

## Antimicrobial polymers for textile products

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Researches concerning the development of polymer biocides represent a great challenge for both academic world and industry. This review will cover most recent advances in antimicrobial polymers for textile coating and finishing. Methods of synthesis, application and grafting of such polymers on textile substrates will be illustrated. Biocidal performances and stability (*i.e.* fastness to washing) will be reported as parameters for comparison when possible. Since the evaluation method of the antimicrobial efficiency of textile materials is a crucial factor, the most used standard test methods will be also discussed in the chapter. There are several recognized protocols in the literature for evaluating the efficiency of biocidal surfaces. Research works dealing with antimicrobial polymers from natural and synthetic sources were examined.

**Keywords** antimicrobial textile; antimicrobial polymer

### 1. Introduction

In recent years antimicrobial textiles have gained interest from both academic research and industry because of their potential to provide high-quality life and safety benefits to people. Textile products are prone to host micro-organisms responsible for diseases, unpleasant odours, colour degradation and deterioration of textiles. Antimicrobial textiles can be used to produce many goods such as sportswear, outdoor apparels, undergarments, shoes, furnishings, upholstery, hospital linens, wound care wraps, towels and wipes. Self-sterilizing fabrics could have potential benefits to reduce disease transfers among hospital populations, biowarfare protection and other applications.

Current antimicrobial products, such as triclosan and silver, suffer from critical weaknesses, for instance short active duration or high cost. Moreover, such low-molecular weight antimicrobial agents generally leach out from the fabrics towards the environment and to the skin of the wearers. Antimicrobial polymers having high molecular weight could overcome these problems reducing or preventing leaching of bioactive substances. Antimicrobial polymers have been increasingly taken into account as a feasible alternative for bactericidal applications. Moreover, antimicrobial polymers are considered an attractive way for the “non-leaching” approach in the production of bactericidal materials. This approach is interesting for many applications, in particular in textile field, where antimicrobial polymers show several advantages with respect to low-molecular weight antibacterial agents, including improved environmental stability, lack of diffusion on the wearers’ skin, low skin irritation, low toxicity, good bio-compatibility, low corrosion of metals and plastics, long residence time and biological activity.

In this review, antimicrobial polymers are defined as polymers having biocidal pendant groups or biocidal repeat units in the polymer chemical structure. The simple addition of a biocide to a polymer matrix should not be deemed as a method for producing antimicrobial polymers. Exhaustive studies on synthesis and application of such “intrinsically” antimicrobial polymers have been started in the 1970s [1, 2], and recently they were proposed for making non-leaching antimicrobial surfaces by cost-effective processes.

The non-leaching approach is attractive for textile applications, although the mechanism of action is not yet fully understood compared to conventional antimicrobial concept. Low molecular weight cationic biocides act to target sites of cytoplasmic membranes of bacterial cells. The following processes have been supposed: (i) Adsorption onto the negatively bacterial cell surfaces, (ii) Diffusion through the cell wall, (iii) Binding to the cytoplasmic membrane, (iv) Disruption of the cytoplasmic membrane, (v) Release of  $K^+$  ions and constituents of the cytoplasmic membrane, (vi) Death of the cell. The adsorption of polycations onto the negatively-charged cell surfaces is expected to take place to a greater extent than that of cationic molecules or monomers because of the much higher charge density carried by the polycations. The presence of a large number of negative charges on the membrane should ease the linkage of the polycations to the cytoplasmic membrane, compared with that by the low molecular weight cations. Thus, the disruption of the membrane and the subsequent leakage of  $K^+$  ions and cytoplasmic constituents would be enhanced [3].

This review will cover most recent advances in antimicrobial polymers for textile coating and finishing. Methods of synthesis, application and grafting of such polymers on textile substrates will be illustrated. Biocidal performances and stability (*i.e.* fastness to washing) will be reported as parameters for comparison when possible. Table 1 summarized the results gathered in literature.

## 2. Antimicrobial activity test methods

Several test methods have been developed to determine the efficacy of antimicrobial textiles [4]. The tests to evaluate the antibacterial properties generally fall into two categories: agar diffusion test (qualitative method) and dynamic shake test (quantitative method). The bacterial species *Escherichia coli* (Gram negative), *Staphylococcus aureus* (Gram positive) and *Klebsiella pneumoniae* (Gram negative) are used in most test methods.

### 2.1 Agar diffusion tests

The agar diffusion tests include AATCC 147-2004 (American Association of Textile Chemists and Colorists), JIS L 1902-2002 (Japanese Industrial Standards), SN 195920-1992 (Swiss Norm) and ISO20645:2004 (International Organization for Standardization). They are only qualitative, but are simple to perform and are most suitable when a large number of samples have to be screened for the presence of antimicrobial activity.

“Parallel Streak Method” AATCC Test Method 147-2004 has the aim to determine the antibacterial activity of diffusible antimicrobial agents on treated textile fabric. In this method, the agar surface is inoculated by making a parallel streak, and then the sample is pressed onto the inoculated plate. The method is used for obtaining an estimate of activity, in that the growth of the inoculum organism decreases from one end of each streak to the other and from one streak to the next resulting in increasing degrees of sensitivity. The size of the zone of inhibition and the narrowing of the streaks caused by the presence of the antibacterial agent allow an estimate of the residual antibacterial activity after multiple washings. Specimens of the material, including corresponding untreated samples of the same material, are placed in intimate contact with nutrient agar which has been previously streaked with an inoculum of test bacterium. After incubation at  $37 \pm 2$  °C for 18–24 hours, a clear area of interrupted growth underneath and along the sides of the test material indicates antibacterial activity of the specimen. The average width ( $W$ ) of a inhibition zone, along a streak, on either side of the test specimen is calculated by the following Eq. (1):

$$W = \frac{T - D}{2} \quad (1)$$

where  $T$  is total diameter of test specimen and clear zone (in mm) and  $D$  is diameter of the test specimen (in mm). Moreover, no bacterial colonies have to grow under the sample in the contact area to be considered acceptable antibacterial activity. The difference in zones of inhibition does not necessarily mean that a specimen is more biocidal or less. The zone of inhibition depends on the migratory property of the antibacterial agent to diffuse into the agar; hence, it does not depend only on the strength of the biocidal agent.

