Advances in Textile Engineering

Chapter 3

Microencapsulation as an Effective Tool for the Design of Functional Textiles

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Abstract

The importance of active coatings for smart textiles increased rapidly in the textile market, due to compétition, gaining added value, and increasing market possibilités. Since the last décade, the consumers do not only search for aesthetic properties, but also Functional properties. In This context, micro encapsulation and microcapsules have been playing an important rôle to achieve the desired properties, due to the own spécificités, i.e., protection of the active substance, controlled release, compatibility, and also providing higher specific surface area to enhance the functionalities. This Technology allows encapsulating a wide range of coré materials, such as aqueous solutions, water-immiscible Liquids, and solid particles. The formulation of microcapsules composed of polymeric material and an encapsulating active principle is demanding though many approaches have been used for a textile application, such interfacial polymerization, in situ polymerization, phase coacervation or solvent évaporation. Now a days, the Most attractive commercial uses are oriented toward the improvement of the textile performances such as the controlled release of the active substance for cosmeto-textiles, insect repellent textiles, or medical textiles, the thermal comfort with the encapsulation of phase change materials, aesthetic effect with the entrapment of thermochromic solution, or wearer's protection.

1. Introduction

These last three decades many reviews have been published on the use of microencapsulation in the textile field [1-9]. It is not the purpose of this chapter to give a comprehensive review of this field, but rather to acquaint the reader with the evolution of this technology in this technical field, and give him a general overview of the capabilities and limitations of the interest to use microencapsulation to enhance the textile properties. In recent years, surface coating technologies have considerably expanded the scope of materials research. As a result, demands from manufacturers are no longer limited to aesthetic or barrier aspects alone but are now moving towards additional functional properties. In this context, microencapsulation, a technology that is enjoying significant commercial success, used in particular in the paper and pharmaceutical industries, provides a complementary possibility to the growing needs of functional coatings [10]. The encapsulation of materials has been primarily inspired by the examples of Nature, where materials are embedded to be protected from the influence of environmental factors, from the macroscopic scale (eggs or seeds) to microscopic scale (cells). The development of microencapsulation began with the preparation of capsules containing pigments (or dyes) that were introduced into the paper for carbonless purposes to replace carbon paper (Green & Schleicher, 1956 cited in [11]). Since the 1950s, the development of microencapsulation, in terms of new technologies, new processes and industrial applications, has grown exponentially [12], particularly in the pharmaceutical field, which has been using it for many decades to prepare capsules containing active ingredients. Over the past 20 years, this approach has also led to extensive research in application areas such as the chemical, pharmaceutics, food, cosmetics and textile industries. One of the main characteristics of this technology is the possibility of combining the properties of inorganic materials with those of organic materials, which is delicate with other technologies. Microencapsulation is not limited to a product or a component of the product alone and can be defined as a process by which fine particles of a solid, liquid or gaseous compound are trapped by an "inert" membrane, which isolates them and protects them from the external environment. This "inert" character is to be related to the reactivity of the membrane concerning the encapsulated substance. This technology is mainly used for protection, controlled release, and compatibility of active ingredients. The encapsulation step preserves the encapsulated substance in the form of a finely divided state, and releases it or not depending on external stimuli. In the case of a liquid product, its conversion into powder form also preserves its reactivity, which facilitates the handling of reactive or sensitive products.

1.1. Definition of micro encapsulatio

From an etymological point of view, the word microencapsulation originates from the Greek "mikros" and the Latin "en" and "capsula" which mean "small in a small box". Thus, according to IUPAC, microencapsulation corresponds to confinement of microscopic particles

with a host; in the early 2000s, Richard and Benoît defined microencapsulation as a method that encompasses all technologies leading to individualized particles consisting of coating material and an active material of a size between 1μm and 1000μm [13]. Over the past two decades, microencapsulation has been a growing field with applications in many technological disciplines. However, the principle of encapsulation is ancient, since if we consider that biochemistry is one of the great founding principles of life, it is due to the presence of a membrane to allow the containment of vital molecules in cells. Nature is full of examples of encapsulation, from macro to nanoscale, to protect materials in the surrounding environment, such as a seed in a mantle, a bird's egg or a cell in a membrane [14]. Therefore, the development of microencapsulation processes is only an imitation of nature to obtain innovative structures to immobilize, structure, release or structure the active ingredient. Since then, encapsulation has been used in various industrial fields; many definitions are depending on the needs in a specific field. Nevertheless, one of the possible generic definitions may be the trapping of a compound or system in a dispersed material for immobilization, protection, transfer control, structure and functionalization [15].

Therefore, microencapsulation is a process by which an active substance is surrounded or coated with a continuous polymeric material, also called shell. The active substance or core material may be a finely ground solid, tiny droplets of liquid, or gaseous material. Microencapsulation makes it possible to prepare microparticles of different morphologies, the simplest of which are identified as microcapsules or reservoir systems, where the active principle at the core of the capsule is entrapped by a solid and continuous membrane of the coating material, and microspheres where the active principle is dispersed in fine particles in a matrix network (**Figure 1**). Other types of morphologies based on the former are also possible in regard to the end use, such as multi-core capsules or nanocapsules dispersed in a bigger one, or multi-layered shell and multicore microspheres. Particles, spherical or irregularly shaped and of average diameter between 1 and 1000 μm [13] or even 5000 μm [16], generally contains 5 to 90% by weight of active ingredients. These different characteristics, as well as the functional properties, are dictated by choice of process and formulation. Microencapsulation technology has many advantages in the formulation of functional products. The main reasons to encapsulate an active compound are driven by its protection before use; the improvement of the conditions of its implementation (solubility, dispersion, fluidity); the increase its shelf life by protecting it from degradation conditions (oxidation, dehydration,...); the control, regulation, or vectorization of its release; the safety improvement to handle it; masking its taste or smell; the immobilization of enzymes or microorganisms; and to transform a liquid into a pseudo-solid to facilitate its manipulation.

