

THE BIOPOLYMERS CHITOSAN AND SERICIN APPLICATIONS IN TEXTILES

Satyam Gupta¹, Lalit Jajpura²

Department of Textile Technology, Dr. B. R Ambedkar National Institute of Technology Jalandhar-144011, India

Abstract: *Biopolymers are naturally occurring materials such as chitin, sericin, starch, alginate, gelatin, cellulose, etc. Biopolymers have numerous promising industrial applications due to their certain valuable properties such as low toxicity, renewability, biodegradability, sustainability, etc. The biopolymers Chitosan and Sericin is discussed in the present article being their valuable characteristics amongst available numerous biopolymers. Chitosan is derived from N-deacetylation of polysaccharide Chitin, which is a natural biopolymer found in the exoskeletons of crustacean like shrimps, crabs, lobsters, and other shellfish. Chitosan possesses various valuable properties for textiles such as biodegradability, metal chelating, non-toxicity, antimicrobial activity, etc being presence of reactive amino group in it. Therefore, it can be used extensively in various wet processing applications in textiles. Sericin is also a natural macromolecular protein derived from silkworm Bombyx mori. The sericin exhibit various useful properties such as hydrophilicity, antibacterial, UV protection, etc which can be used to improve functional properties of textile materials. This byproduct of silk degumming operation can be crosslinked, copolymerized and blended with other materials especially artificial polymers to produce materials with improve properties. Coating of sericin can improve handle properties of wool and moisture absorption properties of hydrophobic synthetic textile materials. Beside these sericin treated fabrics has great applications in medical textiles. Overall, Chitosan and sericin biopolymers have great potential as sustainable dyeing and finishing agents in textiles due to their abundance availability at low cost with numerous functional properties.*

Keywords: *Sericin, Chitosan, Biodegradability, Biopolymer.*

1. Introduction

There is a tremendous pollution occurred due to use of numerous synthetic dyes, chemicals, auxiliaries, finishes, etc in production and wet processing steps of textiles. Thus, there is need to replace these synthetic dyes, finishes and auxiliaries with suitable alternatives. Natural biopolymer can be a good alternatives to synthetic toxic chemicals and auxiliaries in textile wet processing being biodegradable and renewable with abundant availability. Biopolymer such as sericin, chitosan, cellulose, glycogen, starch, gums, proteins can be extracted from natural plants, animals, bacteria, fungi without any adverse effect on environment. Chitosan and sericin are obtained as byproducts waste and have numerous sustainable applications in various industries. The present paper emphasis applications of chitosan and sericin in textiles and allied industries in detail.

Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in outer skeleton of insects, crabs, shrimps and lobsters. It is abundantly available in nature and is cheap to be procured from sea food waste. Chitosan is derived from chitin via deacetylation by alkaline hydrolysis reaction at high temperature. Chitosan is partially N- acetylated Poly beta (1-4) anhydro-D- glucosamine polysaccharide derived from the natural polymer chitin. It shows good biocompatibility, bio-absorbability, wound-healing, anti-infection, anti-bacterial, non-toxicity and adsorption properties. Chitosan is a cationic polyelectrolyte, a natural biopolymer with a molecular structure very similar to cellulose. It resembles the structure of cellulose closely, with the hydroxyl ion at the α -carbon atom replaced by an amine group. The possibilities of Chitosan applications in textiles were initially realized being its close resemblance to the cellulose polymer, which is the most common component of the natural textile fibres. The chemical structures of chitin and chitosan are given below in Fig. 1.

