

# Application of Chitosan Fibre in the Textile Industry



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It is difficult today to pick out a domain in our lives where a fibre doesn't exist. From the living muscles to the bandages, from automobile tyres to river embankments, fibres are playing very important functional roles, besides their extensive usage as wearable and decorative textiles. In the field of medical sciences also, researches involving the developments in the usage of textile fibres is intense. There has been increased inclination towards eco-friendly, biocompatible and biodegradable polymers, as most of the prevalent synthetic polymers lack these properties. Hence, the advantages of chitosan as a textile fibre were realised. Chitosan is a natural biopolymer, abundantly available in nature and is cheap to be produced. It shows good biocompatibility, bio-absorbability, wound-healing, haemostatic, anti-infection, anti-bacterial, non-toxicity and adsorption properties. Besides, it is resistant to thermal decomposition and can act as a good drug delivery carrier. It also exhibits the permeability and selectivity required for medical purposes. It can provide better control of transport and inherent blood compatibility.

Chitosan is gaining popularity as a textile fibre which can be specifically used for medical purposes, despite the problems faced in its process-ability and inferior mechanical properties. It is a unique material with certain special properties, preferred for medical usage. It has been found that wound dressings from chitosan can increase the rate of healing by 75%.

Research is being aimed at modifications of chitosan polymer so as to make its processing as a textile fibre or filament easier. At the same time, the modifications are also being aimed at increasing the tensile properties. Blending chitosan with other natural polymers like cellulose and silk fibroin have been tried, and the results show a lot of promise.

## What is chitosan?

Chitosan is a cationic polyelectrolyte, a natural biopolymer with a molecular structure very similar to chitin and cellulose. It is a linear polymer of  $\alpha$ -(1-4)-linked 2-amino-2-deoxy-D-glucopyranose. It resembles

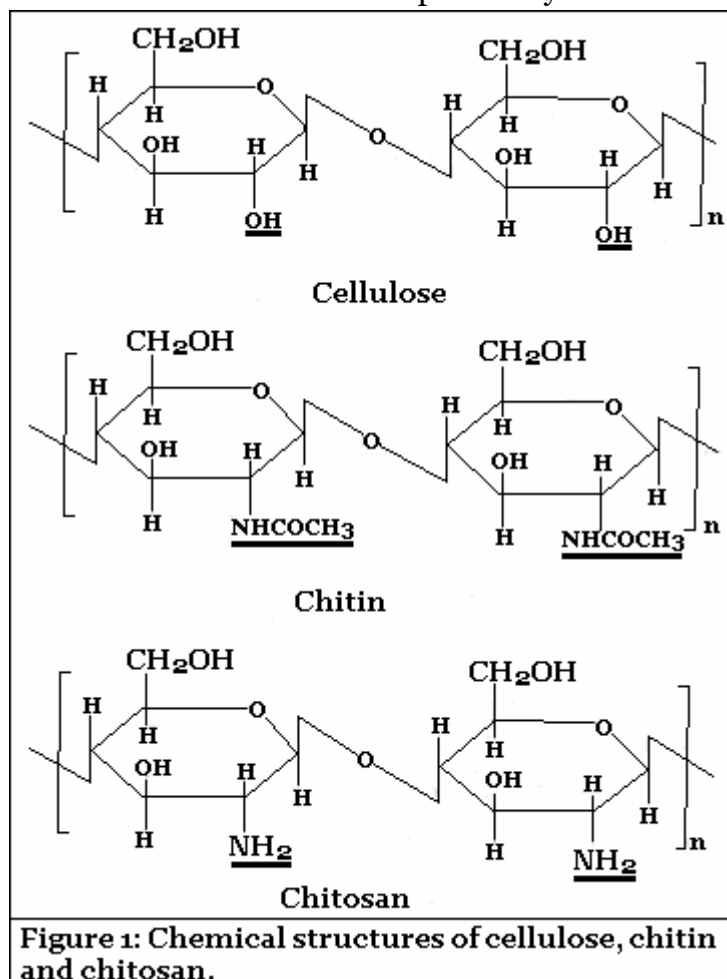
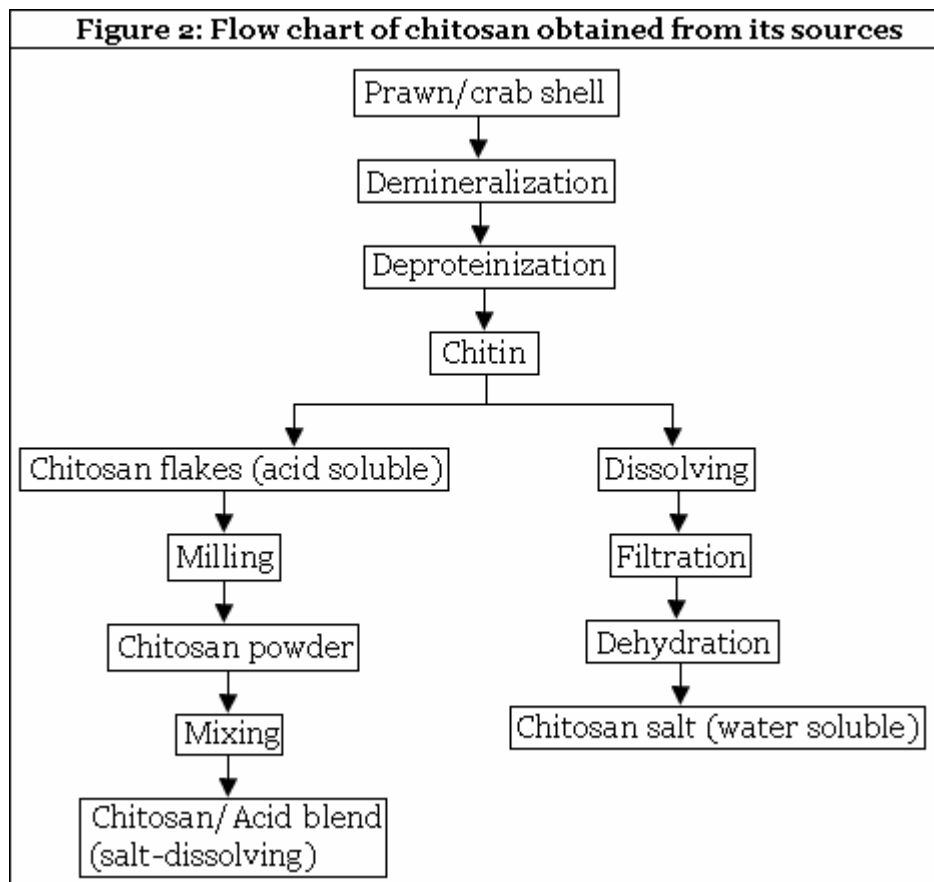


