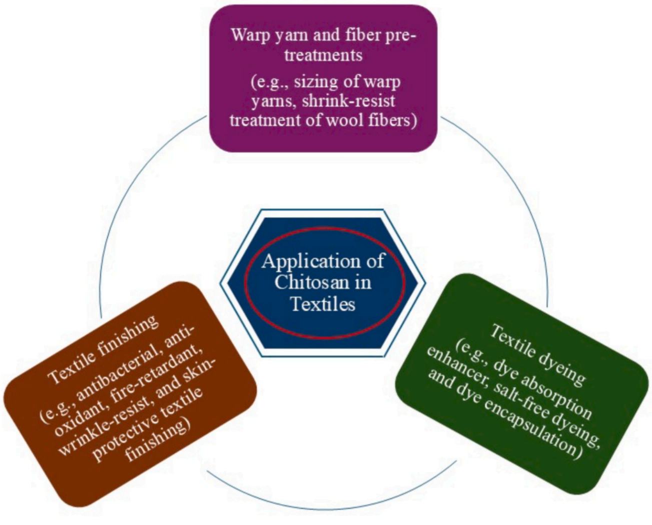

Fig. 1. Application of chitin derivatives at various stages of textile processing.

2. Chitin and its extraction methods

The primary source of commercial chitin is waste biomass from the seafood industry, such as crustacean shells from crabs and shrimp, which serves as a valuable, non-food-competing resource that would otherwise be a waste product [10]. Crustacean shell waste is comprised of proteins, inorganic salts, pigments, and lipids other than chitin [11]. Squid pens are another chitin source, and chitin extracted from them often exhibits greater reactivity towards deacetylation [12]. Vast quantities of crustacean waste, such as shells and other by-products, are generated annually. Their disposal through landfills or ocean dumping leads to significant environmental pollution and severe marine environmental problems, depleting oxygen levels and causing acidification of water and extensive siltation of corals. For example, in 2022, India alone produced around 80,000 tons of shellfish waste, while the processing of shrimp and crabs in the EU alone generated more than 100,000 tons of shellfish waste annually [13]. Upcycling shellfish waste not only addresses the environmental issues associated with the dumping of such waste into the environment but also provides a sustainable feedstock for CS production. Chitin is a rigid and inelastic natural polymeric material, which is found in the exoskeletons of various arthropods, including crustaceans, insects, myriapods, and arachnids, as well as in the cell structures of algae, yeast, and the cell walls of fungi. It can also be extracted from insects, such as cicadas, silkworms, and honeybees, often resulting in higher yields compared to marine crustaceans [14]. Films made from chitin extracted from *C. molossus* L. exhibited higher tensile strength and elongation at break compared to the film made from shrimp-derived CS [15]. The diverse range of raw material sources makes chitin the second most abundant natural polymer on Earth, following cellulose. Shrimp shells contain 30–40% proteins, 30–50% calcium carbonate, 20–30% chitin, and trace amounts of pigments, such as astaxanthin, canthaxanthin, lutein, or β-carotene [16]. The exoskeleton of crustaceans is very rigid and consists of a three-layered cuticle.

Chitin exists in nature in three different crystalline polymorphic forms: α-, β-, and γ-chitin, and their chemical structures are presented in Fig. 2. Among these, α-chitin, featuring strong intermolecular and intramolecular bonds with antiparallel chains, is the most common form found in nature [17]. In contrast, β-chitin, characterized by a parallel arrangement of chains and a lower degree of crystallinity than α-chitin, is primarily found in the pens of *Loligo* squids, pogonophora tubes, and the spines of diatoms. Additionally, γ-chitin is a combination of both α and β chitins and can be found in the stomachs of *Loligo* squids and the cocoon fibers of the *Ptinus beetle* [18].

2.1. *Extraction of chitin*

Chitin extraction involves isolating chitin from shell biomass. Chitin is primarily found in the inner layers of the shell's cuticle, where it is wrapped in proteins. The middle layer consists of chitin mixed with minerals, while the outer layers are composed of calcium carbonate and proteins. To effectively isolate chitin, it is essential to exfoliate the outer and middle layers to free chitin. The chitin extraction process can be divided into three main steps: pre-treatment, demineralization, deproteinization, and decolorization, as shown in Fig. 3 [19]. The collected shells are washed and ground into powder. Demineralization is then carried out by soaking the powder in a strong acid solution to remove mineral contaminants. However, at this stage, chitin still contains various proteins and pigments. To eliminate natural pigments, demineralized shells are treated with strong oxidants, such as hydrogen peroxide (H_2O_2) or sodium hypochlorite. Following this, the shells undergo treatment in strongly alkaline conditions to dissolve and remove protein-based contaminants. The resulting pure chitin is then deacetylated to produce CS. The chitin extraction methods can be classified into the following categories:

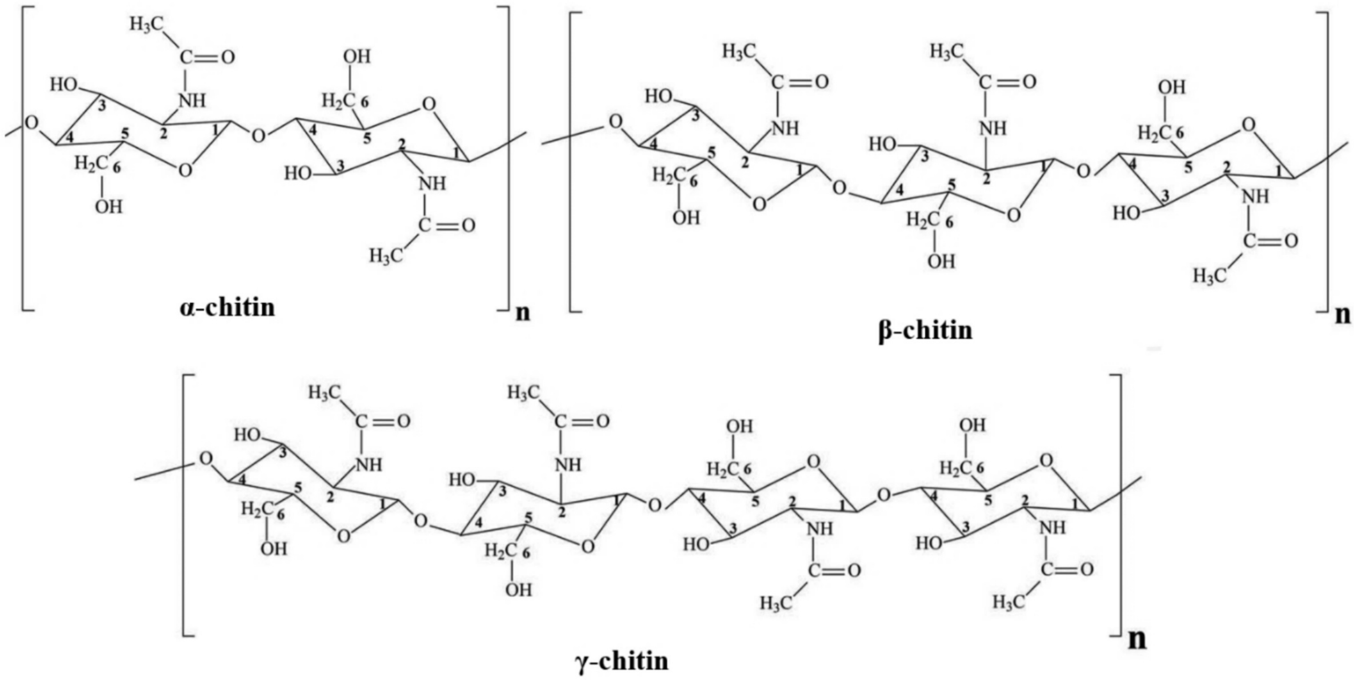

Fig. 2. Chemical structures of various forms of chitin.

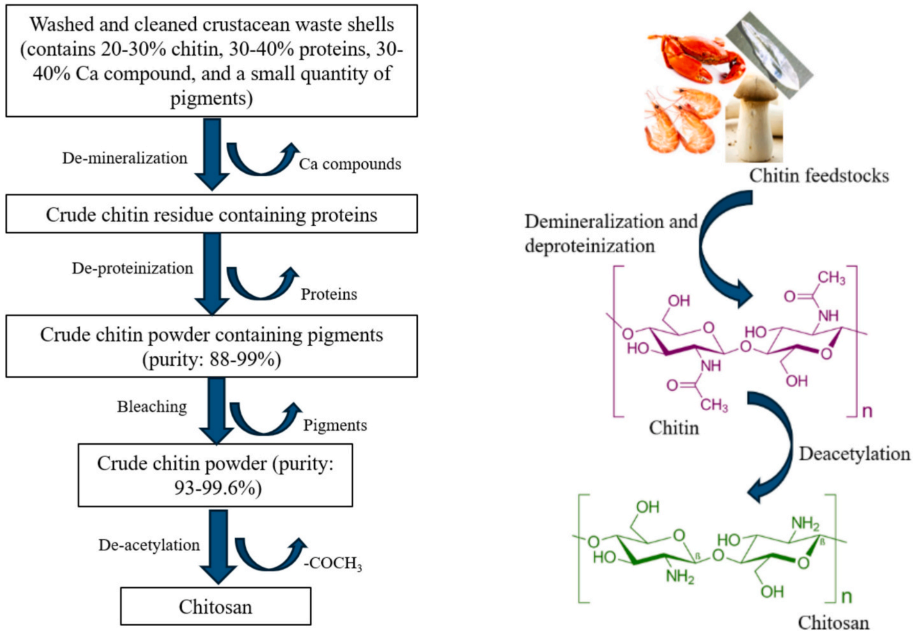

Fig. 3. Flow chart of the extraction of chitin from crustacean biomass shells and its conversion to CS [19].

2.1.1. *Traditional acid-alkali method*

In this method, demineralization is achieved by treating materials with acids, followed by the removal of other organic components found in arthropods, yeast, fungi, squid pens, and marine sponges through an alkaline treatment, which dissolves these components, allowing for the isolation of water-insoluble chitin. Both mineral acids (e.g., hydrochloric acid) and organic acids (e.g., citric and acetic acids) are used for this purpose, with hydrochloric acid being the most common choice. The inorganic component of the chitin feedstocks, calcium carbonate, is dissolved using hydrochloric acid. This reaction produces water-soluble calcium chloride, which separates from the shell materials. This treatment typically takes place at room temperature for 2 to 3 h. When organic acids are employed, the reactions are slower and yield calcium acetate or calcium citrate, which are less soluble in water compared to calcium chloride. After the chitin is recovered, it undergoes further washing and drying. The conventional process for isolating and purifying chitin from crustacean shells needs strong alkaline and acidic solutions, along with relatively high temperatures [20]. While this traditional method is cost-effective, it generates significant amounts of acidic, alkaline, and organic waste that can harm the environment. The subsequent treatment of this waste adds to the overall costs. Additionally, the high-temperature alkaline deproteinization can reduce the molecular weight of chitin, affecting its mechanical properties. As a response, enzymatic and ionic liquid (IL)-based extraction processes are being explored as sustainable alternatives.

2.1.2. Enzymatic extractions

Enzymatic treatments have been explored as a cost-effective and sustainable method for extracting chitin from crustacean biomass. This process involves hydrolyzing proteins, dissolving them, and allowing the separation of chitin from the crustacean shells. The enzymes studied include aspartic protease [21], neutral protease in combination with microwave heating [22], and protease from *Streptomyces griseus* [23]. While enzymatic extraction is relatively straightforward, environmentally friendly, and less expensive, its efficiency in removing proteins is lower compared to chemical methods, and 5–10% of residual protein remains in the isolated chitin.

2.1.3. Two-stage organic acids and discharged barrier plasma

The organic protein components are removed by treating shrimp shells with alkali at a moderate temperature, which dissolves the proteins while leaving the chitin intact. Borić et al. successfully utilized dielectric barrier discharge (DBD) plasma to deproteinate shrimp shell waste for the isolation of chitin from it [24,25]. In this method, the shrimp shells underwent two cycles of different nitrogen-based DBD plasmas to eliminate the protein components, followed by one cycle of acetic or lactic acid at 30 °C for 15 to 30 min to remove the mineral components. The DBD plasma treatment was found to be an efficient method for rapid protein removal that does not affect the chitin biopolymer. However, this developed process is costly, requiring significant capital investment for DBD plasma machinery.

2.1.4. Ionic liquid-based chitin extraction

Ionic liquids (ILs) are salts with melting points below 100 °C, composed of a large organic cation and a smaller anion, which can be either organic or inorganic. They are considered ‘green’ solvents due to their low vapor pressure, thermal stability, low flammability, and ease of recyclability. The extraction of chitin using ionic liquids involves dissolving crustacean shells in an IL and precipitating the chitin with an antisolvent, which helps in the formation of its cell-matrix or mechanically resilient structures [22]. High-purity chitin has been isolated from shrimp shells using pulping liquors made from varying ratios of 1,5-diazabicyclo[4.3.0]-non-5-enium acetate or [DBNH][OAc] and glacial acetic acid [26]. These ILs are employed to deproteinate and demineralize the shrimp shells in a single step. Importantly, the used ionic liquid can be recycled in its original form through distillation. IL disrupts the hydrogen bonding between the amide and hydroxyl groups of chitin, and the addition of urea or thiourea enhances the chitin-dissolving capability of ionic liquids [27]. However, it is important to note that the IL-based extraction process for chitin is generally more expensive compared to traditional alkali or acid extraction methods, and the complete separation of ILs from the isolated chitin is difficult.