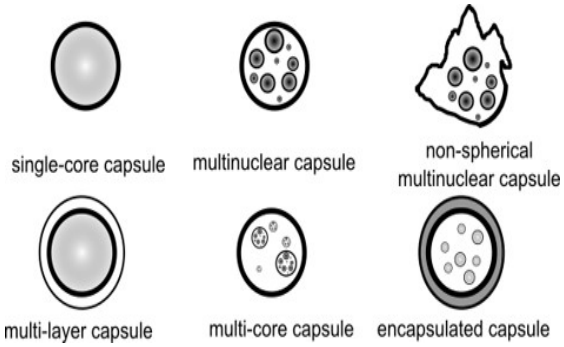

Figure 1: Microparticles morphologies.

1.2. Microencapsulation and Textile

Textile industry has significantly evolved over the last three decades. Thus, textile products were mainly based on conventional technologies in the 80's, where the product had to meet basic specifications, such as a protective barrier for the body of the wearer or to hide it. From the 90's, with the emergence of new materials and fibers, the traditional textile was moved toward technical textile with higher added value. So for the last decade, the textile products have become more and more functional or multifunctional with the development of the smart textile or smart textiles, taking into account ecological criteria. Textiles are structures with outstanding properties, combining flexibility, lightness and mechanical resistance. They are used in many applications such as clothing, insulation, absorption or filtration. However, it is sometimes necessary to add new functionalities to them to give them new properties and increase their added value. Thus, finishing processes make it possible to confer a color, a water-repellent or antibacterial characteristic on them, for example. However, the active principles used may be sensitive to their surroundings. They are also available in liquid form, making their integration into textiles impossible as they are. To avoid any interaction with the environment, limit their reactivity and overcome their volatility, a polymer membrane encapsulates the active ingredients in the product. The transformation of liquids thus simplifies handling into solid powders, which may allow controlled release when necessary.

In this context, textile industry actors have been relatively slow to introduce microencapsulation technology into their field, although this technology has been used since the 1950's in the chemical, paper or pharmaceutical industries [3,17]. The competitiveness of the textile sector depends on its ability to understand and respond to the needs of its customers by adapting to technological developments and human resource mobility. The introduction of a "new technology" such as microencapsulation, in a traditional sector such as textiles, should make it possible to provide products that meet aesthetic and functional requirements in order to fight competition with low labor cost countries where social concerns are lower and therefore offer alternatives to relocation. The implementation of flexible and environmentally friendly processes to respond more quickly to user needs and market demands is based on quality and innovation. In this context, the development of the textile sector in the field of "interactive textiles" or "multifunctional textiles" has increased in recent years, in particular with the use of

the functionalization of supports based on microencapsulation, which represents a technology with high growth potential [18]. Thus, there is growing interest in the use of this technology in the textile field, both from an academic point of view, as illustrated in **Figure 2**, and from an industrial point of view, since the majority of publications are patents, thus demonstrating the strong participation of the latter in the development of high added value textile products [5]. In **Figure 2**, it seems that after reaching a plateau in the 1990s, the number of publications on microencapsulation has increased significantly since 2000. The number of publications in the textile field follows the same trend, mainly due to the emergence of phase change materials technology, and the use of microcapsules in cosmetotextiles. Indeed, the textile field represents 4% of scientific publications concerning microencapsulation. So nowadays, microcapsules are found in various textile fields such as technical, medical or Para-medical textiles, cosmeto textiles for different functional properties such as aesthetic effects, protection, comfort or skin care. Thus, from the last decades, the number of commercial applications, mainly are driven by the use of phase change materials, antimicrobial compounds and controlled release fragrances, increases in order to impart new functional characteristics, which cannot be reached with other technologies.

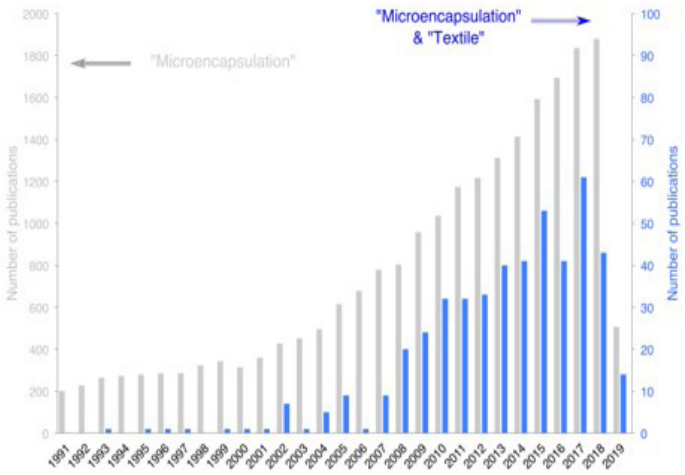

Figure 2: Trends in scientific articles on microencapsulation for textiles applications (realized on Web of Science in 2019, advanced search: TS= (microcapsule* OR microencapsulate*) ANS TS= (textile* OR fabric* OR garment* OR cloth*).

