

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

171,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Introductory Chapter: Functional Textiles

Bipin Kumar and Viraj Somkuwar

1. Introduction

Recent developments in high-performance fibers, fabrics, and manufacturing technologies become the main driving force behind the emergence of functional textiles. The majority of functional textiles were originally used in defense applications, but due to their popularity, they are now available to the general population. The field of functional clothing is vast and varied, with each function having its own set of specifications, material needs, and corresponding technologies and methods. Hence, the designing and from the prospect of manufacturing, the functional clothing becomes a challenge due to limited set of standards and varying requirements according to the needs. Functional textiles have a wide range of applications, including saving lives, adapting to hostile environments, and improving performance and quality of life [1, 2].

The recent COVID-19 epidemic had a significant impact on the world, posing difficulties to the health care infrastructure, society, culture, and economic system. The outbreak has failed all the advance medical treatments, but the crucial role was played by the non-pharmaceutical measures in reducing the transmission of viruses. The functional and smart textile has played a crucial role in designing the personal protective equipment (PPE) and telemedicine for strengthening the healthcare system. The breakthrough research in the field of nanomaterial, surface treatments, and finishing technology has given an edge to the functional textiles to successfully prevent this spread of viruses and disease. The personal protective equipment such as masks, surgical gowns, and gloves are the examples of textile functional clothing used for COVID19 protection. The fabrics were treated with antiviral and antimicrobial treatment to enhance its protection efficiency [3–5]. Another major factors that help the people during the lockdown situation are the telemedicine technology, which again mainly depends upon the smart and wearable textile which contains some electronic sensing functionality. The functional clothing used for telemedicine contains, electronic-embedded sensor, or the textile material itself converted into the sensor, which monitor the human vital parameters, such as heart rate, breathing pattern, blood oxygen level [6].

The focus of this book is to review key materials, manufacturing technologies, and the application methodologies for the designing and development of functional and technical textiles. This chapter will provide an overview of the principles of different types of functional textiles and their applications in various industries.

1.1 Functional textile: definition

All the textile clothing is meant to perform several objectives in our daily life from esthetics to provide basic protection from the various external factors. “Functional clothing” can therefore be defined as “a generic term that includes all

such types of clothing or assemblies that are specifically engineered to deliver a pre-defined performance or functionality to the user, over and above its normal functions” [7]. This type of clothing can be produced by using high-performance fiber, novelty finishes, or intrinsic modification of conventional material. The clothing is expected to perform some specific functions, which can be protecting the person from a hazardous working environment, facilitating the movement during sporting activity, assisting a physically challenged individual or enhancing the endurance of a sports person. Functional clothing can be used for protection against the life-threatening viruses and diseases in medical treatment. It can also have the electronic functionality embedded inside the clothing, which can be used for transmitting the signals wirelessly and monitor the human vital to provide telemedicine facilities [1].

1.2 Classification of functional textiles

The standard technical textile is categorized according to the application, such as Sportech (sports textile), Protech (protective textile), and MedTech (medical textile). Designing a product for a specific end user opens up a new classification system that includes current technology. The classification for the functional textile can be made according to the functionality and requirements. As the material, manufacturing technology may be the same or varied for the specific application. For example, material selection is based on the user’s physiological and psychological needs, whereas technology is chosen based on the required functionality, ergonomics, comfort, and fit (Table 1).

1.2.1 Protective clothing

It is one of the largest areas of functional clothing. The designing of the fabric varies for every function and required special attention. Environmental factors such as heat, cold, snow, and wind demand different types of fiber, fabric construction, and treatment. The challenge in designing the protective clothing is to offer maximum protection without affecting the metabolic heat transmission [8]. A fire protective clothing assembly schematic is shown in Figure 1, depicting the fabric layer arrangement to protect the skin from different hazards and simultaneously maintaining the body’s thermal balance [9, 10]. Some primary requirements are

| Class | Description |
|-----------------------------|--|
| Protective clothing | Environmental protection—extreme heat or cold, rain, snow, dust, UV rays Biological, chemical, and radiation—hazardous chemicals, toxic gases, germs, radioactive substances Injury protection—cut, ballistic, impact protection |
| Medical functional clothing | Surgical protection—viruses, germs, bacterial protection Therapeutic—pressure management in lymphatic and venous disorder, scar management |
| Wearable clothing | Sensing—biological and physiological monitoring, telemedicine Communication—wireless monitoring, remotely tracking |
| Sports clothing | Training—performance enhancement, fatigue management, body shaping Activewear—moisture, sweat management, heat stress management |
| Special needs clothing | Clothing for the elderly, pregnant women, infants, and disabled |

Table 1.
Classification of functional textile clothing.

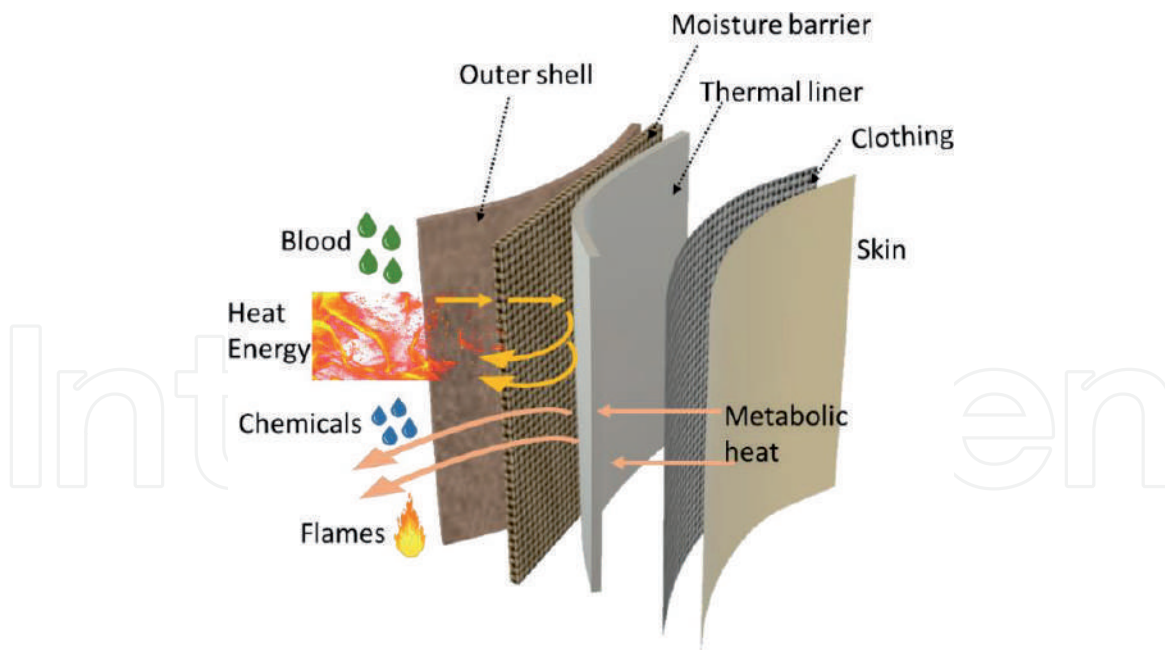


Figure 1.
 Fire-protective functional clothing assembly.

lighter weight and volume, ergonomic design, and better moisture management. The biological, chemical, and radiation protection demands a barrier between the source of radiation and the human skin; hence, the clothing should contain a reflective material or a coating to prevent the penetration of these substances through the clothing [11, 12].

1.2.2 Medical functional clothing

Textiles have been utilized for medical treatment from a long time for surgery, wound protection, etc. The major function of this clothing is to protect from the bacteria, viruses, and body fluid infection. The clothing uses intrinsic antimicrobial textile material or substances coated onto the fabric. The fabric used for therapeutic treatments uses elastic garment to impart a compression on the infected area. The pressure exerted by the compression garments helps in the movement of the blood and lymphatic fluid from the affected area to reduce the venous disease. The pressure garments use elastic yarn and fabric construction, such as knitting to develop compression garments [13–15]. The functional clothing used for COVID19 protection uses a nonwoven fabric as a filter medium in the mask and PPE kit. Nonwoven fabric's porosity can be modified to obtain appropriate virus protection, and they can be coated with antiviral and antibacterial compounds to improve their protective performance [3–5].

1.2.3 Wearable clothing

Textile-based monitoring and treatment devices are becoming more preferable due to comfortability and portability, and use discretely and carefully among children and elderly people. Furthermore, the interactive textiles can be utilized for real-time monitoring and ultra-personalization, such as data measurement and storage for individual customers to have accurate and precise diagnoses [16–18]. There are several textiles-based TENGs applications reported in real-time monitoring, such as heart rate detection (ECG), neurobiological rehabilitation, gait recognition, pulse detection, motion sensors, respiration detection, and thermotherapy [17, 19–21]. E-textiles

constitute two domains—textiles and electronics, which vary in type, material, and behavior from each other. Textiles are soft, flexible, porous, and susceptible to different conditions, while in general, electronics are rigid, precise, and guarded. It is always challenging to achieve material-specific properties for the wearable application while complying with the contrasting properties of electronics and textiles. Triboelectric nanogenerator (TENG) devices constitute one such platform for merging textile with electronics. The TENGs use the triboelectric effect and electrostatic induction to transform mechanical energy into electricity. The self-generation of an electrical signal without any power supply and the response to the health stimulus creates the TENG as a viable alternative for the wearable monitoring applications. The triboelectric effect is well known for almost a thousand years, through which material becomes electrically charged due to friction. The contact between two materials of opposite polarity creates an electrochemical interaction between the surface molecules, which is responsible for the generation of triboelectric charges on their surfaces. However, upon the separation, these triboelectric charges become the driving force for the electron to flow through the electrode to equalize the potential difference created (**Figure 2**) [20, 22].

1.2.4 Sports functional clothing

The growing popularity of textiles in the sports industry has increased the demand for functional clothing, which has become a critical aspect in improving a

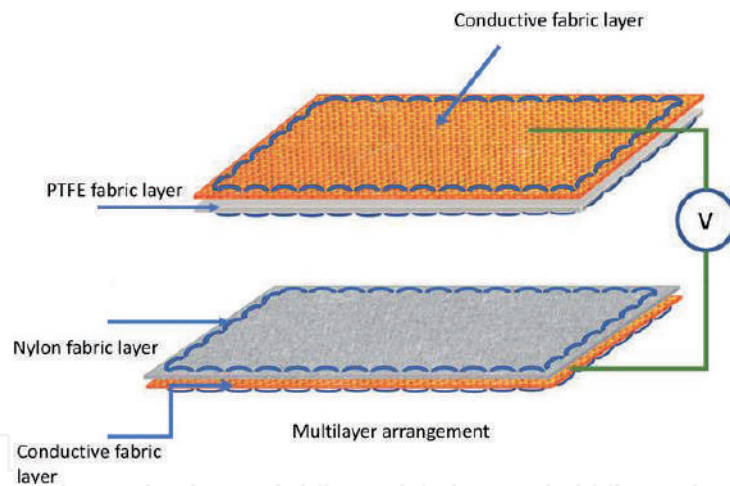


Figure 2.
Schematic of triboelectric nanogenerator arrangement [22].

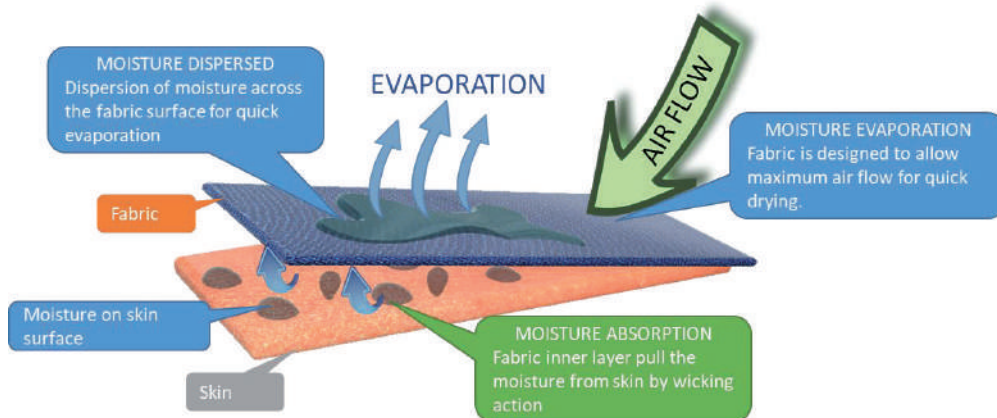


Figure 3.
Mechanism of moisture transport through sports clothing.

sportsperson's overall performance. The main characteristics of sports functional clothing are moisture management, quick moisture transport, temperature management, odor control, lightweight, and fit. The textile fiber is specially modified to enhance its surface area to facilitate moisture wicking helps in maintaining thermal balance during sports activity (**Figure 3**) [23]. Sports functional clothing is also used for enhancing the performance of the sportsperson by the mechanism of compression and aerodynamic design [23, 24]. The compression property of the garment helps in regulating the blood flow to a specific muscle groups providing enhanced energy and oxygen supply, which also helps in faster muscle recovery [14]. The aerodynamic design helps to reduce the wind and air resistance by systematically controlling the morphology of the fiber, shaping the garment, and structural arrangement of the fabric components [16].

2. Market and future scope

The need for functional fibers, processes, and technologies is growing in the 21st century, and such products are not being only used in apparel or garment, but also in other different applications, such as medical, automotive, agriculture, sports, geotextile, and others. The recent outbreak of COVID19 has resulted in more demand for medical textile products. The acceptance of smart healthcare products in daily life will be the next significant technological change going to happen globally. Smart Wearable E-Textile Medical Technology is one of the top-trending technology topics across the globe. It includes the integration of smart sensor/actuator materials in garments for non-invasive health monitoring. Such e-textiles help to detect the individual's vital signs and retransmit them *via* wireless sensor technology to provide continuous feedback on the health status. For the development of any functional or smart textile product, it combines knowledge from interdisciplinary backgrounds including material science, interfacial physics, biomechanics, textile engineering and design, and other engineering stream. Additionally, the need for new technologies is expected to be developed, which could bring down the manufacturing cost and make such products a commercially successful. It has been projected a massive growth rate of over 6% CAGR for the technical and functional textiles from 2020 to 2025, expected to reach over \$222.4 billion global markets by 2025.

Author details

Bipin Kumar* and Viraj Somkuwar
Department of Textile and Fibre Engineering, IIT Delhi, New Delhi, Delhi, India

*Address all correspondence to: bipiniitd18@gmail.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Pan N, Sun G. Functional Textiles for Improved Performance, Protection and Health. Sawston, United Kingdom: Elsevier; 2011
- [2] Majumdar A, Singh SP, Ghosh A. Modelling, optimization and decision making techniques in designing of functional clothing. *Indian Journal of Fibre and Textile Research*. 2011;**36**(4):398-409
- [3] Beesoon S, Behary N, Perwuelz A. Universal masking during COVID-19 pandemic: Can textile engineering help public health? *Preventive Medicine*. 2020;**139**:106236
- [4] Darby S et al. COVID-19: Mask efficacy is dependent on both fabric and fit. *Future Microbiology*. 2021;**16**(1):5-11
- [5] Ha JF. The COVID-19 pandemic, personal protective equipment and respirator: A narrative review. *International Journal of Clinical Practice*. 2020;**74**(10):e13578
- [6] Hollander JE, Carr BG. Virtually perfect? Telemedicine for COVID-19. *The New England Journal of Medicine*. 2020;**382**(18):1679-1681
- [7] Gupta D. Functional clothing—Definition and classification. *Indian Journal of Fibre and Textile Research*. 2011;**36**(4):321-326
- [8] Scataglini S, Andreoni G, Gallant J. Smart clothing design issues in military applications. In: *International Conference on Applied Human Factors and Ergonomics*. Switzerland AG: Springer; 2018
- [9] Song G, Mandal S, Rossi R. Thermal Protective Clothing for Firefighters. United Kingdom: Woodhead publishing, Elsevier; 2016.
- [10] Lawson JR. Fire fighters' protective clothing and thermal environments of structural fire fighting. In: *Performance of Protective Clothing: Sixth Volume*. West Conshohocken, PA, USA: ASTM International; 1997
- [11] Nurfaizey A et al. Functional nanofibers in clothing for protection against chemical and biological hazards. In: *Functional Nanofibers and their Applications*. Sawston, United Kingdom: Woodhead Publishers; 2012. pp. 236-261
- [12] Bhuiyan MR et al. Advances and applications of chemical protective clothing system. *Journal of Industrial Textiles*. 2019;**49**(1):97-138
- [13] Garg H et al. Polyethylenimine-based shape memory polyurethane with low transition temperature and excellent memory performance. *Macromolecular Materials and Engineering*. 2020;**305**(8):2000215
- [14] Kumar B, Hu J, Pan N. Smart medical stocking using memory polymer for chronic venous disorders. *Biomaterials*. 2016;**75**:174-181
- [15] Kumar B, Das A, Alagirusamy R. Study of the effect of composition and construction of material on sub-bandage pressure during dynamic loading of a limb in vitro. *Biorheology*. 2013;**50**(1-2):83-94
- [16] Leutheuser H et al. Textile integrated wearable technologies for sports and medical applications. In: *Smart Textiles*. Switzerland AG: Springer; 2017. pp. 359-382
- [17] Coyle S et al. Textile-based wearable sensors for assisting sports performance. In: *2009 Sixth International Workshop on Wearable and Implantable Body Sensor Networks*. Berkeley, CA, USA: IEEE; 2009

[18] Islam GN, Ali A, Collie S. Textile sensors for wearable applications: A comprehensive review. *Cellulose*. 2020;27(11):6103-6131

[19] Yi F et al. Recent advances in triboelectric nanogenerator-based health monitoring. *Advanced Functional Materials*. 2019;29(41):1808849

[20] Mathew AA, Chandrasekhar A, Vivekanandan S. A review on real-time implantable and wearable health monitoring sensors based on triboelectric nanogenerator approach. *Nano Energy*. 2020;80:105566

[21] Pragya A et al. Designing and investigation of braided-cum-woven structure for wearable heating textile. *Engineering Research Express*. 2020;2(1):015003

[22] Somkuwar VU, Pragya A, Kumar B. Structurally engineered textile-based triboelectric nanogenerator for energy harvesting application. *Journal of Materials Science*. 2020;55(12):5177-5189

[23] Dong Y et al. Materials design towards sport textiles with low-friction and moisture-wicking dual functions. *Materials and Design*. 2015;88:82-87

[24] Raj AN, Yamunadevi S. Application of textile fibres for technical and performance enhancements in sports. *International Journal of Multidisciplinary Research and Development*. 2016;3(12):40-45

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

171,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Antimicrobial Agents for Textiles: Types, Mechanisms and Analysis Standards

*Ahmad Ibrahim, Joseph-Émile Laquerre, Patricia Forcier,
Vincent Deregnaucourt, Justine Decaens
and Olivier Vermeersch*

Abstract

The large surface area, and ability to retain moisture of textile structures enable microorganisms' growth, which causes a range of undesirable effects, not only on the textile itself, but also on the user. Moreover, textiles used in health care environments are required to possess antimicrobial property to minimize spread of pathogenic infection. Anti-microbial property can be imparted via chemical finishing with an antimicrobial agent. Currently the use of antimicrobial agents includes metal compounds (notably copper and silver particle), chitosan, halogenated phenols "triclosan", quaternary ammonium compounds, antibiotics (a class of antimicrobials produced from microorganisms that act against one another), and N-halamines. The possibility of bacterial resistance limits antibiotic use to specific medical applications, and triclosan is known for being dangerous to the environment and is currently under scrutiny for possible endocrine disrupting to human being. Although quaternary ammonium compounds are stable and easily manufactured, microbial resistance is also a concern. Quaternary ammonium compounds (QACs), Polyhexamethylene Biguanide (PHMB), chitosan and N-halamines are listed under bound or non-leaching type antimicrobials. The bulk of current chapter focuses on the different family of antimicrobial agents used for textiles and their mechanisms.

Keywords: Finishing textiles, nanoparticles, silver particles, quaternary ammonium, antibacterial effect, ecological antibacterial

1. Introduction

Microorganisms play both beneficial and harmful roles in our lives. Some of the beneficial roles include production of oxygen via photosynthesis, nitrogen fixation, circulation of carbon by decomposition of dead organic matter, formation of crude oil, and helping animals such as cows digest their food. They are used by humans in making bread, beer, cheese, and antibiotics. Some of the harmful effects are caused by the virulence of pathogenic microorganisms, i.e., infection causing bacteria such as *Staphylococcus aureus* (*S. aureus*), *Escherichia coli* (*E. coli*), and *Enterococcus faecalis* (*E. faecalis*). Health care associated infections can be controlled by inhibiting the

various routes of transmission that causes an infection to spread from an infected person to healthy person. One of the various routes through which an infection can spread is the direct contact with infected individuals; infected water and food; contact with inanimate objects such as textiles used in scrubs, doctor's coats, surgical gowns, bed-sheets, pillow covers, and curtains. The control of the spread of infections via infected individuals, water and food can be achieved by developing hygienic practices.

Textiles have been recognized as a media for the growth of microorganisms such as fungi and bacteria. The growth of these microorganisms on textiles inflicts unwanted effects not only on the textile material, but also on the consumer. These effects can include the generation of unwanted odor, discoloration in the fabric, an increased probability of contamination, and an overall reduction in the fabric mechanical strength [1, 2]. The spread of infections through textile materials can be controlled by the use of antimicrobial textiles that kill pathogens on contact or hinder their ability to reproduce prior to being transferred on to another material or person. Antimicrobial textiles are made by treating textile substrates with antimicrobial agents or by using textile fiber with inherent antimicrobial efficiency. Antimicrobial agents are bound to textiles by different methods depending on the chemistry between the antimicrobial agent and the textile [3]. Consumers' attitudes toward hygiene and their desire for comfort and well-being have created a rapidly increasing market for antibacterial materials. Therefore, there has been extensive research in recent years in this area. Estimations have shown that there was approximately a production of 30,000 tons of antimicrobial textiles in Western Europe and 100,000 tones worldwide in year 2000. It was also estimated that the production increased by over 15% annually in Western Europe between 2001 and 2005, making antimicrobial textiles a rapidly growing sector of the textile market [1]. While synthetic fibers have been known to be more resistant to microorganisms due to hydrophobicity, natural fibers are more vulnerable to microorganism attack. In addition, soil, sweat, and dust can be nutrient sources for microorganisms [2]. Socks, active-wear, shoe linings, and lingerie account for approximately 85% of the total antimicrobial textile production. In addition, there has recently been a large market for antimicrobial fibers in air filters, outdoor textiles, upholstery, and medical textiles [1].

Other than the antimicrobial ability, there are certain basic requirements to be satisfied by an antimicrobial agent for its successful application on textiles rendering them to be used commercially. The basic requirements of a good antimicrobial agent for textile substrates are summarized below [3, 4]:

- Should possess affinity for specific fabric and fiber types.
- Be easy to apply on textile substrates.
- Be able to inactivate undesirable microbes while simultaneously not affect desired microbes.
- Inert to chemicals to which the textile might be exposed during processing.
- Durable to repeated laundering, dry cleaning, ironing and prolonged storage including resistance to detergents used to care for the textiles.
- Stable during usage without degrading into hazardous secondary products.
- Not adversely affect the user or the environment.

2. Antibacterial family

Many antibacterial product and chemistry are available in the current market using different technologies. Most antibacterial agents applied on textiles have been used for many years in food preservatives, disinfectants, wound dressings, and pool sanitizers. The attachment of these compounds to textile surfaces or their binding with the fiber can reduce their activity largely and limits the antibacterial agents' availability. In addition, the antibacterial agent can gradually be lost during the washing and use of the textile material. The most widely used antimicrobial agents for textile applications are based on metal salts (for e.g., silver), quaternary ammonium compounds (QAC), halogenated phenols (for e.g., triclosan), polybiguanide (for e.g., PHMB), chitosan, and N-halamines [5]. The aim of this section is to present the general family of antibacterial textile finishing.

In general, antibacterial agents can either kill the microorganisms (–cidal) or inhibit their growth (–static). Almost all the commercial antimicrobial agents used in textiles (silver, polyhexamethylene biguanide (PHMB), quaternary ammonium compounds, and triclosan) are biocides. They can damage the cell wall or disrupt the cell membrane permeability, and inhibit the activity of enzymes or synthesis of lipids, while all these functions are essential for microorganism's survival [3].

The antibacterial material can be separated in two categories: antimicrobials with controlled release or 'leaching' mechanism and bound or non-leaching type antimicrobials. The mechanism of the leaching type will act upon contact of the cell. On the other hand, the non-leaching types will diffuse a disruptive chemical to the cell. This type is preferred for an environment supporting the diffusion of the chemical, such as water.

2.1 Antimicrobials with controlled release or 'leaching' mechanism

The antimicrobial agents that belong to this category do not form strong bonds with the textile substrate. The chemical species responsible for biocidal activity are released slowly from the treated fabric surface, thus killing all the microbes surrounding the agent. An advantage of leaching antimicrobials effect are their superior antimicrobial activity than compounds based on other modes of action on the same fabric under similar environmental conditions [6]. The flip side is that the antimicrobial agent in the textile substrate is depleted eventually and loses its effectiveness. Metal salts (e.g., silver) and halogenated phenols (e.g., triclosans) are examples of antimicrobial agents that utilize the leaching mechanism [7].

