Manufacture Techniques of Chitosan-Based Microcapsules to Enhance Functional Properties of Textiles

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Abstract

In recent years, the textile industry has been moving to novel concepts of products, which could deliver to the user, improved performances. Such smart textiles have been proven to have the potential to integrate within a commodity garment

advanced feature and functional properties of different kinds. Among those functionalities, considerable interest has been played in functionalizing commodity garments in order to make them positively interact with the human body and therefore being beneficial to the user health. This kind of functionalization generally exploits biopolymers, a class of materials that possess peculiar properties such as biocompatibility and biodegradability that make them suitable for bio-functional textile production. In the context of biopolymer chitosan has been proved to be an excellent potential candidate for this kind of application given its abundant availability and its chemical properties that it positively interacts with biological tissue. Notwithstanding the high potential of chitosan-based technologies in the textile sectors, several issues limit the large-scale production of such innovative garments. In facts the morphologies of chitosan structures should be optimized in order to make them better exploit the biological activity; moreover a suitable process for the application of chitosan structures to the textile must be designed. The application process should indeed not only allow an effective and durable fixation of chitosan to textile but also comply with environmental rules concerning pollution emission and utilization of harmful substances.

This chapter reviews the use of microencapsulation technique as an approach to effectively apply chitosan to the textile material while overcoming the significant limitations of finishing processes. The assembly of chitosan molecules into microcapsules was proved to boost the biological properties of the polymer thanks to a considerable increase in the surface area available for interactions with the living tissues. Moreover, the incorporation of different active substances into chitosan shells allows the design of multifunctional materials that effectively combine core and shell properties. Based on the kind of substances to be incorporated, several encapsulation processes have been developed. The literature evidences how the proper choices concerning encapsulation technology, chemical formulations, and process parameter allow tuning the properties and the performances of the obtained microcapsules. Furthermore, the microcapsules based finishing process have been reviewed evidencing how the microcapsules morphology can positively interact with textile substrate allowing an improvement in the durability of the treatment. The application of the chitosan shelled microcapsules was proved to be capable of imparting different functionalities to textile substrates opening possibilities for a new generation of garments with improved performances and with the potential of protecting the user from multiple harms. Lastly, a continuous interest was observed in improving the process and formulation design in order to avoid the usage of toxic substances, therefore, complying with an environmentally friendly approach.

Key-words Chitosan; Microencapsulation processes; Textile functionalization, Finishing treatments

Abbreviations

1 Introduction

The textile industry and research have continuously been evolving over the past 30 years. From the so-called traditional textile product, resulting from conventional processes, whose function was to protect and/or hide the wearer's body, it evolved into more technical products in the 1990's, to become more functional or multifunctional with the development of intelligent textiles, with regard to consumer demands and ecological criteria in the last decade. In this context, smart textiles have gained more and more research and development interests due to their potential functionalities, which bring high added values and increases the market possibilities. In this context, the use of the microencapsulation technologies to manufacture functional coating plays an important role to achieve smart coating textiles (Salaün 2016).

Nevertheless, the use of microencapsulation as a possible tool for the functionalization of textile supports was introduced very late in the process compared to other industrial sectors (Gordon 2001). Nowadays, it is applied for various textile applications, such as technical, medical or para-medical textiles, cosmetics and textiles for various functional properties such as aesthetic effects, protection, comfort or skin care. Such functional coatings, which provide additional benefits to users without changing the structure and basic characteristics of the product, are becoming necessary in the present highly competitive textile market (Erkan and Sariiski 2004).

The term "microencapsulation" derives from the Greek "mikros" and the Latin "en" and "capsula", small in a little box, respectively. Microencapsulation refers to the formation of polymeric particles entrapping a solid, liquid or gaseous active substance, and exhibiting several types of morphology, ranging from the microscale to nanoscale. This technology aims to immobilize, protect, structure, and release the active principle according to the specific end-use. According to Poncelet, microencapsulation is defined as the entrapment of a compound or system in a dispersed material to its immobilization, its protection, its control of transfer, its structure and its functionalization (Poncelet et al. 2007). Furthermore, the associated terminology to define the obtained particle varies according to the mean diameter. Thus, the term microparticle is used for a range in size between 1 and 1000 µm; macroparticle if it is higher than 1 mm, and for a sub-micronic range the particles are qualified as nanoparticles. The development of the microencapsulation technology is closely related to the progress of many technologies to realize an innovative component for a specific application. Thus, the main characteristics of the microcapsules may be designed as per the application, regarding size and shape, the shell physico-chemical properties, compatibility and permeability. Therefore, microparticles having porous, semi-porous or impermeable shell are used in different applications.

The different synthesis methods proposed in the scientific literature and patents, about 200, describe the formation of microcapsules from 3 stages, i.e., the enclosure of core component, formation of the microparticles, and hardening of it. The microencapsulation processes are divided into three main groups based on the mechanisms formation, i.e., mechanical, chemical and physico-chemical processes. The

cost of processing, the desired size, the use of organic solvents for health and environment considerations, the stability of the active principle are the main criteria to select a method rather than another. Furthermore, the polymer-solvent interactions occurring during the microencapsulation process have probably the stronger effect on morphology and properties of the obtained particles. Thus, the solvency of the oil phase affects each step of the microencapsulation process, and the choice of the solvent needs to take in account its properties to induce the polymer precipitation at in the interface during the first stage of the reaction, and also allows the diffusion of the macromolecular chains through this primary shell to induce it growing.

The functional performances of the microcapsules depend on the morphology, the chemical nature and the surface characteristics of the polymeric shell related to the process parameters (Yadav et al. 1990). Microcapsules can have various geometries and structures. Their morphologies depend on the physico-chemical characteristics of the core material, mainly related to solubility parameters, and the mechanism of the shell formation around it. Thus, these particles have either regular or irregular shapes, and on the basis their morphology, the mononuclear or core/shell structure is distinguished from the multinuclear or polynuclear particles, and matrix particle or microsphere (Fig. 1). The choice of a particular process is determined by the solubility characteristics of the active compound and the shell material for a specific end-use. The bioresourceable and biodegradable polymers, such as chitosan (Chi), gelatin, albumin, and alginate have been already used to encapsulate active substance due to their biocompatibility, good release properties, lack of toxicity, film-forming capacity, high mucoadhesivity, and tensile strength (Pedro et al. 2009; Alonso et al. 2010; Garud and Garud 2010).

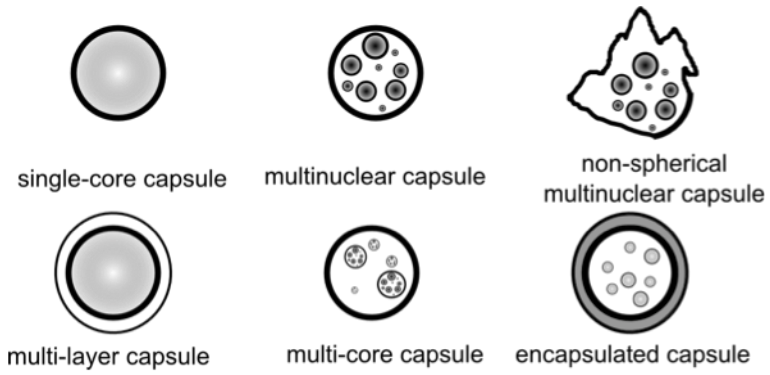


Fig. 1 Schematic representation of possible particle structures modified after Kondo (1979). Microparticles have regular or irregular shapes, and mononuclear or multinuclear structures with one or several layered-shell can be obtained.

