CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Antimicrobial finishes

Textiles are an excellent medium for the growth of microorganisms when the basic requirements such as nutrients, moisture, oxygen, and appropriate temperature are present. The large surface area of textiles also assists the growth of microorganisms on the fabric.

Natural fibers are more susceptible to microbial attack than synthetic fibers. Protein fibers act as a nutrient source for moth worms. Cellulosic fibers themselves are not a direct source of nutrients but, under appropriate conditions, some fungi secrete enzymes that convert cellulose into glucose-a nutrient source for microorganisms. Soil, dust and a few textile finishes can all be a source of nutrients for microorganisms.

Microorganisms attack fiber only when the fiber is damp. Synthetic fibers, because of their high hydrophobicity, strongly resist any attack by microorganisms. These fabrics and their blends possess a greater degree of perspiration wetness than fabrics made solely from cotton fiber because the moisture absorption of polyester fiber is low. In such cases, there is a greater chance of microbial growth on the human body that causes irritation and odor causing problems.

The major problems associated with microorganism growth in textiles are related to hygiene and fabric deterioration. Microorganisms metabolize nutrients, such as sweat and soil present in textile products, producing odor causing intermediates that cause irritation. They can damage fabric by causing stains and discoloration (such as mildew stains on curtains or tents) or by deteriorating the fabric itself-some microbes feed on finishes that are present on textiles and some fungi can eat cotton or latex. Therefore, there is a need to inhibit microbiological growth on fabrics both in industrial and apparel use [11].

A durable antimicrobial finish is a potentially effective means of controlling microorganisms on a textile by providing protection against fabric rotting and reducing odor development. An ideal antimicrobial agent for textiles would have the following basic requirements. It would provide safety in the form of low toxicity to

the consumer; e.g., it would not cause allergy or irritation to the skin. Its application would not adversely affect textile properties or appearance. It would be compatible with common textile processing, and the resulting antimicrobial efficacy has to be durable against repeated laundering [12].

Consumers' demand for hygienic clothing and active wear has created a substantial market for antimicrobial textile products [13]. Estimations have shown that the production of antimicrobial textiles was in the magnitude of 30,000 tones in Western Europe and 100,000 tones worldwide in 2000 [14-15]. Furthermore, it was estimated that the production increased by more than 15% a year in Western Europe between 2001 and 2005, making it one of the fastest growing sectors of the textile market [16]. Sportswear, socks, shoe linings and lingerie accounted for 85% of the total production [14-15]. There is also a broader market for antimicrobial fibers, for instance, in outdoor textiles, air filters, automotive textiles, domestic home furnishings and medical textiles. This high demand, in turn, has stimulated intensive research and development.

2.1.1 Field of application

Any textile finish that inhibits or kills micro-organisms can accurately be described as 'antimicrobial'. (A list of definitions is given in Table 2.1) However, it is convenient to sub-divide this general type of finish into three main groups [17].

(a) Rot proofing is an anti-microbial finish applied to give material protection, either long-term or short-term, against physical deterioration. For plastics, the term 'preservation' is used; it is also often used when referring to the short-term protection of textiles, either natural or synthetic, when mould growth can occur.

(b) Hygiene finishes are concerned with the control of infection and unwanted bacteria; a specialised development is the prevention of dust mites.

(c) Aesthetic finishes are used to control odour development and to prevent staining.

Some finishes fulfil two or even three of the above purposes – for example, cotton socks (prevent degradation, control dermatophytic fungi, inhibit odour development). Some examples of the uses of anti-microbial finishes are given in Table 2.2.

Table 2.1 Terms associated with the field of biocides [17]

Term	Definitions
Anti-microbial	The effect, chemical or otherwise, of inhibiting the growth of or destroying a microscopic organism
Rotproofing	The treatment of a material to prevent decay due to bacterial or fungal action
Hygienic	Promoting health or cleanliness
Fungicide, bactericide, biocide	Substances capable of killing fungi, bacteria or living organisms, respectively
Fungistat, bacteriostat, biostat	Substances capable of inhibiting the growth of fungi, bacteria or living organisms, respectively
Bacteria (plural)	Unicellular micro-organisms
Fungi	A kingdom separate from bacteria, plants and animals. Fungi lack chlorophyll, leaves, true stems and roots, but their cell walls contain chitin, which is only found in the animal kingdom. Fungi reproduce by the production of spores.
Micro fungi	Fungi such as mould, mildew, yeasts and so on, not producing a macroscopic fruiting body like a mushroom
Enzyme	A protein produced by living cells to act as a catalyst in a specific biochemical reaction
Virus	A sub-microscopic entity capable of replication only within a living cell
Pathogen	An agent that can cause disease
Sterilisation	A process that kills living micro-organisms
Disinfection	The process of destroying, inhibiting or removing microorganisms usually by chemical means
Antiseptic	Completely free of contamination by micro-organisms, or the chemical agent that attains this state

Table 2.2 Examples of uses of anti-microbial finishes [17]

Finish type	Problem	Area of application
Material protection (rotproofing)-long-term	Loss of tensile strength in use	Tents, webbings, awnings
	Loss of tensile strength during storage	Storage of all cellulosic goods
Material protection (rotproofing)-short-term	Loss of tensile strength	Cotton, viscose, flax, jute and wool fabrics, fibres and yarns left wet between processing
Aesthetic	Odour	Socks, underwear linings
	Staining	Shower curtains, roller blinds, garden furniture, curtains and curtain linings
	Staining, odour	Storage of fibres, yarns and fabrics with high humidities (climate or storage)
	Staining	Storage of packaged non-cellulosic textiles under fluctuating temperature conditions
	Staining	All textiles left wet between processing
Hygienic	Difficult to launder	Bedding, mattresses, carpets
	Dust mites	Bedding, upholstery, carpets, mattresses
	Cross-infection	Protective clothing

