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Chitosan as Multi Performance Bio Material: Properties and Applications.

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ABSTRACT

Chitosan is a nontoxic, biodegradable, and biocompatible polysaccharide of b (1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. This derivative of natural chitin presents remarkable properties that have paved the way for the introduction of chitosan in the biomedical textile finishing and nanofibers. Chitosan offers remarkable biological properties, which have paved the way for its application in the pharmaceutical and biomedical fields. It has been used for a variety of biomedical applications such as bone implants as a replacement for the nucleus pulposus and artificial organs. An elegant way to improve or to impart new properties to chitosan is the chemical modification of the chain generally by grafting of functional groups, without modification of the initial skeleton in order to conserve the original properties. This review aims to provide an overview of chitosan properties and applications in biomaterials, textile finishing and some also methods of treatment material with chitosan.

Keywords: Chitosan, Nanofibers, Biomedical, Antimicrobial, finishing.

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INTRODUCTION

Chitosan is widely distributed in nature as structural component of exoskeletons of crustaceans and insects, in marine diatoms and algae, as well as in some fungal cell walls. It was discovered by Rouget in 1859[1]. Chitosan solubility, biodegradability, reactivity, and adsorption of many substrates depend on the amount of protonated amino groups in the polymeric chain, therefore on the proportion of acetylated and non-acetylated D-glucosamine units [2]. The amino groups (pKa from 6.2 to 7.0) are completely protonated in acids with pKa smaller than 6.2 making chitosan soluble. Chitosan is insoluble in water, organic solvents and aqueous bases and it is soluble after stirring in acids such as acetic, nitric, hydrochloric, perchloric and phosphoric [3]. Chitosan and its derivatives have been recently proposed as biomaterial for a large number of applications ranging from pharmaceutical, cosmetic, biomedical, food, agriculture, paper and textile [4]. In textile field, the applications of chitosan are mainly related to its antimicrobial properties. In fact, chitosan is a wide-spectrum biocide with high antimicrobial efficacy against both Gram positive and Gram negative bacteria, as well as fungi and yeasts [5]. Mechanisms of the antimicrobial activity of chitosan have been recently reported. The protonation of the amino groups on the chitosan backbone inhibits the electrospinnability of pure chitosan [6]. Recently, electro spinning of nanofibers based on chitosan has been widely researched and numerous nanofibers containing chitosan have been prepared by decreasing the number of the free amino groups of chitosan as the nanofibiers have enormous possibilities for better utilization in various areas [7-9].

Structure of chitosan

Chitosan (i.e. poly-β-(1→4)-2-amino-2-deoxy-D-glucopyranose) is derived from chitin. Chitosan is a derivative of natural chitin the second most abundant polysaccharide in nature after cellulose.Typically, chitosan is obtained by deacetylation of the N-acetyl glucosamine units of chitin, generally by hydrolysis under alkali conditions at high temperature. When the degree of acetylation falls below the value of 60 mol%, chitin becomes chitosan [10,11]. The chemical structure of chitosan shows in figure 1.

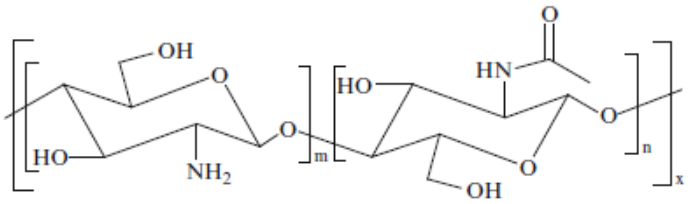

Figure 1: Chemical structure of chitosan [12].

PROPERTIES OF CHITOSAN

Chitosan, considering its unique properties, such as biodegradability, bioactivity, biocompatibility, the fibre grade properties, coating ability, and good miscibility with other polymers. Chitosan is a polycation whose charge density depends on the degree of acetylation and pH. So chitosan chains are able to interact by electrostatic interactions with negatively charged molecules. It can form nanoparticles by ionic gelation with polyphosphates and with nucleic acid. However chitosan suffers from a poor solubility in water, which is a major drawback for drug formulations. Indeed, chitosan is only soluble in acidic solutions of pH below 6.5, required to insure the protonation of the primary amine. In such cases, the presence of positive charges on the chitosan skeleton increases the different polymer chains, facilitating their solubilization [13,14].

Chemical properties of chitosan

The chemical properties of chitosan are as follow:

- Linear polymer
- Reactive amino groups
- Reactive hydroxyl groups available
- Chelates many transitional metal ions

Biological properties of chitosan

The biological properties of chitosan were as follow:

- Biocompatible (natural polymer, biodegradable to normal body constituents, safe and non-toxic, bind to mammalian and microbial cells aggressively)
- Regenerative effect on connective gum tissue.
- Accelerates the formation of osteoblast responsible for bone formation
- Hemostatic
- Fungi static
- Spermicidal
- Antitumor
- Anticholesteremic
- Accelerates bone formation
- Central nervous system depressant
- Immunoadjuvant

APLICATION OF CHITOSAN

Drug delivery

Chitosan and chitosan derivatives have been extensively studied for drug delivery and other biomedical applications due to;

- Their biocompatibility and low toxicity
- Their possible formulation in nanoparticles or in gels
- Their cationic properties

An overview of their use in biomedical applications will be given for gene delivery, solubilization of poorly soluble drugs, tissue engineering, and vaccine delivery. These examples are not exhaustive but clearly demon strate the benefit of chitosan derivatives in drug delivery [15,16].