2.1.1 Metal and metal salts

The interest of metal and metal oxide particle reside in the high antibacterial activity against microorganism, durability and stability, while having a low mammalian cell toxicity, meaning they are safe for close to the skin application. Even at very low concentrations, many heavy metals are toxic to microorganisms. Metal particles are synthesized from different precursor and reducing agent to obtain different end material, morphology or to lower the impact of on cost or environment. Plethora of synthesis reaction are available from the scientific literature. However, the reaction principle is similar for each technique, using a sol–gel. The precursor is usually a water-soluble salt such as silver nitrate, copper chloride, and zinc acetate. The metal ion is reacted with a reducing agent, such as conventional reducer like sodium borohydride, citric acid, citrate, and ascorbic acid, or with bio-based reducer such as glucose, polysaccharide, cellulosic fiber and plant or microorganism

extract. The precursor is mixed with a reducing agent under different conditions such as heat, mixing, sonication to surpass the activation energy of the reaction. Strong reducing agent will require milder reaction condition, while weak reducing agent will require stronger reaction condition. During the reaction, the particle could be stabilized using a capping agent in order to control the shape, size and stability of the final product. In some reaction, the reducing agent will also be used as a capping agent. While metals such as zinc, cobalt and copper have had some applications in past years as antibacterial agents for textiles, silver, having an MIC value of 0.05–0.1 mg/L against *E. coli* is still the most widely used metal in textile applications and wound dressings [3, 7–9]. Moreover, this metal is less toxic in the human body than other heavy elements with a smaller risk for exposure through inhalation, ingestion, or dermatological exposure [10]. It was found that AgNP was much less toxic to human cells than silver ion [11]. A concentration of silver ion higher than 1 µg/ml is toxic to human mesenchymal stem cells while the concentration of AgNP can be higher than 2.5 µg/mL. AgNP can destroy bacteria even at a nano-molar level while silver ion needs to be at a micro-molar level.

Silver can be applied in other forms: silver ion exchangers, silver salts, and silver metals. Silver zirconium phosphate and silver zeolites are examples of ion exchangers. Silver chloride (AgCl), nanosilver chloride, and AgCl microcomposites (AgCl nanoparticles attached to titanium dioxide as a carrier material) are types of silver salts. Silver metal can be used in the form of filaments and silver metal composites [12]. With concerns regarding bacterial resistance to silver [3], there is efforts to increase the efficiency of metal-based antimicrobial. Other metal based antimicrobial agents found to exhibit good antimicrobial properties are based on copper and zinc compounds, in the form of their sulfides and sulfates [13]. Many studies on metal salts have focused on preparation of nano sized metal particles, which has led to the development of new generation of biocides [5]. Above all, AgNP (Silver Nanoparticles), a nanometric form of silver element without an ionic charge, can be used as a catalyst, an optical sensor and an antibacterial agent [14–16]. The antibacterial activities of the silver ion and salts are well studied, but research about antibacterial mechanism of AgNP is relatively recent [14]. Different methods have been developed to synthesize and incorporate AgNP in some biomedical applications, and some reports have proven AgNP to be a potent antibacterial agent, that is effective against both Gram-positive and Gram-negative bacteria [17–19].

2.1.1.1 Mechanisms of metal and metal salts antimicrobial action

All silver-based antimicrobials generate and release different amounts of silver ions, with silver metals releasing the least, silver ion exchangers releasing the most, and silver salts somewhere in between [20]. In the presence of moisture, silver releases ions that bind the bacterial cell's surface with proteins. On binding, the following action occurs [21].

- Denaturing effect of the silver causes DNA to get condensed and lose its replication abilities.
- Induces inactivation of bacterial proteins by reacting with thiol group [21, 61].

The form of the silver used impacts its antibacterial effectiveness. For example, a concentration of AgNO₃ should be higher than 1 mM to kill silver resistant *E. coli*. While only 80 nM of AgNP is necessary for the same result [17]. The antibacterial efficacy of silver is directly proportional to the amount of bioactive silver ions released in the presence of moisture, as well as its ability to penetrate bacterial cell

membranes [10]. Silver is effective at low concentrations and promotes wound healing without appreciable toxic risk. However, there is a small risk of developing allergies to silver [22, 23]. In fact, silver and copper ions can disrupt or kill the microbes via different mechanism path. First, the ions can diffuse through the cell membrane and bond to the enzyme of the cell. The enzymatic activity of the cell is decreased, which inhibits the growth of the cell until the death of the cell. Second, Silver ion can kill microbes by binding to intracellular proteins and inactivating them, can inhibit the synthesis of ATP (Adenosine triphosphate) and lead to DNA (Deoxyribonucleic acid) denaturation [24]. To observe the killing mechanism of silver ion more directly, TEM (Transmission electron microscopy) and X-ray techniques were used to facilitate the investigation. When *Escherichia coli* (E.coli) and *Staphylococcus aureus* (S. aureus) were treated with AgNO₃, the cytoplasm membrane detached from the cell wall. Subsequently, DNA and protein failed to function and finally the cell wall was damaged [21]. Third, the silver cation can damage bacterial cell walls, proton leakage and result in cellular structural changes. It can induce proton leakage through the membrane of the cell and cell death. The silver cation is highly reactive in a concentration between 5 and 40 mg/L [25]. Regarding the AgNP, their exact antibacterial mechanism has not been clearly revealed to date [11, 26]. The reduced nano-silver did not show antibacterial activity toward E.coli, but when it was mixed with partially oxidized nano-silver, the mixture showed significant inhibition to the growth of E.coli. Thus, the antibacterial activity of AgNP is a result of surface oxidization as AgNP is sensitive to oxygen [17].

Others metals oxides of interest are titanium dioxide (TiO₂) and zinc oxide (ZnO). The mechanism of those compounds is believed to be mostly from the generation of reactive oxygen species (ROS). Those compounds prevent the antioxidant defense system and damage the cell membrane of the microbe. This mechanism is catalyzed by ultraviolet light. It is of particular interest as an adjuvant to the UV disinfection, which is of growing usage for disinfection against COVID-19. However, this also means the efficiency of those metal oxides is largely influenced by the environment in which they are used. The efficiency of the metal oxide could be reduced in the presence of antioxidant or pigment, often used in synthetic textile. The morphology of the particle will have a great impact on the stability of the product as well as the antibacterial activity. In general, the greater surface area will provide a greater activity, but decrease the durability for the leaching type.

Currently, silver is used in a large number of antimicrobial commercial textile products at a relatively low cost. The silver is in the form of ultra-fine metallic particles and is mainly applied to polyesters, in the finishing stage. Ruco-BAC®, SilverClear®, UltraFresh®, Silpure®, AlphaSan®, Microfresh®, Solefresh®, GuardYarn®, and SmartSilver® are some of the commercially available antibacterial agents applied on textiles [3, 27, 28]. In the case of synthetic fibers, metal and metal salts particles can be incorporated into the polymer prior to extrusion (or before electrospinning for nanofibers). For example, silver can diffuse into the fiber surface and in the presence of moisture it can form silver ions. Gradual release can lead to an extended period of antibacterial activity. In addition, silver nanoparticles can be padded onto cellulosic and synthetic fabrics, resulting in a durable antibacterial finish [29]. While metals and metal salts has excellent antimicrobial activity, leaching from treated textiles into laundering effluent is problematic. Ionic silver is highly toxic to aquatic organisms, with the EPA setting water quality criteria at 1.9 ppb in salt water and 3.4 ppb in fresh [30]. Effluent from both home laundering and industrial application can transfer silver into sewage treatment facilities, depleting necessary bacterial communities. Research conducted by Geranio et al. found that fabric treated with AgCl released only 2.7 ppb (2.4 ppb for AgCl plus a binder) of total silver per gram of textile after the first wash cycle [31]. As the

effectiveness of silver depends on the release of silver ions, too few ions result in a lack of antimicrobial action, and too many yield an excess leading to pollution and waste. Success depends on finding the balance between minimum antimicrobial concentration and effectiveness.

2.1.2 Halogenated phenols (Triclosan)

2,4,4'-trichloro-2'-hydroxydiphenyl ether, commonly known as Triclosan is a broad-spectrum antibacterial agent, having a Minimum Inhibitory Concentration (MIC) of less than 10 ppm against most kinds of bacterial species. Triclosan has been used since 1960 in a wide variety of consumer products including toothpastes, hand soaps, deodorants, mouthwashes, shower gels, etc. Its mode of action is inhibiting bacterial growth by blocking biosynthesis of lipids. As a relatively small molecule, triclosan can be used by exhaustion, combined with dyes, or applied after dyeing. Through melt-mixing or suspension polymerization, triclosan can be incorporated directly into synthetic polymers (**Figure 1**) [5, 32].

Triclosan inhibits the growth of microbes by using an electrochemical mode of action to penetrate and disrupt the cell wall of microbes. When incorporated within a polymer, it migrates to the surface and protects the material [3, 33]. When embedded in β -cyclodextrin triclosan forms a complex and can exhibit antimicrobial action with minimum quantities [34]. Some researchers claim that triclosan inhibits a specific function i.e., lipids synthesis in a bacteria [35]. Others claim that lower levels of triclosan resistance by strains of bacteria shows that triclosan inhibits bacterial cell function in multiple ways. A decrease in the antimicrobial efficiency of triclosan treated material when the material is subjected to repeated home wash cycles has been reported by [36]. One of the greatest concerns regarding triclosan is that when exposed to sunlight, it breaks down into 2, 8-dichlorodibenzo-p-dioxin, a chemical related to other harmful polychlorinated dioxins. Therefore, it has raised a lot of concern in European governments, and its application in consumer products is banned in some countries [37, 38].

2.2 Bound or non-leaching type antimicrobials

The antimicrobial agents that belong to this category are chemically bound to the textile substrate. Hence, the antimicrobial can act only on the microbe that are in contact with the treated textile's surface. By virtue of its binding nature, these antimicrobials are not depleted and therefore potentially may have higher durability than [39]. However, compounds on a treated fabric might get abraded or deactivated with long-term usage and lose their durability [40]. The antimicrobial agents listed under this category are Quaternary Ammonium Compounds (QACs), Polyhexamethylene Biguanide (PHMB), chitosan and N-halamines.

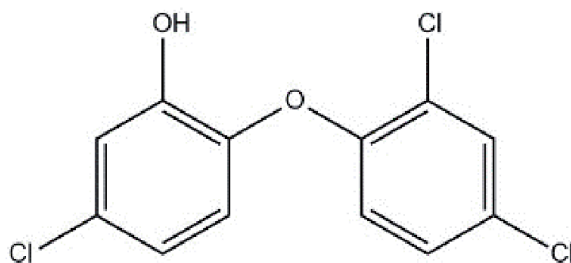


Figure 1.
Molecular structure of Triclosan.

2.2.1 Quaternary ammonium (QAC)

Surface-active agents (surfactants) contain two distinct regions in their molecules: a long chain hydrophobic hydrocarbon tail and a hydrophilic head. Based on the charge of the hydrophilic group, they are classified into cationic, anionic, nonionic, and amphoteric compounds. Among the wide range of these surfactants, the cationic agents (Quaternary Ammonium Compounds or QACs) are known to be the most effective (**Figure 2**). QACs have significant antimicrobial properties and are excellent for deodorization and hard surface cleaning. They are used as biocides in a variety of consumer products, including toothpaste, mouthwash, shampoo, soap, deodorant, etc. The application of QACs as disinfectants goes back to 1936, where Dunn investigated the antibacterial properties of alkyl dimethylbenzylammonium chloride and found the phenol-coefficients against *S. aureus* and *S. Typhosa* (**Table 1**). The most widely used QACs are monoquaternary ammonium such as alkyltrimethylammonium bromide, and diquaternary ammonium salts such as alkanediyl- α,ω -bis (dimethylalkylammonium bromide). Murugan et al. studied the antibacterial behavior of five novel insoluble bead-shaped, polymer-supported multi-quaternary ammonium salts containing two to six quaternary ammonium groups [41]. The QACs showed excellent antibacterial activity against *S. aureus*, *Klebsiella pneumonia* and *Pseudomonas aeruginosa* (*P. aeruginosa*). Murugan et al. also found that the antibacterial activity increased as the number of QACs in the structure increased [41]. However, there are also reports of bacterial resistance to QACs [42, 43]. Following alkyl dimethylbenzylammonium chloride, other QACs such as Cetyl dimethylbenzylammonium halide and N-(acylcolaminoformyl methyl)pyridinium chloride were studied and were found to have high phenol-coefficients. These solutions were known to be both bacteriostatic and bactericidal, according to the period of exposure and concentration [44].

The attachment of QACs to a textile material is known to be predominantly by ionic interactions between the anionic fiber and the cationic QAC. Therefore, in the case of fabrics that contain sulfonate or carboxylic groups, QACs can be attached to fibers by using an exhaustion dyeing process [45–47]. In the case of synthetic fibers, which contain fewer reactive sites and are quite resistant to antibacterial finishing modifications (such as Nylon 66); dye molecules can act as bridges to bind the functional molecules to fibers [48]. For example, acid dyes can be used to dye the fabric and then QACs can be applied under alkaline conditions. This ionic bonding between the QAC and the dye is relatively strong and provides a semi-durable antibacterial finishing [47, 48]. Hence a dyed fabric can achieve higher add on levels of QACs and antimicrobial efficacy as compared with undyed fabrics [48]. One commercial QAC-based antibacterial textile is Bioguard[®]. The active antimicrobial agent is 3-trimethoxysilylpropyldimethyloctadecyl ammonium chloride, also known as AEM 5700 or Dow Corning 5700 Antimicrobial agent, which has an MIC = 10–100 mg/L against Gram-negative and Gram-positive bacteria. This

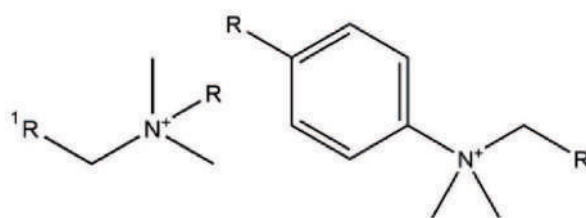


Figure 2.
 General molecular structure of Quaternary ammonium (QAC).

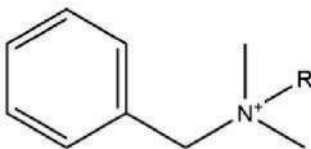
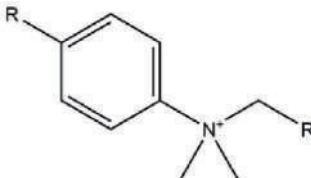
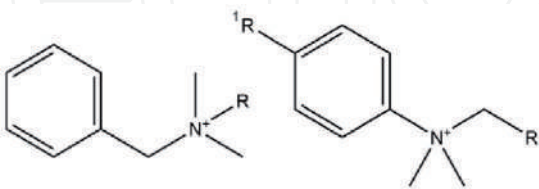
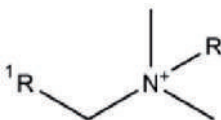
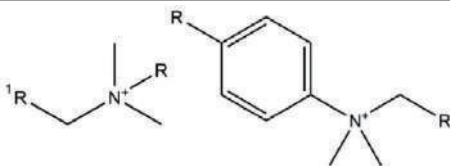
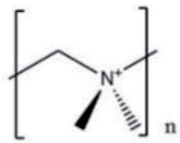
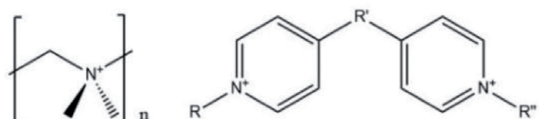
| Generation | Compound example | Description |
|------------|--|--|
| 1st |  | Benzalkonium, alkyl chains, C12 to C18 |
| 2nd |  | Aromatic rings with hydrogen and chlorine, methyl and ethyl groups |
| 3rd |  | Dual QACs; mixture of alkyl dimethyl benzyl ammonium chloride (lower toxicity) |
| 4th |  | Dialkylmethyl aminos with twin chains |
| 5th |  | Synergistic combinations of dual QACs |
| 6th |  | Polymeric QACs |
| 7th |  | Bis-QACs with polymeric QACs |

Table 1.
Molecular structures and description of the different generations of quaternary ammonium (QAC).

compound is made into aqueous solution and applied by spraying, padding, and foam finishing. During drying, silane forms covalent bonds with the textile, resulting in excellent durability. This compound has been commercially used on nylon, cotton, and polyester. Recently, novel quaternary ammonium functional dyes have been applied on textiles in order to combine antimicrobial finishing and dyeing of textiles in a single step [49–51].

2.2.1.1 Mechanisms of Quaternary ammonium (QAC) antimicrobial action

QACs are active against a broad range of microorganisms such as fungi, Gram-positive and Gram-negative bacteria, and some viruses. QACs have a positive charge on the N atom and inflict a variety of effects on microorganisms, including the disruption of cell membrane, denaturation of proteins, and damage to cell structures. It has been proposed that during the inactivation of bacteria, the quaternary ammonium group remains intact and can retain its antibacterial ability as long as

the QAC is attached to the fibers [48]. When a microbe approaches a QAC treated fabric, the free end of the agent's molecule reacts with the cell wall and causes a leakage of the negatively charged species in the microbe cell. It eventually causes the cell's death [39, 52]. The cationic ammonium group and the negatively charged bacteria membrane are attracted to each other. Consequently, the interactions result in the formation of a surfactant-microbe complex that interrupts all the normal functions of the membrane [53]. QACs affect bacterial DNA, causing a loss of multiplication ability [5]. If the long hydrocarbon chain is bonded to the cationic ammonium in the structure of the QAC, two types of interactions between the agent and the microorganism can occur: a polar interaction with the cationic nitrogen of the ammonium group and a non-polar interaction with the hydrophobic chain. Penetration of the hydrophobic group into the microorganism consequently occurs, enabling the alkylammonium group to physically interrupt all key cell functions [5]. The efficiency of the quaternary ammonium depends on the generation and chain substitution. It is known that the germicidal power increases with an increase in carbon chain length, while the surface activity also increases in the same way [44]. The QACs with 12–18 carbons have been used extensively as disinfectants. The typical dosage is under 1%, and even under 0,1% for some application.

To resume, the quaternary ammonium compounds are membrane active agents, their target site is at the inner (cytoplasmic) membrane in the bacteria (or plasma membrane in yeasts) [8, 44]. One of the mechanisms proposed for the antimicrobial action of QACs is in this sequence:

- Adsorption and penetration of QAC in the microorganism's cell wall
- Reaction with the lipid or protein cytoplasmic membrane, which will disorganize the membrane
- The leakage of low molecular weight intracellular material
- Degradation of nucleic acids and proteins
- Wall lysis which is caused by the autolytic enzymes.

Without detailing the studies carried out on the toxicity of quaternary ammoniums, different experiences were carried out on their ocular toxicity [54, 55], contact dermatitis [56], their skin sensitizer (human contact allergen) and asthma [57, 58]. Quaternary ammonium compounds are known to cause occupational asthma. It was found that nurses exposed to a class of QAC and all exhibited early or delayed asthma symptoms when handling disinfectant solutions containing QAC. The same study was done with products lacking in QAC and the results were negative [59]. These results have been confirmed by a multitude of studies [57–59]. In parallel, it has been reported that repeated occupational exposure after handling QACs as powders or solutions could cause sensitization [60]. In conclusion, the studies above all confirm the link between prolonged exposure to quaternary ammonium compounds and asthma. However, regarding ocular and dermal irritation, it seems that the quaternary ammonium compounds allergenicity is likely to be related to the compound's solubility. Apparently, no quaternary ammonium compounds can be regarded as allergens. In most of the studies that classify these compounds as irritants/allergens, the lipid or water-soluble compounds have been studied, while the non-soluble QACs certainly do not have the same properties.

2.2.2 Polyhexamethylene biguanide (PHMB)

PHMB is a hetero disperse mixture of polyhexamethylene biguanide (**Figure 3**). Polyhexamethylene biguanide (PHMB, commercially known as Vantocil) is a broad-spectrum antibacterial agent with low toxicity, having an MIC = 0.5–10 ppm. It has been previously used as a disinfectant in pool sanitizers, mouthwashes, wound dressings, and in the food industry. PHMB can disrupt the integrity of cell membranes [61].

The halide form of PHMB i.e., polyhexamethylene biguanide hydrochloride is applied on cellulosic materials [62]. PHMB is found to form hydrogen bonds with cellulosic fibers. With the increase in the concentration of PHMB there is a dominant increase in hydrogen bond formation between PHMB and fibers [63]. When the fabric treated with PHMB is exposed to a bacterium, the biocide interacts with the surface of the bacteria and is transferred to the cytoplasm and cytoplasmic phospholipids in the bacterial membrane. This biocide is positively charged, and therefore it mainly reacts with negatively charged species and includes aggregation, leading to increased fluidity and permeability. This results in the leakage of inner material from the outer membrane and eventually causes death of an organism [52].

2.2.3 Regenerable N-halamines and Peroxyacids

N-halamines are heterocyclic compounds containing one or two covalent bonds formed between nitrogen and halogen [64]. N-halamines contain one or more nitrogen-halogen covalent bonds formed by the chlorination or bromation of imide, amide or amine groups. The halogen, which is usually chloride, is replaced with hydrogen in presence of water or chloroform and acts as biocide (**Figure 4**) [65]. By using chlorine-containing N-halamine compounds, durable antibacterial finishing can be achieved on textiles. N-halamines are broad-spectrum disinfectants, which have been used previously for water treatment. Their antibacterial activity is known to be due to the oxidative properties of halamine bond (N-Cl). In order to kill the bacteria, N-Cl will be transformed to N-H, which can be recharged with chlorine (during laundering, by using bleach). The product of the reaction is reversible, meaning the N-halamide can be regenerated with the presence of chlorine compound. This function is found in hypochlorite, commonly found in bleach solution. The regeneration with bleach can be done during the washing process. This novel regenerable method was first proposed by Sun and Xu for the treatment of cotton fabric [66]. Since then, many different heterocyclic N-halamines have been applied on polyester, nylon, keratinous fibers, and cotton through covalent bonding. In all these studies, it was demonstrated that regenerable and durable antibacterial activity can be achieved by recharging the fabric in aqueous chlorine solutions.

N-halamine compounds, of which N-chloramine is one form, can provide instant and complete kill of a broad-spectrum of microorganisms. The antibacterial property is based on active chlorine, Cl^+ . Two mechanisms can be used to explain

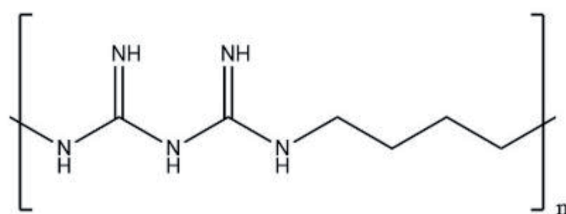


Figure 3.
Molecular structure of Polyhexamethylene biguanide (PHMB).

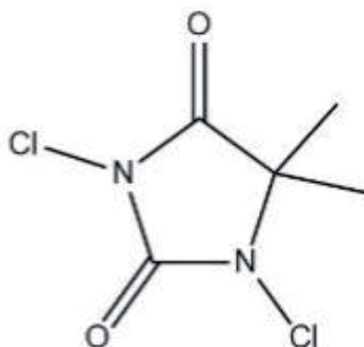


Figure 4.
 Molecular structure of N-halamines.

the antibacterial activity of N-chloramine. One mechanism is that free chlorine is released into water and then forms HClO or ClO^- . The other is that chlorine binds directly to acceptor regions in bacteria and greatly influences their enzymatic and metabolic processes [64]. It was found that the antibacterial activity mainly attributed to the second mechanism because the dissociated chlorine is limited [67]. N-halamines possess stability that is suitable for long-term use, storage and regeneration. N-chloramine can be achieved by the reaction between sodium hypochlorite solution and imide, amide or amine groups. N-halamines have been used in water treatment and incorporated into cellulose-containing fabrics, polyester fibers and polyamide [68–70]. Although no research has directly addressed N-halamine in wound dressing, it has been grafted onto fibers or fabrics so it may be used in wound dressing [69, 70].

Halamine can be applied on different textile including cellulose, polyamide and polyester fibers [71–74]. It has also been found to have extraordinarily durable biocidal functions in a series of laundering tests [75]. However, N-halamine materials are found to be decomposed upon exposure to ultraviolet irradiation as in direct sunlight [76]. The main problem with N-halamines was that they result in a significant amount of absorbed chlorine (or maybe other halogens), which can remain on the fabric surface, resulting in unpleasant odor and fabric discoloration. The use of bleach and the presence of strong oxidizing degrade the dye on the textile, which leads to discoloration of the textile. This antimicrobial technology is best used on bleach resistant textile. One method known to resolve this problem is using a reduction step to remove the residual unbounded halogen from the surface of fabric [75–79]. An alternative antibacterial finishing agent is known to be peroxyacids (such as peroxy acetic acid, which is extensively used in hospitals.) Peroxyacids should convert to carboxylic acid in order to deactivate bacteria, but can be regenerated by reacting with an oxidant (such as hydrogen peroxide). Despite the stability of the peroxyacids on the fabric during prolonged periods, the antibacterial activity reduces largely after a number of washing and recharging cycles [73, 74].

2.2.4 Chitosan

Chitosan is derivatized by the deacetylation of Chitin, the main component of shrimp, crab, and lobster shells. Chitin, a poly (β -(1–4)-N-acetyl-D-glucosamine) is a natural polysaccharide. Chitin is synthesized by many living organisms. Chitin is the second most abundant polysaccharide in nature after cellulose [80]. When chitin is acetylated to at least about 50%, then it is called chitosan [28]. Chitosan (**Figure 5**) contains three reactive sites including a primary amine and two primary or secondary hydroxyl groups per glucosamine unit. As a result, it is readily

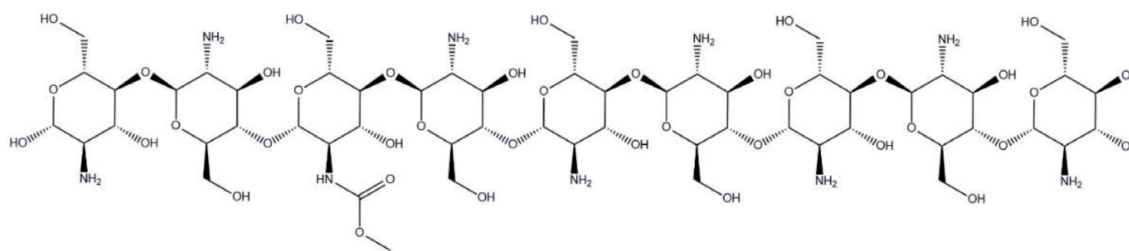


Figure 5.
Molecular structure of chitosan.

subject to chemical modification. The structural characteristics of chitosan mimic glycosaminoglycan components of the extracellular matrix, so the biocompatibility, biodegradability, antibacterial, hemostatic and antioxidant activities and mucoadhesive properties impart versatility [81]. Chitosan's good antibacterial activity along with its biodegradability, biocompatibility, and most importantly nontoxicity makes it an ideal biocidal agent in food science, pharmaceuticals, medicine, and textile applications. Despite all these advantages, chitosan lacks good solubility above pH 6.5. Its applications in a commercial context are not as wide as might be expected [82]. One of the potential problems with an effective chitosan based antimicrobial agent is that chitosan is insoluble in water and possesses high molecular weight. The high molecular weight increases the viscosity of the medium and causes detrimental effect on the hand and feel of the fabric [83]. Chitosan can be used to spin antimicrobial fibers or as a finishing agent for surface modification. Therefore, researchers are exploring chitosan derivatives that are soluble in water over a wide pH range for expanding the chitosan applications.

