Use of Chitosan in Surface Modification of Textile Materials

DANIELA ENESCU
Department of Natural and Synthetic Polymers, "Gh. Asachi" Technical University, 700050 Iasi,
"Petru Poni" Institute of Macromolecular Chemistry, 700487 Iasi, Romania

Abstract

Textiles have long undergone surface modification to improve their softness, dyeability, absorbance, and wettability. Recent advances in textile chemistry have also approached textile surface modification to impart antimicrobial activity, decreased skin irritation, and even enhancing fragrance.

Chitosan is an effective natural antimicrobial agent derived from Chitin, a major component in crustacean shells. Chitosan applied to textiles has been widely studied for effects such as shrink resistance, improved dye uptake, and as auxiliary or anti-static agents, etc., because of the low toxicity and good biocompatibility of this natural polymer. Coatings of Chitosan on conventional fibres appear to be the more realistic prospect since, they do not provoke an immunological response. In this article, I summarize some of the most recent development in surface modification of textile using chitosan.

Keywords: chitosan, textile, surface modification.

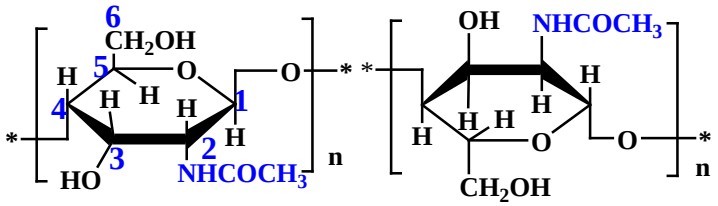
Introduction

Textile goods, especially those made from natural fibers, provide an excellent environment for microorganisms to grow, because of their large surface area and ability to retain moisture. A number of chemicals have been employed to impart antimicrobial activity to textile goods. Those chemicals include inorganic salts, organometallics, iodophors (substances that slowly release iodine), phenols and thiophenols, antibiotics, heterocyclics with anionic groups, nitro compounds, ureas, formaldehyde derivatives, and amines [1]. Many of these chemicals, however, are toxic to humans and do not easily degrade in the environment. The textile industry continues to look for eco-friendly processes that substitute for toxic textile chemicals. From this point of view, chitosan is an excellent candidate for an eco-friendly textile chemical.

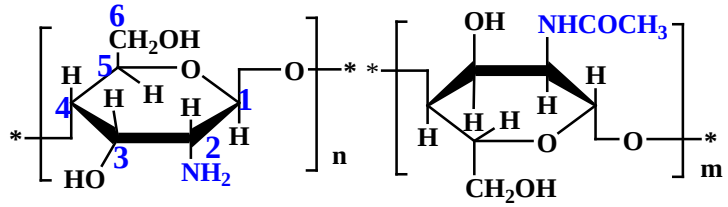
Nowadays, the surface modification of textile fibres is considered as the best route to obtain modern textile treatments [2]. It enables the required level of beneficial effect by the modification of fiber surface only, thus minimizing whole fiber attack, and hence the deterioration in fiber quality could be easily avoided. As one of the most promising treatments, it was suggest by the Jocic & al. [3], the hydrogen peroxide or low-temperature plasma (LTP) pre-treatment combined with biopolymer posttreatment [3]. Among various available biopolymers, the polysaccharide chitosan (CS) is highly recommendable, since it shows unique chemical and biological properties and its solubility in acidic solutions makes it easily available for industrial purposes.

Chitosan is an abundant biopolymer, consisting of poly [β-(1-4)-2-amio-2-deoxy-D-glucopyranose] - which is obtained after alkaline deacetylation of the chitin which is found in the

exoskeletons of crustaceans, arthropods and mollusks, as well as the cell walls of certain fungi (Figure 1) [4, 5]. Its production in nature has been estimated to be ca. 10^9-10^{10} ton/year [6].



CHITIN



CHITOSAN

Figure 1. Chemical structures of chitin and chitosan

1. Preparation of chitosan

Chitosan is commonly prepared by deacetylating chitin using 40-50 % aqueous alkali at 100-160^{o}C for a few hours as described in Figure 2 [7]. The resulting chitosan has a degree of deacetylation (DD) up to 0.95. For complete deacetylation if needed, the alkaline treatment can be repeated but it is rarely achieved. The solubility in dilute aqueous acids is obtained at an extent of deacetylation of = 60 %.

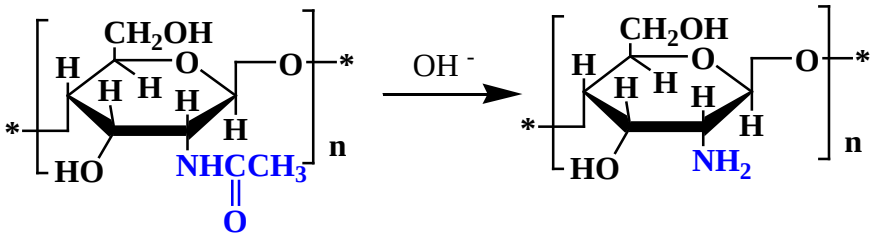


Figure 2. Preparation of chitosan

2. Characterization of chitosan

Chitosan has two important structural parameters, which are degree of deacetylation (DD) and molecular weight (MW). Its performance in physics and chemistry is determined by the influence of these two parameters on such things as solubility, enrichment ions, the mechanics of the chitosan membrane, flocculation, etc. In acidic solvents, the NH_2 group in chitosan becomes a quaternary amino group and allows the chitosan to inhibit the growth of many bacteria, including gram-negative and gram-positive ones.