Figure 1: Chemical structures of cellulose, chitin and chitosan.

the structure of cellulose closely, with the hydroxyl ion at the  $\alpha$ -Carbon atom replaced by an amine group. Due to its close resemblance to the polymer chain of cellulose, which is the most common component of the natural textile fibres, the possibilities of chitosan in applications as textile fibre were initially realised. Chitosan is often derived from chitin by deacetylation [1,8]. Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the outer skeleton of insects, crabs, shrimps and lobsters, and in the internal structures of other invertebrates. It is the most abundant natural acetyl amino polysaccharide and is estimated to be produced annually as much as cellulose [1]. The structure of chitin is that of a cellulose-like polysaccharide of  $\beta$ -linked 2-acetamido-2-deoxy-D-glucose residues, whose hydroxyl groups at C2 position are substituted with acetamide groups (-NH-CO-CH<sub>3</sub>). The chemical structures of cellulose, chitin and chitosan are as shown in figure 1 [4]:

### Sources of chitosan

Chitosan can be obtained by deacetylation of chitin. Chitosan-glucan complexes can be obtained by fermentation and subsequent alkali treatment of *Aspergillus niger*, *Mucor rouxii* and *Streptomyces sp.* The alkali removes the protein and deacetylates the chitin simultaneously. The processing of crustacean shells involves removal of proteins and dissolution of calcium carbonate present in crab shells in high concentrations. The resulting chitin is deacetylated in 40% sodium hydroxide at 120°C for 1-3 hours. This treatment produces 70% deacetylated chitosan [1, 4]. The following figure 2 shows the flow chart regarding processing of chitosan from its main sources [1]:



## **Properties of chitosan**

Almost all the properties chitosan depend on two fundamental parameters:

- (i) Degree of acetylation.
- (ii) Molecular mass distribution.

