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# Chitosan and its derivatives in the functional processing of textiles



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#### Abstract

hitosan, a natural polysaccharide, has received great attention for use in textile applications Because of its exceptional features, including as biodegradability, biocompatibility, haemostasis, antibacterial activity, and other intrinsic functional properties, has gained a lot of attention for usage in textile applications. Chitosan has piqued the curiosity of both scientists and industry. Many researchers have attempted to create new biomaterials based on chitosan derivatives through chemical changes, particularly sulfonation or sulfation processes, in order to modify the physical and biological properties throughout the past decades. Because of the existence of residual amino groups, the resulting numerous derivatives exhibit appropriate biological features such as antioxidant and antiviral activity, which broadens their spectrum of applicability. This study provides an overview of chitosan, techniques for producing it, and strategies for chemically modifying chitosan by adding groups on its backbone, as well as applications in the realm of functional textiles.

# Keywords: chitosan, chitin, Textile finishing, dying, amino group, applications, medical.

# **Introduction**

In the past decade, the market for comfort, healthcare, and aesthetic textiles has grown dramatically. On the other hand, there is a growing understanding of the importance of sustainability and environmental protection. [1] Many methods have been implemented to make safe and functional textiles utilizing cleaner techniques and materials in order to meet consumer and environmental standards. Traditional textile processing processes are giving way to supercritical fluids, plasma processing, and nanotechnology. Traditional synthetic and toxic chemicals are gradually being replaced with bioremediation agents such as sericin, alginate, and cyclodextrin, Chitosan. (CS) is a chitosan biomaterial with outstanding features such as biodegradability, biocompatibility, and antibacterial activity. The compounds formed as a result of CS breakdown are non-toxic, non-allergenic, and noncarcinogenic. Many research have reported numerous applications of CS in many industries, such as pharmaceutical, food, cosmetics, agriculture, chemical, medical, environmental, textile industry, and many others, based on the aforementioned qualities. Chitosan is a biopolymer derived from chitin, one of the most abundant and renewable natural resources on the planet. chitosan is made by deacetylating chitin, which is a linear biopolymer comprised of N-acetyl-D-glucosamine units linked by (1,4) glycosidic connections. [2]

Chitin is nature's second most prevalent polysaccharide after cellulose. Chitin is a fundamental component of cell walls in fungi, the exoskeletons of arthropods such as crustaceans such as crabs, lobsters, and shrimps, and insects, molluscan radulae, cephalopod beaks, and fish and Lissamphibia scales. Another important source of chitin is fungal biomass. Global attention is being paid to recent advancements in fermentation technology for the manufacture of biopolymers from fungal sources. The biomass utilized in chitosan fermentation is a low-cost bio-waste from a plentiful and low-cost source, and it must be managed/treated in some way. extraction of high-performance value-added compounds like chitosan could provide a profitable solution to this biowaste. chitosan has piqued the interest of scientists and industry since the late 1970s due to its unique macromolecular structure. biocompatibility, biodegradability, and other intrinsic functional features. [2, 3] Chitosan and its derivatives find use in the food industry, agriculture, pharmacy, medicine, cosmetology, textile and paper industries, and chemistry. Chitosan has received

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significant attention in a variety of other fields over the last two decades, including dentistry and bioimaging, hygiene and personal care, veterinary medicine, the packaging industry, agrochemistry, aquaculture, functional textiles and cosmetotextiles, the beverage industry, and wastewater treatment. numerous fundamental investigations have also been conducted on chitosan. This is a sign of the biopolymer's extensive use and growing importance. This Paper contains overview of chitosan, we highlight selected research on chitosan applications published in the recent two decades.[4]

## Sources of chitosan

Chitosan can be made from a variety of sources. Chitosan is traditionally derived from leftover crustacean shells from the seafood processing sector, such as crab or shrimp shells. Another source is the exoskeleton of insects such as beetles. Another natural source that is gaining appeal is the fungal kingdom of molds and macro-mushrooms.[4-6]

## Chitosan from crustacean seafood waste

The exoskeleton and cephalothoraxes account for approximately 45% of shrimp manufacturing waste. This sort of trash contains valuable proteins (30%-40%), calcium carbonate (30%-50%), and chitin (20%-30%), and accounts for 50%-70% of the weight of the raw material. This waste also contains lipidic pigments such as carotenoids (lutein, - carotene, canthaxanthin, astaxanthin, and astathin). Chitin is the second most common polysaccharide on the planet, after cellulose. This polymer is composed of a linked linear chain of 2-acetoamido-2-deoxy--D-glucopyranose.[7]

# Chitosan from fungi

Chitin is found in a wide variety of microorganisms, including fungi, protists, and algae. Mycelium from a variety of fungus, including Mucor rouxii, Absidia glauca, Aspergillus niger, Gongronella butleri, Pleurotus sajor-caju, Rhizopus oryzae, Lentinus edodes, and Trichoderma reesei, has been considered as a potential source of chitin and chitosan due to their abundance in cell walls. Chitosan and chitin can be found in high concentrations in (fungi). Their cell walls include more chitin than those of other classes. The chitin microfibril found in the inner fungal cell wall helps to balance the turgor pressure of the cells.[5, 8]