2.1. Degree of N-deacetylation

An important parameter to examine closely is the degree of N-acetylation in chitin, i.e. the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units. This ratio has a striking effect on solubility and solution properties. Chitin does not dissolve in dilute acetic acid, but if it is deacetylated to a certain degree, (approximately 60 % deacetylation) it becomes soluble in acid and it is referred as chitosan.

In chitin, the acetylated units prevail (degree of acetylation typically 0.9). Chitosan is the fully or partially N- deacetylated derivate of chitin with a typical degree of acetylation less than 0.4. To define this ratio, a number of methods have been used such as FTIR spectroscopy [8], UV spectroscopy [9], ^{1}H-NMR spectroscopy [10], ^{13}C solid state NMR spectroscopy [11], gel permeation chromatography [9], titration methods [12], equilibrium dye adsorption [13], elemental analysis [14], acid degradation followed by HPLC [14] and thermal analysis [15].

2.2. Molecular weight (MW)

Molecular weight (MW) is a very important parameter for the application of natural and synthetic polymers. The MW of chitin and chitosan depend on its source and deacetylation conditions (time, temperature and concentration of NaOH), respectively. Chitosan obtained from deacetylation of chitin may have a MW over 100 kD, consequently, it is necessary to reduce the MW by chemical methods to a much lower MW for easy application as a textile finish. The MW of chitosan can be determined by several methods, such as light scattering spectrophotometry [16], gel permeation chromatography and viscometry [17].

3. Surface characterization

The type of analytical tools used in characterizing surface modified polymers depends on the anticipated nature of the modification, the specificity required and the resources available. Not only the quantity and activity of the attached bioactive compound must be measured, but also the surface chemistry must be verified after each step in the modification in order to validate the proposed mechanism by which the bioactive compound was covalently attached.

3.1. Non-spectral methods

The spectroscopic and microscopic methods discussed in *Section 3.2* are precise and accurately describe changes in surface chemistry, but equipment is costly and analyses can be time consuming, because surface functional groups become unstable due to highly reactive which bring to a significant loss of surface reactivity between the time of functionalization and the time of analysis [18-21]. The rapid and simple surface analytical techniques outlined below can be useful during laboratory development prior to spectral confirmation.

3.1.1. Water contact angle

Water contact angle measures surface hydrophilicity by measuring how much a droplet of water spreads on a surface. As shown in Figure 3, the lower the contact angle, the more hydrophilic the surface is. As a surface becomes more oxidized, or has more ionizable groups introduced to it, hydrogen bonding with the water becomes more facile and the droplet spreads along the hydrophilic surface, resulting in a lower contact angle. Advancing contact angle is measured by delivering a droplet of water to the surface and recording the height and the width. Receding contact angle is measured by removing water just prior to a change in droplet width and recording the resultant height.

Contact angle values can then be calculated from Eq. (1) [22,23]:

$$\tan(\theta_s/2) = h/x \qquad (1)$$

in which θs is the static contact angle, h is the droplet height, and x is half of the droplet width.

Contact angle hysteresis can be calculated from Eq. (2):

$$CAH = \theta_a - \theta_r \qquad (2)$$

in which θa is the advancing contact angle, θ_r is the receding contact angle, and CAH is the contact angle hysteresis [24].

By taking contact angle with a range of buffered aqueous solutions varying in pH value, it can be identified the surface pKa, which can be used to identify if a surface contains acidic or basic functionalities [25]. Knowing surface pKa not only helps identify the nature of the surface functional groups, but it aids in determining the proper pH for a conjugation buffer in order to optimize covalent bonding. While contact angle is a simple and rapid measure of the change of a surface's hydrophilicity, it is limited by its inability to distinguish between different hydrophilic functional groups and by the many ways error can be introduced into the measurement, including the following: difference in operator measurement, inconsistent water pH and hardness, and changes in environmental temperature and humidity.

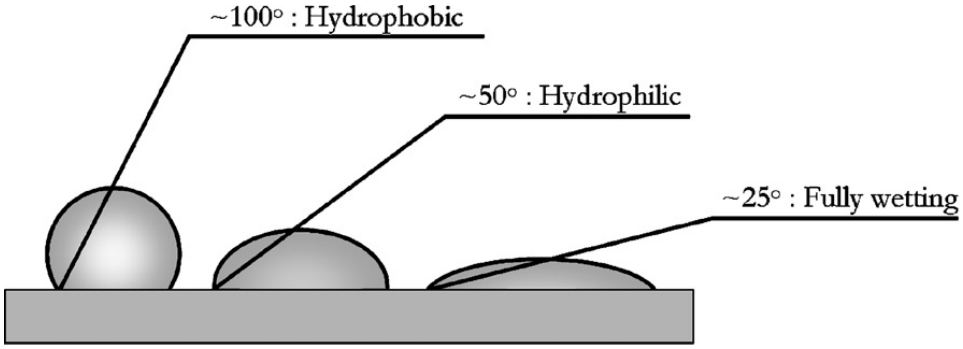


Figure 3. Schematic of contact angle

3.1.2. Zeta potential

The functional groups present on a modified polymer surface can introduce a high surface charge density that is typically not present on untreated polymer surfaces. When such a charged solid surface is in contact with a liquid phase, an electrical potential develops at the interface. A double layer is established, with surface bound ionizable groups and tightly bound liquid phase ions of opposite charge forming the fixed layer, and loosely bound liquid phase ions of opposite charge forming the mobile layer (Figure 4). The zeta potential is the change in potential across this double layer [26]. Commercial zeta potential analyzers are available; bench top units can be set up as well.

Like water contact angle and surface titration, zeta potential can be used to determine surface isoelectric points and quantify a change in surface ionizable groups [27, 28].