Chitosan, a natural linear biopolymer of glucosamine monomers and a small amount of N-acetyl –glucosamine monomers, is obtained by alkaline N-deacetylation of chitin, which is the second most abundant polysaccharide in nature after cellulose (Kasaai 2010). Chitosan is considered to be an attractive biomaterial in the area of microencapsulation technology due to its biocompatible, biodegradable and nontoxic nature (Peng et al. 2010). Chitosan has received significant attention for developing microcapsules, and the main advantages of chitosan-based microcapsules as drug carriers are their controlled release properties and biocompatibility (Rokhade et al. 2007). It is also considered to be a good candidate for wall materials in textile finishing products encapsulation (Alonso et al. 2010). Various methods such as spray drying, phase coacervation have been used for the formation of chitosan microcapsules (Liu et al. 2011); the obtained microcapsules are either single or multilayer depending on microencapsulation method (Pothakamury and Barbosa-Cánovas 1995).

The peculiar chitosan nature, a hydrophilic polymer characterized by the cationic charges in acidic medium, allows designing mild microencapsulation methods in order to obtain micro or nanoparticles. The purpose of this chapter is to analyze the potential use of chitosan to design new textiles substrates and challenges of the chitosan-based textiles products research. The objectives of this paper are (i) to provide data on the interest to use this compound to functionalize the textile, (ii) to detail the main applications of chitosan-based textile processing, (iii) to consider the formation of chitosan particles through microencapsulation methods, (iv) to analyze the improvement of the performances of smart coating with these microparticles.

2 Chitosan-Based Textile Processing

The whole supply chain of textiles requires research efforts on how to establish the sustainability regarding health safety and cost. The use of chitosan is one of the main opportunities to develop new sustainable industrial practice in fiber production and fabric treatments. Thus, the blended and modified chitosan-based materials extend the availability of various high-end functional textiles with reasonable cost, and then improve the development of the finishing process.

Over the last decade, chitosan has been used in the textile field either under fiber form or in the finishing process as a substitute to conventional polymeric binders. Chitosan fibers are obtained either from spinning processes, i.e., wet spinning, dry spinning, or electrospinning. Chitosan is solubilized in an acid solution before extrusion in an alkaline coagulation bath during the two first methods. The use of chitosan as a binder in the finishing treatment allows protecting the fabric from degradation against the attack of the oxidizer and maintains similar mechanical properties to the untreated bleached fabric. Moreover, it finds some applications in various processes such as a sizing and desizing agent for textile pretreatment (Stegmaier et al. 2008), an auxiliary for dyeing (Ramadan et al. 2011), or a binder for printing (Bahmani et al. 2000).

Cotton fabric has a high shrinkage characteristic, corresponding to an irreversible change in the dimensions, during wetting, washing or drying processes. In most cases, crosslinking agents are used to overcome this phenomenon, and to increase the elastic shrinkage, which is reversible to it. Fragmented chitosan, with an oxidizing agent, allows its diffusion into the textile substrate to create a network with fibers, resulting in the recovery angle increase, and therefore reducing the wrinkle property of fabric, and develop durable press finishing process (Huang et al. 2008).

Chitosan has a high moisture regain value, and therefore it may be applied as an antistatic finishing agent on the textile surface (Abdel-Halim et al. 2010). Therefore, chitosan treated fabrics enable to absorb a very significant amount of water from the surrounding medium, which results in the increase in electrical conductivity following the lower propensity to produce static charges.

Chitosan-treated fabrics and fibers are used for the production of antibacterial fabrics for a working environment such as a hospital, biotechnology research lab, cosmetics, industries, and so on. The charged amino group of chitosan interacts with the cell wall of microbes leading to the degradation of protein and intracellular constituents, and thus their causing cell death (Alonso et al. 2009). These antibacterial properties required significant interactions between chitosan amino groups and cell wall; for this reason, a high concentration of chitosan, which led to the synthesis of nanosized chitosan particles having a higher specific surface area was proposed as a strategy to increase the chitosan-cell interactions. Nevertheless, chitosan is often coupled with other antibacterial compounds such as silver, to fight against large varieties of the microbes (Ali et al. 2011). In most of the cases, the chitosan formulation required the use of a coupling agent, such as glutaraldehyde, butane tetracarboxylic acid, citric acid, potassium permanganate, and sodium hypophosphite, to be covalently bonded to the textile fibers, either cellulose or wool.

The adding of graphene particles into a chitosan coating allows developing a cotton fabric as UV blocker (Tian et al. 2015). The modification of the surface fabric state by the incorporation of nanoscale chitosan coating has been found to increase the substrate roughness to provide water repellent properties. Nevertheless, to maintain the shelf life of the hydrophobic behavior, this treatment is usually coupled with silicon and/or fluoride treatment (Ivanova et al. 2013).

Chitosan, being a nitrogen-containing polysaccharide, can provide a char-forming property for use as intumescent additives. Furthermore, it can also act as a blowing agent with the release of nitrogen compounds during its degradation. Nevertheless, to be effective, it needs to be coupled with phosphorous species, such as phytic acid (Laufer et al. 2012), sodium polyphosphate (Charuchinda and Srikulkit 2005), orthophosphoric acid (Abou-Okeil et al. 2007), phosphate-nickel (Hu et al. 2012), melamine phosphate (Leistner et al. 2015), diammonium hydrogen phosphate (El-Tahlawy 2008), etc. The presence of ammonium in the mixture may provide a synergistic effect with phosphate groups for flame retardancy properties (Kandola et al. 1996).

3 Chitosan-Based Microencapsulation Methods for Textile Applications

Microencapsulation technology is in growing expansion in the textile field due to the potentiality and versatility in terms of applications. The process allows coating some tiny particles of an active substance with a continuous film of a determined size range. Furthermore, it allows the core materials to be released under controlled conditions enhancing their specific functionalities. The release kinetics mainly depends on the selection of the wall materials, microencapsulation methods, and also the specific end uses. The delivery of the active substance can be achieved by shell permeability changes or degradation from external stimuli, i.e., friction, pressure, temperature, diffusion through the polymer wall, dissolution of the polymer wall coating, or biodegradation.

The advantages of implementing functionalities onto textiles via microencapsulation are as follows:

1. protection of unstable and sensitive agents from the external environment before and during use, i.e., heat, acidity, alkalinity, moisture, or evaporation;
2. controlled or sustained release of the active substance if required through various media;
3. improvement of shelf-life against degradative reactions, i.e., oxidation and dehydration mechanisms;
4. increase in the compatibility between active substances of different nature;
5. increase in the effectiveness of the functionality with the increase of the specific contact surface area,
6. increase in the compatibility of finishes with other chemical processes and the possibility of combined-bath treatments;
7. improvements in solubility, dispersibility, and flowability for better finishing treatments ;
8. and convenience in the handling of active substances.

The main suitable microencapsulation methods used for a textile application are based on physical-chemical methods, since they lead to the formation of particles with a mean diameter lower than 40 micrometers. They can be applied onto the surface substrate by conventional finishing processes. Therefore, they include simple and complex phase coacervation, emulsion precipitation or chemical crosslinking (**Table 1**). Spray drying method may also be used, as a mechanical process, for specific applications or to obtain dried powder.

Table 1 Examples of core-shell materials used in chitosan-based microencapsulation for textile applications

Simple coacervation			
Polymer	**Coacervation agent**	**Active substance**	**Reference**

Chitosan	NaOH	Essential Oil	Souza et al. 2014b
		Berberine	Lam et al. 2013
		Miconazole nitrate / Jojoba oil	Yuen et al. 2012
Chitosan	SDS	Linseed Oil	Chatterjee et al. 2012; Chatterjee et al. 2014b, 2014a; Chatterjee et al. 2014c
Chitosan	Sodium tripolyphosphate	Flagrance	Hu et al. 2011
Chitosan	Glutaraldehyde	Herbal extract	Chandrasekar et al. 2014

Complex coacervation

Polymer 1	**Polymer 2**	**Active substance**	**Reference**
Chitosan	Gum Arabic	Dye	Butstraen and Salaün 2014
		Lime oil	Wijesirigunawardana and K. Perera 2018
		Limonene/vanillin	Sharkawy et al. 2017
		Lemon essential oil	
Chitosan	Silk fibroin	PCM	Deveci and Basal 2009
Chitosan	Gelatin	Antibacterial compound	
		Citronella oil	Specos et al. 2010
		Patchouli oil	Liu et al. 2013
		Limonene	Prata and Grosso 2015
		Lemon oil	Chelaru et al. 2015
		Zanthoxylum limonella oil (Genipin)	Maji and Hussain 2008
Chitosan	Collagen	Lavender oil	Ocak 2012
Chitosan	Carboxymethyl cellulose	n-hexadecane	Roy et al. 2018a
Chitosan	clay-nano particles	n-eicosane	Genç and Alay Aksoy 2106

Emulsion - precipitation

Shell	**Precipitation agent**	**Core substance**	**Reference**
Chitosan	NaOH	Essential oil	Javid et al. 2014

Emulsion-chemical crosslinking

Shell	**Shell crosslinker**	**Core substance**	**Reference**
Chitosan	Glutaraldehyde	polyurethane photochromic microcapsules	Fan et al. 2015
	TPP	Neem extract	Rajendran et al. 2012

Miscellaneous microencapsulation process.