2.1.2 Requirements for Antimicrobial Finishing

In order to obtain the greatest benefit, an ideal antimicrobial treatment of textiles should satisfy a number of requirements [18]. Firstly, it should be effective against a broad spectrum of bacterial and fungal species, but at the same time exhibit low toxicity to consumers, e.g. not cause toxicity, allergy or irritation to the user. Antimicrobial-treated textiles have to meet standards in compatibility tests (cytotoxicity, irritation and sensitization) before marketing. Secondly, the finishing should be durable to laundering, dry cleaning and hot pressing. This is the greatest challenge as textile products are subjected to repeated washing during their life. Thirdly, the finishing should not negatively affect the quality (e.g. physical strength and handle) or appearance of the textile. Finally, the finishing should preferably be compatible with textile chemical processes such as dyeing, be cost effective and not produce harmful substances to the manufacturer and the environment.
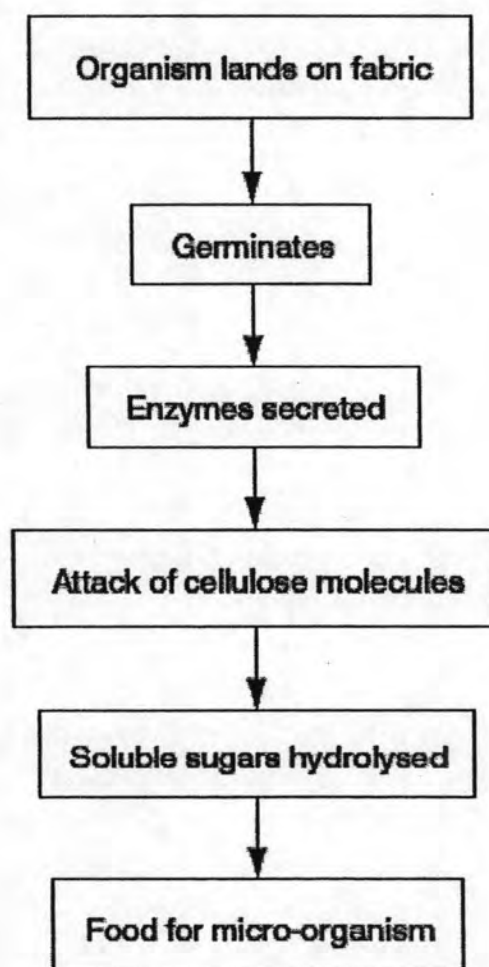
One further consideration is that the antimicrobial finishing of textiles should not kill the resident flora of nonpathogenic bacteria on the skin of the wearer. The skin resident flora consists of several bacterial genera, which are important to the health of the skin as they lower skin surface pH and produce antibiotics to create an unfavorable environment for the growth of pathogenic bacteria [19]. Fortunately, antimicrobial agents on textiles may only reduce the density of the skin resident flora but do not completely eliminate them. To date, no evidence exists that the use of antimicrobial textiles changes the ecology of skin resident flora leading to the outgrowth of pathogenic bacteria [19].

2.1.3 Modes of antimicrobial action

In order to live and multiply, micro-organisms need moisture, warmth and a food source. Therefore, if the micro-organisms can be deprived of any one of these, or if the micro-organism itself can be destroyed or prevented from multiplying, then it follows that an anti-microbial effect will be in force. For practical purposes, keeping material permanently dry or very cold is impossible although it is worth noting that degradation of materials in deserts or Polar Regions is very slow. Normally micro-organisms are present all around us and, being airborne, are constantly landing on textiles and materials. Given an adequate food source they will then start to multiply,

producing deleterious effects as described above. The food source may be the textile itself (for example, cellulose or polyurethanes) or another chemical present on the substrate (for example, spinning oils or soiling).

The latter category includes dirt deposited from the atmosphere, perspiration, skin scales and soap residues. The level of soiling varies considerably depending on the environment; consider the difference between greasy deposits that accumulate near cooking areas and ordinary dust accumulation in a bedroom. The foodstuff may be in a form that is immediately useable by the micro-organism; an obvious example of this is the breakdown of sugars by yeast in the fermentation process. More usually, however, it is necessary for the micro-organism to break down more complicated molecules into a form that is accessible as food. To do this the micro-organism produces an enzyme that is a biocatalyst [17]. A typical sequence in connection with the breakdown of cotton is shown in Figure 2.1.

Figure 2.1 Degradation process (cotton) [17]

It follows, therefore, that in order to prevent degradation of textile materials, four possibilities are available:

(a) kill organism;

(b) block enzyme;

(c) insert a barrier (for example, coating);

(d) modify fibre (top surface or whole).

Only the first option applies to hygiene and aesthetic finishes while all four options apply theoretically to a rot proofing finish designed to prevent breakdown of fibres. The process of destroying a micro-organism is achieved with a biocide in one of two ways. There can be a chemical reaction with the cell membrane, which stops the metabolic process; for example, silver- and mercury-based biocides work by displacing hydrogen ions from bacteria with the relevant metallic ion. Alternatively, the biocide can penetrate the cell wall and poison the cell from within.

A second approach is to block the enzymes elucidated by the micro-organisms. This is an important consideration. The mechanism whereby the microbe recognises the presence of a food source and produces the relevant enzyme is still not understood. However, it is possible for enzymes to be produced that will break down a material even when it has been treated with a biocide. This is obvious when one considers a tent fabric. If buried in the ground these will eventually rot almost irrespective of what treatment is given to them, and before the biocide has leached out of the fabric. Many of the enzymes produced by micro-organisms have been identified, particularly those associated with the breakdown of cellulose but blocking these is not yet practical.

Some substrates can be protected by coating or impregnation. Such a process will substantially change the physical properties of the fabric but this may be desirable for other reasons. A coating may be required in order to give water-repellent or waterproof properties and this will lend a considerable degree of protection to the fabric against microbial attack, but it is usual to also include a biocide to give aesthetic protection and to prevent degradation of the coating material itself. The degree of protection will depend on how much strike there is of the coating into the substrate or whether the substrate is coated both sides.

The alternative barrier method is to use a treatment that gives the fabric direct surface contact activity against microbial growth. The only example of this to date is

the use of an organo-silicon polymer that contains quaternary ammonium groups and forms a bio-barrier on the fabric. The chemical process involves a condensation reaction and needs available hydroxyl groups for permanent bonds to be formed. This is only available in cellulosic fibres and therefore has limited applicability. The fourth approach is to modify a biodegradable fibre. In the case of cellulose this involves reacting a chemical with the appropriate site on the molecule so that the biochemical reaction carried out by the micro-organism, via its enzyme, can no longer take place. The earliest practical example of this was in 1920 when Doree discovered the resistance of cellulose acetate to micro-organisms [17]. Full acetylation to the diacetate or triacetate results effectively in new fibres with substantially different properties to cellulose. Partial acetylation still produces some loss of physical properties and because of other problems and high processing costs this route for producing a rotproof fabric has never become commercially viable.

To protect against rot-producing fungi, disease-causing bacteria or aesthetic-destroying microbes it is necessary to use an anti-microbial treatment. This can take several forms.

2.1.4 Antimicrobial Finishing Methodologies

In the frame of antimicrobial polymers, antimicrobial polymer finishing for textiles is a particular situation, as the textile is a macromolecule as well. This latter can be a natural (cotton, wool, silk, linen, etc.) or a synthetic one (polyester, polyamide, etc.). However, the situation of small molecules like quaternary ammonium salts, halogenated derivatives, metallic substances or others, either covalently or electrostatic linked or immobilised onto the macromolecular fibres will not be considered as an antimicrobial polymer. These kinds of systems will not be regarded hereafter[20].