2.2. Biosynthesis of chitin

Chitin can be obtained not only through the extraction from various naturally derived biomasses, but also it can be synthesized through a biosynthetic route. The biosynthesis of chitin is a highly conserved process among different organisms. It plays a crucial role in growth, development, and reproduction, particularly in insects, fungi, and oomycetes. Chitin biosynthesis involves a series of enzymatic reactions that convert uridine diphosphate-*N*-acetylglucosamine (UDP-GlcNAc) into chitin [28], and a membrane-integrated glycosyltransferase transfers GlcNAc from UDP-GlcNAc to a growing chitin chain. Chitin synthase (CS) is the enzyme that catalyzes the vital polymerization of *N*-acetylglucosamine from its activated precursor, UDP-GlcNAc, into the growing chitin polymer. One of the main advantages of chitin biosynthesis is that it is not dependent on seasonal changes, resulting in a lower level of inorganic materials, and facilitates simpler extraction of CS, as it does not require biomineralization, unlike extraction from crustacean biomass.

The typical biosynthesis route is presented in Fig. S1 (Supplementary Information) [29], which initiates from glycogen, catalyzed by the phosphorylase enzyme, and converts to glucose-1-phosphate. In the next step, glucose-1-phosphate is converted into glucose-6-phosphate in the presence of phosphomutase. This glucose-6-phosphate is then converted to fructose-6-phosphate by hexokinase. Following this, glutamine-fructose-6-phosphate amino transferase converts fructose-6-phosphate into *N*-acetylglucosamine, producing glutamic acid as a byproduct. In the next step, *N*-acetylglucosamine-6-phosphate is formed by glucosamine-6-P-*N*-acetyl transferase enzyme. It then transforms into *N*-acetylglucosamine-1-phosphate, followed by the generation of UDP-*N*-acetylglucosamine and *N*-acetylglucosamine through an isomerization step, where phosphate is transferred from C6 to C1, catalyzed by phospho-*N*-acetylglucosamine mutase. Furthermore, UDP-*N*-acetylglucosamine is formed through the utilization of uridine triphosphate (UTP). Finally, chitin is synthesized from UDP-*N*-acetylglucosamine in the presence of chitin synthase. The deacetylation of chitin leads to the formation of CS. This deacetylation in the cell wall of fungi is catalyzed by the chitin deacetylase enzyme (EC 3.5.1.41), which removes the acetyl groups from GlcNAc residues by catalyzing the hydrolysis of acetamido groups.

2.3. Challenges of chitin extraction

Extraction of chitin from marine sources and other materials presents several challenges, making it relatively expensive. Issues such as limited availability, seasonal supply fluctuations, and environmental pollution contribute to this problem. However, insects offer a promising and sustainable alternative that can help meet the growing demand for chitin and CS [30]. Insect farming has the potential to provide a more stable and environmentally friendly source compared to traditional seasonal aquaculture. In addition to crustaceans and insects, fungi are also a significant source of chitin. Fungal cell walls contain about 1–15% chitin, and their structure closely resembles that of crustacean cell walls. Currently, small-scale production of CS derived from both fungi and insects is available. The biosynthetic route of chitin production is generally considered a green and environmentally friendly alternative to chemical extraction methods, but is less efficient on an industrial scale, with limitations in scalability, high production cost, long processing time, and difficulty in getting highly pure chitin [31].

2.4. Scalability of chitin production

Industrial-scale chitin, CS, and carboxymethyl-CS (CM-CS) production predominantly uses conventional chemical methods involving strong acids and alkaline solutions as solvents due to their efficiency and low cost. Several industries in China also utilize emerging “green” alternative solvents, including deep eutectic solvents (DESs) and ionic liquids (ILs) to reduce the environmental impact of the traditional processes [32]. Both batch and continuous processing are feasible for chitin and CS production, with the optimal choice depending on the raw material source (e.g., crustacean vs. fungal) and target production scale. Continuous processes generally offer higher efficiency and lower costs at high volumes, while batch processes provide flexibility for lower volumes or specific process steps. Over 75% of commercial chitin globally is sourced from crustacean waste, such as the shells of shrimp, crayfish, crabs, and lobsters, which are readily available as a byproduct of the large seafood industry. The yield varies from 1.3% to 15.5% depending on various factors, including the extraction methods and feedstocks [33]. A mass-energy balance for the chemical production of CS shows that the extraction of each kg of chitin or 0.7 kg of CS from shrimp requires 8 kg of acid, 5 kg of alkali, and > 2 kWh of electricity, which also produces 1 ton of effluent containing >4 kg of protein and almost 2 kg of calcium [34]. The carbon footprint of chitin and its various derivatives also varies depending on location and other factors. For example, using SimaPro LCA software, Riofrio et al. showed that the carbon footprint of CS production in India, Europe, and Ecuador is 12, 77, and 59 kg CO_2 eqv/kg CS [35]. The cost of chitin production varies widely from under $1/kg to over $100/kg depending on the raw material source (e.g., cheap shellfish waste vs. fungi), extraction efficiency, scale (large-scale is cost-effective than a small batch), processing methods (chemical vs. greener enzymatic), purity required, and location, with major factors being operational costs, reagent reuse, and taxes, though newer insect-based methods promise significant cost reductions. In the case of the traditional acid/alkali method, the solvent is not recovered, but for IL and DSE, most of the solvents are recovered and reused.

3. Chitin derivatives

While many CS derivatives have been developed over the years, this article focused specifically on those studied for textile applications. These derivatives can be broadly classified into two categories: chemically modified CS and polymer-grafted CS.

3.1. Chemically modified CS

In this type of CS derivative, synthesis occurs through a reaction with chlorine compounds. This process modifies the amino groups and/or the primary C-6 hydroxyl groups of the glucopyranose monomer unit in CS via hydrogen abstraction. Examples of these derivatives include CM-CS and quaternized CS (Q-CS).

3.1.1. Conversion of chitin to CS

CS is the simplest chitin derivative, which is soluble in diluted acetic acid solution. To convert chitin into CS, the acetamide ester linkage of chitin is broken down, converting the *N*-acetyl group into a primary amine by a process called deacetylation. When the conversion of *N*-acetyl groups to amine groups in chitin exceeds 50%, then it is considered CS, which dissolves in an aqueous solution of acetic acid (AA). Deacetylation of chitin can be carried out under acidic or alkaline conditions. However, the alkaline method is preferred because cellulosic materials are more stable in alkaline environments than in acidic ones. Acidic conditions are not ideal since acids can damage glycosidic bonds, leading to polymer chain breakdown [36]. Purified chitin is typically dispersed in a strong sodium hydroxide solution and heated at 120 °C for varying durations, depending on the required degree of deacetylation (DD). It is necessary to note that temperatures above 100 °C can degrade the CS polymer through oxidative breakdown, and therefore, the reaction is conducted in an inert atmosphere to minimize degradation [37]. The antimicrobial and antioxidant properties of CS improve with an increased DD. However, greater deacetylation also results in decreased thermal stability. Additionally, the tensile strength of CS is influenced by CS's molecular weight, which varies depending on the chitin source, as well as the temperature and time of the deacetylation treatment [38]. Interestingly, the antibacterial properties of CS are also affected by its molecular weight, and lower molecular weight CS and CS oligomers tend to exhibit stronger antibacterial effects compared to their higher molecular weight counterparts [39]. To classify a substance as CS, the DD must be at least 50%, which allows it to be water-soluble in acidic conditions; anything below this threshold is still considered chitin. The DD and the average degree of substitution can be assessed using solid-state NMR techniques. Techniques, such as ^{1}H NMR and ^{13}C NMR, can quickly determine the degree of substitution in CS solutions.

3.1.2. Carboxymethylation

It is synthesized by reacting CS with chloroacetic acid in an alkaline medium [40]. In the process of carboxymethylation, some of the hydroxyl (–OH) and/or amine (−NH_2) groups on the CS molecule are replaced with carboxymethyl (–CH_2COOH) groups. This occurs when CS is reacted with chloroacetic acid under alkaline conditions. During this reaction, carboxyl groups are introduced by the binding of chloroacetic acid (CAA) with either C6-hydroxyl groups or amino and C6-hydroxyl groups, as illustrated in Fig. 4 (top). CM-CS is a derivative of CS that offers enhanced water solubility across a wide range of pH levels, as well as modified properties. It was mostly studied to enhance the dyeability and antibacterial properties of textiles. The carboxymethylation of CS enables its dissolution at a wide pH range, from acidic to alkaline conditions.

3.1.3. Phosphorylation

In this method, phosphonate groups are introduced in CS polymer by reacting with a phosphorylating agent, primarily targeting the hydroxyl and amino groups, to create phosphorylated CS. The common phosphorylating agents are phosphoric acid, phosphorous pentoxide, or phosphorous trichloride, which react with CS at elevated temperatures in the presence of an activator (e.g., urea or methanesulfonic acid). Fig. 4 (bottom) represents the phosphorylation of CS with phosphorous trichloride, and during this reaction, phosphonium groups are introduced by the conversion of either C6-hydroxyl groups or both amino and C6-hydroxyl groups. Phosphorylation of CS enhances CS's thermal stability, mechanical properties, fire-retardancy, and ionic conductivity, making it suitable for applications in textiles, bone repair, and fuel cells.

3.1.4. Quaternization

Quaternization of CS involves the replacement of some of its primary amino groups with quaternary ammonium groups [41]. The examples of Q-CS are: N-(2-hydroxy-3-dimethyl dodecyl ammonium)propyl CS chloride (HDCC), and O-acrylamide methyl-N-(2-hydroxy-3-dimethyl dodecyl ammonium) propyl] CS chloride [42], O-acrylamide methyl-N-(2-hydroxy-3-trimethylammonium)propyl] CS chloride [43], n-2-hydroxypropyl trimethylammonium chloride modified CS [44], glycidyltrimethylammonium chloride grafted CS or GTMAC-g-CS [45], and silane-modified quaternary ammonium CS [46]. This process results in a permanent positive charge, which enhances the solubility and antimicrobial properties of CS. During quaternization, specific primary amino groups on C2 are substituted with quaternary ammonium groups, leading to improved water solubility, as well as enhanced antimicrobial, antiviral, and antioxidant properties [47]. Quaternization of CS can be achieved through various methods, such as directly reacting with the amino groups of CS with alkyl halides,

forming Q-CS. An example is the trimethylation of CS's amino groups using methyl iodide, forming Q-CS 1, as shown in Fig. 5. Furthermore, quaternary ammonium groups can be introduced to CS by reacting with compounds like N-2-hydroxypropyl trimethylammonium chloride (NHTAC) or 4-(carboxybutyl)triphenyl phosphonium chloride (CBTPC), forming Q-CS 2 and Q-CS 3, respectively, as represented in Fig. 5 [48]. The quaternization of CS enhances its ability to interact with biological systems, significantly expanding its applications in medical textiles, drug delivery, and biomedical devices [49,50]. Quaternized CS was mostly studied as an antibacterial agent to make textiles antibacterial.

3.2. Polymeric grafting

In this type of CS derivative, a polymer is primarily grafted to the primary hydroxyl groups of the glucose unit in CS. However, in some cases, the primary amine groups may also participate in the grafting reaction. Examples of such derivatives include poly(NIPAM)-grafted CS [51], poly2-(acryloyloxy)ethyltrimethyl-ammonium chloride-grafted CS [52], phosphonate polymer-grafted CS [53], CS-based waterborne polyurethane [54], cyclodextrin-grafted CS, and CS nanoparticles [55,56]. Among these, poly(NIPAM)-grafted-CS (pNIPAM-g-CS) and poly[2-(acryloyloxy)ethyl]-trimethylammonium chloride grafted CS (pATAC-g-CS) can be prepared by grafting poly(NIPAM) and poly[2-(acryloyloxy)ethyl]-trimethylammonium chloride, respectively, onto the macromolecular chains of CS according to the scheme shown in

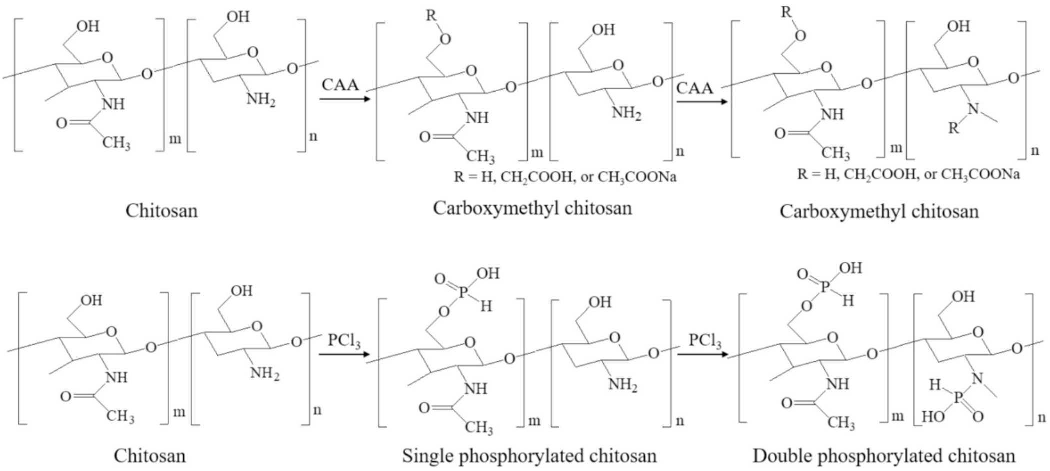

Fig. 4. Carboxymethylation (top) and phosphorylation (bottom) of CS with chloroacetic acid and phosphorous trichloride, respectively.