Source	Advantages	Limitations
Crustacean shell	Chitosan synthesis process that has been industrialized and commercially accessible chi- tosan	<ol> <li>Seasonal and restricted supply of basic materials.</li> <li>Chemicals in large amounts, such as alkali and acids, are required. The procedure is also time-consuming and energy-intensive. A high alkali, as well as a temperature of more than 100 °C.</li> <li>Because of the significant volume of calcium carbonate, demineralisation treatment is required.</li> </ol>
Fungi	<ol> <li>No seasonal variation exists. Chitosan derived from fungi can be generated at any time of year.</li> <li>No heavy metals such as nick- el or copper, and (3) No allergic animal source protein.</li> <li>Controlling the molecular weight and degree of deacetyla- tion during fungal chitosan syn- thesis is important for highly spe- cialized applications.</li> <li>A low polydispersity index and homogenous preparation.</li> <li>It is biocompatible.</li> <li>Fungal chitosan may be pro- duced as a byproduct of fungi- based industry.</li> </ol>	<ol> <li>The availability and quantity of fungal raw material are not comparable to those found in marine or animal sources.</li> <li>The cost of production is higher than that of crustacean-based manufacture.</li> <li>There are a limited number of commercial manufacturers.</li> </ol>

Table 1. shows the advantages and limitations of the sources from which chitosan is extracted

# <u>Structure and physiochemical properties of chi-</u> tosan

Chitosan has a chemical structure similar to chitin; the primary variation is the amount of acetyl groups. chitosan is a linear polymer of -(14)-linked 2-amino-deoxy--D-glucopyranose made up of two relatively common sugars, glucosamine and Nacetylglucosamine (Figure 1), the proportion of which depends on the alkaline treatment used to make it. This cationic polysaccharide has a primary amine and two hydroxyl groups in each monomer and has a unit formula of C<sub>6</sub>H<sub>11</sub>O<sub>4</sub>N.The presence of amino groups in its structure confers several advantages, such as improved solubility (e.g., in aqueous acidic solutions). the ability to form ionic connections, as well as being a useful chemical substrate for obtaining a wide range of derivatives and conjugates. Aside from the proclivity to create intramolecular and intermolecular hydrogen bonding interactions, the abundance of hydroxyl groups and the reactivity of amino groups result in the creation of linear aggregates and hard crystalline domains. As a result of the creation of these stiff and unique structures, chitosan exhibits polymorphism, where these structures differ depending on the packaging and polarity of the neighboring chains. Furthermore, the variety of structures might alter the compound's qualities, notably its solubility.[6, 9-16]

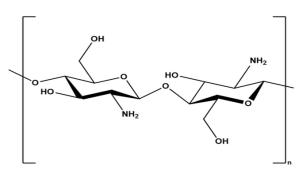


Figure 1. General structure of chitosan

The physicochemical characteristics determine the relationship that exists between the structure of CS compounds and their potential use in many branches of science and industry. The deacetylation degree (DD) and molecular weight (MW) are the most important parameters influencing CS properties such as flexibility, surface area, porosity, conductivity, tensile strength, biodegradability, biocompatibility, adsorption, antimicrobial and antioxidant. Other characteristics that are frequently examined include solubility, crystallinity, viscosity, nitrogen concentration, and water retention value. Other important considerations in determining CS use include its heavy metal and protein content, as well as the quantity of endotoxins.[17, 18]

### **Preparation of Chitosan**

#### **Biological method**

The alkaline deacetylation of chitin yields CS, a natural polysaccharide. As a result, chitosan synthesis must be resource-intensive. Simple, costeffective, time-saving, and ecologically friendly, with numerous superior characteristics the purity, DA, MW, and polydispersity index of chitosan all have a significant impact on it. Applications in a variety of fields.[19] The extraction of chitin, followed by two primary phases of demineralization and deproteination, and ultimately the removal of pigments and lipids using KMnO<sub>2</sub>, is the first step in processing and valorizing this material. Demineralization or decalcification commonly includes treating soluble calcium salt with HCl or other acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, or HCOOH. Deproteination is often accomplished by mixing with NaOH at temperatures as high as 160°C. These treatments, however, induce the chitin backbone to cleave at random. The biological technique can lessen the environmental impact of the alkali/acid phases while also avoiding undesirable chitin structural changes. Natural lactic acid is used for demineralization, and proteases are used for deproteination in this process. Furthermore, entire bacterial extraction processes incorporating the cofermentation of proteolytic and lactic acid bacteria have been devised, resulting in softer treatment conditions and a better-defined chitin product. [5, 6, 191

#### **Chemical methods**

Chemical processes are commonly used for commercial purposes due to their low cost and suitability for large-scale manufacture. Because glycosidic connections are easily destroyed by acids, alkaline deacetylation is more commonly used; however, chitin can be deacetylated by both acids and bases. Chitin N-deacetylation can be classified into two types: homogeneous and heterogeneous. Chitin is commonly processed for a few hours (6 h) at a temperature between 70 and 150°C with a 10-60% NaOH solution in the heterogeneous technique. This produces chitosan, an insoluble residue that is deacetylated to 85-93%. The degree of deacetylation rises with increasing temperature or NaOH concentration. Using the homogeneous method, alkaline chitin is first prepared by dissolving it in a solution of 13-24% NaOH. It was placed on ice (zero degrees Celsius), yielding soluble chitosan with a deacetylation degree of 48-55%. Two markers of chitosan solubility are the distribution of Nacetyl groups and the amount of 2-acetamido-2deoxy-D-glucose in the molecule.[6, 8, 11]

### **Microwave irradiation**

Microwave irradiation has recently gained a lot of attention since it can speed up reactions by an order of magnitude faster than regular heating. To fully extract chitosan, the traditional demineralization, deproteinization, decolorization, and deacetylation procedure could take up to two days. Microwave heating is based on the production of an electromagnetic field that causes vibrations at the molecular level of materials. Microwave irradiation was shown to be more efficient than typical heating methods for chitin deacetylation. Furthermore, by using microwave heating for a few minutes, a substantial degree of deacetylation was achieved.