Chitosan and chitosan derivatives in tissue engineering

Tissue engineering aims to develop functional substitutes for damaged or diseased tissues through complex constructs of living cells, bioactive molecules, and 3Dporousscaffolds that support cell attachment, proliferation, and differentiation. The natural biopolymer chitosan is an excellent candidate for the preparation of wound dressings and hydrogel scaffolds for tissue engineering. There are different ways to form hydrogels from chitosan. Chitosan could be used alone but this is rarely the case because pure chitosan hydrogel is fragile and has low mechanical strength, which limits its application in tissue engineering [17]. Chitosan has therefore been combined with other compounds or chemically modified to improve its properties for tissue engineering applications, in particular to create thermo sensitive hydrogels that will gel in situ [18,19].

Artificial vessel

Chitosan accelerating effects of wound healing to small animals such as rat and dog was applied for a hemostatic agent for vascular grafts [20].

Abscess

Chitosan cotton was used as a filling agent for subcutaneous abscess. Subcutaneous abscess were cured in all cases with single chitosan cotton was gradually contracted by granulated tissue formation and was cured within a mounth no recurrence or suppuration of the wounds were observed [21].

Dermatitis

Chitosan also can use effectively as a topical treatment for certain types of infections. B.K.ghosh has used it in acetic acid solution to treat monkeys suffering from dermatitis caused by mite infestations. The dermatitis cleared up in two days and new hair growth started in 10 days .unlike conventional topical treatment. Treatment with chitosan appears to clear up the condition permanently. It works on athletes foot infections, too [22].

APPLICATION OF CHITOSAN FOR TEXTILE FINISHING

Antibacterial

Chitosan has been found to inhibit the growth of microbes in a large body of work that has been extensively reviewed by Lim and Hudson [23]. It has a MIC of 0.05–0.1% (w/v) against many common bacterial species; although the activity can be affected by its molecular weight and degree of deacetylation. many techniques are available to determine the degree of deacetylation, such as:

- Elemental analysis
- Titration
- Hydrolytic methods
- HPLC – Ultraviolet
- Infrared
- 1H nuclear magnetic resonance
- CP-MAS 13C NMR
- CP-MAS 15N NMR
- Many other methods are described in the literature but with a somewhat smaller appeal [24].

Some of these methods are: steric exclusion chromatography, nitrous acid deamination thermal analysis gas chromatography with columns packed with chitin and chitosan, etc. [25]. Antimicrobial efficacy was evaluated following the shake flask method against S. aureus (ATCC 6538) and K. pneumonia (ATCC 4352). Chitosan-treated cotton fabrics showed antimicrobial activities close to 100 % of bacteria reduction [26,27]. Fabrics showed good antibacterial properties also after 25 laundering cycles [28,29]. The bacteria reduction of S. aureus and K. pneumonia were 91 and 93 %, respectively. Chitosan has been also grafted to wool after acylation with succinic anhydride and phthalic anhydride [30,31].Antimicrobial properties were evaluated by a qualitative method against S. aureus and E. coli [32,33]. It was found that antimicrobial activity is more efficient against E. coli. Fibres of poly(ethylene terephthalate) (PET) were irradiated with 60Co-ray and grafted with acrylic acid [34,35].The resulting fibres were further grafted with chitosan and collagen by means of esterification [36,37]..Antimicrobial tests were carried out using Methicillin-resistant S. aureus (MRSA), S. aureus, P. aeruginosa (ATCC 10145) and E. coli O-157:H7 (ATCC 43894) at concentration of 1.5 ± 0.3 × 105 CFU/ml for contact times of up to 24 hours [38,39]. The order of bacteria reduction of chitosan-grafted PET fabrics is E. coli > P. aeruginosa> S. aureus> MRSA [40].The concentration of MRSA started to diminish after 6 hours of contact for PET grafted with collagen and chitosan, while the bacteria concentration started to decrease after 4 hours of contact time with of PET grafted with chitosan only. It is known that chitosan derivatives with quaternary ammonium groups possess high efficacy against bacteria and fungi [41].It is now widely accepted that the target site of these cationic polymers is the cytoplasmic membrane of bacterial cells [42,43].

Several mechanisms for the antimicrobial activity by chitosan

- Polycationic structure of chitosan which can be expected to interact with the predominantly anionic components (lipopoly-saccharides and proteins of microorganism surface) resulting in changes in permeability which causes death of the cell by inducing leakage of intracellular components.
- The chitosan on the surface of the cell can form a polymer membrane which prevents nutrients from entering the cell.
- The chitosan of lower molecular weight enters the cell, binding to DNA and inhibits RNA and protein synthesis.

- Since chitosan could adsorb the electronegative substance in the cell and flocculate them, it disturbs the physiological activities of the microorganism leading to death of the cells [44,45].