2. Microencapsulation Methods for Textile Applications

The multiplicity of microparticle synthesis processes allows the formulator to design and control the elaboration of particles of variable mean diameter according to the final application, of various morphologies, and to control the encapsulated active rate, the membrane thickness or their physico-chemical properties. There are more than 200 microencapsulation methods described in the scientific literature and patents. Whatever these methods, they are based on three main steps that correspond to the coating of the active ingredient, the formation of Microparticles or shells, and their hardening. The choice of one process over another depends mainly on the cost of the microcapsules, the desired volume, the impact of the process cost on the added value of the final product, the consideration of environmental aspects, the

functionality integrated in the capsules, the compatibility (or adhesion) between the capsules and the other formulation compounds (binders, resins,...), the optimal concentration of the active substance in the capsule, the methods of application of these products on or in the final substrate, the release or impermeability properties, the desired release profile, and the size, density or thermal and/or chemical stability of the encapsulated compound. Microencapsulation processes are generally divided into two main classes, i.e., chemical and physical, although the latter can be subdivided into techniques based on physico-chemical or physico-mechanical methods. Encapsulation based on chemical processes (interfacial polycondensation, in situ polymerization) and physico-chemical processes (simple or complex coacervation) are most suitable for textile applications (**Figure 3**). These processes allow obtaining the formation of particles with a mean diameter lower than 40 micrometers, which is the size limit to avoid any deterioration of the microcapsules during the finishing processes. Nevertheless, in most cases, the size of the microcapsules varies from a few Hundred namometers to about ten micrometers.

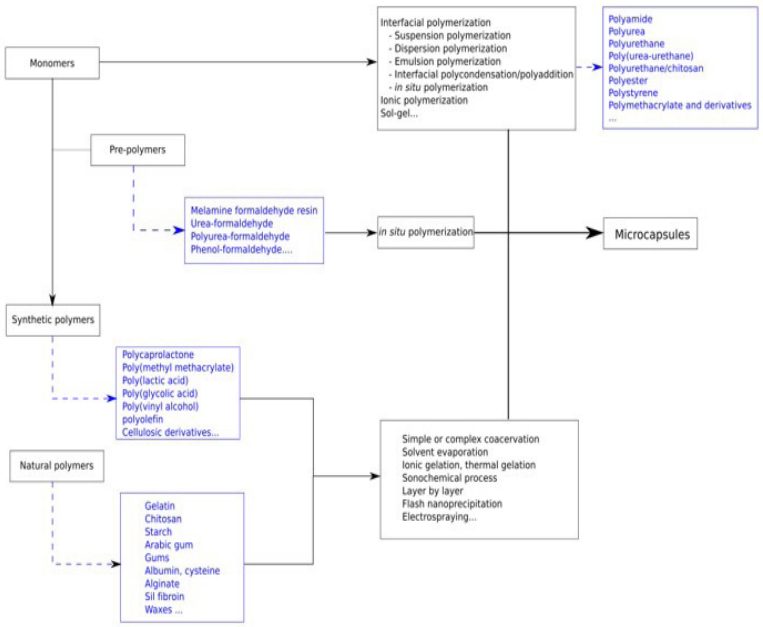

Figure 3: Microencapsulation processes based on raw materials for textile applications.

Regardless of the method used, the encapsulation process includes two main steps, i.e., the emulsion step which determines the size and size distribution of the microcapsules, and then the formation of the capsule membrane. The emulsion step can be influenced by both the system configuration, the shear rate, the volume ratio of the two phases present, and the physico-chemical properties of the system such as interfacial energy, viscosity, density and chemical composition of the two phases. The formation of microcapsules is strongly affected by the presence of surfactants, which determine not only the average particle diameter but also the stability of the dispersion. The surfactants used in the system have two leading roles, namely to reduce the interfacial energy between the dispersed phase and the continuous phase allowing the formation of small particles, and also to prevent any phenomenon leading to the destabilization of the emulsion such as coalescence, by adsorbing at the interface, and

consequently by creating a layer on the surface of the droplets. The second step of the process, or the synthesis of core/crown particles (or other morphologies), is mainly governed by kinetic parameters, i.e., the ability of monomers, oligomers or pre-polymers to react or crosslink, and by thermodynamic factors, i.e., the minimization of free energy exchanges in the system. Spreading coefficients are one of the thermodynamic prediction tools used to design the system and predict the coating of core droplet with a polymer in a third immiscible phase [19,20].

2.1. Chemical Processes

Chemical processes use monomers or pre-polymers that polymerize in situ to form the membrane [21]. They are thus different from physico-chemical processes that are based on the use of preformed polymers such as polysaccharides or proteins and their interactions and solubility.