Microwave heating, rather than traditional heating, would reduce chitosan extraction time from hours to minutes while maintaining the same degree of deacetylation. During typical heating, the reactants are stimulated in a non-uniform and sluggish manner, whereas Microwave heating takes place at the molecular level, resulting in a uniform and quick temperature rise. As a result, the deacetylation time for chitosan isolation using microwave heating was reduced from 180 minutes to 60 minutes. Furthermore, the same percentage of deacetylation (DDA) was obtained with the same amount of heat. In comparison to the conventional procedure, which used 40-50% sodium hydroxide (NaOH), the deacetylation approach employed 30% NaOH. As a result, microwave heating is more environmentally friendly, poses fewer risks of harm, and necessitates fewer chemical expenditures.[2]

#### Some of Chitosan Derivatives

The most prevalent chitosan alteration is acvlation modification. Chitosan acylation is the reaction of chitosan with a range of organic acids and organic acid derivatives (mostly acyl anhydride and chloride), resulting in the introduction of aliphatic or aromatic acyl groups into the molecular chain. The acylation reaction breaks down chitosan's intramolecular and intermolecular hydrogen bonds, reducing its crystallinity and increasing its water solubility. The chitosan molecular chain has two hydroxyl groups: one primary hydroxyl group (C6-OH) and one secondary hydroxyl group (C3-OH). The main hydroxyl group may rotate in the spatial conformation with low steric hindrance, whereas the secondary hydroxyl group cannot spin with high steric hindrance, resulting in a large number of derivatives. Chitosan derivatives have emerged, [20] including the following:

#### **Carboxymethl Chitosans**

There have been far too many investigations on carboxymethyl chitosan (CM-chitosan), a chitosan derivative. Carboxymethyl chitosan, a water-soluble chitosan derivative, has piqued the interest of researchers in a variety of domains, including in vitro diagnostics, theranostics, bioimaging, biosensors, wound healing, gene therapy, and tissue engineering. Chitosan is converted into N-carboxymethyl chitosan by treating it with glyoxylic acid and a reducing agent. It is an amphoteric (a molecule or ion that may respond as both an acid and a base) polymer, and the pH determines its solubility. Oand N-carboxymethylation occurs under controlled reaction circumstances with sodium monochloracetate in the presence of NaOH. This reaction expands the pH range above 7, where chitosan is water-soluble, but due to the balance of positive and negative charges, A phase separation occurred on the polymer at 2.5 pH 6.5. It was established that the preponderance of positive or negative charges along the polymer chains at each pH, and hence the polymer's solubility, is governed by the balance between protonation of amino groups and carboxvmethyl group dissociation. As a result, whether the medium was mildly acidic to neutral or alkaline, negative charges predominated, whereas positive charges predominated in acid media. The excess of positive or negative charges appears to be the most important element regulating polymer solubility at a particular pH. the insolubility of the polymer arising of an insufficient excess of charge. As a result, the more substituted carboxymethyl chitosan samples had a broader range of solubility.

(CM-chitosan) is a method of increasing the antibacterial activity of chitosan by concurrently inserting a carboxymethyl group and a quaternary ammonium group into the chitosan molecular chain.[20]

#### Trimethylchitosan Ammonium

This cationic derivative, which is water soluble across almost the entire pH range, was created by quaternizing chitosan. It was created through the controlled reaction of a low acetyl content chitosan with methyl iodide and sodium hydroxide. This reaction resulted in a significant drop in molecular weight under all studied settings. These polymers are soluble in water regardless of pH for a degree of quaternization greater than 25%. These polymers had good flocculating characteristics. However, several quaternized derivatives possessed antistatic characteristics. [21]

#### Lactic-Glycolic Acid-Chitosan Hydrogels

Chitosan hydrogels were created by grafting D, L-lactic and/or glycolic acid directly onto chitosan without the need of catalysts. After grafting with lactic and/or glycolic acid, they demonstrated a greater interaction between water and chitosan chains. Because both the polyester side chains and the chitosan are biocompatible and biodegradable, these hydrogels are potentially advantageous for biomedical applications such as drug delivery systems and wound dressings.[20]

### Carbohydrate-Branched Chitosans

Carbohydrate attachment to chitosan changes it from a water-insoluble linear polymer to a branched-chain water-soluble derivative. Reductive alkylation was used to graft carbohydrates on the chitosan backbone at the C2 position: disaccharides (cellobiose, lactose, etc.) with a reducing end group and in the presence of a reductant were introduced to chitosan in the open chain form. These compounds were soluble in water.[20, 22]