Anti-shrinking

The shrinkage of the untreated fabrics in both the warp and the weft direction is larger than that of the treated fabrics. This result is because the yarn of the untreated fabrics is stretched taut during weaving, whereas the treated fabrics have reactive polymers completely covering the fiber scales or an even layer of protective thin membrane formed over the surface. In turn, the latter would make the tightness of the yarn, the structure of the fabric, and weaving density more restrictive to the movement of individual fibers. Under such circumstances, the fibers in the treated fabric would, of course, become much more resistant to outside forces and not glide against each other; that is, the fabric would become more shrink proof [46]. Therefore, when the osmosis of chitosan in fabric is better, the area covered by chitosan on the surface of the fiber becomes larger. Nano chitosan-treated fabric has better shrink proofing properties [47].

CHITOSAN TREATMENT

Padding

For the chitosan treatments, chitosan solutions were freshly prepared by dissolving the desired amount in distilled water containing acetic acid (3%). The treatments were performed by padding fabrics (100% WPU). After treatment, the samples were squeezed and dried at 40°C [48].

Crosslinking

Fabric was completely immersed in a solution containing 1% chitosan (ca. 600 kDa), and the cross-linking agent tested (2.5%). Impregnation was achieved by the pad-dry-cure method. The pickup was determined by weighing the fabric before and after impregnation and found to be 79%. The fabric was allowed to dry at 100 C for 4 min, after which it was thermo fixed at 140 C for 4 min. It is at this stage that the cross-linking agent will reticulate and “link” the chitosan to the fabric [49].

Chitosan based core-shell

Chitosan based core-shell particle, with chitosan as the shell and a soft polymer as the core, has been designed as a novel antibacterial coating for textiles by Ye et al. The core-shell particles were synthesized via a graft copolymerization of n-butyl acrylate from chitosan in aqueous solution. Properties of the particles, including composition, particle size and distribution, surface charge as well as morphology, were characterized. The treatment of cotton with poly (n-butyl acrylate) (PBA)-chitosan particles confers the fabric with excellent antibacterial property. It is well recognized that chitosan has good antimicrobial activity, especially against the growth of Staphylococcus aureus (S. aureus). As expected, the untreated fabric gave a negligible antibacterial activity of less than 5% while all finished cotton showed over 99% bacterial reduction.

Electrospinning

Electrospinning is a fiber forming process by which either polymer solutions or melts are charged byhigh voltage to form fine jets. It was first reported by Formhals in 1934. Fiber formation by electrospinning of polymer solutions has been extensively studied in terms of voltage, tiptocollectordistance, feeding rate of polymer solution, and polymer solution properties.[50] The electrospun composite nano fibers have been developed using chitosan and synthetic polymers such as poly(vinyl alcohol) (PVA),poly(ethylene oxide) (PEO), poly(ethylene terpthalate) (PET), polycaprolactone (PCL), poly(lactiacid) (PLA), nylon-6 and others. These composite nanofibers are more advantageous over the electro spun nanofibers of pure chitosan, because the mechanical, biocompatible, antibacterial and other properties of the nanofibers were drastically enhanced by the addition of these polymers. Because PVA has good fiber forming characteristics, many nanofibers of the blends of PVA and chitosan have been fabricated by electrospinning [51]. The proteins which can be mixed with chitosan to form electrospun nanofibers have similar characteristics with the polymers mentioned above: they can be conveniently electrospun to nanofibers and can interfere with the association of the chitosan molecules. Pure electrospun collagen nanofibers have been fabricated in HFIP. Zein/chitosan/Poly (vinyl

pyrrolidone) (PVP) composite fibrous membranes were also fabricated from aqueous ethanol solutions by electrospinning .PVP was introduced tofacilitate the electrospinning process. Increasing zein and PVP concentrations led to an increase in average diameter of the fibers. In order to improve stability in wet stage and mechanical properties, the composite fibrous membranes could be crosslinked by hexamethylene diisocyanate (HDI). The crosslinked membranes showed slight morphological change after immersion in water for 24 h. The tensile strength and elongation at break of the membranes were increased after crosslinking, whereas Young's modulus was decreased.[52,53].

CONCLUSION

Chitosan is considered one of the most valuable polymers for biomedical and pharmaceutical applications due to its biodegradability, biocompatibility, antimicrobial, non-toxicity, and antitumor properties. Nanoparticles, microspheres, hydrogels, films, and fibers are typical chitosan based forms for biomedical and pharmaceutical applications. The purpose of this study is introduction of chitosan, properties of chitosan. Application of chitosan and chitosan treatment. Chitosan can improve antibacterial properties and anti-shrinking in the textile fibers and fabrics. Also it can used in the biomaterials such as drug delivery, tissue engineering, artificial vessel, abscess, dermatitis and nanofibers Chitosan treated fabric showed better antibacterial and anti-shrinking properties than untreated fabric. There are several methods for finishing on fabric such as padding, cross-linking, core-shell and Electrospinning.by the electrospinning methos we can product nano fibers that used in filtration showed good erosion stability in water and high adsorption affinity for metal ions in an aqueous solution.

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