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Chitosan-Based Sustainable Textile Technology: Process, Mechanism, Innovation, and Safety

Jagadish Roy, Fabien Salaün, Stéphane Giraud,
Ada Ferri and Jinping Guan

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Abstract

This chapter reviews relevant findings regarding the activities and contributions of chitosan in different textile processing following the varieties of process, mechanism, and applications. Chitosan is a better candidate in both aspects of biodegradability and efficiency instead of synthetic polymers. The technical and scientific discussions behind the role of chitosan in all the processes and treatments have been explored in the chapter. Over the last few years, enormous efforts and challenges are being practiced in research and industry to design and development of eco-friendly and sustainable technologies. Therefore, the chapter emphasizes on chitosan-based formulations of fibers, fabrics, coatings, and functional textiles.

Keywords: chitin, chitosan, textile, fiber, fabric, antibacterial, nanofibers, electrospun

1. Introduction

The first discovery of chitin was traced by Braconnot, a French professor, in 1811 in research on the mushroom. Later on, Rouget discovered the solubility test through chemical and thermal treatment of chitin fiber in 1859 [1]. Ledderhose identified the chitin molecular structure, which consists of glucosamine and acetic acid, in 1878 and Hoppe-Seyler announced the name 'chitosan' of the modified chitin in 1894.

Chitin is a very common bio product produced naturally in the exoskeleton of crustaceans and insects (spiders, shrimps, crabs, and lobster), the radulae of mollusks and the cell wall of mushrooms, algae, and fungi. The amount of chitin produced naturally each year is 10^{10} ton

of which 70% comes from oceans. Therefore, the by-product of the fishing industry is enough to support the huge commercial demand of chitin and chitosan with a long-term potential supply. The main advantages of using chitosan are biodegradable [2, 3], biocompatible [4, 5], and nontoxic because it degrades as sugar after being metabolized.

Chitosan is a biomaterial which possesses the superior mechanical property and very diverse biological activity. The chitosan-derived products have a slow-growing market for poor reproducibility in product development. The first- and second-generation chitosans have been used as a biomaterial and biological functionalities for wastewater treatment and agricultural applications, but the scenario alters now. The third phase of chitosan exhibits strong relationship in molecular structure-function. Up to date, studies and investigations are approaching to understand the cellular mode of action to reveal every biological and biomedical activity of chitosan which will open the door for new material applications. Chitin and chitosan have very diversified use in applications (**Table 1**) and in the form of nanofibers, membranes, micro-/nanoparticles, scaffolds, beads, hydrogels, and sponges. Due to the growing concern about health, environment, and economics, enzymatic synthesise of chitosan is continuously studied as an alternative to the hazardous process and nonspecificity for chitosan fictionalization. Besides, the sustainability and safety in textile technology are being practiced and equipped by innovating new process, machinery, and designs from raw materials to the end of life cycle.

Application	System
Antibacterial cotton fibers	Fiber-reactive chitosan derivative
Cell culture	Chitosan-based nanofiber
Biodegradable and biocompatible nonwoven wound dressing	Chitin and chitosan nanofibers [spinning solvent: 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)]
Bioactive and biodegradable Wound dressing	Dibutylchitin fibers

Table 1. Chitosan fibers and their applications.

2. Chemistry of chitin and chitosan

According to the chemical structure of chitin (**Figure 1**) and chitosan (**Figure 2**), they are the modified form of cellulose (**Figure 3**) in which an acetamide and an amine group takes the place of C-2 hydroxyl group, respectively. Chitosan is derived from natural chitin which consists of *N*-acetyl glucosamine and glucosamine units distributed randomly in a linear polysaccharide chain. In nature, it is very rear to exist 100% acetylated amino groups and 100% deacetylated free amine groups. Therefore, less than 10% degree of deacetylation (DD) may exist in chitin structure, while 40–98% DD is found for chitosan. The average molecular weight of chitin and chitosan mainly depends on the degree of deacetylation and degree of polymerization. Besides, the achieved properties from different applications and products vary according to the two parameters. The polymorphic structures of chitin and chitosan change due to different packing and orientation of polysaccharide chain. Every individual chain

undergoes a full rotation along 10.1–10.5 Å of the chain axis due to the presence of chiral glycosidic units. These units link between C-1 oxygen atoms of one unit and C-4 of the adjacent unit in parallel and anti-parallel directions. The characterization of those structures using X-ray diffraction and NMR spectroscopy reveals three types of allomorphs: α , β , and γ form where a higher percentage of α form exists [6].

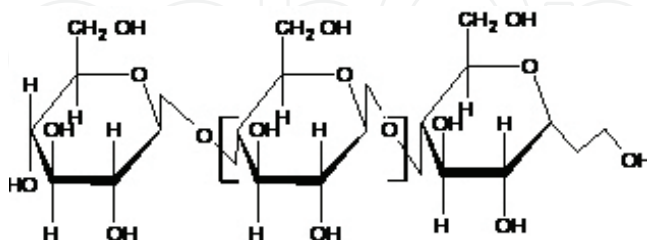


Figure 1. Molecular structure of chitin.

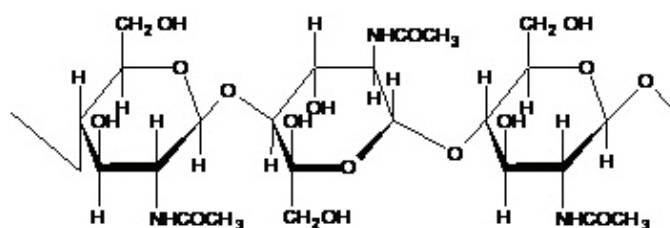


Figure 2. Molecular structure of chitosan.

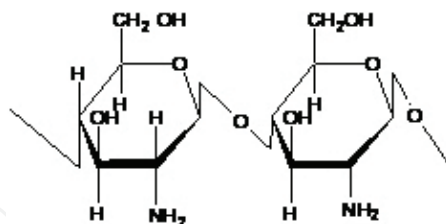


Figure 3. Molecular structure of cellulose.

The physico-chemical behaviors of chitin and chitosan are quite different even though they show many similarities in the structures. Due to the presence of acetamide group, chitin mostly shows an inert behavior, while chitosan is highly reactive for free active amine groups. Also, the behavior also attributes to the degree of crystallinity because chitosan is less crystalline compared to chitin. Moreover, there are very few solvents allowing the dissolution of chitin, whereas the chitosan dissolve in almost all aqueous acid solvents. The chitosan carries positive charges after interacting with acid for the presence of free amino groups and dissolves at $\text{pH} \leq 6.0$. Over the $\text{pH} 6.0$, more than 50% of dissolved chitosan molecules lose its positive charges and become insoluble.

3. Chitosan-based fiber production

3.1. Spinning process

3.1.1. Wet spinning

3.1.1.1. Introduction

Chitin is an acetylated form of polysaccharide. The presence of acetyl groups increases the interchain forces and the percentage of crystallization which leads to a better dry and wet strength compared to semi-crystallize chitosan fibers. Besides, the chitosan fibers having higher moisture regaining property show poor performance in developing the desired strength.