2.2.4.1 Chitosan derivatives

Given that chitosan does not dissolve in aqueous media at neutral and alkaline pH's and its antimicrobial activity likewise is not particularly good in neutral or alkaline solutions, so there is many causes to chemically modify chitosan. These modifications were made with the aim of proposing more soluble chitosan derivatives better suited for textiles. Recent researchers reported that chitosan derivatives have better water solubility, antibacterial and antioxidant properties [84]. Chitosan can be modified to include quaternary ammonium groups, alkyl and aromatic groups, substituents having free amino or hydroxyl groups, carboxy-alkyl groups and amino acids and peptides [85]. And different applications have been found for these chitosan derivatives. Among the derivatives of chitosan we cite: Carboxymethyl Chitosan, N,N,N,-trimethyl chitosan (TMC) and Chitosan nanoparticles (CSNP).

The modification of the structure of chitosan by the addition of carboxymethyl in the structure of chitosan allows the manufacture of carboxymethyl chitosan (CMC). Compared to chitosan, CMC is characterized by high solubility at neutral and alkaline pHs. This modification does not affect its characteristic properties [86]. In addition, CMC has superior antimicrobial activity, biocompatibility and safety for humans. Usually, there are O-CMC, N-CMC, N, singlet O and N, N-dicarboxymethyl chitosan that have different chemical structures (Figure 6). For antimicrobial properties, the antimicrobial activity of different types of CMCs against *E. coli* has been shown to increase by converting NO-CMC < Chitosan < O-CMC due to the reduced number of protonated amino groups in NO-CMC [86]. And against *S. aureus*, O-CMC and N-CMC also have improved antimicrobial properties [86–88].

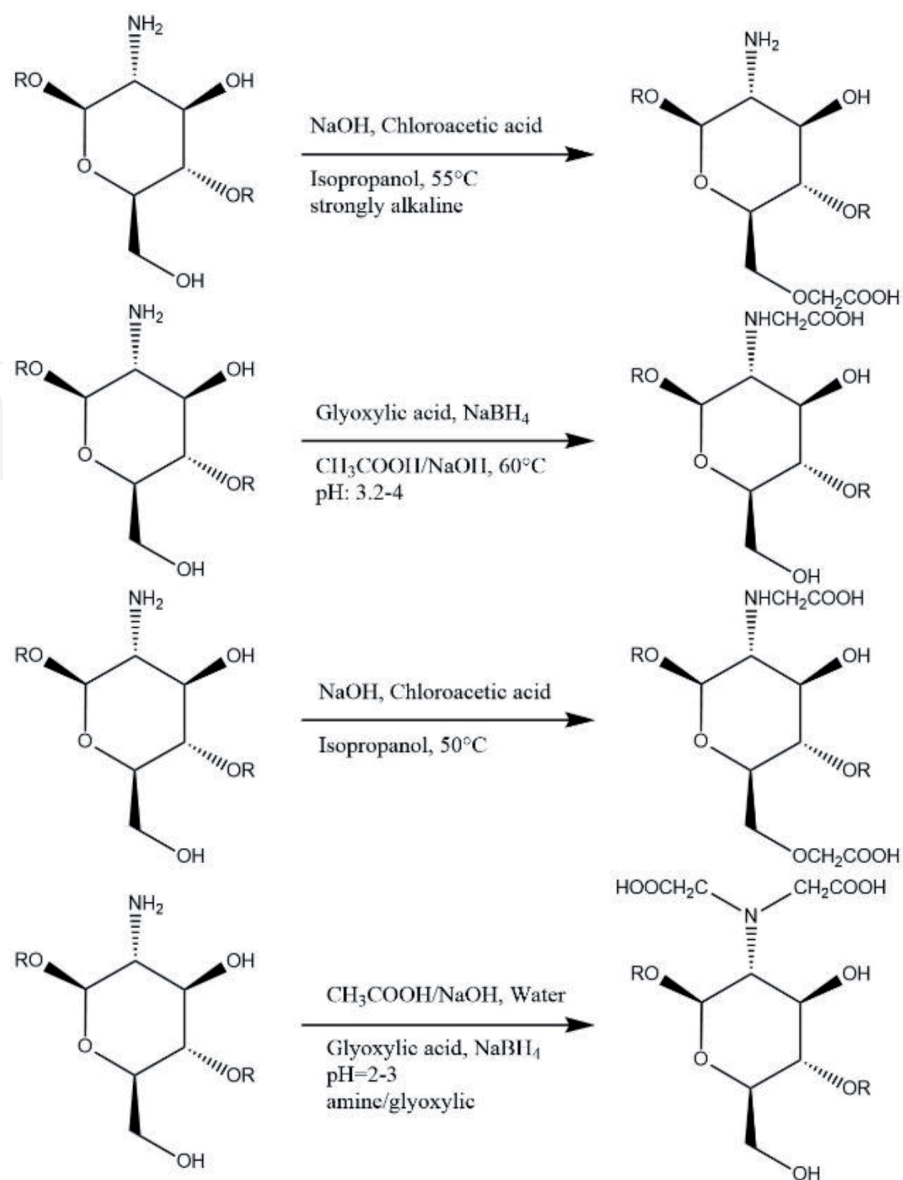


Figure 6.
As example, some carboxymethyl derivatives of chitosan [86].

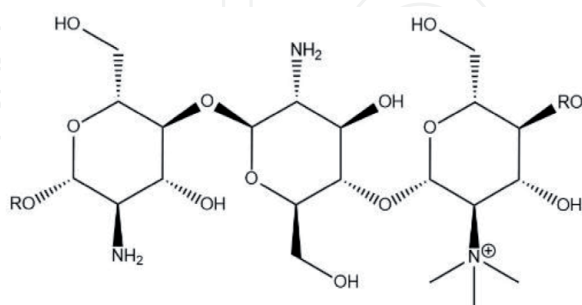


Figure 7.
Molecular structure of N, N, N-trimethyl chitosan [89].

The second chitosan derivative fairly presented in the literature is TMC (**Figure 7**). It is a partially quaternized derivative [89]. It is obtained by nucleophilic substitution of the primary amino group in position C-2 by a quaternary amino group [89]. This modification facilitates the aqueous solubility of TMS at neutral and basic pH due to the presence of a permanent positive charge independent of pH (the quaternary amino amino groups) [90, 91]. This high positive

charge density is responsible for the high antibacterial performance reported for TMC compared to Chitosan [92–94]. It is essential to point out that this modification takes place under alkaline conditions using sodium iodide as catalyst and N-methyl-2-pyrrolidone as solvent [95]. In addition, it can take place by reaction with dimethyl sulfate [96, 97] or dimethylformamide [98].

Among the derivatives of Chitosan, which have a higher antimicrobial activity than the chitosan solution, there are the chitosan nanoparticles (CSNP). For the moment, there is no clear explanation for this high efficiency, but one of the hypotheses given is based on the high specific surface area of nanoparticles as well as their better affinity for the microbial cell wall [99]. Unlike TMC, CNSPs are prepared with simple methods, without organic solvent or high shear force. Among these methods there are: emulsion crosslinking, coacervation (precipitation), ionic gelation, spray drying, microemulsion, diffusion of emulsifying solvent and polyelectrolyte complex [100]. The degree of deacetylation of chitosan and its molecular weight are factors that affect the formation and size of CNSPs [101].

2.2.4.2 Mechanisms of chitosan's antimicrobial action

Chitin is a film-forming polymer with antibacterial and fungi-static property. It triggers the defensive mechanism in host inducing certain enzymes like phytoalexins, chitinases, pectinases, glucanases, and lignin in plants [28]. Chitosan and its derivatives have been studied as antimicrobial agents against bacteria, fungi and viruses, in experiments involving in vivo and in vitro interactions with chitosan in different forms (solutions, nanoparticles, films, fibers and composites). Chitosan can react in two different mechanisms, killing or inhibiting the growth of microorganisms (biocide or Biostatic). However, its action often takes place without distinction between activities [102]. The antimicrobial performance of Chitosan or one of its derivatives depends largely on its molecular structure and its properties such as molecular weight [103], the degree of deacetylation and its water solubility [104–108]. In addition, its pH and its concentration in solution affect its effectiveness against microorganisms [109]. Chitosan has MIC of 0.05–0.1% (w/v) against most common kinds of bacteria. The mode of its antibacterial action is not yet fully understood [110–112], but it is possible that the amine groups provide positive charges which can react with the negatively charged surface of microbes; therefore, they can change the cell permeability, which finally leads to intracellular substance leakage [113, 114]. Chitosan acts primarily as a disruptor of the outer membrane and not as a penetrating agent. Using transmission electron microscopy, impaired membrane function was demonstrated by shrinkage, implying that water and ion leakage had occurred. However, other studies have proposed a mechanism by encapsulation where chitosan forms a polymeric substance around the bacterial cell preventing nutrients from entering the cell and its subsequent death [115]. In addition, a third mechanism based on metal chelation, removal of spore elements and binding to nutrients essential for microbial growth is proposed. This mechanism is based on the strong binding capacities known for chitosan to metals. This absorption of cations occurs by metal chelation favored by the amino groups present in the chitosan molecules [115]. The efficiency of this mechanism depends largely on the pH of the medium. A high pH favors this absorption mechanism by the fact that the amino groups of the chitosan will not be protonated under these conditions. This will allow the pair of electrons on the nitrogen atom to be available for donation to metal ions. Some studies have assumed that the metal can behave as an electron acceptor which connects via $-NH_2$ functions to one or more chitosan chains, forming bridges with hydroxyl groups [116].

2.2.4.3 Chitosan and chitosan nanoparticles (CSNP) on textiles applications

Even though, chitosan has already been utilized for the treatment of fibrous materials, a comprehensive research on their use for antimicrobial functionalization of viscose fibers for development of modern medical textiles for applications in medical devices is still missing. There is a lack of information regarding the behavior of different chitosans in contact with the cellulose materials. In addition, in-depth knowledge of their physical, chemical, and biological properties is missing [117, 118].

For textiles, chitosan and its derivatives could constitute one of the products that can be used for the finishing processes [116]. In addition, they could be used for the production of raw materials such as chitin and chitosan fibers [116]. The latter are widely used, alone or in admixture with other products such as viscose, in the medical field for the manufacture of non-woven, which can be used for dressings, or as a carrier for medicaments in the form of hollow fibers [119, 120]. Microbiological tests showed antimicrobial activity, no cytotoxicity was detected for a chitosan-polypropylene nonwoven [119]. Viscose tampons treated with chitosan were utilized for maintaining the physiological pH of vagina and acting as moisturizing agent, while simultaneously providing antimycotic and antibacterial activity [121]. Textiles treated in such a way were effective against gram-negative and gram-positive bacteria [122]. Some studies have shown that chitosan-based products provide rapid healing and less dense skin lesions compared to standard products [122–124]. By way of example, it has been found that the treatment of cotton with a carboxymethyl chitosan derivative at a concentration of 0.1% provides antibacterial protection against *E. coli* and *S. aureus*, as well as an improvement in the wrinkle recovery. Alternatively, core-shell particles based on chitosan (shell) and poly (n-butyl acrylate) (PBA) (core) have been designed as a novel antibacterial coating for textiles [125]. These particles applied to a cotton fabric showed an antibacterial performance of over 90% against *S. aureus*. The application of chitosan on cotton takes place without the need for a crosslinking agent. Studies have shown that an intermolecular hydrogen bond between the hydroxyl groups of cotton and the amino groups of chitosan [125]. Antibacterial efficacy against *S. aureus* was examined for chitosan nanoparticles loaded with silver (CSNP) applied to polyester. An efficiency of 100% was obtained. This efficacy is attributed to the synergistic effect of silver and CSNP [126].

2.2.5 Natural antibacterial

In addition to chitin and chitosan, antibacterial performance has been identified for other naturally occurring products such as honey. The latter and because of its antibacterial activity allows the treatment of certain burns [127–129]. This antibacterial performance, against certain large bacteria-infecting wounds such as *S. aureus* known for its resistance to methicillin, is attributed to the presence of certain molecules such as hydrogen peroxide and bioflavonoids. The latter have the capacity to inhibit the synthesis of nucleic acids [130].

At the same time, we must not forget the products of plant origin (*Aloe Vera*, tea tree oil and eucalyptus, extracts of neem, grapefruit seeds and tulsi leaves, etc.) which have a high antibacterial performance. This efficiency is attributed to their content in certain phenol type products (simple phenols, phenolic acids, quinines, flavonoids, flavones, tannins and cumarins), terpenoids, essential oils, alkaloids, lectins, polypeptides and polyacetylenes [131]. In addition to their antibacterial performance, these components are known for their antioxidant properties. The combination of these two functionalities constitutes an important advantage

for biomaterials that can be used for medical applications such as dressings. It ensures a reduction in the formation of reactive oxygen species, which are strongly involved in the pathogenesis of injury. Usually these species cause the formation of biomolecules (lipids, proteins and nucleic acids) at the level of injury as well as the depletion of mitochondrial DNA in human skin [132]. Among the powerful anti-oxidants are the flavonoids, which are used as anti-inflammatory, antimicrobial and anticancer agents [132]. But, durability and resistance to washing remains the weak point for the antimicrobial finish based on natural agents. This weakness results from their difficulty in forming bonds with textile materials [133]. Certain methods have been developed to increase this durability. Among these methods, mention may be made of microencapsulation [133–135], the use of a crosslinking agent [131] and the immobilization of bioactive liquids in sol–gel matrices are also described in the literature [135]. For example, antimicrobial activity against *S. aureus* has been recorded for cotton fabrics treated with *Aloe Vera* extract by a dry drying process. This effectiveness was sustainable even after 50 wash cycles [136].

3. Standard tests for antimicrobial activity

The antimicrobial efficacy of textiles could be characterized by different methods of analysis. These methods are standardized and divided into two categories: 1) qualitative, such as AATCC TM147, AATCC TM30 (American Association of Textile Chemists and Colorists Test Method), ISO 20645, ISO 11721 (International Organization for Standardization) and SN 195920, SN 195921 (Swiss standard) and 2) quantitative, such as AATCC TM100, ISO 20743, SN 195924, JIS L 1902 (Japanese industry standards) and ASTM E 2149 (or its modification).

Qualitative methods are characterized by their speed and simplicity. They are mainly based on the agar diffusion test. As diffusion through agar occurs at different rates depending on the textiles and the nature of the antimicrobial agents used, this category of methods is not suitable for all types of textiles. Some differences could be identified between the different qualitative methods. As an indication, we can mention that the textile is laid on an inoculated agar plate for AATCC TM147. While it is placed between two agar plates, with one side inoculated for ISO 20645. Usually the qualitative method has an incubation period. After this period (24–48 h) depending on the type of microorganisms tested, the plates are examined for bacterial growth directly underneath the fabric and around its edges (zone of inhibition). The appearance of the zone of inhibition depends on the ability of the antimicrobial agent to diffuse into the agar and its binding to the textiles. The appearance of a zone of inhibition and its size are indicative of the rate of release of the active agent and its antimicrobial efficacy. It is important to specify that zone of inhibition does not necessarily imply that microorganisms have been killed; they might have only been prevented from growing. By qualitative methods, the efficacy of different agents cannot be compared [137].

On the other hand, quantitative methods can be used for the majority of antimicrobial agents and textile supports. However, they require a longer time compared to qualitative methods. In addition, they are more expensive because they involve a real count of the microbes to measure the antimicrobial effectiveness. This method of measurement makes it easier to compare the effectiveness of different antimicrobial agents on the same textile support, for example [138–141]. Quantitative methods are much more specific depending on the mechanism of action of the antibacterial agent. For example, ISO 20645 can be tested with only leaching types because the configuration does not allow observation under the textile [141]. AATCC TM100 and JIS L 1902 can be tested with leaching and non-leaching type's antimicrobial. These

methods (AATCC TM100, ISO20743 and JIS L 1902) are based on similar principle: specified amount (weight, size, and surface area) of sample swatches or substrate are inoculated with a specified number of microorganisms [142]. The inoculum is put in contact with the treated surface via three different methods: absorption, transfer and printing (ISO 20743). The absorption method uses an inoculated broth with a standardized species and concentration. The broth is absorbed by the textile sample. The sample is incubated in different condition depending on the method, to promote the bacterial growth. This method allows testing a leaching, non-leaching or a combination of antibacterial textile as well as bacteriostatic and bactericidal. However, this method is not recommended for textile with hydrophobic treatment or low absorption capacities [143]. While, the transfer method uses an agar plate who is inoculated with the tested bacteria. The contaminated plate is put in contact with the textile for 60 seconds, and after the sample is incubated. This method is used to replicate the contact of the antimicrobial textile with a contaminated surface. Whereas, the printing method apply the bacteria via a printer. This method allows faster incubation time (1 to 4 h, ISO 20743) and faster sample preparation with the automated printer (ISO20743). Finally, the dynamic shake flask method (ASTM E 2149 (or its modification) is particularly appropriate for non-leaching antimicrobials whilst the dynamic contact conditions are applied to the samples [140]. It can be used to assess the activity of the antimicrobial textile as a qualitative test. This method has been used for testing antimicrobial activity of cotton fabrics (or cellulose fibers) treated with the nanoparticles [144, 145], as well as functionalized wool [146], cotton and viscose fibers coated with chitosan [147, 148], and some other fabrics.

Once the microorganism and incubation application protocol are applied according to the desired method, the microorganism count will take place via two different techniques: the plate count method and the luminescence method. The count plate method consists of recovering the microorganism from the broth by re-plating and the number of surviving organisms. The number of colonies forming unit (CFU) is counted and the bacteria concentration is obtained by multiplying the dilution rate. The ATP concentration is quantified via a spectrophotometer according to the luminescence method. This measurement will be compared with a calibration curve prepared according to the ATP standard. The quantification of the ATP of the inoculum is carried out before and after exposure to the antimicrobial treatment. The number of surviving organisms is counted as CFU and results are usually presented as percentages or log₁₀ reduction in contamination relative to the initial inoculum of microorganisms or the untreated control.

It should be noted that antimicrobial analysis methods are quite sensitive to contaminate. For this reason, tests are usually done under tightly controlled conditions to ensure reproducibility of results. However, carrying out tests in such a standardized environment does not reflect the reality of using textiles treated with antimicrobial agents [137]. Another factor that affects these tests is the efficiency of microbial extractions from the sample tissues. In addition, the absence of an absolute standard of effectiveness facilitates changes in the protocols applied creating inconsistencies between laboratories at national and international levels. Taking into account all the factors affecting the effectiveness of antimicrobial tests, certain additional methods are applied in complementarity. These methods include colorimetric analyzes [149], viability test [150], viability staining and microscopy [151], and fluorescent staining coupled with flow cytometry [152]. Despite the advancements made to date, the poor reproducibility of test results is the Achilles point of these tests. Over time, some attempts to establish a correlation between the different analytical techniques have taken place. For example, AATCC TM147 and JIS L 1902 were found to give the same result for a textile sample with a non-leaching antimicrobial [137]. Nevertheless, the strong differences are always an obstacle.

4. Conclusion

In conclusion, the microorganism presence on textile can be eliminated or the growth can be slowed by treating with a variety of antimicrobial agent. Multiple antimicrobial families were presented in this chapter, including synthetic and natural chemicals (**Table 2**). Textiles are susceptible to microorganism growth because of the structure and the ability to retain moisture of the textile. Therefore, the microorganism growth can generate multiple undesired consequence, such as hosting and transmitting harmful microbe, creating odor, mold, degradation, discoloration and biofouling for example. Textile can be treated with antimicrobial agent to reduce, slow or eliminate the microbial growth and spread. The antimicrobial was categorized in two types in this chapter, leaching and non-leaching. The non-leaching types are bound to the textile and react with the microbes upon direct contact. On the other side, the leaching types release antimicrobial in the environment at a controlled rate to disrupt the microorganism at proximity of the textile. A summary of the common reagents discussed in this chapter is gathered in the **Table 3**.

The antimicrobial efficiency, the durability and skin compatibility of the treated textile must be assessing during the development of an antimicrobial treatment to minimize the risk. The antimicrobial activity testing can be categorized by quantitative and qualitative method. The qualitative method is useful for routine quality control and for the screening of multiples iterations during the development of a product, such as determining the wash durability. However, this method can lead to subjective determination. Instead, the quantitative method eliminates the possible subjectivity with plate count and luminescence technique. In addition, the skin should not be harmed be the treated textile. The safety for the skin can be evaluated with cytotoxicity test to human cell and irritation test in-vitro and in-vivo. The properties of the antimicrobial should be assessed before commercialization of an antimicrobial treated product.

| Mechanism | Reagent | Fiber | Remarks |
|--------------|-----------------|---|--|
| Leaching | Metals (silver) | Nylon, Wool, Polyester and Regenerated- cellulose | Slow release, durable, depletion of Ag might occur |
| | Triclosan | Polyester, Nylon, Acrylic, Polypropylene and Cellulose- acetate | Breaks down into toxic dioxine, large amount needed, bacterial resistance, banned in some European countries |
| Non-Leaching | QACs | Cotton, wool, Nylon, Polyester and Acrylic | Very durable, covalent bonding, possible bacterial resistance |
| | PHMB | Nylon, Polyester and Cotton | Large amount needed, bacterial resistance |
| | N-halamine | Wool, Nylon, Cotton and Polyester | Requires regeneration, unpleasant odor from residual Cl |
| | Peroxyacids | Cotton and Polyester | Poor durability, requires regeneration |
| | Chitosan | Wool, Polyester and Cotton | Low durability, adverse effect on fabric handle |

Table 2.
Conventional reagents used in the antimicrobial finishing of textiles.

| Test | Method | Title | Principle | Antimicrobial type | Uses |
|-------------|---------------------------|---|---------------------------------------|---------------------------|---|
| ASTM E2149 | 20 | Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions | Dynamic shake flask test | Non-leaching type | Qualitative: Screening, routine quality-control |
| AATCC 147 | Parallel Streak | Antibacterial Activity of Textile Materials: Parallel Streak | Zone diffusion assay: Agar | Leaching-types | Qualitative: Screening, routine quality-control |
| AATCC 100 | — | Test Method for Antibacterial Finishes on Textile Materials: Assessment of | Cell suspension intimate contact test | Leaching and non-leaching | Quantitative |
| XP G 39-010 | — | Propriétés des étoffes - Étoffes et surfaces polymériques à propriétés antibactériennes - Caractérisation et mesure de l'activité antibactérienne | Cell suspension intimate contact test | Leaching and non-leaching | Quantitative |
| JIS L 1902 | Absorption method | Testing Method for Antibacterial Activity of Textiles Quantitative Test | Cell suspension intimate contact test | Leaching and non-leaching | Quantitative |
| JIS L 1902 | Transfer method | Testing Method for Antibacterial Activity of Textiles Quantitative Test | Transferred Agar plate contact test | Leaching-types | Quantitative |
| JIS L 1902 | Printing method | Testing Method for Antibacterial Activity of Textiles Qualitative Test | 'Dry' inoculum intimate contact test | Non-leaching | Quantitative |
| JIS L 1902 | Halo Method | Testing Method for Antibacterial Activity of Textiles Qualitative Test | Zone diffusion assay: Agar | Leaching-types | Qualitative: Screening, routine quality-control |
| ISO 20645 | Agar diffusion plate test | Textile fabrics — Determination of antibacterial activity — Agar diffusion plate test | Zone diffusion assay: Agar | Leaching-types only | Qualitative: Screening, routine quality-control |
| ISO 20743 | Absorption Method | Textiles - Determination of antibacterial activity of antibacterial finished products: Absorption Method | Cell suspension intimate contact test | Leaching and non-leaching | Quantitative |

| Test | Method | Title | Principle | Antimicrobial type | Uses |
|-----------|-----------------|--|---------------------------------------|--------------------|--------------|
| ISO 20743 | Transfer Method | Textiles - Determination of antibacterial activity of antibacterial finished products: Transfer Method | Cell suspension intimate contact test | Leaching-types | Quantitative |
| ISO 20743 | Printing Method | Textiles - Determination of antibacterial activity of antibacterial finished products: Printing method | 'Dry' inoculum intimate contact test | Non-leaching | Quantitative |

Table 3.
Comparison of antimicrobial test method for textile.

Antimicrobial resistance should also be a concern when developing an antimicrobial treatment for a textile because of the large quantity of antimicrobial agent required achieving the antimicrobial activity and durability. The risk/reward should always be considered before applying antimicrobial product to a textile. The risk of antimicrobial resistance can be minimized. First off, the antimicrobial should not come close to the minimal inhibitory concentration (MIC) of the treatment during the useful life of the product to guarantee an effective product. The MIC of the antimicrobial product can be reached because of poor wash durability of the antimicrobial product. Second of, the synergy, mechanism of different antimicrobial product can be combined to reduce the resistance of a gene to a pathway. A complex antimicrobial mechanism is believed to be more efficient and more complex for the microbe to develop a set of successful mutated gene against the antimicrobials [153].

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (COVPJ 553781 - 20), and the MEI-Québec (Ministère de l'Économie et de l'Innovation).