2.1.1. Interfacial polymerization

Interfacial polycondensation or interfacial polymerization is based on the dispersion of a phase containing a solvent, the active principle and a monomer in a second phase containing a second solvent. A second monomer soluble in the second solvent is added in the mixture so as to modify the volume ratio between the phases slightly. The polymerization reaction can then proceed. Two mechanisms are then observed. In the first one, polymerization takes place at the interface where the monomers are in contact [22]. A thin film of polymerization is produced at the interface where the monomers are in contact, and the monomers then diffuse through this film to continue the polymerization and allow the membrane to grow. In the second mechanism, the monomers of the continuous phase diffuse into the dispersed phase where they polymerize with the other monomers. As the solubility of oligomers decreases as the chain length increases, they precipitate and migrate at the interface to form the protective film. The continued diffusion of the monomers of the continuous phase and polymerization allows the formation of a matrix network and the formation of spherical particles. Monomers, with functionality higher than 2, allow the formation of a dense and solid reticulated network. Cross-linking agents can also be used to promote the formation of solid particles. The porosity of the membrane is adjustable and modifiable according to the monomers and cross-linking agents chosen. The choice of surfactants and monomers must be made following the possible interactions between the active ingredient, monomers, and solvents. The disadvantage of this technique is the time required for the diffusion of monomers limiting membrane growth, which can be reduced by using some solvents that increase the reaction kinetics.

Interfacial polymerization is mainly used as an alternative method to the use of *in situ* polymerization, and in particular to compensate for the use of formaldehyde [23], for the encapsulation of pigments, essential oils [24], fragrances [25], plant extract [26], anti-microbial agents [27], flame retardants [28,29], cosmetic compounds [30, 31] or phase change

materials [32]. In most cases, polyurea or polyurethane shells provide excellent encapsulation efficiencies, and porosity control allows for the adjustment of active release kinetics.

2.1.2. *In situ* polymerization

The main difference with interfacial polycondensation is the presence of monomers in a single phase (in the continuous phase or the dispersed phase). It is based on the production of an emulsion under high agitation and in the presence of surfactants. Two monomers are solubilized in the continuous or dispersed phase. In the case of melamine-formaldehyde (MF) microcapsules, when the emulsion step is established, agitation is reduced, and membrane formation is initiated by temperature rise or pH adjustment resulting in a change in the solubility of the oligomers in water and initiating membrane formation [33]. During synthesis, polymers and oligomers diffuse at the interface to form the capsule wall [34]. Depending on the solubility of the monomers, pre-polymers, and polymers formed in each of the two phases, various cases are observed. Since monomers and pre-polymers can be soluble in the continuous phase; however, the polymer must not be soluble to allow its migration at the interface and the formation of particles. If it is soluble in the dispersed phase, spheres are formed, if it is not, core/membrane capsules are obtained.

For the two last decades, melamine-formaldehyde microcapsules have been successfully commercialized because of their its low price, simple fabrication route, good thermal and mechanical properties, high fire resistance, and acid and basic pH resistance. Even if, the residual formaldehyde is considered as the main drawback of this process, it can be reduced to meet the requirement of free formaldehyde in textiles by using modified MF pre-polymer, heat treatment or addition of scavengers [35]. The brittle rigid MF shell was used to entrap most of the active principle having a potential action in functional textiles. Thus, these recent years, many research works focused on the microencapsulation of phase change materials [36-40], fragrant oils [41-47], thermochromic and dyes [39, 48, 49], antimicrobials [24, 43, 50], and flame retardant [43, 51].

2.2. Physico-chemical processes

Physico-chemical processes are based on phase separation. It is obtained by reducing the solubility of polymers by modifying some parameters such as pH, temperature, and the presence of a non-solvent or electrolytes. It leads to their precipitation. Two phases are then present in the medium, i.e., a solvent rich and low polymer phase, and a polymer rich and low solvent phase at the origin of the membrane.

2.2.1. Coacervation Methods

Phase coacervation, including simple and complex coacervation, is one of the oldest

and widely used microencapsulation techniques. This technic is base on the separation of a macromolecular solution into two immiscible liquid phases corresponding to the coacervate and the dilute equilibrium phases. The simple coacervation method requires the use of one colloidal solute, whereas in the complex coacervation two oppositely charged colloid polymers are used. The microencapsulation process is carried out in three or four consecutive steps under stirring, i.e., (i) dispersion of the active principle in a solution containing the surface-active hydrocolloid; (ii) precipitation of the hydrocolloid onto the dispersed droplets by decreasing the solubility of the hydrocolloid, with the use of a non-solvent, a pH or/and temperature change, or the addition of an electrolyte solution; (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 microcapsule shell by crosslinking agent addition, such formaldehyde, glutaraldehyde, tripolyphosphate or genipin. Essential oils are one of the most active principles, for textile applications, encapsulated via either simple coacervation with gum Arabic [52] or ethyl cellulose [53], or via complex coacervation with chitosan/gum arabic [54-56], chitosan/carboxymethyl cellulose [57], gelatin/gum Arabic [58, 59], or gelatin/carboxy cellulose [45, 60].

2.2.2. Solvent evaporation

This technique is based on the evaporation of a volatile solvent (such as chloroform or dichloromethane). First, the solvent, active ingredient, and coating polymer are mixed. This mixture is dispersed in a continuous medium in which the polymer and active ingredient are not miscible, and the solvent is not miscible. This step is generally carried out by mechanical agitation, but can also be obtained by extrusion or by using static mixers, which allow the rapid and continuous production of an emulsion with a narrow size distribution.

The formation of the microparticle is obtained by removing the solvent, causing the solubility of the polymer to decrease and then precipitate. The solvent can be extracted by diluting the medium, adding a co-solvent. The microparticles obtained are then recovered by filtration, rinsed and dried. This process easily achieves excellent yields, close to 100%, rapid production of large quantities of suitable quality capsules (with few surface defects, few breakage and satisfactory encapsulation) and predictable release of the active ingredient. Some parameters such as low pressure contributing to extraction the high viscosity of the solvent or the high viscosity of the dispersed phase thus favor the quality the encapsulation of active drug ingredients. However, it is limited by using a volatile solvent (which must be recycled) and a polymer that is not soluble in the continuous phase. The particles obtained are microspheres containing 30 to 40% by weight of the active ingredient. They generally contain traces of solvent that must be removed in an additional step. The particle size depends on the formulation and solubility of the polymer, emulsion parameters, evaporation conditions, and physico-chemical parameters of the products used. Solvent evaporation was used to encapsulated essential with

ethyl cellulose for cosmeto-textile application [61].