The most popular method for chitin and chitosan fiber production is a wet spinning method. In this process (**Figure 4**), the fibers of chitosan are produced using viscous chitosan solution by the extrusion process in a coagulation bath. The chitosan dissolution occurs in 1–10% acetic acid below the pH 6, and a viscous dope is formed. It passes through a candle system filtration unit to remove the undesired impurities and a reservoir for degassing under vacuum around 30 mbar for 5 h to confirm the complete removal of the air bubble. Then, the extrusion process starts to obtain fibers where the extrusion chamber is comprised of a reservoir, a metering pump, and a spinneret. The chitosan dope is extruded less than 1.5 bar pressure into a coagulation bath. The coagulation bath contains an aqueous solution of the coagulant such as NaOH [7], KOH [8], cupric ammonia [9], alcohol/calcium chloride/acetate [10], NaOH–Na₂SO₄, NaOH–AcONa [11], NaOH-40% methanol, CuSO₄–NH₄OH, CuSO₄-concentrated ammonia [12], etc. The presence of tailors mentioned above chemicals acts as coagulation retardants. In this process, the take-up rollers, drawing system, drying rollers, and winding up are optimized according to the production rate and required properties of fibers. The excess amount of coagulant on fiber is washed off using distilled water or aqueous methanol and ethanol. This washing bath is also called predrying bath. Some additional physical and chemical processes are practiced to enhance the desired mechanical property in drying treatments.

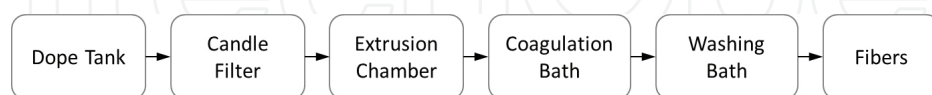


Figure 4. A typical block diagram of wet spinning.

3.1.1.2. Solvent system

A proper selection of solvent system and coagulation bath leads to produce desired fiber structures and properties. Many researchers have studied (**Table 2**) different types of solvent systems such as dichloroacetic acid-isopropyl ether-formic acid, trichloroacetic acid, dimethylacetamide-lithium chloride; a mixture of trichloroacetic acid-chloral hydrate-dichloromethane

(DCM) is used for dissolving chitin. Besides, the pH-sensitive behavior of chitosan is very useful in the processing of fiber. Acetic acid is efficient enough to dissolve chitosan, a simple solvent system, especially <pH 6. Moreover, coagulation bath containing NaOH is easier to prepare and strengthens the chitosan fibers within a short time.

Chitin dissolution (solvent system)	Chitosan dissolution (solvent system)
Trichloroacetic acid (40%)-chloral hydrate (40%)-methylene chloride (20%)	Dilute aqueous organic acid (acetic acid, formic acid)
LiCNS/Ca(CNS) ₂ /CaI ₂ /CaBr ₂	Dimethylsulfoxide/ <i>N,N</i> -dimethylformamide (DMF)
Lithium thiocyanate	<i>p</i> -Toluene sulfonic acid
Formic acid-dichloroacetic acid-isopropylether	Guanidine hydrochloric acid-urea
Sodium <i>N</i> -acylchitosan xanthate [O-(sodium thio) thiocarbonyl <i>N</i> -acylchitosan]-xanthate [O(sodium thio) thiocarbonyl cellulose]	Ionic liquid, 1-butyl-3-methylimidazolium bromide ([BMIM][Br])

Table 2. Solvent system for the dissolution of chitin and chitosan.

3.1.2. Dry spinning process

The chitosan used for dry spinning [13] should have the initial concentration over the critical concentration of chain entanglement which is equal or more than 0.5% (w/w). Acetic acid is frequently used for the dispersion of chitosan. Similarly, the above-mentioned process is followed up by the extrusion process. During the coagulation process, 125 ml of concentrated ammonia (20% w/w) in the gaseous state comes in contact with chitosan monofilament. The flow of gaseous ammonia is around 0.24 m³/h for 7.5 s based on the relation between extruder and speed of the first roller around 3.4 m/min. The stretching is done by maintaining 14% of the maximum first roller speed that produces a straight fiber line during coagulation. It is important to maintain the speed exactly to avoid un-stretching. A second roller having higher speed is used to maintain a stretching ratio of 1:12 to the produced monofilament. In the drying process (**Figure 5**), the hot air around 110°C is passed through a 65 cm oven, while the air flow of 1.5 m³/h is used and the retention time of monofilament in the oven is around 10 s. Then, the chitosan fiber is treated in the wet air circulating at 25°C and water content is 55% w/w for one week before final storage [13].

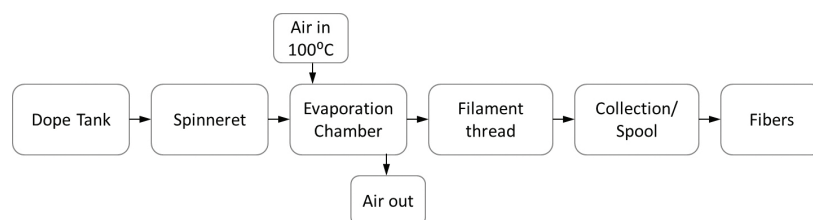


Figure 5. A typical block diagram of dry spinning.

3.1.3. Electrospun

In 1934, Antonin Formhals applied for a patent to manufacture textile yarn. The fabrication process is called electrostatic spinning or electrospinning. The central principle of this process is to apply an electrostatic potential to a polymer solution to overcome the surface tension which results in the formation of the nanofibers. An external high voltage source delivers the required electric potential in this process. The first step of the process (**Figure 6**) is to prepare the chitosan solution by placing in a pipette, which is charged by a positive electrode of the source. As a result, a repulsive force is developed that causes splitting of a charged jet from the pendant polymer droplet at the pipette tip. The single jet splits into multiple jets due to radial-charge repulsion which is driven electrically to the collector and neutralizes. The multifilament fluid jet dries, while the solvent evaporates as soon as the mixture comes out of the pipette tip. The solidified polymers are deposited in the collector.

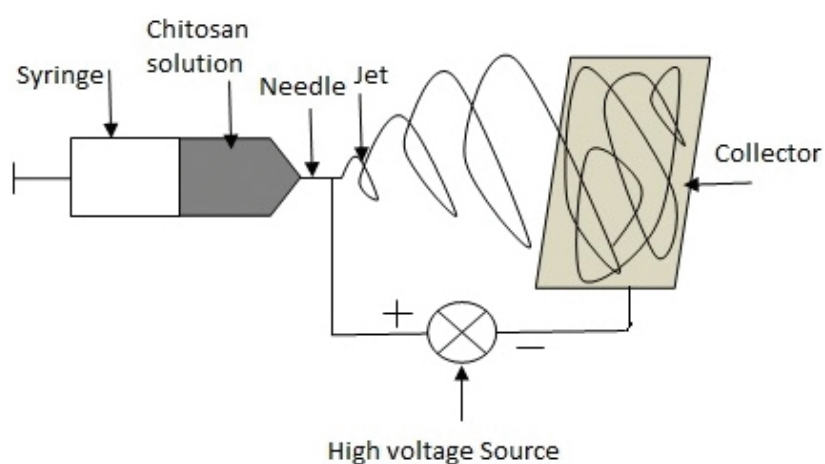


Figure 6. A typical diagram of electrospinning process.

In this process, solvent plays the main role in the spinnability of chitosan. Many physical and chemical properties of chitosan such as solution viscosity and conductivity affect the rheology of chitosan fibers. Many studies have been conducted for choosing suitable solvents such as acetic acid, dilute hydrochloric acid, formic acid [14], dichloroacetic acid, trifluoroacetic acid (TFA), etc., for the dissolution of chitosan. The understanding of solvent-chitosan interaction and the effect of solvent ionic strength, pH, and viscosity would help on the proper selection of the solvent.