Author details

Ahmad Ibrahim*, Joseph-Émile Laquerre, Patricia Forcier, Vincent Deregnaucourt, Justine Decaens and Olivier Vermeersch
Groupe CTT, Saint-Hyacinthe, QC, Canada

*Address all correspondence to: aibrahim@gcttg.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Majeti, K.; Ravi, N.V. A review of chitin and chitosan applications. *Reactive and Functional Polymers*, 2000, 46, 1, 1-27.
- [2] Deepti, G.; Adane, H. Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan. *Carbohydrate Polymers*, 2007, 69, 1, 164-171.
- [3] Gao, Y.; Cranston, R. Recent advances in antimicrobial treatments of textiles. *Textile Research Journal*, 2008, 78, 60-72.
- [4] Kramer, A.; Guggenbichler, P.; Heldt, P.; Junger, M.; Ladwig, A.; Thierbach, H.; Weber, U.; Daeschlein, G. Hygienic relevance and risk assessment of antimicrobial impregnated textiles. *Current Problems in Dermatology*, 2006, 33, 78-109.
- [5] Simoncic, B.; Tomsic, B. Structures of novel antimicrobial agents for textiles-A review. *Textile Res. J.* 2010, 80, 1721-1731.
- [6] Kut D.; Orhan, M.; Gunesoglu, C.; Ozakin, C. Effects of environmental conditions on the antimicrobial activity of treated cotton knits. *AATCC Review*, 2005, 5, 25-28.
- [7] Wolfgang, S.D.; Peter, H. J. Antimicrobial finishes. in *Chemical Finishing of Textiles*. Woodhead Publishing, 2004, 213.
- [8] McDonnell, G.; Russel, A. Antiseptics and disinfectants: activity, action and resistance. *American Society of Microbiology*, 1999. 12, 147-179.
- [9] Purwar, R.; Joshi, M. Recent Developments in Antimicrobial Finishing of Textiles-A Review. *AATCC Review*, 2004. 4: 22-26.
- [10] Lansdown, A.; Hipler, U.; ed, Elsner, P., ed. "Silver in Health Care: Antimicrobial Effects and Safety in Use." *Biofunctional Textiles and the Skin. Current Problems in Dermatology*, 2006, 33, 17-34
- [11] Kittler, S.; Greulich, C.; Koller, M.; Epple, M. Synthesis of PVP-coated silver nanoparticles and their biological activity towards human mesenchymal stem cells. *Materialwissenschaft und Werkstofftechnik* 2009, 40, 258-264.
- [12] Windler, L.; Height, M.; Nowack, B. "Comparative Evaluation of Antimicrobials for Textile Applications." *Environment International*, 2013, 53, 62-73.
- [13] Nakashima, T.; Sakagami, Y.; Ito, H.; Matsuo, M. Antibacterial activity of cellulose fabrics modified with metallic salts. *Textile Research Journal*, 2001, 71, 688-694.
- [14] Kim, J.S.; Kuk, E.; Yu, K.N.; Kim, J.H.; Park, S.J.; Lee, H.J. Antimicrobial effects of silver nanoparticles. *Nanomed-Nanotechnol.* 2007, 3, 95-101.
- [15] Pradhan, N.; Pal, A.; Pal, T. Silver nanoparticle catalyzed reduction of aromatic nitro compound. *Colloid Surface A.* 2002, 196, 247-257.
- [16] McFarland, A.D.; Van Duyne, R.P. Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity. *Nano Letters* 2003, 3, 1057-1062.
- [17] Lok, C.N.; Ho, C.M.; Chen, R.; He, Q.Y.; Yu, W.Y.; et al. Proteomic analysis of the mode of antibacterial action of silver nanoparticles. *J. Proteome Res.* 2006, 5, 916-924.
- [18] Baker, C.; Pradhan, A.; Pakstis, L.; Pochan, D. J.; Shah, S.I. Synthesis and antibacterial properties of silver nanoparticles. *J. Nanosci. Nanotechnol.* 2005, 5, 244-249.

- [19] Aymonier, C.; Schlotterbeck, U.; Antonietti, L.; Zacharias, P.; Thomann, R.; Tiller, J. C.; Mecking, S. Hybrids of silver nanoparticles with amphiphilic hyperbranched macromolecules exhibiting antimicrobial properties. *Chem. Commun.* 2002, 3018-3019.
- [20] Height, Murray. "Silver Use in Textiles." VA. Proc. of Nano Release Steering Committee Workshop, U.S. EPA Potomac Yard Conference Center, 2777 S. Crystal Drive, Arlington. http://205.251.124.92/ResearchFoundation/Documents/NanoRelease%202011%20Workshop%20Presentation%20PDF%20Files/HeightNanoreleaseWorkshop_SilverTextiles_10May2011_print.pdf.
- [21] Feng, Q.L.; Wu, J., Chen; G.Q., Cui; F.Z., Kim; T. N.; Kim, J.O. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *Biomedical Material Research*, 2000, 52, 662-668.
- [22] Lansdown, A. B. G. Silver I: Its antimicrobial properties and mechanism of action. *Journal of Wound Care*, 2002, 11, 125-130.
- [23] Lansdown, A. B. G. A review of the use of silver in wound care: facts and fallacies. *British Journal of Nursing* 2004, 13, S6-S19.
- [24] Leaper, J.D. Silver dressings: their role in wound management. *Int. Wound J.* 2006, 3, 282-294.
- [25] Klasen, H.J. Historical review of the use of silver in the treatment of burns. I. Early uses. *Burns* 2000, 26, 117-130.
- [26] Vimala, K.; Mohan, Y.M.; Sivudu, K.S.; Varaprasad, K.; Ravindra, S.; Reddy, N.N.; Padma, Y.; Sreedhar, B.; MohanaRaju, K. Fabrication of porous chitosan films impregnated with silver nanoparticles: A facile approach for superior antibacterial application. *Colloid Surface B.* 2010, 76, 248-258.
- [27] Thomson Research Associates. Available from: <http://www.ultra-fresh.com/tra/>.
- [28] Rinaudo, M.; Chitin and Chitosan: Properties and Applications. *Progr. Polymer Sci.*, 2006, 31, 603-632.
- [29] Williams, J.F.; HaloSource, V.; and Cho, U.; Antimicrobial Functions for Synthetic Fibers: Recent Developments. *AATCC Review*, 2005, 5, 17-21.
- [30] Troy M.B.; Westerhoff, P. "Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics." *Environmental Science & Technology* 2008, 42, 4133-4139.
- [31] Geranio, L.; Heuberger, M.; Nowack, B. The Behavior of Silver Nanotextiles during Washing." *Environmental Science & Technology*, 2009, 43, 8113-8118.
- [32] Kalyon, B.D; Olgun, U., Antibacterial Efficacy of Triclosan-incorporated Polymers. *Am. J. Infect. Contr*, 2001, 29, 124-125.
- [33] Mansfield, R. G. Keeping it fresh. *Textile World*, 2002, 152, 42-45.
- [34] Lu, J.; Hill, M. A.; Hood, M.; Greeson, D. F.; JR.; Horton, J. H.; Orndorff, P. E., Herndon, A. S.; Tonelli, A. E. Formation of antibiotic, biodegradable polymers by processing with Irgasan® DP300R (triclosan) and its inclusion compound with β -cyclodextrin. *Journal of Applied Polymer Science*, 2001, 82, 300-309.
- [35] Mcmurry, L.M.; Oethinger, M.; Levy, S.B. Triclosan targets lipid synthesis. *Nature*. 1998, 94, 531-532.
- [36] Orhan, M.; Kut, D.; Gunesegulu, C. Use of triclosan as antimicrobial agent in textiles. *Indian Journal of Fibre and Textile Research*, 2007, 32.114-32.118.
- [37] Glaser, A. The Ubiquitous Triclosan- A common antibacterial

agent exposed Available from: <http://www.beyondpesticides.org/pesticides/factsheets/Triclosan%20cited.pdf>.

[38] Williams, R.M. Triclosan - A Controversial Antibacterial. Available from: <http://www.townsendletter.com/May2006/healthrisk0506.htm>.

[39] Malek, J. R.; Speier, J. L. Development of organosilicone antimicrobial agent for the treatment of surfaces. *Journal of Coated Fabrics*, 1982, 12, 38-46.

[40] Shindler, W. D.; Hauser, P.J. Antimicrobial finishes. Chemical finishing of textiles. Cambridge England: Woodhead Publishing Limited, 2004, 165-174.

[41] Murugan, E.; Gopinath, P.; Shanmugayya, V.; Mathivanan, N. Antibacterial activity of novel insoluble bead-shaped polymer-supported multiquaternary ammonium salts. *J. Appl. Polym. Sci.* 2010, 117, 3673-3678.

[42] Townsend, D.E.; Greed, I.; Ashdown, N.; Grubb, W.B. Plasmid-mediated resistance to quaternary ammonium compounds in methicillin-resistant staphylococcus aureus. *Med. J. Australia* 1983, 2, 310.

[43] Tennent, J.M.; Lyon, B.R.; Gillespie, M.T. Cloning and expression of Staphylococcus-aureus plasmid-mediated quaternary ammonium resistance in Escherichia-coli. *Antimicrob. Agents Chemother.* 1985, 27, 1, 79-83.

[44] Resuggan, J.C.L.; The antibacterial activity of quaternary ammonium compounds. *Journal of Applied Microbiology*, 1952, 15, 166-171.

[45] Cai, Z.S.; Sun, G. Antimicrobial Finishing of Acrilan Fabrics with Cetylpyridinium Chloride: Affected Properties and Structures. *Journal of*

Applied Polymer Science, 2005, 97, 1227-1236.

[46] Kim, Y.H.; Sun, G. Functional Finishing of Acrylic and Cationic Dyeable Fabrics: Intermolecular Interactions. *Textile Research Journal*, 2002, 72, 1052-1056.

[47] Son, Y.A.; Sun, G. Durable Antimicrobial Nylon 66 Fabrics: Ionic Interactions with Quaternary Ammonium Salts. *Journal of Applied Polymer Science*, 2003. 90, 2194-2199.

[48] Kim, Y.H.; Sun, G. Dye Molecules as Bridges for Functional Modifications of Nylon: Antimicrobial Functions. *Textile Research Journal*, 2000, 70, 728-733.

[49] Liu, J.; Sun, G. The synthesis of novel cationic anthraquinone dyes with high potent antimicrobial activity. *Dyes and Pigments*, 2008, 77, 380-386.

[50] Ma, M.; Sun, G. Antimicrobial cationic dyes. Part 3: simultaneous dyeing and antimicrobial finishing of acrylic fabrics. *Dyes and Pigments*, 2005, 66, 33-41.

[51] Ma, M.; Sun, Y.; Sun, G. Antimicrobial cationic dyes: part 1: synthesis and characterization. *Dyes and Pigments*, 2003, 58, 27-35.

[52] Mulder, G. D.; Cavorsi, J. P.; Lee, D. K. Polyhexamethylenebiguanide (PHMB): An addendum to current topical antimicrobials. *Wounds*, 2007, 19, 173-182.

[53] Tiller, J.C.; Liao, C.J.; Lewis, J.; Kilbanov, A.M. Designing surfaces that kill bacteria on contact. *Proc. Natl. Acad. Sci. U.S.A.* 2001, 98, 5981-5985.

[54] Cserhati, T., Alkyl Ethoxylated and Alkylphenol Ethoxylated Nonionic Surfactants: Interaction with Bioactive Compounds and Biological Effects. *Journal of Environmental Health Perspectives*, 1995, 103, 358-364.

- [55] Yanni, J.M. Ophthalmic, anti-allergy compositions suitable for use with contact lenses. 2002, Alcon Universal Ltd.: U.S. Patent 5641805.
- [56] Schallreuter, K.U.; Schulz, K.H.; Wood, J.M. Induction of Contact Dermatitis in Guinea Pigs by Quaternary Ammonium Compounds: The Mechanism of Antigen Formation. *Environmental Health Perspectives*, 1986, 70, 229-237.
- [57] Reynolds, J. Martindale: the extra pharmacopoeia, ed. 31. 1996, London: Pharmaceutical Press.
- [58] Bernstein, J.A.; Stauder, T.; Bernstein, D.I.; Bernstein, I.L. A combined respiratory and cutaneous hypersensitivity syndrome induced by work exposure to quaternary amines. *J Allergy Clin Immunol*, 1994, 94, 257-259.
- [59] Purohit, A.; quaternary ammonium compounds and occupational asthma. *International Archives of Occupational and Environmental Health*, 2000, 73, 423-427.
- [60] Marple, B.; Roland, P.; Benninger, M. Safety review of benzalkonium chloride used as a preservative in intranasal solutions: an overview of conflicting data and opinions. *Otolaryngol Head Neck Surg* 2004, 130.
- [61] Feng, Q.L.; Wu, J.; Chen, G.Q.; Cui, F.Z.; Kim, T.N.; Kim, J.O. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *J.Biomed. mater. Res.* 2000, 52, 662-668.
- [62] Payne, J. D.; Yates, J. E. U.S. Patent No. A1 0271,707. Washington, DC: U.S. Patent and Trademark Office, 2007.
- [63] Blackburn, R. S.; Harvey, A. L.; Kettle, L.; Payne, J. D.; Russell, S. J. Sorption of poly (hexamethylenebiguanide) on cellulose: mechanism of binding and molecular recognition, *Langmuir*, 2006, 22, 5636-5644.
- [64] Lin, J.; Winkelman, C.; Worley, S. D.; Broughton, R. M.; Williams, J. F. Antimicrobial treatment of nylon. *Journal of Applied Polymer Science*, 2001, 81, 942-947.
- [65] Qian, L.; Gang, S. Durable and regenerable antimicrobial textiles: Chlorine transfer among halamine structures. *Industrial and Engineering Chemistry Research*. 2005, 44, 4, 852-856
- [66] Sun, G.; Xu, X.J., Durable and Regenerable Antibacterial Finishing of Fabrics: Biocidal Properties. *Textile Chemist and Colorist*, 1998, 30, 26-30.
- [67] Williams, D.E.; Elder, E.D.; Worley, S.D. Is free halogen necessary for disinfection? *Appl. Environ. Microbiol.* 1988, 54, 2583-2585.
- [68] Sun, Y.Y.; Sun, G. Novel regenerable N-halamine polymeric biocides. I. Synthesis, characterization, and antibacterial activity of hydantoin-containing polymers. *J. Appl. Poly. Sci.* 2000, 80, 2460-2467.
- [69] Sun, Y.Y.; Sun, G. Novel regenerable N-halamine polymeric biocides. II. Grafting hydantoin-containing monomers onto cotton cellulose. *J. Appl. Poly. Sci.* 2001, 81, 617-624.
- [70] Lin, J.; Cammarata, V.; Worley, S.D.; Broughton, R.M.; Tzou, Y. M.; Huang, T.S. Infrared characterization of biocidal Nylon. *Polymer* 2001, 42, 7903-7906.
- [71] Sun, Y.Y. and Sun, G., Regenerable N-halamine Polymeric Biocides. III. Grafting Hydantoin-containing Monomers onto Synthetic Fabrics. *J. Appl. Polymer Sci.*, 2001. 81: 1517-1525.
- [72] Sun, Y.Y.; Sun, G., Novel Refreshable N-halamine Polymeric Biocides: Grafting Hydantoin-containing

Monomers onto High Performance Fibers by a Continuous Process. *J. Appl. Polymer Sci.*, 2003. 88, 1032-1039.

[73] Huang, L.K.; Sun, G., Durable and Oxygen Bleach Rechargeable Antimicrobial Cellulose: Sodium Perborate as an Activating and Recharging Agent. *Ind. Eng. Chem. Res.*, 2003. 42, 5417-5422.

[74] Huang, L.K.; Sun, G., Durable and Regenerable Antimicrobial Cellulose with Oxygen Bleach: Concept Proofing. *AATCC Review*, 2003. 3, 17-21.

[75] Sun, G.; Xu, X.; Bickett, J. R.; Williams, J. F. Durable and regenerable antibacterial finishing of fabrics with a new hydantoin derivative. *Industrial Engineering and Chemical Research*, 2001, 40, 1016-1021.

[76] Kocer, H.B.; Akdag, A.; Worley, S.D.; Acevedo, O.; Broughton, R.M.; Wu, Y. Mechanism of photolytic decomposition of N-halamine antimicrobial siloxane coatings. *ACS Applied Material Interfaces*. 2010, 2, 2456-2464

[77] Liu, S.; Sun, G., Durable and Regenerable Biocidal Polymers: Acyclic Nhalamine Cotton Cellulose. *Ind. Eng. Chem. Res.*, 2006, 45, 6477-6482.

[78] Qian, L.; Sun, G., Durable and Regenerable Antimicrobial Textiles: Improving Efficacy and Durability of Biocidal Functions. *J. Appl. Polymer Sci.* 91, 2588-2593.

[79] Sun, G.; Allen, L.C.; Luckie, E.P.; Wheatley, W.B.; Worley, S.D. Disinfection of Water by N-Halamine Biocidal Polymers *Ind. Eng. Chem. Res.*, 1995. 34, 4106-4109.

[80] Choi, C.; Nam, J.; Nah, J. Application of chitosan and chitosan derivatives as biomaterials. *Journal of Industrial and Engineering Chemistry*, 2016, 01, 33, 1-10.

[81] Dragostin, O. M.; Samal, S. K.; Dash, M., Lupascu, F.; Pânzariu, A.; Tuchilus, C.; Profire, L. New antimicrobial chitosan derivatives for wound dressing applications. *Carbohydrate Polymers*, 2016, 05, 141, 28-40.

[82] Wang, X.; Du, Y.; Luo, J.; Yang, J.; Wang, W.; Kennedy, J. .. A novel biopolymer/rectorite nanocomposite with antimicrobial activity. *Carbohydrate Polymers*, 2009, 07, 77, 449-456.

[83] El-tahlawy, K.F.; El-bendary, M.A.; Elhendawy, A. G.; Hudson, S. M. The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan, *Carbohydrate Polymers*, 2005, 60, 421-430.

[84] Alves, N.; Mano, J. Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. *International Journal of Biological Macromolecules*, 2008, 12, 43, 401-414.

[85] Sahariah, P.; Másson, M. Antimicrobial Chitosan and Chitosan Derivatives: A Review of the Structure–Activity Relationship. *Biomacromolecules*, 2017, 18, 3846-3868.

[86] Upadhyaya, L.; Singh, J.; Agarwal, V.; Tewari, R. P. Biomedical applications of carboxymethyl chitosans. *Carbohydrate Polymers*, 2013, 91, 452-466.

[87] Anitha, A.; Rani, V. D.; Krishna, R.; Sreeja, V.; Selvamurugan, N.; Nair, S.; Jayakumar, R. Synthesis, characterization, cytotoxicity and antibacterial studies of chitosan, O-carboxymethyl and N,O-carboxymethyl chitosan nanoparticles. *Carbohydrate Polymers*, 2009, 11, 78, 672-677.

[88] Mishra, D.; Bhunia, B.; Banerjee, I.; Datta, P.; Dhara, S.; Maiti, T. K.

Enzymatically crosslinked carboxymethyl–chitosan/gelatin/nano-hydroxyapatite injectable gels for in situ bone tissue engineering application. *Materials Science and Engineering: C*, 2011, 10, 31, 1295-1304.

[89] Dehousse V.; Garbacki N.; Colige A.; Evrard B. Development of pH-responsive nanocarriers using trimethylchitosans and methacrylic acid copolymer for siRNA delivery. *Biomaterials*, 2010, 31, 7, 1839-1849.

[90] Jintapattanakit A.; Mao S.; Kissel T.; Junyaprasert V.B. Physicochemical properties and biocompatibility of N-trimethyl chitosan: effect of quaternization and dimethylation. *European Journal of Pharmaceutics and Biopharmaceutics*, 2008, 70, 2, 563.

[91] Prezottoda, S.L.; Douglas, B.; Regali, S.M.H.; Odilio B G. In vitro activity of water-soluble quaternary chitosan chloride salt against *E. coli*. *World Journal of Microbiology and Biotechnology*, 2010, 26, 11, 2089-2092.

[92] Tao, X.; Meihua, X.; Mingchun, L.; Huili, H.; Shengquan. Z. Synthesis, characteristic and antibacterial activity of N,N,N-trimethyl chitosan and its carboxymethyl derivatives. *Carbohydrate Polymers*, 2010, 81, 4, 931-936.

[93] Sadeghi A.M.M.; Dorkoosh F.A.; Avadi M.R.; Saadat P.; Rafiee-Tehrani M.; Junginger H.E. Preparation, characterization and antibacterial activities of chitosan, Ntrimethyl chitosan (TMC) and N-diethylmethyl chitosan (DEMC) nanoparticles loaded with insulin using both the ionotropic gelation and polyelectrolyte complexation methods. *International Journal of Pharmaceutics*, 2008, 355, 1-2, 299-306.

[94] Vidar, R.O.; Jukka H.; Tapio, N.; Martha, H.; Tomi, J.; Thorsteinn, L.; Einarsson Jón M.; Sigrídur, J.; Margrét,

V.; Már. M. Antibacterial activity of methylated chitosan and chito oligomer derivatives: Synthesis and structure activity relationships. *European Polymer Journal*, 2007, 43, 6, 2660-2671.

[95] Sieval A.B.; Thanou M.; Kotze´ A.F.; Verhoef J.C.; Brussee J.; Junginger H.E. Preparation and NMR characterization of highly substituted N-trimethyl chitosan chloride. *Carbohydrate Polymers*, 1998, 36, 2-3, 157-165.

[96] Douglas, D.B.; Odílio B.G. A novel method for obtaining a quaternary salt of chitosan. *Carbohydrate Polymers*, 2007, 69, 2, 305-310.

[97] Pattarapond, G.; Warayuth, S.; Uracha, R.; Nuttaporn, R.P.; Issara, S.; Onanong, N.; Somsak, S.; Saowaluk, C.; Satit, P. Novel quaternized chitosan containing β -cyclodextrin moiety: Synthesis, characterization and antimicrobial activity. *Carbohydrate Polymers*, 2011, 83, 2, 905-913.

[98] Vidar, RO.; Jukka, H.; Sigrídur, J.; Hákon, S.; Már, M. N-selective ‘one pot’ synthesis of highly N-substituted trimethyl chitosan (TMC). *Carbohydrate Polymers*, 2008, 74, 3, 740-744.

[99] Lifeng, Q.; Zirong, X.; Xia, J.; Caihong, H.; Xiangfei, Z. Preparation and antibacterial activity of chitosan nanoparticles. *Carbohydrate Research*, 2004, 339, 16, 2693-2700.

[100] Sunil A.A.; Nadagouda N.M.; Tejraj M.A.; Recent advances on chitosan-based micro- and nanoparticles in drug delivery. *Journal of Controlled Release*, 2004, 100, 1, 5-28.

[101] Quan, G.; Tao, W.; Colette, C.; Paul, M. Modulation of surface charge, particle size and morphological properties of chitosan–TPP nanoparticles intended for gene

delivery. *Colloids and Surfaces B: Biointerfaces*, 2005, 44, 2-3, 65-73.

[102] Rejane C.G.; Douglas, B.; Assis Odilio B. G. A review of the antimicrobial activity of chitosan. *Polímeros*, 2009, 19, 241-247.

[103] Nan, L.; Xi-Guang, C.; Hyun-Jin, P.; Chen-Guang, L.; Cheng-Sheng, L.; Xiang-Hong, M.; Le-Jun, Y. Effect of MW and concentration of chitosan on antibacterial activity of *Escherichia coli*. *Carbohydrate Polymers*, 2006, 64, 1, 60-65.

[104] Ming, K.; Xi-Guang, C.; Yu-ping, X.; Cheng-Sheng, L.; Le-Jun, Y.; Qiu-Xia, J.; Su, C.D.; Jin, P.H. Preparation and antibacterial activity of chitosan microspheres in a solid dispersing system. *Frontiers of Materials Science in China*, 2008, 2, 2, 214-220.

[105] Tomoki, T.; Masanao, I.; Isao, S.; Jun, S. Growth inhibitory effect on bacteria of chitosan membranes regulated with deacetylation degree. *Biochemical Engineering Journal*, 2008, 40, 3, 485-491.

[106] Avadi M.R.; Sadeghi A.M.M.; Tahzibi A.; Bayati Kh; Pouladzadeh M.; Zohuriaan- Mehr M.J.; Rafiee-Tehrani M. Diethylmethyl chitosan as an antimicrobial agent: Synthesis, characterization and antibacterial effects. *European Polymer Journal*, 2004, 40, 7, 1355-1361.

[107] Caiqin, Q.; Huirong, L.; Qi, X.; Yi, L.; Juncheng, Z.; Yumin, D. Water solubility of chitosan and its antimicrobial activity. *Carbohydrate Polymers*, 2006, 63, 367-374.

[108] Dina, R.; Kristine, B.; Albert, H.; Hans-Georg, S. Insights into the Mode of Action of Chitosan as an Antibacterial Compound. *Applied and Environmental Microbiology*, 2008, 74, 12, 3764-3773.

[109] Xiaohui, W.; Yumin, D.; Hui, L. Preparation, characterization and antimicrobial activity of chitosan-Zn complex. *Carbohydrate Polymers*, 2004, 56, 1, 21-26.

[110] Rabea E.I.; Badawy M.E.T.; Stevens C.V.; Guy, S.; Walter, S. Chitosan as Antimicrobial Agent: Applications and Mode of Action. *Biomacromolecules*, 2003, 4, 6, 1457-1465.

[111] Liu X.F.; Guan Y.L.; Yang D.Z.; Li Z.; Yao K.D. Antimicrobial action of chitosan and carboxymethylated chitosan. *Journal of Applied Polymer Science*, 2001, 79, 1324-1335.

[112] Lim, S., H.; Hudson, M. Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals. *Journal of Macromolecular Science*, 2004, C43, 223-269.

[113] Young, D.H.; Kohle, H.; Kauss, H. Effect of Chitosan on Membrane Permeability of Suspension-Cultured Glycine max and Phaseolus vulgaris Cells. *Plant Physiology*, 1982, 70, 1449-1454.

[114] Helander, I.; M., Nurmiäho-Lassila, E. L.; Ahvenainen, R.; Rhoades, J.; Roller, S. Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria. *International Journal of Food Microbiology*, 2001, 71, 235-244.

[115] Simona, S.; Olivera, S.; Lidija, F.; Anita, J.; Karin, S.K. Chitosan-universally applicable biopolymer. *Tekstilec*, 2007, 50, 10, 243-261.

[116] Claudia, V. The use of mucoadhesive polymers in vaginal delivery. *Advanced Drug Delivery Reviews*, 2005, 57, 1692-1712.

[117] Elisabetta, G.; Vanna, S.; Claudia, J.; Cristina, B.M.; Paolo, G.