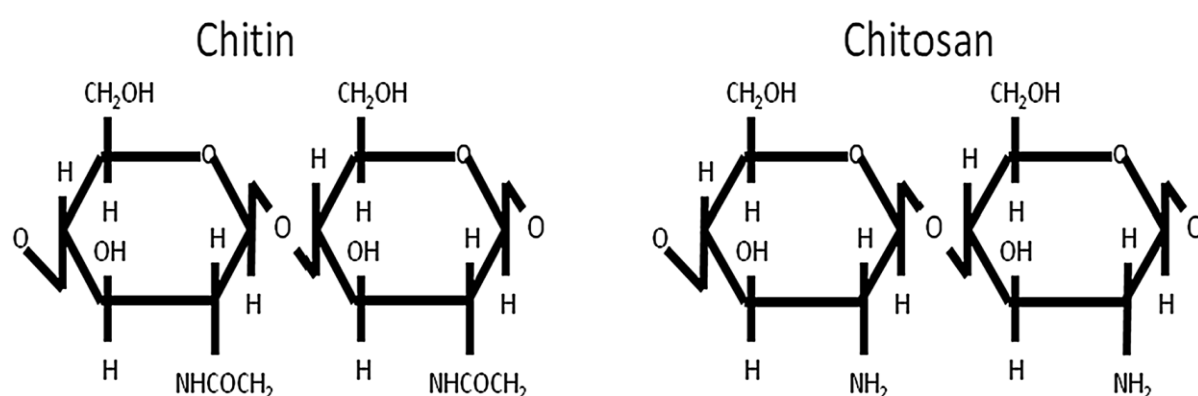


Figure 1: Structure of Chitin and Chitosan [9]

Silk fibre is made of two types of proteins – Silk fibroin and Sericin. Silk fibroin is the crystalline protein chains that forms the silk filament and gives its unique physical and chemical properties. Silk filament, a double strand of fibroin, is held together by a gummy substance called silk sericin or silk gum. In preparatory wet processing sericin needs to be removed from silk to get appropriate lustre on silk filament. Thus, sericin is a waste byproduct of silk industries. It is characterized by its high content of serine and other 18 amino acids. It has a combination of many unique properties such as biodegradability, nontoxicity, oxidation resistance, antimicrobial activity, UV resistance and moisture absorption. There are different methods of isolation of sericin from silk filament. Solubility, molecular weight and gelling properties of sericin depend on the method of isolation. Silk sericin is a highly hydrophilic proteinaceous macromolecule having molecular weight ranges from 24 to 400 kDa. Its consists of polar side chains made of hydroxyl, carboxyl and amino groups that enables easy cross linking, copolymerization and blending with other polymers to form improved biodegradable materials. The carbon, hydrogen, oxygen and nitrogen composition in sericin and fibroin varies a little as given below in Table1.

Table 1: Composition of Fibroin and Sericin [2]

	Fibroin %	Sericin %
C	47.6	46.5

H	6.4	6.0
N	18.3	16.5
O	27.7	31.5

Sericin contains different amino acids such as in fibroin but the amount of different amino acids is not same as in fibroin. The different amino acids are present in sericin are given below as in table 2.

Table 2: Different amino acids present in Sericin [2]

Amino acid	Percentage
Lysine	20-30
Serine	7-16
Glycine	10-20
Aspartic acid	7-10
Glutamic acid	4-6
Threonine	3-10
Histidine	3-6
Arginine	5-15
Tyrosine	4-6

2. Properties

The properties of chitosan and sericin are given below as follows:

2.1 Chitosan properties

Chitosan, the deacetylated product of chitin in which mostly nitrogen occurs in the form of primary aliphatic amino groups. Therefore it undergoes various types of amine reactions such as N-acylation and Schiff reactions. Chitosan is soluble in dilute acids such as acetic acid, formic acid etc. The properties of chitosan are dependent on various parameters as follows:

2.1.1 Degree of Acetylation

Chitin is N-deacetylated such an extent that it becomes soluble in aqueous dilute acetic and formic acids by formation of chitosan. Chitosan is a partially or fully N- deacetylated chitin with a degree of acetylation less than 0.35. The degree of acetylation depends on the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units.

2.1.2 Molecular Mass distribution

The weight average molecular weight (M_w) of chitin and chitosan is determined by light scattering and viscometer. When chitin converts into chitosan then molecular weight reduces due to change in degree

of acetylation. The weight reduced from chitin to chitosan is from $(1.03 - 2.5) \times 10^6$ to $(1 - 5) \times 10^5$. The other properties of chitosan are given below as following-

- Mostly naturally occurring polysaccharides are neutral or acidic in nature but chitosan is a highly basic polysaccharide.
- Chitosan solubilizes in various acidic acids solvents. It has been also reported that it is also soluble in N-methyl morpholine-N- oxide (NMMO) / H₂O.
- Chitosan forms aldimines and ketimines with aldehydes and ketones respectively, at room temperatures. They retain the film-forming property of chitosan.