During their life time, textiles are confronted to various constraints, indeed, such as washing, drying, ironing, body fluids, microbial attacks. The long lasting character will then be an important parameter for the quality and the efficacy of the antimicrobial finishing. Compared to treatment with substances of low molecular weight with permanent controlled release, the macromolecules are already of more permanent solution as explained earlier, nevertheless the contact between the fibres and the polymer can be more intimate or not. Different binding concepts exist:

(a) Textile fibres are treated with antimicrobial polymers after production as an after-treatment. The adherence of the finishing will vary with the method used. On the one hand, it will be relatively low for impregnation methods like: coating, padding, pad-dry-cure, film casting, padding, spraying or dipping methods. However, a better fixation of the antimicrobial polymer can be achieved by addition of a binder or a plasticiser. For example, Kim et al. carry out the finishing of cotton fabrics with a quaternary derivative of chitosan by padding, the use of binder such as dimethyloldihydroxyethylene urea (DMDHEU) or polyurethane resin, improve the resistance to washing [21].

On the other hand, the antimicrobial polymer can be covalently attached to the fibres. This can be achieved either by grafting the monomer and subsequent polymerisation of this latter, or by polymerisation directly onto the fibre as done by Kanazawa et al. [22] with 3-(trimethoxysilyl) propyltrialkyl phosphonium chloride onto cotton fibres. The use of a crosslinking agent [23], or an organic reaction between functionalities borne by the polymer and the fibre like the reaction between polyethylenimine and hydroxyl or amino groups onto cotton, nylon or wool, as described by Lin et al. [24-25] allow a permanent linkage of the antimicrobial species. A technique such as plasma process is an easy way to improve the number and nature of functionalities along the fibres [26].

(b) The antimicrobial macromolecules are introduced into the fibre bulk during fibre production.

This second situation is possible in the case of synthetic fibres and leads to a rather high cohesion between the fibre and the polymer. Three situations arise: either the polymer and the fibre are co-extruded (mixed before spinning) or they are blended (mixed after spinning), or the fibre is only composed with the antimicrobial polymer. This latter can only be possible when antimicrobial polymer can be spun.

2.1.5 Test methods and assessment

Testing anti-microbial finishes on textiles is more difficult and more complicated than many other tests. The two main difficulties are reproducibility of results and establishing a meaningful correlation between laboratory results and actual conditions in the field. The current British Standard on preservative textile treatments (BS 2087) is purely analytical in content. It is based on field experience over many

years and does not have any references to anti-microbial tests. While in some ways this is an unbeatable approach, it provides no scope for swift development. Laboratory testing is essential to provide reasonably rapid screening of new preservatives and to check the effectiveness of existing preservatives under new conditions or when used in combination with other finishes. For example, the use of a melamine formaldehyde resin could result during curing in the crosslinking of not only the resin but the biocide present and its consequent inactivation [17].

There are four main test methods for evaluating anti-microbial finishes. The description of each method is given below. In all cases, controls as well as treated materials must be tested.

2.1.5.1 Agar plate method

In the agar plate method, a nutrient gel containing a micro-organism is poured into a plate and, when set, a piece of the fabric under examination is put on the surface of the gel and the whole plate is then incubated under conditions ideal for microbial growth. (Alternatively the inoculums is sprayed onto the sample after it has been placed on the agar plate.) For bacteria, this could be 18–24 hours at 37 °C; for fungi, 3–14 days at 28 °C, or up to 4 weeks for materials such as PVC coated fabrics. At the end of the incubation period samples are assessed either visually or by performance loss. The visual assessment is normally a comparison between uninhibited growth of the micro-organism in the dish and the growth on, or in contact with, the sample. There may be a reduction in growth or a complete absence of growth on the sample. There may also be a zone of inhibition (or 'halo') around the sample where the biocide has diffused into the gel and prevented the micro-organisms from developing. Large zones of inhibition are not desirable; they indicate that either the material has been over-loaded with biocide or that the biocide is diffusing rapidly and easily into the gel, an indication that durability will not be good.

Because of possible variations, samples will always be tested at least in quadruplicate with controls to check the viability of the organism. Care must be taken to prevent contamination from outside bacteria or fungi.

The agar plate method provides a reasonably economical and swift method for assessing materials. The test method is flexible and many variants are possible:
(a) the test can use single bacteria or fungi or mixed cultures;

(b) a wide range of textiles both coated and non-coated and cellulosic and non-cellulosic can be tested;

(c) a mineral salts agar can be used so that the only carbon source is the material under test and development of the micro-organism will indicate that degradation is taking place;

(d) quite large numbers of samples can be handled so that it is possible to compare a range of treatments and their durability – for instance, leaching, washing, dry-cleaning and exposure to UV light.

Assessment by performance loss is done by measuring loss of tensile strength or weight loss but this type of assessment is not relevant to all materials. For instance, with a polyurethane-coated nylon fabric the nylon substrate may be completely unaffected by micro-organisms so that the tensile strength of the material is unaffected during tests and weight losses are minimal. However, fungal attack of the polyurethane can result in cracking and a loss of waterproofness.

The agar plate method, when used with bacteria, relies on the biocide on the material under test migrating or diffusing into the agar gel. If the diffusion rate is very low – for example, with certain coated materials or with water-repellent finishes – misleading results may be obtained particularly with bacteria with growth occurring before the biocide has had time to diffuse out. This problem can be partly overcome by holding a sample on the plate at 5 °C for 24 hours prior to incubation. The test organism does not develop during this period but the biocide on the material has more time to diffuse into the gel.

2.1.5.2 Soil burial test

The soil burial test is a relatively crude method for assessing anti-microbial finishes and is very severe. It is, however, particularly suitable for assessing products that come into direct contact with soil such as tents, tarpaulins and sandbags, or other applications that will be subject to exposure to micro-organisms. Strips of the material under test are buried in prepared soil for 7, 14, 21 or 28 days (or longer for plastics and coated fabrics) and after burial the samples are then tested for loss of tensile strength.

Different test standards require up to 20 of each sample to be tested so the method as a whole is time-consuming and expensive. It is essential to use a control

material that must rot quickly to confirm the efficacy of the micro-organisms within the soil. There are a number of inevitable variants in this method – for example, the type of soil, moisture, pH, type and number of microorganisms present. The most meaningful results come from assessment based on comparisons rather than looking for absolute standards.

The soil burial test cannot be used for assessing aesthetic anti-microbial finishes but if the fungicide performs well in this test it will almost certainly perform well in less severe procedures.