Mucoadhesive vaginal tablets as veterinary delivery system for the controlled release of an antimicrobial drug, acriflavine. AAPS PharmSciTech, 2002, 3, 3, 1-7.

[118] Antoni, N. Chitosan Medical Dressings. *Fibres & Textiles in Eastern Europe*, 2005, 13, 6, 16-18.

[119] Subhash, A. Medical Textiles and Biomaterials for Healthcare: Incorporating Proceedings of MEDTEX03 International Conference and Exhibition on Healthcare and Medical Textiles. Woodhead. Vol. 2006.

[120] Zemljič Lidija, F.; Olivera, Š.; Igor, B.; Andrej, Z.; Lusicky. M. Viscose Material Functionalised by Chitosan as a Potential Treatment in Gynaecology. *Textile Research Journal*, 2011, 81, 1183-1190.

[121] Hayano, S.; Fujieda, Y.; Yoshioka, S. Chitosan-Coating of Cellulosic Materials Using an Aqueous Chitosan-CO₂ Solution. *Polymer Journal*, 2002, 34, 3, 144-148.

[122] Muzzarelli R.A.A.; Muzzarelli C. Chitosan Chemistry: Relevance to the Biomedical Sciences. in *Polysaccharides I*, Heinze Thomas, Editor. Springer Berlin Heidelberg, 2005, 151-209.

[123] Sang-Hoon, L.; Samuel M.H. Synthesis and antimicrobial activity of a watersoluble chitosan derivative with a fiber-reactive group. *Carbohydrate Research*, 2004, 339, 2, 313-319.

[124] Weijun, Y.; Fai, L.M.; John, X.; Leung, K.T.; Len, L.D.K.; Pei, L. Novel core-shell particles with poly(n-butyl acrylate) cores and chitosan shells as an antibacterial coating for textiles. *Polymer*, 2005, 46, 23, 10538-10543.

[125] Mingxi, W.; Yuanbin, S.; Zuobing, X.; Jing, H.; Rujun, Z.; Jia, Z. The green

adsorption of chitosan tripolyphosphate nanoparticles on cotton fiber surfaces. *Carbohydrate Polymers*, 2014, 101, 812-818.

[126] Wazed, A.S.; Subbiyan, R.; Mangala, J. Synthesis and characterization of chitosan and silver loaded chitosan nanoparticles for bioactive polyester. *Carbohydrate Polymers*, 2011, 83, 2, 438-446.

[127] Efem, S.E.E. Clinical observations on the wound healing properties of honey. *Br H Surg*. 1988, 75,679-681.

[128] Wilkinson, J.M.; Cavanagh, H.M.A. Antibacterial activity of 13 honey against *Escherichia coli* and *Pseudomonas aeruginosa*. *J. Med. Food* 2005, 8, 100-103.

[129] Cooper, R.A.; Molan, P.C. Antibacterial activity of honey against strains of *Staphylococcus aureus* isolated from infected wound. *J Soc Med*. 1999, 92, 283-285.

[130] Tim Cushnie, T.P.; Lamb, A.J. Antimicrobial activity of flavonoids. *Int. J. Antimicrob. agents* 2005, 26, 343-356.

[131] Mangala, J.; Wazed, A.S.; Subbiyan, R. Antibacterial Finishing of Polyester/Cotton Blend Fabrics Using Neem (*Azadirachta indica*): A Natural Bioactive Agent. *Journal of Applied Polymer Science*, 2007, 106, 793-800.

[132] Lidija, F.Z.; Vanja, K.; Čakara. D. Antimicrobial and antioxidant properties of chitosan-based viscose fibres enzymatically functionalized with flavonoids. *Textile Research Journal*, 2011, 81, 1532-1540.

[133] Thilagavathi G.; Kannaian T. Combined antimicrobial and aroma finishing treatment for cotton, using micro encapsulated geranium (*Pelargonium graveolens* L' Herit. Ex. Ait.) leaves extract. *Indian Journal of*

Natural Products and Resources, 2010, 1, 348-352.

- [134] Alonso D.; Gimeno M.; Sepulveda-Sanchez J.D.; Shirai K. Chitosan-based microcapsules containing grapefruit seed extract grafted onto cellulose fibres by a non-toxic procedure, Note. Carbohydrate Research, 2010, 345, 854-859.
- [135] Haufe H.; Muschter K.; Siegert J.; Böttcher H. Bioactive Textiles by Sol-Gel Immobilized Natural Active Agents. Journal of Sol-Gel Science and Technology, 2008, 45, 97-101.

[136] Jothi D. Experimental study on antimicrobial activity of cotton fabric treated with aloe gel extract from *Aloe vera* plant for controlling the *Staphylococcus aureus* (bacterium). African Journal of Microbiology Research, 2009, 3, 5, 228-232.

[137] Tijana, R.; Lidija, F.Z.; Monika, N.; Marjetka, K.K.; Silva, S.; Nina, G.C.; Simona, S. Antimicrobial efficiency of functionalized cellulose fibres as potential medical textiles. in Science against microbial pathogens: communicating current research and technological advances, Méndez-Vilas A., Editor. Formatex: Badajoz, Spain, 2011, 36-51.

[138] Diana, C.; Simona, O.; Narcisa, V. Biofunctionalization of textile materials by antimicrobial treatments: a critical overview. Romanian Biotechnological Letters, 2010, 15, 4913-4921.

[139] Swofford H.W. An Overview of Antimicrobial Testing for Textile Applications: A look at commonly used antimicrobial testing protocols for textiles. AATCC Review, 2010, 10, 6, 5.

[140] Linda, T.; Bernhard, R. Improved methods for the investigation of the

interaction between textiles and microorganisms. Lenzinger Berichte, 2006, 85, 54-60.

[141] Pinho, E.; Magalhães, L.; Henriques, M.; Oliveira, R. Antimicrobial activity assessment of textiles: standard methods comparison. Annals of microbiology, 2011, 61, 493-498.

[142] Askew, P. D. (2007). Analysis and assessment of current protocols to develop harmonised test methods and relevant performance standards for the efficacy testing of treated articles/ treated materials. ENV/JM/MONO.

[143] Microchem Laboratory, ISO 20743 - Assessment of Antibacterial Finished Products, Available from <http://microchemlab.com/test/iso-20743-assessment-antibacterial-finished-products>.

[144] Kim H.W.; Kim B.R.; Rhee Y.H. Imparting durable antimicrobial properties to cotton fabrics using alginate-quaternary ammonium complex nanoparticles. Carbohydrate Polymers, 2010, 79, 1057-1062.

[145] Daoud W.A.; Xin J.H.; Zhang Y-H. Surface functionalization of cellulose fibres with titanium dioxide nanoparticles and their combined bactericidal activities. Surface Science, 2005, 599, 69-75.

[146] Wang Q.; Jin G.; Fan X.; Zhao X.; Cui L.; Wang P. Antibacterial functionalization of wool via mTGase-catalyzed grafting of ϵ -poly-L-lysine. Applied Biochemistry and Biotechnology, 2010, 160, 2486-2497.

[147] Lidija, F.Z.; Tijana, R.; Tkavc, T. Adsorption and antibacterial activity of soluble and precipitated chitosan on cellulose viscose fibers. Journal of engineered fibers and fabrics, 2012, 7, 1, 50-57.

[148] Lidija, F.Z.; Simona, S.; Olivera, Š.; Karin, S.K. Characterization of Amino Groups for Cotton Fibers Coated with Chitosan. *Textile Research Journal*, 2009, 79, 3, 219-226.

[149] International ASTM. Standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions, 2001, ASTM.

[150] Ozer R.R.; Hill W.C.; Rogers M.E., Evans M. Development of colorimetric analytical methods to monitor quaternary amine grafted surfaces. *Journal of Applied Polymer Science*, 2010, 118, 2397-2407.

[151] Knittel D.; Schollmeyer E. Chitosans for permanent antimicrobial finish on textiles. *Lenzinger Berichte*, 2006, 85, 124-130.

[152] Hewitt C.J.; Franke R.; Marx A.; Kossmann B.; Ottersbach P. A study into the antimicrobial properties of an amino functionalised polymer using multi-parameter flow cytometry. *Biotechnology Letters*, 2004, 26, 549-557.

[153] Morais, D. S.; Guedes, R. M.; opes, M. A. Antimicrobiasl approaches for textiles: from research to market. *Materials*, 2016, 9, 498.

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

171,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Textiles Functionalization - A Review of Materials, Processes, and Assessment

Mukesh Kumar Singh

Abstract

Conventionally, textiles are known to cover up the human skin, but by scientific administration, clothing can be extended to serve other human skins' functions. Accepting the chemical and dermatological complexity of human skin, the effect of humidity, microbes, pH, temperature, and wind can be engineered by wrapping it by functional clothing. In this regard, the latest class of textile material has been added called functional textiles. Such clothing materials consist of the potential of delivering more than one functionality apart from its primary function to cover-ups the human body. This present chapter offers state-of-the-art viewpoints on the application of functional textiles, including assorted concerns. First, the skin responds to various environmental stimuli and then overviews various techniques to incorporate functionalities in textiles. Finally, the applications and future scope and possibilities of research in this field are included in this chapter. Miniaturisation to small micro to nanometre scale is registered as one of the most exciting meadows in engineering and science over the past few decades. This drift also grasps colossal potential to functionalise the textiles. Various techniques are available now to develop a thin uniform film of functional materials on clothing surface to offer extra functionalities hitherto unrevealed to textile processors. These technologies are based on layer-by-layer assembling, immobilisation of enzymes on textile surfaces, nanocoating of textile substances, plasma for nanoscale modifications, and loading of various functional biomaterials micro and nanoencapsulation by minimum influence on breathability, feel, handle, and strength. The manufacturing of functional textiles can be classified into two groups. One is to functionalise the fibre by adding dope additives, modifying the fibre forming polymer, and then converting it to clothing. The fibre surface is also functionalised by adding some resins on the fibre surface. The other is to modify the textile surfaces by functional biomaterials, resins, finishes.

Keywords: cosmetic textiles, skin care, skin moisturising, active textiles, microencapsulation, natural dyes, smart textile, enzyme immobilisation, wellness textiles

1. Introduction

The functionalisation of different surfaces is of curiosity since the chronicle emergence of various technologies in the antiquity. Different surface coatings and painting materials and techniques were developed to alter the aesthetic

appearance, functional potential, and protection against the environment like resistance against oxidants [1, 2].

Initially, durability was prime criteria for selecting any fabric by the customer in the ancient era, and then aesthetic values and comfort index were primary attributes to decide the fabric choice. Now, customer's approach about clothing and textiles is shifting to search some additional functionality apart from traditional attributes in textiles. The functionality may come from protective clothing, cosmetotextiles, and temperature regulating textiles, industrial textiles, sports textiles, and automotive textiles. All the above textile materials must keep at least any one specific functionality to register as functional textiles.

The functional textiles market is growing with an excellent growth rate of 33.58% between 2015 to 2020. The global functional textile market was reached 4.72 billion US\$ by 2020. India is a prime manufacturer in apparel and textile manufacturing and fourth-largest exporter in the international sector.

The functional textile sector has encountered a compound annual growth rate (CAGR) of 30% from 2015 to 2020 due to strong automotive, fitness, fashion, healthcare, military, and sports textiles.

The physical finishing process includes three methods: impregnation, padding, and coating, and its main drawback are that the bonding force is weak between the finishing agent and textiles. However, its strength is more durable, and functionality can be maintained for a long time. The chemical finishing method involves grafting a functional monomer onto a polymer substrate, to obtain a new functional textile. The advantage is that its functionality can be maintained for a long time. Biological, ecological finishing is a finishing method which has emerged in recent years, and it adopts biological enzymes with biological activity in the finishing of textiles.

Smart textiles do not necessarily imply a less sustainable option to ordinary textiles if they offer better user value, user attachment and longevity. This chapter discusses the difference between ordinary sustainable methods based on saving energy and resources and methods that tackle excessive consumption, such as user involved design to enhance product durability. It discusses the theoretical model of user involved design through a practical example of developing a smart, lightweight tracking tent and concludes with a set of general guidelines for developing sustainable smart- textile products.

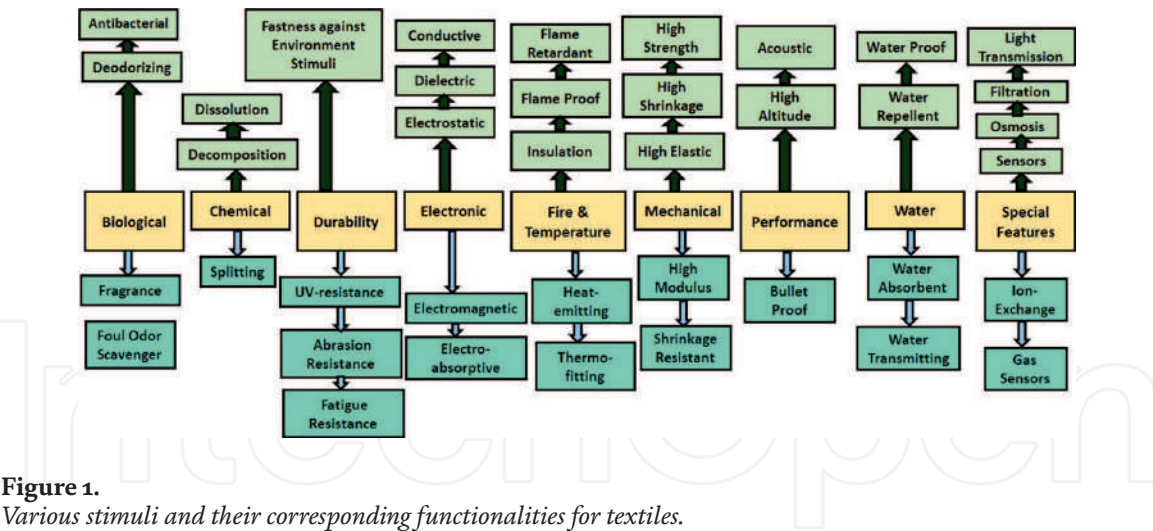
The functional textiles can be defined as textiles consist of additional functions of adjusting and regulating various attributes like temperature, humidity, colour and controlled release of some additives from fibres. The most popular fibres used to manufacture various types of functional textiles are polyester and viscose. Other fibres are also used to manufacture functional textiles as the need for some specific functions. The significant demand for functional textiles arises from active and high-performance wear sectors.

Some leading manufacturer of functional textiles at the international horizon are Dyntex GmbH, Eclat Textile Corporation Ltd., Harvest SPF Textile Company Ltd., Kelheim Fibres GmbH, Sofileta, Trevira GmbH, Toung Loong Textile MFG.

2. Classification of functional textiles

Various authors and researchers have tried to classify the functional textiles on their own time, but it is not easy to propose an ideal classification [3].

Functional textiles have become instrumental for the advancement of the conventional technical textiles segment, representing a sector where traditional clothing crosses the usual frontiers and connects with the spheres of biotechnology, cosmetic science, computing potentials, flexible electronics, medicine, and



nanotechnology among some more, to achieve the multidimensional and complex demands of the customers. By definition, Functional textiles are user-governed specified and customised or engineered products manufactured to fulfil the customer’s performance needs under extreme conditions.

Gupta [3] classified the functional textiles logically in six categories. Now including three more, present classifications consist of nine different functional classes, as shown in **Figure 1**. It is essential to clarify that some more classes will introduce functional textiles classification as per the demand and availability of various functional textiles shortly. There is a slight difference between functional and technical textiles. All functional textiles may belong to technical textiles, but all technical textiles may not be functional. For example, protective functional textiles may belong to protective surgical masks for doctors, healthcare workers, and sports armour.

3. Functional textile market

The aerothermal concept has been adopted in functional textiles to control the heat containing airflow through fabrics. These functional textiles are manufactured and marketed by Adidas, and Peak Performance of the IC group. The Schoeller Technologies AG developed far infrared-based functional textiles’ Energear’ to collect the energy employed by the human body. Remarkable developments and innovations polymer and fibre science, coating and finishing technologies are the major driving forces for the growth of functional textiles. The initial demand for functional textiles was originated from various sports wear used in cycling, ski sports, swimming. The latest development in functional textiles turned the customer highly demanding for functional textiles. The higher cost of functional textiles stamped it textiles of premium class. Thus, the challenge of cost reduction in functional textiles manufacturing chain is the need for the present era to make it available for the common man and accelerate functional textiles’ global market. Geographically, the functional textiles market is divided into five regions the Asia Pacific, Middle East and Africa, European Union, Latin America, United States of America. European Union secured the first position in manufacturing Functional Textiles mainly in Germany, France, Italy, and the United Kingdom. The USA also has a healthy manufacturing and market for functional textiles.

The Asia Pacific and Middle East Africa have the immense opportunity to grow the functional textile market. Japan, Malaysia, South Korea, Turkey, and Taiwan are predicted to be a promising market for functional textiles. The maximum number of functional textiles is manufactured by the application of various finishing agents

on textiles. Thus, the international market for finishing agents is expected to grow to 4.52 billion US\$ by 2025. The protective textile segment, including health care and protection, is an up-and-coming field of functional textile is anticipated to manoeuvre the market rise in the next years. Enhancing buying potential and expendable income in emerging countries like Brazil, China, India, Russia, Taiwan, and Indonesia is another driving force of the growth of the functional textile market. However, the strict regulatory norms to restrict harmful and toxic chemicals will remain the requisite provocation for functional textile manufactures.

Functional textile finishing agents are dominated by various repellent and release agents in recent years and expected to grow with CAGR of 4.8% till 2028. The application of flame retardant chemicals was 22% of global textile finishing chemicals in the year 2020.

The major functional finishing agent manufacturers are Archroma, BASF SE, Covestro, CHT Group, Evonik Industries, Huntsman Corporation, Sumitomo Chemicals, Dow Chemical Company, HT Fine Chemical, FCL, KAPP-CHEMIE, NICCA CHEMICAL CO., Ltd., OMNOVA Solutions, Tanatex Chemicals B.V., Wacker Chemie AG, Zydex Industries, Sarex and others.

4. Functionality in textiles

4.1 Functionality by micro and nano encapsulation

A technique in which an active substance is stored in tiny space covered or coated with a thin polymeric material to protect the core material along with controlled release, is called microencapsulation.

Particles obtained by this process are called microparticles, microcapsules and microspheres according to their morphologies and internal structure. For particles with a size range below one μm , the terms ‘nanoparticles’, ‘nanocapsules’ and ‘nanospheres’ are used, respectively. Furthermore, particles larger than 1000 μm are designed as microcapsules. The nomenclature used to define different parts of the encapsulated product includes terms for the shell, ie, ‘wall’, ‘coating’, ‘membrane material’; and for the core material, ie, ‘active agent’, ‘payload’, ‘internal phase’, respectively. Different kinds of compounds such as dye, protein, fragrance, monomers, the catalyst can be encapsulated with various shell wall materials like natural polymer (gelatine, cellulose, chitosan, etc.), artificial polymers (cellulosic derivatives, etc.) and synthetic polymers (polyamide, polyester, etc.), with a loading content between 5% and 90% of the microparticles in weight (Figure 2).

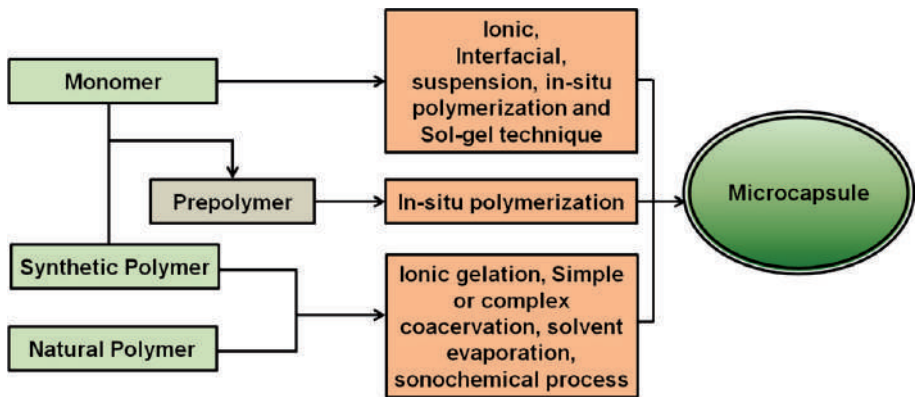


Figure 2.
Functionality by microencapsulation.

| Sheath polymer | Core active material | Function | Reference |
|--------------------------|------------------------|--|----------------------------|
| Poly (urea urethane) PUU | Sensitive dye | To get colour as a function of time | [4] |
| Poly (urea urethane) PUU | Cooling agent | To get cool feel during wearing | Salaün et al. [5] |
| Poly (urea urethane) PUU | Fragrances | To get controlled fragrance release | Teixeira et al. [6] |
| Poly urethane/ polyurea | Antimicrobial | To get bacterial protection | [7], and Vroman et al. [8] |
| Polyurea | Flame retardant | To get improved flame protection | |
| Polyurethane/chotopsan | Thermochromic | Colour change as a function of temperature | Fan et al. [9] |
| Cellulose derivative/PU | Phase change materials | To control environmental temperature fluctuation | Salaün et al. [10] |
| Polyurethane | Cosmetic Ingradient | To get skin care functionality | Azizi and Chevalier [11] |

Table 1.
Microencapsulation by interfacial polymerisation.

Micro and Nanoencapsulation is a technique in which a thin wall surrounds a tiny amount of active ingredient or droplets. The capsule wall's active material is called core material while the coating material is known as shell or membrane. Microcapsules have a diameter of few microns whereas nanocapsules have diameters of some hundreds of nanometres. Micro and nanoencapsulation is an up-and-coming technology to functionalise the textiles by potential core material for desires functionality. Micro and nanoencapsulation have permitted biocides, insecticides, essential oils, moisturisers, energisers, moisturisers, therapeutic oils, and vitamin E to be uploaded into fabrics. Some other applications are agrotextiles, cosmetics, industrial textiles, food additives, essences, herbicides, nutraceuticals, and sealants. The microencapsulation by interfacial polymerisation is given in **Table 1**.

4.2 Chemical grafting

The traditional binder application binds some functional compound on textile surfaces and creates a three-dimensional network and starts hindering the release of functional ingredient from the surface. The absence of strong chemical linkage between the capsule sheath and substrate surface exhibits inferior wash fastness and low air and moisture transmission. During pad-dry-cure, some of the capsules get burst due to the presence of applied pressure on substrate. Microcapsules are covalently connected onto textile surfaces by opting multifunctional crosslinking (coupling) reagents to enhance the fastness against wash and wear.

Microcapsules with ethylcellulose sheath are grafted on cotton fabric surface using 1,2,3,4-butane tetracarboxylic acid as crosslinking agents that react with a hydroxyl group cellulose to configure ester bonds [12].

Dimethyloldihydroxyethylene urea was opted as a coupling agent between chitosan and cellulose to form a covalent bond to enhance washing fastness [13].

Citric acid was another choice to crosslink chitosan microcapsules on cellulosic surfaces [9, 14].

Grafting strategies from the particle surface modification can be performed by introducing reactive chemical groups like α -Bromo-acrylic acid, adipic acid, 2,4,6-trichlorotriazine and dichloroquinoxaline, to react with the microcapsule sheath materials to offer further grafting possibilities onto natural, manmade fibres. Polyamide capsules and silica microspheres with 2,4,6-trichlorotriazine were functionalised to be deposited on cotton fibre surface [15].

Microcapsules were dispersed in water and glycidyl methacrylate monomer, and potassium persulfate was added to initiate an outer shell of poly(glycidyl methacrylate). The microcapsules were then applied by exhaustion in alkali medium to jersey cotton knitwear with a liquor ratio of 1:10 at 75 °C for 30 min. After rinsing, the sample was dried at 120 °C. The functional groups of the poly(glycidyl methacrylate) on the outer surface of the microcapsules are directly reacted with the functional groups of the fibres, which also conveyed durability of the PCM microcapsule-incorporated fabric even when subjected to physical processes involving frictional forces, or chemical processes such as domestic and industrial washing, or dry cleaning [16]. Gouveia used a sonication method to produce and simultaneously bind the microspheres onto textile materials [17].

Polyamide microcapsules are directly synthesised on cellulosic surfaces with 80% high encapsulation [18].

4.3 Functionality by layer by layer (LbL) deposition

Some studies were planned to modify the textile surfaces through layer by layer deposition to get nanocomposite textile fibre and protective clothing. Various functional molecules like enzymes, dyes and charged nanoparticles are deposited on textile surfaces in a controlled manner. Various finishing processes are based on Ag, TiO₂, Zn nanoparticles to functionalised various textile surfaces [19]. Layer by layer deposition technique is a distinctive technique invented to develop ultrathin composite films on the surface of solid materials. A series of layer-by-layer deposition of polyanions and polycations on oppositely charged surfaces occurs in this method [20].

This process involves the charging of substrate sufficiently, followed by dipping in a conversely charged polyelectrolyte. The process begins by charging a substrate appropriately, followed by immersion in an oppositely charged polyelectrolyte solution and rinsing. Strong electrostatic bonds between charged surface and polyelectrolyte become the main instrumental in getting it to bind. The process begins with rinsing followed by monolayer coating of polyelectrolyte which gets bind by electrostatic bonds and process may repeat to be deposited 20 ultrathin layers [21–23].

Unlike pad-dry-cure, radiation, and thermal deposition methods, different finishing techniques are used to deposit various nanoparticles on textile substrates. The chemical coating on textile surfaces has some limitations due to higher thickness, which suppresses textiles' breathability. The LbL technology offers moderate chemical deposited surfaces to keep transmission, thickness and stability up to the desired extent. Various textile surfaces are modified by LbL technique.

Cotton, Kevlar, Nylon, Nomex, Silk and Wool fabrics were opted to functionalised for different applications by platinum atomic layer deposition. The platinum layer by layer deposition on textile surfaces was targeted to fabricate resistive heating devices with high stability and long life. The platinum deposition was found uniform layer by layer except for nylon fabric surface. [(1,2,5,6- η)-1,5-Hexadiene]-dimethyl-platinum(II) (HDMP; Tanaka Kikinzoku Kogyo K.K., Japan) and O₂ gas were used as a Pt precursor and counter-reactant, respectively. The substrate temperature was maintained at 145 °C during the ALD process. Field emission scanning electron microscope integrated with energy dispersive spectroscopy (EDS) was

used for quantitative and elemental deposition conformation on textile surfaces. The atomic-scale crystalline and chemical structures of treated fabric specimen were analysed using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS), respectively [24].