The main problem of chitosan is its higher viscosity at higher concentration. For example, above 2% (w/w) of chitosan is highly viscous and loses its ability to flow. In contrast, low concentration of chitosan does not contain enough material to obtain solid and stable fibers. In the molecular level, every chitosan contains -NH_2 and -OH groups which interact promptly at high viscous level. Therefore, the interchain interactions are higher among the chitosan chains at a higher concentration which results in a three-dimensional network formation and highly viscous gel formation [15]. The trifluoroacetic acid (TFA) is a proposed solvent that

could dissolve around 8% of pure chitosan which is perfectly spinnable. A mixture of TFA and dichloromethane provides fibers in a range of 200–650 nm diameter [16].

3.2. Mechanical properties of fibers

The electrospinning process provides nanofibers for nonwoven. The diameter of fibers, uniform deposition at the nanolevel, thickness of the fibers, and bead formation are essential to validate a process. Concerning these morphological and structural properties, the tensile strength and tenacity are crucial parameters to quantify the quality of chitosan fibers. The chitosan fiber was obtained with 82 g/denier modulus of elasticity while 2 g/denier tenacity at a final dry jet stretching ratio of 3.7 [17]. Besides, chitosan fiber having the dry tenacity of 2.1 g/denier was obtained by the wet spinning process [8]. Ionic liquid, [Bmim]Cl (1-butyl-3-methylimidazolium chloride), is used as a solvent for the fabrication of the pure chitosan fibers by both wet and dry-wet processes. The dry fiber exhibits the strength and modulus at 1.5 and 71 cN/dtex, respectively, for the wet process, while 2.1 cN/dtex and above 3.5 cN/dtex are, respectively, found for the dry-wet process. The results are attributed to the orientation of the crystallites, which is increased by 40% due to the dry-jet-stretched ratio and inter-fibrillar amorphous zone restricting the inter-fibrillar sliding that causes plastic deformation [17]. Moreover, the polymorphism and crystallinity of chitosan membrane depend on the used solvent, the processing conditions, the form of dry or wet [18]. Synchrotron X-ray diffraction experiment confirms two types of allomorph existing in chitosan—tendon and annealed forms [17, 18]—depending on stretching ratio. In addition, the chitin fibers are also influenced by its polymorphism; α -chitin is profoundly hard, while β - and γ -chitin show superior quality on toughness and elasticity [19]. A very poor tensile strength is observed for the chitosan fibers, which are obtained after spinning process and exist in wet condition. Different processes are applied to improve mechanical strength such as epichlorohydrin in coagulation bath, glutaraldehyde in posttreatment, phosphate and phthalate ions containing the solution.

Physical, chemical, and mechanical characters of chitosan fibers and the ability to build in different forms facilitate chitosan nanofibers for the filtration process, for example, metal and dyes separation from water [20, 21], capturing of virus in air [22], etc. In addition, the technological developments in textile processing associated with chitin and chitosan would impact on reinforcing microfibers composite [23], dressing for wound skin [15, 24–26], carrying and delivering drugs [22, 27], tissue engineering [15, 28–30], vascular grafts [31], etc.

3.3. Chitosan blends for electrospinning process

Apart from the pure chitosan processing, many studies have reported on mixtures of chitosan with different polymers such as polyvinyl alcohol (PVA) [32], polyacrylamide [33, 34], polyethylene oxide (PEO), polyacrylonitrile (PAN) [35], caprolactone [14], and Zein (an agro-based protein) [36] to modify the chitosan solution property and facilitate the spinnability by easy flowing through the capillary tip. For example, the viscosity of chitosan solution decreases with the increasing amount of PEO. The main reasons for the change in viscosity is the reduction of intra- and intermolecular attraction among the chitosan chains and the formation of new bonding of PEO with the backbone of chitosan. The presence of PEO on chitosan

structure interferes the intra- and intermolecular association, while new hydrogen bonds are formed between –OH group of chitosan and water. It results in a drastic reduction in the viscosity of chitosan solution [15]. Furthermore, PVA also facilitates interaction with chitosan in molecular levels that restrict the intra- and intermolecular interaction among chitosan chains and provide a better spinnable solution [16]. Moreover, inorganic nanoparticles such as sodium chloride, potassium chloride, or ions such as calcium and iron are used in doping chitosan in the electrospinning process [33]. The metal ions also help to break down the intra- and intermolecular hydrogen bonds and reduce the viscosity of chitosan solution that would enhance the chain entanglements. As a result, lower number of beads and reduced diameter of fibers are obtained from chitosan electrospinning process [33]. Some processes of chitosan blends and mechanical properties have been demonstrated below.

3.3.1. *Nylon-6/chitosan blends fiber*

Two solvents, 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and formic acid at a ratio of 90/10, have been used to dissolve nylon-6 and chitosan for the electrospinning process. The total weight of polymer has been maintained 6% by varying the concentrations of both polymers. The similar electrospinning (Section 3.1.3) process has been operated at room temperature [37]. The properties of the blend fibers depend on the blending weight ratio. The increased amount of chitosan increases the functional sites for capturing water molecules. A unique molecular interaction between nylon-6 and chitosan is formed due to developing a hydrogen bond which affects the mechanical property of the blend fibers. The tensile strength and crystallization behavior decrease due to the formation of an amorphous polymer during the electrospinning process. For example, 25% of chitosan in the blends shifts the melting point at 258.1°C, while pure nylon-6 exhibits the temperature at 268°C [37].

3.3.2. *Chitosan-agarose blend fibers*

Chitosan and agarose, one kind of red algae, are dissolved in a mixture of solvents, trifluoroacetic acid (TFA) and dichloromethane (DCM). The polymer has been maintained at 7%, while the solvent ratio between TFA and DCM is 7:3. In the electrospinning process, the operating electrostatic potential is 15 kV/12 cm and the solution flow rate is 0.5 ml/h. The blending contents of 30 and 50% agarose provide fibers with smooth and uniform surfaces. The main advantage of blending of chitosan and agarose is the production of nanosized fibers. The achieved fiber diameter is 520 ± 35 nm and 140 ± 9 nm for using 30 and 50% agarose, respectively. Besides, the pure chitosan fibers from electrospinning process exhibit around 1.76 ± 0.59 μ m in diameter [38].

3.3.3. *Poly lactic-co-glycolic acid (PLGA)-chitosan-PVA blends*

The PVA and chitosan are dissolved in 2 wt.% acetic acid separately and blends at a ratio of 60:40. The mixture is used for the electrospinning process. Besides, PLGA of 6 wt.% is dissolved in a mixture of solvents, tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF). The electrospinning process is modified by adding an extra tip or syringe parallel to another tip for holding two polymer solutions separately. The collector collects the spinning fibers from

both tips. In this process, chitosan/PVA and PLGA solutions are used separately in these tips and run the electrospinning process. The tensile strength values of three different electrospun nanofibers—PLGA, chitosan/PVA, and PLGA-chitosan/PVA—achieved by electrospun are 7.3, 4.3, and 2.6 MPa, respectively. The reason behind the result is no interaction present between PLGA and chitosan/PVA. Besides, PLGA-chitosan/PVA and chitosan/PVA nanofibers are crosslinked separately using 25% glutaraldehyde. The tensile strength of crosslinked PLGA-chitosan/PVA is found higher compared to uncrosslinked nanofibers. In contrast, the cross-linked chitosan/PVA nanofibers have lower tensile strength than that of uncrosslinked nanofibers. In the case of crosslinked PLGA-chitosan/PVA, some bonds are formed after crosslinking with glutaraldehyde [39].