Methods	Shell hardener	Core substance	Reference
Ionic gelification	NaOH, TPP	Rose fragrance	Hu et al. 2011
Sonofication	Alginate (layer-by-layer)	Antimicrobial	Antunes et al. 2014
Spray drying		Vanilin	Yang et al. 2014
		Orange oil	Li et al. 2013
Surfactant-free dispersion copolymerization	PolyNiPAAM-chitosan	---	Kulkarni et al. 2010

3.1 Coacervation and Precipitation Methods

Phase coacervation is one of the oldest and widely used microencapsulation techniques and can be divided into two groups, i.e., simple coacervation implying the use of one colloidal solute, and complex coacervation, in which the polymeric solution is obtained from the interactions of two oppositely charged colloids. Coacervation corresponds to the separation of a macromolecular solution into two immiscible liquid phases, i.e., a dense coacervate phase and a dilute equilibrium phase. These methods are carried out in four consecutive steps carried out under stirring, i.e., (i) dispersion of the active substance in a solution of a surface-active hydrocolloid; (ii) precipitation of the hydrocolloid onto the dispersed droplets by lowering the solubility of the hydrocolloid, e.g., non solvent, pH change, temperature or electrolyte; (iii) addition of a second hydrocolloid to induce the polymer-polymer complex in the case of complex coacervation; and (iv) stabilization and hardening of the microcapsules by crosslinking agent additions.

3.1.1 Simple coacervation

The simple coacervation is based on the desolvation phenomenon occuring by blowing a chitosan solution into an alkaline precipitation medium, on the addition of a poor solvent to the hydrophilic colloidal solution, resulting in the formation of two phases, i.e., one rich in colloid particles or coacervate, and (ii) the other without coacervate. To induce this, sodium sulfate, alcohol or acetone may add gradually into the solution with continuous stirring.

Chatterjee et al. have studied the formation of multilayer microcapsules carried out by phase coacervation method based on ionic interactions between oppositely charged chitosan and sodium monododecyl sulfate (SDS) as wall materials (Chatterjee et al. 2014a). The microencapsulation method started with the preparation of an oil in water emulsion using SDS as an anionic emulsifier. The dilution

during microcapsule formation was applied to reduce the repulsion between positively charged microcapsules and free chitosan macromolecules during the microencapsulation process and decrease the viscosity of the microcapsules suspension. The microcapsules formed after 11 alternated additions of chitosan and SDS by phase coacervation process were treated with alkali for drying in a liquid medium to solidify the outermost shell and charge neutralization of amine groups of chitosan on the microcapsules surface. Nevertheless, they observed that this treatment led to the formation of flocculi in the suspension rising to some undesired gel formation. This is the main drawback for commercial use of this slurry in various applications especially for textiles. A small amount of butanol was added in alkali solution to overcome this drawback. The alcohol allows restricting swelling of the outermost shell of microcapsules. After that, the samples were subject to react with trisodium citrate solution for buffering action and ionic cross-linking. Cationic polyamine may attain ordered microcapsule structure under specific salt solutions, and the presence of counter-ion in the solution leads to the formation of ordered microcapsules structure from ionically cross-linked polymers (Rana et al. 2004).

3.1.2 Complex Coacervation

When microcapsules were prepared by complex coacervation, the process consists in four consecutive steps. The first step involved the solubilization or dissolution of the biopolymers in aqueous solution. Thus, low concentrated chitosan solution was prepared by dissolving chitosan powder in acetic acid, and left under magnetic stirring for several hours until complete dissolution. The required amount of anionic polymer, Arabic gum or gelatin (**Fig. 2**) was also solubilized in an aqueous medium. In the second step, the two aqueous solutions were mixed together, prior adding of core substance to be emulsified at high shearing rate. In most the cases, the bath temperature is relatively high to decrease the viscosity of the solutions and to favor the obtaining of narrow size distribution and low mean diameter of the dispersed core substance droplets. The induction of the polymers coacervation, by decreasing the pH with acid at low stirring rate is done in the third step. For example, the maximization of the cationic charges of chitosan is obtained in a pH range between 2.8 to 4, whereas for Arabic gum, the negative charges are found at a pH higher than 2.2. The next step is the gelation of the system by reducing the bath temperature between 5 to 10°C, and before introducing the cross-linkers such as tannic acid, glutaraldehyde, or genipin (Fig. 3).

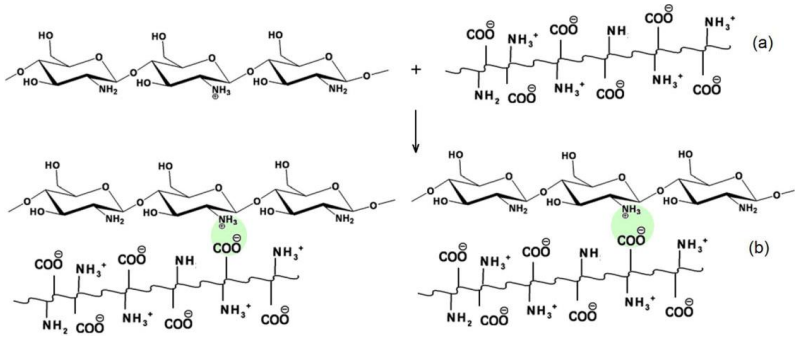


Fig. 2 Possible reaction mechanisms: (a) chitosan and gelatin microstructure and (b) ion exchange in acetic acid and possible reaction mechanism between chitosan and gelatin (Samimi Gharaie et al. 2018).

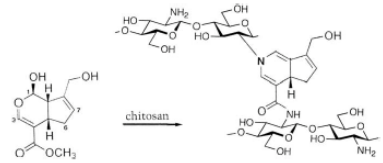


Fig. 3 Genipin reacts with chitosan to yield two main crosslinking reactions. On the right, two chitosan chains (represented by their structural units) are crosslinked by one mole of genipin: the formula shows the two newly formed chemical groups, namely the monosubstituted amide and the tertiary amine (Muzzarelli 2009).

The synthesis of microcapsules from Pickering emulsion approach is an attractive way to design the particles. This process is based on the preparation of a particle-stabilized emulsion. The diffusion of the particles, solid or coacervates, stabilize the interface against droplet coalescence by reducing the interfacial energy of the system.

Zhang et al. (2018) have studied the ability of functionalized reduced graphene oxide to stabilize chitosan emulsions in w/o Pickering emulsifications, in which toluene is the continuous phase and a chitosan aqueous solution is the discontinuous phase. They observed that the use of functionalized reduced graphene oxide as a stabilizer provides a flexible way to design hydrophilic polymer droplets or microcapsules for controllable drug release behavior. Chitosan-type B gelatin may also be used as Pickering particle to stabilize emulsion (Roy et al. 2018b). The increase of gelatin B amount in the biopolymer ratio, as well as the biopolymer concentration, narrows the particle size distribution, due to the capture of the obtained droplets after the homogenization step in denser emulsions. The formation of chitosan-gelatin complex occurs via non-Coulombic interactions (Kovach et al. 2016). These coacervated particles stabilize the interface, and after coalescence and by introducing a cross-linkers, hardened particles can be obtained.