2.2 Sericin properties

Silk sericin is a unique protein due to its various non-conventional properties, which are given below as following:

2.2.1 Solubility

Sericin is partial soluble protein in hot water. Solubility of sericin may be increased by addition of poly sodium acrylate and it may be decreased by addition of formaldehyde, polyacrylamide or resin based finishes. Sericin is also categorized as α -sericin and β -sericin by some researchers depends on the sericin position within the layer of cocoon. The first one is located in the outer most layer and it has high solubility in hot water due to presence of smaller amount of carbon and hydrogen atoms. The second one is the inner layer having large amount of nitrogen and oxygen atoms keeps it less soluble compared to α -sericin. [2]

2.2.2 Property of gelling

Sericin consists of random coil and β -sheet structure. Random coil structure soluble in hot water, on decreasing the temperature its converts into the β -sheet structure, this results in gel formation. So Sericin has sol-gel property as it easily dissolves into water at 50-60°C and again returns to gel on cooling.

2.2.3 Isoelectric point

The pH of solution at which molecule carries no net electric charge is refereed to isoelectric of that molecule or polymer. The isoelectric point of sericin has been reported between 3.5 to 4 due to greater amount of acid-amino acids than basics. [2]

2.2.4 Molecular weight

The molecular weight of sericin depends on extraction methods such as acidic, alkaline, and enzymatic along with process parameter of degumming such as pH, temperature, pressure and processing time. When it is extracted from cocoons it is ranges from 40-400 kDa and when it extracted from the worms it ranges from 80-310 kDa.

3. Applications of Chitosan and Sericin

3.1 Chitosan Applications

Chitosan finds broad applications in the different fields, such as biomedical, pharmacy, cosmetics, agriculture, food industry, environmental protection and textile industry due to its fibre grade properties, coating ability, excellent biocompatibility, biodegradability, nontoxicity and good miscibility with other polymers. It has multiple applications in textile processing such as antibacterial, anti-wrinkle, dyeing and antistatic finishing of textiles. The brief discussion about the applications of chitosan in several industries are given below as following: [14]

3.1.1 Food Industry

In the food industry, chitosan is used as antimicrobial and antioxidant agent (food protection), for antimicrobial coatings of fruits and vegetables, also used as nutritional ingredient (food additives, functional foods). It shows outstanding antimicrobial activities and coating against microorganisms because it is cationic in character and bioactive in nature.

3.1.2 Cosmetics

Chitosan is used in cosmetics due to its bacterostatic, film-forming, fungistatic, antistatic, and moisture retaining properties. It is of great interest in cosmetic formulations because it is compatible with other ingredients such as starch, glucose, oils, fats, waxes, acids, and non-ionic watersoluble gums, etc. So it is used in solution form for functional additives, in powder form for moisturizers to maintain skin moisture and tone skin, also used in different products such as shampoo, creams, skin creams, creams for acne treatment, hair sprays, hair colourants, soap, bath agent, etc.

3.1.3 Agriculture

Chitosan is extensively used in plant protection, antifungal, antibacterial, and seed soaking materials for agriculture. It is used in spray form for coating materials in seeds, fruits, and vegetables, in powder form for increase of crop yields, in gel form for to reduce the growth of phytopathogenic fungi, in pesticide formulations bio-pesticides, bio-fungicides, spray for pesticide removal, and also used in fertilizers and biocontrol agents.

3.1.4 Pharmacy and Medicine

In pharmacy, the main properties required is the controlled release of drug. Chitosan and its derivatives may be used as solutions, gels, tablets, capsules, fibres, films, and sponges. It is used in various drugs in the form of gels for cross linking reactions (lidocaine), tablets for matrix coating (salicylic acid), in capsules (insulin) and in the medicines chitosan is used for biocompatible and biodegradable materials for use as implants, blood substitutes, blood vessels, wound dressing materials , sutures, surgical threads, bandages, and dental implants, etc.

3.1.5 Textile Applications

Due to various suitable properties of chitosan such as cost effective, nontoxic, biocompatible, biodegradable, antistatic activity, antimicrobial activity, chelating property, deodorizing property, film forming ability, chemical reactivity dyeing improvement ability, thickening property and also wound healing property it has too many applications in textile industries. The broad applications of chitosan in textile industries are given below in Table 3.