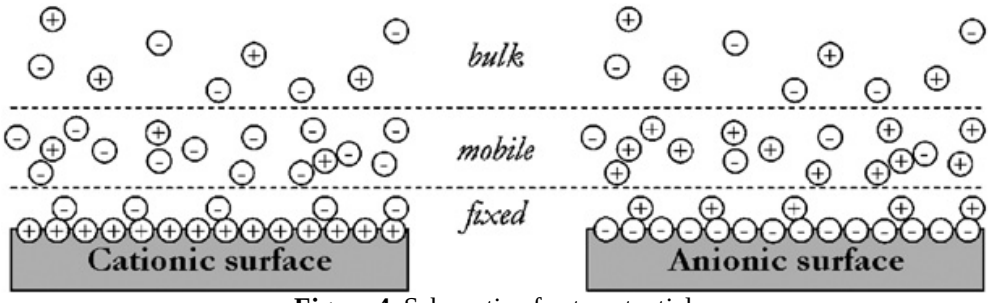


Figure 4. Schematic of zeta potential

3.2. Spectroscopic and microscopic analysis

3.2.1. X-ray photoelectron spectroscopy (XPS)

XPS, or Electron Spectroscopy for Chemical Analysis (ESCA), determines the atomic composition of a solid's top several nanometers. Upon exposure to X-ray photons, a surface

emits photoelectrons whose binding energies can be compared to known values to identify the element and its oxidation state [29]. The resulting spectrum is a plot of intensity (arbitrary units) versus binding energy (eV). The intensity of the ejected photoelectrons relates directly to the material surface atomic distribution and can therefore be used to quantify percent atomic composition and stoichiometric ratios [30, 29]. In addition to quantifying change in surface atomic composition, XPS can be used to estimate extents of reaction by dividing measured atomic concentrations by theoretical values calculated by assuming complete conversion [31, 32].

In polymer surface modification, it is of interest to identify the presence of specific functional groups. Curve synthesis can be used on high resolution scans to better understand the nature of a bond, but curve fitting models must be chosen carefully, functionalities are typically present in low concentration, and fitted curves overlap, making quantification complex [33, 34]. A different approach to identifying presence of specific functional groups is through the use of chemical derivitizing agents [32, 35-37].

3.2.2. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

Time-of-flight secondary ion mass spectrometry (ToF-SIMS)ToF-SIMS uses mass spectrometry to determine the type and quantity of ionizable chemical groups of a surface's top nanometer [38]. When a surface is subjected to a beam of primary ions, it ejects secondary ions, which are separated according to their mass to charge ratio in a mass spectrometer. The resulting spectrum depicts signal intensity versus mass to charge ratio (m/z) and can be used to gauge relative intensities of chemical species. It can also provide two-dimensional chemical maps for use in establishing surface homogeneity [32] or designing micropatterning for genomic arrays and biosensors [39]. The detection limit of ToF-SIMS is more sensitive than XPS, on the order of parts per billion, however ionization of surface molecules is dependent on sample matrix, and is therefore not quantitative. ToF-SIMS can be used to complement XPS results by offering identification of chemical species [40]; it may also be used to differentiate samples that have similar XPS spectra [38].

3.2.3. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) uses infrared radiation to determine the chemical functionalities present in a sample. When an infrared (IR) beam hits a sample, chemical bonds stretch, contract and bend, causing it to absorb IR radiation in a defined wavenumber. In attenuated total reflectance (ATR) FTIR, the incident IR beam first passes through a ZnSe, Ge, or diamond crystal, improving the surface sensitivity of the technique. The resulting plot is of absorbance (or transmittance) versus wavenumber. Sampling depth is dependent on the infrared transmitting crystal used to internally reflect the incident IR beam as well as the refractive index of the sample and is on the order of microns [38]. Although ATR-FTIR has a relatively deep sampling depth, it does not require ultra high vacuum conditions, as do XPS and ToFSIMS, and an analysis can therefore be conducted in less than ten minutes [41]. ATR-FTIR can also be used to monitor migration of functional groups to the polymer bulk [42].

3.2.4. Atomic force microscopy (AFM)

In AFM, a tip attached to a flexible cantilever moves across the sample surface to measure surface morphology on an atomic scale. The change in surface height is then measured by the location of the reflected laser beam in the quadrant photodetector, and a surface topographical map is generated from which surface roughness values can be

calculated [43]. AFM can operate with a resolution of thirty by less than one angstroms (lateral by vertical) [43]. Surface roughness is an important parameter in biomedical materials, as it may affect cell adhesion [44]. In the case of vascular prostheses, increased surface roughness can compromise hemocompatibility as turbulent blood flow may initiate hemolysis [45]. Because AFM has subnanometer resolution and is capable of conducting measurements in physiological conditions, it has been used to study a range of biological molecules (proteins, DNA, RNA, tissues, etc.). This ability to observe biofunctionalized surfaces in their native environment would benefit from faster scan rates such that the activity of immobilized biomolecules could be directly observed.

3.2.5.Scanning electron microscopy (SEM)

When a sample is bombarded with electrons, it emits secondary electrons and X-rays. The intensity of the secondary electrons is detected to generate a high resolution three dimensional surface image. X-rays can be detected to conduct elemental analysis. SEM is not as surface sensitive as other techniques, and non-conducting polymers must be sputter-coated prior to analysis [38, 46]. Nevertheless, it is one of the more widely available tools in surface analysis, and it is thus often used to measure surface topography [47-50].

4. Application of chitosan in surface modification of textile materials

Chitosan applied to the textile industry, as an antimicrobial finish, became popular due to its ability to provide protection against allergies and infection diseases, coupled with moisture retention and wound healing capabilities.