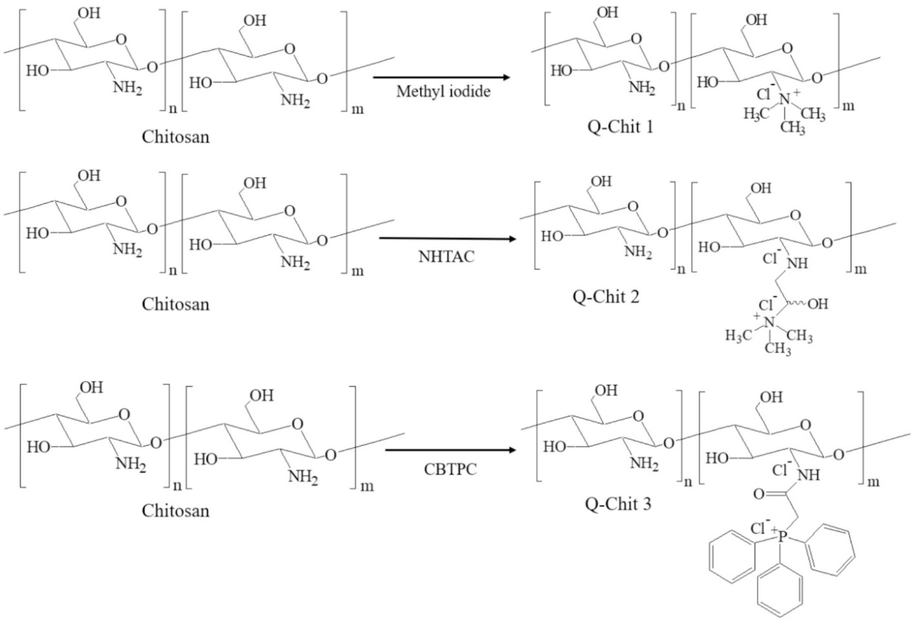

Fig. 5. Quaternization of CS with methyl iodide (top), N-2-hydroxypropyl trimethylammonium chloride (middle), and 4-(carboxybutyl)triphenyl phosphonium chloride (bottom) compounds [48].

Fig. 6 (top). This process is carried out through free-radical polymerization in the presence of a free-radical initiator.

The phosphonate polymer-grafted CS can be prepared through the nitroxide-mediated polymerization (NMP) of methacrylate dimethyl (methacryloyloxy)methyl phosphonate or DMMAMP in a CS solution using an SG1-terminated alkoxyamine initiator, as illustrated in Fig. 6 (bottom) [51,52,57]. This process led to the formation of a living poly (dimethyl(methacryloyloxy)methyl phosphonic acid) following the deprotection of the SG1-capped poly[dimethyl(methacryloyloxy) methyl] phosphonic acid. Subsequently, this polymer was grafted onto CS (CTS) to create phosphorus polymer-grafted CS, which possesses fire-retarding, anticorrosive, and metal ion-binding properties. CS with quaternary ammonium and phosphonate moieties was mostly studied for the antibacterial and flame-retarding treatment of textiles.

3.3. Nanochitin

Another important derivative of chitin is nanochitin, which is considered an assembly of semicrystalline chitin nanofibrils that show highly oriented nanocrystals embedded in an amorphous matrix [58]. Nanochitin could be of two types: chitin nanofiber (ChNF) and chitin nanocrystals (ChNC). The most common route to produce nanochitin is the top-down approach, where the chitin bundles are disintegrated into ChNC via controlled chemical reactions or into ChNF through mechanical treatments without the removal of disordered, nanocrystalline regions [58]. Nanochitin is small in size, ultralight, chemically stable, renewable, and biodegradable, along with excellent physical, chemical, and biological properties [59]. They also exhibit low toxicity and high chemical reactivity due to their large surface area and abundance of functional groups (acetylamino and hydroxyl groups). It has been studied as a functional coating to enhance various properties of textiles.

4. Application of chitin derivatives in green processing of textiles

4.1. Sizing of warp yarns

Sizing is exclusively used to protect the warp yarn from mechanical

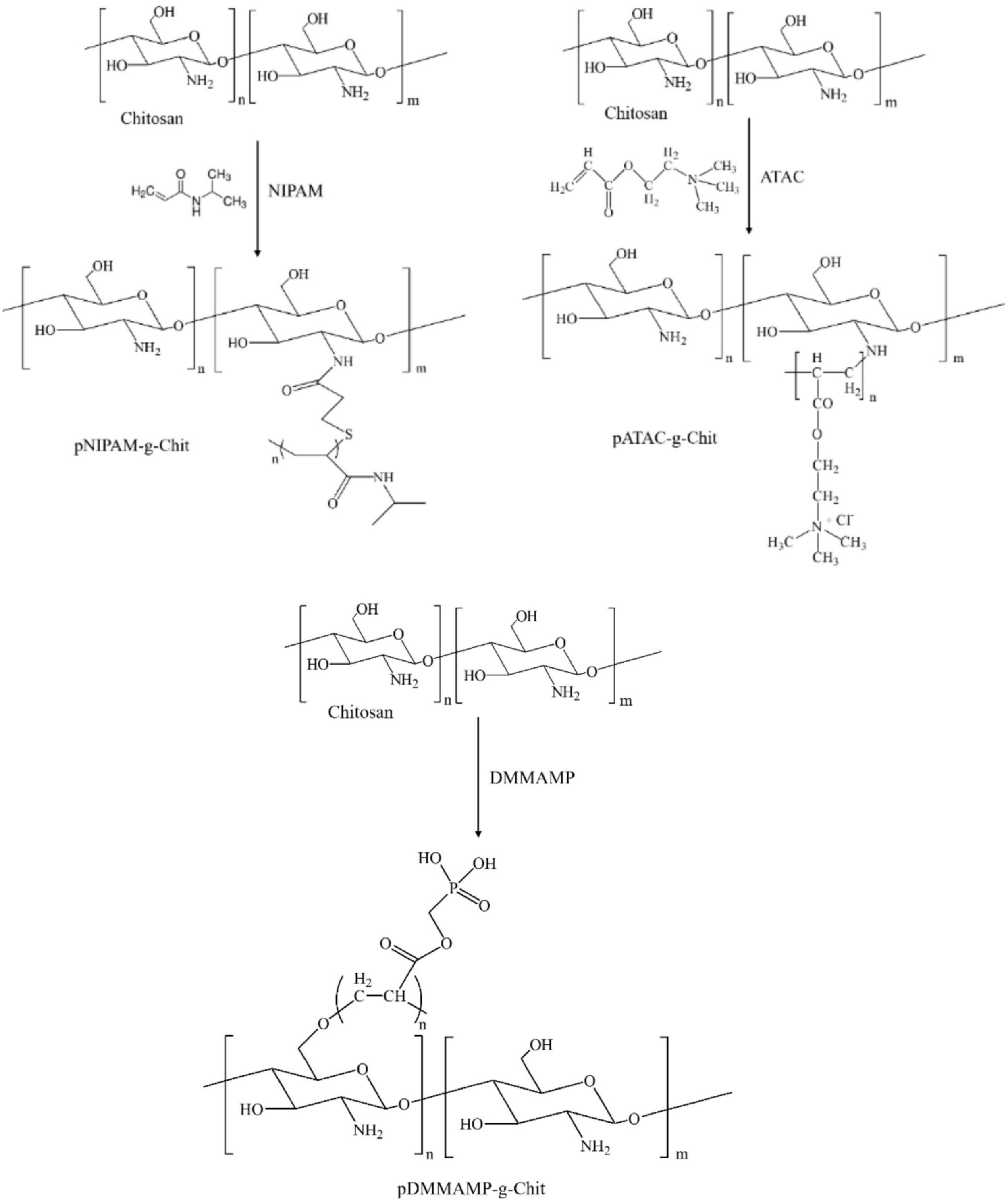

Fig. 6. Grafting of poly(NIPAM), pATC, and phosphorus-containing pDMMAMP to CS [51,52,57]. Reproduced with copyright permission from the Royal Society of Chemistry, UK (RSC), and Elsevier.

loads during the weaving process. Shedding creates an opening for the weft yarn to pass through, but it also increases the risk of warp breakages due to high tension. Therefore, warp yarns are reinforced by coating with sizing agents so that they do not break during shedding in weaving. However, after weaving, sizing materials are removed by a treatment called desizing; otherwise, they may cause uneven treatments during bleaching, dyeing, printing, and finishing. Starch and polyvinyl alcohol (PVA) are popular sizing agents in the textile industry. Although starch is natural, unlike polyvinyl alcohol, it is insoluble in water, and therefore, it is carboxymethylated by reacting with highly concentrated CAA to make it water-soluble. Textile sizing effluent creates environmental issues by contaminating water and soil with dyes, chemicals, and high levels of organic matter and salts, contributing to increased turbidity, which can disrupt photosynthesis in aquatic environments, depleting oxygen levels, and potentially harming aquatic life. They also present challenges for conventional wastewater treatment due to their complex composition and low biodegradability. The introduction of new spinning and weaving technologies, as well as the environmental concerns regarding the discharge of effluent in local streams and wastewater treatment plants, are prompting the search for new sizing materials.

The suitability of CS, a derivative of chitin, has already been demonstrated as a sizing agent to produce a coating on natural and synthetic fibers, especially on cotton fibers [7]. The sizing of cotton warp yarns with CS is shown by a schematic diagram in Fig. S2 (Supplementary Information). A strong adhesion formation between fibers and sizing materials, and high moisture absorbency make CS a suitable alternative as a sizing agent, as some of the conventional sizing agents, such as PVA, do not biodegrade or biodegrade only under certain conditions. Hydrolyzed CS with lower apparent viscosity was studied as a sizing agent, which significantly decreased elongation at break of cotton warp yarns, and the 100% removal efficiency was achieved only with water at 90 °C, eliminating the need for desizing treatment [59]. CS can also be added to traditional sizing agents, such as starch, to reduce the surface tension of the sizing liquor, which improves the wettability and the adhesion behavior of the modified sizing agent [7]. The application of CM-CS was studied as a sizing agent, which enabled easy desizing due to its high water-solubility [60]. Similarly, CS, modified by grafting with polyacrylamide, markedly improved the mechanical properties of the sizing film and its adhesion to textile fibers [61].

4.2. *Shrink-resist treatment of wool fibers*

Wool fabrics tend to shrink during laundering due to felting. Shrinkage causes changes in the shape and appearance of the fabric. To achieve shrink resistance, the scales of wool fibers are fully or partially etched and then coated with a polymeric resin to prevent the scales from locking. The most successful shrink-resist treatment is the so-called chlorine/Hercosett process, in which the edges of scales are etched, and a hydrophobic 18-methyl eicosanoid acid layer is removed from the fiber cuticle surface by chlorination so that the surface of wool fibers becomes hydrophilic, enabling compatibilization of wool fiber surface with the fiber-reactive hydrophilic poly(chlorohydroxypropyldiethylene adipamide ammonium chloride) or Hercosett resin [62]. However, the chlorination treatment produces effluent containing absorbable organohalogens (AOX) that are toxic and are classified as persistent organic non-degradable pollutants [63]. Various synthetic pre-polymers, such as Bunte-salt-terminated polyether or Securlana K [64], and diacrylate [65], have been studied as an alternative to Hercosett resin to provide wool fabrics with shrink-resistance. However, they are all petroleum-derived, possibly non-biodegradable, and have some level of toxicity, making them unsustainable.

4.2.1. *Shrink-resist treatment with CS*

CS treatment can improve the shrink resistance of wool fabrics to some extent by forming a layer and altering the scaly surface of wool fibers, but CS alone is ineffective in making wool fabric machine washable. Its effectiveness is enhanced by enzyme or oxidation pretreatments, which offer an alternative to the traditional but hazardous chlorine/Hercosett process. Alkaline hydrogen peroxide pre-treatment significantly modifies the wool cuticle structure, leading to wool fiber tip smoothening and disrupting disulfide bonds of the keratin protein within the cuticle, forming cysteic acid and making the fiber surface more hydrophilic [66]. However, enzyme treatments can etch the cuticle edges of wool fibers, providing better shrink-resistance, but can cause uneven treatment and excessive damage to wool fibers as enzymes can enter the fibers [67]. The use of modified enzymes, such as CS-grafted papain (CS-g-Pap), reduced damage to wool fibers but with a loss in enzyme activity [4]. It was reported that CS coating, followed by protease treatment, can further enhance the shrink-resistance of wool fabrics and can also repair the damage caused by enzymes to some extent [68]. The wool fabric pre-treated with H_2O_2 or papain (Pap) enzyme, followed by Schiff base treatment with glutaraldehyde (GDH) and CS, provided excellent shrink-resistance [69]. A pre-treatment of wool fabric with peroxymonosulfuric acid or PMS at 5% on the weight of fiber (owf), followed by coating with CS, showed that PMS pre-treatment and the molecular weight of CS both affect the shrink-resist performance of the fabric [70]. The molecular weight or level of *N*-acetylation did not affect the shrink-resist performance of wool fabrics treated with CS, but an increasing number of hydrophobic groups in CS through the incorporation of several long-chain N-acyl groups reduced shrinkage at the same level of add-on [71]. To enhance CS adsorption into wool fibers, wool fabric was pre-treated with a water-vapor low-temperature plasma [72]. It was found that low-temperature plasma treatment alone only modified the cuticle surface of the wool fibers and improved the surface wettability and shrink-resist performance, but failed to make the wool fabric machine-washable. However, plasma in combination with CS treatment made the wool fabric machine-washable. For example, the wool fabric pre-treated with water-vapor low-temperature plasma, followed by treatment with CS, exhibited excellent shrink-resistance [73]. The plasma treatment made the wool fiber surface hydrophilic, allowing uniform spreading of CS on the wool fiber surface, creating a uniform coating. CS can also be combined with other sustainable biopolymers, such as gum Arabic and wheat starch biopolymers, to impart shrink-resistance to wool fabric without any oxidation treatment [74]. The wool fabric treatment with CS in combination with other polymers (e.g., water-borne polyurethane) by the pad-dry-bake method offered excellent shrink-resistance with good durability to washing [75].