Table 3: Applications of Chitosan and its derivatives in Textile Industry [14]

Topic	Forms	Applications
Textiles	Microcapsule	Dye binders for textiles
Functional textiles	Gel	Impregnated Textile material
Cosmetotextiles	Gelatinous Dispersion	Binding agent for nonwoven
Medical textiles	Coating	Surface modification of textiles
	Fibre	Textiles with antibacterial properties
		Textile printing and antimicrobial finishing
		Textile preservative and deodorant agent
		Non-allergenic fibres
		Sanitary fibrous products
		Surgical threads

3.1.6 Chitosan Applications in Textile processing

The functional properties such as antibacterial, anti-wrinkle, dyeing, antistatic, etc. provided by chitosan make it suitable ecofriendly agents for textiles. The applications of chitosan are as follows [9, 16, 17] -

- Chitosan in antibacterial finishing of textiles by using citric acid as a cross linking agent and sodium dihydrogen phosphate as a catalyst onto cotton textiles to give them effective antibacterial properties.
- Application of chitosan in conjunction of anti-wrinkle finishing agents reported to give suitable modification on textile surface. It was observed that when fabric is treated with chitosan solution in 1% w/v acetic acid then it forms water insoluble protective layer on the fabric surface on drying and make the fabric stronger and less deformable.
- In textile dyeing chitosan is used as dye deepening agent because it is a cationic polymer so it is best suited for anionic dyes for fixing agent. It also improves the surface properties of the fabric.
- Chitosan is excellent hygroscopic agent being presence of strong polar groups such as hydroxyl and amino acids in its structure. The chitosan layer on fabric surface forms continuous water

film which also dissolve electrolyte present in the atmosphere. Thus, it imparts antistatic properties to hydrophobic fabrics by increasing the electrical conductivity of the fabric surface.

- Chitosan can be used as bio-mordanting agent in applications of natural dyes as alternative to heavy metals as well as for improving the antibacterial properties of the dyed fabric [18-20].

3.2 Sericin Applications

Due to various valuable properties like gelling, moisture absorption, antioxidant, anti-bacterial, etc in Sericin has got wide application in different industries such as food, cosmetics, medical, pharmaceuticals, textile, etc. due to its gelling, moisture absorption, antioxidant, anti-bacterial, etc. properties. The details of various sericin applications [21] in different industries are as follows:

3.2.1 Food Industry

Sericin has so many applications in food industries due to its antioxidant properties. It is useful in improving the presence of some important minerals (Zn, Mg, Fe, Ca) in food or food additives. It is also used for fruit protection from ageing due to its antioxidant activity by applying sericin layer. It is good cholesterol controlling agents hence wide applications in weight control food additives and medicines.

3.2.2 Cosmetic Applications

Sericin is used in cosmetic products for skin, hair and nails being its important biocompatible, hygroscopic, biodegradable, antioxidant, etc. properties. It is used in skin care products for improving skin elasticity, anti-wrinkle, anti-ageing, moisturizing, cleansing and UV protection effect. In hair care it is used for conditioning, cleansing and hair damage prevention. In nail care products, it is used in prevention of nail cracks, brittleness and to increase the inherent brightness.

3.2.3 Medical Applications

Sericin has antioxidant and anticoagulant properties hence it can be used widely in medical textiles as well as in bioremediation. It is also used in cancer prevention, drug delivery, wound healing, fat control and in constipation treatment [13].

3.3.4 Textile Applications

Sericin textile applications are very versatile and the applications are given below as following [11] -

- Sericin can be used as finishing agent in filter fabrics. It can be coated on nylon and polyester which are used for indoor air filters to reduce the amount of fungi and bacteria. Hence simple coating of sericin waste increases the value of air filters.
- Sericin improves the touch and antibacterial activity of wool and other fabrics.
- Sericin improves the frictional and hygroscopic property of synthetic fibres.
- Sericin is used as raw material for the development of contact lenses. Oxygen permeable membranes are made up of sericin with water used for contact lenses and artificial skin.

- Sericin has wound healing property so it can be used as wound healing covering material in the form of film or sutures.
- Sericin derived from waste biomass is low cost and effective for removal of acidic dyes and other anionic dyes from water.
- Sericin, fibroin and PVA blended hydrogel gives better moisture absorbing and desorbing properties and increases elasticity also.

4. Conclusion

This review summarized the properties and applications of biopolymers chitosan and sericin. Both the biopolymers are sustainable being renewable and biodegradable as well as available abundantly. Both are harvested from waste or byproduct hence their production or extraction itself is bioremediation. Due to numerous valuable functional properties such as antibacterial, antioxidant, hygroscopic and biocompatible nature both has wide applicability in various industries. In textile they are widely used as auxiliaries and finishing agents. They have tremendous applications in personal hygiene, medical textiles, bio implants and other biomaterials being biocompatible. Thus the future of both biomaterials chitosan and sericin is very promising and exploration further in this field will definitely increase their applications in value added textile products.

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