### Chitosan Biocomposite with Cadmium Sulfide

The biopolymer chitosan was utilized as a matrixto create cadmium sulfide (CdS) quantum dots (QDs) with a restricted size distribution under mild circumstances, yielding a unique QDs biocomposite. whose size can be adjusted by altering the reaction duration and precursor concentration. The UV-vis spectrum and TEM data suggested that chitosan limits CdS particle development and agglomeration. The CdS QDs and chitosan formed strong hydrogen bonds, according to FTIR-(ATR). This interaction was also shown in the results. The solubility and stability of the chitosan-capped CdS QDs were improved. In the presence of CdS QDs, however,It also changed the temperature of chitosan thermal degradation to 50 °C. A. [23]

The CdS QDs capped with chitosan synthesis process was modified from earlier literature reports. To achieve a chelating equilibrium, 0.1 g of chitosan and 0.0114 g Cd (Ac)2 were dissolved in 50 mL of 1% HAc aqueous solution and stirred for 24 hours. Under magnetic stirring, the solution was purged with pure nitrogen gas for at least 30 minutes. The vortex of the mixed solution was then slowly filled with 0.0120 g Na2S9H2O dissolved in 10 mL water. Finally, the colloidal solution was sealed and incubated at 35 degrees Celsius for 5 hours. To eliminate unreacted inorganic ions, the produced solution was dialyzed against water. For two weeks, the colloid solution was held at room temperature with no evidence of precipitation.[24]

## Solubility of chitosan and its derivatives

CS solubility is strongly related to its MW and DD, as well as the aqueous pH value. CS is insoluble in water and the majority of organic solvents. It can, however, be easily dissolved in acidic aqueous solutions with pH less than 6.3, such as acetic, formic, and lactic acids. Even at low concentrations, the aqueous solution of CS has a high viscosity. Degrading CS to reduce its MW helps to increase its solubility in water.[11]

Because CS is poorly soluble in organic solvents, its application is restricted. As a result, several studies have focused on changing its chemical structure. There are three types of reactive functional groups in CS: two hydroxyl groups on C-3 and

C-6 in each repeating unit, and one amino group on C-3 Each deacetylated unit contains C-2. Many substituents can be conjugated in these groups, resulting in novel modified derivatives of CS. The key processes are quaternization (which is important for increasing CS solubility in neutral water), acetylation, reductive amination, acylation, phosphorylation, Schiff's bases, and cross-linking modifications.

Quaternary ammonium CS salts, carboxymethyl-CSs, carboxyalkyl-CSs, aryl-CSs, hydroxyalkyl-CSs, sulfated derivatives, phosphorylated CS, succinyl CS, and thiolated CSs are the most common[9, 17]

## Multi-functional textile finishing with chitosan

Surface modification with CS is used to create highly active textile surfaces with a variety of functionalities, including antimicrobial and antiviral activities, deodorizing, flame retardancy, antistatic, shrink-resistance, water repellency, and UV protection. There are two main ways to use CS in surface modification formulations: as an active agent imparting the desired property to the textile and, on the other hand, as a compound supporting the efficiency of active agent release (microencapsulation) or as a carrier or binder material.[17]

### Antimicrobial finishing

CS Widely effective against gram-positive and gram-negative bacteria, fungi, yeasts, and other microorganisms, CS is a broad-spectrum biocide that kills microorganisms and biostatic that prevents the growth of microbes. CS's antibacterial efficacy is mostly determined by its positive charge, degree of N-deacetylation, mean polymerization degree, and kind of chemical modifications. Similar to this, CS has gained popularity as an antibacterial agent for textiles because of its ability to retain moisture well and exhibit antibacterial properties. in contrast to other antimicrobial agents, such halogenated phenols (like triclosans) and metal salts (like silver), CS is a non-leaching antimicrobial agent that is chemically bonded to the textile substrate. Because of its binding properties, CS does not quickly run out.[15, 16, 25-41]

Because of the amino groups it contains, chitosan has a positive charge that is beneficial for cell adhesion and proliferation. Since bacteria are typically thought of as negatively charged entities, their interaction with chitosan can have a positive inhibitory effect. Three mechanisms underlie chitosan's antimicrobial properties: (1) cationic amino groups in chitosan bind to anionic groups in microorganisms, disrupting the physiological activities of the bacteria and inhibiting growth; (2) chitosan forms a polymer membrane on the cell surface, blocking the entry of nutrients; and (3) chitosan with a lower molecular weight permeates the cell. The degree of chitosan-finished fabric's antibacterial action is not correlated with the level of chitosan deacetylation. The fabric hand is negatively impacted by chitosan treatment, particularly with high molecular weight chitosan, which is one drawback of chitosan utilized in textiles.

And study has been conducted on the correlation between the molecular weight and antibacterial activity of chitosan. According to studies, the molecular weight of chitosan and the bacterial strains that are examined have an impact on its antibacterial effectiveness. The greater the chitosan molecular weight, the more potent the antibacterial action becomes against such as Staphylococcus aureus. On the other hand, as chitosan's molecular weight increases, the antibacterial efficacy against Escherichia coli is reduced. At low treatment concentrations, the impact of molecular weight was more noticeable. In order to achieve the desired antimicrobial finishing effect, it is crucial to select the appropriate chitosan molecular weight balance between the hand property and the antibacterial activity of the materials.