4.2.2. *Shrink-resist performance*

The shrink-resist performance of wool fabrics pre-treated with H_2O_2 or enzyme, or plasma, followed by treatment with CS, is presented in Table 1. Of them, wool fabric treated with a special proteolytic enzyme (2 g/L Perizym AFW) at pH 8.0 and 70 °C for 1 h and then treated with CS exhibited the best shrink-resist performance [68]. The shrinkage exhibited in warp and weft directions was 1.5% and 3.1%, respectively, and the average area shrinkage was 2.3% along with a tensile strength loss of 21.2%. Conversely, other protease enzymes provided lower shrinkage, but the loss in tensile strength was excessive (~75%). Wool fabric pre-treated with H_2O_2 and then treated with CS, followed by crosslinking with GDH, provided excellent shrink-resist performance, and the area shrinkage was reduced to only 2.5% [69]. The wool fabric treated with papain, followed by treatment with CS and then with GDH, also provided similar shrink-resist performance. Peroxide treatment followed by coating with 1% CS solution reduced the shrinkage to 4% after 2 cycles of washing [67], but plasma treatment in combination with CS showed slightly better shrink-resist performance [68]. On the other hand, the glutaraldehyde-crosslinked CS treatment provided very poor shrink-resistance as the shrinkage reduced to 13.5% [70]. Wool fabric pre-treated with plasma, then treated with CS followed by enzymatic treatment with protease, showed excellent shrink-resist property; the shrinkage reduced to 2.8% only [71]. On the other hand, Rani et al. found that wool fabric treated with 0.5% CS by the pad-dry-bake method exhibited only 0.55% shrinkage after 1 cycle of washing. However, the test method used to assess the shrinkage was different [72].

4.2.3. *Shrink-resist mechanisms*

The wool fiber surface has many unidirectional scales, making the fiber surface rough, and the fabric made from it becomes prone to shrinking. During laundering and tumble-drying in hot and humid conditions, by agitation and friction, the scale edge of one fiber locks into the inter-scale gap of another fiber, not allowing the fibers to return to their original positions, causing irreversible shrinkage of the fabric. The coating of wool fibers with CS fills these inter-scale gaps, making the wool fiber surface relatively smooth, as shown in Fig. 7 (left). In humid conditions, the CS deposited in the inter-scale gaps of wool fibers swells, covering the inter-scale gaps, allowing no interlocking of fibers during laundering, and therefore, no shrinkage of wool fabric occurs. The

Table 1

Shrink-resist performance of wool fabrics coated with CS alone or in combination with other treatments.

Treatments	Pre-treatments	CS conc. (%)	Tensile strength loss (%)	Test methods	Shrinkage (%)	Ref.
CS-g-Pap	At 60 °C for 2 h	n/a + 75 U/mL	Batch exhaust	IWS TM 31	4.9	[6]
H_2O_2 + CS	18 mL/L H_2O_2 at pH 9 and 60 °C for 1 h	1.0	Pad-dry-bake	IWS TM 31	4 after 2 cycles	[67]
Perizym AFW + CS	2 g/L enzyme at pH 8.0 and 70 °C for 1 h	1.0	Exhaustion	IWS TM 31	2.3 after 1 cycle	[68]
H_2O_2 + CS + GDH	H_2O_2 + Pap	1.0	Batch	IWS TM 31	2.5	[69]
Pap + CS + GDH	Pap					
PMS + CS	5% owf PMS at pH 4.0 and 25 °C for 0.5 h	1.0	Exhaustion	IWS TM 31	5 after 2 cycles	[70]
CS + glutaraldehyde	CS-treated fabric was x-linked with GDH	3 g/L	Exhaustion	IWS TM 31	13.5	[71]
H_2O_2 + CS + glutaraldehyde	H_2O_2/CS-treated fabric was x-linked with GDH	3 g/L	Exhaustion	IWS TM 31	8	
Plasma + CS + Esperase 8.0 L	Water vapor plasma/100-watt/120 s	1 + 0.25	–	IWS TM 31	2.8 after 1 cycle	[72]
Plasma + CS	Air plasma	1.0	Exhaustion	IWS TM 31	3 after 2 cycles	[73]
CS		0.5	Pad-dry-bake	ISO 6330	0.55 after 1 cycle and 3.92 after 3 cycles	[74]

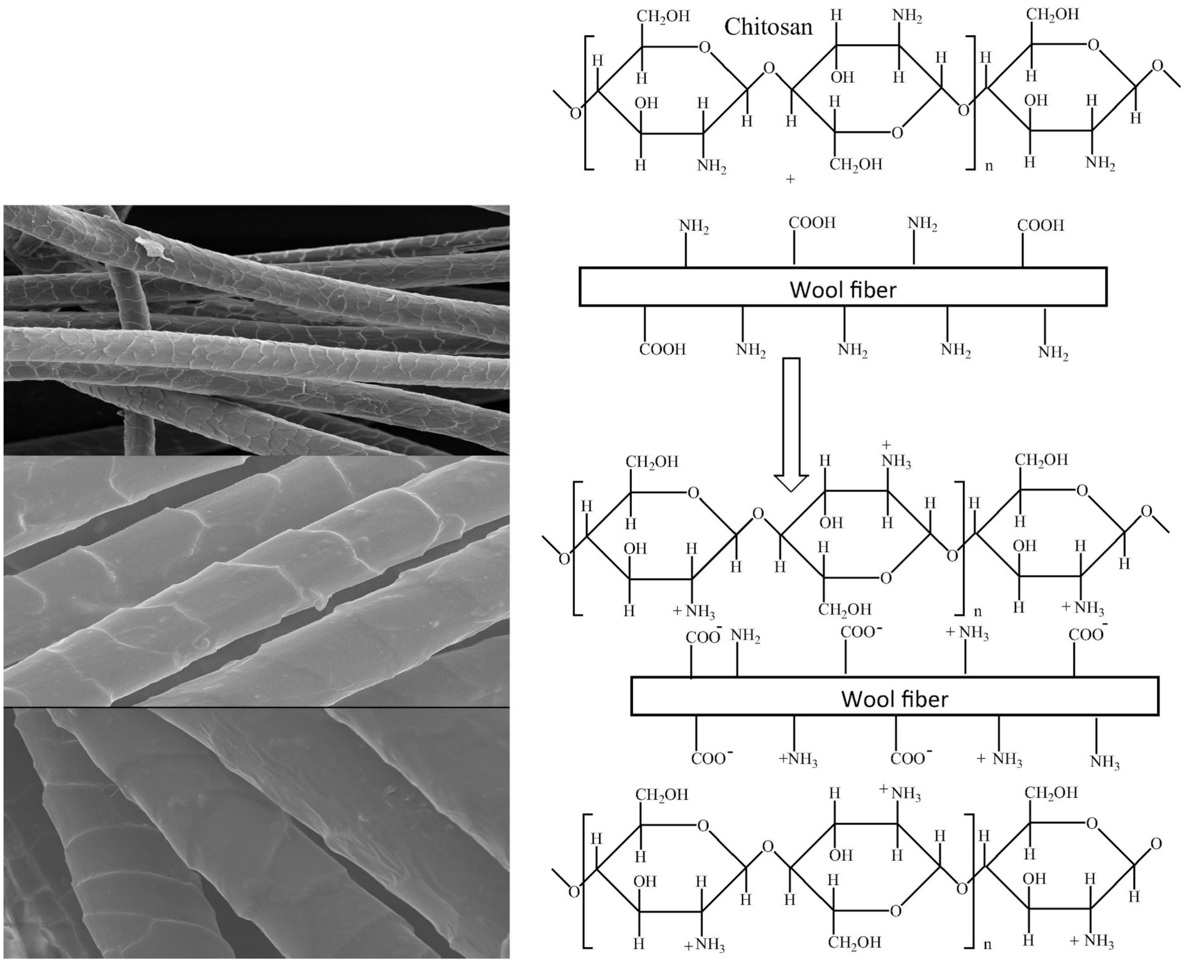

Fig. 7. SEM micrographs (left) of untreated (top), chlorinated (middle), and CS-coated (bottom) wool fibers, and mechanism (right) of binding of CS to the surface of the wool fiber [62]. Reproduced with permission from Elsevier.

cationic amino groups of CS are ionically bonded to the anionic carboxyl groups of wool fibers at neutral to alkaline conditions, as shown in Fig. 7 (right), providing some level of durability of the CS coating to washing.

5. Application of chitin derivatives in sustainable dyeing

Over the years, various zero-effluent dyeing [76] and replacement of persistent synthetic dyes with bio-derived alternatives, such as lignin [77], polyphenols of cacao husk, mango seed kernels, and feijoa skin [78,79], and toxic finishing agents with bio-derived ones having anti-microbial and antioxidant properties [79], were explored with some level of success. However, they are not yet used in industrial manufacturing because of various issues, including the necessity of using new machinery or modifying existing machinery, high capital and operational costs, and also performance and durability to washing. CS has been studied as a fiber surface modifier to enhance dye absorption, for salt-free dyeing with anionic dyes, and as a mordanting agent to bind the dye to fibers or make the dye insoluble through complexation.

5.1. Dye absorption enhancer for salt-free dyeing

Cellulosic fibers are usually dyed with reactive dyes under alkaline conditions, at which fibers and dyes are both anionic. To increase dye exhaustion, cellulosic fibers are modified with cationic polymers so that anionic dye molecules are attracted to the surface of the cationic fibers, increasing the exhaustion and absorption of dye molecules into the fibers. In cellulosic fiber dyeing with reactive dyes, a large amount of salt is used to neutralize the negative charges of the cellulosic fiber surface so that reactive dyes can be absorbed into the fiber. To eliminate salt use, cellulosic fibers are mostly cationized with fiber-reactive quaternary ammonium compounds, which are toxic and foul-smelling, and their treatment produces toxic effluent. To overcome the issue, textile fibers, such as cellulose [80], polypropylene [81], silk [82], and wool fibers [83], are modified with cationic CS for dyeing with anionic acid, reactive, and natural dyes. The ultrahigh molecular weight polyethylene fibers modified by DBD plasma, followed by coating with CS, not only adsorb the dye but also enhance wettability [84]. The modification of flax fabric with low molecular weight CS quaternary ammonium salt showed enhanced dyeing affinity and dye absorption capacity [85]. The silk fibers modified with CS by using anhydrides enhanced the dyeability of the treated silk fibers [86]. Similarly, wool fibers coated with polypropylene imine dendrimer [87] and polyacrylamide [88], modified CS provided enhanced dyeability of wool fibers with cochineal and reactive dyes, respectively, along with enhanced colorfastness to washing. CS-modified cotton and polyamide fabrics not only showed enhanced absorption of natural carmine dye but also enhanced the fabric's antibacterial activity [89]. Similarly, CS pretreatment of flax fabrics enhanced their ability to absorb peanut skin dye [90]. Cotton fabric pre-treated with a fiber-reactive CS derivative containing quaternary ammonium groups, *O*-acrylamidomethyl-N-(2-hydroxy-3-trimethylammonium)propyl CS chloride (NMA-HTCC), enabled dyeing with reactive dyes without using any electrolyte [81]. CS was also studied for modifying other natural fibers to increase the dye uptake and color yield. For example, tussah silk fabric coated with CS exhibited enhanced acid dye uptake along with improved colorfastness to light and washing, but with a slight increase in yellowness [82].

5.2. Bio-mordant

As CS is an amphoteric polymer due to the presence of both anionic and cationic functional groups, it works as a bridge (mordanting agent) between the fiber and the dye, eliminating the need to use toxic heavy metals as a mordant in dyeing of natural dyes. CS was studied as a bio-mordant to bind turmeric root extract [91], spent coffee ground [92], and onion peel and pomegranate rind extract [93] dyes to cotton fibers, which also increased their substantivity towards cotton fibers. Different molecular weight CS was also studied as a biomordant for the dyeing of cotton fabrics with *Curcuma longa* and *Pterocarpus santalinus* natural dyes [94]. CS derivatives, such as CS-poly(amidoamine) dendrimer [95] and CS-polypropylene imine dendrimer [87], were also studied as bio-mordant for the dyeing of wool with cochineal and madder natural dyes.