The prime focus for chitosan as an antimicrobial treatment has been on cotton. Early work indicated that the antimicrobial effect was potent against a range of microbes, but the finishing was not durable [51]. To improve durability, chitosan has been crosslinked to cotton using chemicals such as dimethyloldihydroxyethyleneurea (DMDHEU), citric acid, 1,2,3,4-butanetetracarboxylic acid (BTCA) or glutaric dialdehyde [52-55]. These chemicals, some of which are used in cotton durable press, crosslink chitosan to cotton through hydroxyl groups. Antimicrobial activity with a durability of up to 50 washes has been reported in some of these studies. Ye & al. [56, 57] synthesized nanoscale core–shell particles of poly(*n*-butyl acrylate) cores and chitosan shells and applied them to cotton fabrics in a pad–dry–cure process. The antibacterial activity was maintained at over 90 % reduction levels after 50 washes.

Mehta & al. [58] reported that chitosan improves the dye coverage of immature fibres in cotton dyeing and that it could be successfully used as a thickener and binder in pigment printing of cotton [59].

Since cotton fibers contain large amounts of hydroxyl groups they are highly hydrophilic. In addition, the fiber crystallization is low, so that when cotton fibers absorb water, the bonding force among cellulose molecules is reduced markedly, which causes swelling. Therefore, when cotton fabrics are twisted or rubbed when being washed or worn, the cellulose macromolecules shift and undergo plastic deformation. Consequently, the fabric shrinks and wrinkles. The primary method of minimizing creases in cotton fabrics when washed or worn is to use appropriate agents to cross-link the cellulose molecules in the fiber. This prevents the relative displacement of the cellulose molecules in cotton fibers when washed or worn. Crease resistance results from increasing the elasticity of the fibers [60].

Kuo-Shien Huang & al. [61] used H_2O_2 to degrade chitosan to low molecular-weight chitosan (LWCS), which was then mixed with an anti-creasing agent (dimethylol dihydroxyl ethylene urea) to produce the finishing agent, and then applied in the anti-creasing treatment of cotton fabrics. The results showed that the antiwrinkle property of all process fabrics is

decreased obviously after washing 20 times, the softness of the fabric was improved, and the strength of the fabric decreased slightly after the wash treatment.

Sang-Hoon Lim & al. [62] created a fiber-reactive chitosan derivative, O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (NMA-HTCC), which was applied to cotton fabrics by a cold pad-batch method in the presence of an alkaline catalyst to evaluate its use as a durable antimicrobial textile finish. The antimicrobial activities of the NMA-HTCC treated cotton fabrics were evaluated quantitatively against Staphylococcus aureus. The cotton treated with NMA-HTCC at a concentration of 1% on weight of fabric showed 100% of bacterial reduction. The activity was maintained over 99% even after being exposed to 50 consecutive home laundering condition [62].

A method of improving the dyeability of cellulosic fabric with reactive dyes was proposed by Weltrowski [63] involves pretreating the fabric with an oxidizing agent, applying chitosan oligomers to the fabric, stabilizing the product of this step by treatment with a reducing agent solution, and dyeing the resultant product with a reactive dye.

In addition to improving dyeability, chitosan has been used for durable press and antimicrobial finishing of cotton with citric acid by means of the conventional pad-dry-cure process [55]. Citric acid was expected to react with hydroxyl groups in cellulose and chitosan or with amino groups in chitosan to form ester crosslinking or interionic attraction. The treatments improved durable press appearance and antimicrobial properties, and the properties were retained through twenty washing and tumble-drying cycles.

Lee & al. [54] treated samples with chitosan and fluoropolymers using the pad-dry-cure and pad-cure methods, respectively, to impart barrier properties against microorganisms and blood to 100 % cotton and 55/45 % wood/polyester spunlaced nonwoven fabrics. They assessed the antimicrobial activity and blood repellence of the samples and measured the mechanical properties to investigate the effect of finishing on handle with the KES-F system.

Huh & al. [64] prepared chitosan-grafted poly(ethylene terephthalate) (PET) (C-PET) and quaternized chitosan-grafted PET (QC-PET) [64] against S. aureus, C-PET and QC-PET showed high growth inhibition in the range of 75–86 % and still retained 48–58 % bacterial growth inhibition after laundering. Several other studies confirmed [65-71] the effect of chitosan as an antibacterial finishing agent.

While the application of chitosan on cellulosic textiles improves dyeability, soil release properties, and antimicrobial activity, treatment of polyester fabrics with chitosan imparts a significant antistatic effect. Matsukawa & al. [72] treated polyester fabric with chitosan, hydrolyzing the surfaces with caustic soda solution to incorporate the functional groups (-COOH). They reported that the strength of the polyester fabrics decreased greatly with the alkali treatment but recovered with the chitosan treatment.

Recent studies in medical textiles have resulted in progress in modification of traditional materials that are widely used as wound care products [73-79]. Alginate filaments coated by chitosan are developed for advanced wound dressings [80].

Cotton fabric surface modified by chitosan absorbs antibiotic molecules from aqueous solution. The quantity of absorption depends on the degree of modification of the samples. The higher degree of modification the higher amount of antibiotic can be bonded by the textile. Such cotton textile finishing enables to achieve therapeutic new generation dressings for protection of surgical wounds against infections [81].

Wound dressings have also undergone surface modification to impart antimicrobial activity. Chitosan has been covalently linked to carboxylic acid functionalized poly(propylene) (PP) using water soluble carbodiimide chemistry. The resulting material showed enhanced wettability and antimicrobial activity against Pseudomonas aeruginosa [82].

Hirano & al. [83] recently reported on their study of chitosan fibers combined with acidic glycosaminoglycans namely hyaluronic acid, chondroitin sulfate, dermatan sulfate and heparin [89]. Filaments of approximately 25 cm were fabricated into cotton-like staple fibers. The fiber materials were found to contain between 5 % to 33 % of glycosaminoglycans. The presence of glycosaminoglycans made the fiber mechanically weaker, but the glycosaminoglycans was found to be released indicating an alternative wound healing approach.