In addition to molecular weight, chitosan concentration and deacetylation degree influence antibacterial efficacy. In other words, antibacterial action gets stronger with increasing chitosan content and degree of deacetylation. Poor launder time is another drawback of chitosan applied to fabrics. Binder or crosslinker addition can raise the percentage of add-on. The chitosan's amino groups, however, could be obscured by the binder or react with them through the crosslinker, reducing the chitosan's antibacterial action. For the same reason, adding additional auxiliaries can help improve the fabric's bad hand following chitosan treatment. However, the chitosan's antimicrobial action cannot be impacted by the addition of chemicals. exposed chitosan-coated textiles to ultraviolet light, it produced excellent hand qualities and strong antibacterial qualities. By dilution with an acetic acid solution prior to spreading on fabrics, and allowing sufficient time for the chitosan to permeate fibers before curing, fastness can be enhanced.

Chitosan can be used as a deodorant for textiles, an antimicrobial for antimicrobial finishing, and a preservative in yarn sizing prior to weaving because of its antimicrobial, biodegradable, and non-toxic qualities. It is possible to enhance the properties of chitosan-treated textiles, such as their tensile strength, stiffness, and moisture [42]

Cotton and viscose fabrics treated with 3, 6 percent concentrations of chitosan and chitosan nanoparticles were dyed with two popular acid colors to impart absorption and antibacterial properties. The impact of chitosan and chitosan nanoparticles on the dyeing qualities of cotton and viscose was investigated by analyzing the color strength expressed in K/S values of the treated substrates at varying chitosan and dye concentrations. In comparison to untreated fibers, fabrics treated with chitosan and chitosan nanoparticles revealed higher dye uptake and exhaustion. When chitosan and chitosan nanoparticles are applied to cotton and viscose fabrics, bacteria production is reduced. revealed chitosan, chitosan nanoparticles, and the two acid dyes killed bacteria; and that antibacterial effectiveness varies depending on the bacterium strainsand fungus; and that the rate of the inhibitory zone rises with increasing quantities of chitosan and chitosan nanoparticles. The amount of growth is determined by the types of fungus and bacteria present. One method for determining an antibiotic's efficiency is to measure the area that is inaccessible to bacteria and fungi. The amino groups of chitosan nanoparticles interact with DNA at the cell surface, preventing bacteria from generating mRNA. When the concentration of dve molecules is raised, they bind to chitosan nanoparticles more readily. This is due to the dye molecules' increased access to amino groups. Because of the structure of bacterial cell walls, chitosan-coated fabrics are more effective against Gram-positive bacteria than Gram-negative bacteria. Chitosan nanoparticle-treated fabrics, on the other hand, are More effective against Grampositive and Gram-negative bacteria.[43]

Fabrics treated with chitosan and chitosan nanoparticles have the best antimicrobial qualities, as indicated by improved antibacterial activity compared to untreated fabrics. When dyed cotton and viscose fabrics, as well as pre-treated fabric with chitosan nanoparticles and chitosan, were tested for rubbing, washing, and sweat fastness, the results revealed that all of the dyes previously mentioned range from acceptable to outstanding, and salt-free dyeing is also acceptable.[44, 45]

Wool fabrics coated with chitosan have antibacterial characteristics since it contains a lot of amino groups that destroy bacteria.

Chitosan with a 2weight percent concentration has antibacterial capabilities against both Gram positive and Gram-negative bacteria because amino groups are transformed into ammonium ions, which can cling to bacterial cells and cause bacterial death. Furthermore, due to the composition of bacterial cell walls, chitosan-treated wool materials are more effective against Gram positive bacteria than Gram negative bacteria.[46]

Recently, researchers described the preparation and application of new chitosan nanoparticles on bioactive polyester fabric to impart increased antibacterial activity at extremely low concentrations. The effects of chitosan type and nanochitosan concentrations on the anti-bacterial and shrink-proofing capabilities of wool fabric have also been explored; nanochitosan-treated wool fabric and polyester fabric has better anti-bacterial and shrink-proofing properties.[47]

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Chitosan nanoparticle dispersion solution was produced and development as a novel multifunctional agent to change Antheraea pernyi silk. The surface of the chitosan-nanoparticle-treated A. pernyi silk fiber was rougher than the bulk chitosantreated and untreated ones, and a greater specific surface could be attained. Furthermore, the antibacterial activity, breaking strength, and wrinkle resistance of the chitosan-nanoparticle-treated A. pernyi silk fabric were improved. Previous research shown that chitosan nanoparticles improve the dyeability of silk with acid as well as reactive dye and the adsorption capabilities of several acid dyes.[47]

# Other functional

Chitosan-containing PU/poly (NIPAAm) thermosensitive membranes have recently been produced. To achieve this, hydroxyl-terminated polybutadiene (HTPB)-based polyurethane (PU) was created, and the PU solution was then UV-modified with N-isopropylacrylamide to produce thermosensitive membranes (PUNIPAAm). Chitosan was then infused onto the surface of PUNIPAAm and freezedried to create chitosan-containing PUNIPAAm. These membranes have very low cytotoxicity, promote the growth of 3T3 fibroblasts, and are antimicrobial, according to the findings. As a result, these materials may be useful for wound dressing.[48]

In another study, microporous polyamide (nylon) membranes were activated by bisoxirane and then bonded with chitosan to promote hydrophilicity and reactive sites. These membranes include a high concentration of reactive groups such as -OH and -NH2. By activating 1,1'-carbonyldiimidazole (CDI), polylysine (PLL) as a ligand was adsorbed onto chitosan-coated nylon membranes. CDI is highly reactive with several functional groups, including amino, carboxyl, and hydroxyl groups. These affinity membranes can adsorb bilirubin from bilirubin-phosphate buffer and bilirubin-albumin solutions. The results reveal that monolayer adsorption is the mechanism of adsorption and that adsorption capacity improves with increasing temperature.[48]

Recently, quaternized chitosan was used as a selective layer, polyacrylonitrile membrane as a support layer, and an anhydride mixture as a crosslinking reagent to create another form of composite membrane. The results suggest that raising the anhydride mixture concentration enhances rejection while decreasing pure water permeability and swelling in water. indicating the positively charged nature of these membranes. These membranes could be effective for lowering water hardness.