Lee et al. [25] developed a pressure sensor atomic layer deposition on the cotton surface by depositing [(1,2,5,6-η)-1,5-hexadiene]-dimethyl-platinum(II) (HDMP) and O₂ as the Pt precursor and counter reactant. The research group developed a useful atomic layer deposition technique. The deposition process may repeatedly apply up to 10,000 times. This technique helps produce various E-textiles by combining and connecting the number of sensors in a textile item that may be proved as propitious applicants for a range of smart and wearable electronics.

Stawski et al. [26–28] deposited oppositely charged polyelectrolytes; poly(acrylic acid) and poly(allylamine hydrochloride) layer-by-layer on a polypropylene knitted fabric, which had areal density 80 g/m², diameter per filament 14.9, 18 courses per centimetre, 14 wales per centimetre, 56 dtex multifilament yarn.

The polypropylene (PP) fabric was activated as per the protocol opted by Połowiński [29] and [30–32] by heat-treating the fabric samples in an aqueous solution (20 g/L) of ammonium persulfate for 30 minute at 80 °C, and saturated with nitrogen), rinsing thoroughly with distilled water, and grafting with concentrated acrylic acid (52 g/L) for 60 minutes at 80 °C, saturated with nitrogen. After completing the grafting process, the PP fabric samples were dipped in an aqueous polyelectrolyte solution (10–2 mol/L). This process may repeat many times as per the need of desired end applications. Before initiating a new layer, deposition fabric specimens were rinsed with distilled water. In this way number of polyelectrolyte layers was coated on PP fabric surface [28, 29]. The PP samples functionalised by LbL technique were found to significantly reduced the static charge half-disappearing time, from 46 to 5.7 minutes. The degradation temperature shifted from 330 to 420 °C. The capillary rise has increased from 50 to 400 mm in the case of surface-modified knitted fabric samples. SEM and wide-angle X-ray diffraction was used to confirm the layer by layer deposition on PP fibre surface. It was found that the layer-by-layer deposition of polyelectrolyte considerably modifies dyeability, electrostatic shielding potential, and hydrophilicity of PP fabric samples.

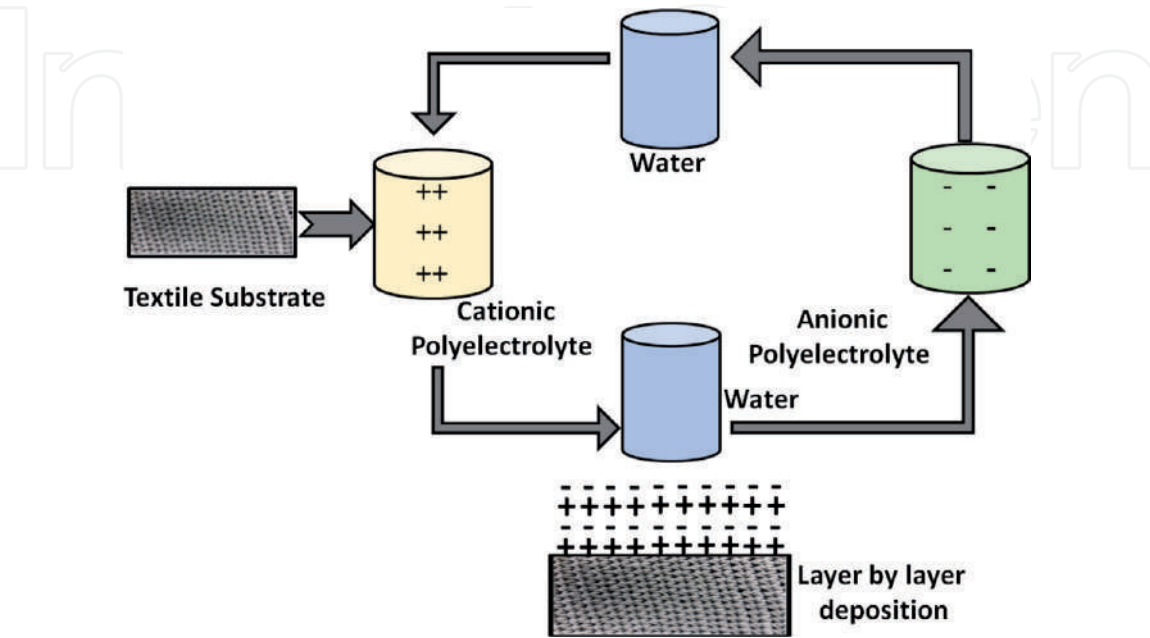


Figure 3.
Concept of layer by layer (LbL) Technology for Functional Textiles.

Highly durable hydrophobic polyester fabric surfaces were created by LbL nanoparticle coating on the fabric surface. Electrophoretic deposition (EPD) technique was used to modify the fabric surface with deposition of silica nanoparticles. The deposition of silica nanoparticles remains challenging on non-conductive surfaces like polyester due to undue cracks and poor adhesion. Thus electrostatic self-assembly layer-by-layer technique was opted to overcome these issues as shown in **Figure 3**. The polyester fabric modified by LbL silica NPs deposition offers a very high contact angle in static condition along with low contact angle hysteresis. The superhydrophobicity was remained intact ever after 500 h skin friction [33]. This method provides fast and customisable deposition of superhydrophobic surface coatings. The coating thickness can be controlled by the electric field intensity and deposition time. Furthermore, the modified surface's morphology can be altered by changing the suspension stability during EPD [34]. Three significant routes achieve sustainable surface functionalisation; by alternating a charged substrate's immersion in aqueous solutions containing interacting charged particles, chemical vapour deposition, and spraying the interactive solutions on charges surfaces.

4.4 Functionalisation by fabric engineering

Fabric Comfort, good low-stress mechanical properties, pleasant aesthetic appeal, elasticity and recovery, favourable formability, desired crease-resistance are some attributes can be achieved by fabric engineering. These attributes are required for various applications like formal wear, party wear, ladies wear and sportswear.

The PBT (polybutylene terephthalate), yarns have good elastic potential with high recovery after heat treatment, have been adopted to manufacture highly elastic cotton-like fabric. The effect of PBT elastic yarn, weave and fabric structure was observed on physical, elastic, UPF, comfort) properties of the fabric. PBT yarns have found it appropriate to introduce elasticity in selected areas of the fabrics. The fabric had quick-drying, easier folding and storage and perfect fit to all dimensions [35].

3D printing is another way to introduce various functionalities in a different range of textiles. 3D printing has opted in case of defence, protective, sports, flexible electronics and safety clothing.

3D printing is used to customise the product for specific applications. Various types of additives can be loaded on fabric surfaces as a part of printing inks or pastes. A variety of hard and soft flexible materials can be printed directly on the textile surfaces. A combination of additives can also incorporate some functionality on a common textile substrate by 3D printing. The effect of family of twill weave and different weft densities on adhesion potential of printed objects on polyester/cotton fabric surfaces was studied. A range of 3D objects was printed with polylactic acid (PLA) filament on textile surfaces. T - Peel adhesion test was conducted by Instron dynamometer. It was found that the 1/3 broken twill fabric has the maximum impact on the adhesion perspective [36].

The worldwide health consciousness has enhanced natural dyes' use to avoid the threat of allergy, mutagenicity, and carcinogenicity. Cotton fabric was dyed with an extract of forty different plants with zero mordant. Some plants were able to record great wash and lightfastness like pomegranate peel and turmeric for yellow, madder and quince for yellow, indigo for blue, myrobalan for green, white onion peel and catechu for brown colour. White onion peel or turmeric dyed cotton fabrics have registered significant improvement in ultraviolet protection functionality [37].

4.5 Functional textiles by enzyme immobilisation

Enzyme driven textile functionalisation has attracted the attention of textile manufacturers worldwide. Nonpolluting, non-toxic, and biodegradable nature of enzymes make it appropriate for the green processing of textiles. The enzyme production can be enhanced commercially anytime as per the need in industry. Enzymatic bleaching, scouring, bio-washing, and bio-polishing cotton fabric have become quite popular in the textile industry. Recently cotton fabrics are modified through transesterification by Proteinase subtilisin enzymes. Woollen fabrics are made shrink-proof by transesterification by the use of proteinase subtilisin enzymes. The Laccase enzyme is used to functionalise the wool in multiple order with antibacterial, antioxidant and water repellent for grafting alkyl galleates. The hydrophilicity and antistatic charge potential are introduced in polyester fabrics by treating it with cutinases and esterases enzymes. The nylon and acrylic fabrics are functionalised by treatment with amidase and nitrilase. The functionalisation of textile surfaces is made by 'enzyme immobilisation' on textile surfaces to introduce some special functions to textile surface. The immobilised enzymes work better than free enzymes on the textile surface to impart long term functionalities on textile substrates. As compared to free enzymes, immobilised enzymes are permanently attached to the textile, thereby adding unique functionalities to its surface.

5. Functional materials

5.1 Phase-change materials

The micro and nanoencapsulation of phase change materials can alter the core material from solid to liquid and liquid to stable by changing the entropy within a specific temperature span. This technique is used to suppress the effect of temperature variation on the targeted subject. The encapsulation of phase change materials is used to keep the temperature of clothing at a constant level. Microencapsulated phase change materials enhance the comfort delivery of blankets, duvets, mattresses, snowsuits, and vests [38].

5.2 Fragrance finishes

Fragrance finishes are applied straight on textiles, but aroma stability lasts maximum up to a couple of wash cycles. The micro and nanoencapsulation of fragrances are used to prolong the fabric's aroma functionality for a much more extended period. This technique is mainly adopted to encapsulate various essential oil flavours like lavender, rosemary, pine and others on for aromatherapy to treat headaches, insomnia, and prevent bad odour.

5.3 Fire retardants

Encapsulation of flame retardant materials does not allow sacrificing the softness and other low-stress mechanical properties seeded by direct application of flame retardant chemicals. Scientific selection of core and sheath materials for flame retardancy can offer synergistic effect; organophosphorus compound as core and nitrogenous compound as a sheath. Some intumescent flame retardant coatings can also be generated by micro and nanoencapsulation technique. This flame retardancy technique is widely used in the military sector to treat the tentage, upholstery and firefighting dresses.

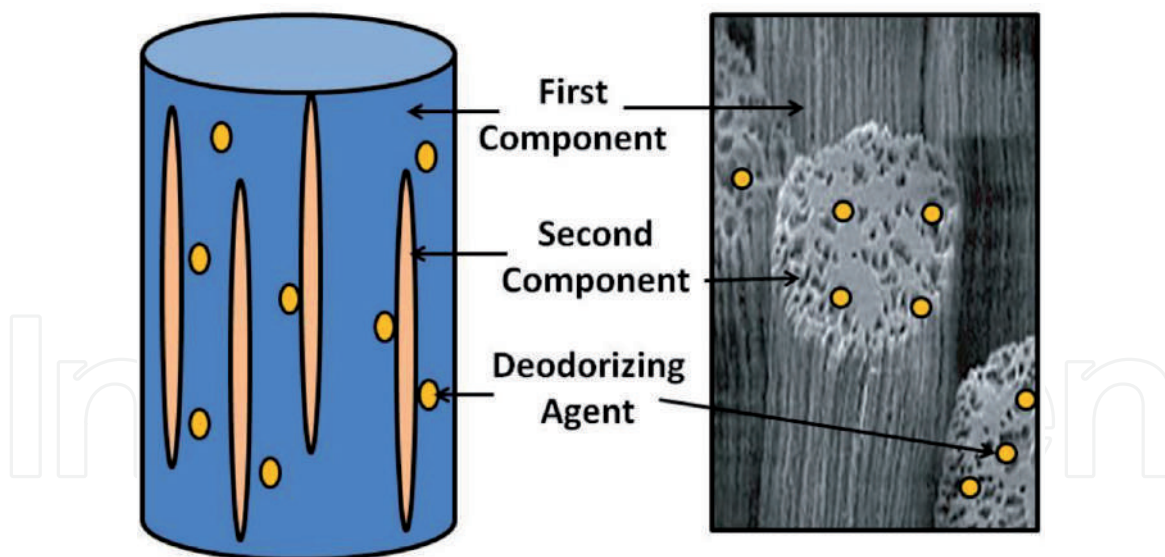


Figure 4.
Concept of inherent deodorant textile fibre.

5.4 Deodorant functional textiles

The deodorant fibres are manufactured by modifying the polymer molecular chain during polymerisation, by adding deodorant additives during fibre extrusion and by applying deodorant finish on fibre surface after spinning. The addition of deodorant additive as dope additive is simplest method to impart deodorancy in fibres as shown in **Figure 4**.

The polyester staple fibres were modified by photocatalyst and blended with cotton and bamboo fibre to produce several fabrics. The photocatalyst fibre contents were varied from 0 to 100% at a step of 20% increment in different samples. The deodorant potential of produced fabric samples was tested and examined. The conclusion is explained that as the photocatalyst fibre content reached 80% or 100%, the fabrics get better deodorant potential, but the photocatalyst content remains 40% to 60% in fabric samples, it shows low deodorant effect. It is established that at least 80% photocatalyst is essential to produce acceptable deodorant fabric [39, 40].

5.5 Polychromic microcapsules

The colours and dyes responsive against temperature are called as polychromic or thermochromatic dyes. The dyes and colours changes by a change in ultraviolet light are called as photochromatic dyes. The thermochromic or photochromic dyes are encapsulated inside the shell material used for product labelling, forensic purposes, and fashion applications. Many dyes and chemicals are available, which change colour by changing temperature and UV light exposure.

5.6 Antimicrobials

Microbes cause severe damage to various textile items. Some chemicals used to decay the microbial effects of fabrics are called as antimicrobials. These antimicrobials can be uploaded with textiles by microencapsulation technique in which antimicrobials remains in the core of the capsules. High-value textiles are treated by this method to prolong the life of these textiles.

5.7 Textiles for refreshing and relaxing

Refreshing and relaxing attributes are incorporated in textiles by uploading the *Aloe vera*, menthol, and essential oils with suitable emulsifiers in the capsule core. *Aloe vera* has found an appropriate finishing ingredient of textiles to achieve a refreshing and relaxing feel in textiles. These functional textiles are used to offer pleasant wear, wellness, and high energy levels.

Various plants and fruit-based aromas are also used by encapsulating and loading on fabrics for a functional point of view.

5.8 Textiles for cosmetics

A class of textiles responsible for imparting skincare, ageing combating, and wellness feeling is known as cosmetotextiles. Cosmetotextiles is one of the significant members of the functional textile family. The demand for cosmetotextiles increases every year due to the increase in self-wellbeing and purchasing power globally [41].

Cosmetotextiles are resultant of combining cosmetics and the textiles through different techniques, in which microencapsulation is the prime. Cosmetotextiles is a consumer textile product with a long lasting cosmetic ingredient released as a function of time.

5.9 Skincare functional textiles

Skincare is the most potent aspect of modern globally. The glowing skin is the desire of every person of the universe. The potential of skincare in textiles can be incorporated very easily by finishing the route. The functional textiles are capable of caring for human skin in various ways, and some are described here.

Skin soft 415 New:

This fabric finish is based on water-soluble phospholipid developed by Daiwa Chemical Inc., Japan. The finishing bath mainly consists of 2-methacryloyloxyethyl phosphorylcholine (MPC) with phosphatidylcholine polar groups to retain moisture on human skin for a long time [42]. A gentle softener is also used in Skinsoft 415 New to give a soft feeling to the wearer.

The skinsoft 415 finish has the potential to enhance the antibrowning and antistatic potential of textile surfaces [43].

Ohara Paragium Chemicals Kyoto, Japan, have floated a wide range of skincare and anti-ageing functional finishes to treat different fabrics. Some selected skincare finishes for textiles are;

- Parafine Skincare –1000: This finish was developed by Ohara Paragium Chem. Japan and that primly consists of silk-based amino acids. The amino acids are rich in moisture retaining properties that promote skin well-being by enhancing skin moisture.
- Parafine Skincare-3000: This finish offers cellulite reducing functionality by the presence of capsaicin, along with moisture-retaining and skincare effect by the presence of raspberry and squalane, respectively.
- Parafine Skincare-5000: The Parafine SC-5000 finish primly based on extracts of rice germ oil (ferulic acid and g -oryzanol) and vitamin E. The mixture

of ferulic acid, g-oryzanol and vitamin E offers anti-oxidation attributes to impart skin anti-ageing. This finish accelerates the anti-oxidation, blood circulation, and bio-membrane stabilisation in human skin.

- **EVOTM Care Vital:** This skincare finish recipe mostly contains *Aloe Vera*, Jojoba oil and Vitamin E to impart anti-ageing functionality in the finished fabric. This skincare finish was developed by Dystar Auxiliaries GmbH, Frankfurt, Germany. Some natural bio-substances are added with silicone matrix, which is an essential component of most softeners to enhance the washfastness of treated fabric surfaces. This finish is applied as the final treatment in the standard exhaust and pad-dry-cure process sequence. DyStar has introduced a similar finish with the commercial name of Evo Care BeeWell with beewax, Evo Care AVP and Evo Care AVS. Primarily, these finishes are based on *Aloe Vera* and Jojoba oil. Evo Care finish can finish a wide range of textile materials to impart anti-ageing functionality in innerwear that come directly in skin contact.

5.10 Insect repellent

The purpose of insect repellent functionality on textiles is to protect the wearer and cloth both from insects. The insect repellent materials are used to finish the traditional textile surfaces either by natural materials like (essential oils) such as citronella, eucalyptus, lemon, and neem or synthetic materials such as picaridin (1-piperidine carboxylic acid 2-[2-hydroxyethyl]-1-methylpropylester) or permethrin and (*N,N*-diethyl-3-methylbenzamide) (DEET). Direct application of these ingredients possesses very poor wash fastness. Thus most of them are applied through microencapsulation route by melamine-formaldehyde, sodium alginate, and silica as sheath material by pad-dry-cure method [44–47]. The efficacy of DEET was tested under laboratory conditions to inhibit blood feeding and killing mosquitoes for six months. This formulation was found very useful for mosquitoes got resistance against pyrethroid.

Textiles loaded with microcapsules containing citronella as the active ingredient has found better insect repellency (more than 90% for three weeks) than fabric sprayed with citronella oil and ethanol solution directly on fabric surfaces [48]. Lemongrass oil extract was uploaded on polyester fabric in microcapsule form and found 92% insect repellency. The mosquito-repellency was 80% when the polyester fabric was treated through pad-dry-cure route microcapsules containing methanolic lemongrass leaves extract as an active ingredient in capsule core.

5.11 Wellness

A cosmetotextile is a textile containing a substance or preparation targeted to be released permanently on different epidermis parts. It claims one or several unique properties such as cleansing, fragrance, skin appearance change, protection and upkeep, or foul body odour correction.

Some multinational companies like Oracle (France) and Dim launch fabrics with moisturising agent containing microcapsules grafted on textile surfaces. Global companies; Cognis in 2001 and Invista in 2003 floated their products as cosmetotextiles solution. Some other companies like Lytess (France), supplier for L'Oréal since 2009 with Mixa (2010), Mennen Garnier (2011), Biotherm, and then Nivea (2014) are continuously involved in this business. These companies are exclusively dedicated to the development and commercialisation of cosmetotextiles and have become a European market leader as a textile brand in this area. The Cosmetotextiles market was estimated at 500 million Euros in 2013, in which the slimming garments

contribute about 10% share. France is the first producer and consumer of cosmetotextiles, with 64% of the market in 2012. The development and manufacturing of new products will open new market opportunities, cosmetotextile manufacturers. Cosmetotextiles can be broadly divided into two major classes: (1) dermocosmetics (skin care) and (2) aromatherapy (release of essential oil and fragrances). Furthermore, a broad classification of cosmetotextiles is presented by Singh [49]. Grafting, padding, coating, spraying or screen printing are the major ways of applying microcapsules containing fragrance or cosmetic agents onto a textile [50].

5.12 Aromatherapy

Aromatherapy is considered an alternative route of medicine that uses volatile materials like essential oils by various peoples. Essential oil or fragrance is released from the microcapsule when any external stimuli actuate the fabric's microcapsule to promote the healing. The functional textiles for aromatherapy are found appropriate to affect the feelings, emotions and mood. Textile substrate works as a medium to deliver aroma conveniently at the desired moment. Various curtains, furnishings, handkerchiefs, and masks are treated with aroma finishes to incorporate functionalities. The microcapsules containing essential oils or fragrance are loaded on such textiles. Perfumed microcapsules are fixed on textile surfaces wither by the use of a binder or chemical grafting. Variety of essential oils like peppermint to get the exact thinking mood, lavender to get feeling of getting relax, similarly other oils for different purposes.

5.13 Photochromic textiles

Photochromic materials are uncoloured initially and do not absorb light. These materials are activated only by high energy photons of ultraviolet rays present in the close surrounding of it. Organic substances like fulgides, spiropyrans, and spirooxanines are primarily used as sensor in textiles.

For a textile application, organic compounds such as spiropyrans, spirooxanines and fulgides are mainly used to act as sensors [51]. The last category has found application in garments, toys and logos on T-shirts. Microencapsulation is used to improve the compounds' fatigue resistance as a result of deterioration after numerous repetitive cycles of irradiation and is affected by environmental factors [52, 53].

Photochromism is used in textiles to provide new functional smart fabrics such as garments capable of blocking UV radiation and sensing environmental changes, and also for aesthetics or functional effects such as camouflage, security printing, brand protection [51] and anticounterfeiting. Microencapsulated photochromic compounds can be applied by screen printing or grating onto a textile surface.

Di Credico et al. worked on a microencapsulation process to entrap a photochromic UV-sensitive dye dissolved in sunflower oil as a core material. After optimising the microcapsule shell's UV screening properties by tuning the core material's chemical composition, they demonstrated the use of such UV screening microcapsules in functional coatings for the nondestructive in situ visual detections of mechanical damage by colour change.

6. Benefits of functionalisation by microencapsulation

According to the desired functionality in textiles through microencapsulation route, microcapsules are planned and engineered. Nature of active ingredient core material, nature of sheath polymer, particle size, compatibility between core

and sheath material are some prime parameters that drive microencapsulation. Microcapsules with porous, semiporous or impermeable shells are used for different applications.

6.1 Protection and shelf life enhancement

Most of the active substances available are volatile, chemically fragile, or chemically, physically or thermally unstable, and cannot be applied directly on the textile substrate without being covered inside a shell. The micro or nano encapsulation not only provide the safety to the active substance from environmental stimuli; acidity, alkalinity, heat, moisture, oxidation) To restrict interaction with other chemicals remains present in the system to enhance the functionality delivery period.

The capsule shell is used to block the evaporation of active ingredients.

The capsules can also prevent the dissipation of volatile compounds. Additionally, the microcapsules save human resources at manufacturing and users side from exposure to harmful substances. Microcapsules allow safe handling of active ingredients before processing and permit a soluble substance to be transformed in a temporarily insoluble form. This technique permits an unpleasant fragrance from active compounds to be masked before end application during manufacture.

6.2 Controlled release

The microencapsulation of active substances is one of the best routes to enhance the efficiency and minimise environmental damage by controlled release.

This technology prolongs an active ingredient's delivery until an external stimulus like heat, moisture; pressure is actuated at a specific rate, time or situation. The microcapsules are desired to escape the core ingredient to the wearer under a range of controlled situations, which mainly depend on the choice of shell materials, the microencapsulation process opted and final applications.

6.3 Compatibility

The compatibility of core and shell material assists in microencapsulation. A binder's efficiency in connecting microcapsules to the textile surface depends on compatibility between various interphases of each component's microcapsules and finishing and chemical nature.

7. Microencapsulation technologies

The micro and nano encapsulation involve three necessary steps: enclosure of active ingredient as core material, the formation of microparticles and hardening. Again, these processes are further divided into three main groups depending on microparticles formation mechanisms. These three mechanisms are mechanical, chemical and physicochemical. The selection of one mechanism depends on various factors in which processing cost and selection of organic solvent is a significant point of considerations (**Table 2**).

Some multifunctional ingredients impart a range of functionalities on textiles after uniformly coating on it. Zinc oxide can introduce collective functionalities like antimicrobial activity, electrical conductivity, flame retardancy, hydrophobicity, moisture management, photocatalytic self-cleaning, and UV protection. In the development of wearable electronics, the enhancement of the piezo-photocatalytic activity of ZnO NRs by controlling the structure grown on conducting textile

| Basic Ingredient | Functionality | Reference |
|--|--|-----------|
| Pro-vitamin C soluble in sebum | Cosmeto-clothing: Pro-vitamin C converts into vitamin C in the presence of sebum and is applied on blouses, and men and women's shirts | [54] |
| <i>Aloe Vera</i> , and Chitosan with other PCMs | <i>Aloe Vera</i> , and Chitosan with other PCMs Leg wear and intimate clothing for both men, women and Yoga Lines: Delivering cosmetic and well-being benefits like freshness, moisturising and massage for leg wear and intimate apparel. Stretch and recovery function through the use of Lycra | [49] |
| Distilled oils of plants, fruits and leaves | Textile has the functionality to provide gentle care to tired feet and legs with the special effects of invigorating aromas | [55] |
| Ultra-thin cloth with extracts of <i>Padina Pavonica</i> | The cosmetically inspired fluid lingerie "Hydrabra" provides moisturising and firming effects | [56] |
| Seersucker Woven Fabrics with Therapeutic Properties | Seersucker woven fabrics provide anti-cellulite functional knitted. The fabrics were measured in the range of their structural, mechanical, comfort-related and functional properties. These fabrics offer sufficient air transmission and good thermal resistance with gentle micro-messaging functionality | [57] |
| Chitosan microencapsulation with essential oils and bio-surfactants on cotton fabric | Smaller size microcapsules are obtained in presence of bio-surfactants. The antibacterial activity of fabric increases with the increase the add-on of chitosan and essential oil concentrations. The presence of essential oil decreases the stiffness but has no effect on wrinkle recovery | [58] |
| Deodorising Textiles | Photocatalyst modified polyester staple fibre, cotton, bamboo fibre, and photocatalyst modified polyester blended woven fabrics were offered good deodorancy at 80% or 100% photocatalyst fibre content. | [39, 40] |
| Wearable and textile electronics | Wearable and textile electronics was developed by thermal atomic layer deposition (ALD) at 300 °C with highly reactive counter reactants, including plasma radicals and O ₃ . High functional cotton fabrics are developed. | [25] |
| Temperature responsive functional textiles | A series of stimuli sensitive polymers were applied on various fabric surfaces to make them thermal responsive | [59] |
| Radar absorbers, microwave | Polypyrrole coated fabrics and fibres becomes able to absorb various waves sensitive in radar range | [60] |
| Camouflage electrochromic functional textiles | Polymers have a higher ion exchange capacity, higher hydrophilic/intensely coloured in the charged state are used to coat the textile surfaces. Coated textile colour is dramatically altered by application of small quantities. | [61] |
| Flexible wearable pressure sensitive textiles | Piezoresistive properties are incorporated to detect the loacal pressure on the fabric. These functional textiles become useful for injury prevention, rehabilitation, sports and medical applications | [62, 63] |

Table 2.
Details of some selected functional ingredients, functions in functional textiles.

substrates will be crucial [64]. Silver nanoparticles and titanium dioxide nanoparticles functionalised Cotton-cellulose-spandex fabrics with various weaving configurations like plain, twill and satin with ester crosslinking agent, silicone

micro-emulsion. The treated fabric samples offered sufficient antibacterial, soft-handle, water/oil repellence, UV-protection and self-cleaning functionalities. The functionalised fabric samples retained these properties even after ten washing cycles [65]. Effective analytical techniques like scanning electron microscope with EDX confirmed the effective interaction between cellulosic surface and finishing nanoparticles.