2.1.5.3 Saturated atmosphere test

This method is suitable for assessing fabrics that will come into contact with airborne microorganisms but will not be in contact with the ground. The method consists of hanging the test specimens over water in a kilner-type jar, spraying the specimen with a single or mixed fungal spore suspension and then incubating for a minimum of 14 days at 28 °C. A visual assessment is made at the end of the test period.
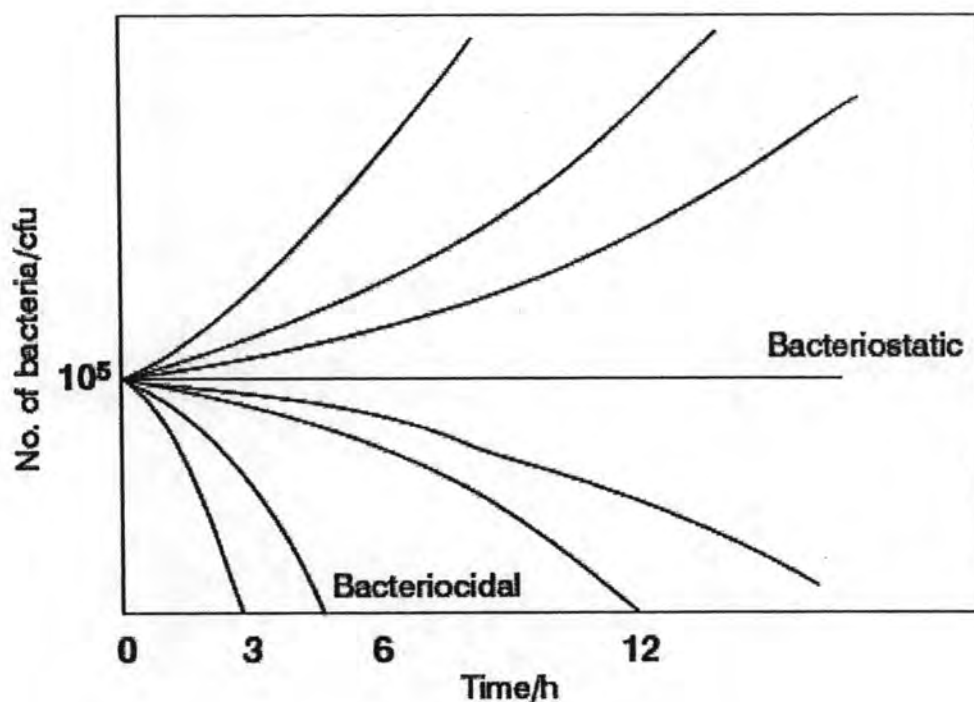
This test method is suitable for assessing anti-microbial finishes intended for aesthetic purposes or those intended for use to prevent mould or mildew development during storage. It is fairly easy and economical to perform but is not as precise as the agar plate method.

2.1.5.4 Count test (bacterial challenge)

The previous test methods are all qualitative or at best semi-quantitative. In contrast, the count test is quantitative although its application is more limited.

The count test involves inoculating swatches of the test fabric with a bacterial culture containing typically 104–106 colony-forming units (cfu) per ml. An extraction is made at time zero to establish the number of cfu present, and then further counts are made after, say, 6, 12, 18 and 24 hour periods of incubation so that a pattern of growth is established. A control sample will show a large increase in the number of cfu after incubation (although there is normally an induction period and the rate of growth eventually plateaus); an ineffective biocide will also show an increase. If the cfu value is more or less the same after incubation then the antibacterial agent is

bacteriostatic; if its value is significantly reduced then the agent is bacteriocidal. This is illustrated in Figure 2.2.

Figure 2.2 Graph to show possible results of count tests to measure the effectiveness of antibacterial agents [17]

The count test is only suitable for testing hygienic finishes and cannot be used with fungi. It is the least severe of the four basic test methods described and, because of the time needed to make the individual counts, is expensive.

There are some limitations to this test method. In order to give valid results the biocide must be able to leach fairly readily into the aqueous medium. It is not, therefore, suitable for coated fabrics nor, often, for fabrics where other finishes have also been applied – for example, a fluorocarbon. Also, depending on the structure (physical and fibre) of the fabric, as well as factors such as soiling, bacteria can 'hide' in the fabric, so that the biocide appears to be ineffective particularly in the short term.

There are several variants on these test methods as well as variations in national standards. In the UK, BS 6085: 1992, Methods for determination of the resistance of textiles to microbiological deterioration [27], gives methods for three of

the above tests but other countries have other standards. Details on test methods and standards are widely available [28-29].

It is important for exporters to be aware of these variations and to ensure that any textiles intended for overseas markets meet the required standard.

In addition to assessing the efficacy of biocide treatments, testing the durability of such finishes is also frequently required. This can be done via field trials but more practically in the laboratory. Samples are evaluated microbiologically before and after various treatments such as washing or leaching to check fastness, heating to ensure thermal stability, exposure to carbon arc or xenon lamp to evaluate susceptibility to actinic degradation, and Q panel to test weathering. The latter piece of equipment allows samples to be exposed to light (UVA or UVB), humidity and spraying with water, in different settings, combinations and cycles.

2.1.6 Antimicrobial Agents for Textiles

Several major classes of antimicrobial agents are used in the textile industry. They are generally not new materials and have been in use in other industries, e.g. as food preservatives, disinfectants, swimming pool sanitizers or in wound dressings. These agents are potent in their bactericidal activity, as indicated by their Minimal Inhibitory Concentration (MIC) values. However, their attachment to a textile surface or incorporation within the fiber substantially reduces their activity and limits their availability. Furthermore, the biocide can be gradually lost during the use and washing of the textile. For these reasons, large amounts of these biocides need to be applied to textiles to effectively control bacterial growth and to sustain durability [13].
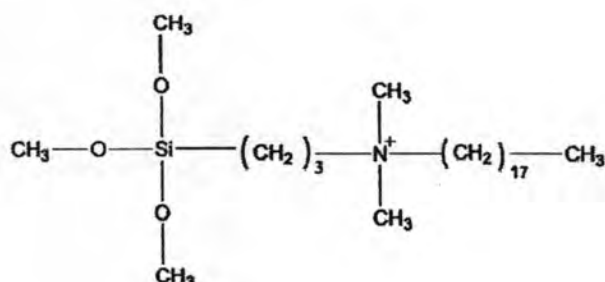
2.1.6.1 Metals and Metal Salts

Many heavy metals are toxic to microbes at very low concentrations either in the free state or in compounds. They kill microbes by binding to intracellular proteins and inactivating them [30]. Although some other metals, such as copper [31], zinc [32,-33] and cobalt [34], have attracted attention as effective antimicrobial agents for textiles, silver is by far the most widely used in general textiles as well as in wound dressings [35]. It has a MIC value of 0.05– 0.1 mg/l against *E. coli* [36]. Some

concerns have been expressed about the development of bacterial resistance to silver [37, 38].

However, such treatments of textiles with metal ions have serious limits due to technical and environmental problems and therefore have not been adopted in commercial production.