### **Degree of acetylation**

Chitosan is the universally accepted non-toxic N-deacetylated derivative of chitin, the deacetylation being to such an extent that it becomes soluble in dilute aqueous acetic acid and formic acid. The degree of N-deacetylation depends on the ration of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units.

### **Molecular mass distribution**

The weight-average molecular weight,  $M_w$ , of chitosan can be determined by light scattering. Viscometry can also be applied to determine the molecular weight. The constants  $\alpha$  and  $K$  in the Mark-Houwink equation have been determined in 0.1M acetic acid and 0.2M sodium chloride solution. The intrinsic viscosity is expressed as:

$$[\eta] = K.M_v^{\alpha} = 1.81 \times 10^{-3}.M_v^{-0.93}.$$

The charged nature of chitosan in acid solvents and the propensity of chitosan to form aggregation complexes require care when applying these solvents. Furthermore, conversion of chitin to chitosan lowers the molecular weight, changes the degree of acetylation, and thereby alters the charge distribution, which in turn influences the agglomeration. The weight-average molecular weight of chitin is  $1.03 \times 10^6$  to  $2.5 \times 10^6$  kDa, which comes down to  $1 \times 10^5$  to  $5 \times 10^5$  kDa [14].

Chitosan of higher molecular weight, i.e., of higher degree of polymerisation, causes a decrease in wrinkle recovery angle (WRA) of DMDHEU or DMDHEU-chitosan treated samples. Also, a higher molecular weight chitosan gives higher breaking strength retention due to the binding effect of the fabric structure [1].

Thus, the important properties of chitosan can be discussed as follows:

### **Basicity**

Although most of the naturally occurring polysaccharides are essentially neutral or acidic in nature, chitosan is a highly basic polysaccharide [1].

### **Solubility**

Chitosan has ready solubility in various acidic solvents [8]. Its solubility in N-methyl morpholine-N-oxide (NMMO)/H<sub>2</sub>O has also been reported.

### **Reaction with acid anhydrides and halides**

Chitosan undergoes reactions typical to amines, of which N-acylation and Schiff reactions are important. N-acylation with acid anhydrides or acyl halides introduces amido groups at the chitosan Nitrogen. Linear aliphatic N-acyl groups higher than propionyl permit rapid acetylation of the hydroxyl groups in chitosan.

### **Reaction with aldehydes and ketones**

Chitosan forms aldimines and ketimines with aldehydes and ketones respectively, at room temperatures. Chitosan and simple aldehydes produce N-alkyl chitosan upon hydrogenation. The presence of more or less bulky substituent weakens the hydrogen bonds of chitosan. So, N-alkyl chitosans swell in water in spite of the hydrophobicity of alkyl chains. They retain the film-forming property of chitosan.

### **Use of chitosan in textiles**

Chitosan degrades before melting. So, they cannot be prepared by melt-spinning technique. Chitosan fibres can be prepared by wet spinning of chitosan in 2% aqueous acetic acid. Parameters such as spin strength ratio, coagulation bath composition and drying conditions play important roles in determining fibre properties. One problem in wet spinning is the choice of a suitable solvent system. Among the many solvents available, only a handful is of practical use, due to toxicity, corrosiveness and mutagenic properties. The object is to achieve a homogeneous non-gel solution with a maximum polymer-to-solvent ratio. Polymer concentration, pH, counter-ion concentration and temperature effects on the solution are important parameters to be controlled. In order to spin a fibre, a coagulant is also required whose nature depends highly on the solvent and solution properties.

Various modifications have been tried to get superior properties of the fibres. Chitosan fibres were acetylated with acetic anhydride in methanol, producing regenerated chitin fibres. The acetylation process was affected by parameters such as reaction temperature, treatment time and molar ratio of anhydride to amine groups. The acetylated fibres were found to have improved thermal stability and tensile strength.

Fibres produced from pre-saturated solutions of chitin in lithium thiocyanate (saturated at 60°C) at 95°C showed very low tensile strength but high degree of orientation was observed through X-ray analysis. However, solvent removal was not successfully done, even at 200°C.