“Testing method for antibacterial of textiles” JIS L 1902-2002 Test Method has the aim to evaluate the antibacterial efficacy of textiles on which both antibacterial and deodorizing treatment and bacteriostatic treatment have been given. Treated and untreated fabrics are put into a 30 ml vial with a screw cap. After sterilization in an autoclave at 121 °C for 15 minutes, 0.2 ml of inoculum, the number of which is adjusted to  $1 \pm 0.3 \times 10^5$  CFU (colony-forming units)/ml, is applied to both fabric samples and cultivated at 37 °C for 18 hours. The number of living bacteria on the fabric is evaluated just after the inoculation and again after 18 hours of cultivation by measuring the optical density of diluted suspensions.

“Determination of antibacterial activity - Agar diffusion plate test” ISO 20645:2004 is a test method in which bacteria are “printed” onto the surface of textiles without them being in an aqueous suspension. The printed samples are then incubated under humid conditions at 20 °C for a specified time (18–24 hours) after which the surviving cells are counted. In particular, specimens of the material to be tested are placed on two-layer agar plates. The lower layer consists of a culture medium free from bacteria and the upper layer is inoculated with the selected bacteria. The textiles are tested on both sides. The level of antibacterial activity is assessed by examining the extent of the inhibition zone around the specimen.

### 2.2 Dynamic shake tests

The dynamic shake tests include ASTM E 2149-01 (American Society for Testing and Materials) and AATCC Test Method 100-1999 (American Association of Textile Chemists and Colourists). They provide quantitative values on the antimicrobial finishing, but are more time-consuming than agar diffusion tests.

“Standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions” ASTM E 2149-01 is designed to evaluate the resistance of non-leaching antimicrobial treated specimens to the growth of bacteria under dynamic contact conditions. This dynamic shake flask test was developed for routine quality control and screening tests in order to overcome difficulties in using classical antimicrobial test methods to evaluate substrate-bound antimicrobials. These difficulties include ensuring contact of inoculum to treated surface (AATCC 100), flexibility of retrieval at different contact times, use of inappropriately applied static conditions (AATCC 147), sensibility and reproducibility. The incubated test culture in a nutrient broth is diluted with a sterilized

0.3 mM phosphate buffer (pH 7.2) to give a concentration of  $1.5\text{--}3.0 \times 10^5$  CFU/ml (working dilution). Each fabric (about 1 g) is transferred to flask containing 50 ml of the working dilution. All flasks are shaken for 1 hour at 190 rpm. After a series of dilutions of the bacterial solutions using the buffer solution, 1 ml of the solution is plated in nutrient agar. The inoculated plates are incubated at 37 °C for 24 hours and surviving cells are counted. The antimicrobial activity is expressed in % reduction of the organisms after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control.

The percentage reduction is calculated using the following Eq. (2):

$$\text{Reduction \% (CFU/ml)} = \frac{B - A}{B} \times 100 \quad (2)$$

where  $A$  are the surviving cells (CFU/ml) for the flasks containing the treated substrate after the specified contact time and  $B$  are “0” contact time CFU/ml for the flasks used to determine  $A$  before the addition of the treated substrate.

“Antibacterial finishes on textile materials” AATCC 100-1999 provides a quantitative procedure for the evaluation of degree of antibacterial activity. Samples of test and control textile materials are inoculated with the test organisms. After inoculation, the bacteria are eluted from the swatches by shaking in known amounts of neutralizing solution. The number of bacteria present in this liquid is determined, and the percentage reduction by the treated specimen is calculated.

### 2.3 Non standard methods

Among the non standard methods, the “spraying test method” evaluates the antimicrobial activity by spraying a bacterial suspension of  $10^5$  CFU/ml of distilled water on the fabrics. After drying under air, the fabrics are placed in Petri dishes, covered with agar (yeast–dextrose broth) and incubated at 37 °C for 2 days. Then the colonies are counted.

In the “sandwich test method” 25  $\mu$ l of the bacterial suspension is placed to the centre of a fabric sample with  $\sim 2.5$  cm of diameter in a sterile Petri dish. A second identical fabric is placed on the first one and hold in place by a sterile weight. Samples are exposed for a fixed time (e.g. from 1 to 30 minutes). The solutions are diluted with 100  $\mu$ M phosphate buffer at pH 7, plated and incubated at 37 °C for 24 h. The bacterial colonies are counted for evaluating antibacterial efficiency.

## 3. Natural polymers

Although a wide range of synthetic agents are used for antimicrobial finishing of textile products (e.g. triclosan, metal and their salts, organo-metallics, etc.), they are a cause of concerns about their side effects as action on non-target microorganisms and water pollution. For these reasons, there is a great demand for antimicrobial textiles based on eco-friendly, natural polymers. The most studied natural polymer for antimicrobial finishing of textiles is chitosan; anyway, other natural products can be used for this purpose.

### 3.1 Chitosan

Chitosan (i.e. poly- $\beta$ -(1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucopyranose) is derived from chitin, which is widely distributed in nature as structural component of exoskeletons of crustaceans and insects, in marine diatoms and algae, as well as in some fungal cell walls. Chitin is an insoluble linear polysaccharide consisting of *N*-acetyl-D-glucosamine repeat units, linked through  $\beta$ -(1 $\rightarrow$ 4) glycosidic bonds. The chemical structure of chitin is highly related to that of cellulose. Chitosan was discovered by Rouget in 1859 [5], it is a linear polycationic polysaccharide with molecular weights that range from 50 to 2000 kDa. It can be produced by alkaline deacetylation of chitin. Deacetylation occurs by boiling chitin in high alkaline solutions for 1–3 hours. Since this N-deacetylation is almost never complete, chitosan is considered as a partially N-deacetylated derivative of chitin. In fact, chitosan usually consists of two monosaccharides, *N*-acetyl-D-glucosamine and D-glucosamine. The relative amount of the two monosaccharides in chitosan depends from the degree of deacetylation (75-95 %) [6].