2.2.3. Layer by layer

The electrostatic self-assembly processes layer by layer of polyelectrolytes of opposite charges are based on the successive immersion of the particles in a solution of cationic then anionic polyelectrolytes until the desired number of layers is achieved.

This technique is easy to implement. It allows the manufacture of microcapsules with a size between 1 and 1000 μm in diameter and adjusted membrane thickness. It is often used to make hollow capsules, the core being dissolved. They have a selective permeability since they allow small molecules such as dyes to pass through but are impermeable to polymers. Also, specific parameters, such as pH, modify the degree of electrolyte association and therefore, the porosity of the membrane and allow controlled release of active ingredients.

2.3. Miscellaneous microencapsulation process

Miscellaneous microencapsulation processes are most of the time designed for particular applications, such as a double-walled formation [62], the formation of microspheres [63], or nanoparticles [64], and they are mainly based on the previous ones. Nevertheless, these last years, two of them are received particular attention from the researchers inspired by the pharmaceuticals field, *i.e.,* the nanoflash precipitation or solvent displacement [65] and the electrosprayed route [66].

2.3.1. Flash nano precipitation

The solvent-displacement or flash precipitation technique is based on dissolving the active principle and the polymer in a solvent and mixing the solution with an immiscible solution or antisolvent to induce the precipitation of the polymer containing the active substance. The main interests of this method are the use of low toxic solvents since water is mainly used as the anti-solvent, the control in terms of particles size and size distribution, and high loading content without the use of additives, and the fact that the method is fast and economical. These recent years, menthol [67], caffeine [68], as hydrophilic compounds were encapsulated in PCL shell for textile purpose.

2.3.2. Electrospraying

Electrospraying is novel electrohydrodynamic atomization achieving the stretching and breakup of the polymeric solution to prepare polymeric microspheres or microcapsules as well as further achieve their functional coatings on materials surface means of electrical force. The solution containing the solubilized polymer, with or without the active principle, is polarized in the applied electric field, and the charged droplets were stretched and accelerated into the

charged jet due to the electrostatic forces generated on their surfaces. After that, the charged jet breakups into tinnier charged droplets due to Coulomb repulsion forces, and after completed solvent evaporation, particles in the nano- to micrometer range are collected [69].

The electrospraying, as a nanotechnology process, is also used to confer to the textile some finishing nano-chemical treatments [70, 71], such as water and oil repellent [72], antimicrobials with or without chitosan [73, 74], moisture management [75], and for textile functionalization [76] and functionalized non-woven production [77], medical and filtration application [78, 79], without altering the physical properties of the textile fabrics and the agglomeration of the particles during the process.

The properties of particles, size and morphology, and in particular their influences on the kinetics of active release, are strictly related to the formulation parameters and machine parameters used in electrospraying. For textile applications, spherical morphologies are considered more suitable for the release of active ingredients, compared to those of irregular shape. The use of electrospraying and coaxial electrospraying are recognized to be a suitable process for the entrapment of various active substances such as phase change materials [80], fragrances and essential oils [9], dyes or pigments [81], or drugs [82].

3. Textiles and Fibers Functionalization and Properties

Microcapsules can be applied to any textile support (fabric, knitwear, non-woven, clothing made) regardless of the chemical nature of the fibers, by conventional finishing techniques or incorporated into the fiber during the spinning stage. They are also sometimes applied during a rinsing cycle of a washing machine. However, the incorporation of microcapsules into any textile substrate can only be achieved by controlling the physico-chemical characteristics of the particles to optimize their compatibility with other compounds in the formulation according to the final application [83]. The choice of the process is based on both efficiency and durability criteria for microcapsules. Thus, for specific uses in the clothing sector, microcapsules must have a wash life of at least 20 cycles, with thermal stability allowing ironing or tumble drying. During washing, the chemical action of alkaline products, friction and temperature can alter the microcapsules.

Nevertheless, optimizing the formulation of the finishing bath, and in particular by choosing the appropriate binder polymer for each type of textile support may achieve the improvement of the shelf life of the particles. However, the best way to preserve the integrity of microcapsules remains hand-washing fabrics to minimize the loss of active ingredients and optimize their effects while they are worn. Also, the limitation of this technology is that when the capsules are “empty”, they cannot be recharged. Therefore, the microcapsules are integrated or fixed on the textile according to the technique that best matches the finish of the product, the textile itself or the expected wash resistance.