3.2 Water-in-Oil Emulsion and Chemical Cross-Linking

The water-in-oil emulsion followed by chemical cross-linking reaction in one the first method used to the synthesis of chitosan nanoparticles (**Fig. 4**). Chitosan is firstly dispersed in an aqueous acidic phase containing an active substance, emulsified in an organic solvent, such as toluene or paraffin, with a suitable surfactant such Span 80. The emulsion was cooled below 10°C to induce gelation, and the pH was adjusted to 9-10 with soda. In the last stage, the addition of a cross-linking agent allows the formation of hardening particles. The stirring speed, as well as the amount of cross-linkers, are the main factors affecting the mean diameter and particle size distribution (Agnihotri et al. 2004). One of the main drawbacks of this method is the use of toxic cross-linkers, such as glutaraldehyde (**Fig. 5**). In some cases, the addition of aqueous of methanolic NaOH can also further harden the obtained particles.

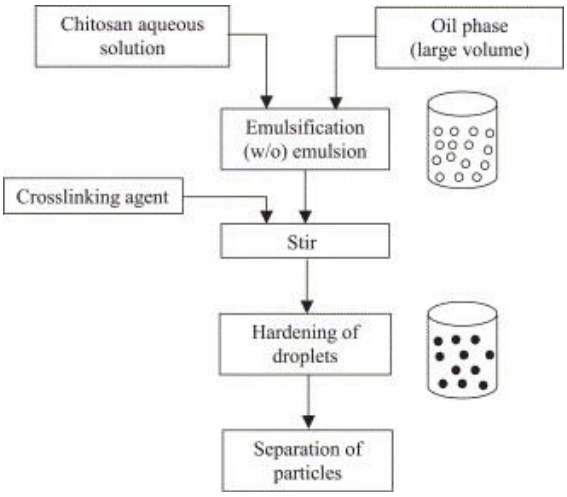


Fig. 4. Schematic representation of preparation of chitosan particulate systems by emulsion cross-linking method (reprinted with permission from Agnihotri et al. (2004))

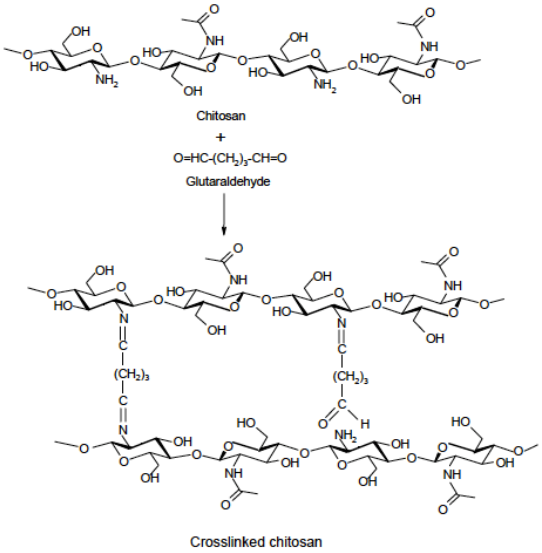


Fig. 5 Chitosan molecules reacting with glutaraldehyde to form crosslinked chitosan (reprinted with permission from Yang et al. (2004))

Emulsion cross-link method presents few drawbacks, the method is tedious and involves the use of harsh cross-linkers, which can react with the polymer or the active substance. Furthermore, the particle size distribution is sometimes higher than the required one for a textile application.

3.3 Ionic Cross-Linking Method

Ionic cross-linking method represents one of the mild ways to synthetize chitosan micro and nanoparticles loaded with an active substance. The formation of the particles is due to the ionic interaction between the positively charge amino groups of chitosan and the anionic charges molecules, such as sodium tripolyphosphate, cyclodextrin derivative, or anionic macromolecules. Thus, this method is based on the ionic attractions of differentially charge macromolecules to synthesize particles. Tripolyphosphate is one of the main common compounds used to induce cross-linking, since it is a multivalent nontoxic molecule, and its tripolyphosphoric groups form gelates through ionic interaction with positively charged amino groups of chitosan. Sodium tripolyphosphate solution is added dropwise to the acidic solution of chitosan, which induces ionic gelation and droplet precipitation (Fig. 6). The concentration of chitosan, ratio of chitosan/ sodium tripolyphosphate, ionic strength, shear strength, stirring time and pH of the solution are the main parameters influencing the kinetics and the gel formation step. The particle size as well as the surface

charge density may be designed or controlled to modify the release behavior and the functionality of the microcapsules.

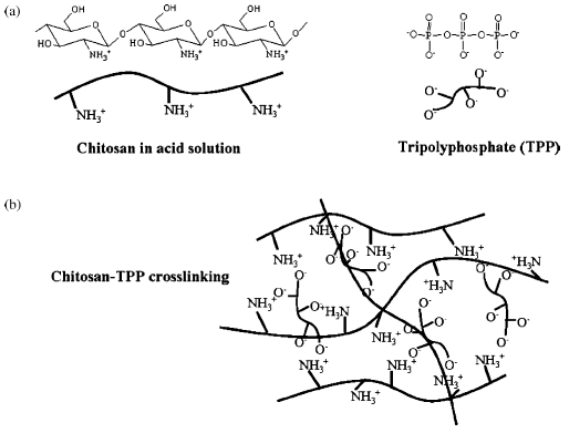


Fig. 6 (a) Molecular structure of chitosan in acid solution and that of tripolyphosphate (TPP). (b) Ionic crosslinking between chitosan and TPP (reprinted with permission from Hsieh et al. (2008))

3.4 Miscellaneous Microencapsulation Process

Chitosan miscellaneous microencapsulation processes are most of time designed for particular applications, such as a double walled formation, the formation of microspheres, or nanoparticles.

4 Textiles Functionalization and Properties

Textile fabrics can be functionalized with chitosan microcapsules by using one of the following finishing treatment (Yip and Luk 2016):

1. prior padding the fabric, it is immersed into the microcapsule suspension followed by curing for fixation;
2. exhaustion method in which the fabric is soaked in the microcapsule suspension for a given time under controlled, the exhaustion process is usually followed by curing for fixation;
3. spraying the microcapsules onto the fabric followed by fixation and/or curing;
4. screen printing microcapsules with an appropriate binder and thickener onto the fabric followed by curing for fixation;

5. and embedding microcapsules onto fabric that has undergone surface modification, such as via atmospheric pressure plasma by using one of the techniques listed in (1) to (4), followed by thermal fixation with a fixing agent that contains a monomeric or oligomeric cross-linker.

4.1 Textiles Finishing Treatments

The step of encapsulation allows manufacturing textiles containing microcapsules by various ways to fix the microcapsules within the fiber structure permanently, to embed them into a binder, to mix them into foam or to graft them according to the expected end-use and the microcapsules shell properties. The microcapsules should have some suitable characteristics to be used in the textile field, i.e, a narrow size distribution, a core to shell ratio with a core content as high as possible; stability to mechanical action and high thermal and chemical properties; and also adequate compatibility or affinity with the textile substrate and the binder used. The choice of the textile finishing process to functionalize the fabrics needs to take into account (i) the characteristics of the textile in terms of chemical nature, fiber type, construction design, (ii) the durability of the microcapsules in regards to their effectiveness, (iii) the availability of the machinery, (iv) the cost to benefits ratio, and (v) the environmental considerations and legislation as well as compatibility with other finishes.

Chitosan microcapsules can be applied by conventional finishing techniques or during the rinse cycle of a washing machine on any fabric (woven, nonwoven, knitted or garments) regardless of its nature (natural, synthetic) (**Table 2**). On the other hand, one of the challenges of the textile research is to ensure the durability of the functional properties of the microcapsules treatment with repeated used, when in some applications they may be damaged during washing cycles (at least 20 washing cycles), ironing or tumble drying.