Wool fibre, based on a protein called keratin, consists of two major morphological parts: cortex cells (90 % of the wool's weight) and the surrounding cuticle cells (10 % of the wool's weight). The surface of the cuticle cells is highly hydrophobic due to covalently bound fatty acids [84]. The morphology of the wool fibre surface plays an important role in textile finishing processes. The covalently bound fatty acids and the high amount of disulphide bridges make the outer wool surface highly hydrophobic. Especially in the printing and dyeing of wool, the hydrophobic character of the wool surface is disturbing. Diffusion of the hydrophilic dyes at and into the fibres is hindered [85]. For this reason, the hydrophilicity and dyeability properties of the wool fibre should be developed.

A method for improving the dyeability of wool fabric with reactive dyes was proposed by Julia & et. [86], involves pre-treating the fabric with an oxidising agent, applying chitosan to the fabric. Other authors reported that the dyeability of wool fabrics pre-treated with a chitosan/nonionic surfactant mixture improved, and their colour strength with reactive dye increased [87].

In wool finishing, chitosan has been used as a shrinkresist agent [88, 89] and as an agent for improving the dyeability of wool [90-97]. The modified fibre always shows somewhat different dyeing behaviour, so the influence of the biopolymer to the fibre dye ability has to be examined in detail [98] and the best way to achieve this is to investigate the interaction between chitosan and dye in the solution [99, 100].

Park & al. [101] investigated the antimicrobial and deodorant activities of chitosan-treated wool fabric, treating the wools with chitosans of varying molecular weights and degrees of deacetylation (DD) by pad-dry method. They reported that wool treated with chitosan of DD > 70 % showed good antimicrobial activity regardless of the molecular weight of the chitosan. Deodorant activity of the chitosan-treated wool increased as the DD of the chitosan increased. A previous study concluded that the optimum molecular weight of the chitosan for excellent deodorant activity was in the range of 100-400 kD. Additionally, wool treated with chitosan showed relatively high durability to laundering, probably because of the strong ionic bonding between the chitosan and wool keratin.

In addition to native chitosan, a number of chitosanderivatives have been synthesized and used as antimicrobial agents on textiles. These include chito-oligosaccharide [102, 103], N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride [104-106] and N-p-(N-methylpyridinio)methylated chitosan chloride and N-4-[3-(trimethyl-ammonio) propoxy]benzylated chitosan chloride [107]. Many of these derivatives contain a quaternary ammonium group to enhance the antimicrobial activity. Another derivative is *O*-acrylamidomethyl- N-[(2-hydroxyl-3-trimethylammonium)propyl] chitosan chloride [108]. The acrylamidomethyl group is fiber reactive and can form a covalent bond with cellulose in cotton, resulting in excellent durability. Kenawy *et al.* attached several compounds to the reactive amino group of chitosan [109]. These modified chitosans were highly active against microbes, in particular fungi species.

Despite such active research and recent patents covering the use of chitosan on cotton [110] and polyester [111], chitosan has yet to be used as a finishing agent on any commercial

textiles. The poor handle, among other factors, may be limiting its application on textiles. Nevertheless, the Swiss company Swicofil manufactures a composite fiber of chitosan and viscose, Crabyon®, that has durable antimicrobial efficacy and it is suitable for a range of textile products [112].

Conclusion

Chitosan, the deacetylated derivative of chitin, has a number of properties, such as biocompatibility, biodegradability, nontoxicity and antimicrobial activity which have attracted much scientific and industrial interest. Taping new potential antimicrobial substances, such as Chitosan, can considerably minimize the undesirable activities of the antimicrobial products. Scientists all over the globe are working in the area and few of them reported to have used antimicrobial finishes to make the fabric having antimicrobial properties. Chitosan was reported to be suitable finishing agent for textile materials with barriers against microorganisms.