Chitosan and its derivatives have been recently proposed as biomaterial for a large number of applications ranging from pharmaceutical, cosmetic, biomedical, food, agriculture, paper and textile. In textile field, the applications of chitosan are mainly related to its antimicrobial properties. In fact, chitosan is a wide-spectrum biocide with high antimicrobial efficacy against both Gram-positive and Gram-negative bacteria, as well as fungi and yeasts. Mechanisms of the antimicrobial activity of chitosan have been recently reported [7].

Chitosan and water soluble carboxymethyl chitosan with different molecular weights and degrees of deacetylation were applied to cotton fabric by padding and curing at 150 °C for 3 minutes [8]. The antimicrobial activity of treated fabrics was tested against Gram-negative *E. coli* and Gram-positive *S. aureus* following the ASTM E 2149-01 method. The percentage of reduction was related to the add-on of active polymer on the fabric. In particular, the percentage of reduction with an add-on of 0.5–0.6 % was  $\sim 60$  % for both carboxymethyl chitosan and chitosan, and no significant

increase in efficiency was obtained by increasing the add-on against *E. coli*. On the contrary, the bactericidal efficiency against *S. aureus* increased to ~75 % and ~79 % with an add-on of 1.6–1.8 % of carboxymethyl chitosan and chitosan, respectively. Moreover, the antimicrobial activity decreased to a large extent after dyeing with anionic dyes.

Carboxymethyl chitosan was also applied to cationized cotton [9]. Cationization of cotton was carried out using a commercial cationic agent, namely Quab® 151 (2,3-epoxypropyl-trimethyl ammonium chloride) by pad-dry-cure method. Cationized cotton was then treated with carboxymethyl chitosan. Carboxymethyl chitosan forms ionic bonds with cotton due to the opposite charges. Antimicrobial activity for the treated cotton was carried out using *E. coli* (DSMZ 498) and *Micrococcus luteus* (ATCC 9341). Antimicrobial activity increased by increasing the concentration of Quab® 151 in comparison with the control, as well as the antibacterial activity of carboxymethyl chitosan on cationized cotton fabrics increased by increasing the amount of carboxymethyl chitosan.

Chitosan was modified producing O-quaternized-N-benzylidene-chitosan and applied to cotton fabrics by pad-dry-cure method using citric acid as crosslinking agent [10]. The antimicrobial efficiency of the treated cotton fabrics were evaluated by GB/T 20944.3-2008 shake flask method (National Standards of the People's Republic of China) against *S. aureus* and *E. coli*. At a concentration of 2 % of chitosan derivatives, the percentage reduction were 99.7 % for *S. aureus* and 97.7 % for *E. coli*. The antimicrobial activity was close to 100 % for both the bacteria increasing the concentration of chitosan derivatives to 3 %. The fastness to washing of antibacterial properties was evaluated according to GB/T 8629-2001 (National Standards of the People's Republic of China for textile). One cycle of laundering by this method is considered equivalent to five home machine launderings. In absence of the cross-linking agent, the antimicrobial activity sharply dropped after five launderings. On the contrary, the antimicrobial efficiency of chitosan derivatives cross-linked cotton was found to be greater than 75 % after 20 home-launderings.

Two different cross-linking agents, namely butanetetracarboxylic acid (BTCA) and Arkofix NEC (by Clariant), were used to chemically bind chitosan to cotton fabrics [11]. Antimicrobial activity of the treated fabrics was evaluated against *Bacillus subtilis*, *Bacillus cereus*, *E. coli*, *Pseudomonas aeruginosa*, *S. aureus* and *Candida albicans* using a disc diffusion method. The maximum antimicrobial activity was obtained when the cotton fabrics were treated with 0.5–0.75 % chitosan with 1.5–5 kDa molecular weight, and cured at 160 °C for 2–3 minutes.

Dimethylolhydroxyethyleneurea was used as cross-linking agent in order to covalently link chitosan to cotton [12]. Fabrics were tested against *E. coli* and *S. aureus* according to “diffusion agar test” of the American Society for Microbiology, and “shake flask test” ASTM E 2149-01. Chitosan-treated fabrics showed 100 % percentage reduction for both *E. coli* and *S. aureus*. In order to evaluate fastness to laundering, the fabrics were washed by means of an automatic washing machine at 60 °C for 45 minutes using soap and sodium carbonate. The test results showed a decrease of the antimicrobial activity after 5 and 10 washing cycles to 90 and 83 %, respectively. Antibacterial properties disappeared after 15 washing cycles.

Another cross-linking agent to bind chitosan to cotton was epichlorohydrin [13]. Antimicrobial efficacy was evaluated following the shake flask method against *S. aureus* (ATCC 6538) and *K. pneumoniae* (ATCC 4352). Chitosan-treated cotton fabrics showed antimicrobial activities close to 100 % of bacteria reduction. Fabrics showed good antibacterial properties also after 25 laundering cycles. The bacteria reduction of *S. aureus* and *K. pneumoniae* were 91 and 93 %, respectively.

Chitosan has been also grafted to wool after acylation with succinic anhydride and phthalic anhydride [14]. Antimicrobial properties were evaluated by a qualitative method against *S. aureus* and *E. coli*. It was found that antimicrobial activity is more efficient against *E. coli*.