The basic mechanism of bio-mordanting of CS in the dyeing of cellulosic and protein (e.g., wool) fibers with a natural dye is shown by a schematic diagram in Fig. 8. CS works as a bridge between the carboxyl groups of protein fiber and the anionic groups of dye, as shown in Fig. 8 (top). At mild acidic conditions, CS binds to protein fibers by forming ionic bonding between the carboxyl groups of protein and amine groups of CS, making the fiber surface cationic and attracting anionic natural dyes. The anionic groups of natural dyes bind to the cationic amino groups of CS, binding the dye molecules to protein fibers, increasing the colorfastness to washing. Similarly, in the case of cellulosic fibers, CS binds to the cellulosic fibers by forming hydrogen bonds with the amino groups of CS, as shown in Fig. 8 (bottom). Like protein fiber dyeing, anionic groups of natural dyes bind to the cationic amino groups of CS, binding the dye molecules to cellulosic fibers.

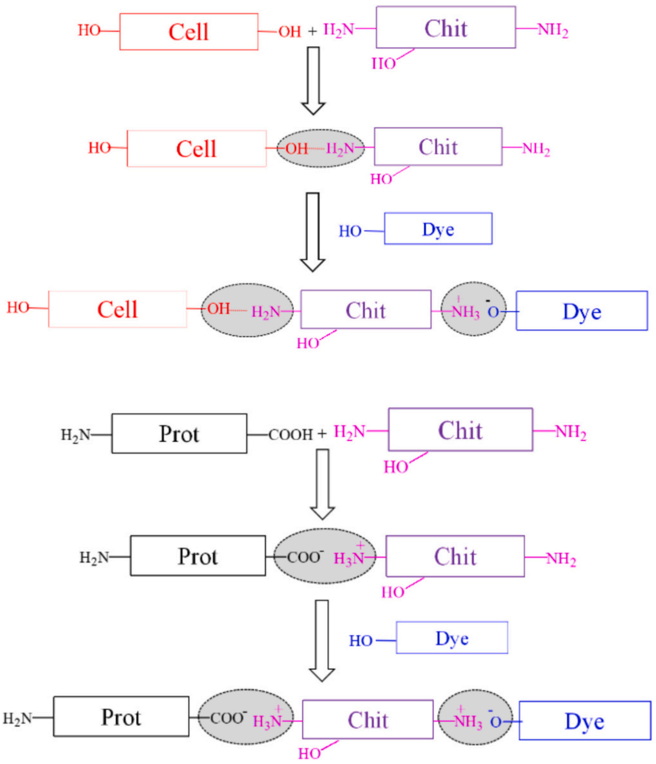

Fig. 8. Mechanism of CS working as a mordant in the dyeing of protein (left) and cellulosic (right) fibers with a natural dye.

5.3. Encapsulation of dyes

Human skin can be sensitive to synthetic dyes used for the dyeing of various textiles, as they come into contact with human skin. When dyed clothes encounter skin, sweating can release a small fraction of dye from the fabric into human skin, causing an allergic effect. Dye molecules were micro- or nano-encapsulated to prevent them from coming directly in contact with human skin. Very little research has been published in this area, as the difficulty in binding capsules to the fiber surface and possible low colorfastness to washing could be the reasons. The nano-encapsulation of several disperse and vinyl sulfone-type reactive dyes with CS through ionic gelation using tripolyphosphate as a crosslinker reached 90% dye entrapment efficiency [96]. The cytotoxicity of the dyes was tested against HaCat cells. The encapsulated dyes showed no cytotoxicity to HaCat cells, whereas the non-encapsulated dyes showed high cytotoxicity. However, no color yield and colorfastness to washing and rubbing of the dyed cloths were reported. The dyeing performance of fabrics dyed with these nano-encapsulated dyes was not compared with fabrics dyed with the same dye using the traditional dyeing method. Such dyeing will not dye the whole fiber; rather, it will only coat the fiber surfaces, and a binder will be needed to bind the dye capsules to the fiber surface.

6. CS derivatives in functional coating of textiles

Numerous finishing agents are applied in textile processing, such as antimicrobials, benzophenone-based UV absorbers, formaldehyde-releasing anti-crease finishing agents, fluorocarbon-based water repellents, polybrominated diphenyl ethers, and other halogen- and phosphorus-based flame-retardants. Many of them are toxic, recalcitrant, and pose health and environmental risks throughout their lifecycle. Some of them, such as polybrominated diphenyl ether and formaldehyde, are possible carcinogens. Many synthetic antimicrobial agents, including 2,4,4′-trichloro-2′-hydroxydiphenyl ether or triclosan, cause drug resistance. Many textile finishing chemicals contain toxic volatile organic compounds that are released during their production and use. To overcome these issues, CS and other chitin derivatives were studied as an alternative to these finishing agents.

6.1. *Antimicrobial treatments and their performance*

Clothing stays in contact with human skin for a long period of time each day, and its prolonged contact with skin and skin humidity can facilitate the transfer of microorganisms from clothing to the human body. Clothes can be vectors for spreading diseases from one person to another through contact. The use of antimicrobial agents in textiles not only protects textiles from damage but also prevents the spread of disease and prolongs their hygienic conditions. Although the incorporation of antimicrobial agents into textile materials was effective in protecting humans from bacterial infection, the addition of such components to textile clothing can compromise the balance of the skin microbiota of the wearer [97]. As a polycationic biopolymer, CS and its derivatives have good anti-microbial and anti-fungal properties against Gram-positive and Gram-negative bacteria, filamentous fungi, and yeast. Table 2 lists the antibacterial activity of textiles treated with CS and other derivatives of chitin against a wide range of bacteria.

6.1.1. *Unmodified CS as an antibacterial agent*

CS of various molecular weights, alone or with other antibacterial agents, was studied for the antibacterial treatment of cotton [98.99], polyester [100], acrylic [101], viscose [102], and wool fabrics [103] against a range of Gram-positive and Gram-negative bacteria. Besides CS, its nanoparticles were also studied to render textiles antibacterial [95,104]. Exhaustion or pad-dry-bake is the conventional method of application of CS to textiles to make them antibacterial. The textile samples, after pre-treatment with enzymes or enzyme+hydrogen peroxide, are immersed in CS aqueous solution. The samples are then passed through the padding mangle and dried. The treated fabric demonstrates efficient antimicrobial activity against *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) bacteria [105]. Cotton and viscose fabrics treated with CS nanoparticles (CS NPs) showed considerably better antibacterial activity against *S. aureus*, *E. coli,* and *Candida albicans* (*C. albicans*) than the fabric treated with CS [102], but no durability of the treatment to washing was reported. Conversely, nettle fabric treated with CS showed excellent antibacterial activity against *S. aureus*, but against *E. coli*, the antibacterial performance was quite poor (only 56.9% killed) [100]. The maximum antimicrobial activity was obtained when the cotton fabrics were treated with 0.5–0.75% CS of molecular weight

Table 2
Antibacterial performance of wool fabrics coated with CS and its derivatives.

Treatment	Type of fabric	CS dosage (% owf)	Test methods	Antibacterial performance against						Ref.
				E. coli		*S. aureus*		*P. aeruginosa*		
				0 wash	20 washes	0 wash	20 washes	0 wash	20 washes	
Unmodified CS										
CS	Cotton	2.0	ASTM E 2149–13	99.8%	n/a	100%	n/a	n/a	n/a	[89]
	Nylon 6,6			100%		100%				
CS	Cotton	0.5	AATCC TM 61	26 mm	25 mm	18 mm	18 mm	n/a	n/a	[99]
CS coated	Cotton	2.0	Kirby-Bauer disk diffusion	11 mm	2.0 mm	12.0 mm	4.0 mm	n/a	n/a	[108]
CS x-linked		2.0		13 mm	11.0 mm	15.0 mm	12.0 mm	n/a	n/a	
CS	Acrylic	10 g/L	Disc diffusion	25 mm	21 mm	21 mm	16 mm	n/a	n/a	[101]
CS	Cotton	0.3	Disc diffusion	7 mm	n/a	13 mm	n/a	n/a	n/a	[105]
CS NPs		0.3		14 mm	n/a	15 mm	n/a	n/a	n/a	
CS	Cotton	0.5	Disc diffusion	14 mm	n/a	18 mm	n/a	23.5 mm	n/a	[102]
	Viscose			13 mm	n/a	18 mm	n/a	23.5 mm	n/a	
CS NPs	Cotton			24 mm	n/a	26 mm	n/a	25 mm	n/a	
	Viscose			21 mm	n/a	22 mm	n/a	25 mm	n/a	
CS composites										
CS + AP	Cotton	n/a + 3.0	GB/T 20944.3–2008	99.8%	n/a	n/a	n/a	n/a	n/a	[110]
CS + melamine + SPP	Cotton	200 g/L	AATCC 100	n/a	n/a	98.7%	n/a	n/a	n/a	[111]
CS + SiNP	Cotton	0.8/1.0	Disc diffusion	n/a	n/a	17 mm	n/a	n/a	n/a	[113]
ZnO + CM-CS	Cotton	4.0	Disc diffusion	22 mm		26 mm				[118]
ZnO + CM-CS	PT-cotton	1.0	AATCC 100	n/a	n/a	99.9%	99.8%	n/a	n/a	[119]
CS derivatives										
GTMAC-m-CS	PP	n/a	Disk diffusion	0	n/a	64%	n/a	n/a	n/a	[45]
pATC-g-CS	pSS-g-wool	0.5	AATCC TM 147	n/a	n/a	5 mm	5 mm	n/a	n/a	[52]
PS-CS	Cotton	6 g/L	AATCC 100	99.9%	80%	99.9%	80%	n/a	n/a	[114]
CE-CS	CS fiber	8.0	ASTM E 2149–01	13 mm	n/a	18 mm	n/a	18 mm	n/a	[115]
CM-CS	Cationized cotton	50 g/L	Tetrazolium/ formazan test	61.3%	n/a	n/a	n/a	n/a	n/a	[120]
CS	CM-Cotton		ASTM E2149	14 mm	n/a	17 mm	n/a	n/a	n/a	[123]
O-QCTS-DEBn	Cotton	3.0	GB/T 20944.3–2008	99.7%	n/a	100%	n/a	n/a	n/a	[116]
PCS	Cotton	7.0	GB/T 20944.3–2008	93.7%	n/a	100%	n/a	n/a	n/a	[117]
ZnO/CM-CS	Cotton	2.0	n/a	6 mm	n/a	12 mm	n/a	n/a	n/a	[132]
CS-g-pAA	Wool	1.0	ASTM E2149	3.1	n/a	0.2 mm	n/a	n/a	n/a	[88]
		10.0		3.2	n/a	0.9 mm	n/a	n/a	n/a	

1.5–5 kDa and cured at 160 °C for 2–3 min. Zhang et al. reported that cotton fabric treated with 0.3 and 0.5 g/L CS showed antibacterial activity against *Escherichia coli* and *Hay bacillus,* respectively [106]. The nylon fabric treated with CS exhibited excellent antibacterial activity, but the authors did not report the durability of the treatment to washing [89].

As CS does not bind to textiles permanently, various crosslinking agents were studied to bind CS to textiles and to enhance the durability of the antibacterial treatment to washing. The fabric treated with CS using butane tetracarboxylic acid (BTCA) as a crosslinker exhibited excellent antibacterial activity against *E. coli* and *S. aureus*, which only negligibly diminished after 30 cycles of washing, and the size of the zone of inhibition decreased by only 1 mm [98]. The cotton fabric treated with CS showed excellent antibacterial activity. However, the antibacterial performance was highly diminished after 30 cycles of washing, which considerably improved after CS was bonded to fibers via crosslinking with triethyl orthoformate [107]. The acrylic fabric treated with CS using polyurethane (PU) as a binder showed excellent antibacterial activity, which diminished after 30 washes [101], suggesting ineffectiveness of PU as a binder.

Published literature reveals that the molecular weight of CS can affect its antibacterial activity. A low molecular weight CS often shows greater antibacterial efficacy than a high molecular weight CS due to better bacterial cell wall penetration, disrupting their metabolism [108]. El-Tahlawy et al. investigated the effect of molecular weight of CS on its antibacterial activity and the durability of CS bonded to cotton fabric by butane tetracarboxylic acid (BTCA) crosslinker to washing, as illustrated in Fig. 9 [99]. The molecular weight of CS had a mixed effect on the antimicrobial performance, which was dependent on the types of bacteria. For instance, antimicrobial performance diminished with an increase in molecular weight of CS for *E. coli*, *S. aureus*, and *Pseudomonas aeruginosa* (*P. aeruginosa*) bacteria, but for *Bacillus subtilis (B. subtilis),* no change in antimicrobial performance was observed. Conversely, for *Bacillus cereus (B. cereus)*, a marginal increase in zone of inhibition (ZI) was observed up to 30 KDa.

6.1.2. CS in combination with other additives

To introduce functionalities other than antibacterial properties, CS was studied in combination with various additives, such as ammonium phytate (AP), melamine+sodium pyrophosphate (SPP), and silica nanoparticles. However, the combined treatment showed slightly diminished antibacterial performance compared to CS treatment alone [109–111]. The cotton fabric treated with CS and AP showed excellent antibacterial activity against *E. coli* (99.8% killing), but the durability of the treatment to washing was not reported. Nano-CS in combination with acyclovir, and also with clove oil was studied as an antibacterial and antiviral finish for cotton fabrics [112].