2.1.6.2 Quaternary ammonium compounds

Quaternary ammonium compounds (QACs), particularly those containing chains of 12–18 carbon atoms, have been widely used as disinfectants [33]. These compounds carry a positive charge at the N atom in solution and inflict a variety of detrimental effects on microbes, including damage to cell membranes, denaturation of proteins and disruption of the cell structure [33]. During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antimicrobial ability as long as the compound is attached to textiles [39].
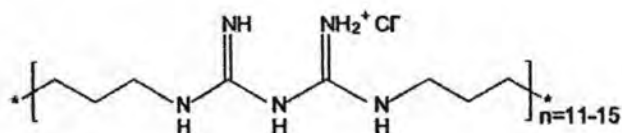

Figure 2.3 Structure of 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride [13].

2.1.6.3 PHMB

PHMB is a heterodisperse mixture of polyhexamethylene biguanides with an average molecular weight of approximately 2500 Da. Being a potent and broad spectrum bactericidal agent with low toxicity (MIC = 0.5–10 ppm, Arch technical information), it has been successfully used as a disinfectant in the food industry and in the sanitization of swimming pools and is being explored as a biocide in mouthwashes and wound dressings . PHMB impairs the integrity of the cell membrane in its action,

and its activity increases on a weight basis with increasing levels of polymerization .
To date, bacterial resistance to PHMB has rarely been observed although resistance to
the bisbiguanide chlorhexidine is well known [13].

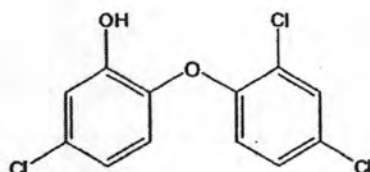**Figure 2.4** Structure of polyhexamethylene biguanide (PHMB) [13].

2.1.6.4 Triclosan

Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether) is a broad-spectrum
antimicrobial agent with a MIC of less than 10 ppm against many common bacterial
species . Unlike most other cationic biocides used on textiles, triclosan is not ionized
in a solution. It has been in a wide array of professional and consumer products
including hand soaps, surgical scrubs, shower gels, deodorants, healthcare
handwashes, toothpastes and mouthwashes. It inhibits microbial growth by blocking
lipid biosynthesis [13].

In 2004, Payne patented the treatment of cotton or cotton blends with triclosan
mixed with a polyurethane resin and a plasticizer. Being a relatively small molecule,
triclosan can also act like a disperse dye and can be used by exhaustion prior to
dyeing, together with dyeing or after dyeing of polyester and nylon fibers. During
fabric use, the agent migrates to the surfaces of the treated textiles at a slow yet
sustained rate to provide antimicrobial efficacy. To achieve a more durable finishing,
triclosan has been inserted into the hydrophobic cavity of β-cyclodextrins to form an
inclusion complex which was then embedded in a polymer film or fiber, or
encapsulated in microspheres which were subsequently attached to viscose. Triclosan
can also be directly incorporated into synthetic polymers through melt-mixing or
suspension polymerization.

Furthermore, when exposed to sunlight in the environment, triclosan breaks
down into 2,8-dichlorodibenzo-p-dioxin which is chemically related other toxic
polychlorinated dioxins. Owing to such health and environmental issues, a number of

leading retailers as well as governments in Europe are concerned about or have banned the "unnecessary use" of triclosan in textiles and some other products.

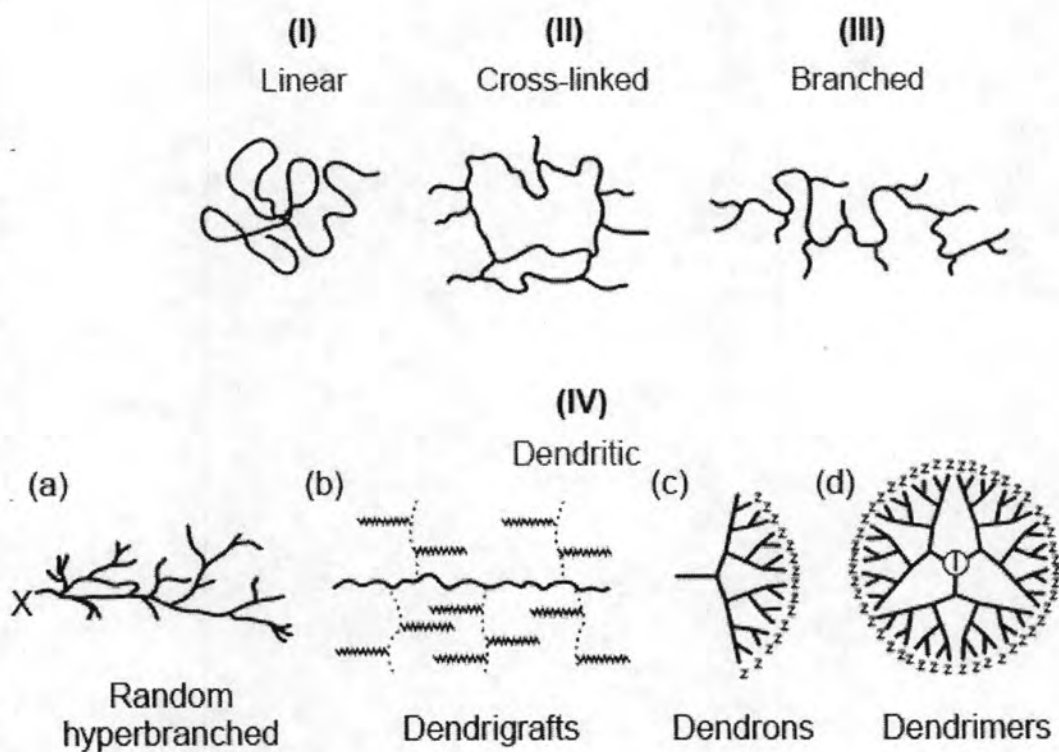**Figure 2.5** Structure of triclosan [13]

2.1.6.5 Dyes

Some synthetic dyes used in the textile industry, e.g. metallic dyestuff, exhibit antimicrobial activities. Therefore, dyeing and antimicrobial finishing can be simultaneously achieved by choosing specific dyes. Some synthetic dyes have been specifically made with antimicrobial activity. For examples, a new series of azo disperse dyestuffs, prepared by the reaction of sulphanilamidodiazonium chloride derivatives with indan-1,3-dione, gave excellent dyeing and antimicrobial results on wool and nylon . Another approach to achieve simultaneous dyeing and antimicrobial finishing is to covalently attach a biocide to a dye via a linker. For example, novel cationic dyes were synthesized by linking quaternary ammonium group to the aminoanthraquinioid chromophore. These dyes showed varying levels of antimicrobial activities, depending on their structures, but when applied to acrylic fabrics the antimicrobial durability generally did not last for more than five washes. Some natural dyes have also been examined for antimicrobial ability. Curcumin, a common dye used for fabric and food colorations, a dye isolated from *Quercus infectoria* and the colorant Berberine, which contains the quaternary ammonium group, all exhibit durable antimicrobial efficacy when attached to textiles.