4. Chitosan-based textile processing

4.1. Chitosan: a sizing and desizing agent for textile pretreatment

Sizing is the conventional process of fiber pretreatment for the resistance of warp breakage caused by highly stressed weaving process. In general, a sizing agent adheres to the surface of yarn and forms a coating. It provides the required strength and hydrophilicity for a successful weaving process. Polyvinyl alcohols and acrylics including all synthetic sizing agents need to be washed out at the end for a smooth finishing process, to avoid complications in the subsequent steps of fibers or fabric treatment. Chitosan is a better candidate in both aspects of biodegradability and efficiency, while synthetic agents are not. Chitosan is soluble in pH less than 6.0 since the pKa is 6.5 where more than 50% of chitosan molecules deprotonated and become insoluble.

Chitosan is hydrolyzed by concentrated hydrochloric acid 0.1 N [40], 0.2 N [41], 0.5–1 N [42] at high temperature (30–90°C) to achieve soluble chitosan which exhibits lower apparent viscosity. The temperature is associated with the activation energy, which catalyzed the hydrolyzing action of HCl. Besides, the content of nitrogen reduces from 7 to 6.5% since the hydrolysis of chitosan continues around 60 min. It attributes to chain scission at 1–4 glycosidic bonds of chitosan for the regular attack of concentrated HCl resulting in the lower molecular weight. In addition, the dissolution of short chain chitosan shows lower and stable apparent viscosity to 110 MPa s after 60 min probably due to the retention of crystallinity after degradation. The conformational change is attributed to the result of a transformation rod to coil transition [40]. In general, the sizability and desizability processes are expressed as size add-on and removal percentages, respectively. The add-on proportion of size mainly depends on the apparent viscosity and the solid content of size materials in the liquor. The tensile strength is found higher after drying the size coating by heat treatments, while the elongation at break decreases significantly. The effects attribute to the diffusion and deposition of the size materials in the fiber thread which increase the brittleness and rigidity. On the other hand, the removal efficiency of hydrolyzed chitosan is found 100% only with water at 90°C. Carboxymethylated chitosan, a modified form of chitosan, is readily soluble in water at neutral pH and could be used as sizing agent [42]. On the other hand, in combination with wax or starch by an extrusion

process, a form of sizing agent is obtained [43]. The viscosity of chitosan solution increases with increasing chitosan concentration and limiting its performance as sizing agent arises from the high viscosity of chitosan at room temperature above 2% in the acidic medium. Carboxymethylated chitosan is achieved via hydrolysis using 0.5 N hydrochloric acid at a minimum of 90°C for 2 h. The NaCO_3 is used for the neutralization, and then, the filtration with washing is necessary for removing the sodium chloride salt. The final form is used as sizing agent [42]. Apart from the carboxymethylated chitosan, the addition of wax with the modified chitosan provides a reduction in surface tension which results in improved wetting property including adhesion behavior of modified sizing agent [43]. The viscosity is reduced by 0.5% of pure chitosan after the small proportion of wax addition. Moreover, the sizing film also reduces the friction between metal and fibers resulting in the better performance in the weaving process. Some modified chitosans such as *N*-[(2-hydroxy-3-trimethyl ammonium) propyl] chitosan chloride (HTACC) and *N*-[(4-dimethyl aminobenzyl)imino] chitosan (DBIC) have been developed for better performance of solubility and pretreatment of polyester fabric [44].

4.2. Chitosan: an auxiliary in textile dyeing process

The dyeing process is a major step in fabric processing, especially for consumer esthetic test. In this process, dye molecules diffuse and interact with functional sides of fibers or fabrics. Therefore, various types of fibers or fabrics made of cotton [45], polyester [46], rayon [46], nylon [47], wool [48, 49], silk [50], and composites [51] are processed using different functional dyes such as sulfur dye, vat dye [46], reactive dyes [45, 46, 52–54], etc. Therefore, the methodological variations are found based on dyes and fibers/fabrics such as Jig dye, Pad dye, and Jet dye [46] for the dyeing process. All methods require quite high energy, large amount of water and salts until the dye molecules distribute and diffuse uniformly. In addition, these processes release a high amount of complex effluents containing all chemicals together. Therefore, the loss of untreated dye and salt and highly efficient effluent treatment all have very high equivalent cost. Moreover, the drawbacks also impact on aquatic environment-related health. The use of chitosan or modified chitosan has beneficial effects on dyeing process which reduces the amount of untreated dye in the bath without using any salt. As a result, a simple effluent treatment would be enough to process released effluent from dye house.

In the dyeing process of cotton fibers or fabrics, reactive dyes are the mostly used due to its better-wet fastness, brilliance, hue variability, easy processability, and applicability [55]. In addition, reactive dye molecules form covalent bond through reaction with hydroxyl groups of cellulose via nucleophilic addition or substitution reaction. In general, reactive dyes and cotton fabrics or fibers hold anionic groups which affect the reaction due to charge repulsion in the dye bath. As a result, large quantities of salts are used for the screening of charges in dying process. A comprehensive and comparative optimization process studies have been conducted by Ramadan et al. [56] regarding dyeing treatment of chitosan-treated cotton fabrics. A cotton fabric is immersed in an aqueous solution of 2% chitosan and 50 mg/100 ml sodium periodate (NaIO_4). The liquor ratio is maintained at 1:50 for 60 min when the dye bath temperature is kept constant at 60°C. The treated cotton fiber is washed with 1% aqueous acetic acid solution and rinsed with water for several times, and the drying temperature was

maintained at 60°C. Two steps are followed for the fabric treatment with chitosan to compare the dyeing and mechanical properties of the treated fabrics. The underlying mechanism of the process is to create aldehyde groups in the molecular structure of chitosan at C1 through the action of NaIO₄. In addition, C3 and C4 positions hold secondary hydroxyl groups; position C6 contains primary hydroxyl and C2 holds the amino groups. Moreover, the chain scission occurs at C3, C6, C2 positions and 1–4 glycosidic linkage under the attack of oxidizer [57]. The IR analysis confirms the presence of aldehyde and carboxyl groups in the molecular structure of treated cotton, which interacts with chitosan strongly. There is a possibility to degrade the fabrics due to oxidizing, but the presence of chitosan may reduce this drawback. The presence of chitosan also protects the fabric from degradation against the attack of the oxidizer and maintains similar mechanical properties (i.e., tensile strength, elongation at break) to the untreated bleached fabric [56]. In addition, highly soluble, uniform structure, low viscous, and better film-forming chitosan is achieved from the fragmented chitosan [58].

In the second step, the dyeing process is conducted using the dried cotton fabric in 1% reactive dyes while 5% sodium chloride in a liquor ratio of 1:50 at room temperature. The temperature of the dye bath is increased at 60°C and left it to be stable for 45 min. After the process, the fabric is rinsed with water for several times and treated with 1% wetting agent using a liquor ratio of 1:50 for half an hour at 60°C. Several washes are required using hot and normal water after the treatment and dried at room temperature. The enhanced color yield (K/S) is observed compared to the untreated fabric due to the Coulombic attractions between positively charged cotton surface modified by chitosan and anionic dye molecules (reactive and acid).