Some modified chitosans, such as hydroxyethyl chitosan and hydroxypropyl chitosan membranes, have been examined for their ionic conductivity and tensile characteristics. The membranes were created by combining alkali-chitosan with 2-chloroethanol and propylene epoxide. The results reveal that the crystallinity of the modified chitosan membranes decreased progressively as the degree of hydroxyl group substitution increased, resulting in a gradual increase in the swelling index. Membranes with a higher degree of substitution had a one-order-ofmagnitude improvement in ionic conductivity. Furthermore, there was no substantial change in tensile strength or elongation at breakage for these changed membranes. The degree of deacetylation affects the ionic conductivity of the modified membranes, which should not be too high.[49]

Recently, environmentally friendly ultrasonication approach was successfully used to manufacture graphene sheets coated with O-carboxymethyl chitosan nanoparticles. The produced graphene sheets (O-GRP) were then used as a green binder for covering the Ppy-Ag nanocomposite on the surface of textile. The Ppy-Ag nanocomposite on the graphene-modified textile was synthesized using a newly invented vapor polymerization for the fabrication of ternary modified cotton fabrics. The ascoated fabrics were examined for conductivity, antimicrobial, flammability, and mechanical characteristics. As an indication of the high conductive fabrics, the as-fabricated textile composites had lower electrical resistance than the virgin textile. The inhibition diameter zone for modified textiles was measured to be 24 and 28 mm for Ecoli and S. aureus bacterial strains, respectively, indicating excellent antibacterial activity. Furthermore, as compared to uncoated textile (149.3 mm/min, 17.8%) and blank CT/O-GRP200 (79.2 mm/min, 19.9%), the rate of burning and LOI values for CT/O-GRP200-Ppy-Ag were dramatically improved to 30.9 mm/min and 22.8%, respectively, showing the greater retardation against fire growth. When compared to bare CT, the elongation of the coated textiles was maximized, demonstrating that the coating with O-GRP-Ppy-Ag composite increases the elasticity of the textile. The amount of CMCh employed in the preparation of graphene sheets, as well as the efficient synergism between graphene and Ppy-Ag nanocomposite, have been investigated. This process could provide an excellent trial for obtaining a green flame retardant for coating the smart textile in order to achieve promising antibacterial and conductive qualities for use in a variety of sophisticated applications.[50]

In another study, polyamide textiles with multifunctional properties have attracted a lot of interest in the technical textile area Because of their good physical features however, their simple ignition and rather hydrophobic nature limit their practical application. Thus, using metal-oxide nanoparticles, namely TiO2 and SiO2 in the presence of chitosan (CS) in a simple dip-coating approach, bi-functional polyamide 66 (PA66) textiles with better flame retardant and wettability qualities were developed in this work. The use of TiO2 and SiO2 nanoparticles with CS increased the limiting oxygen index (LOI) while lowering the peak heat release rate (pHRR). As a result of the substantially lower water contact angle value of 10, an increased level of wettability was realized. In sum, in the laundering test, such a finishing was found to be semi-durable, with a small loss in the handle and tensile qualities.

the treated fabrics demonstrated adequate resistance to home laundering. As a result, metal-oxide nanoparticles in a hybrid application with CS show great promise as a promising family of chemicals for imparting functional qualities to synthetic textiles other than cellulosic and protein textiles.

# <u>Medical Application of Chitin and Its Deriva-</u> <u>tives</u>

Chitin and chitosan have been used to create medicinal (biomaterials). Figure.2 depicts the most prominent medical applications of chitin and its derivatives.[51, 52]

## **Primary and Secondary Wound Dressings**

- Primary wound dressings should provide an appropriate environment for wound healing. There is an increasing demand for bioactive materials that protect the wound in a synergistic manner and have strictly and clearly defined bioactive qualities, such as:[51-53]
- Promotion of wound healing
- Antimicrobial characteristics (antibacterial, bacteriostatic, antifungal)

- Controlling connective tissue regeneration (due to scar avoidance)
- Local hemostatic activity
- Boost the activity of polymorphonuclear leukocytes, macrophages, and fibroblasts
- Matrix metalloproteinase inhibition
- Chitin derivatives have various advantages related to passive infection prevention and wound healing, including:
- Gel formation to prevent over-adhesion to the wound bed
- Pain relieften. Physical entrapment of germs in gel structures
- Absorption of excess exudate
- Non-adherent to the wound and easily removed after use
- Creation of clear or semi-transparent gels or films
- Wound healing in a controlled wet environment

When compared to competitive controls, histological investigations using chitosan wound dressings demonstrated that the regenerated collagen fibers were more developed. The collagen fiber configurations were identical to those found in healthy skin. When compared to controls, the tensile strength of regenerated connective tissue was much higher, indicating complete reepithelialization and granulation.