2.2 Dendritic architecture

2.2.1 Synthesis of dendritic architecture [40]

The macromolecular architecture is divided into four major classes, namely: linear (class I), cross-linked (bridged; class II), branched types (class III) and dendritic type class IV). The three architectural classes (class I to class III), are recognized as traditional synthetic polymers. In all these classes, structures or architectures are produced by largely statistical polymerization processes, rather than exact distribution processes (Figure 2.6).

(I)
Linear

(II)
Cross-linked

(III)
Branched

(IV)
Dendritic

(a)

(b)

(c)

(d)

Random
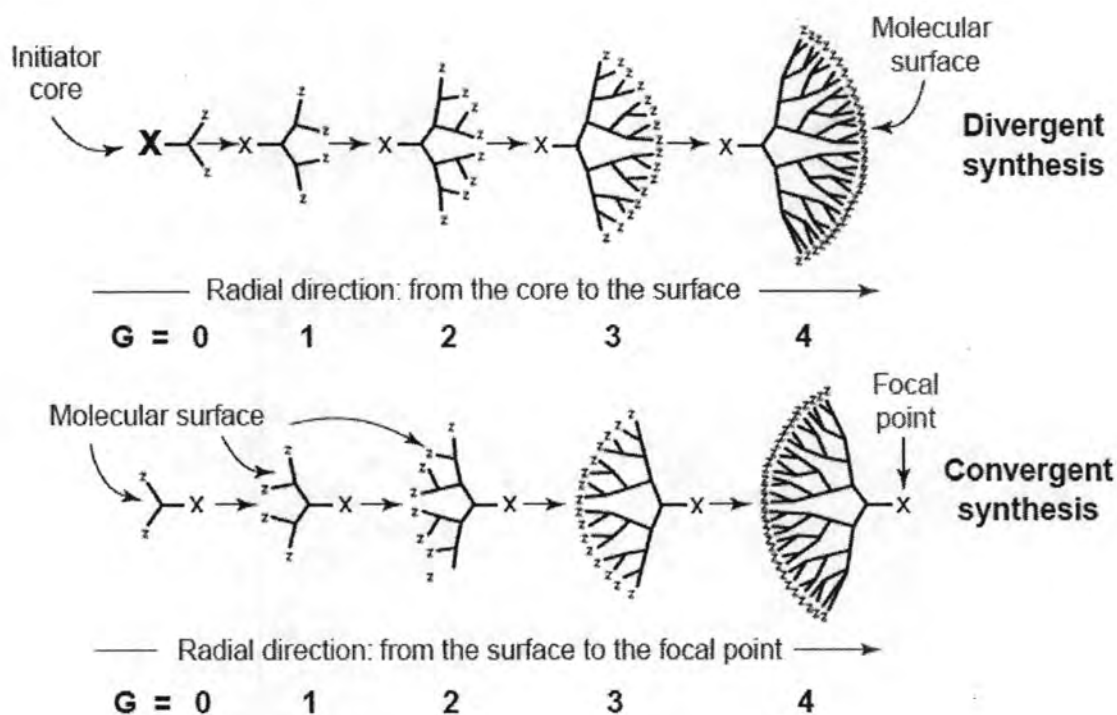hyperbranched

Dendrigrafts

Dendrons

Dendrimers

Figure 2.6 Four major classes of macromolecular architecture. (I) linear, (II) cross-linked (bridged) and (III) branched. Structure controlled polymers (IV) dendritic [40].

These processes produce polydispersed (i.e. Mw/Mn >2−10) products of many different molecular weights. In general, these are not structure-controlled macromolecular architectures such as those observed in biological systems. However, considerable progress has occurred recently in the areas of living anionic, cationic and radical polymerizations. As early as 1979, the first synthetic strategies to produce monodispersed, structure-controlled, dendritic macromolecules in ordinary laboratory glasswar were initiated. Although dendrimer structures exhibit structural control reminiscent of biological systems, the synthetic approaches did not require biological components. They did, however, involve significant innovation and digression from classical organic synthesis methods. Commercial quantities (kg) of controlled macromolecular structures with polydispersities of 1.0005−1.10 are now routinely synthesized using traditional organic reagents and monomers, such as ethylenediamine and alkyl acrylates. These new structures are referred to as dendrons or dendrimers.

The first was the divergent method in which growth of a dendron (molecular tree) originates from a core site (root) (Figure 2.7). All dendritic polymers were produced by construction from the root of the molecular tree. This approach involved assembling monomeric modules in a radial, branch-upon-branch motif according to certain dendritic rules and principles.
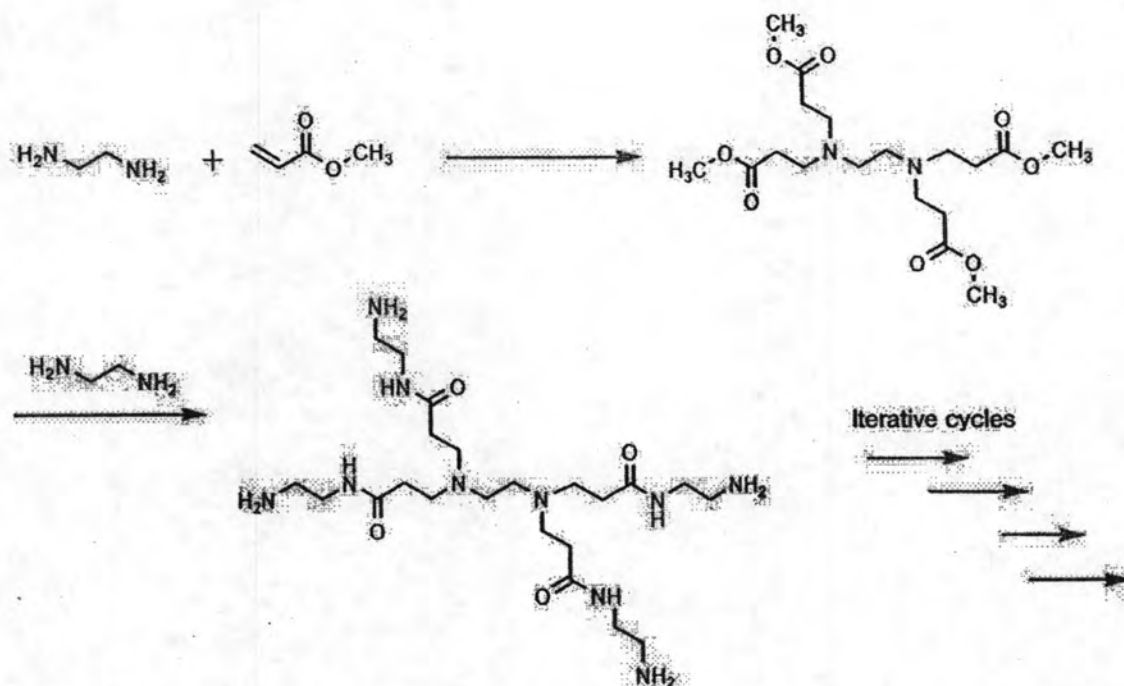
A second method is the convergent growth process. It proceeds from what will become the dendron molecular surface (i.e. from the leaves of the molecular tree) inward to a reactive focal point at the root (Figure 2.7). This leads to the formation of a single reactive dendron. To obtain a dendrimer structure, several dendrons are reacted with a multi-functional core to yield such a product.