The role of weave structure was also found crucial to enhance functionalities of treated fabric follows the descending sequence Satin (4) > Twill (2/2) > Plain (1/1) nevertheless of the used functional ingredients. The treated fabric samples showed bi-functional potentials like easy care-water and oil repellent, comfortable care-soft touch, or easy-care/antibacterial finish. The fabric finished with citric acid/NaH₂PO₂/TiO₂-Nanoparticles to get easy care/antibacterial/anti-UV/Self-cleaning effect was stable regardless of fabric weaves.

The in-line characterisation of flame retardant and polyvinyl acetate based stiffed polyester and cotton fabrics were scanned by a hyperspectral camera (1320–1900 nm) based on chemometric approaches using the partial least squares (PLS) algorithm. The finish was applied to enhance the areal fabric density from 10–50 g.m⁻². For both the fabrics, the root mean square prediction error (RMSEP) was estimated at 1.5–2 gm – 2. These results were found a very close correlation with gravimetry results also. The near-infrared imaging technique was also opted to detect the finishing agents' traces after washing the treated fabric surface. It was proved that a very thin layer of areal density between 0.4 and 5.5 g m – 2 was found intact even after many wash cycles [66].

8. Functional textile assessment

Functionality is a broad term used to assess the specific needs of clothing customers. The assessment of functional textiles primarily depends on the satisfaction of the customer. Customer demands water-proof breathable fabrics, flame-retardant deodorant textiles, antimicrobial-perfumed textiles, soft-skin glowing textiles and others. Creativity, reliability, and aesthetics are three significant points of consideration during functional textile assessment planning. Some features must be considered as a part of the assessment is:

- Low-Stress mechanical properties
- Breathability
- Thermal Transmission
- Air transmission
- Presence of active ingredients on the fabric surface
- Colour Index
- Scavenging potential of foul odours and toxic gases

8.1 Low-stress mechanical properties

The alacrity desire for comfortable fabrics has become steering of the increasing demand for functional textiles. A dramatic shift in apparel goods has registered

from durability to functional aspect and increasing purchase power and customer awareness fueled it up. The rapid change in fashion trends and market demand has compelled the fabric manufacturer to follow the functional textiles design right from fibre manufacturing stage rather than relying upon experienced cloth manufacturing with conventional fibre design. The concept of high-quality apparel fabrics to achieve desired level appearance, handle and wearing comfort was finalised by Hand Evaluation Standardisation Committee (HESC).

Consumers' purchasing decisions are usually based on feel fabrics for their tactile properties because, during daily wearing, low-stress mechanical action like bending, shear, compression, tensile, and hysteresis occurs on clothing. These common low-stress mechanical attributes significantly impact the feel, movement, sensory and tactile comfort. Other fabric and yarn properties like yarn counts; twist, coefficient of mass variation, neps, hairiness, thin and thick places, and strength and elongation also influence the clothing functionality.

Tactile properties of fabrics affect the functional aspect of apparel products and influence consumers' decision-making when purchasing textile clothing [67].

In the textile industry, tactile comfort is known as "handle" or in a broader sense "skin sensational wear comfort" or "sensorial comfort". Sensorial or tactile functionality, mostly identified by "hand or handle", is an inference of quantity of stress is generated in the fabric during use [68]. Tactile functional attributes are complex theories which incorporate dimensional alterations by small forces like bending, compression, shear, surface properties, and tensile. The feel of warmth and cool also influence the functionality of the fabrics.

Kawabata Evaluation system for fabrics (KES-FB) and Fabric Assurance by Simple Testing (FAST) systems are used to test the low-stress functional properties from a comfort point of view.

8.2 Breathability

The breathability of functional textiles is an essential parameter to be tested to assure the efficacy. The breathability of textiles is mostly referring to the moisture vapour transmission rate through the fabric. A series of instruments are available in the textile world, but moisture management tester of SDL Atlas is considered the prime instrument followed by some other concepts in which inverted cup method [69].

8.2.1 Sweating guarded hot plate tests

The sweating guarded hot plate's moisture vapour transmission resistance can be measured as per ISO 11092 testing standard [70]. This apparatus comprises the water supply unit and measuring unit in which the measuring unit is fixed with a metal block which consists of an appropriate heating element. The measuring unit is a permeable square metallic plate with area of 0.04 m² and 3 mm. The specimen holder remains at the centre of heating plate which is surrounded by a guarded heating device. As shown in **Figure 5**, the guarded heating systems block any lateral heat escape from the samples' edges. The resist heater is fixed at the bottom of the heating plate to avert the descending heat loss from the specimen and guard section.

This positioning of various components operates heat or moisture transmission only upward along the specimen thickness direction. Distilled water is used to feed the surface of the porous plate through an appropriate dosing system. Water impermeable but water vapour permeable cellophane ultrathin membrane is fitted over the plate. The 300 X 300 mm² sample is mounted over the membrane. The heating of square porous plate at the constant heating rate is started that mimics the

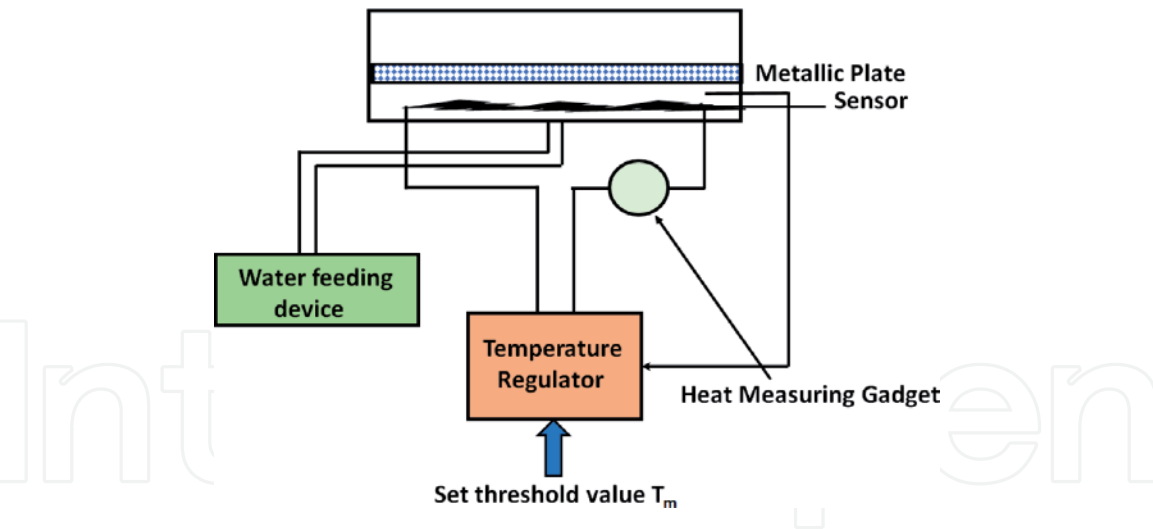


Figure 5.
Sweating guarded hot plate concept.

human body skin temperature, 35 °C, which is measured by a sandwiched sensor directly which is fixed underneath the plate surface. The entire system is closed in a chamber to control the micro-environment conditions very carefully. In order to simulate the actual condition, the air flow is kept at 1 m/s. The air temperature and relative humidity are maintained at 35 °C and 40% respectively.

8.2.2 Upright cup method

The water vapour transmission rates are measured as per ASTM E96, procedure B, and standard test methods by upright cup method. 100 ml distilled water is filled in a shallow cup and a specimen of size 74 mm is mounted on the cup by covering the gasket and fixing it in appropriate position. The cup and other accessories are housed inside an environmental chamber as shown in **Figure 6**. The temperature of circulating temperature is set to 23 °C with controlled relative humidity at 50%. The air flow is maintained with a velocity of 2.8 m/s. The cup assembly is

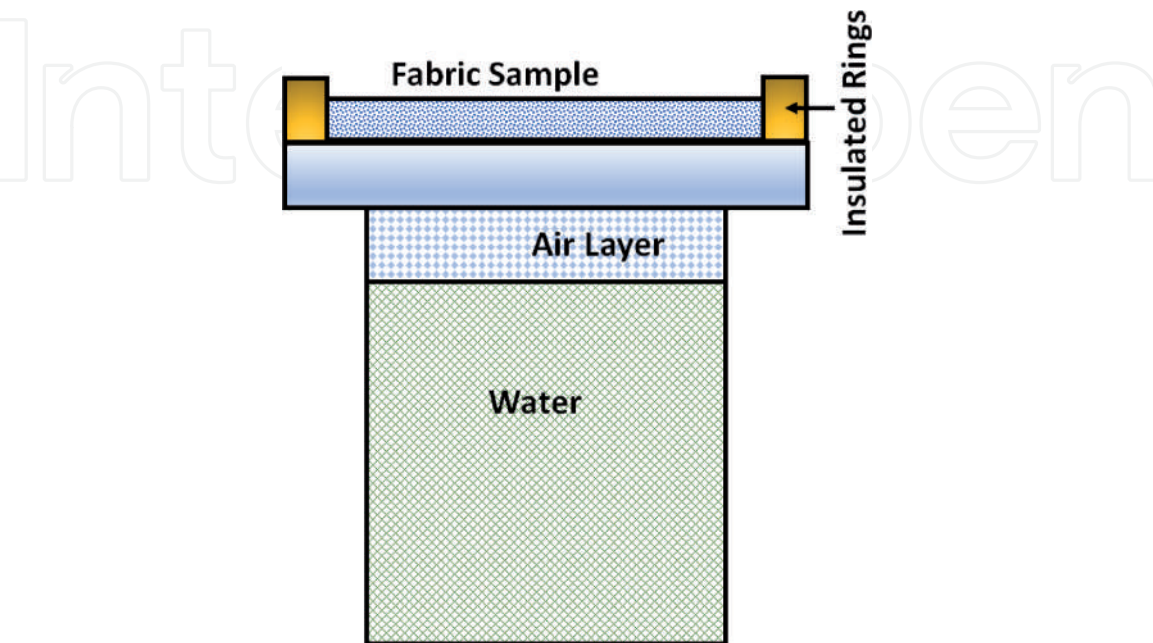


Figure 6.
Upright cup method.

weighed with accuracy of 0.001 g with the assistance of periodically top loading balance for 24 h. Finally the water vapour transmission rate is estimated by estimating the weight change g, in a time period of 24 h through a test area in m².

$$WVT = G \times 24 / t \times A \quad (1)$$

WVT = water vapour transmission rate, g/m²/day.

G = weight change, g.

t = time during which G occurred, h.

A = test area, m².

8.3 Antimicrobial assessment of functional textiles

Assessment of antimicrobial functional textiles can be completed by testing the following attributes as summarised in **Table 3**:

Colour.

The antimicrobial finish application on textile surfaces should not alter the colour, which becomes the cause of significant quality deterioration. It is preferred to add an antimicrobial agent in dye bath if the dye and antimicrobial agent's chemistry allows for this.

Chemical Effects.

The antimicrobial agent must have zero chemical effects on the functional textiles. The tensile strength, elongation, bending rigidity, fullness and surface smoothness must be maintained for a long time.

Efficacy.

The efficacy of bacteriostatic/fungistatic or bactericidal/fungicidal treatments must be appropriately checked. Variety of chemicals is available to destroy the microbes, but their logical selection is required to prolong the fabric's functionality in a controlled manner. Apart from that, the antimicrobial agent should be effective at a relatively small quantity to control the add-on and cost of the material under permissible limits.

Odour.

The antimicrobial finishes should not release an annoying odour to the finished product, especially in apparel class. Many antimicrobial agents are prone to transmit unpleasant odour, while some are entirely free from foul odour feature.

Fastness.

The fastness or stability of antimicrobial finish is calculated in terms of resistance to abrasion, heat, light, laundering, oxidising agents, and ultraviolet rays. The deficient number of antimicrobial agents possesses all the above features. The antimicrobial molecule must be stable as a compound in a manufacturing environment. It should be steady not only for the finished functional textiles' purposeful life but also for the long storage period.

Hand.

The antimicrobial treatment of functional fabrics should not deteriorate the functional fabric's low-stress mechanical behaviour, particularly in the apparel sector's manufacture. The fabric should not attain a rough hand after antimicrobial treatment.

Toxicity.

The antimicrobial functional textiles must be free from toxicity or of a short order of toxicity. The antimicrobial potential is an essential feature for kids clothing where any type of toxicity is not permissible.

| Test | Test Description and Expected Inferences |
|--|--|
| AATCC 100–2004 Antibacterial Finishes | <p>The microorganism growth is completed in liquid culture, followed by dilution in a sterile nutritive solution. Inoculation is essential for sample and glassware. Bacteria quantity is examined at “time zero” by elution in a neutralising broth, followed by dilution and plating. A standard sample run is essential to confirm the neutralisation/ elution method effectiveness. Suppression of microorganisms reference to initial concentrations and the control sample is estimated.</p> <p>Percent reduction of bacteria $R = 100 (B - A)/B$ where: R is % reduction A is the number of bacteria recovered from the inoculated treated test sample, B is the number of bacteria recovered from the jar immediately after inoculation (at “0” contact time)</p> |
| AATTC Test Method 147–2004 Parallel Streak Method | <p>Control and treated both samples are placed in close contact with the inoculated agar surface with test bacteria. A logical zone of heckled growth below and along the sample sides represents antibacterial potential of the fabric sample. A usual bacterial strain must use for test. The mean width of a zone of inhibition along a streak on either side of the sample is calculated by: $W = (T - D)/2$ where: W is width of zone of inhibition (mm), T is total diameter (mm) of sample and D is diameter of the test specimen in mm.</p> |
| AATTC: 30–2004 Antifungal Activity of Textiles | <p>This test method includes four methods for antifungal assessment on textiles.</p> <ul style="list-style-type: none">• One method involves testing fabric properties after burial in soil that contains fungi.• Second includes the cellulosic fabrics exposed to Chaetomium globosum in an agar plate and examination of subsequent growth.• The third method exposes textiles to Aspergillus niger in an agar plate and visually determines any fungal growth.• The fourth method uses a humidity jar to expose textiles to mixture of fungi spores. Any growth on the textile is visually determined. |
| AATCC TM30 Test IV | <p>A dry, 1 × 3 inches strip of nutrient saturated treated and untreated fabric, sprayed with a mixed-spore suspension of mildew is suspended and incubated with sterile water in the standard moist conditions. The percent fungal growth is recorded after the incubation period. This test allows more clear differentiation between treated and untreated samples.</p> |
| SN 195920 | Determination of antimicrobial activity on textile fabrics: Agar diffusion plate test |
| SN 195921 | Determination of antimycotic activity on textile fabrics: Agar diffusion plate test |
| SN 195924 | Determination of the antibacterial activity on textile fabrics: Germ Count Method |
| JIS L 1902 | Testing for antibacterial activity and efficacy on textile surfaces |
| ISO 20743 | Testing for antibacterial activity and efficacy on textile surfaces |
| BS EN ISO 20645 | Determination of antibacterial activity: Agar diffusion Plate test |
| BS EN ISO 11721-1 | Determination of resistance of cellulose-containing textiles to micro-organisms- Soil Burial Test – Assessment of rot-retardant finishing |
| ASTM D 4300 | Antimicrobial Testing for ability of adhesive Films to support or resist the growth of Fungi |
| ASTM E2149 | Determining the Antimicrobial Activity of Immobilised Antimicrobial Agents under Dynamic Contact Conditions |
| ASTM E2180 | Determining the activity of Incorporated Antimicrobial Agents in Polymeric or Hydrophobic Materials |

Table 3.
Various tests for antimicrobial assessment [71–74].

9. Enzyme immobilisation for functionality on textiles

Various enzymes have been immobilised on various textiles surfaces, cotton, polyester wool, and flax, to achieve additional functionalities. Enzymes are biological catalytic materials used to keep up biochemical reactions by expediting the catalytic potential. Enzymes are proteins, which remains available in cells of living entities that are proficient in reducing the stimulation energy needed by chemical reactions in organic medium and living creatures [75]. The demand for enzyme application has been

triggered in all industrial segments, but the textile industry demands high performance, extremely stable enzyme at the uttermost pH and temperatures [76]. A physically attached enzyme on a water-insoluble surface, auxiliary material or carrier is called an immobilised enzyme [77]. These enzymes remain stable with the attached surface due to a proper linkage [78]. Various latest approaches appear regularly to immobilise various enzymes on surfaces to achieve improved efficiency, stability and applications. Many materials opted as carrier, substrate or support to immobilise the enzymes are inorganic, organic and organic synthetic carriers. Most inorganic carriers are aluminium oxide, activated carbon, bentonite, hydroxyapatite, kaolinite, nickel, titania, zirconia, silica gel, and glass. Inorganic carriers are less reactive with high stability and sound diffusion, and flowing potential. These carriers are very cost-effective also.

The organic carriers are mainly carbohydrates and proteins. The carbohydrate-based carriers are alginate, chitin chitosan, cellulose, dextran, and starch; however, the protein-based carriers are albumin, collagen, and keratin. These organic carriers offer little diffusion and flow potential. These organic carriers are effected easily by microbial contamination and pH.

Organic synthetic carriers are polyamide (PA), polypropylene (PP), polyvinyl, polyacrylate, polystyrene, copolymers of ethylene, polypeptides and polyaldehydes primly [79]. The organic synthetic carriers are appropriate for a wide range of enzymatic applications because they are not sensitive to microbial contamination [80].

9.1 Essential features for a substrate for enzyme immobilisation

The characteristics of immobilised enzymes are defined by the interaction between enzyme and substrate characteristics. Important characteristics to consider are the following.

Solubility.

The immobilised enzymatic system should be insoluble and rigid with the substrate surface to avoid biological contamination and enzymes' loss.

Functional groups.

The abundance, existence and activation of functionality are essential features of the matrix. These attributes are responsible for deciding the potential of the immobilised enzyme activity, stability under application situations. Generally, the immobilisation activity is performed via the nucleophilic reaction between the enzyme and substrate functional groups because the enzyme does not react with other organic reagents.

Dimensions and porosity/permeability

In general, the bigger the matrix surface area per mass unit, the greater the probability for the enzyme and substrate to get into contact. In terms of permeability, or porosity, the higher the porosity, the better the penetration of molecules between the enzyme and the substrate. Matrix pores bigger than 30 nm appear to support enzyme immobilisation by facilitating enzyme accessibility to the matrix's internal area [80].

Mechanical strength

This property takes importance depending on the reactor or the industrial vessel where the chemical reactions take place. When using immobilised enzymes in a stirring tank, the matrix is desired to be strong enough to prevent abrasion. Particle sizes lower than 50–100 µm may result in filters and sieve plugging.

Resistance to microbial contamination

The support material must be resistant and not affected by microbial attacks. It should be stable and inert to microbial contamination for an extended period.

Reuse

One of the benefits and thus a desirable feature of immobilised enzymes is their ability to be reused. This property makes them less expensive and compensative for

any extra cost than soluble enzymes, which is especially important when using an expensive matrix or support materials in some specific applications. Proper orientation of immobilised enzymes and support from crosslinking agents improves reusability.

Hydrophobicity and/or hydrophilicity

The hydrophobicity and/or hydrophilicity of the carrier, supporting material, or matrix is vital because such characteristics affect the strength and affinity of enzyme-carrier interactions noncovalent interactions [78]. This characteristic can also affect surface assimilation, dissemination, and obtainability of the product and substrate.

Matrix size and shape

These properties are significant for operating times. In general, the size and shape are dependent on the applications. Commercially, the matrix size can be available in the range of 150–700 μm particle size. A spherical shape matrix with a particle size range of 150–300 μm is preferred for stirred tank batch productions.

9.2 Enzyme immobilisation for textile processing

Different enzymes are tried to immobilise textile surfaces to achieve various functionalities, as summarised in Table.

9.2.1 Cellulases

Cellulase enzymes recorded global identity in textile processing due to their potential to functionalised the cellulosic fibres in a regulated fashion, manufacturing improved quality fabrics without significant compromise in structural damage [81]. Cellulases, a group of enzymes, can cause cellulose hydrolysis via β -(1–4) linkages degradation of the biopolymer, consequently releasing reduced sugars [82–84]. The cellulase enzyme's multicomponent tendency finds its most application in removing fluffy and protruding fibres from cotton fabrics (biopolishing) and for a stonewashed look in fabrics by efficient abrading of indigo-dyed denim [85]. A soluble–insoluble reversible polymer, Eudragit L-100, was successfully opted for cellulase immobilisation on cotton fabric surfaces and found an alternative to be used in bio-polishing and/or bio scouring of cotton fabrics [86].

9.2.2 Pectinases

Based on their mode of action, polygalacturonases degrade the complicated pectins found in plant tissues into simpler molecules like galacturonic acids [87, 88]. Pectinase has found its way in textile processing in the 21st century; otherwise, it was a known enzyme for the food industry [89]. Many non-cellulosic impurities are found in the primary wall of cellulosic fibres and less in the secondary wall, restricting the penetration of dyes and other functional finishes in the fibre interior [87]. The bioscouring of cotton is applied to degrade the cuticle and primary wall constituents from the cotton fibre surface to improve the hydrophilicity [90].

Pectinase immobilised on the cotton fabric surface for bioscouring in a reverse micellar system with pectinase dose of 10% (2.8 IU/g of the fabric) on the weight of the fabric at 60 °C for 120 min, pH 7 to produce a hydrophilic fabric [91].

9.2.3 Amylases

Amylases are the enzymes, which split the starch molecules and starch related compounds in either exo or endo positions by hydrolysing α -1,4- and/or α -1,6-glucosidic linkages in either endo- or exo-locations [92]. The removal of starch from warp threads of the fabric in which unsized weft yarn also remains present is safely possible by the amylase enzyme's selective action [93]. The immobilised amylases

| Enzyme | Support System | Immobilisation | Benefits | Ref. |
|-----------------|--|-------------------------------------|---|-------------------------------|
| Amylase | Alkylamine glass beads coated with zirconia | Adsorption followed by GLUTAL | Immobilised enzymes with better washing fastness till 100 launderings without any considerable loss of activity | Dhingra et al. [94] |
| Cellulase | Polyvinyl alcohol coated chitosan beads, | Epichlorohydrin-Adsorption | Acid cellulase became a neutral cellulase | Dinçer and Telefoncu [82, 83] |
| | Chemically modified pumices particles | ZrOCl ₂ - Adsorption | Gives stonewashed finish on indigo-dyed denim fabrics by efficient abrading | Pazarlioglu et al. [81] |
| Catalase | Alumina pellets | Covalent-GLUTAL | Higher stabilities and surfactant inactivation | Costa et al. [99] |
| | Alumina pellets | Covalent-GLUTAL | 93% protein bound and 87% activity retained | Paar et al. [100] |
| | α- and γ-Alumina balls, Novalox saddles and Raschigrings | Covalent-GLUTAL | Higher porosity and shape of the carriers are two main parameters to influence the enzyme immobilisation stability. | Fruhwirth et al. [101] |
| | Cotton fabric or Nylon 6 | Adsorption and covalent-GLUTAL | Low cost and flexible construction | Opwis et al. [102] |
| | Poly(ethylene terephthalate) or polyamide 6.6 | Covalent -Photo chemical | After 20 application cycles, the immobilised enzyme showed an integral activity around 3.5 higher than free catalase | Opwis et al. [103, 104] |
| | Poly(ethylene terephthalate) | Chemical and Covalent-Photochemical | Enzyme modification before the immobilisation; photochemical technique may be able to compete with conventional immobilisation procedures | Opwis et al. [105] |
| Peroxidase | Polyethylene | Covalent-GLUTAL | Reusability was studied for 15 cycles and the half-life was found to be 60 h | Shaffiqu et al. [106] |
| Laccase | poly amide 6,6 | Cross linking-GLUTAL and spacer | Potential for application in the continuous decolorisation of textile effluents, where it can be applied into a membrane reactor | Silva et al. [98] |
| Glucose oxidase | Cotton | Covalent binding | Recycling of desizing liquors into bleaching liquors | Opwis et al. [107] |
| | polypropylene | plasma activated, -OH Bond | To produce enzymatically active films, activity prolong upto 30 days of storage | [108] |

Table 4.
Enzyme immobilisation on textile surfaces, (GLUTAL: Gluteraldehyde).

enzyme has opted in the detachment of starch and detergents from cotton fabrics. All detergents' performance enhances in the presence of immobilised amylase on cotton fabric surfaces [94].