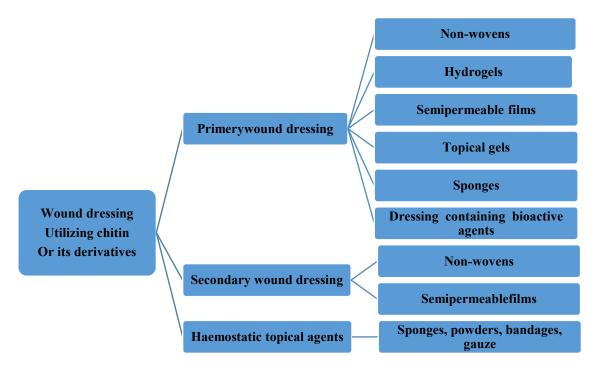


Figure 2. Types of wound dressings utilizing chitin or its derivatives

The fundamental wound dressing effect of chitin and its derivatives is linked to the synergistic mechanism of their physical qualities (moisture management, production of absorbent exudate gels, etc.) and bioactivity.

Secondary wound dressings containing chitin and its derivatives have two key properties: antibacterial protection (bioactivity) and the ability to generate semipermeable or absorbent exudate useful forms of biopolymers.[51]

Between 2005 and 2010, various forms of secondary wound dressings were developed but not yet commercialized. The wound dressing studies were chosen based on properly presented preclinical data (harmonized standards, including biocompatibility tests). Except for hemostatic topical medicines.

Composite wound dressings were produced in the form of needle-punched nonwovens and sponges incorporating antibacterial fibers and/or various functional forms of chitosan. They can be utilized throughout the first healing period, especially on wounds that are accompanied by inflammations. Antibacterial agents such as bioactive staple polypropylene fibers containing triclosan, or aluminosilicate with Ag+ and Zn2+ would suppress the infection, but chitosan would promote wound healing and shorten the recovery time. Antibacterial activity was examined in modified staple polypropylene fibers and chosen chitosan forms, such as microcrystalline chitosan (MCCh) or chitosan fibers. The dressings were tested for bacteriostatic characteristics against E. coli and Staphylococcus aureus.

There is Preliminary research on the production of composite films incorporating chitosan, sodium alginate, and anti-inflammatory compounds Agents suggested that this material could be used to treat bedsores in the early stages of wound healing.

The UV-photocrosslinking of a chitosan solution with azide groups and lactose moieties with integrated paclitaxel is described. The generated hydrogel could be used to create hydrogel wound dressings with integrated fibroblast growth factors or paclitaxel for tumor treatment. During in vivo experiments, the bioactive chemicals are gradually released. Furthermore, the modified chitosan hydrogels efficiently reduce carotid artery bleeding and lung air leakage in examined animals. Hydrogels have a stronger sealing strength than fibrin glue.[51, 53]

as well as Validated research on nonwoven wound dressings constructed of dibutyrylchitin (a soluble product of chitin substitutions by butyric anhydride). These studies included estimations of performance (sorption, mechanical characteristics, etc.) as well as safety (EN-ISO biocompatibility). Infrared spectroscopy, size exclusion chromatography, and viscometry were also used to investigate dibutyrylchitin particles. In most cases, satisfactory results were obtained during the clinical research of wound healing, particularly in cases of burn wounds, postoperative/posttraumatic wounds, and numerous other disorders causing skin/epidermis loss.

The effects of chitosan topical gels with varying molecular weights (M w) and degrees of deacetylation (DD) on wound healing have been studied. The treated wounds were discovered to contract at the fastest pace, with a high M w and DD of Chitosantreated rats were compared to untreated rats. Wounds treated with chitosan had much higher epithelialization as well as faster wound closure. In wounds treated with high M w chitosan, histological analysis and collagenase activity assessment demonstrated progressed granulation tissue development and epithelialization. However, the mode of action may be synergistic via bioactivity of chitosan oligomers as well as appropriate moisture remaining for wound healing by chitosan gel with high fluid handling capacity.

A study conducted there described unique chitin/nanosilver composite materials for wound healing applications. The antibacterial activity of these -chitin/nanosilver composite materials against E. coli was outstanding and S. aureus, as well as the ability to coagulate blood.

Antibacterial capabilities (E. coli and S aureus), whole blood clotting, swelling, and lack of cytotoxicity define and composite of -chitin hydrogel containing silver nanoparticles. Furthermore, chitin/nanosilver hydrogels were tested for cell adhesion utilizing epithelial cells (Vero cells).

EN 13726 standards specify the performance of the specified wound dressing. The study assesses the overall performance of various chitosan prototypes of innovative wound dressings (such as sponges, hydrogels, and films) made of various usable forms of chitosan (microcrystalline chitosan, chitosan fibers, chitosan/alginate fibers, and chitosan/carboxymethylcellulose mixture). The abovementioned wound dressing prototypes were evaluated using recommendations from the EN 13726 family of standards. the scope of:

- Absorption capacity for free swell
- Capacity to handle fluids
- Gelling characteristics
- Dispersion properties
- The wound dressing's moisture vapor transmission rate (MVTR) when in contact with water vapor or liquid.
- Waterproofness
- Extensibility
- Set in stone

### **Topical Hemostatic Agents**

Chitosan and its oligomers' hemostatic capabilities have been commercially utilized in a variety of topical hemostatic dressings that differ in their usable form. Many studies have demonstrated the potential of chitosans, which vary in molecular weight and degree of deacetylation, to localize platelet activation and turnover of the intrinsic blood coagulation cascade. Furthermore, chitosans' gelling characteristics assist the creation of a physical barrier against major bleeding. Chitosan's hemostatic activity is significantly influenced by its chemical as well as physical nature and structure. The topical hemostatic medications that are commercially available.[51, 52].