Figure 2.7 Two principle synthetic methods for constructing dendritic macromolecules (dendrons): the divergent method (a), the convergent method (b) [40].

2.2.2 Polyamidoamine dendrimers (PAMAM)

PAMAM dendrimers were the first complete dendrimer family to be synthesized, characterized and commercialized [6, 14]. They are synthesized by the 'divergent' method. This method involves a two-step iterative reaction sequence that produces concentric shells (generations) around a central initiator core (Figure 2.8). This PAMAM core-shell architecture grows linearly in diameter as a function of added shells (generations). Meanwhile, the surface groups amplify exponentially at each generation according to dendritic-branching mathematics described in Table 2.3.

Figure 2.8 Synthesis of PAMAM dendrimers (according to Tomalia *et al.*) [41]

Table 2.3 Increase of PAMAM parameters with the number of generations [42]·

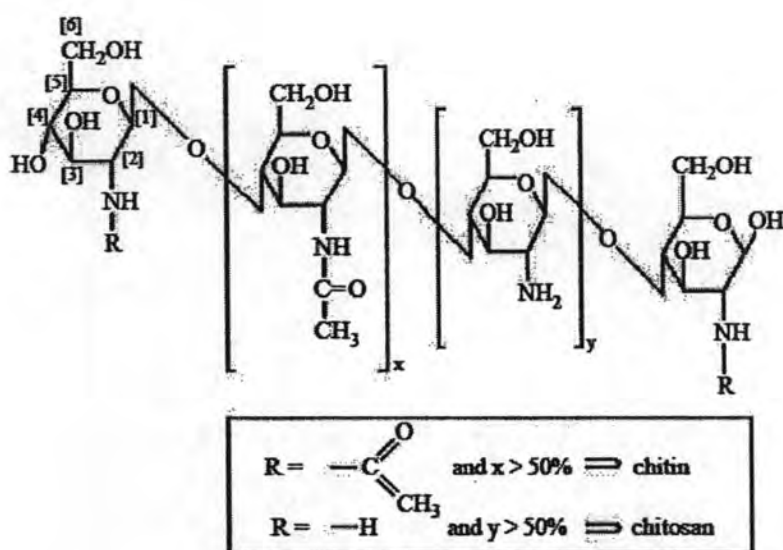| Generation	Surface Groups	Molecular Formula	MW	Diameter (nm)
0	4	$C_{11}H_{48}N_{10}O_4$	517	1.4
1	8	$C_{62}H_{126}N_{26}O_{12}$	1,430	1.9
2	16	$C_{142}H_{288}N_{58}O_{28}$	3,256	2.6
3 ·	32	$C_{302}H_{608}N_{122}O_{60}$	6,909	3.6
4	64	$C_{622}H_{1248}N_{250}O_{124}$	14,215	4.4
5	128	$C_{1262}H_{2528}N_{506}O_{252}$	28,826	5.7
6	256	$C_{2542}H_{5088}N_{1018}O_{508}$	58,048	7.2
7	512	$C_{5102}H_{10208}N_{2042}O_{1020}$	116,493	8.8
8	1,024	$C_{10222}H_{20448}N_{4090}O_{2044}$	233,383	9.8
9	2,048	$C_{20462}H_{40928}N_{8186}O_{4092}$	467,162	11.4
10	4,096	$C_{40942}H_{81888}N_{16378}O_{8188}$	934,720	~13.0

2.2.3 Antimicrobial dendrimer researches

Cooper S.L. et al. [43] reviewed a recent progress in antimicrobial dendrimers. Dendrimers were able to create more potent antimicrobial agents for both industrial and biomedical applications. The special architecture of dendrimers can be used to design effective antimicrobial agents and efficient biocide delivery systems.

In 2002, They invented quaternary ammonium functionalized dendrimers which were utilized to control the growth of microorganisms [44]. The quaternary ammonium functionalized dendrimer biocides were effective against various microbial species consist of bacteria, spores, yeast, fungi, mold and multicellular microorganisms. In addition, they also studied the interactions between dendrimer biocides and bacterial membranes[45].

Balogh L. and co-workers [46] used silver complexes of poly(amidoamine) (PAMMAM) dendrimers and silver-PAMAM dendrimer nanocomposites as antimicrobial agents. They were tested in vitro against *Staphylococcus aureus, Pseudomonas aeruginosa, and Escherichia coli* bacteria, using the standard agar overly method. Both PAMAM silver salts and nanocomposites showed displayed considerable antimicrobial activity without the loss of solubility and activity, even in the presence of sulphate or chloride ions.
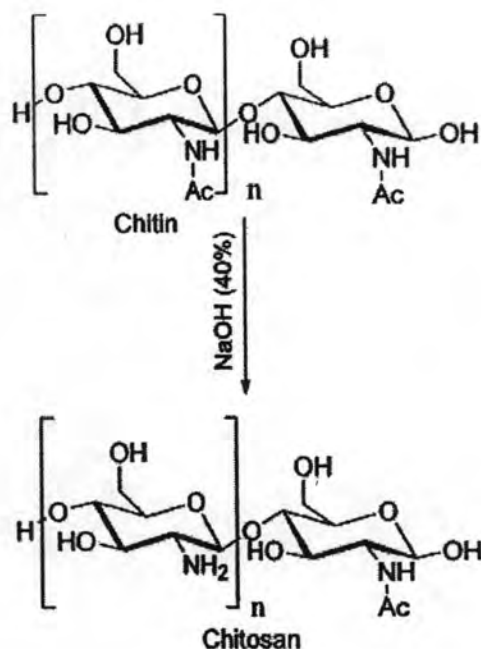
2.3 Chitosan

Chitosan is a natural polysaccharide derived from chitin. Chitin is a co-polymer of N-acetyl-glucosamine and N-glucosamine units randomly or block distributed throughout the biopolymer chain depending on the processing method used to derive the biopolymer (Figure 2.9) When the number of N-acetyl-glucosamine units is higher than 50%, the biopolymer is termed chitin. Conversely, when the number of N-glucosamine units is higher, the term chitosan is used [47].

