REVIEW

THE OUTLOOK FOR CHITOSAN IN TEXTILES: A REVIEW OF THE LITERATURE SINCE THE START OF THE 2020'S

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1. Introduction

The textile field is immense. We could argue that clothing should be placed on the list with food and housing as critical needs. Textiles by definition are anything made from fibres. Traditionally, we classify textiles by use: apparel, home furnishings, and industrial. Worldwide, about 115 million metric tons of fibres will be manufactured in 2023. Of these, about 28 million metric tons are of natural fibres, such as cotton, silk, and wool. The incorporation of chitosan into textile products and processes continues to expand. Chitosan has a chemical affinity for these fibres compared with synthetic fibres such as polyester or polypropylene. Both cellulose and chitosan are β–(1→4)–linked polyglucopyranoses and wool as for any protein-based fibre have an excess of negative to positive charges.

Chitosan is used directly in textiles in two manners. First, it can be applied as a surface coating, to modify fibre properties, which is referred to as finishing. Because of the fine diameters of textile fibres, textile fabrics have relatively large surface areas compared with a film. Finishes are typically applied by dipping the fabric in a bath containing the finish agent and then running the fabric through pad rolls that squeeze out excess liquid. Finally, the fabric is sent through an oven to dry and cure the finish if it is chemically reactive with the substrate fibre. Second, chitosan can be converted directly to fibre or incorporated into bicomponent fibres, usually by mixing chitosan with cellulose in the viscose process. This article summarises the developments of these uses of chitosan since the beginning of the 2020s.

The primary uses of chitosan found in the literature since 2020 are:

- antimicrobial fibre finishes;
- flame retardant finishes;
- finishes for colour fastness;
- the use of chitosan microcapsules in finishing;
- medical textiles;
- chitosan fibres;
- decolourisation of textile waste water from dyeing operations.

There are a number of in depth review articles that thoroughly cover several of these applications [1–5].

2. Antimicrobial Fibre Finishes

The surfaces of textile fibres may provide ideal conditions to support bacteria and mildews. Hydrophilic fibres such as cotton found in many garments retain moisture and may be contaminated with sebum, the grease-like material that rubs off of skin. Sebum supports bacterial growth, which can lead to odours. This is also a critical problem for medical implant materials used in the human body.

When applied to the surface of a fibre, chitosan creates a bacteriostatic surface, when cationic, that resists colonisation by bacteria or mildew. Chitosan is only in the cationic state when in an acidic environment. Therefore, much work has focused on creating quaternary ammonium salts that maintain a cationic charge at a higher pH. These antimicrobial finishes have been developed for most if not all of the common apparel fibres. They are used primarily to control odour resulting from bacterial growth. The second area of focus has been for implantable medical devices. It is difficult to sterilise some devices because of their fragility or in the case of a textile hernia mesh, the large surface area provides refuge for some bacteria. Antimicrobial finishes are reported for many different medical implant materials.

Wang *et al.* [6] recently described the synthesis of a durable antimicrobial cotton fabric finished with a carboxymethyl chitosan modified with (3-carboxypropyl) trimethylammonium chloride. A critical aspect of many applied finishes like this is that they are removed by laundering. A garment may be laundered 50–100 cycles during use. In this case, the authors used the carboxy methyl moiety to form an ester link with cellulose to provide wash fastness, or resistance to being removed with laundering. They demonstrated a resistance to gram-negative and gram-positive bacteria and the fabric still had a bacterial reduction capacity of 99.9% after 120 laundering cycles.

3. Flame Retardant Finishes

Another functional finish is flame retardance. Cellulosic fibres are flammable and many injuries have occurred when curtains or furniture upholstery catch fire, a phenomenon that may occur when an individual falls asleep while smoking. Most synthetic fibres are melt extruded, so low-molecular-weight flame retardant compounds are mixed into the molten polymer and thus encapsulated inside the fibre structure. In the past some of these compositions were found to be carcinogens. TRIS BP, a brominated propyl phosphate, has been banned from polyester sleep wear since the 1970s.

Li *et al.* [7] described the use of phosphorylated chitosan for this use on cotton. It is the combination of the chitosanic nitrogen and the added phosphorus that provide the flame retardant action. The goal is that when the fabric is removed from an applied flame, it does not continue to burn, that is, it is self-extinguishing. The authors provided a comprehensive review of flame retardants used in cellulosic and synthetic fibres. As above, when we discussed the antimicrobial finishes, wet fastness is an important attribute. In this case, the authors ensured wash fastness by incorporating the phosphoryl groups. These groups are capable of covalently bonding chitosan to cellulose, which provides the self-extinguishing properties of a flame retardant.