4.3. Chitosan: a binder in printing process

Fabric printing process requires a dye or a pigment, a binder and thickener. The main function of binder is to maintain a stable viscosity, enhances the droplet formation, provides adequate adhesion to the textile surface by forming a film, and binds the color or pigment molecules. In the industrial application, most of the binders are synthesized from styrene-butadiene, or vinyl acetate-acrylate copolymers or styrene-acrylate. Very few researchers have conducted experiments on using chitosan as binder and thickener due the weak performance compared to commercial binders. In the first step of preparation, 3% (w/w) chitosan solution is prepared using preferred amount of water and acetic acid. The pigment is added to the solution and stirred to achieve a 3% homogeneous pigment paste for printing. In the case of poor dispersion of pigments, the amount of acetic acid is increased. Additionally, a very high amount of chitosan (≥3%) in acetic acid generates very highly viscose solution. The achieved properties of the process exhibit lower efficiency and effectiveness of chitosan as a binder compared to the commercial Alcoprint pastes (BASF). The tendency of yellowing is higher after the treatment with increased amount of chitosan and the increase of the curing temperature. Moreover, same process parameters in different batches show variation in yellowing propensity. Furthermore, a share thinning property is exhibited by chitosan solution when the viscosity is measured. Besides, the viscosity is lower than commercial Alcoprint pastes (BASF) when the share rate is less than 50 per s. In contrast, almost similar viscosity profile is found at higher share rate, but yield point is lower than the commercial paste. It indicates that the

required force or stress of the chitosan to start flowing is very low. Besides, the wet pick-up ratio of chitosan solution is 75%, while the commercial paste shows 85%. It results in 50% less color strength using chitosan solution after the determination of K/S values. It probably attributes to the aggregation of colorant in the chitosan solution where the dispersion is tough to maintain. In addition, the bending length and stiffness are higher for chitosan-used printed fabric compared to Alcoprint pastes, the commercial one. Eventually, the wash fastness and spreading behavior are not significantly different between chitosan and commercial tested binders [59].

4.4. Chitosan: a finishing agent for durable press for textile

The cotton fabric is hydrophilic due to a high amount of hydroxyl groups. Therefore, the cotton cellulose becomes flexible and exhibits lower crystallinity when it is swelled. A plastic deformation occurs due to the shifting of cellulose molecules during washing treatment. It results in shrinkage and wrinkles of fabric. For overcoming the problem, the crosslinking agent is used to increase the elasticity and prevent the displacement of cellulose which reverses the plastic deformation. Chitosan exhibits similar molecular structure to cellulose and would be applied to cotton finish. During this process, chitosan is fragmented by oxidizing agent such as hydrogen peroxide (H_2O_2). The fragmentation process is carried out using a mixture of hydrochloric acid and chitosan. After 30 min of stirring, hydrogen peroxide is added with an increased temperature of 60°C for 2 h. A vacuum filter is used for the separation of two phases. The residue is washed with water to neutralize, and the filtrate is mixed with ethanol to precipitate the chitosan for 24 h. All precipitates are dried and stored in airtight container. The main application of the fragmented chitosan is to develop durable press finishing process on fabric. In this process, the fragmented chitosan is added to distilled water and stirred until it dissolves completely. The finishing agent contains 8–10% (w/w) dimethyloldihydroxyl ethylene urea (DMDHEU), 0.8% MgCl_2 , required amount of softener, and the fragmented chitosan solution. The fabric is then immersed in the finishing solution maintaining a pick-up ratio of 80%. The treated fabric is preheated at 80°C for 5 min and then cured at 150°C for 3 min [60].

The fragmentation of chitosan chain facilitates its diffusion into the fabric to form a network with fibers that results in increased recovery angle. The curing time and temperature have a significant effect on the result of final wrinkle property of fabric.

4.5. Chitosan: an antistatic finishing agent on textile

Static surface charge is developed on polymers due to very less amount of moisture content. Moreover, the electrical conductivity is also an important factor on developing static charge along the synthetic filament through a mechanism induced by an electric field. Therefore, antistatic chemical compounds influence the propensity of accumulating static charges by aborting the production of electrostatic charges or by enhancing the electrical conductivity or by both mechanisms. Chitosan can hold in high moisture content regardless the extent of humidity that opens the opportunity to apply chitosan as an antistatic finishing agent on textile surface. In general, the polymers show the resistance of specific electrical resistance in the order

of $10^{16} \Omega \text{ cm}$ that is very close to the value of a good insulator. On the other hand, deionized water exhibits a magnitude that is 10^8 times lower than that of polymers but mineral water shows 10^3 times higher electrical conductivity compared to pure water. Therefore, chitosan-treated fabrics enable to absorb a very significant amount of water from the atmosphere after exposure to the humid environment and result in the increase in electrical conductivity following the lower propensity to produce static charges. Chitosan having excellent moisture content property is an excellent antistatic agent [61]. Antistatic fabric is developed by fixing the chitosan on the fabric. In the fixing process, butane-1,2,3,4-tetracarboxylic acid (BTCA) is used in the presence of the catalyst, sodium hypophosphite (SHP). Chitosan (1% w/v) dissolution in acetic acid (1%) is the first step of the process. Liquor is produced by the addition of 6 g BTAC and 6 g SHP in the chitosan solution. A sample of fabric is then immersed into the liquor and padded to maintain wet pick-up ratio 100%. The treated fabric is required to dry at 80°C for 5 min, and the curing process is done at $140\text{--}170^\circ\text{C}$ for 5–20 min according to the final finish of the fabric. At the end of the process, the temperature of the fabric decreases at room temperature and it is washed with acetic acid for removing extra chitosan. It is then washed again with deionized water and dried by air. The qualitative and quantitative analyses are done by potentiometer and compared with the untreated fabric. Another study has been carried out for the antistatic fictionalization of PET film and fabric by applying oligochitosan. The processes are almost similar except the drying and curing temperature and time. In the later process, drying temperature is maintained at 70°C for 1 h and the curing process is done at 110°C for 30 min [62]. A new *N*-substituted quaternary ammonium chitosan derivative facilitates for the utilization of antistatic functional textile. The chitosan derivative is synthesized through the *N*-alkylation of 4-formyl-*N*-methylpyridinium iodide and [3-(4-formylphenoxy)propyl]trimethylammonium iodide [63].

4.6. Chitosan: an antimicrobial agent for textile

Innovative ideas are in practice to develop a new form of chitosan for improving the efficacy of conventional chitosan applications in textile. Chitosan-treated fabrics and fibers are used for the production of antibacterial fabrics for working environment such as a hospital, biotechnology research lab, cosmetics, fundamental industries, and so on. The charged amino group of chitosan interacts with the cell wall of microbes that causes degradation of protein and intracellular constituents. It also affects the permeability of essential nutrients by altering the cell membrane and causes their death finally [64]. For example, chitosan exhibits direct interaction with the cell wall of *Aspergillus niger*. As a result, a controlled fungal growth and delays in the spore germination occur.

Despite having the potential as antibacterial property, it requires, at a high concentration, for desired efficacy without having any release property in bandage, sutures, etc. The innovation in synthesis, production, and application leads to form nanosized chitosan that could be beneficial for the presence of high amount of active sites available due to the large amount of surface area. In general, a single antibacterial agent has some limitations to perform against both gram positive and gram negative including a broad range of microbes. Therefore, the combination of chitosan and other antibacterial components such as silver has gained more

and more attention to fight against large varieties of the microbe by focusing on easier the synthesis and highly efficient in the application [65]. For example, chitosan and silver particles both are used for the synthesis of chitosan-silver nanoparticles which provide excellent antibacterial property on textile application. The application of chitosan and its derivatives on fabric/fiber is followed by the covalent crosslinking into cellulose or wool substrates. The durable press finishing is one of the conventional processes to fix chemicals on fiber surface that also enhances the quality of textiles such as low-shrinkage capacities, anti-odor, wrinkle resistance, and antibacterial properties. For this purpose, a suitable crosslinking agent is required. It should be nontoxic and nonirritating during the use and storage; nevertheless, formaldehyde is one of the mostly used compounds and presents the limitation in those aspects due to its spontaneous toxic vaporization [64]. There are some other crosslinkers such as glutaric dialdehyde, butane tetracarboxylic acid, citric acid (CA), potassium permanganate, and sodium hypophosphite that form the covalent bond between chitosan and the cellulose fabrics by an ester bond.