Impregnation is one of the more appropriate finishing methods to embed microcapsules onto the textile surface due to a lack of affinity between the microcapsules and the textile substrate (Monllor et al. 2007). In most of time, microcapsules solutions are mixed with a dispersant to promote their diffusion through the textile material, followed by the addition of a crosslinking agent in order to bind them to the substrate. In an exhausting process, the fabrics or garments are introduced in a dyeing apparatus with water. A formulation containing the microcapsule dispersion, the polymeric binder, the auxiliaries and acids/bases for pH adjustment, is then introduced in the apparatus at defined times, speeds, temperature, and pH to allow the fixation onto the textiles. In a padding process, the fabric goes through the finishing bath containing the microcapsules, a softener, wetting agents and a binder. After emerging from the bath, the fabric is squeezed by a pair of mangles or rubber rolls at a constant pressure to reach a determined wet pick-up level. The presence of the rolls allows ensuring the contact between the microcapsules and the fibers (Fig. 7). Thermal treatment with hot air in an oven is applied to remove water and to cure

the resin or binder, and therefore to induce microcapsules adhesion on the fiber surface.

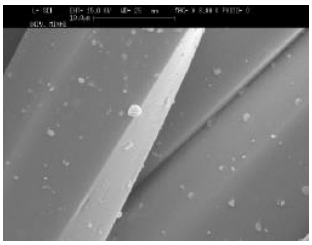
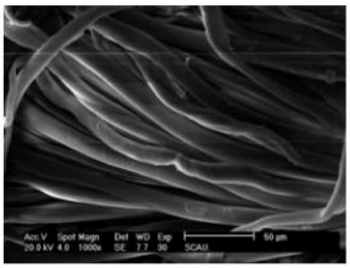


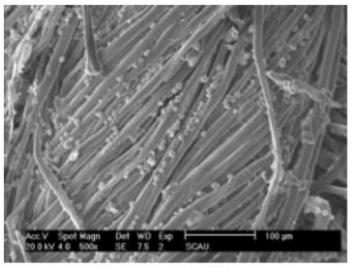
Fig. 7 SEM micrographs of polyester fabrics containing microcapsules. Microcapsules are physically linked onto the fiber surface after heating treatment.

Ionic bonding is another solution to fix charged capsules, such as chitosan, onto the fiber having surface potential, such as polyamide in acidic conditions (Chatterjee et al. 2014a). The capsules are synthesized to have cationic or anionic functional groups on the external surface of the membrane, and therefore imparting affinity and strong ionic bonds between microcapsules and fibers during bath exhaustion treatment without binder. In this case, also, one advantage is that the method may be carried out straightforwardly. The major drawback is the low resistance to wetting since, after a few washes, the capsules disappear from the surface of the fibers.

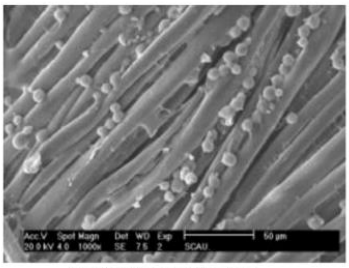
In some cases, if the function of the microcapsules is to control the release behavior with a porous or semi-porous shell, the use of binder creates a three-dimensionally linked network and is a hindrance of the active substance release. Furthermore, the lack of strong chemical bonding between the capsules and textiles results in poor washing durability and poor air permeability. Even if padding is a simple way to functionalize textile, the applied pressure may break the microcapsules. Chemical grafting represents an efficiency finishing method to overcome these various drawbacks, and therefore to covalently linked the microcapsules onto textile fibers by using polyfunctional crosslinking reagents.



(a) 1000×magnification



(b) 500×magnification



(c) 1000×magnification

Fig. 8 SEM photographs of cotton fabrics before (a) and after being treated (b and c) with chitosan–gelatin microcapsules (reprinted with permission from Liu et al. (2013))

Table 2 Examples textiles finishing treatments for chitosan based microcapsules

Application	Incorporated substance	Textile material	Finishing method	Reference
Antimicrobial	Silver	Polyester	Bath exhaustion	Ali et al. 2011
Antimicrobial / antioxidant	Iodine	Viscose	Padding	Zemljič et al. 2017
Antimicrobial	Pyrazole	Cotton	Pad dry curing	Nada et al. 2018
Antimicrobial	Berberine	Cotton	Spraying	Lam et al. 2013
UV-Protection / antimicrobial	Zinc oxyde	Cotton	Pad dry curing	AbdElhady 2012
UV-Protection / antimicrobial	Zinc oxyde	Cotton	Synthesis of nanoparticles onto fabrics	Perelshtein et al. 2013
Antimicrobial / insect repellent	Limonene Oil	Cellulose	Padding	Souza et al. 2014b
Antimicrobial / insect repellent	N,N-Diethyl-3-methylbenzamide	Cotton	Spraying	Fei and Xin 2007

Antimicrobial / insect repellent	Dodecyltrimethylammonium chloride	Wool	Pad dry curing	Hassan and Sunderland 2015
Cosmetic	Rose fragrance	Cotton	Dipping	Hu et al. 2012
Cosmetic	Vanillin	Cotton	Chemical grafting	Yang et al. 2014
Cosmetic	Aromas	Cotton	Chemical grafting	Sharkawy et al. 2017
Medical	Clindamycin 2-phosphate	Viscose	Padding	Ristić et al. 2016
Medical	Gallic acid	Cotton	Padding	Hui et al. 2013
Antimicrobial / thermal regulation	Silver zeolites+preformed phase change material	Cotton	Pad dry curing, Citric acid as cross-linker	Scacchetti et al. 2018

4.2 Smart End-Uses of Textile Substrates Containing Microcapsules

4.2.1 Improving Textile Performances

The research in the field of textile technology has been focusing over the last decades toward the design of garments which can deliver to the user better performances regarding wearability and comfort while imparting functional properties of different kinds (Oliveira and Cunha 2019). In the context of improving the performance of textile materials, microencapsulation was revealed to be a practical approach to combine functional substances with commodity fabrics. In facts the encapsulation process showed the capability of improving the effect of functional substance while easing the binding to the fabric, leading to better performance and durability of the treatments (Salaün 2016). Chitosan represented a very advantageous polymeric shell for the preparation of capsules for functional textile finishing; its natural biodegradability and biocompatibility have made it suitable for encapsulation of bioactive ingredients while its positive surface charge lead to a better affinity for many textile substrates especially the cellulosic ones (Roy et al. 2017). Furthermore, it showed a natural antimicrobial activity that can be combined with the peculiar properties of the core substance to impart multiple functionalities to the textiles (Konuklu and Paksoy 2015). Scientific literature evidenced how chitosan-based particles have been intensely studied to improve the performances of garments, in particular they found application in the production of medical and cosmetic textiles, moreover significant interest is arising in using chitosan to encapsulate phase change materials as thermal storage devices to improve the comfort of the garment user (Hu et al. 2011; Ristić et al. 2016; Scacchetti et al. 2018).

Cosmeto-textile is a textile material that incorporates particular substances or preparations intended to be released on the outermost layers of skin of the human skin; it holds properties such as cleaning, perfume, modification of appearance, protection, maintenance or repair of body odor. The preparation of cosmeto-textiles has mostly exploited microencapsulation technique in order to avoid the burst release of the active substance and to effectively bind the system to the textile making more effective over longer usage times (Mathis and Mehling 2011).

In the work of Hu et al. (2011), rose fragrance was incorporated into chitosan nanoparticles and applied to cotton fabrics. The synthesized fragrance was incorporated into chitosan nanoparticles by ionic gelation method and attached to the fabrics by dipping them into the nanosuspension under vacuum for 2 hours. Release test was conducted by leaving the fabrics in an oven at 70°C so that the fragrance could be released, at given time interval the fabrics were removed from the oven, and the residual fragrance was extracted in ethanol, the amount of extracted fragrance was analyzed by UV-visible spectroscopy. It was proved that the encapsulated fragrance was retained on the textile while in case of direct application onto the textile substrate all the fragrance vaporized in 10 hours.