4. Finishes for Colour Fastness

Frequently, the choice of colour is the last decision made in the manufacture of a garment. The application of dyestuffs to obtain these colours is a major activity within the textile industry. A large number of different classes of dyestuffs have been evaluated for all the various textile fibres. Chitosan has an affinity for cellulose as noted above, so we will focus on the use of chitosan in the dyeing of cotton fibres, a substantial fraction of the fibre used in apparel.

Each dyestuff class presents distinct chemistry. Direct and reactive dyes are two of the major classes used to dye cotton. Each class presents its own problems, but the general issues are exhausting or transferring the dye from the dye solution to the fibre surface. Then during use, the dye should not wash off or bleed. Furthermore, to process 1 kg of cotton fabric, up to 100 kg of water is consumed. Chitosan plays several roles in this process.

Again, it is the cationic nature of chitosan that makes it useful for these applications. Rehman *et al.* [8] recently demonstrated the enhancement of the dyeability of cotton with reactive dyes by precoating the fibre with chitosan using the pad dry method described above. Reactive dyes are based on cyanuric acid and have two reactive groups that form ethers with alcohols. They also bear ionic groups such as sulphates, which help with water solubility. Direct dyes also rely on sulphate groups for solubility in a dyebath. Reactive dyes have two problems. First, a percentage of the dye hydrolyses in the dyebath and loses its reactivity. Second, they tend to have lower molecular weights (about 500 g/mol) than direct dyes (about 700 g/mol). Hence, less reactive dye exhausts onto the fibre and more stays in the dyebath, because it is more soluble. Large quantities of salt may be added to the dyebath to force the dye onto the fibre. Chitosan improves both of these situations. First, any hydrolysed dye is still capable of forming an insoluble salt with the chitosan via its sulphate groups. The reactive dye can also form ether links with chitosan and possibly act as a crosslinker to bind the chitosan and dye to the cellulose in the cotton. All this results in greater exhaustion of the dye from the bath, which lowers pollution concerns and increases the colour fastness of the dye to cotton.

5. The Use of Chitosan Microcapsules in Finishing

The use of microcapsules to deliver textile finishes to fibre surfaces is a relatively recent innovation. An early example was the use of immobilised phase change materials to provide warming and cooling effects in response to environmental changes. Recently, Valle *et al.* [4] provided a comprehensive review of the manufacture and use of chitosan microcapsules (including 166 references cited). The use of chitosan microcapsules in textiles is motivated by the need to functionalise fabrics to provide a durable aroma, insect repellence, antimicrobial activity, and, as noted above, thermal comfort. Chitosan is valued in this application because it is biocompatible, nontoxic, and has inherent antimicrobial activity. The authors described the major methods to form microcapsules, which in many cases also work to yield nanoparticles. The purpose of the chitosan shell is to contain the active agent, to preserve it for some length of time, and then to control its release rate. Most of the methods employed with chitosan are ionic in nature, either coacervation or ionic gelation. There are also layering techniques to construct more complicated shells. All of these processes involve salt formation. In the case of coacervation, an anionic polyelectrolyte is added and a gel results. In other cases, chitosan may be ionically crosslinked with tripolyphosphate to obtain the microcapsule. Since 1988, when the first paper on microcapsules was published, to now, there has been an exponential growth in the number of published papers.

Valle *et al.* [4] included detailed tables that list the applications for which chitosan microcapsules have been used to modify fabrics. They can be classified into four (4) topics:

- to provide antimicrobial and antioxidant properties;
- to provide insect repellence;
- to provide durable fragrances;
- to provide a thermoregulating property by encapsulating materials that melt (to provide cooling) or freeze (to provide warming) at useful temperatures, so-called phase change materials.

One of the most active areas is the application of vitamins, skin moisturisers, and deodorants to sports and medical garments. These textiles are more technical and provide new markets and growth. Chitosan is just beginning to penetrate these new market opportunities.

6. Medical Textiles

The medical textile application of chitosan is the most active topic of publication in the textiles field. From 1 January 2020 to 15 April 2023, a search of chitosan medical textiles yielded 299 papers, including 47 review articles. These applications of chitosan, which are based on its chemical properties, reflect much of what has been discussed above. The antimicrobial properties are important for the surfaces of medical textile fibres, to prevent infections. Chemical methods to apply chitosan to most of the synthetic fibres have been developed. Due to its haemostatic properties, chitosan fibres have been incorporated into various wound dressings. The majority of the work seems to relate to the formation of nanoparticles to functionalise fabric and fibre surfaces.