A high intensity of UV lamp at a wavelength of 254 nm is applied to the raw fibers and exposed for 4 h before the crosslinking treatment. The content of chitosan is 40% less in the final treated fiber compared to the raw fibers without UV irradiation before the treatment with chitosan. It usually changes the surface polarity of fibers via photooxidation and forms active carboxylic groups by photodestruction of glycosidic bonds and rings. The fixation of chitosan with UV-irradiated cellulose fiber is more stable than the raw fibers according to the thermogravimetric analysis. In this process, a fixed amount of chitosan and NaH_2PO_4 is mixed in distilled water. Then, citric acid (CA) is added to the aqueous solution as an acidifier and crosslinking agent. The process could be carried out excluding NaH_2PO_4 based on the requirement of mechanical properties. The raw cellulose fibers are dipped in the solution and raised the temperature at 70°C in the pH range from 3.8 to 4.1. The pH is not recommended over 4.5 to perform the crosslinking reaction and avoids fibers deterioration. The treatment continues for 5 min, and fibers are removed for curing at 130°C up to 3 min. After the curing process, the samples are dried at room temperature under vacuum, before rinsing with distilled water and washing with acetic acid to remove the excess unreacted chitosan. The treated samples are rinsed again with distilled water and dried at room temperature under vacuum until to reach a stable mass.

The mechanism involved in the process follows two steps. In the first step, the crosslinking reaction between cellulose and polycarboxylic acid/CA takes place by the formation of carboxylic anhydride. In the second step, the rings open to react with the polysaccharide through the alcohol groups and form the ester bond. The use of maximum 2.3 w/w% NaH_2PO_4 accelerates the fixation through esterification due to the presence of the phosphate and the partial sodium salt of the polycarboxylic acid. The increased amount of NaH_2PO_4 affects the chitosan loading with fibers due to the neutralization of free carboxylic groups and inhibits esterification of the hydroxyl moieties present in chitosan. The unreacted amino moieties act as active antibacterial property.

Sustainability requires a process safer in terms of raw materials and finished products excluding any toxic by-product. In this aspect, reference [64] proposes UV radiation for

generation of reactive sites on chitosan that can fix many compounds through crosslinking without using any toxic chemical compounds.

Moreover, the antibacterial colloid is prepared by blending chitosan and AgCl–TiO₂ at a ratio of 1:5. A cotton fabric is dipped, and a padder is used to nip the treated fabric as though 70% pick-up ratio is achieved. The predrying temperature is maintained at 120°C and run for 2 min. Subsequently, a curing process is done at 150°C for 3 min. The tensile strength and bending length of chitosan-treated cotton fabric enhanced with the increasing of chitosan concentration. It affects the stiffness of the treated fabric by increasing the value. Moreover, chitosan-treated cotton fibers exhibit lower whiteness index (WI) with the increase in chitosan concentration from 1 to 5 g/L. The degree of WI is found six times lower than that the concentration of 5 g/L [66]. Modified chitosan is also used for the hydrophobic drug delivery [67].

4.7. Chitosan: a flame and fire retardant material for textile

Flame retardant textiles are highly recommended, especially where the working environment is highly concerned regarding fire or flame. The flame retardant property is considered when the flame is not permitted to propagate and extinguished at the same time of withdrawing the fire source. Phosphorus-based materials are interesting and well known as flame retardant due to low toxicity and absence of halogen compounds. These materials are quite efficient as a flame retardant for cellulose and its derivatives through dehydration and char production. In phosphorylation process, cellulose is treated with diammonium phosphate in the presence of urea.

Chitosan could be paired with phosphorous derivative to build an intumescent flame retardant compound. Chitosan is a nitrogen-containing polysaccharide, biodegradable, biocompatible, and environmentally nontoxic. It provides a char-forming property when it is used as intumescent additives due to its hydroxyl and amino groups on molecular skeleton. In addition, it functions as blowing agent and releases nitrogen as a result of molecular destruction. Therefore, a potential nitrogen-phosphorous bonding could be established as flame retardant materials. Chitosan-based flame retardant materials have been designed by chitosan-phytic acid [68], chitosan-sodium polyphosphate [69], chitosan phosphate (chitosan-orthophosphoric acid) [70], chitosan phosphate-nickel [71], chitosan melamine phosphate (chitosan-melamine-sodium hexametaphosphate) [72], chitosan-diammonium hydrogen phosphate [73], etc. It is expected that the presence of ammonium nitrogen in chitosan would provide the synergistic effect with phosphate groups against flame or fire [74]. The preparation of chitosan phosphate has been conducted using many processes. For example, 23 g chitosan has been added to a solution that contains urea (40 g), phosphoric acid (40 ml), and dimethylformamide (350 ml) at 100°C for 5 h. At the end of the process, the product is filtered and washed with isopropyl alcohol (50%) and dried at 60°C. In this process, a commercial resin, knittex FLC, has been provided by Ciba-Geigy (Switzerland). The resin allows the capturing of phosphate by crosslinking and by forming a network to fix the chitosan with cellulose. In addition, the increased amount of resin concentration (2–8%) leads to a reduction in tensile strength (140–114 kg) and elongation at break (21–15%). In contrast, the tensile strength and elongation at break increase for using a higher concentration of chitosan phosphate. It also guides to increase

the amount of phosphate (0.095–0.314%) content in the coated fabric and shows higher residue contents by releasing very less volatile components compared to untreated fabric. A compensation effect works between the concentration of chitosan phosphate and resin. The cotton surface treated with 8% chitosan phosphate and 6% resin shows 36.557% residue, while the decomposition temperature is reduced by 25°C compared to the untreated fabric [70].

Furthermore, apart from a reaction mixture, layer-by-layer (LBL) deposition processes are also examined for developing a nanolayer formation [68] on substrate or fabric. In this process, the solution of chitosan is prepared using HCl and phytic acid salt (2 wt.%) in deionized water. The branched polyethyleneimine (1 wt.%) is used to increase the adhesion of cotton fabric as a primary layer. The fabric is dried and dipped sequentially in positively and negatively charged solutions. The process continues up to desired level of the bilayer to achieve effective layers for flame retardancy. After the dipping process, it is wrung to release excess solution and dried at 70°C for 2 h. The thinnest coating which is approximately 10 nm thick has been achieved at pH 4. The thickness contains 30 bilayers on the cotton fabric surface where one bilayer consists of one positive and negatively charged layers. More than 90% residues were left, while the flame propagation is completely stopped during the vertical burn test. In addition to chitosan phosphate, Shuang and his coworkers have focused on the metal ion binding ability of chitosan phosphate that results in a synergistic effect and enhanced flame retardant property by adding nickel ions [71]. The process involves 2 g chitosan and 30 ml methanesulfonic acid in magnetic stirrer putting on an ice bath in inert atmosphere to avoid moisture, by adding phosphorus pentoxide (10 g). The chitosan phosphate is achieved from the reaction and washed with acetone, methanol, and ether. The drying process is realized at 60°C using vacuum. Nickel (II) nitrate hexahydrate and the dried chitosan phosphate react in the ratio of 10:1 with each other at 60°C for 1 h in the presence of ethanol. The final product is washed with fresh ethanol to remove extra nickel (II) nitrate hexahydrate and dried at 60°C in a vacuum dryer. It is then blended with polyvinyl alcohol (PVA) that provides film or fibers or nanofibers [75] to synthesize flame- and chemical-resistant materials. The heat release rate of nickel chitosan phosphate (NiPCS) blended PVA decreases substantially compared to the raw PVA. The microscale combustion calorimeter test has exhibited the peak of heat release for PVA at 155 W/g, while NiPCS blended PVA having a peak at 40 W/g [71]. Besides, the total heat release rate is decreased by NiPCS from 18.2 to 10.4 kJ/g, which underlines the main action of NiPCS. Moreover, the increased amount of NiPCS enhances the char formation that resists the transfer of oxygen and heat. This process leads to delay the thermal decomposition of materials due to the improvement in thermal stability at high temperature.