For conventional finishing methods such as scarfing, printing or bath immersion, the textile support is impregnated with a solution, dispersion or emulsion of microcapsules. Whatever the process is chosen, it requires the use of a binder polymer such as acrylic, polyurethane or silicone, with or without a catalyst, to allow the capsules to be fixed on the textile and to maintain them during the post-treatment stages or use. Fixation is only achieved after the drying and rigidification of the polymer on the surface of the substrate. The use of a binder has certain disadvantages, particularly about the physical (touch, permeability, drape,...) and mechanical properties of the substrate. The quantity used must be sufficient to ensure proper adhesion to the substrate without affecting the release of the active ingredient. A microcapsule covered with binder may become more difficult to break, or the binder may limit the diffusion of the encapsulated substance when the membrane is broken. Another option used to improve the functionality of microcapsules, and more particularly for those that diffuse the active ingredient, is to graft the reactive membranes onto the fibers chemically. However, this choice is limited since it is necessary that the microcapsules resist synthesis conditions and have reactive surface functions. In some specific cases (e.g., gelatin or chitosan microcapsules), it is advantageous to use ionic interactions to fix the microcapsules on the supports. Lamination and coating processes are relatively well suited to the incorporation of microcapsules on textile substrates, especially for applications that require large quantities of particles such as the use of phase change materials (PCM) or flame retardants (FR). Depending on the method used, the viscosity of the formulation and the compatibility of the coatings with the membranes of the microcapsules, the latter are either wholly trapped in the coating or remain partially on the surface. When fully integrated into the coating, the diffusion of the active ingredient is controlled not only by the resistance of the membrane but also by the thermo-mechanical and barrier properties of the polymer used. During surface integration, the particles can either diffuse spontaneously by mechanical pressure, or the membranes can degrade slowly under the influence of the environment. In most cases, the aim is to optimize the binder/microcapsules mass ratio to impregnate as many microcapsules as possible with a minimum of the binder while preserving the main thermo-mechanical characteristics of the textile, without excluding aesthetics, touch,... and by promoting textile/binder/microcapsules adhesion.

The incorporation of microcapsules into the core of fibres during the spinning stages, either wet (4 to 40% by weight) or melt (3 to 24% by weight) spinning, has attracted the attention of many researchers since the late 1980's, particularly for the design of thermoregulated structures [84,85]. These types of processing require the formulation of microcapsules with average diameters of less than 10 µm, and excellent thermo-mechanical properties. The solvent route was initially preferred not only to limit the tendency of microcapsules to aggregate in dry powder form but also to avoid thermal degradation of the shells [86]. Thus, acrylic fibers containing 7% by weight of microcapsules have been available on the market since 1997 [87], other types of viscose or lyocell-based fibers are produced on a pilot scale [88]. The

melting process requires increasing the thickness of the microcapsules membranes to improve their thermal stability. These particles are first extruded in polyethylene, polypropylene or polybutylene terephthalate and then spun [89, 90]. However, for charging rates higher than 10% by weight, the process destroys some of the microcapsules.

Therefore, the development of a textile structure containing microcapsules is particularly complicated. The choice of processes for encapsulating and applying microcapsules must be the subject of compromises between different parameters such as economic aspects, the performance of the desired functionality, the preservation or improvement of the physical properties of the textile, knowing that these various points are interrelated. Thus, the development of functional textile materials requires a global approach to the problem, which cannot be reduced to a single property without ignoring that the multitude of other parameters conditions the functional properties of the material.

The use of microencapsulation for the functionalization of textile substrates has been the subject of particular attention in recent years. The choice of the encapsulation process, correlated to the chemical nature and physico-chemical properties (stability, porosity,...), must be considered not only by considering the characteristics of the active principle to be encapsulated but also the final application and the functionalization step on or in the textile fibers. Based on these different criteria, original solutions have been studied mainly for applications aimed at textile comfort for the improvement of thermoregulation [91-94], fire protection with or without the concept of the formulation of intumescent microcapsules [43, 51, 95], or the delivery of active ingredients for cosmetotextile applications [45, 96-98].

Textile fabrics can be functionalized with chitosan microcapsules by using one of the following finishing treatment [99]:

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. Smart End-Uses of Textile Substrates Containing Microcapsules

Research in the textile field has focused mainly in recent decades on the design of clothing that offers the wearer better performance in terms of portability and comfort while combining functional properties of different kinds [100]. In the context of improving the performance of textile materials, microencapsulation is a practical approach to combine the functional side of active ingredients with the intrinsic properties of textile structures. Also, microencapsulating the active ingredients also improves their effect while facilitating their incorporation into the fabric, which has led to better performance and durability of the treatments [6].

Table 1: Recent examples textiles finishing treatments for microcapsules

Application	Incorporated substance	Textile material	Finishing method	Reference
Insect repellent	Citronella oil	Polyester & cotton	Padding	[101]
Insect repellent	Citronella oil	Polyester	Pad dry curing	[102]
Insect repellent	Essential oils / diethyl toluamide	Cotton	Immersion	[103]
Cosmeto-textile	Jasmine oil	Cotton	Impregnation	[104]
Cosmeto-textile	Neroline	Cotton	Impregnation	[30, 31]
Color	Phthalocyanine	Cotton & viscose	Printing	[105]
Color	Thermochromic solution	Cotton	Pad dry curing	[106]
Color	Liquid crystal	Cotton	Coating	[49]
Fragrance	Citrus unshiu oil	Cotton	Pad dry curing	[46, 107]
Fragrance	Chinese arborvitae	Cotton	Padding	[108]
Fragrance	Male and female fragrance oils	Cotton	Printing	[42]
Fragrance	Cologne essential oil	Cotton	Impregnation	[109]
Fragrance	Limonene	Leather & cotton	Immersion	[45]
Fragrance	Essential oils	Silk	Impregnation Dip-pad curing Exhaustion Spray-drying Spray-curing	[98]
Fragrance	Peppermint oil	Cotton	UV curing	[110]
Medical	Ozonated oils	Cotton	Padding	[111]
Medical	Green tea & Viola tricolor	Linen	Spraying	[61]
Comfort	N-octadecane	Leather	Spraying	[112]
Comfort	N-eicosane	Cotton	Pad dry curing	[113]
Comfort	N-octadecane	Cotton	Pad dry curing	[114]
Comfort	N-octadecane	Polyester	Printing, coating, padding	[115]
Comfort	Paraffin	Polystyrene foams	Coating	[116]
Flame retardant	Resorcinol bis(diphenyl phosphate)	Polyester	Impregnation	[51]