Reference

[1] T. L. VIGO, *Protection of textiles from biological attack. Handbook of Fiber Science and Technology. Chemical Processing of Fibers and Fabrics, Functional Finishes. Part A.* In M. LEWIN, S. B. SELLO, eds., Marcel Dekker, inc., New York, vol. II, 1983, pp. 367–426.
[2] D. JOCIC, P. JOVANCIC, Z. PETROVIC, E. BERTAN, A. NAVARRO, M. R. JULIA, P. ERRA. *The influence of surface modification on wool functional and dyeing properties*. In Proceedings of the World Textile Conference 2nd AUTEX Conference, Textile engineering at the dawn of a new millennium: an exciting challenge, Bruges, Belgium, 1–3 July 2002, pp. 297–312.
[3] P. ERRA, R. MOLINA, D. JOCIC, M. R. JULIA, A. CUESTA, J. M. D. TASCON, *Textile Res. J*., **69**, 811–815 (1999).
[4] N. LIU, X.-G CHEN, H.-J PARK, *Carbohydr. Polym.*, **64**, 60-65 (2006).
[5] H. K. NO, N. Y. PARK, S. H. LEE, **74**, 65-72 (2002).
[6] Y. C. CHUNG, Y.-P SU, C. C CHEN, *Acta Pharmacol. Sin*., **25**, 932-36 (2004).
[7] D. HORTON, D. R. LINEBACK, *Carbohydr. Chem.*, **5**, 403 (1965).
[8] A. BAXTER, M. DILLON, K. D. A. TAYLOR, G. A. F. RONERTS, *Int. J. Biol. Macromol.*, **14**, 166- 169 (1992).
[9] S. AIBA, *Int. J. Biol. Macromol.*, **8**, 173-176 (1986).
[10] A. HIRAI, H. ODANI, A. NAKAJIMA, *Polym. Bull.*, **26,** 87-94 (1991).
[11] L. RAYAMOND, F. G. MORIN, R. H. MARCHESSAULT, *Carbohydr. Res*., **246,** 331-336 (1993).
[12] H. TERAYAMA, *J. Polym. Sci.*, **8**, 243-253 (1952).
[13] G. MAGHAMI, G. A. F. ROBERTS, *Makromol. Chem.*, **189**, 2239- 2243 (1988).
[14] F . NIOLA, N. BASORA, E. CHORNET, P. F. VIDAL, *Carbohydr. Res*., **238**, 1-9 (1993).
[15] I. G. ALONSO, C. PENICH-COVAS, J. M. NIETO, *J. Therm. Anal.*, **28,** 189-193 (1983).
[16] R. A. A. MUZZARELLI, C. LOUGH, M. EMANUELLI, *Carbohydr. Res*., **164**, 433-442 (1987).
[17] J. Z. KNAOUL, M. R. KASSAI, V. T. BUI, K. A. M. CREBER, *Can. J. Chemistry*, **76**, 1699-1706 (1998).
[18] C. M. CHAN, T. M KO, H. HIRAOKA, *Surf. Sci. Rep.*, **24**, 3–54 (1996).
[19] J. G. A TERLINGEN, H. F. C. GERRITSEN, A. S. HOFFTMAN, F. J. JEN, *J. Appl. Polym. Sci*., **57**, 969–82 (1995).
[20] B. D. RATNER, D. G. CASTNER, *Surface modification of polymeric biomaterials.* New York: Plenum Press, 1997.
[21] H. MAKAMBA, J. H. KIM, K LIM, N. PARK, J. H. HAHN, *Electrophoresis*, **24**, 3607–3619 (2003).
[22] F. E. BARTELL, H. H. ZUIDEMA, *J. Am. Chem. Soc*., **58**, 1449–1554 (1936).
[23] G. L. MACK, *J. Phys. Chem*., **40**, 159–167 (1936).
[24] C. W. EXTRAND, *Langmuir*, **20**, 4017–4021 (2004).
[25] S. R, HOLMES-FARLEY, R. H. REAMEY, T. J. McCARTHY, J. DEUTCH, G. M. WHITESIDES, *Langmuir*, **1**, 725–740 (1985).
[26] D. HARVEY, *Modern analytical chemistry*. New York:McGraw-Hill, 2000.

[27] B. J. KIRBY, E. F. HASSELBRINK, *Electrophoresis*, **25**, 187–202 (2004).
[28] B. J. KIRBY, E. F. HASSELBRINK, *Electrophoresis*, **25**, 203–213 (2004).
[29] L. SABBATINI, P. G. ZAMBONIN, *Surface characterization of advanced polymers*. New York: VCH Publishers, inc., 1993.
[30] E. KISS, C. G. GOLANDER, J. C. ERIKSSON, *Prog. Coll. Pol. Sci*., **73**, 113–119 (1987).
[31] M. CROMBEZ, P. CHEVALLIER, R. C. GAUDREAULT, E. PETITCLERC, D. MANTOVANI, G. LAROCHE, *Biomaterials*, **26**, 7402–7409 (2005).
[32] P. KINGSHOTT, J. WEI, D. BAGGE-RAVN, N. GADEGAARD, L. GRAM, *Langmuir*, **19**, 6912–6921 (2003).
[33] D. BRIGGS, D. M. BREWIS, R. H. DAHM, I. W. FLETCHER, *Surf. Interface Anal.*, **35**, 156-167 (2003).