4.8. Chitosan: a hydrophobic material for water repellent textile

Superhydrophobicity is observed in duck feather, wings of butterflies, the legs of water striders, etc. The specific energy of surface is a quantitative value to comprehend the understanding of how water droplets interact with a surface. It is highly relevant to the contact angle and roughness factors [76]. Nanoscale chitosan coating may be applied on the surface of cotton and polyester fibers to achieve rough surface. These rough surfaces are further treated with silicon [77] and fluoride [78] to reduce the surface energy. The fabrics are dipped for 1 min in

a chitosan solution in 1% acetic acid before being squeezed. The wet fabric is neutralized by ammonia gas for 1 min and dried 80°C for 5 min [79]. The dipping-padding process with chitosan allows forming a thin film on the fabric surface. Later on, ammonia treatment changes the pH of the wet fabric, and insoluble-nanoscaled chitosan is precipitated on the fabric surface. The SEM study confirms that nanofiber-like shapes are deposited on the fiber surface, resulting in rough surface on microscale cotton fiber structure. Also, nanoflower-like precipitation is found for the same treatment with polyester fabrics. The deposition of chitosan nanosized particles forms proper roughness on cotton and polyester fibers. Besides, an emulsion of polysiloxane may be used for reducing the surface energy of the chitosan-treated fabric. The emulsion is prepared by hexadecyltrimethoxysilane (HDTMS, 85%), 3-glycidol-propyl-trimethoxysilane (GPTMS, 97%), and sodium dodecyl sulfate (SDS). A mixture of 8 g HDTMS, 2 g GPTMS, and 1 g SDS is stirred at 75°C for 2 h maintaining pH about 2 using HCl. The operation temperature is reduced to room temperature, and the pH is maintained at 8.0 by ammonia. After the dipping, padding, washing, and drying, the curing process is done at 150°C for 1 min. Further washing is necessary if excess SDS is present on the fabric surface and need to cure again following the same process. In characterization, water contact angles (WCA) are found 152° and 148° for cotton and polyester, respectively. The cotton and polyester fabrics having WCA at 130° and 102°, respectively, after processing only with chitosan do not exhibit long duration hydrophobicity.

Another process based on fluorocarbon to reduce the surface energy has been developed for the preparation of superhydrophobic textile. In this process, anionic heptadecafluoro-1-octanesulfonate has been synthesized from a surfactant, $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{Li}$. Chitosan nanoparticles are formed using 0.2% chitosan solution and mixed with soluble heptadecafluoro-1-octanesulfonate in acetic acid. The dispersion is stirred for 1 h and left it for 2 h before characterization. The size and surface charge of the chitosan NPs are controlled by the ratio of chitosan and $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{Li}$ concentrations. For the treatment of fabric, the nanoparticles dispersion sprayed over the textile surface. The contact angle of the treated fabric is $157^\circ \pm 2.2^\circ$. It has been noticed that long-term water contact would degrade the particles due to the presence of hydroxyl groups in the chitosan complex. The hydroxyl groups are blocked by treating the fabric with chlorodimethyl-1H,1H,2H,2H-perfluorodecylsilane (90%) in 1% heptane solution. The contact angle has been improved after this treatment and found at $160^\circ \pm 2^\circ$ [78].

4.9. Chitosan: a coating on textile for UV blocking

A coating of chitosan-graphene is designed for the process of developing a cotton fabric as UV blocker. A graphene nanosheet (1–3 nm) is added to chitosan solution by stirring vigorously around 5 h. A cotton fabric is submerged in the dispersion of chitosan-graphene for 2 h. In padding process, the fabric passes through two dips and two nips for achieving 80% wet pick up on average. The washing and drying treatments are maintained separately. The predrying process is continued at 70°C for 10 min and curing process at 110°C for 10 min. The ultraviolet protection factor (UPF) of the treated fabric using 1% graphene is 60 times greater than that of

untreated cotton. The well-dispersed graphene particle in the chitosan matrix without any aggregation is considered for the high value of UPF [80].

5. Chitosan microcapsules for textile applications

The microencapsulation technique is widely used in pharmaceutical, cosmetic, food, biotechnology, textile industries to obtain control release of active components for a particular purpose. In general, the microencapsulation process is applied to fabrics for improving durability, desirable aroma, hygienic use, fire resistance, wound healing activity, and so on. A tiny amount of active components is surrounded by a continuous polymeric phase in the microencapsulation process. The active component is introduced in different terms such as core, internal phase, encapsulated, while the continuous polymeric phase is described as coating, wall, shell, external phase, and membrane. The continuous polymeric phase is one of the vital issues for application-based microencapsulation process. Chitosan is very efficient to encapsulate the core materials in microencapsulation process. The core materials are usually found in two different phases—solid and liquid—and chosen for specific application. The grapefruit seed oil, a liquid core material, is used to attain durable fragrance and antibacterial properties by microencapsulation process in the textile application [81]. Chitosan is one of the shell materials which are used for microencapsulation due to nontoxic, biodegradable, and naturally extracted. Depending on the process, different types of solvents, crosslinking agents, and surfactants could be used to modify the mechanical strength of chitosan shell for releasing active core materials.

5.1. Microencapsulation processes

There are many different microencapsulation techniques such as coacervation [82], interfacial polymerization or *in situ* polymerization, air suspension coating, emulsion hardening process, pan coating, spray drying [83, 84], centrifugal extraction [85], etc. (**Figure 7**).

The simple coacervation technique is usually followed by single colloidal solute while complex coacervation process involving more than one colloidal solute. The coacervation is one of the mostly used techniques for the development of smart textile and will be discussed. Coacervation can be defined as the separation of a macromolecular solution into two immiscible liquid phases: a dense coacervate phase and a dilute equilibrium phase. The general outline of this method consists in four consecutive steps carried out under stirring, i.e., (i) dispersion of the active substance in a solution of a surface-active hydrocolloid; (ii) precipitation of the hydrocolloid onto the dispersed droplets by lowering the solubility of the hydrocolloid (nonsolvent, pH change, temperature, or electrolyte); (iii) addition of a second hydrocolloid to induce the polymer-polymer complex in the case of complex coacervation; and (iv) stabilization and hardening of the microcapsules by crosslinking agent. Chitosan is used as shell material that is sensitive to the pH and ionic strength of the solution. The pKa value of chitosan is 6.5 and becomes insoluble above this pH since more than 50% chitosan molecules are deprotonated. The complex coacervation technique requires anionic materials that are used for the ionic

interaction with protonated chitosan such as vanillin [83], carrageenan [82], alginate [86], gelatine [87, 88], gum Arabic [89], etc. Besides, the addition of crosslinking agent improves the mechanical property of chitosan microcapsules such as sodium tripolyphosphate [90–92], sodium hydroxide [93, 94], genipin [87, 88, 95] glutaraldehyde [96], tannic acid [97], etc. In the processing of microcapsule with chitosan, a soluble chitosan is prepared in solvent such as acetic acid [89], citric acid [83], etc. In an acid medium, chitosan is protonated and bears a positively charged group below pH 6.0. Besides, O/W emulsion is prepared separately using an anionic material which can interact with chitosan. The anionic material stabilizes the emulsion and resists the droplets from aggregation. A homogenizer of high-speed rpm provides the desired droplet size. After that, the chitosan solution is added into the emulsion and using around 800–1000 rpm neutralization of charge and formation of coacervate are achieved in the chitosan solution. The coacervation process can produce fine particles after the charge neutralization and deposition on the surface of emulsion droplets. A crosslinking agent is used to form a strong network by binding the deposited chitosan complex and form a shell around the droplets. The pH, temperature, and concentration ratio vary according to specific system. For example, a chitosan-gum arabic coacervation process requires pH 3.6 for the high yield of coacervation and homogenization speed at 11,000 rpm for less than 10 μm average capsule size [89].