6.1.3. CS derivatives

Various chitin derivatives, including thiolated CS and imido CS, prepared by reacting with thioglycolic acid and iodoacetic acid, respectively, were found effective against *E. coli* with a minimum inhibitory concentration (MIC) of 400 μg/mL [113]. Anionic polystyrene sulfonate (pSS)-grafted wool fabric treated with poly[2-

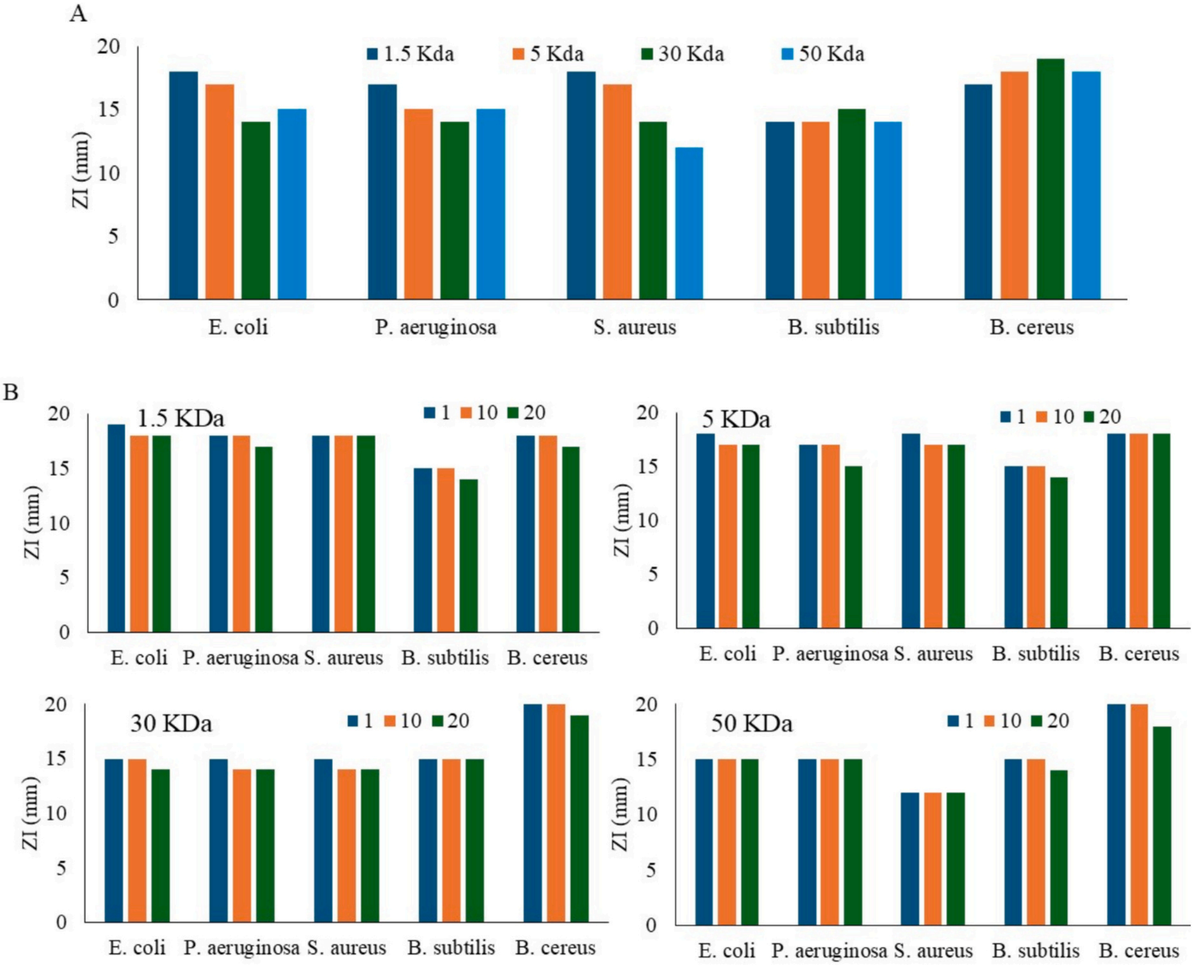

Fig. 9. Effect of molecular weight of CS (A) and number of washes (B) on the antimicrobial performance of CS bonded to cotton fabric by crosslinking with BTCA (the charts were generated from data extracted from [99]. Antibacterial performance generally decreased with an increase in CS molecular weight and number of washes.

(acryloyloxy)ethyl]-trimethylammonium chloride-grafted-CS or pATC-g-CS exhibited excellent antibacterial performance, as the zone of inhibition (ZE) observed was 5 and 5 mm for *S. aureus* and *E. coli*, which did not diminish even after 20 domestic washes [52]. Natural pterostilbene-grafted-CS (PS-CS) was applied to cotton fabric by the layer-by-layer assembly coating to provide a durable antibacterial property [114]. Similarly, cyanoethyl CS (CE-CS) non-woven membrane was found effective against *S. aureus*, *B. subtilis*, *B. cereus*, *E. coli*, and *P. aeruginosa* [115]. The cotton fabric treated with CS quaternized with O-quaternized-N,N-biethyl-N-benzyl ammonium CS chloride (O-QCTS-DEBn) exhibited excellent antibacterial activity, as the bacterial killing of *E. coli* and *S. aureus* was more than 96% and 99%, respectively, when crosslinked with citric acid. However, the antibacterial activity decreased to 75% after 20 home launderings, suggesting weak binding of modified CS to cotton fibers [116]. The polypropylene (PP) fabric treated with glycidyl trimethyl ammonium chloride-modified-CS (GTMAC-m-CS) showed very poor antibacterial activity against *E. coli*, as only 64.5% of the bacteria were killed [45]. The cotton fabric treated with phytic acid protonated CS (PCS) showed excellent antibacterial activity against *S. aureus*, but against *E. coli* was unsatisfactory [117]. The cotton fabric coated with ZnO/CM-CS showed very good antibacterial properties against Gram-positive and Gram-negative bacteria and also enhanced UV protective properties [118], but ZnO/CM-CS applied to plasma-treated cotton (Pt-cotton) showed considerably better durability to washing [119]. The cationized wool fabric treated with CM-CS exhibited good antibacterial activity that was durable to washing [120]. The wool fabric treated with polyacrylamide grafted CS (pAA-g-CS) showed poor antibacterial activity against *E. coli* and *S. aureus* at 1% owf concentration, but the activity against *S. aureus* was considerably enhanced when the applied dosage was increased to 10% owf [88]. The cotton fabric treated with *O*-acrylamidomethyl-N-(2-hydroxy-3-trimethylammonium)propyl CS chloride (NMA-HTCC) by a cold pad-batch method in the presence of an alkaline catalyst provided durable and excellent antimicrobial activity against *S. aureus* [44].

To enhance the durability of the CS antibacterial treatment to washing, CS was made anionic by carboxymethylation to bind to cationized cotton, but this reduced the antibacterial activity [121]. Conversely, the cotton fabric treated with CS/poly(NIPAM) core-shell type nanoparticles exhibited excellent antibacterial activity against *S. aureus*, and this antibacterial activity did not decrease even after 50 washes, as the treated fabric still showed 99.5% bacterial death [40]. CS bonded to cotton fabric by modifying the primary hydroxyl groups on the C6 position in glucose units of cellulose with H_3PO_4/HNO_3-$NaNO_2$ mediated oxidation, which produced monocarboxy cellulose and binding sites for binding CS to cellulose, showed high antimicrobial activity and excellent antibacterial washing durability [122]. Polystyrene sulfonate-grafted-wool (pSS-g-wool) fabric treated with pATC-g-CS exhibited excellent antibacterial activity against *S. aureus* and *Klebsiella pneumoniae (K. pneumoniae)*, and also some level of antifungal activity against *Aspergillus fumigatus* (*A. fumigatus*), and the antimicrobial performance was not diminished after washing [52]. CS applied to carboxymethylated cotton fabric (CM-Cotton) showed quite good antibacterial activity, but the durability of the treatment to washing was not reported [123]. Gawish et al. modified wool fabrics by grafting with low-molecular-weight deacetylated CS using citric acid as a crosslinking agent, which not only enhanced the antimicrobial activity of the treated fabric but also increased its tensile strength [124]. The layer-by-layer coating of cotton fabric with CS, phytic acid, ionic liquid, copper, and epichlorohydrin-modified aramid nanofibers showed excellent antibacterial properties [113]. Although the treatment with CS introduces antibacterial functionalities to cotton fabric, it decreases the tensile strength and elongation of the treated fabrics due to the depolymerization of cellulose macromolecules in acidic conditions. The unmodified and modified CS both show excellent antibacterial activity against a wide range of bacteria but are ineffective against fungi.

6.1.4. Antibacterial mechanisms

Fig. 10 illustrates the antibacterial mechanisms of CS (left) and Q-CS (right) [125,126]. The most acceptable mechanism of the antimicrobial activities of CS is that the positively charged amino groups of CS bind to the negatively charged cell membrane of microorganisms, damaging their barrier properties, disrupting their integrity, leading to leakage of their intracellular contents, and ultimately causing cell death. The chelating ability of CS inhibits the metabolic enzymes of microbial cells by blocking their active centers and.

reducing microbial growth. The high and low-molecular-weight CS can exhibit different synergistic effects. For example, high molecular weight CS can form a polymer membrane to change the cell permeability and prevent the entry of nutrients into the cell, while a low molecular weight CS penetrates and binds with the DNA of the cells, interfering with the synthesis of mRNA and proteins, causing cell death. The quaternization improves CS's antimicrobial activity, but the antibacterial mechanism of Q-CSs is very similar to the antibacterial mechanism of CS, except that positively charged quaternary ammonium groups, as well as protonated amino groups, interact with the negatively charged cell membrane of microorganisms, enhancing cell disruption and causing cell death [127].

6.2. Flame-retarding treatments

Flame retardancy is an essential attribute of textiles, as accidental combustion can be fatal, which is very important for children's wear and firefighter dress. As CS is rich in nitrogen, its combustion may release inert nitrogen gas, and therefore, it may provide some level of increase in flame-retarding properties to textiles. CS was studied alone or with other natural flame retarding agents to enhance the flame retarding properties of textiles. Other than CS, a range of CS derivatives including phosphite-protonated CS (PPC) [116], phosphorylated CS (Phos-CS) [128], ammonium vinyl phosphonate-grafted CS (AVP-g-CS) [129], melamine and sodium pyrophosphate- modified CS (M-SPP-CS) [111], melamine salt of CS phosphate (MCP) and nano CS (Nano-CS) [130], and also CS in combination with lignin sulfonate (LS) and boric acid (BA) [131], sodium polyborate (SPB) and polydimethylsiloxane (PDMS) [132], and phytic acid (PA) and epichlorohydrin-modified aramid nanofibers (EAN) [114], were studied as a flame retarding agent. A cotton fabric coated with CS/ammonium phytate (CS/AP) layer-by-layer [110], and CS in combination with rice husk biochar (RHB) and phytic acid (PA) [133], exhibited excellent flame-retarding properties.

The flame retardancy of textiles is measured by the vertical flame test, limiting oxygen index (LOI), and cone calorimetry. LOI is the minimum concentration of oxygen (expressed as a percentage in a mixture of oxygen and nitrogen) that is needed to sustain the flaming combustion of a material under specified test conditions, and the higher the LOI value, the higher the flame-retardancy. In the vertical flame test, a vertically suspended fabric sample is exposed to a controlled flame for a specific time, and various parameters, including after-flame time, after-glow time, and char length, are measured. The results indicate how well a fabric will resist ignition and burning after the source of flame is removed. The lower the after-flame time, after-glow time, and char length, the higher the fabric's resistance to burning. In the cone calorimetry test, the peak heat release rate (pHRR) is measured. The lower the pHRR value, the better the flame-retardancy of the fabric.