Yang et al. (2014) incorporated vanillin in chitosan microparticles by spray drying attached the products onto cotton fabrics by crosslinking reaction carried out with citric acid, the crosslinking reaction was carried out using sodium hypophosphite as a catalyst at a temperature of 160°C. The release test was conducted on the textile for 2 hours at different temperature and relative humidity, after the given time the vanillin was extracted from the textile and quantified by gas chromatography. Washing fastness test was conducted in parallel on the textile microcapsule system and on a control sample obtained by directly applying vanillin onto the cotton fabrics. The release test evidenced that the amount of vanillin released is proportional to temperature and relative humidity; the encapsulation process allowed vanillin to be kept onto the cotton fabric for ten washing cycles more than respect to the free vanillin. The author interpreted the data by mean of density functional theory calculation and ascribed the encapsulation and release behavior to the inclusion complexes formed between chitosan and vanillin.

Given the promising results regarding performances some researchers focused on upscaling the production of cosmeto textiles; in doing that it is of crucial importance to properly select the chemical substances involved in the production to avoid harmful and reactants. Therefore, several studies were devoted to the green production of cosmeto textiles in the vision of the industrial process.

The procedure proposed by Alonso et al. (2010) significantly reduced the environmental impact of the process by substituting the chemical grafting with UV curing. Essential oils were loaded in chitosan microcapsules by oil in water emulsion technique, after that, the textile sample was UV irradiated, dipped in the capsules suspension and heated to allow the crosslinking by the esterification reaction.

An in-depth study of the green production of cosmeto textiles was conducted by Sharkawy et al. (2017), which proposed alternatives to toxic crosslinkers and employed both in the capsules production and grafting to fabrics. The main idea of the

work was to substitute aldehyde based substances such as glutaraldehyde and melamine formaldehyde with polycarboxylic acids such as tannic and citric acid. The particle preparation was performed by complex coacervation of chitosan and Arabic gum by using tannic acid as a hardener, the process allowed to load vanillin and limonene successfully. The grafting was performed by using citric acid as cross-linker, and the esterification reaction was conducted by employing sodium phosphate monobasic monohydrate as a catalyst in mild temperature conditions (50°C) after the bath the fabric underwent thermofixing at 90°C.

The work showed the effectiveness of the green processing since the properties of the cosmeto-textile was not compromised and it represents a good point toward the industrial production of cosmeto textiles.

Similarly to cosmeto-textiles also medical textiles are materials that incorporate bioactive substances, however, while cosmeto-textiles incorporate substances for aesthetic purposes medical textiles aim to have a specific therapeutic target (Shah and Halacheva 2016; Massella et al. 2017). They range of application can be both topical and systemic, in the first case the therapeutic target is the outer skin layers, for example, textile materials have been widely exploited as wound healing devices to treat burns or skin ulcers (Mostafalu et al. 2017). On the other hand, systemic action deals with substances that are released through the skin to reach blood circulation and there exploit therapeutic effect; typical examples of such devices are transdermal patches (Mihailiasa et al. 2016). The first commercialized examples of these devices were based on polymeric films that acted as drug reservoir and could be applied to the patient skin for several days; this however caused skin irritation due to the lack of breathability of the polymeric films. Therefore, textile-based transdermal release system has been gaining significant interest in the recent years. The significant advantage of such materials consisted of the capability of exploiting the high surface area of the skin (the largest organ of the human body) as administration route while making the drug delivery device wearable, therefore no further administration was required by the patient allowing him to be easily compliant to the therapy. Medical textiles have been usually produced by combining commodity fabrics with drug carriers with suitable for topical or transdermal release (Rubio et al. 2010). Such carriers include liposomes, cyclodextrins, polymeric micro and nanoparticles (Martí et al. 2012; Mihailiasa et al. 2016). The already mentioned properties of chitosan made it suitable for dermatological applications, not only for its antimicrobial activity and its ability to incorporate drug (Donalisio et al. 2018). In facts chitosan tends to be degraded in mildly acidic environments, given the normal skin pH to be of about 5.5 the polymer can slowly degrade in the skin environment thus effectively releasing the drug. Furthermore, the positive surface charge of chitosan eases its ability to cross the skin barrier, which can lead to more effective transdermal release (Khadjavi et al. 2015). Several chitosan-shelled drug carriers have been studied evidencing is good compatibility with skin tissue and no cytotoxicity against skin cells (Argenziano et al. 2017).

In the work of Ristić et al. (2016), clindamycin 2-phosphate was loaded into chitosan nanoparticles by ionic gelation method. The nanoparticles were then used to functionalize viscose fibers by dipping, padding and oven drying. The effectiveness

of functionalization was assessed by acid dye adsorption technique. Given the application of the viscose fibers as vaginal tampons, they were tested for antimicrobial activity against Candida Albicans and tested for controlled release in neutral pH at which symptomatic of infection occurring. The study reported the successful loading of the drug in the nanosized carriers and is adsorption on the fiber surface. Furthermore, an excellent antimicrobial efficiency was observed, while the release kinetic was quite fast with a not high delivery of the drug. This can be attributed to fast diffusion of the hydrophilic drug and reduced erosion of the polymer matrix at the pH at which the release test was conducted.

Hui et al. (2013) developed bio-functional textile for the treatment of atopic dermatitis by applying chitosan-sodium alginate microparticles loaded with gallic acid onto cotton fabrics. The gallic acid was extracted from a mixture of Chinese traditional herbs and incorporated in the polymers by emulsion cross-linking process. The application on the cotton fabrics was performed by dipping, padding and oven curing, and a resin binder was employed to enhance the fixation of particles of the textile surface. The drug release test was conducted at pH=5.5, and the cytotoxicity was assessed on skin keratinocytes cell cultures both by MTT cell viability and LDH membrane integrity tests. The obtained particles displayed a controlled release over 72 hours with the release of 90% of drug loaded; this is in accordance with the solubilization of chitosan in acidic pH, which allows a total release of the loaded drug. The cell cultures showed that the biofunctional textile is nontoxic to human skin.

The great potential of the usage of chitosan as material for dermatological applications and the interest in the production of bio-functional textiles makes the application of chitosan based nanocarriers to fabrics a topic of great interest for future research.

One of the recent advancements in textile technologies consisted in the production of garments with improved thermal regulation properties (Dotti et al. 2016). Providing thermal regulation to the human body is the primary objective of garments and nowadays thank innovative finishing it is possible to improve thermal comfort to the user with significant benefits on his performances and health (Mantegazza et al. 2018). Such technologies are of significant interest in developing sportwears for extreme environments. Microencapsulation has been exploited in this sense with the aim of incorporating in the microcapsules the phase changing materials. They are substances of various natures, which can undergo a phase change (usually fusion) in a range of temperature close to the human skin one (35-38°C).

Moreover, they usually present high enthalpies of phase change (Alay Aksoy et al. 2016). These materials can, therefore, absorb thermal energy from the human body in the form of latent heat, then in case of external temperature change the inverse phase transition occurs and the stored latent heat is released toward the body, therefore phase change materials can contribute to thermal comfort by avoiding heat dissipation if applied to textiles (Yang et al. 2018). Commonly used phase change materials for textiles applications include fatty acids and paraffins; therefore the proper encapsulation in a polymeric shell that can effectively be bound to the

fabric is of crucial importance in the scope of imparting fastness and effectiveness to the phase change materials finishing. Recent research has inquired the possibility of using chitosan as polymer shell to entrap phase change materials, the possibility of combining on the same garment the heat management of phase change materials together with the antimicrobial effect of chitosan (Konuklu and Paksoy 2015; Paulo et al. 2018).