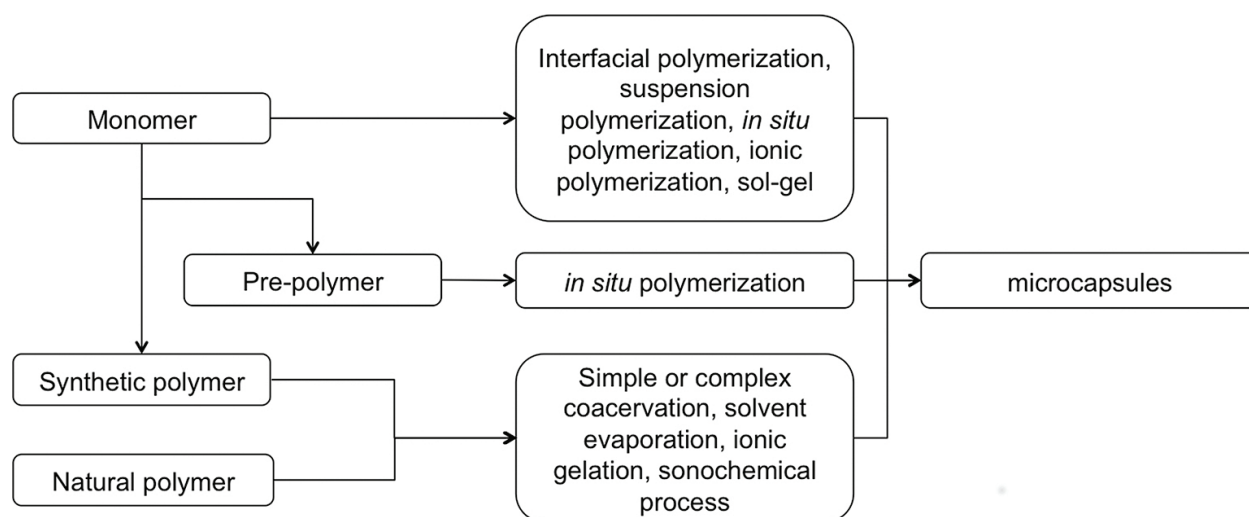


Figure 7. Different textile applications and techniques of chitosan-based microcapsules.

5.2. Textile processing with chitosan-based microcapsules

Citronella essential oil, a mosquito repellent agent, is extracted from *Cymbopogon nardus*, a crop which is mostly found in Argentina. The natural repellent is usually volatile which limits the direct applications on the textile surface. Hence, chitosan-encapsulated citronella essential oil is applied on textile for the fabrication of mosquito repellent textile [93]. Moreover, linseed oil [98], phase change materials [99], and lemon essential oil (*Citrus limon* L.) [94] are also encapsulated by using chitosan for the formation of shell material in textile applications (Table 3).

Apart from the microcapsule formulation, textile processing with the microcapsules is also important for achieving the real benefit of smart textiles. The mosquito repellent textile would be a proper example to review the textile processing with the chitosan-based microcapsules below.

Fei and Xin [100] have developed a DEET-containing textile made of cotton for the application of mosquito repellent and antibacterial activity. Chitosan and polyacrylate copolymers have been involved in the process for encapsulating the DEET *in situ*. Chitosan solution (0.5% w/v) is prepared using 0.6% (w/v) acetic acid in a flask which is equipped with a condenser, magnetic stirrer, and nitrogen flow facility. Butyl acrylate (BA) and *N,N*-diethyl-*m*-toluamide (DEET) are added to the chitosan solution, and the temperature is maintained at 80°C for 10 min with stirring. In general, DEET is easily dissolved in poly butyl acrylate, and the dissolution is uniformly homogeneous. Tert-butyl hydroperoxide is added to the mixture at 80°C for 4 h. A white emulsion will be achieved, and the emulsion is sprayed on a 4-mm cotton fabric. The fabric sample should be bleached before the treatment, and maximum 10 mg/cm² emulsion is maintained. Chinese standard GB/T 17322.10-1998, a standard test, is followed to check the mosquito repellency at 25°C and 65% humidity compared to untreated fabric sample. The percentage of mosquito repellency is determined based on the difference between control and treated fabric. For example, ED₉₀ indicates 90% effective dose. In this process, 4% DEET is enough to achieve the ED₉₀ value, while the content is 1.5 mg/cm² for 4 h protection. Apart from the formulation, *Vitex negundo* leaf extract is also used as a mosquito repellent and is encapsulated using chitosan as shell materials [101]. Sodium alginate (95 ml, 0.6% w/v) and 18 mM calcium chloride are added to the leaf extract. Chitosan is added to this solution by stirring for 30 min and left overnight at room temperature. It is then centrifuged at 1500 rpm for 15 min. The coacervate phase will be separated out, washed, and stored at 5°C for further analysis.

Application	Microencapsulation technique
Limonene oil microencapsulated textile for antibacterial activity	Coacervation process by NaOH dripping technique
Cosmato textile-chitosan/vanillin microcapsules	Spray drying technique
Microcapsulation of citronella oil	Coacervation process by NaOH dripping technique
Microcapsulation of linseed oil	Multilayer coacervation method
Phase change material encapsulation	Chitosan as binder

Table 3. Different techniques and applications of chitosan-based microencapsulation processes for textile.

The release rate of the core materials through the chitosan shell depends on the temperature, humidity, and time. On top of that, the release property of active component depends on chitosan concentration and temperature [93]. For example, the release of citronella oil is 20–25% when the operational temperature is maintained at 40–60°C. Besides, chitosan wall membrane concentration 0.2–0.5% is considered as a good microcapsule for a better release property. The release property is entirely inhibited when the operational temperature is 80°C. The mechanism underlying the release behavior is the contraction of chitosan membrane due

to increase in temperature. As a result, the pore size reduced and the release of core materials stopped [93]. On the other hand, the chitosan-core material interaction also affects the release property. In this regard, the concentration of chitosan and crosslinking agent should be optimized properly.

6. Conclusion and future perspectives

Chitosan is biodegradable in human health, plant, and environment organisms. Concerning economic aspect, it is a by-product of fishing industry. Textile is one of the most usable consumer products in our daily life although the processes are mostly hazardous. The whole supply chain of textiles still requires more research on how to establish the sustainability regarding health safety and cost. The use of chitosan could open the door for developing a sustainable industrial practice in fiber production and fabric treatments for its nontoxic property and low cost. Moreover, the blended and modified chitosans that extend the availability of various high-end functional textiles with reasonable price will enhance the research and development on chitosan-based textile processing.

Author details

Jagadish Roy^{1,2}, Fabien Salaün^{1,2*}, Stéphane Giraud^{1,2}, Ada Ferri³ and Jinping Guan⁴

*Address all correspondence to: fabien.salaun@ensait.fr

1 University Lille Nord de France, Lille, France

2 ENSAIT, GEMTEX, Roubaix, France

3 Department of Materials Science and Chemical Engineering, Polytechnic University of Turin, Turin, Italy

4 College of textile and Clothing Engineering, Soochow University, Suzhou, Jiangsu, China

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