Fibres of poly(ethylene terephthalate) (PET) were irradiated with <sup>60</sup>Co- $\gamma$ -ray and grafted with acrylic acid. The resulting fibres were further grafted with chitosan and collagen by means of esterification [15]. Antimicrobial tests were carried out using Methicilin-resistant *S. aureus* (MRSA), *S. aureus*, *P. aeruginosa* (ATCC 10145) and *E. coli* O-157:H7 (ATCC 43894) at concentration of  $1.5 \pm 0.3 \times 10^5$  CFU/ml for contact times of up to 24 hours. The order of bacteria reduction of chitosan-grafted PET fabrics is *E. coli* > *P. aeruginosa* > *S. aureus* > MRSA. The concentration of MRSA started to diminish after 6 hours of contact for PET grafted with collagen and chitosan, while the bacteria concentration started to decrease after 4 hours of contact time with of PET grafted with chitosan only.

### 3.2 Other natural products

Besides chitosan, other natural polymers at antimicrobial activity are for example sericin from silk, natural polyphenols (e.g., tannins) or products extracted from plant such as Aloe vera.

Sericin is a macromolecular protein created by silkworms in the production of silk and constitutes 25-30 % of silk protein; the sericin molecular weights range from 30 to 300 kDa. This protein, that cements the two fibroin filaments, is removed during raw silk production (degumming process). The sericin recovered from the degumming liquor finds applications in creams, shampoos and as moisturizing agents. Recently, it has been found that PET fabrics treated with sericin (4 % w/v) show 51 % reduction of *Proteus vulgaris* and 38 % reduction of *S. aureus* [16].

Tannins are natural and water soluble polyphenols contained in herbaceous and woody plants, that have molecular weights ranging from 500 to over 3000 kDa. Tannins have been reported to be bacteriostatic and bactericidal against a wide range of fungi and bacteria (e.g. *S. aureus*, *E. coli*, *K. pneumoniae*) [17].

Among the natural products, also Aloe vera possesses antibacterial activity against *S. aureus*, *P. aeruginosa*, *C. albicans*. Aloe vera of family *Liliaceae*, also known as “Lily of the desert”, has been used in medicinal practices such as wounds healing and for cosmetic purposes. There are different polysaccharides in Aloe vera, among them the acemannan is responsible for antimicrobial activity. Recently, Wasif *et al.* [18] tried to impart antimicrobial finishing on cotton wovens using Aloe vera extract at different concentrations, in the presence of a cross-linking agent glyoxal, by pad-dry-cure technique.

## 4. Synthetic polymers

### 4.1 Quaternized polymers and pyridium-type polycations

Cationic surfactants, particularly quaternary ammonium salts (QASs), are important biocides that have been known to be effective against a broad spectrum of micro-organisms for years. The antimicrobial efficacy of QASs mostly depends on the length of the alkyl chain [19]. Polymers containing ammonium salt groups are one of the most studied class of antimicrobial polymers.

Klibanov's research group is one of the most active group on the study of the development of ammonium-based polymers. In 2003, Lin *et al.* [20] covalently bound alkylated polyethylenimine (PEI) on cotton, wool, nylon, and polyester fabrics by means of acylation with 4-bromobutyrylchloride. Micro-organisms used were fungi *Saccharomyces cerevisiae* (ATCC 4040004) and *C. albicans* (ATCC 90028), Gram-positive *S. aureus* and *Staphylococcus epidermidis*, and Gram-negative *E. coli* and *P. aeruginosa*. Microbiocidal efficiencies ranged from 88 to 99 % using alkylated 750-KDa PEI. Moreover, the work demonstrated that the PEI used for immobilization must have high molecular weight to be bactericidal, in fact bactericidal action decreased with the decrease of the chain length. Interestingly, the Authors calculated that the 750-kDa PEI should be ~6  $\mu\text{m}$  in length; that is, more than enough to penetrate even the bacterial cell. The 25-kDa PEI is up to 0.2  $\mu\text{m}$  in length. The 2- and 0.8-kDa PEIs, are 0.02 and 0.007  $\mu\text{m}$  in length, respectively, and they are too short to be harmful for the wall cell.

More recently, Hsu and Klibanov [21] synthesized a photosensitive hydrophobic polycationic salt starting from branched polyethylenimine (PEI). Positive charges were maximized by methylating the nucleophilic amino groups into quaternary ammonium groups, yielding the final photosensitive *N*-alkyl-PEI. Plain cotton fabric was then dipped into a solution of the polymer in dichloroethylene and dried in the dark. The polymer can be covalently bonded to the cotton fabric by means of UV light. Antimicrobial efficiency of the coated-fabric was determined against Gram negative *E. coli* (Coli Genetic Stock Center, CGSC4401) and Gram positive *S. aureus* (ATCC 33807) shaking 2.5  $\times$  2.5 cm pieces of fabric with 10 ml of a  $4 \times 10^4$  CFU/ml bacterial suspension in phosphate-buffered saline at 250 rpm at 37 °C for 2 h with *E. coli* and at room temperature for 4 h with *S. aureus*. Then five-fold serial dilutions were plated onto yeast-dextrose broth agar plates and incubated overnight at 37 °C. The coated fabric showed 100 % bactericidal activity against waterborne *S. aureus*.

In a previous work Klibanov and co-workers [22] proposed a procedure for covalently binding poly(vinyl-*N*-hexylpyridium bromide) (hexyl-PVP) onto polymer surfaces (i.e. polyolefin, polyamide and polyester). The first step consisted in the insertion of -SiOH groups by chemical vapour deposition on the polymer surface. The following step was the amination of the surface by the reaction with 3-aminopropyltriethoxysilane. Next, the surface was bromo-alkylated with 1,4-dibromobutane. The last step consisted in the derivatisation with hexyl-PVP. The hexyl-PVP-modified surfaces were tested on *S. aureus* (ATCC 33807) and *E. coli* (ZK 650 by Harvard Medical School, Boston, MA) following two procedures: for (1) airborne and (2) waterborne bacteria. (1) A suspension of bacteria (concentration of  $10^6$  CFU/ml for *S. aureus* and  $10^5$  CFU/ml for *E. coli*) in water was sprayed on the surface to simulate natural deposition of airborne bacteria; the material was incubated overnight in nutrient agar, then the surviving bacteria were counted. (2) Bacteria were suspended in PBS at concentrated  $2 \times 10^6$  CFU/ml *S. aureus* and  $4 \times 10^6$  CFU/ml for *E. coli*. The antibacterial materials was plugged in the suspension and shaken at 200 rpm at 37 °C for 2 hours, incubated overnight in nutrient agar, and then the surviving bacteria were counted. The method also evaluated the adhesion of the bacteria on the polymer surfaces. Antibacterial materials killed 90 to 99 % of the bacteria deposited on the surfaces through air or water.