# Application of a chitosan and derivatives to dyeing

Chitosan was first employed in the textile industry as a color deepening agent. Chitosan, as a cationic polymer, is thought to be an excellent fixing agent for anionic dyes. Salt-free.

Dyeing is accomplished with the help of chitosan and other ingredients. The presence of chitosan results in a homogeneous layer on the surface of the fiber, which may explain the level of coloring effect. It enhances the surface characteristics of the fiber and decreases the Coulomb repulsion between the fiber and the anionic dyes, resulting in a significant increase in dye uptake rate. The protonation of the free amino group on the chitosan molecule in acidic circumstances also contributes to the deepening impact. When the material is When the fiber is immersed in chitosan solution, its positive charge increases, reducing the repulsive force between the fiber and the anionic dyes.[54-56]

Henna, a natural pigment with established bactericidal effects, was combined with chitosan to give antimicrobial capabilities to wool garments. Applying chitosan to wool fabrics before dyeing has two effects: the first is that it improves dye absorption; the second is that it significantly improves dye antimicrobial activity, as chitosan has been shown to increase dye absorption rate and dye exhaustion of woolen fabrics in the case of acidic and reactive dyes. Chitosan is a naturally occurring biopolymer that is increasingly being utilized as a functional finish on textile substrates to impart antibacterial properties and enhance dye uptake.[45]

Cotton fabric was treated with O-acryl amidomethyl-N- [(2-hydroxy-3 trimethylammonium) propyl] chitosan chloride (NMA-HTCC), a fibrereactive chitosan derivative containing quaternary ammonium groups. Cotton treated with NMA-HTCC was dyed without the addition of salt with direct and reactive dyes. Despite the use of a substantial amount of salt in the later example, the colour yield was higher on treated cotton. Cotton treated with NMA-HTCC after dyeing had improved wash fastness than untreated cotton. the creation of ionic bonds between the cationic groups of NMA-HTCC and the anionic groups on the dye is thought to be responsible for the greater colour yield on treated cotton. However, the light fastness was inferior to that of untreated cotton. Cotton treated with NMA-HTCC has significantly decreased antibacterial activity against Staphylococcus aureus after treatment dyeing, most likely because the cationic group's antibacterial activity on NMA-HTCC is hindered by its mixture with the anionic dye.[57]

Cotton fabrics with acid dye have been improved by finishing them with chitosan nanoparticles (CSNPs). CSNPs were synthesized from chitosan and tripolyphosphate using an ionotropic gelation process of chitosan (0.2 g/100 ml) and tripolyphosphate (0.1 g/100 ml). TEM imaging and FT-IR spectroscopy are used to identify CSNPs. The dyeability and antibacterial activity of cotton fabrics dyed with AR and AO acid dyes after treatment with various concentrations of CSNPs were examined. Because chitosan nanoparticles could create new cationic charges from amino groups protonation on the cellulosic cotton fabrics surfaces, the pad-dry-cure method was used for cotton fabric treatment with different Chitosan nanoparticles treatment was improved and enhanced the dveability of cotton fabrics with AO and AR acid dyes. Furthermore, the physicochemical and mechanical qualities of cotton fabrics have been improved as a result of the high power penetration of nanoparticles and physical crosslinking within cotton fabrics (presence of OH and NH2 groups in CSNPS moiety). The optimal chitosan concentration was 0.2 wt.% for both dyeability and antibacterial activity enhancement. Finally, chitosan nanoparticles offer antimicrobial activity to these dyed cotton fabrics against Gram-positive, Gram-negative bacteria, and fungus.[58, 59]

#### <u>Summary</u>

The range of chitosan modification methods reported demonstrates that a number of new compounds with widely diverse chemical and physical properties can now be created from a single biopolymer. The main applications of chitin and chitosan depend on their good functional qualities, which can be achieved by modification. Better physical, chemical, and biological effects, such as the ability to dissolve in water and non-toxic solvents, antibacterial capabilities, biocompatibility, or non-toxicity, are all beneficial properties. Furthermore, since it is a natural polymer, it is completely biodegradable and has no negative impact on the environment. Due to the active functional groups, the molecular structure of chitosan can be altered to generate derivatives with superior physical, chemical, and/or physiological capabilities. Various chemical processes produce chitosan derivatives, and they are often used in many aspects of our lives. Chitosan, a natural polymer, is one of the main materials used to build many advanced structural and functional materials based on electronic principles found in nature. This natural polymer has many beneficial health benefits, including powerful antioxidant, antimicrobial, antioxidant, and anti-inflammatory effects, and can be used as a new-generation drug due to its ability to biodegrade in the body, lack of adverse responses, and high biocompatibility.

As a result of its increasing popularity and researchers' ongoing efforts to improve various functional qualities, it may one day replace many synthetic polymers currently in use. Chitosan is one of the polymers of the future that has piqued the interest of researchers. For many years, new publications have been published detailing new ways to create various forms of the polymer after changes have been implemented, allowing chitosan to increasingly find new applications.[60]

# **Conflict of Interest**

There is no conflict of interest in the publication of this article.

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