### **Chitosan fibre in medical textile**

Chitosan has many useful biological properties because of its good biocompatibility. These properties, along with its abundance and easy sourcing makes it extremely fit for biomedical uses. Chitosan has high biocompatibility, bio-absorbability, wound healing, haemostatic, anti-infection and anti-bacterial effects [9]. In addition, chitosan is easy to handle for clinical uses because of its resistive nature to heating due to intra-molecular hydrogen bonding formed between the hydroxyl and amino groups. Therefore, much attention has been paid to chitosan-based biomedical materials, for example, drug delivery carriers, wound healing agents, etc. However, clinical applications are limited due to low mechanical strength. [3]

Fibres from chitosan have been useful for absorbable sutures and wound dressings. It has been claimed that wound dressings from chitosan fibres accelerate the healing of wounds by 75%. Chitosan has also been applied successfully in artificial kidney systems and artificial skin. Chitosan shows the required permeability and selectivity for these membranes. These novel membranes need to be developed for better control of transport, ease of formability and inherent blood compatibility. One of the problems of

these artificial membranes is surface induced thrombosis, where heparization of blood is needed to prevent clotting, and people who are liable to internal haemorrhage can be dialyzed only at great risk. Hence, one of the challenges to be solved remains the inherent blood compatibility. In this respect, chitosan has an edge as it is haemostatic and causes blood clot [1, 4].

Some popularly used derivatives of chitosan and their specific uses are given in table 1.

<b>Derivative</b>	<b>Examples</b>	<b>Potential uses</b>
N-acylchitosan	Formyl, acetyl, butyryl, hexanoyl, acetanoyl, decanoyl, etc.	Textiles membrane and medical aids.
N-Carboxyalkyl (aryl) chitosan	N-Carboxybenzyl, glycine-glucan, N-Carboxy-methyl, alanine glucan, phenylalanine glucan, etc.	Chromatographic media.
N-Carboxyacyl chitosan	From anhydrides such as maleic, itaconic, glutaric, cyclohexane, etc.	Molecular sieves, viscosity builders.
o-Carboxyalkyl chitosan	o-Carboxymethyl, cross linked $\alpha$ -Carboxymethyl, etc.	Molecular sieves, viscosity builders.
Sugar derivatives	1-deoxy-galactic, chitosan products obtained from ascorbic acid, etc.	Molecular sieves, viscosity builders.
Metal ion chelates	Palladium, copper, iodine, silver.	Catalyst, photography, health products, insecticides.

Various researches are being carried out to get a suitable wound dressing out of chitosan fibres or filaments. An artificial skin was designed for long term chronic use, which focuses on the development of a non-antigenic membrane that performs as a biodegradable template for synthesis of neo-dermal tissue. Chitosan polysaccharides with structural similarities to glycosamino glycans are very suitable for such substratum for skin replacement.

Another attempt included development of chitosan-glucan complex for surgical dressing. Chitosan was dissolved in water in acidic conditions (pH 2-3) followed by adding gelatine dissolved in water. The weight ratio of chitosan to gelatine was 3:1 to 1:3. To reduce stiffness, sorbitol or glycerol was used as plasticisers. The dressing film was cast out of this solution on a flat plate and dried at room temperature. Compared to conventional dressings, this new one displayed excellent adhesion to subcutaneous fat. Nonwoven made of chitosan fibres were also used as dressings. Chitin was treated with 1(N) HCl for 1 hour at 4°C. It was then heated to 90°C at which it was treated for 3 hours in a 0.3% NaOH solution to remove calcium and protein. It was then dissolved in dimethylacetamide solution containing lithium chloride of 7%. After filtration and defoaming, filaments were extruded from it through spinnerets of diameter 0.06 mm, into butanol at 60°C at 2.2 g/min. Filaments of 0.74 dtex with tensile strength of 2.8 g/den were obtained. The filaments were then cut into staple fibres and using polyvinyl alcohol binders, the nonwoven dressing was made.

In 1988, Beschitin W, a new dressing was developed based on chitin non-woven fabric. Wound dressings were also developed from polyelectrolyte complexes of chitosan with sulphonated chitosan. Wound healing is accelerated by the oligomers of degraded chitosan by tissue enzymes.

N-carboxybutyl chitosan dressing was developed for treating of plastic surgery donor sites. A solution of N-carboxybutyl chitosan was dialyzed and freeze-dried to give 10 X 20 X 0.5 cm<sup>3</sup> soft and flexible pad, which was sterilised and applied on wounds. This dressing can promote ordered tissue regeneration at the donor sites. Better histoarchitectural order, better vascularisation and absence of inflammatory cells were observed.