Martin *et al.* [23] deposited poly(dimethylaminomethylstyrene) (PDMAMS) on nylon fabrics by initiated chemical vapour deposition (iCVD). This surface treatment involves the introduction of monomer vapour above the surface through the vapour phase and the formation of a polymeric film directly on a cooled substrate by means of the introduction of free radical initiator species that are thermally cracked. The iCVD process can coat substrates sensitive to heat as textile materials. Streams of monomer and initiator (i.e. di-tert-amylperoxide) in vapour phase were metered and mixed before entering the reactor. The deposition was carried out for 20–27 minutes for each side of the fabric. About 5 % of the monomer was transformed to polymer in the reactor, and ~27 % of the produced polymer coated the fabrics. Antimicrobial properties were evaluated according to ASTM E 2149-01 using *E. coli* (ATCC 29425) and *B. subtilis* (ATCC 6633). The coating was found to be >99.9999 % effective against both *E. coli* and *B. subtilis* after 1 hour of contact. Further testing showed that the coating was >99.99 % effective against *E. coli* after just 2 minutes.

3-(Trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride monomer (AEM 5700) was dissolved at room temperature in distilled water at pH 4 adjusted with acetic acid [24]. Polyester fabrics were placed in the solution of AEM 5700 and squeezed obtaining a wet pick-up of ~100 %. Polymerisation of AEM 5700 was carried out in an oven at temperatures ranging from 70 to 140 °C for 30 min. Weight add-ons of ~1 % resulted from the polymerisation of AEM 5700 were determined by weighing specimens before and after treatment. In particular, as polymerisation temperature increased the add-on decreased. Moreover, the coating produced at low polymerisation temperature was more hydrophilic because of a large amount of residual silanol groups. On the contrary, at temperature >100 °C the coating showed a hydrophobic behaviour. ASTM E 2149-01 method was used to measure the antimicrobial efficacy against *E. coli* (ATCC 8439). Excellent antimicrobial action was demonstrated with microbial reduction of >99.5 %.

Monomers of 4-vinylpyridine (4VP) and pentachlorophenyl acrylate (PCPA) were polymerised by reversible addition-fragmentation chain transfer (RAFT) polymerisation obtaining block copolymers (P(4VP-b-PCPA)) [25]. P(4VP-b-PCPA) was electrospun from a solution in mixed tetrahydrofuran and dimethylformamide producing fibres with diameters in the range of 0.5–4.0 µm. Quaternarisation was carried out by *N*-alkylation of pyridine groups of P4VP block and chloroaromatic compounds of PPCPA block. Antibacterial efficiency tests were carried out using *S. aureus* and *E. coli*. Electrospun fibres exhibit good antibacterial activities against both *E. coli* and *S. aureus* with percentage reductions of 96 and 99 %, respectively, after being in contact with 50 mg nanofibers in 10 minutes.

#### 4.2 Polymers with *N*-halamine moieties

*N*-halamines are heterocyclic organic compounds containing one or two halogen atoms (*e.g.* chlorine) covalently bound to nitrogen. N–Cl bonds can be formed by chlorination of amine, amide or imide groups in dilute sodium hypochlorite solutions. *N*-halamines are active for a broad spectrum of bacteria, fungi and viruses [4], and their action differs from those of the other polymeric biocides. In fact, the antimicrobial properties are based on the reaction of electrophilic substitution of chlorine in the N–Cl bonds with hydrogen atoms (usually from water), and results in the release of reactive Cl<sup>+</sup> ions. Cl<sup>+</sup> ions link to acceptors on micro-organism wall hindering enzymatic and metabolic processes of proteins. The electrophilic substitution between chlorine and hydrogen is a reversible reaction, therefore an N–H group, which does not have antimicrobial properties, can be regenerated for its antimicrobial activity by exposition to sodium hypochlorite [19]. *N*-halamines are commonly used as disinfectants and swimming pool sanitizers. Moreover, *N*-halamine groups were easily grafted into cellulose [26, 27]. Sun and Sun [28] co-polymerised *N*-halamine monomers with other monomers in order to produce rechargeable antimicrobial polymers. It is known that cyclic *N*-halamines (with amine, amide and imide groups) show antimicrobial efficiency against a broad spectrum of micro-organisms. Acyclic *N*-halamines possess comparable antimicrobial activities as the cyclic *N*-halamines. The chlorine content of the *N*-halamine groups can be determined by iodometric/thiosulfate titration.

Acyclic *N*-halamine polymers were also produced by co-polymerisation of vinyl acetate (VAc) with acyclic amide monomers, methacrylamide (MAM) and acrylamide (AM) [29]. Small amounts of acyclic amide monomers were added during co-polymerisation to maintain the properties of poly(vinyl acetate) but providing the co-polymers with sufficient amide groups required for the antimicrobial function upon chlorination. The co-polymers (*i.e.* poly(VAc-co-MAM) and poly(VAc-co-AM)) were dissolved in acetone and coated onto polyester fabrics. Coated fabrics were chlorinated by soaking in a 10 % aqueous solution of NaOCl at pH 7 at room temperature for 1 hour. The chlorinated samples were rinsed with distilled water and dried at 45 °C for 1 hour. Antimicrobial activities of both chlorinated and not chlorinated coated polyester fabrics were tested with *S. aureus* (ATCC 6538) and *E. coli* (ATCC 43895) carrying out a “sandwich test”. Poly(VAc-co-MAM)-coated polyester fabrics after chlorination inactivated both *S. aureus* and *E. coli* completely, with log reductions of 6.17 and 6.00, respectively, within 1 minute of contact. In the case of poly(VAc-co-AM)-coated polyester fabrics after chlorination, *S. aureus* was completely inactivated with log reduction of 6.17 within 1 min, but these fabrics were unable to completely inactivate of *E. coli* within 1 minute, in fact the log reduction was 4.19.