Deveci and Basal (2009) studied the encapsulation of n-eicosane by complex coacervation of chitosan with silk fibroin using glutaraldehyde as cross-linker. The study focused on the particles preparation rather than on the testing of system performances. The factorial design of the experiment evidenced how the relative amounts of fibroin and chitosan and silk fibroin are the main factors in determining the final size and encapsulation efficiency of the microcapsules. In the following study, the authors focused on the characterization of the microcapsules, with a particular focus on studying the phase change behavior by DSC analysis (Basal et al. 2011). The enthalpy of melting of the encapsulated PCM was proportional to the quantity of encapsulated n-eicosane with no significant shift in the temperature of fusion which found at 37°C for the micro PCM system. The authors concluded that the produced microcapsules were suitable as potential heat storage materials for textile application.

Chaiyasat (2018) prepared octadecanone loaded PMMA by exploiting microsuspension iodine transfer polymerization using chitosan as the stabilizer with the aim of preparing a multifunctional thermoregulating and antimicrobial material. The DSC analysis evidenced how the melting enthalpy of the encapsulated octadecanone does not change respect to bulk material, mainly due to hydrophilic nature of the polymer shells which can undergo phase separation during the heating cycle, such results showed the suitability of microcapsules as heat storage system. The testing of antibacterial properties, however, showed scarce inhibition of bacterial growth, attributed to the scarce availability of surface amino groups. The overall system needs to be optimized before being applied to textiles.

An example of a combination of chitosan and PCMs applied to textile substrates is reported by Scacchetti et al. who produced chitosan-silver zeolites microparticles by ionic gelation procedure and applied to cotton fibers together with preformed PCM microcapsules (Scacchetti et al. 2018). The finishing consisted in pad-dry cure process, which employed citric acid as cross-linker. The fabric was also functionalized with silver zeolites and silver zeolites with chitosan film as a control. The thermoregulatory capabilities of the textiles fabrics were assessed both by differential scanning calorimetry and infrared thermography, which provided information on the heat distribution over the fabric surface. The bioactive properties were tested both in term antimicrobial activity and silver ions released. The work reported how the different properties were synergic, in facts thermal regulation, bacterial inhibition, and silver ions controlled release was obtained.

4.2.2 Textiles for Protection

In the last decades, several efforts have been made to impart functional properties to textile materials in order to make them beneficial to people health (Li et al. 2015; Mostafalu et al. 2017; Yao et al. 2018). In the context of bio-functional garments, a significant amount of studies have been conducted to develop innovative finishing that can protect the human body from potential harms (Bui et al. 2017; Fornasiero 2017). The growth of bacteria and other microorganisms onto the textile surface has been a common issue occurring due to the fact the usage condition of the garments are the ones that usually favors the cell growth of several pathogens (Morais et al. 2016). Besides being a potential threat to human health the growth of microorganism onto textile also lead to a series of side effects such as unpleasant odors, stains and ruining of the materials (Yuan and Cranston 2008). For this reason, several innovative finishing has been developed to impart antimicrobial properties to textile materials. Concerning the possible strategies to inhibit the microbial growth several approaches have been developed; concerning the use of antibiotics, several concerns have aroused in the last years due to the proven capability of several bacteria to evolve and developing antibiotics resistance (Parisi et al. 2017). Therefore great interest was paid in textile technology to substitute the antibiotics drugs with inorganic nanomaterials such as silver, zinc and titanium-based nanoparticles (Bashari et al. 2018). Such materials can release positively charged ions that can interact with the negatively charged bacterial cell wall; this leads to the rupture of the cell wall and the bacterial death (Hoseinzadeh et al. 2017). However, some issues were also aroused concerning the potential toxicity of metal-based nanomaterials and their side effects (Bouwmeester et al. 2018). Chitosan was found to be an exciting alternative to inorganic antimicrobial materials being a natural biocompatible and biodegradable polymer, moreover, its abundance in nature makes it much more convenient from an economic point of view if compared to silver and titanium (Ruocco et al. 2016; Tokatlı and Demirdöven 2018). In the context of using polymeric nanomaterials for antimicrobic application, chitosan has presented the advantage of being intrinsically antimicrobic. Therefore there is no need to chemically modify or conjugate it with drug molecules as it is done with other polymers (Parisi et al. 2017; Verlee et al. 2017). The intrinsic antibacterial activity of this polymer lies in its chemical structure which is rich in amino groups that get protonated in the biological environment; therefore it can easily bind to the microbial cell wall, altering its structure and permeability and inhibiting the DNA replication (Helander et al. 2001; Li et al. 2016). Moreover, Chitosan is a very versatile polymer that can be easily chemically modified to enhance its functional properties or employed as a polymeric shell to incorporate various substances in the forms of micro and nanoparticles (Divya et al. 2017; Wang et al. 2017). Indeed, using chitosan as shell material for micro and nanocarrier production presented several advantages due to the mucoadhesive properties of this polymer, this showed an enhancement of the interactions between the particles and the target tissue improving the release of the encapsulated substance (Ma et al. 2017; Parisi et al. 2017). Moreover, the assembly of

chitosan in micro and nanoparticles was proved to the available surface area for cell wall interaction and leads to improvement in the antibacterial properties (Ali et al. 2011; Perelshtein et al. 2013). The application of micro and nanoparticles to textile fabrics is an up-and-coming technology, which has been deeply studied in the recent years to impart functional properties to the commodity garments (Salaün 2016; Massella et al. 2017). The nature of the core material to be encapsulated determines the properties and the application of the produced material; these functional properties of the core substance combined with the antimicrobial properties of chitosan have been giving the chance to produce a new generation of multifunctional garments. Studies in this area have a wide approach that starts from the formulation of the particles and the characterization of their properties to the application of the particles to the textile substrate and the assessment of the properties of the functional textile. Ali et al. (2011) attempted to combine and improve the antimicrobial properties of silver by encapsulating it in chitosan nanoparticles. The particles were produced by an ionic gelation method and applied to polyester fabrics. Given the scarce reactivity of polyester, the textiles were surface activated with a sodium hydroxide pretreatment before applying the nanoparticles by an exhaustion bath treatment carried on for 45 min at 60°C. The extent of chitosan adsorption on the fabric was assessed by carrying out dyeing with an acid dye (Navy blue), which interacts with the $–NH_3^+$ groups of chitosan. The color intensity measured by spectrophotometry and correlated to the amount of chitosan-grafted. The antimicrobial assay carried onto the textile evidenced how the combination of silver and chitosan in the nanoparticle form delivery better bacterial neutralization for the single materials, evidencing a synergistic antimicrobial effect. In antimicrobial textile functionalization, it is important to take into account that some antibacterial substances agents many cause skin irritation in case of high dosage and uncontrolled release. In the work of Zemljič et al. (2017), the powerful antimicrobial I_2 was incorporated in chitosan nanoparticles to control its release and exploit its antimicrobial and antioxidant activity without irritating side effects. The particles were produced by an ionotropic gelation method and attached to the viscose fibers by immersion and padding protocol. Fibers were previously treated with sodium chlorite to form carboxylic group onto the surface which could better interact with amino groups of chitosan. The nanoparticles functionalized fibers displayed better antimicrobial and antioxidant properties than the ones functionalized by iodine and chitosan alone, showing that the polymer exerts no inhibition of iodine activity. The two species then acted synergistically, and the encapsulation allowed controlling the I_2 dosage, reducing the risk of irritation. The innovative approach of using chitosan to stabilize the phospholipid membrane of liposomes prior to attaching them on textile is presented in the work of Nada et al. (2018). In this case, the molecular chains of chitosan were broken down by oxidative degradation in $NaNO_2$. The depolymerized chitosan was then used to hydrate the thin phospholipid film during liposome production. The chitosan stabilized liposome incorporated an appositively synthesized Pyrazole active compound, the particle emulsion was then attached to cotton fabrics by padding followed by air drying curing, citric acid was employed as a non-toxic crosslinker. The textile material was investigated for its mechanical properties and biological

one by assessing antimicrobial activity and cytotoxicity on skin melanocytes. The fabrics were non-toxic for skin cells and displayed antimicrobial activity. However, no synergistic effects of chitosan and pyrazole were observed, probably due to the degradation of the molecular chains during the pretreatment. A loss of the hand of the cotton was noticed as a consequence of the finishing. The hand loss and in general the alteration of the mechanical properties of the textiles upon the application of the antimicrobial finishing is a factor that could negatively influence the comfort and wearability of the mentioned bio-functional garments. Varan (2017) studied how the chitosan finishing could influence the mechanical properties of nylon/elastane pressure garment for rehabilitation and burn scar management. In this work, chitosan was applied in bulk form, and the parallel test of antibacterial and mechanical properties was conducted to inquire how imparting antibacterial finishing influences the mechanical response of the material. The binding of chitosan with the fibers caused a slight increase in stiffness together with a small decrease in air permeability, bursting strength and drapeability; porosity values instead decreased significantly upon chitosan application. The antimicrobial activity was successfully proven.