Figure 2.9 Schematic representation of the chitin and chitosan depicting the co-polymer character of the biopolymers [47]

Chitin is one of the most abundant biopolymer derived from exoskeletons of crustaceans and also from cell walls of fungi and insect [48], is well known to consist of β-(1,4)-2-acetamido-2-deoxy-D-glucose and β-(1,4)-2-amino-2-deoxy-D-glucose units. Chitin is a white, hard, inelastic, nitrogenous polysaccharide and can be degraded by chitinase [48].

Chitosan is a product derived from N-deacetylation of chitin in the presence of hot alkali (Figure 2.10). The characteristics of chitosan that may be varied as required for a particular application are the degree of deacetylation (compared to chitin) and the molecular weight. The viscosity of solutions containing chitosan is affected by the degree of deacetylation, the molecular weight, the concentration, the ionic strength, the pH, and the temperature. Generally, an increase in temperature causes a decrease in the viscosity of the solution. The effect of the pH on the viscosity depends on the particular acid used. Native chitosan is soluble in organic acids when the pH is <6 and insoluble in water, in alkaline medium, or in organic solvents. However, water-soluble salts of chitosan may be formed by neutralization with acids such as hydrochloric acid, acetic acid, lactic acid, or formic acid [49].

Figure 2.10 Preparation of chitosan from chitin [49]

2.3.1 Antimicrobial activity of chitosan

Because of the positive charge on the C-2 of the glucosamine monomer below pH 6, chitosan is more soluble and has a better antimicrobial activity than chitin. The exact mechanism of the antimicrobial action of chitin, chitosan, and their derivatives is still unknown, but different mechanisms have been proposed. Interaction between positively charged chitosan molecules and negatively charged microbial cell membranes leads to the leakage of proteinaceous and other intracellular constituents. Chitosan acted mainly on the outer surface of the bacteria. At a lower concentration (<0.2 mg/mL), the polycationic chitosan does probably bind to the negatively charged bacterial surface to cause agglutination, while at higher concentrations, the larger number of positive charges may have imparted a net positive charge to the bacterial surfaces to keep them in suspension. The antimicrobial activity of chitosan was observed against a wide variety of microorganisms, The antimicrobial activity of chitosan against fungi and bacteria was present in Table 2.4 and 2.5.

Table 2.4 MIC of Native Chitosan against fungi [49]

Fungi	MIC (ppm)
Botrytis cinerea	10
Fusarium oxysporum	100
Drechstera sorokiana	10
Micronectriella nivalis	10
Piricularia oryzae	5000
Rhizoctonia solani	1000
Trichophyton equinum	2500

Table 2.5 MIC of Native Chitosan against bacteria [49]

Bacteria	MIC (ppm)
Agrobacterium tumefaciens	100
Bacillus cereus	1000
Corinebacterium michiganence	10
Erwinia sp.	500
Erwinia carotovora subsp	200
Escherichia coli	20
Klebsiella pneumoniae	700
Micrococcus luteus	20
Pseudomonas fluorescens	500
Staphylococcus aureus	20
Xanthomonas campestris	500

MIC = minimum growth inhibitory concentration

Chitosan has been found to inhibit the growth of microbes in a large body of work that has been extensively reviewed by Lim and Hudson [50]. It has a MIC of 0.05–0.1% (w/v) against many common bacterial species, although the activity can be affected by its molecular weight and degree of deacetylation [50-53]. The antimicrobial mechanism is not clear but is generally accepted that the primary amine groups provide positive charges which interact with negatively charged residues on the surface of microbes. Such interaction causes extensive changes in the cell surface and cell permeability, leading to leakage of intracellular substances [50]. This antimicrobial ability, coupled with its non-toxicity, biodegradability and biocompatibility, is facilitating chitosan's emerging applications in food science, agriculture, medicine, pharmaceuticals and textiles [50].

2.3.2 Chitosan as antimicrobial agent in textile

The primary focus for chitosan as an antimicrobial treatment has been on cotton. Early work indicated that the antimicrobial effect was potent against a range of microbes, but the finishing was not durable [50]. To improve durability, chitosan has been crosslinked to cotton using chemicals such as dimethyloldihydroxyethyleneurea (DMDHEU), citric acid, 1,2,3,4-butanetetracarboxylic acid (BTCA) or glutaric dialdehyde [53-54]. These chemicals, some of which are used in cotton durable press, crosslink chitosan to cotton through hydroxyl groups. Antimicrobial activity with a durability of up to 50 washes has been reported in some of these studies. Ye *et al* synthesized nanoscale core–shell particles of poly(*n*-butyl acrylate) cores and chitosan shells and applied them to cotton fabrics in a pad–dry–cure process. The antibacterial activity was maintained at over 90% reduction levels after 50 washes.

Chitosan has been applied to wool as a shrink-proofing polymer, although antimicrobial activity of the treated wool was not examined in these studies [54-60]. Given the intrinsic antimicrobial activity of chitosan, it is envisaged that the shrink-proofing treatment will dually lead to antimicrobial function. Owing to the hydrophobic and non-reactive nature of the wool fiber surface, treatment with chitosan requires pre-treatments so that the polymer can adhere to the surface. Pre-treatments include oxidation with peroxide [55- 57], protease digestion [58-59] and plasma treatment [60]. Hsieh *et al.* reported oxidizing wool with potassium permanganate and crosslinking chitosan onto it using citric acid in a pad–dry–cure treatment [61]. Although chitosan conferred durable antimicrobial ability and shrink resistance, the disadvantage was that the handle of the fabric, together with some other physical properties, was adversely affected [57, 62-63].

In addition to native chitosan, a number of chitosan derivatives have been synthesized and used as antimicrobial agents on textiles. These include chito-oligosaccharide [63-64], N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride [66-67] and N-p-(N-methylpyridinio)methylated chitosan chloride and N-4-[3-(trimethyl-ammonio) propoxy]benzylated chitosan chloride [68]. Many of these derivatives contain a quaternary ammonium group to enhance the antimicrobial activity. Another derivative is *O*-acrylamidomethyl-N-[(2-hydroxyl-3-trimethylammonium)propyl] chitosan chloride. The acrylamidomethyl group is fiber reactive and can form a covalent bond with cellulose in cotton, resulting in excellent

durability. Kenawy *et al.* attached several compounds to the reactive amino group of chitosan [69]. These modified chitosans were highly active against microbes, in particular fungi species.

Despite such active research and recent patents covering the use of chitosan on cotton [70] and polyester [71], chitosan has yet to be used as a finishing agent on any commercial textiles. The poor handle, among other factors, may be limiting its application on textiles. Nevertheless, the Swiss company Swicofil manufactures a composite fiber of chitosan and viscose, Crabyon®, that has durable antimicrobial efficacy and is suitable for a range of textile products [72]. Furthermore, chitosan can be spun into fibers but their applications seem to be limited to medical uses (e.g. medical gauzes, sutures and wound dressings) [73-74].