6.2.1. Flame-retarding performance

The flame retarding performance is indicated by higher LOI, and lower char length and pHRR values. The flame-retarding performance of various textiles treated with unmodified and modified CS is listed in Table S1 (Supplementary Information). The untreated cotton fabric has a very low flame-retardancy and a LOI value of 18, which increased to 29.9 after treatment with PPC, and the peak heat release rate decreased from 171.5 to 83.5 [117]. The fabric coated with melamine salt of CS phosphate and polyvinyl alcohol also showed excellent fire-retarding

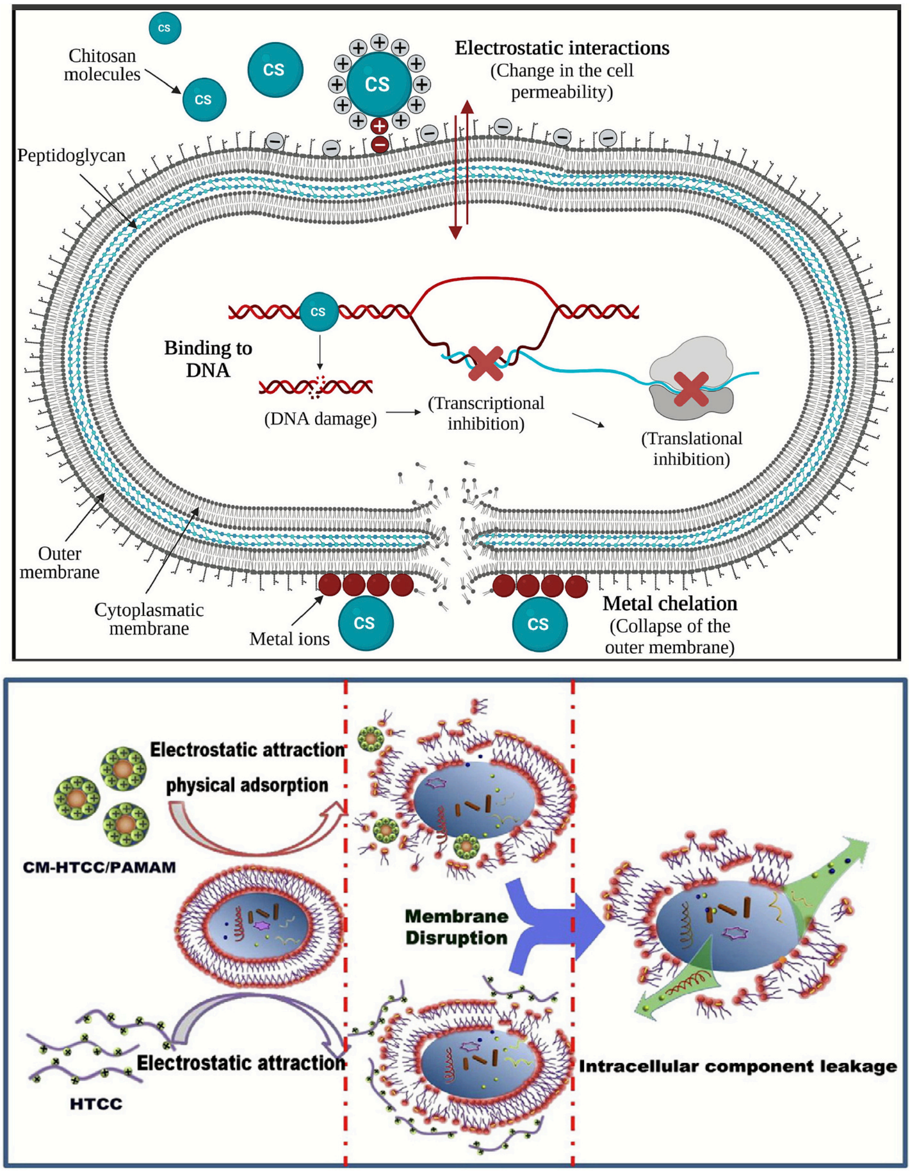

Fig. 10. Antibacterial mechanisms of CS (top) and Q-CS (bottom) [116,126]. Reproduced with permission from Cell Press and Elsevier, respectively. CS and Q-CS disrupt bacterial cell walls, killing bacteria.

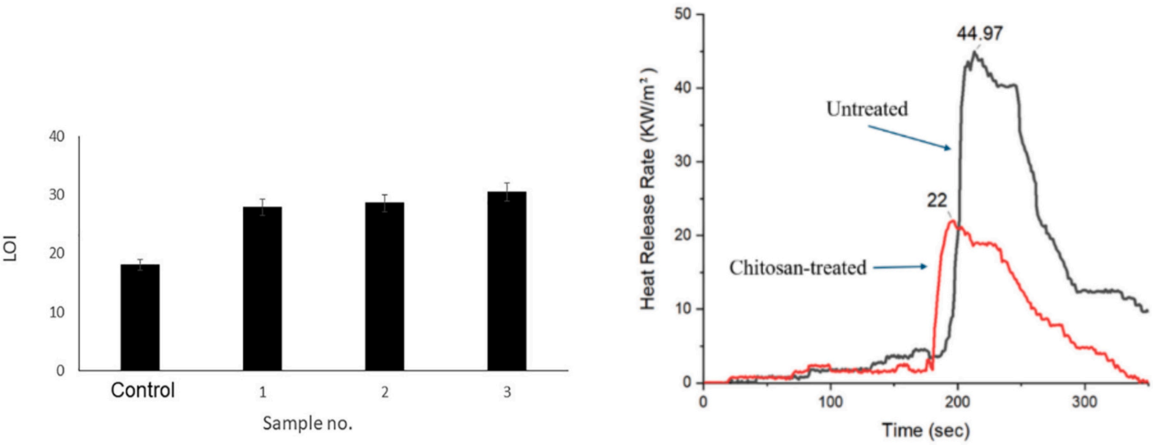

Fig. 11. LOI (left) and heat release rate (right) of cotton fabrics layer-by-layer coated with CS, lignin sulfonate, and boric acid [131]. The flame-retardant fabrics exhibit a lower heat release rate compared to non-flame-retardant fabrics. Reproduced with permission from Elsevier.

properties as the limiting oxygen index of the cotton fabric increased by 58.2% [130]. Safi et al. found that cotton fabric coated layer-by-layer with CS, lignin sulfonate (LS), and boric acid (BA) increased the limiting oxygen index (LOI) of the treated fabric from 18 to 30.5, along with a decrease in heat release rate from 44.97 kW/m^2 to 22 kW/m^2, as shown in Fig. 11 [131]. Similarly, Li et al. reported that polyester/cotton fabric coated with phosphorylated CS (Phos-CS) exhibited an LOI increase from 17.6 to 30 and a heat release decrease from 149 to 86 kW/m^2, i.e., the treated fabric showed excellent flame-retardancy [128]. Cao et al. also observed that the LOI value of cotton fabric coated with phosphite-protonated CS (PCS) increased from 18 to 29.9 [117].

6.2.2. Flame retarding mechanisms

CS's flame retardancy depends on a combination of factors, including the release of non-combustible nitrogen gas during burning, which helps to extinguish the fire. CS also creates a protective and stable carbonaceous char layer on the surface of the fabric, which acts as a diffusion barrier to inhibit gaseous products from diffusing to the flame and protects the fabric's surface from heat [134]. It also acts as an intumescent material, which swells with the degrading textile, forming a porous foamed structure over the fabric that acts as a barrier to heat, air, and pyrolysis products [135,136]. CS can also act as a heat sink when it decomposes endothermically, cooling the pyrolysis zone located at the combustion surface of the fabric, which helps extinguish fire [137]. Additionally, CS is modified to incorporate phosphorus-containing functionalities, further enhancing its flame-retardant properties. Phosphorus is known to act in the condensed phase by enhancing charring, yielding intumescence, or through inorganic glass formation, and in the gas phase through flame inhibition, reducing combustion efficiency [138]. In the condensed phase, many phosphorus-containing flame retardants become volatile and undergo decomposition and/or chemical reactions. Their decomposition products may form volatile or solid products based on the chemical surroundings in the pyrolysis zone [139]. The combination of phosphorus with additional nitrogen-containing additives provides synergistic effects during combustion by forming phosphorus–nitrogen intermediates or increased charring [140]. Thus, CS with phosphorus-containing flame retardants inhibits, suppresses, or delays the combustion process of materials, enhancing their flame retardancy.

6.3. Wrinkle-resist finishing of cotton fabrics

Some fabrics, especially those made of cotton fibers, exhibit poor wrinkle-resisting properties. Wrinkle formation affects the aesthetic properties of the fabric, and to remove crease marks, cotton fabrics need frequent ironing. The fabrics used for shirting and suiting need high wrinkle-resistance properties to maintain the aesthetic of the garments. To improve the wrinkle-resisting property of cotton fabrics, many treatment methods have been developed over the years. The most successful and popular method is treating the fabric with dimethylol dihydroxy ethylene urea (DMDHEU). However, the treated fabric releases some levels of formaldehyde, which is harmful to human health. CS was studied as a sustainable alternative to DMDHEU to improve the wrinkle-resistance property of cotton fabric. The ionic crosslinking of chloroacetic acid-modified cotton fabric with quaternized CS considerably increased its wrinkle recovery [141], but the developed method is impractical for industrial application. Arik et al. studied treated nettle cellulosic fabric with CS using 1,2,3,4-butane tetracarboxylic acid (BTCA) as a crosslinker and sodium hypophosphite as a catalyst. Although 6% BTCA alone provided slightly better wrinkle recovery performance, 6% BTCA with 1% CS provided lower tensile strength loss, higher bending rigidity, and excellent antibacterial properties. Gupta and Haile reported that cotton fabric treated with CS increased the crease recovery angle of the treated fabric from 118° for the untreated to 172° for the treated fabric, with a small loss in the whiteness index [142]. Aly et al. used CS citrate as a crosslinker for cotton fabric which showed an increase in combined warp and weft-wise crease recovery from 140° for the untreated to 231° for the fabric treated with 35° CS but the tensile strength of the fabric decreased from 42 kgF for the control to 19 kgF for the treated fabric with a considerable decrease in whiteness index [143]. Ibrahim et al. used CS in combination with ZnO_2, TiO_2, and SiO_2 nanoparticles to enhance the wrinkle resistance of a polyester/cotton fabric [144]. CS in combination with TiO_2 nanoparticles provided the best wrinkle resistance for cotton fabric by increasing its crease recovery angle. The authors did not report the effect of the treatment on the whiteness index and tensile strength of the fabric. Wei et al. used CS and Q-CS nanoparticle-based crosslinking to enhance the wrinkle-resistance property of cotton fabric [145]. The warp and weft-wise combined dry crease recovery angle increased from 150° for the untreated control to 200° and 235° for the CS and Q-CS nanoparticles, respectively.

6.4. UV protection

The ultraviolet (UV) irradiation of solar light not only damages textile fibers but also affects human skin, causing dangerous sunburn [146]. The solar radiation that enters the Earth's atmosphere can be divided into UV-A (320–400 nm), UV-B (280–320 nm), and UV-C (200–280 nm), but UV-C has the most damaging effect. The use of clothing with high UV protection can protect human skin from the destructive effects of solar UV irradiation. To improve the UV protection properties of textile materials, the use of natural dyes, optical brighteners, or organic UV absorbers was studied. CS coating alone or with other additives was also studied to improve the UV protection factor (UPF) of textiles due to its ability to absorb or reflect UV radiation. The use of antioxidants in textiles also quenches free radicals generated by exposure to UV irradiation, protecting from free-radical damage [147]. CS demonstrated antioxidant properties, primarily due to its ability to scavenge free radicals and inhibit oxidative chain reactions [148]. Various CS derivatives, such as M-SP-CS [111], and CS modified with salicylaldehyde and titanium dioxide (SCSB-Si-TiO_2) were also studied to enhance the UPF value of cotton fabrics [149]. CS in combination with onion skin dye [150], *Opuntia ficus-indica* L. fruit peel [151], ZnO nanoparticle [118], Q-CS Schiff base-TiO_2-ZnO nanocomposites [152], *Solidago gigantea* Aiton extract [153], polyaniline (pAn) [154], black rice extract [155], milk thistle extract-loaded liposomes (MTLL) [156], and CS oligo saccharide (COS) and CS oligosaccharide-based waterborne polyurethane(CWPU) [157], were also studied to improve the UPF value of cotton and silk fabrics. Not only CS, but CM-CS was also studied in combination with ZnO to enhance the UV protection capability of cotton fabric [119]. Nano-CS in combination with polyurethane dispersions (NCS-PUs) was explored as an antibacterial, UV-protective, and strength-enhancing finish for polyester/cotton fabrics [158]. It was also studied in combination with ZnO as an anti-UV and lightfastness improver for the natural indigo-dyed cotton fabric [159].

Table 3 illustrates the antioxidant activity and UPF values of textile fabrics treated with modified and unmodified CS alone, and with other additives. The antioxidant activity of textiles has been less explored than the UV protection capability, as it is a dominant attribute for outdoor textiles. CS alone is not effective in improving the flame-retardancy of textile fabrics. Verma et al. studied CS in combination with onion skin dye, which increased the UPF value of the cotton fabric to 84.8 [150]. CM-CS, in combination with ZnO, provided low UV protection capacity, whereas CS, in combination with black rice extract, M-SP-CS, and SCSB-Si-TiO_2, provided excellent UV protection ability.

6.5. Functional coatings

CS has also been studied as a stimulus-responsive polymer with other additives for the functional coating of textiles to make them superhydrophobic, self-cleaning, super-hydrophilic, free-radical quencher, and stimuli-responsive. Suryaprabha et al. coated cotton fabric with CS

Table 3
Anti-oxidant activity and UPF of textile fabrics with CS alone and with other additives.