In a new attempt, chitosan fibres were prepared from micro fungi instead of conventional source of shrimp shells. Micro fungal mycelia was obtained from a nutrient solution of *Mucor mucedo* and washed and treated with NaOH to remove protein and precipitate chitosan. After bleaching and further washing, fibre dispersion was produced, which after filtration and wet-laid mat preparation was mixed with other fibres to give mechanical strength. Here, a non-animal source was used as raw material and the resulting micro fungal fibres were totally different from normal spun fibres. They exhibited branched and irregular structure. They were very brittle when dried and required to be treated with plasticisers.

Dressings were made from 5-methylpyrrolidinone chitosan also showed promise. This polymer was compatible with a host of other polymers like gelatin, polyvinyl alcohol, polyvinyl pyrrolidone and hyaluronic acid. The advantages claimed were healing of wounded mensical tissues, decubitus ulcers, etc. This polymer could also be fabricated to many different forms like filaments,. nonwoven fabrics, etc.

Dressings were also attempted from dibutyrilchitin, which was obtained by treatment of krill chitin by butyric anhydride in presence of perchloric acid as a catalyst. The reaction was carried at 25-30<sup>o</sup> C. Samples of high molecular weights were obtained to produce fibres by dry spinning 20-22% solution of acetone. Fibres exhibited better tensile properties than chitin itself or some of its derivatives. Alkaline hydrolysis of dibutyril chitin without destroying the fibre structure yielded fibres with even better tensile properties.

A skin equivalent was obtained by co-culturing fibroblasts and keratinocytes on a collagen-glycosaminoglycan-chitosan biopolymer and grafted on dorsal wounds generated by full thickness resection. The results show that the vascularisation precedes the innervations process. These data are consistent with the view that the development of nervous tissue is driven by nutritional and trophic factors provided by the vascular system.

Water soluble chitin (WSC) was prepared by controlling degree of deacetylation (DD) and molecular weight of chitin through alkaline and ultrasonic treatment. The WSC was found to be more efficient than chitin or chitosan as a wound healing accelerator. The wound treated with WSC solution was completely re-epithelialized, granulation tissues

in the wound were nearly replaced by fibrosis and hair follicles were almost healed at 7 days after initial wounding. Also, the WSC-solution treated skin had the highest tensile strength and the arrangement of collagen fibres in the skin was similar to normal skins. The WSC solution is considered to be a suitable wound healing agent due to its easy application and high effectiveness [10].

## Conclusion

Nowadays, emphasis is being given to the developments of eco-friendly materials having inherent biodegradability. The synthetic polymers lack not only biodegradability but also biocompatibility, as they generally have little compatibility with living body skin and lack haemostatic and antibacterial properties. Hence, the need of natural polymers were always felt which will show biocompatibility and biodegradability along with haemostatic, antibacterial and wound healing activities. It was for these reasons that the novel properties of chitosan were rediscovered. Chitosan is a naturally occurring biopolymer and present in abundance so that its processing does not involve high cost. It is gaining popularity as a textile material (filaments, fibres, nonwovens, etc.) especially in biomedical uses because of the unique properties it exhibits.

Although the useful properties of chitosan have been realised, its uses are limited to intensive researches even today. This is basically due to the difficulties in the process ability of the fibre. It is difficult to find out a suitable solvent system for wet spinning or dry spinning of chitosan. Fibres which are dry spun are brittle in nature. Due to instability of the polymer at high temperature, it cannot be melt spun. Modifications with aldehydes and ketones have been done to improve upon the process ability. N-modifications have been done (N-acetyl, N-aryl, N-acyl derivatives) in order to achieve the same purposes. The results have been satisfactory in many cases with an increase in the tensile properties (strength and elongation), thus resulting in better process ability of the polymer. Blends have also been tried with cellulose or silk fibroin with this aim. Modifications of the blended materials have also been done.

Chitosan shows high promise as a biomedical textile fibre, especially wound dressings. It is because of the improved drug delivery systems exhibited by the fibre, as well as other properties inherited by it that makes it conducive to the living body systems. More developments of the tensile properties will obviously lead to easy manufacturing of chitosan wound dressings, thus leading to its enhanced usage. Chitosan wound dressings are still very few in the market, but an increase in its usage in future can be hoped for.

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