4.1. Improving textile performances

The choice of the material microcapsules shell should be carried out in the function of the desired microcapsules functionality and the finishing process used. Thus, natural shell such as chitosan is useful to confer natural antimicrobial activity, and its biodegradability and biocompatibility allow envisaging its use to encapsulate bioactive principles. Furthermore, the presence of positive surface charge lead a good affinity for cellulosic substrates, and confer much functionality to enhance the textile performances [117], and more especially in the manufacture of medical and cosmetic textiles [118], or also to encapsulate phase change materials as thermal storage devices to improve the thermal comfort of the user [119].

4.1.1. Cosmeto-textiles

A cosmetic-textile is generally defined as a textile material containing various specific substances or preparations to be released on the most superficial layers of the skin. Its actions are mainly focused on cleaning, perfume, appearance modification, protection, maintenance, or masking of body odors. This field of application has mainly developed by taking advantage of microencapsulation technology and in particular for the control of substance release, and the possibility of effectively binding the encapsulated systems to the textile support, making it possible to increase its efficiency over more extended periods of use. Given the first promising commercial results regarding performances, some researchers focused on upscaling the production of cosmeto-textiles taking in account the selection of the chemical substances involved in the synthesis to limit the use of harmful and reactants. Therefore, these last years, the research works have turned towards the green production of cosmeto-textiles. To succeed in, various natural substances, either animal derivatives such as chitosan, sericin, or squalene, or plant derivatives, mostly essential oils such as peppermint, caffeine, lavender, thyme or eucalyptus are used for slimming, moisturizing, refreshing and relaxing, energizing, perfuming, vitalizing, UV protection, improving the firmness and elasticity of skin [120].

Regardless of the encapsulated active ingredient or membrane used, the objective of many studies in recent years has focused on washability. Thus, the encapsulation of vanillin with chitosan and the fixation of microcapsules by chemical grafting using citric acid and using sodium hypophosphite as a catalyst on cotton obtained stability of 10 wash cycles [121]. These authors also observed that remarriage kinetics were influenced by temperature and relative humidity. Liu et al. have prepared polysiloxane-modified aromatic nanocapsules, with a mean diameter of about 100 nm, via a two-stage emulsion polymerization method containing jasmine oil as an essential oil [104]. The capsules contain 26.25 % of essential oil, and the impregnation onto cotton fabric allows obtaining washing durability after 15 washing cycles with a residual rate of oil about 25.3%, with much better washing durability than their previous study [109]. The study of Azizi et al. focuses on the improvement of the application of fragrant

polyurethane microcapsules onto 100% cotton jersey fabric by impregnation showing its efficacy for the production of cosmeto-textile articles due to the addition of a cationic surfactant and a polyurethane cross-linking solution during the finishing process [31]. Thus, they have observed that washing durability was increased compared to their previous research work [30]. Sharkawy et al. proposed alternatives to toxic crosslinking chemical compounds, which have been used both in the microencapsulation and finishing processes [55]. In their study, they have substituted aldehyde based substances such as glutaraldehyde with polycarboxylic acids such as tannic to entrapped vanillin and limonene by complex coacervation. The grafting was performed by using citric acid as a crosslinker, to initiate the esterification reaction with sodium phosphate monobasic monohydrate as a catalyst at 50°C prior after thermofixing the fabric underwent at 90°C.

4.1.2. Medical textiles

Medical textiles consist in textile substrate containing bioactive substances for topical or systemic application, where the active substance is released at the outer skin layers for wound healing devices to treat burns injuries or skin ulcers [122], or through the skin such as transdermal patches [123], as well as biological adaption. For this type of development, chitosan as a carrier plays a main role, since it is suitable for dermatological applications, with its ability to degrade in an acidic environment, or slowly at the pH of the skin, and the presence of cationic charges allowing its diffusion through the skin barrier [124-126]. Clindamycin 2-phosphate was entrapped into chitosan nanoparticles by ionic gelation method, or antimicrobial activity against Candida Albicans [118]. The nanoparticles were then used to functionalize viscose fibers by dipping, padding and oven drying, to be used as vaginal pads. The functionality of this textile is related to the fast diffusion of the hydrophilic drug and reduced erosion of the polymer matrix at the pH tested. Simple phase coacervation was used by Beşen et al. to encapsulate ozonated vegetable oils in gum arabic shell. These microcapsules were applied by padding process onto cotton fabric [111]. The purpose of this study was to develop a disposable textile intended to be used as an adhesive plaster or compression dressing, with antibacterial and wound healing properties, and being biologically adapted. Zimniewska et al. have developed a functional garment for the therapy of dermatological diseases [61]. The natural fibers clothing was functionalized with ethylcellulose microcapsules containing plant extracts, such as tea extract and viola tricolor, by a spraying process. They found that their textile was safe for sensitive, non-cytotoxic or keratinocyte no irritant skin, protected against UV radiation, improved lubrication and hydration of the skin and was suitable for treating dermatoses in wearer's tests.