[34] D. BRIGGS, N. FAIRLEY, *Surf. Interface Anal.*, **33**, 283–290 (2002).
[35] V.TERLINGEN, J. G. A. GERRITSEN, H. F. C. HOFFMAN, F. J. JEN, *J. Appl. Polym. Sci*., **57**, 969–982 (1995).
[36] M. CROMBEZ, P. CHEVALLIER, R. C. GAUDREAULT, E. PETITCLERC, D. MANTOVANI, G. LAROCHE, *Biomaterials*, **26**, 7402–7209 (2005).
[37] A. CHILKOTI, B. D. RATNER, D. BRIGGS, *Chem. Mater*., **3**, 51–61 (1991).
[38] S. DESAI, R. P. SINGH, *Surface modification of polyethylene*. In: Albertsson AC, (eds). Long-term properties of polyolefins. New York: Springer, 2004, p. 231–293.
[39] J. HYUN, Y. J. ZHU, A. LIEBMANN-VINSON, T. P. BEEBE, A. CHILKOTI, *Langmuir*, **17**, 6358–6367 (2001).
[40] J. P. SIBILIA, *A guide to materials characterization and chemical analysis*. New York: VCH Publishers, inc., 1988.
[41] C-PS HSU, Chapter 15: infrared spectroscopy. In: Settle F, (eds). *Handbook of instrumental techniques for analytical chemistry*. Upper Saddle River, New Jersey: Prentice-Hall, inc., 1997, p. 247–283.
[42] J. R. RASMUSSEN, E. R. STEDRONSKY, G. M. WHITESIDES, *J. Am. Chem. Soc*., **99**, 4736–4745 (1977).
[43] A. ALESSANDRINI, P. FACCI, *Meas. Sci. Technol*., **16**, 65–92 (2005).
[44] N. FAUCHEUX, R. SCHWEISS, K. LUTZOW, C. WERNER, T. GROTH, *Biomaterials*, **25**, 2721–2730 (2004).
[45] L. CEN, K. G. NEOH, Y. L. LI, E. T. KANG, *Biomacromolecules*, **5**, 2238–2246 (2004).
[46] K. C. DEE, D. A. PULEO, R. BIZIUS, *An introduction to tissuebiomaterial interactions*. Hoboken, NJ: Wiley-Liss, 2002.
[47] D. S. BAG, V. P. KUMAR, S. MAITI, *J. Appl. Polym. Sci*., **71**, 1041–1048 (1999).
[48] E. SHENG, I. SUTHERLAND, D. M. BREWIS, R. J. HEATH, *J. Adhes. Sci. Technol*., **9**, 47-60 (1995).
[49] S. DESAI, D. BODAS, K. R. PATIL, M. PATOLE, R. P. SINGH, *J. Biomat. Sci. Polym. E*, **14**, 1323–38 (2003).
[50] A. KONGDEE, T. BECHTOLD, L. TEUFEL, *J. Appl. Polym. Sci*., **96**, 1421-1428 (2005).
[51] S. H. LIM, S. M. HUDSON, *J. Macromol. Sci. Polym. Rev.*, **43**, 223-269 (2003).
[52] K. F. EL-TAHLAWY, M. A. EL-BENDARY, A. G. ELHENDAWY, S. M. HUDSON, *Carbohydr. Polym.*, **60**, 421–430 (2005).
[53] Z. T. ZHANG, L. CHEN, J. JI, Y. L. HUANG, D. H. CHEN, *Textil. Res. J*., **73**, 1103–1106 (2003).
[54] S. LEE, J. S. CHO, G. S. CHO, *Textile Res. J*., **69**, 104–112 (1999).
[55] Y. S. CHUNG, K. K. LEE, J. W. KIM, *Textil. Res. J*., **68** (10), 772–775 (1998).
[56] W. J. YE, *Polymer*, **46**, 10538–10543 (2005).
[57] W. J YE, *J. Appl. Polym. Sci*., **102**, 1787–1793 (2006).
[58] R. D. MEHTA, R. COMBS, *American Dyestuff Reporter*, **86**(7), 43–44 (1997).
[59] S. A. BAHMANI, G.C. EAST, I. HOLME, *J. Soc. Dyers Colourists*, **116**, 94–99 (2000).
[60] H. MARK, N. S. WOODING, S. M. ATLAS, *Chemical aftertreatment of textiles*. New York: Wiley, 1971, pp. 184–216.
[61] K. S. HUANG, W. J. WU, J. B. CHEN, H. S. LIAN, *Carbohydr. Polym*., **73**, 254–260 (2008).
[62] S. H. LIM, S. M. HUDSON, *Carbohydr. Polym*., **56**, 227–234 (2004).
[63] M. WELTROWSKI, M. S. MASRI, U.S. patent 5, 501, 711 (1996).
[64] M. W. HUH, I. K. KANG, D. H. LEE, W. S. KIM, L. S. PARK, K. E. MIN, K. H. SEO, *J. Appl. Polym. Sci*., **81**, 2769–2778 (2001).
[65] El-R. KENAWY, F. I. Abdel-Hay, A. A. El-Magd, Y Mahmoud, *J. Bioactive Compatible Polym.*, **20**(1), 95-111 (2005).
[66] K.S. HUANG, W. J. WU, J. B. CHEN, H, Shan, *Carbohydr. Polym.*, **73**, 254–260 (2008).
[67] Y. MA, T. ZHOU, C. ZHAO, *Carbohydr. Res.*, **343**, 230–237 (2008).