In another work [30], 3-(4'-vinylbenzyl)-5,5-dimethylhydantoin (VBDMH) monomer was synthesised and polymerised by admicellar polymerisation on cotton fabric at 80 °C for 8 hours in water. The coated cotton fabric was immersed in a 10 % aqueous sodium hypochlorite solution at pH 11 for 1 hour at room temperature for chlorination. Antibacterial properties were evaluated with *S. aureus* (ATCC 6538) and *E. coli* 0157:H7 (ATCC 43895) using a “sandwich test” with contact times of 1, 5, 10, and 30 minutes. The 0.12 wt% Cl<sup>+</sup> coated-cotton fabric inactivated 99.98 % *S. aureus* within 1 minute and 100 % within 5 minutes, and 99.94 % *E. coli* within 5 minutes and 100 % within 10 minutes of contact time.

#### 4.3 Biguanide-based polymers

Polymers based on biguanides (polybiguanides) are polycationic amines composed of cationic biguanide repeat units separated by aliphatic chains. Polybiguanides kill bacteria by electrostatic attractions occurring between the positively charged biguanide groups and the negatively charged bacterial cell surface. Moreover, cationic biguanide groups are also involved in binding the polymer to the fabric surface by electrostatic interactions with negatively charged groups (*e.g.* carboxylic groups in cellulose fibres) [19]. One of the most used biguanide-based polymer is poly(hexamethylene

biguanide) (PHMB) that is already commercially available (Lavasept® by Fresenius-Kabi and BBraun, Vantocil™ FHC and Cosmocil™ CQ by Arch Chemicals) with an average of 11-15 biguanide units [4]. It has been widely used as antimicrobial agent in cosmetics, as sanitizer, and in contact-lens solutions because of its low toxicity. PHMB is water soluble, and most conventional processes, such as padding and exhaustion, are suitable application methods in many fields. Commercial products based on PHMB has been marketed with the trademarks Reputex 20™ and Reputex 48™, and Purista™ particularly for textile treatments by Arch Chemicals [31].

In 2000, Huang and Leonas [32] examined the effectiveness of PHMB applied to polypropylene and cellulose/polyester non-woven fabrics after a fluoro-chemical water-repellent finish (*i.e.* perfluorakyl acrylic copolymer Zonyl® 8300 from Ciba Corp.). Parallel Streak Method (AATCC Test Method 147-1993) was used to determine the antimicrobial property of the finished fabrics against *S. aureus*. Both treated fabrics showed that an add-on of 0.75 % in PHMB was sufficient to inhibit the growth of *S. aureus* beneath the fabric. Moreover, inhibition zones surrounded the fabric edges because of PHMB was probably released from the fabrics.

In 2001, Wallace [33] tested the antimicrobial efficiency of PHMB against Gram positive *S. aureus* and Gram negative *K. pneumoniae*. PHMB was applied to cotton fabric, and the treated fabric was subjected to 1, 5, 10, and 25 laundering cycles following AATCC Test Method 143-96 using Tide detergent before antimicrobial tests. The results showed that PHMB reduced *S. aureus* by 98 % after more than 10 laundering cycles and had >99 % of reduction against *K. pneumoniae* after 5 laundering cycles and more.

PHMB was also applied to a 65/35 polyester/cotton blend fabric by padding and drying processes [34]. The fabric was plugged in an aqueous solution of PHMB at a concentration of 2.3 w/v %, passed through rollers and dried in an oven at 120 °C for 5 min. Antimicrobial performances were determined against *S. aureus* (ATCC 6538) and *K. pneumoniae* (ATCC 4252) bacteria following the AATCC Test Method 100-1999. Percentage reductions were 99.99 % for *S. aureus* and 99.97 % for *K. pneumoniae*. Moreover, PHMB consistently exhibited reductions more than 99 % of *S. aureus* and ~94 % of *K. pneumoniae* even after 25 laundering cycles following AATCC Test Method 143-96.

Recently, Gao and Cranston [35] reported that PHMB can be applied to wool only after a chemical modification, which increases anionic groups of the wool. In the proposed procedure, fabrics were treated with solutions of peroxymonosulphate (PMS) and sodium sulphite. The fabrics, including the untreated fabrics, were dried in an oven at 80 °C for 45 minutes. Then, PHMB was applied to untreated and PMS/sulphite-treated wool fabrics by plunging in a PHMB solution. The treatments were carried out at room temperature for 1 hour. The PHMB uptake was evaluated to be 3.25 % of the initial weight of the fabrics for PMS/sulphite-treated wool. Quantitative antimicrobial activities were performed following the AATCC Test Method 100-1999 with Gram negative *E. coli* (ATCC 4352) and Gram positive *S. aureus* (ATCC 6538). The fabrics were able to reduce both bacteria by 99.9 %. The paper also reported that with a content of PHMB below 1.4 % there is no antibacterial activity. Washing tests on PHMB-coated PMS/sulphite-treated wool [36] were carried out at 40 °C in a washing machine using 5A cycles according to the test method ISO 6330:2000. After 25 washing cycles, the fabrics had a reduction of 67 % for *E. coli*.

#### 4.4 Conjugated polymers

Conjugated polymers, such as polypyrrole (PPy) and polyaniline (PANI), are generally employed in textile field for their electrical properties [37]. They can be easily produced by chemical oxidative polymerisation in aqueous solutions of the monomer. Materials (e.g. fibres, fabrics) plunged in the polymerisation bath are coated with an even and uniform layer of conjugated polymer by *in situ* chemical oxidative polymerisation. The presence of anions in the polymerisation bath improves the formation of positive charges along the backbone chain of the polymer. The positive charges seem to be responsible for the antimicrobial activity of such kind of polymers.