Types of fabric	Treatments	Additives	Applied dosage (% owf)	UPF value	Antioxidant (%)	Ref.
Cotton	CM-CS	ZnO	0.25	30+	n/a	[119]
Cotton	M-SP-CS	None	200 g/L	125	n/a	[111]
Cotton	SCSB-Si-TiO2	n/a	n/a	110.9	n/a	[151]
Cotton	CS	Onion skin extract		84.8	n/a	[150]
Cotton	CS	*Solidago gigantea* Aiton extract	2 g/L	51.6	56.1 ± 0.3	[153]
Silk	CS	pAn	1.5% + 6.0	50	n/a	[154]
Cotton	Unmodified CS	Black rice extract	7 g/L	140	n/a	[155]
Cationized cotton	CS	MTLL	12 layers	30.6	n/a	[156]
Cotton	COS	None	6.0	101.9	11.2	[100]
	CWPU	None	6.0	29.6	71.0	

in a combination with polyaniline, ZnO, and stearic acid, which provided excellent super-hydrophobicity and self-cleaning properties [160]. Cellulose acetate and polyester fabric coated with stearic acid-modified CS produced a superhydrophobic surface without using any *per-* and polyfluoroalkyl substances (PFAS) [161,162]. Cotton fabric coated with CS in combination with TiO_2 and ZnO also provided self-cleanability. On the other hand, Bukit et al. used CS coating in combination with boiler ash and TiO_2 to create self-cleanable cotton fabric [163]. Polyethylene fabric coated with O-benzoylated dihydroxypropyl CS exhibited stain release property [164]. Textiles spray-coated with CS nanoparticles produced a superhydrophobic but antibacterial surface [165]. CS is inherently a hydrophilic biopolymer and is widely used to create superhydrophilic coatings for textiles [166]. CS can create free radical scavenging (antioxidant) coatings for textiles by leveraging its natural properties, often enhanced by adding agents like silver nanoparticles (Ag NPs) or phenolic compounds, to develop functional fabrics that neutralize harmful reactive oxygen species (ROS) for applications in medical dressings or protective wear [167,168]. CS is widely used in textiles to create stimuli-responsive (or "smart") fabrics, primarily through the application of CS-based hydrogels or nanoparticles. These smart textiles are designed to alter their properties (e.g., swelling, color, drug release) in response to external environmental changes, most commonly pH and temperature. Kulkarni et al. produced pH- and temperature-responsive cotton fabric by functional coating with the surface-modifying system based on stimuli-responsive poly-NiPAAm/CS (PNCS) microparticulate hydrogel [169].

7. Mechanical properties

The application of CS and other derivatives of chitin to textiles can enhance or weaken the mechanical properties of textiles, with outcomes depending on the fiber type, concentration of CS and derivatives, and treatment conditions, such as molecular weight of CS, treatment pH and temperature, and the use of crosslinking agents. Table 4 lists the mechanical properties of various textiles treated with CS and other derivatives alone or in combination with additives and crosslinkers. CS treatment generally increases fabric stiffness and bending rigidity due to binding fibers together, but it can also increase or decrease tensile strength. The decrease in tensile strength occurs, especially for cellulosic fabrics [159], at elevated temperatures under acidic conditions due to the degradation of chitosan. The unmodified CS is usually applied to textiles at acidic conditions. Patankar et al. also observed that the breaking tenacity of cotton fabric decreased from 58 kgf to 51 kgf when the concentration of M-SPP-CS increased from 50 to 200 g/L [110]. The cotton fabric coated with 6% CS showed a decrease in tenacity from 86 kgf to 53.3 kgf, but increased to 66.2 kgf when 6% BTCA was added to CS as a crosslinker [99]. Similarly, wool fabric functionalized with CS by crosslinking with laccase in combination with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation showed lower tensile strength than the untreated wool fabric [103].

Table 4
Mechanical properties of textiles treated with CS and its derivatives alone and with other additives.

Treatment	Type of fabric	CS conc. (% owf)	Tenacity in warp direction (kgF)		Elongation (%)		Ref.
			Before treatment	After treatment	Before treatment	After treatment	
Chitin alone							
CS	Cotton	1.5	24.7	20.4	18.3	16.2	[170]
CS	Cotton	n/a	53.5	38.2	n/a	n/a	[171]
CS	Cotton	6.0	86.0	53.3	n/a	n/a	[99]
Nano-CS	Cotton	30.0	33.7	27.9	n/a	n/a	[130]
CS crosslinked with							
O-CS-C	Cotton	n/a	18.1 MPa	40.5 MPa	n/a	n/a	[98]
CS + BTCA	Cotton	6.0 + 6.0	86.0	66.2	n/a	n/a	[99]
H_3PO_4/HNO_3–$NANO_2$	Oxidized cotton	n/a	63.6	53.9	34.3	31.2	[122]
CS	CM-Cotton	n/a	58.1	51.0	n/a	n/a	[123]
Citric acid + CS	Cotton	10 + 0.5	43.0	50.3	34.5	20.8	[124]
CS composites							
$CS/TiO_2/Ag$	Cotton	5 g/L	24.3 MPa	27.2 MPa	n/a	n/a	[174]
CS + LS + BA	Cotton	16% add-on	82.7	68.5	n/a	n/a	[131]
CS + SPB + PDMS	Cotton	14.9 add-on	25.2	23.6	n/a	n/a	[132]
CS derivatives							
M-SPP-CS	Cotton	200 g/L	59.8	51.0	15.9	22.3	[111]
CM-CS	Cotton	n/a	24.5	32.4	13.3	18.4	[120]
Phos-CS	Poly/Cotton	n/a	93.8	105.0	n/a	n/a	[128]
AVP-g-CS	Poly/Cotton	26.6% add-on	55.2	160.2	n/a	n/a	[129]
MCP	Cotton	30.0% add-on	33.7	29.1	n/a	n/a	[130]

The cotton fabric treated with oxidized CS containing carboxyl groups (O-CS-C) exhibited increased tenacity, which increased from 18.1 MPa for the untreated to 40.5 MPa for the fabric treated with O-CS-C [98]. The cotton fabric coated with CS/TiO_2/Ag NPs exhibited an increase in tensile strength from 24.3 MPa to 27.2 MPa when the CS concentration was increased from 0 to 5 g/L [170]. Conversely, when CM-CS is applied to cotton fabric, the tensile strength increases as CMC can dissolve in water at neutral pH and uniformly coat the fabric surface.

The tensile strength of cotton fabric increased from 24.5 kgF for the untreated to 32.4 kgF for the cotton fabric treated with 50 g/L CM-CS [120]. The formation of a CS coating can affect the fabric's hand-feel and drapeability, sometimes reducing these properties. The key disadvantage of CS modification of textiles is that it negatively affects the tensile strength of cellulosic and natural polyamide fabrics. Therefore, their application will need to be optimized without compromising other performance results, with tensile strength. Overall, CS derivatives that are soluble in water at neutral to alkaline conditions (e.g., O-CS-C and CM-CS) can increase the tensile strength of textiles. Otherwise, even crosslinking reactions carried out at acidic conditions caused a substantial stress loss.

8. Key challenges and future directions

The investigation and use of CS and other derivatives will continue to grow within the textile industry. At this point, various functional properties that the treatment of textiles with CS and other derivatives can offer, and the merits of their application are well known. The uses of CS as a fiber modifier to enhance dye adsorption and as an auxiliary to enable salt-free dyeing of reactive dyes, as a bio-mordant to bind natural dyes to textile fibers, and as a finishing agent to make textile fabrics shrink-resistant (only wool), antibacterial, wrinkle-resistant, UV-protective, and fire-retardant, are well established. Many examples of such applications of CS to textile manufacturing are discussed above, and this list will continue to expand as innovations are made.

The key challenges for using CS in textile manufacturing are not only the scaling up of production of chitin and other derivatives, but also its high price, performance, and allergic effects on human skin. Although chitin is extracted from biomass, its various derivatives, including CS, are still expensive due to the lengthy multi-step chitin extraction process and then conversion to various chitin derivatives. The manufacturing of CS and other derivatives has high energy, water, and chemical consumption, which increases the manufacturing cost. Their manufacturing also generates toxic effluent, as many chemicals used in their manufacturing end up in the effluent. Chitin is not a single polymer but a family of molecules with varying compositions, sizes, and monomer distributions, which can affect its performance and make it difficult to achieve consistent results. However, these variabilities can be minimized by adopting proper source selection, screening, grading, and optimizing extraction parameters using methods like IL and enzymatic processes. Standardizing conditions like reagent concentration, reaction time, and temperature during deproteinization, demineralization, and deacetylation reduces degradation and enhances the consistency of the final product's molecular weight and degree of acetylation. Numerous green extraction technologies have been developed recently, paving the way for sustainable extraction of chitin. However, they have not been adopted for scale-up or mainstream commercial production.

CS's solubility is restricted to only acidic conditions, which limits its use in various applications where neutral or alkaline conditions are required. For example, cotton fabrics are usually treated at neutral to alkaline conditions to minimize cellulose degradation by acidolysis, especially at elevated temperatures. Many chitin derivatives, including CS, are mainly soluble in acidic conditions, limiting their applications to textiles. As a finishing agent, CS treatment provides limited durability to washing because of the lack of fiber-reactive groups. To increase the durability of the treated fabrics to washing, either new reactive groups need to be created in chitin derivatives, or they need to be bonded to fibers by crosslinking. Fiber-reactive groups will need to be introduced by the modification of the primary alcohol groups; otherwise, the antibacterial properties of the CS will be affected. Moreover, the creation of such a type of reactive group in CS does not allow it to be considered ‘natural’, and therefore, biochemical routes will need to be explored to make them sustainable. Most of the crosslinking agents studied to bind CS and its derivatives to textiles are toxic, expensive, and increase the environmental impact of the treatment. The pH of the surrounding environment can affect the charge of the CS molecule, impacting its ability to interact with bacterial cell membranes. The molecular weight of CS and the temperature can also affect the antimicrobial performance of CS, as lower molecular weight and higher temperatures promote stronger interactions between CS and microbial cells [170,171]. As a fire-retardant, CS alone is ineffective, but in combination with other fire-retardants, it exhibits synergistic effects. CS has poor mechanical properties, partly due to its random copolymeric structure, which can be partially improved through chemical modifications, derivatization, blending with other polymers, and also by polymeric grafting.

The utilization of chitin derivatives as fiber modifiers, sizing agents, and finishing agents has numerous advantages over traditional petroleum-based chemicals and polymers. Chitin offers a lower carbon footprint precursor compared to many petroleum-derived precursors due to its natural origin and biodegradability, leading to more energy-efficient and less environmentally damaging synthesis processes for materials, such as sizing agents, antibacterial, wrinkle-resist, and flame-retarding agents. Chitin nanofibrils extracted from fungi had a carbon footprint of 18.5 kg CO_2-equiv/kg, well below the 177.9 kg CO_2-equiv/kg for cellulose nanocrystals [172].

Chitin will find other applications in the manufacturing of textiles, especially in medical textiles and wound care materials. The future demographics will have an impact on the expanded use of chitin and its derivatives. In many countries, including the US and the UK, people over 80 are the most rapidly growing demographic group. The demand for medical textiles and wound care materials is increasing significantly, driven by the growing global ageing population. Chitin is usually inert and non-toxic, but its primary derivatives, notably CS, CM-CS, and Q-CS, are also generally considered to be non-toxic, biocompatible, and biodegradable for a wide range of applications, including textile, food, and medicine. Hydrophobic Q-CS is known to be nontoxic but can penetrate cells. Similarly, negatively charged CS and its derivatives penetrate the cells efficiently and stimulate cell proliferation [173]. However, their biological effects, including potential adverse responses, are highly dependent on the specific application method, molecular weight, and degree of deacetylation. CS is known to cause allergic reactions by intra-articular injection [174,175]. Contamination from trace proteins and endotoxins has been shown to account for many of these incidents. However, CS bandages applied to patients allergic to at least one shellfish showed no adverse effects or inflammation, and no patient had a positive IgE skin prick testing [176]. It was reported that shellfish allergies are caused by IgE antibodies to antigens in the flesh of the shellfish and not the shell [177]. The survival of these antibodies, through the hydrolysis of chitin to CS, is not possible due to the use of high concentrations of alkali and high heat. Many unsolved challenges remain for the application of chitin derivatives to textiles; nevertheless, a positive future for CS continues to develop.

9. Conclusions

In this work, we have reviewed the potential for employing chitin as a biomass feedstock for textile sizing agents, fiber modifiers, dyebath additives, and finishing agents. The recent developments in CS extraction from various biomasses and microorganisms, the synthesis of various CS derivatives, and applications of these derivatives in sustainable textile manufacturing are highlighted. Textile manufacturing needs to reduce environmental impacts not only by reducing energy and water usage but also by utilizing dyes and finishing agents derived from renewable, non-toxic, and biodegradable feedstocks, to make future textiles and fashion sustainable. CS extracted from crustacean biomass plays a role as a sustainable feedstock for developing textile pretreatment, dyeing auxiliaries, and finishing agents. CS was studied as a sustainable feedstock for fiber production, but as a fiber modifier to introduce various beneficial functionalities in textile fabrics. CS fibers are already commercially produced by several manufacturers and can be used not only for textile manufacturing but also have already found applications in medical fields. Modification of cellulosic textiles with CS enables their salt-free dyeing, considerably reducing the environmental impacts of effluent and minimizing the liberation of salt in discharged effluent. Low-molecular-weight CS was found against a wide range of Gram-positive and Gram-negative bacteria. CS-modified textiles also exhibited good fire-retarding, UV-protective, and antioxidant properties. CS alone has a modest fire-retarding ability, but with other fire-retarding agents, it exhibits synergistic effects. This review demonstrates that chitin is a viable feedstock for future textile manufacturing. It is anticipated that novel technologies will be developed to solve the mentioned issues, and CS will find wider application in textile manufacturing. At least some of the future textiles will be manufactured from CS fiber, and many multifunctional textiles will be treated with CS.

CRediT authorship contribution statement

Mohammad Mahbubul Hassan: Writing – review & editing, Writing – original draft, Validation, Resources, Formal analysis, Data curation, Conceptualization. **Samuel Hudson:** Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that may influence the work reported in this review article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2026.173420.

Data availability

No data was used for the research described in the article.

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