9.2.4 Proteases

Proteases enzymes are used to carry out the protein degradation through hydrolysis of the peptide bonds in the polypeptide molecular chains [56, 95]. The traditional chlorination process in woollen fabric to achieve shrink-proofness causes ecological issues due to chlorine release is successfully replaced by immobilisation of proteases enzyme. The proteases action on woollen fabric enhances the dyeability, whiteness index and hand behaviour [96]. Some researchers have reported excessive damage in strength and weight loss in woollen fabrics [97]. Immobilisation of proteases enzyme on the textile surface typically enhances the molecular size, constraining proteolytic attack to the cuticle.

The modified protease is immobilised on the cuticle layer region to hydrolyse just the cuticle layer, producing higher tensile strength and a lower felting of the wool fibres. Silva et al. [98] used a commercial protease (Esperase) covalently linked to Eudragit S-100 as summarised in **Table 4**. This novel approach is a promising alternative for wool shrink-resist finishing, replacing the conventional chlorine treatments. Under optimised conditions (Eudragit, 2.5% w/v, carbodiimide, 0.2% w/v, coupling time 1 h and blocking agent concentration, 0.05%), the conjugate activity yield was about 45%, and its operational stability at 60 °C was increased by 1.7 times. Recently different enteric polymers are coupled with Esperase using carbodiimide coupling. More recently, Smith et al. [96] demonstrated that different enteric polymers could also be successfully coupled with Esperase using carbodiimide coupling on woollen fabric.

9.2.5 Glucose oxidase

Glucose oxidase is a dimeric glycosylated flavoprotein enzyme that can accelerate the oxidation of glucose to gluconolactone, which in turn, spontaneously yields gluconic acid as H_2O_2 as a side-product [109]. Therefore, glucose oxidase has been considered a possible method for producing H_2O_2 for green-bleaching, targeted at enhancing the fibre performance before colouration by tear down the pigments initially present in the natural fibres that possess greyness. Enzymatically produced H_2O_2 also gives a comparative bleaching effect with chemical bleaching. The immobilised.

9.2.6 Catalases

Catalases enzymes are known to cleave H_2O_2 into water and oxygen. H_2O_2 is a powerful bleaching agent and oxidises reactive dyes if H_2O_2 does not remove properly from cotton fabric [110]. Catalases enzyme cannot withstand commercial bleaching conditions like temperature 60 °C and pH 9 and above [111]. Alkalothermophilic and thermophilic microorganisms generated catalases enzyme is used as a successful alternative to commercial chemical bleaching. The immobilisation of catalase enzyme on fabric surface counters this issue and offers enzyme for re-application, saving energy and water both. Catalase immobilisation has been practiced by various researchers [109, 112, 113], with different carriers like organic and inorganic materials such as porous glass, cellulose, alumina, silica gel and hydrogels. Some biopolymers like gelatin and chitosan; additionally, some

synthetic polymers like polyacrylamide, were also used for bleaching treatments as summarised in **Table 4** [101]. In a remarkable work Kiehl et al. [114].

Opted catalase enzyme to immobilised on polyester, polyamide (Nylon 6, Nylon 66), cotton textile surfaces opting different strategies as mentioned in **Figure 7**. The catalase enzyme was loaded with 20–70 mg enzyme/g textile carrier to achieve reactivity upto 20% and excellent stability against enzyme desorption. The strategies like grafting, application of bifunctional coupling agents, monomeric and polymeric crosslinking agents were planned to achieve covalent fixation of the enzyme on textile carriers as shown in **Figure 7**.

9.3 Decolorisation of dyes and effluent treatment

9.3.1 Peroxidases

Peroxidases are oxidoreductases used to consume H_2O_2 to initiate the oxidation of a wide variety of organic and inorganic chemicals. Several studies covering general properties, biochemical and molecular characterisation, and industrial and environmental applications have been discussed and reviewed elsewhere [115–118].

The majority of the matrices currently used for the immobilisation of enzymes such silica, controlled pore glass, polyvinyl alcohol, polyacrylamide and chitosan beads were not suitable because of dye adsorption onto the matrices, probably inactivating the enzyme [106].

9.3.2 Laccases

Laccases enzymes are copper-containing oxidoreductases, which belong to the group of small blue oxidases. They are widely distributed in higher plants, fungi and bacteria [119, 120]. These enzymes are used to functionalised the various aromatic compounds (particularly phenols) and inorganic compounds, with concomitant reduction of oxygen to water. Laccases enzymes have found in various textile as well as other industries. The application laccase enzyme is expanding fast, decolourising textile effluents and bleaching textile substrates.

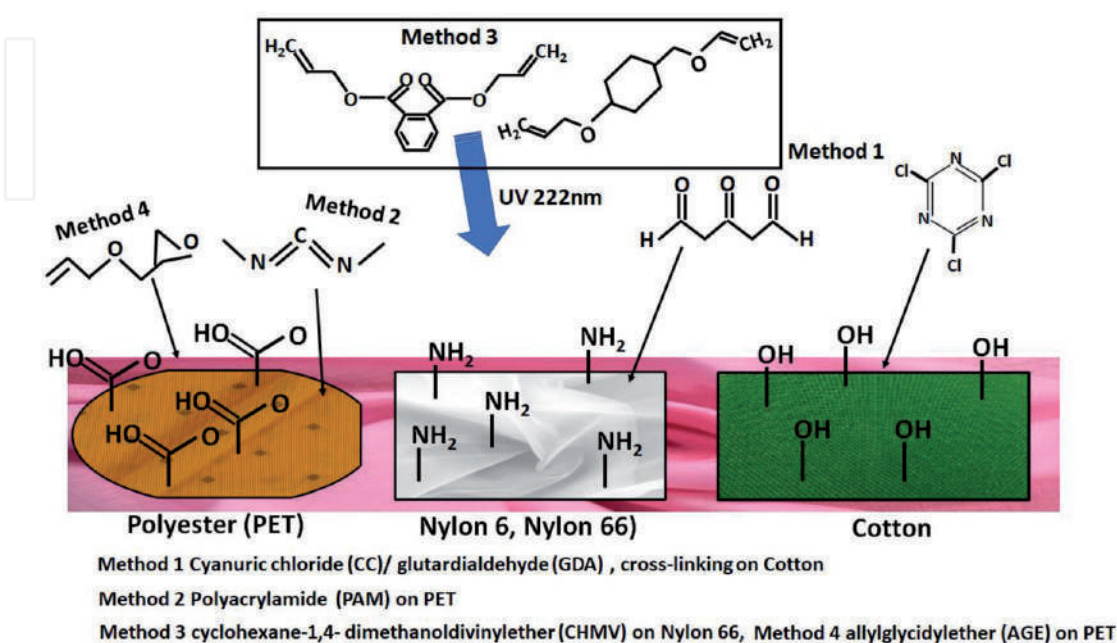


Figure 7.
 Immobilisation of catalase enzyme on various textiles materials by different methods (Kiehl et al. [114]).

Most of the laccase enzymes are produced by white-rot fungi, which are efficient in decolourising dyeing effluents [121]. Research has shown that the subsequent coating of the alumina-immobilised laccase with polyelectrolyte layers considerably increased laccase stability.

In the initial stages of laccase action, decolorisation was primly due to the adsorption of the dyes molecules onto the support system, but the support enzymatic decolorisation was apparent after the saturation of support. Acid stable laccase enzyme works well in decolouration of low pH wool dyeing effluents with water recycling opportunity. Silva et al. [98] revealed the potential application of woven nylon 66 fabrics as a carrier for laccase immobilisation to be used in a membrane reactor.

10. Conclusions

Functional textiles are one of the most critical fields in the textile industry and textile materials science. They include breathable, heat and cold-resistant materials, ultra-strong fabrics (e.g., reinforcement for composites), new flame-retardant fabrics (e.g. intumescent materials), and optimisation of textile fabrics for acoustic properties. Functional textiles became more critical materials for various applications, and interest in them grew year by year.

Human skin offers the crucial first defence mechanism for the body to safeguard against external threats. Clothing fabrics and the human skin surface form a cushioning network that creates a thermal and sensorial state of comfort to keep a human being in the state of wellness.

The microencapsulation is the most versatile technique to impart various functionalities in textiles. Microencapsulation suppresses the compatibility between active ingredients and fibre surface by enhancing the functional durability, efficacy and sustainability. This technique's vast use can be witnessed in functional finish fabrics, medical and healthcare textiles, aromatherapy, cosmetic textiles, and many more functional textiles.

The moderate stability of these bio-catalysts primly restricts the immobilisation of enzymes on textile surfaces. The immobilisation of various enzymes on textile surfaces gives a sustainable solution of surface functionalisation for easy processing. Enzyme immobilisation twinning with other surface modifying techniques gives a synergistic effect in textile functionalisation. Various researchers are trying to enhance the temperature and pH range of enzymes for more effective immobilisation. The immobilisation allows the recovery of enzymes with increases stability to reduce the operation cost of different processes. Recent developments in the synthesis and fabrication of supporting materials with customised pore size and surface functionality have licenced more precise control of enzyme immobilisation. Perfectly oriented and highly rigid enzyme molecules are needed for better immobilisation and integration with different surfaces.

Acknowledgements

This work is supported financially by Technical Education Quality Improvement Program-III (TEQIP-III), Ministry of Education, Govt. of India.

IntechOpen

IntechOpen

Author details

Mukesh Kumar Singh
Uttar Pradesh Textile Technology Institute, Kanpur Affiliated to Dr. APJAK
Technical University, Lucknow, India

*Address all correspondence to: mukesh70ster@gmail.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Lee D, Rubner M F, and Cohen R E (2006), *Nano Letters*, 6(10), 2305-2312
- [2] Michel M, Toniazzo V, Ruch D, and Ball V (2012), *ISRN Mat. Sci.* 1-7
- [3] Gupta D (2011), *Ind J of Fib and Text Res.* 36 (4), 321-326
- [4] Chang C P, Yamamoto T, Kimura M, Sato T, Ichikawa K, Dobashi T, (2003) *J of Contr. Rel.* 86 (2-3), 207-211
- [5] Salaün F, Bedek G, Devaux E, Dupont D L, (2011b) *J of Memb. Sci.*, 370 (1-2), 23-33
- [6] Teixeira M A, Rodríguez O, Rodrigues S, Martins I, Rodrigues A E (2012), *AlChE J*, 58 (6), 1939-1950
- [7] Giraud S, Rochery B M, Vroman I, Tighzert L, Delobel R, PoutchF (2005) *Poly. Degra. and Stab.* 88 (1), 106-113
- [8] Vroman I, Giraud S, Salaün F, Bourbigot S (2010) *Poly. Degr. and Stab.*, 95 (9), 1716-1720
- [9] Fan F, Zhang W, Wang C (2015) *Cellulose*, 22 (2), 1427-1438
- [10] Salaün F, Devaux E, Bourbigot S, Rumeau P (2010), *Carbohydrate Poly.* 79 (4), 964-974
- [11] Azizi N, Chevalier Y, Majdoub M (2014) *Isosorbide-based microcapsules for cosmetotextiles Industrial Crops and Products*, 52 (0) (2014), pp. 150-157
- [12] Badulescu R, Vivod V, Jausovec D, Voncina B (2008), *Carbohydrate Polymers*, 71 (1), 85-91
- [13] Liu J, Liu C, Liu Y, Chen M, Hu Y, Yang Z (2018), *Colloids and Surfaces B: Biointerfaces*, 109 (0), 103-108
- [14] Yang Z, Zeng Z, Xiao Z, Ji H. (2014) *Flav. and Frag. J*, 29 (2), 114-120
- [15] Cuevas J M, Gonzalo B, Rodríguez C, Domínguez A, Galán D, Loscertales I G, (2014), *J of Exp. Nanosci.*, 10 (11), 868-879
- [16] Naylor RGJI, Magalhaes VVRM, Pinto CBS (2006), *Microcapsules with Functional Reactive Groups for Binding to Fibres and Process of Application and Fixation*, WO 2006117702 A2
- [17] Gouveia I C (2012), *Poly. for Adv. Tech.*, 23 (3), 350-356
- [18] Salaün F, Vroman I, Elmajid I (2012) *Chem. Eng. J*, 213 (0) (2012), pp. 78-87
- [19] Kathirvelu S, D'Souza L & Dhurai B, (2009) *Materials Sci*, 15,
- [20] Uğur S S, Sarıışık M, Aktaş A H, Uçar M C & Erden E (2010) *Nanoscale Res Lett*, 5, 1204
- [21] Bertrand P, Jonas A, Laschewsky A & Legras A, (2000), *Macromol Rapid Commun*, 21. 319
- [22] Lvov Y, Price R, Gaber B & Ichinose I, (2002), *Coll Surf A Physicochem Eng*, 375, 198
- [23] Ou R, Zhang J, Deng Y & Ragauskas A J, (2007) *J Appl Polym Sci*, 102, 1987
- [24] Oh K, Park J S, Khan M R, Kim K, Lee Z, Shong B, and Lee H (2019) *Chem. of Mat.* 31, 8995-9002
- [25] Lee J, Yoon J, Kim H G, Kang S, et al., (2016), *NPG Asia Materials*, 8, e331, 1-8
- [26] Stawski D, Zielinska D, Simon F, Polowinski S, Puchalski M (2014) *Industria Textila* 65 (4), 2-9
- [27] Stawski D, Połowiński S (2011). In: *Vlákna a Textil*, 18 (1), 16
- [28] Sánchez L S, Rodríguez J F, Carmona M, Romero A, Sánchez

- P (2011) *J of Appl. Poly. Sci.*, 120 (1), 291-297
- [29] Połowiński, S (2007) In: *J of Appl. Poly. Sci.*, 103(3), 1-7
- [30] Stawski D, Bellmann C (2009) In: *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 345 (1-3), 191
- [31] Stawski D, Halacheva S, Bellmann C, Simon F, Połowiński S, Price G (2011) In: *Journal of Adhesion Science and Technology*, 25 (13), 1481
- [32] Stawski D, Połowiński S, Herczyńska L, Sarna E, Rabiej S (2012), 123 (3), 1340
- [33] Joung Y S and Buie C R (2015), *ACS Appl. Mat. & Interfaces*, A-I
- [34] Joung Y S, Buie C R (2011), *Langmuir*, 27, 4156-4163
- [35] Kostajnshek K, Dimitrovski K, Kadoglu H, Çelik P, Bayraktar G B, Üte T B, Duran D, Ertekin M, Demšar A and Bizjak M, (2013), *Polymers*, 13, 260, 1-18
- [36] Čuk M, Bizjak M, Muck D, Kočevlar T N (2020) 3D Printing and Functionalisation of Textiles, DOI: 10.24867/GRID-2020-p561-4
- [37] Karabulut K and Atav R (2020) *Fib. and Poly.*, 21(8), 1773-1782
- [38] Nelson G (2002), *Int. J of Pharma.* 242, 55-62
- [39] Zhang H, Ge C, Zhu C, Li Y, Tian W, Cheng D, and Pan Z, (2012a), *Physics Procedia* 25, 240-244
- [40] Zhang H, Ge C, Zhu C, Li Y, Tian W, Cheng D, Pan Z, (2012b) *Physics Procedia* 25, 240-244
- [41] Singh M K, Varun V K, and Behera B K (2011) *Cosmetotextiles: State of Art, Fib. & Text. in East. Euro.* 19(4), 27-33
- [42] Kanjana S, Nalankilli G (2018), *J of Text. Eng. & Fash. Tech.* 4(4), 316-318
- [43] Nakamura S, Nishioka K, Otsuki T, (2010) Interview available at http://textileinfo.com/en/chemicals/daiwa/01_06.html.
- [44] Anitha R, Ramachandran T, Rajendran R, Mahalakshmi M (2011), *Elixir Bio Physics*, 40, 5196-5200
- [45] Boh B, Kardos D (2003) *Microcapsule patents and products: innovation and trend analysis R.* Arshady, B. Boh (Eds.), *Microspheres, Microcapsules and Liposomes*, Citus Books, London, 47-83
- [46] Chan ASC, Valle J del, Lao K , Malapit C, Chua M, So RC, (2009), *Philippine Journal of Science*, 138 (1), 13-21
- [47] İnceboz T, Erkan G, Türkoğlu G C , Sarıışık A M, Bakırcı S , Üner S, Üner A (2015) , *Text. Res. J*, 85 (19), 2071-2082
- [48] Specos M M, Garcia JJ, Tornesello J, Marino P, Vecchia MD, Tesoriero MV, Hermida LG (2010) *Trans. of the Roy. Soc. of Trop. Medi. and Hyg.*, 104 (10), 653-658
- [49] Singh M K (2005) "Sun protective clothing" Jan-Feb, 91-97
- [50] Theberge K, Goudreault I, Quirion F, Perron G (2010) *Articles of Manufacture Releasing an Active Ingredient*, US 20100226947 A1
- [51] Billah S M, Christie R, Morgan M (2008), *Coloration Tech.* 124, 229-233
- [52] Fan F, Wang C (2014), *J of Appl. Poly. Sci.*, 131 (20), 211-216
- [53] Zhou Y, Yan Y, Du Y, Chen J, Hou X J (2013) *Sensors and Actuators B: Chem.*, 188 (0) 502-512
- [54] Fuji Spinning Co. Ltd Japan in *European Patent EP 1 251202*

- [55] Tiwari D, Upmanyu N, Malik J and shukla S (2017), *Int. J of Pharma & Chem. Res.*3(4), 814-827
- [56] Singh J, Batra N, Sobti RC (2001) Serine alkaline protease from a newly isolated *Bacillus* sp. SSR1. *Process Biochem* 36: 781-785
- [57] Matusiak M, Wilk E, Zieliński J (2018) Seersucker Woven Fabrics with Therapeutic Properties, *Fib. & Text. in East. Euro.* 26, 5(131), 54-58.
- [58] Javid A, Raza Z A, Hussain T, and Rehman A (2014) *J Microencapsul*, 31(5): 461-468
- [59] Save N S, Jassal M, Agrawal A K, (2005) *J. Appl. Polym. Sci.*, 95(3), 672-680
- [60] Kuhn H H, Child A D & Kimbrell WC (1995) *Synth. Met.*, 71, 2139-2142.
- [61] Invernale M A, Ding Y & Sotzing G A, (2011) *Coloration Tech.*, 3, 167-172
- [62] Mazzoldi A, De Rossi D, Lorussi F, Scillingo EP & Paradiso R, (2002) *AUTEX Res. J.*, 2, 199-204
- [63] De Rossi D, Della Santa A & Mazzoldi A, (1999), *Mater. Sci. Eng.*, C7, 31-37
- [64] Verbic A, Gorjanc M and Simoncic B (2019) *Recent Advances, Coatings* 9 (550), 1-25
- [65] Salaün F, Bedek G, Devaux E D (2011a) *Mat. Lett.*, 65 (2), 381-384
- [66] Mirschela G, Daikosa O, Scherzera T, Steckert C (2018) Near-infrared chemical imaging used for in-line analysis of functional finishes on textiles, *Talanta*
- [67] Behera B K, Ishtiaque S M, and Chand S, (1997) *J of Text. Inst.*, 88 (3), 255-264
- [68] Behera B K, and Singh M K (2014), *J of Text. Inst.*,105 (4), 365-376
- [69] ASTM E96 (1995) Standard Test Methods for Water Vapour Transmission of Materials, in. "Annual Book of ASTM Stand- ards 4.06". American Society for Testing and Materials, West Conshohocken, PA, 1995
- [70] ISO 11092 (1993), "Textiles Physiological Effects Measurement of Thermal and Water Vapour Resistance under Steady state Conditions (Sweating Guarded Hot Plate Test)". International Organization for Standardization, Geneva, Switzerland (1993)
- [71] AATCC Test Method 100-2004 (2012), Amer. Ass. of Text. Chem. and Colo., Res. Tria. Park, NC, 148-149
- [72] AATTC Test Method 30-2004 (2012), Amer. Ass. of Text. Chem. and Colo., Res. Tria. Park,, NC., 80-82
- [73] Shinde S (2010), *Man-made Text. of Ind.*, July, 247-248
- [74] Sathianarayanan MP, Bhat NV, Kokate SS, Walunj VE. (2010), *Ind. J of Fib. and Text. Res.*, 35, 50-58
- [75] Hettiarachchy N S, Feliz D J, Edwards J S, Horax R (2018) *Protiens in Food Processing*, 569-590
- [76] Conesa A, Punt PJ, van del Hondel CA, (2002) *J Biotechnol* 93:143-158
- [77] Bayindirli A, (1995) Immobilisation of enzymes and potential applications in food industry.
- [78] Datta S, Christera L R, Rajaram YRS, (2013) *Biotech.* 3, 1-9.
- [79] Costa SA, Azevedo H S, Reis R L, (2005) Enzyme immobilisation in biodegradable polymers for biomedical applications. *Biodegradable Systems in Tissue Engineering and Regenerative*

Medicine. CRC Press/Taylor & Francis Group/LLC, Boca Raton, FL. 301-324

[80] Tischer W, Wedekind F, (1999) Topics in Current Chemistry. 200. Springer-Verlag, Heidelberg, Germany, 95-126.

[81] Pazarlioglu NK, Sariisik M, Telefoncu A. (2005) Process Biochem 40, 767-771

[82] Dinçer A, Telefoncu A. (2006a), J Mol Catal B Enzymatic 45, 10-14

[83] Dinçer A, Telefoncu A. (2006b) J Mol Catal B Enzymatic 45:10-14

[84] Sinegani AAS, Emtiazi G, Shariatmadari H, (2005) J Colloid Interface Sci. 290:39-44

[85] Gusakov AV, Sinitsyn AP, Markov AV, Sinitsyna OA, Ankudimova NV, Berlin AG. (2001) J Biotechnol 87:83-90

[86] Dourado F, Bastos M, Mota M, Gama FM, (2002) J Biotechnol 99:121-131

[87] Hoondal GS, Tiwari RP, Tewari R, Dahiya N, Beg QK, (2002) Appl. Microbiol Biotech. 59:409-418

[88] Kashyap DR, Vohra PK, Chopra S, Tewari R. (2001) Bioresour Technol 77:215-227

[89] Gummadi SN, Panda T. (2003) Process Biochem 38:987-996

[90] Wang Q, Fan X, Hua Z, Gao W, Chen J. (2007) Carbohydr Polym 67:572-575

[91] Joshi M, Badhe P, Adivareker R, (2013) J of Mole. Cata. B: Enzymatic, 98 (12), 106-113

[92] Hamilton LM, Kelly CT, Fogarty WM, (2000) Enzyme Microb Technol 26:561-567

[93] Gupta R, Gigras P, Mohaptra H, Goswami VK, Chaulan B, (2003) Process Biochem 38:1599-1616

[94] Dhingra S, Khanna M, Pundir CS, (2006) Ind. J Chem Technol 13, 119-121

[95] Gupta R, Beg QK, Lorenz P. (2002) Appl. Micro- biol Biotechnol 59:15-32

[96] Smith E, Schroeder M, Guebitz G, Shen J, (2010) Enzyme Microb Technol 47:105-111

[97] Queiroga A C, Pintado M M, Malcata F X, (2007) Enzyme Microb Technol 40:1491-1495

[98] Silva C, Silva CJ, Zille A, Guebitz GM, Cavaco-Paulo A, (2007) Enzyme Microb Technol 41:867-875

[99] Costa SA, Tzanov T, Paar A, Gudelj M, Gübitz GM, Cavaco-Paulo A. (2001) Enzyme Microb Technol 28:815-819

[100] Paar A, Costa S, Tzanov T, Gudelj M, Robra K-H, Cavaco-Paulo A, Gübitz GM. (2001) J Biotechnol 89:147-153

[101] Fruhwirth GO, Paar A, Gudelj M, Cavaco-Paulo A, Robra K-H, Gübitz GM, (2002) Appl Microb Biotechnol 60:313-319

[102] Opwis K, Knittel D, Schollmeyer E. (2004) Biotechnol J 2:347-352.

[103] Opwis K, Knittel D, Bahnert T, Schollmeyer E, (2005a) Eng Life Sci 1:63-67.

[104] Opwis K, Knittel D, Bahnert T, Schollmeyer E, (2005b) Eng Life Sci 1:63-67

[105] Opwis K, Knittel D, Schollmeyer E, (2007) Biotechnol J 2:347-352

[106] Shaffiqu T S, Roy J J, Nair R A, Abraham T E, (2002) Appl Biochem Biotech. 102:315-326

- [107] Opwis K, Knittel D, Kele A, Schollmeyer E, (1999) *Starch* 51:348-353
- [108] Vartiainen, J.; Rättö, M.; Paulussen, S (2005) *Packag. Tech. Sci.*, 18, 243-251
- [109] Betancor L, López-Gallego F, Hidalgo A, Alonso-Morales N, Dellamora-Ortiz G, Guisán JM, Fernández-Lafuente R. (2006). *J Biotechnol* 121:284-289
- [110] Thompson VS, Schaller KD, Apel WA, (2003) *Biotechnol Prog* 19:1292-1299
- [111] Oluoch KR, Welander U, Andersson MM, Mulaa FJ, Mattiasson B, Hatti-Kaul R. (2006) *Biocatal Biotransform* 24:215-222
- [112] Opwis K, Knittel D, Schollmeyer E. (2004b) *AATCC Rev* 4:25-28.
- [113] Wang Y, Caruso F, (2005) *Chem Mater* 17:953-961
- [114] Kiehl K, Straube T, Opwis K, Gutmann J S, (2015) Strategies for permanent immobilization of enzymes on textile carriers, *Eng. Life Sci.*, 15, 622-626
- [115] Atack JM, Kelly DJ (2006) *Adv Microb Physiol* 52:73-106
- [116] Moreira PR, Bouillenne F, Almeida-Vara E, Malcata FX, Frère JM, Duarte JC (2006a) *Enzyme Microb Technol* 38:28-33
- [117] Matto M, Husain Q, (2006) *J Chem Technol Biotechnol* 81:1316-1323
- [118] Moreira PR, Bouillenne F, Almeida-Vara E, Malcata FX, Frère JM, Duarte JC (2006b) *Enzyme Microb Technol* 38:28-33
- [119] Alexandre G, Zhulin I B, (2000) *Trends Biotechnol* 18, 41-42
- [120] Duran N, Rosa MA, d'Annibale A, Gianfreda L (2002), *Appl Catal B Environ* 28:83-99
- [121] Kandelbauer A, Maute O, Kessler RW, Erlacher A, Gübitz GM, (2004) *Biotechnol Bioeng* 87:552-563