Antimicrobial activity of conjugated polymers was first reported by Seshadri and Bhat in 2005 [38, 39]. They deposited PANI [38] and PPy [39] on cotton fabrics by *in situ* chemical oxidative polymerisation at cold temperature (0-5 °C). The fabrics were first impregnated in monomer solutions for 2 hours, then the solution was cooled and oxidant solutions was added. The oxidant for PANI was ammonium persulphate, while the oxidant for PPy was ferric chloride. After deposition, PANI-coated fabric was plunged in a 1 M acid solution, and washed with water. Some samples of PPy-coated fabrics were also treated with a solution of CuCl<sub>2</sub> as additional antimicrobial agent. The antibacterial and antifungal properties were tested by “Parallel Streak Method” AATCC Test Method 147-1993 and ASTM E 2149-01 procedure using Gram positive *S. aureus* (ATCC 6538), Gram negative *E. coli* (ATCC 11229) and *C. albicans*. The percentage reductions for PANI-coated fabrics was ~95 % against *S. aureus*, 85 % against *E. coli* and 92 % against *C. albicans*. The percentage reductions for PPy-coated fabrics were 65 % against *S. aureus*, 59 % against *E. coli* and 73 % against *C. albicans*. The addition of CuCl<sub>2</sub> to PPy increased the efficacies up to 93, 98 and 100 % for *S. aureus*, *E. coli* and *C. albicans*, respectively.

Recently, our research group coated cotton fabrics at room temperature with PPy using different oxidising agents in order to assess their influence on the antimicrobial efficacy [40]. The fabrics were plunged in water solution of one of the oxidants used (*i.e.* ferric chloride, ferric sulphate, ammonium persulphate). While the fabric was soaking, the monomer was added drop-wise to the stirred bath, and the reaction immediately started. After 4 hours, the fabrics were squeezed, rinsed in cold water, and dried at room temperature. Antibacterial activity was evaluated following the ISO

20645:2004 procedure using Gram negative *E. coli* (ATCC 8739). No inhibition zone was observed for all the samples: the colonies of bacteria grew around the fabric. Removing the specimen from the agar, it was observed the absence of bacteria in the contact zone under all PPy-coated fabrics. Therefore, the oxidising agent used to synthesise PPy had no effect the final high antimicrobial activity, and this activity took effect just by contact because PPy was directly linked to the fabric.

Following the ASTM E 2149-01 procedure we quantified the antimicrobial activity of PPy, demonstrating that PPy possessed actually high antimicrobial efficiency (>99 %) against *E. coli* also without the use of additional antimicrobial agents [41].

#### 4.5 Dendrimers

Dendrimers are a class of low-molecular weight highly-branched polymers discovered in the 1985 by Tomalia and co-workers [42]. Dendrimers have several functional groups with a central core and terminal end groups. Synthesis and modification of dendrimers have been of great interest to scientists in various applications. Quaternization of dendrimers was reported in the 2000 by Chen *et al.* [43] that synthesised quaternary ammonium functionalised poly(propylene imine) dendrimers with high biocide properties.

Recently, dendrimers have been proposed to develop antimicrobial properties for applications to textiles [44]. Poly(amidoamine) dendrimer was modified to provide antimicrobial properties by (a) converting primary amine end groups into ammonium functionalities and (b) producing silver nanoparticles/poly(amidoamine) complexes. These materials were applied to a 50/50 nylon/cotton woven fabric by coating process using a laboratory knife and dried for 6 h in ambient condition. The antimicrobial properties of the fabric were tested following the AATCC Test Method 147-1993 with *S. aureus* ATCC 6538. Fabrics treated with dendrimers having ammonium groups showed a 12-mm wide inhibition zone. Moreover, the silver nanoparticles/dendrimers complexes showed effective antimicrobial activities, but the zone of inhibition was smaller than that of dendrimers alone.

### 5. Potential applications for textiles of other polymers

In this Section, information about some antimicrobial polymers that have not yet applied to textiles are briefly reported.

#### 5.1 Natural polymers

Antimicrobial peptides are widely distributed in nature, existing in organisms from insects to plants to mammals and non-mammalian vertebrates. This observation suggests that they acted a crucial role in the successful evolution of complex multicellular organisms. The great diversity of antimicrobial peptides, discovered over the past 30 years, made difficult to classify them, excepting for their secondary structure. In fact, in antimicrobial peptides, hydrophobic and cationic amino acids cluster in distinct domains spatially arranged in the molecules [45, 46]. Antimicrobial peptides have been proposed as coating agents for many devices. They can be linked to solid materials by layer-by-layer assembly or covalent bonding [47]. For instance, *Cecropin B*, (NH<sub>2</sub>)-NGIVKAGPAIAVLGEAAL-CONH<sub>2</sub>, an antimicrobial peptide isolated from the pupae of Chinese oak silk moth (*Antheraea pernyi*), has been recently covalently bound onto silk fibroin films [48]. The proposed procedure could be easily applied to silk fabrics.

#### 5.2 Synthetic polymers

Several antimicrobial synthetic polymers have been synthesized in recent years but not yet employed in textile field.

The potentialities of these polymers for producing antimicrobial fabrics and garments have therefore to be assessed, as well as the process for depositing them on textile materials.

Kanazawa *et al.* [49] synthesized poly(*p*-vinylbenzyl tetramethylenesulfonium tetrafluoroborate) and poly(*p*-ethylbenzyl tetramethylenesulfonium tetrafluoroborate) with different molecular weights. The polymers showed high antimicrobial efficacies against Gram-positive *S. aureus*, whereas they were less active against Gram-negative *E. coli*. It was found that the activity of polymeric sulfonium salts was much higher than that of corresponding monomers, and the efficacy increased with the increase in molecular weight.