In the design of a bio-functional textile it also of crucial importance to assess the durability of the microcapsules treatment, as a matter of facts the washing fastness is a critical parameter in determining the product life. Lam et al. (2013) investigated how multiple washing cycles influence the properties of cotton fabrics functionalized with berberine loaded chitosan microparticles. The study showed that a loss of about 40% of the finishing was occurring in the first 20 washing cycles, while 50 washing cycles were necessary in order to remove the finishing entirely. The antimicrobial activity was maintained for 20 washing cycles; the authors explained this phenomenon by taking into consideration the limited diffusion of the drug from the microparticles.

As discussed the primary interest in producing such innovative textile materials was mainly driven by the goal of producing garments that could protect the user from sources of harm for its health, and beyond the biological risk other potential harms were identified and tackled by the textile technologist. Therefore, significant efforts were made to design protective garments against UV-radiations, insects, and parasites. The usage of chitosan in the production of these textiles has been proved to be a smart way to incorporate the functional substance on the textile while imparting a further antimicrobial effect to the textile garments.

Zinc oxide is versatile that has found application in many fields (Cauda et al. 2014; Laurenti and Cauda 2017), in the context of textile it has been employed to impart antimicrobial properties, UV protection and hydrophobicity (Ashraf et al. 2014; Doumbia et al. 2015). In the work of AbdElhady (2012), the ZnO was incorporated in chitosan nanorods by an ultrasound-assisted method. The nanorod was applied to cotton fabrics by padding drying and curing protocol. The UV spectroscopy analysis showed a functional capability of the material of acting as UV shield. Furthermore, the material displayed marked antibacterial effect. However, this research did not inquire whether a synergic interaction between the antimicrobial effects of zinc ions and chitosan was occurring which was instead highlighted by

Perelshtein et al. (2013). In this work, a novel sonodynamic approach is presented in order to form the Chitosan-ZnO nanoparticles directly onto the textile material, without the need of using any binging chemicals. The higher surface area of the obtained particles allowed to boost the antibacterial activity of the raw bulk materials.

Another possible threat for which protective garments could be helpful are insects, as a matter of several insects such as mosquitoes are responsible for the transmission and spreading of infectious diseases like malaria. The encapsulation of insect repellent substances in suitable carriers followed by functionalization of the textile material was, therefore, the adopted strategy to design insect protective garments (Peila et al. 2017). In the work of Souza, the insect repellent limonene oil was encapsulated in chitosan microcapsules by oil in water emulsion technique; capsules were then padded on cellulose non-woven fabric. The release profile of the volatile limonene oil was studied by putting the textile material in a controlled temperature oven and measuring the weight loss at given time intervals. This work marked how the encapsulation in the polymer is crucial in avoiding the burst release of active volatile substance and increase the durability of the insect repellent finish (Souza et al. 2014a). In the study of Fei and Xin (2007), N,N-Diethyl-3-methylbenzamide was encapsulated in chitosan and sprayed on cotton fabrics. The mosquitoes repellency was tested by putting the textile on the arms of volunteers which were then placed in a mosquitoes cage, after a while the number of bites on the person's arms was counted to evaluate the effectiveness textile; antimicrobial activity was tested as well. Good results were found regarding mosquitoes repellency and antimicrobial activity. Hassan and Sunderland (2015) encapsulated dodecyltrimethylammonium chloride in chitosan with the aim of making wool fabrics better withstand the degradation due to microorganism and insects like moths. Before finishing the wool fabrics were attached scoured, and then the microcapsules were applied by a pad-dry-curing process. The finishing treatment was proved to be effective in terms protecting wool from insects and bacteria but had some slighted influences the hand of the fabrics.

To sum up, chitosan-based capsules have been proved to be advantageous materials for protective garments applications. The intrinsic antimicrobial activity of the shell material was generally enhanced when assembled in micro and nanoparticles due to the increase in available surface area, this, combined with the functional properties of the core material allowed the design of improved protective garments. When an antimicrobial substance was incorporated in the particles, an improvement of the overall performance concerning raw materials was observed thanks to a synergic effect. Instead, if core materials with other functionalities were incorporated, it was possible to impart multiple protective effects to the textile garment, such antibacterial and UV protection or antibacterial and insect repellency.

5 Conclusions and Future Perspectives

Microencapsulation has been proven to be a versatile technique which can enhance the performance of several substances for a wide range of applications. The research in this field if therefore really active toward the proposal of innovative solutions for bringing to market microcapsules based products. A big focus is being paid nowadays to develop productive encapsulation processes that exploits green chemicals with the aim of making the production easily up scalable. From the formulation point of view it is of great interest to propose methodologies that could display effective loading of the active substance while controlling the release kinetic. In the present chapter the efforts of the scientific community toward the achievement of effective and environmentally friendly microcapsules production evidencing the progress in the field over the last decades and trying to forecast the future trends. Among the various fields in which microcapsules found application a special attention was paid on the production of smart textiles. In this context our review highlighted how significant efforts were made toward the production of durable microcapsule based finishes that could avoid toxic chemicals during the fixation process. Given the strict contact between the smart textile the exploitation bio sourced materials was proposed to be an effective solution in textile finishing. A very interesting trend was then observed in the use of chitosan which was widely exploited both because of its intrinsic antimicrobial activity and good performances as shell material for capsules production. The present work evidenced how this polymer owns peculiar properties that both eases the encapsulation process and control the release kinetics, furthermore the technologies employed to produce chitosan particles deeply explained. Then the analysis focused on how the chitosan capsules can be easily attached to textile substrates evidencing how the chemical nature of this polymers allows effective grafting on textiles surface while avoiding toxic chemicals. A wide range of application of capsules to textile materials was reviewed evidencing how this kind of materials displayed promising experimental results. Such results allow to conclude that the combination of chitosan and micro encapsulation technology could play a determinant role in the design of the garments of future that could satisfy the consumer needs while complying to new regulations in terms of process safety and environmental impact. The way in which textile research opened up to other sectors to provide functional properties to commodity garments will definitely have a significant impact on people life and society in the upcoming years.

Microencapsulation as research axis still has excellent potential for development, particularly in the formulation of more environmentally friendly methods, the choice of the active ingredients to be coated, the formulation of a structuring polymer membrane, or on methods textile finishing for the fixing of the particles and/or the functionalization of the supports. Since the last decade, the main issues are the evolution of legislation in terms of toxicity the products used, the biocompatibility of the raw materials for the textile finishing systems development in response to

environmental stimuli ("smart" membranes), the extension of encapsulation methods for water-soluble active without the use of volatile organic solvent, and the integration of these functional coatings (microcapsule-textile) in other application areas.

In this context, the use of chitosan as well as shell forming material to entrap the active substance and to protect it until the final use, and as antimicrobial compounds represents a wide opening to design new textile materials with added values. Thus, future work will focus not only on chitosan purification in term of molecular mass to better control of the shell formation mechanism but also the textile finishing processes under mild conditions. Therefore, exploiting the potential of chitosan for microencapsulation pass through research, process control, but also by the combination and adaptation of different technology. Research in the textile industry must continue to open up other sectors to develop the textiles of the future desired by the consumer in accordance with the legislation. Nevertheless, the microencapsulation methods using chitosan as shell forming material has a sort synthesis time and is cost-effective.

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