4.1.3. Thermal regulation microcapsules for textiles

A phase-change material (PCM) absorbs or releases a large amount of latent energy

repeatedly during its phase transitions, whether solid-solid or solid-liquid. Among all energy storage techniques, the use of this type of material is particularly attractive because of their high storage density, allowing the implementation of compact energy storage systems under quasi-isothermal conditions. In addition, they have a high melting enthalpy. Thermal energy can be stored or released efficiently and repeatedly by PCM depending on ambient temperature variations and the availability of hot or cold sources. Their action is “temporary” or “transient”, i.e., it is useful as a barrier to thermal energy until all the latent heat stabilizing the exchange temperature is absorbed or released during the phase change of the material [127]. The microencapsulation of PCM has many advantages since the spherical morphology promotes the temperature gradient and increases their shelf-life. Also, the product is always in a “confined” state when the phase change takes place in the core of the coated material. The dispersion of microcapsules is relatively simple, and different PCM formulations can be used to establish the optimal working temperature for phase change. The use of microcapsules increases the heat exchange surface, which enhances the efficiency of heat transfers. A more considerable amount of thermal energy can thus be stored and/or released at a temperature considered constant without significant volume change since the particle size remains constant. Besides, the presence of a free volume within the particles allows the phase change to be complete. This encapsulation step also reduces or eliminates problems generated by subcooling and phase separation. Therefore, impermeable membranes allowing the reversibility of thermal effects throughout use encapsulate these products.

These last years, various organic PCM, such as n-octadecane, n-eicosane, paraffin oil or butylstearate, have been encapsulated via in situ polymerization, ionic gelation, emulsion polymerization or suspension-like polymerization for applications in geopolymer coating [128], thermoregulated textile for thermal comfort [114, 115, 119, 129-131], or thermoregulated foams heat insulation materials [116]. In these various studies, the authors have searched to increase the thermal stability of the microcapsules, the core/shell ratio, or to modify the capsules shell materials to improve the durability of the finishing processes, while maintaining the physical properties of the fabrics, such as mechanical properties, water transfer and air permeability.

4.2. Textiles for protection

One of the main interests in the manufacture of functional or multifunctional textiles is mainly focused on protecting the wearers in hostile environments such as biological hazards, UV rays, insects or fires.

4.2.1. Microencapsulation of flame retardants

Flame retardants (FR), used in many textile applications to limit the flammability and release of toxic and corrosive gases from the majority of synthetic polymers during combustion, are also commonly encapsulated. The capsules Can be fixed to textiles using a

variety of methods. They can be mixed with the polymer during spinning or incorporated into manufactured textiles by conventional finishing processes such as scarfing or coating without modifying the intrinsic properties of the textile. Thus, the latest studies have focused on the encapsulation of phosphate derivatives such as triphenyl phosphate bisphenol-A bis (diphenyl phosphate) and resorcinol bis (diphenyl phosphate) [133] by an in situ process with one or two layers depending on the choice of finishing trématent. Microencapsulation is an appropriate method to avoid any leakage of the liquid RF, and the choice of the melamine formaldehyde Shell increases the thermal stability properties. However, a high content of microcapsules is required to obtain appropriate flame retardant properties, which is not possible without modifying the physical properties of the textile fabric. The fields of application are therefore limited.

4.2.2. Microencapsulation of insect repellent

Insect repellent compounds are primary encapsulated, before the textile finishing process, to improve their wash fastness as well as to reduce their toxicity. Repellents compounds may be divided into two main families according to their origins, i.e., natural sources which are recognized as eco-friendly and biodegradable, such as essential oils come from the extraction of citronella, lemon, thyme or orange; chemical origins, such as N,N-diethyl-m-toluamide (DEET), or permethrin [134]. Nevertheless, most of these substances are toxic in high doses and therefore causing adverse effects on human. Thus, these repellents were encapsulation in chitosan [135], gelatin [136], or Arabic gum [103] to prevent their evaporation, before imparting to fabric by immersion [103], pad dry cure [102] or spraying method, or addition to rinsing cycle. The encapsulation allows their release over time during product use.

5. Conclusion

Microencapsulation is a versatile technique for enhancing the functional performance of active principles 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 textile-based products. Nowadays, the focus lays on the development of new processes exploiting green chemistry to make the production easily up scalable. From the formulation point of view, the high interest is to propose methodologies displaying effective loading of the active substance while controlling the release kinetics. In the present chapter, the efforts of the scientific community toward the achievement of useful microcapsules production evidencing the progress in the field over the last five years and trying to forecast the future trends in the production of smart textiles. Given the contact between the smart textile and the human skin, the exploitation of bio-sourced materials was proposed to be an effective solution in textile finishing. An exciting 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. 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 concluding that the combination of microencapsulation process and textile science plays a determinant role in the design of the garments of future to satisfy the consumer needs while complying to new regulations in terms of process safety and environmental impact.

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 polymer shell, or on methods textile finishing for the functionalization of the fabric substrates. 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, the extension of encapsulation methods for water-soluble active without the use of volatile organic solvent, and the integration of these functional coatings.

Thus, future works will focus not only on bio-sourced polymer, green microencapsulation processes, but also the textile finishing processes under mild conditions. Therefore, exploiting the potential of microencapsulation pass through research, process control, but also by the combination and adaptation of different technology.

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