Erol [50] described the polymerisation of (benzofuran-2-yl)(3-mesityl-3-methylcyclobutyl)-*O*-methacrylketoxime monomer. The resulting polymer was found to be effective in inhibiting the growth of micro-organisms, such as *P. aeruginosa*, *E. coli*, *C. albicans*, and *S. aureus*, because of oxime esters and carbonyl groups might have inhibited enzyme production.

New methacrylate monomers containing pendant quaternary ammonium moieties based on 1,4-diazabicyclo-[2.2.2]-octane (DABCO) were synthesised by Dizman *et al.* [51]. The polymers showed good antimicrobial activities against *S. aureus* and *E. coli*. The activity increased as the *N*-alkyl chain length increased from four to six carbons.

Cao *et al.* [52] developed a series of polymeric silver sulfadiazines with durable and rechargeable antibacterial and antifungal activities. Acryloyl sulfadiazine was copolymerized with methyl methacrylate. The sulfadiazine moieties



formed complexes with silver ions by contact to dilute silver nitrate aqueous solutions producing poly(methyl methacrylate)-based polymeric silver sulfadiazines. The antibacterial activity of the polymeric silver sulfadiazines was evaluated according to AATCC Test Method 100-1999 against *S. aureus* (ATCC 6538) and *E. coli* (ATCC 15 597). *Candida tropicalis* (ATCC 62690) was employed for evaluating antifungal activity. The polymeric silver sulfadiazines showed 100 % biocidal activity against bacteria and fungi for contact time >10 minutes. Moreover, Kirby–Bauer tests indicated that no silver ions leached out of the polymers, and the antibacterial and antifungal functions took place by contact kill.

Novel acrylamide-type monomer (*N*-(4-hydroxy-3-methoxy-benzyl)-acrylamide) was obtained by Friedel-Craft alkylation between guaiacol and *N*-hydroxymethylacrylamide and with a three-step synthesis from vanillin. The monomer was then successfully polymerised following conventional radical polymerisation technique by Liu *et al.* [53]. Antibacterial tests of polymers were carried out using Gram-negative *B. subtilis* (ATCC 6633) bacteria showing promising antibacterial effects.

**Table 1** Results on antibacterial efficiency and fastness to washing of antimicrobial textiles

Polymer	Substrate	Bacteria	Efficiency (%)	Deposition method	Efficiency after washing	Refs.
Chitosan and carboxymethyl chitosan	Cotton	<i>E. coli</i> <i>S. aureus</i>	60 <sup>a</sup> 75-79 <sup>a</sup>	Pad-dry-cure	Unknown	[8]
Chitosan	Cotton	<i>E. coli</i> <i>S. aureus</i>	~100 <sup>a</sup> ~100 <sup>a</sup>	Chemical grafting	83 % after 10 cycles at 60 °C for 45 minutes	[12]
Chitosan	Cotton	<i>S. aureus</i> <i>K. pneumoniae</i>	~100 <sup>a</sup> ~100 <sup>a</sup>	Chemical grafting	91 and 93 % after 25 laundering cycles	[13]
N-alkyl-polyethyleneimine	Cotton	<i>S. aureus</i>	98 <sup>c</sup>	Chemical grafting	<i>S. aureus</i> : 98 % after 1 cycle in methanol and water 98 % after stirring in water at 55°C overnight	[20]
		<i>S. epidermidis</i>	97 <sup>c</sup>			
		<i>E. coli</i>	99 <sup>c</sup>			
		<i>P. aeruginosa</i>	98 <sup>c</sup>			
		<i>S. cerevisiae</i>	97 <sup>c</sup>			
<i>C. albicans</i>	96 <sup>c</sup>					
N-alkyl-polyethyleneimine	Cotton	<i>S. aureus</i> <i>E. coli</i>	100 <sup>b</sup> ~100 <sup>b</sup>	UV curing	Unknown	[21]
Poly(dimethylaminomethylstyrene)	Nylon	<i>E. coli</i> <i>B. subtilis</i>	~100 <sup>a</sup> ~100 <sup>a</sup>	Chemical vapour deposition	Unknown	[23]
Quaternized ammonium polymer	Polyester	<i>E. coli</i>	~100 <sup>a</sup>	Pad-dry-cure	Unknown	[24]
Acyclic N-halamine polymer	Polyester	<i>E. coli</i>	100 <sup>d</sup>	Coating	Unknown	[29]
		<i>S. aureus</i>	100 <sup>d</sup>			
N-halamine polymer	Cotton	<i>E. coli</i>	~100 <sup>d</sup>	Coating	Unknown	[30]
		<i>S. aureus</i>	~100 <sup>d</sup>			
Poly(hexamethylene biguanide)	Polyester/cotton	<i>S. aureus</i>	~100 <sup>c</sup>	Pad-dry-cure	~100 % after 25 cycles AATCC 143-96 94 % after 25 cycles AATCC 143-96	[34]
		<i>K. pneumoniae</i>	~100 <sup>c</sup>			
Poly(hexamethylene biguanide)	Wool	<i>E. coli</i>	~100 <sup>c</sup>	Pad-dry-cure	67 % after 25 cycle A5 ISO 6330:2000	[35, 36]
Polypyrrole	Cotton	<i>S. aureus</i>	65 <sup>a</sup>	Chemical deposition	Unknown	[39]
		<i>E. coli</i>	59 <sup>a</sup>			
		<i>C. albicans</i>	73 <sup>a</sup>			
Polyaniline	Cotton	<i>S. aureus</i>	95 <sup>a</sup>	Chemical deposition	Unknown	[38]
		<i>E. coli</i>	85 <sup>a</sup>			
		<i>C. albicans</i>	92 <sup>a</sup>			

Note. Test methods: <sup>a</sup> ASTM E 2149-01; <sup>b</sup> spray methods (non standard method); <sup>c</sup> AATCC 100-1999; <sup>d</sup> sandwich test(non standard method).

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