There are too many references to cite here, but for example, the most recently published paper, as of this writing, was a study of the fabrication of chitosan-polyethylene oxide based nanofibre hydrogels as a scaffold for bone tissue engineering by Hakimi *et al.* [9]. Piekarska *et al.* [5] published a very recent review addressing medical applications, among others, of chitosan and chitin, including life cycle assessments.

7. Chitosan Fibres

The conversion of chitosan into fibres and films is well known. Chitosan is also incorporated into fibre structures, particularly with cellulose, as chitosan is compatible with the viscose process to obtain composite rayon-type fibres. In their two recent articles, Luo *et al.* [1, 2] discussed single component chitosan fibre and supply-side issues in the use of chitosan in the form of a textile, including many of the applications already discussed above.

There are several issues to keep in mind regarding the use of chitosan fibres for apparel. First, chitosan dissolves in weak acids, such as vinegar, which is problematic. The fibre can be crosslinked to avoid this, but that is an additional step in the manufacture of these fibres. Second, chitosan is a co-polymer of two sugars. Cellulose and all the synthetic textile fibres are homopolymers. This ensures that they crystallise well, which is key to fibre properties. Unless chitosan is highly deacetylated (>95%), it has a lower crystallinity compared with all these other fibres. This translates to poor mechanical properties and a large loss of strength when wet.

Luo *et al.* [1] noted that the functional textile market was valued at $175 billion in 2020. Fibres with superior performance or with additional unconventional functions are becoming mainstream in consumers' lifestyles. The authors noted that a single-component chitosan fibre compared with chitosan-modified cotton/wool/manmade fibres has advantages of better comfort, launderability, and abrasion resistance. Further they noted that as functional fibres enter the market, manufacturers in the middle and lower stream of the market need to identify the raw materials carefully. At present, there is no system for testing and evaluating functional fibres. Luo *et al.* [1] proposed such a system with a list of recommended tests to evaluate chitosan fibres as a functional textile fibre. They purchased six commercial chitosan fibre samples and tested them according to this protocol. As expected, they found that as the degree of deacetylation increases, the fibre strength and antimicrobial activity increase. In their 2022 paper, Luo *et al.* [2] provided an excellent review and road map for sourcing chitosan textiles.

8. Decolourisation of Textile Waste Water from Dyeing Operations

It is difficult to achieve 100% exhaustion of dyestuff from the dyebath onto the textile. Even if you do, not all of the dye will be bound to the fibre, so some dye will wash off during the final rinses. Thus, it is inevitable that there will be colour in the waste water, which first presents an aesthetic pollution problem. One milligram of dye per litre produces water with the appearance of cherry soda. There may also be other pollutants present, such as heavy metals.

In general, dyestuffs are not toxic. They are designed to be very stable molecules to last in the environment and to not fade. Methods that break the dye down and destroy the colour are not useful because the degradative products are likely to be more toxic than the dye. Adsorption to a substrate, a physical process, converts a water pollution problem into a solid waste problem. This is the preferred way to remove dyes from waste water.

Sirajudheen *et al.* [3] reviewed work utilising chitin- and chitosan-based beds for this purpose. It is a comprehensive treatment of this subject including over 200 references cited. The discussion of the nature of industrial water pollution is a very useful aspect of this article. The authors also discussed the myriad ways that chitin and chitosan are used as adsorbents. This includes pure chitin and chitosan and materials derivatised with chitin and chitosan. Also included is the use of mixtures composed of these polymers and various inorganic materials that enhance the action of the adsorbents. The authors also considered the physical form of chitin and chitosan, ranging from hydrogels to nanoparticles to granules.

9. Conclusions

The uses of chitosan as a textile chemical and fibre continue to increase. When considering the promotion of functional textiles, the issue of sustainability is well met by chitosan. The majority of uses of chitosan are for the surface treatments of fibres. Certainly, the COVID-19 pandemic has created opportunities for chitosan due to its antimicrobial properties when applied to fibre surfaces. Indeed, chitosan has been utilised in protective clothing for first responders and health care workers. Chitosan's structure and chemical properties mean that it is a multi-functional material on the surface of a textile. The cationic nature that renders a fibre surface bacteriostatic also improves colour fastness in cellulosic fibres. Chitosan fibres are commercially available. They provide new combinations of properties for designers to work with, especially for functional textiles. The most active aspect of this is the use of these fibres in medical textiles, especially those electrospun to fine diameters. This is the most active area in the literature. Moreover, since 2020, 22 patents that have 'chitosan' and 'textile' in the claim language have been issued. This averages out to a new patent every other month. The outlook for chitosan as a textile material is very positive, with so many possible applications that have already discovered.

10. References

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