[68] S. STRNAD, O. ŠAUPER, A. JAZBEC, K. STANA-KLEINSCHEK, *Textile Res. J*., **78**(5), 390–39 (2008).
[69] Y. SHIN, D. I. YOO, J. J. JANG, *J. Appl. Polym. Sd.*, **80**(13), 2495-2501 (2001).
[70] Y. GAO, R. CRANSTON, *Textile Res. J*., **78**(1), 60–72 (2008).
[71] W. YEA, M. F. LEUNGB, J. XINA, T. L. KWONGA, D. K. L. LEEB, P. LIB, *Polymer*, **46** 10538–10543 (2005).
[72] S. MATSUKAWA, M. KASAI, Y. MIZUTA, *Sen' Gakkaishi*, **51**, 17-22 (1995).
[73] K. KAIFU, N. NISHI, T. KOMAI, S. TOKURA, O. SOMORIN, *Polym. J.*, **13**, 241–245 (1981).
[74] C. W. LOU, C. W.LIN, Y. S. CHEN, C. H. YAO, Z. S. LIN, C. Y. CHAO, J. H. LIN, *Textile Res. J.*, **78**, 248-253 (2008).
[75] S. TOKURA, J. YOSHIDA, N. NISHI, T. HIRAOKI, *Polym. J*., **14**, 527–536 (1982).
[76] D. N. S. Hon, *Chitin and chitosan: medical applications*. *Polysaccharides in medicinal applications*, In S. DUMITRIU, eds., Marcel Dekker, New York, 1996, pp. 631–649.
[77] M. MATTIOLI-BELMONTE, B. MUZZARELLI, R. A. A. MUZZARELLI, *Carbohydr. Eur*., **19**, 30–36 (1997).
[78] R. A. A. MUZZARELLI, M. MATTIOLI-BELMONTE, A. PUGNALONI, G. BIAGINI *Biochemistry, histology and clinical uses of chitins and chitosans in wound healing*. *Chitin and chitinases*, In P. JOLL`S, R. A. A. MUZZARELLI, eds., Basel: Birkha¨user Verlag; 1999, pp. 251–264.
[79] C. J. KNILLA, J. F. KENNEDYA, J. MISTRYA, M. MIRAFTABB, G. SMARTB, M. R. GROOCOCKC, H. J. WILLIAMS, *Carbohydr. Polym*., **55**, 65–76 (2004).
[80] H. TAMURA, Y. TSURUTA, S. TOKURA, *Materials Science and Engineering*, 20 (1-2), 143-147 (2002).
[81] E. RYBICKI, B. FILIPOWSKA, M. KOZICKI, A. JEZIORSKI, J. JAKUBIC, *New generation therapeutic dressings on the basis of surface modified textiles*. Proceedings of 5th International Scientific Conference Medtex. Lodz: Printing-Office of Scientific Publications, 2005, pp. 118-121.
[82] J. M. YANG, H. T. LIN, T. H. WU, C. C. CHEN, *J. Appl. Polym. Sci*., **90**, 1331–1336 (2003).
[83] S. HIRANO, M. ZHANG, M. NAKAGAWA, *J. Biomed. Mater. Res*., **56**, 556–561 (2001).
[84] E. HEINE, B. HOLLFELDER, W. LORENZ, H. THOMAS, G. WORTMANN, H. HOCHER, *Chapter 23, 'Enzymes for Wool Fibre Modification'*, ISBN: 0-8412-3547-3, 1998, pp. 279-293.
[85] E. HEINE, B. HOLLFELDER, H. HOCKER, *Alternative Wool Treatment by means of Enzymes and Combined Processes*, DWI-Report, (1996).
[86] M. R., JULIA, *Textile Chem. Colorist*, **30**(8), 78-83 (1998).
[87] M. S. YEN, *J. Appl. Polym. Sci*., **80**(14), 2859-2864 (2001).
[88] M. R. JULIA, E. PASCUAL, P. ERRA, *J. Soc. Dyers Colourists*, **116**, 62–67 (2000).
[89] M. S. MASRI, V. G. RANDAL, A. G. PITTMA, *Use of crosslinked chitosan in the finishing treatment of wool fabric for launderingshrinkage control*. In R. A. A. MUZZARELI, eds., Proceeding of the 1st International Conference on Chitin and Chitosan, Boston, USA Ancona: University of Ancona, 1978, pp. 306–311.
[90] B. FILIPOWSKA, A. WALAWSKA, E. RYBICKI, *Teinture et chitosan. L'industrie Textile*, **1323**, 79–81 (2000).
[91] D. JOCIC, M. R. JULIA, P. ERRA, *J. Soc. Dyers Colourists*, **113**, 25–31 (1997).
[92] M. S. YEN, *J. Appl. Polym. Sci.*, **80**, 2859–2864 (2001).
[93] N. ONAR, M. SARUSIK, *Fibers Tex. East. Eur*., **13**(49), 54-59 (2005).
[94] E. PASCUAL, M. R. JULIA, *J. Biotechnol*., **89**, 289-296 (2001).
[95] G. A. F. RONERTS, F. A. WOOD, *J. Biotechnol*., **89**, 297–304 (2001).
[96] E. RYBICKI, B. FILIPOWSKA, A. WALAWSKA, *Fibres Tex. East. Eur.*, **8**, 62–65 (2000).
[97] N. ONAR, M. SARIISIK, *J. Appl. Polym. Sci*., **93**, 2903–2908 (2004).
[98] S. VILCHEZ, A. NAVARRO, D. JOCIC, P. ERRA, *Estudio de processo de tintura de lana tratada con plasma y/o quitosano*. In Proceedings of 2001 International Textile Congress, Terrassa, 18-19-20 June 2001, vol. 2, pp. 522–530.
[99] D. JOCIC, S. VILCHEZ, R. MOLINA, P. JOVANCIC, A. NAVARRO, M. R. JULIA, P ERRA, *Adv. Chitin Sci*., **4**, 317–325 (2001).
[100] D. JOCIC, S.VILCHEZ, T. TOPALOVIC, R. MOLINA, A. NAVARRO, P. JOVANCIC, M. R. JULIA, P. ERRA, *J. Appl. Polym. Sci*., **97**, 2204-2214 (2005).
[101] W. H. PARK, K. Y. LEE, J. H. CHOI, W. S. HA, B. H. CHANG, *J. Korea Fiber Soc.*, **33**, 855-860 (1996).
[102] H. S. SEONG, H. S. WHANG, S. W. KO, *J. Appl. Polymer Sci.*, **76**, 2009–2015 (2001).
[103] J. Y. KIM, J. K LEE, T. S. LEE, W. H. PARK, *Int. J. Biol. Macromol.*, **32**, 23–27 (2003).
[104] Y. H. KIM, H. M., CHOI, J. H. YOON, *Textile. Res. J*., **68**, 428–434 (1998).
[105] Y. H. KIM, C. W. NAM, J. W. CHOI, J. H. JANG, *J. Appl. Polymer Sci*., **88**, 1567–1572 (2003).
[106] M. MONTAZER, M. G. AFJEH, *J. Appl. Polym. Sci*., **103**, 178–185 (2007).

[107] K. SUZUKI, D. ODA, T. SHINOBU, H. SAIMOTO, Y. SHIGEMASA, *Polym. J.*, **32**, 334–338 (2000).
[108] S. H. LIM, S. M. HUDSON, *Carbohydr. Polym.*, **56**, 227–234 (2004).
[109] E. R. KENAWY, F. I. ABDEL-HAY, A. ABOU EL-MAGD, Y. MAHMOUD, *J. Bioact. Comp. Polym.*, **20**, 95–111 (2005).
[110] C. LIANG., "*Anti-microbial Chitosan Composition for Textile Products*", United States Patent Application no 20060008515 (2005).
[111] M. C. JOERGER, R. F. KONIZ, S. SABESAN, J. PENNIAS, "*Antimicrobial Polyester-containing Articles and Process for their Preparation"*, United States Patent 7,081,139 (2006).
[112] CRABYON®, A Fibre with Crab's Pulp, http://www.swicofil.com/products/055chitosan.html (accessed June 2007).