Chapter 7
Antimicrobial Fibers and Fabrics Obtained by Electro/Melt Spinning

Abstract Nanotechnology and nanoscience involve different aspects including the manipulation, control, and assembly of nanoscale components to produce materials, systems, and/or devices. In this context, the fabrication of micro/nanofibers has attracted huge interest. In particular, micro/nanofibers have different properties such as high porosity, small pore size, high surface area, and compatibility with functionalizing additives that enables their use in multiple applications. These include their use as enzyme carriers, membranes for filtration purposes, as barriers to liquid penetration, sensors, delivery purposes, and catalysts. Polymer fibers have also been explored in a large variety of medical applications such as tissue engineering or in regenerative medicine.

In this chapter, we will provide an overview of the most extended fabrication approaches and their use in medical applications, in particular to prevent microbial contamination. The fabrication of fibers treated with antimicrobials is today a standard finish for many different textile products employed in such uses as medical, institutional, and hygienic. More recently, antimicrobial fibers have been extended to other applications including women's wear, sportswear, and aesthetic clothing to impart anti-odor or biostatic properties.

Keywords Antimicrobial fibers • Micro/nanofibers • Melt/emulsion spinning • Electrospinning • Hybrid nanofibers • Responsive fibers • Biodegradable fibers

7.1 Introduction

Nanotechnology and nanoscience involve different aspects including the manipulation, control, and assembly of nanoscale components to produce materials, systems, and/or devices. In this context, the fabrication of micro/nanofibers has attracted huge interest. In particular, micro/nanofibers have different properties such as high porosity, small pore size, high surface area, and compatibility with functionalizing additives that enables their use in multiple applications. These include their use as enzyme carriers, membranes for filtration purposes [1], as barriers to liquid penetration [2], sensors [3], delivery purposes [4], and catalysts. Polymer fibers have also

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been explored in a large variety of medical applications such as tissue engineering [5] or in regenerative medicine [6].

In this chapter, we will provide an overview of the most extended fabrication approaches and their use in medical applications, in particular to prevent microbial contamination [7]. Moreover, as reported by Kenawy et al. [8], the fabrication of fibers treated with antimicrobials is today a standard finish for many different textile products employed in such uses as medical, institutional, and hygienic. More recently, antimicrobial fibers have been extended to other applications including women's wear, sportswear, and aesthetic clothing to impart anti-odor or biostatic properties [9, 10].

7.2 Approaches for Fiber Fabrication

While it is true that there exist a large number of techniques to produce fibers with diameter sizes at the micrometer scale and below, herein we will limit our discussion to the most extended methodologies employed currently. Nanofibers from polymers have been for instance prepared using approaches based on the use of a particular template. In general, these are either aluminum oxide [11] or mesoporous silica [12]. However, one of the major drawbacks of these methodologies is related to the length of the fibers obtained with remains in the best case in millimeter range. In contrast to those methodologies, different "spinning" techniques that permit the fabrication of continuous fibers with submicron diameters have been developed [13]. As will be depicted later, this procedure requires the consideration of the experimental conditions such as solution viscosity or the solution conductivity and electric-field intensity when applying an electric current to generate the fibers.

7.2.1 Melt, Solution, and Emulsion Spinning

Spinning approaches refer to those fiber fabrication techniques based on extrusion of a polymer (dissolved, melted, or in an elution) through a spinneret in a continuous mode thus allowing the production of single or, in most sophisticated setups, even multifilament materials. Within this spinning approach three alternatives have been explored for the fabrication of fibers depending on the mechanism of solidification of the extruded material [14].

Melt spinning (also found in literature as melt blowing) takes advantage of a temperature cooling to produce solid filaments. In order to allow the filament to cool, the spinneret to collector distance (TCDs) is relatively high. In melt spinning, a single filament is continuously wound onto a spool, where mechanical drawing of the solidified filament reduces the average fiber diameter. More importantly, several parameters have to be considered since they govern the mechanical properties of the resulting filaments. These include the temperature, the take-up speed, and the dray

ratio. Important advantages of this approach include their reproducibility that allows to prepare extremely long fibers or the no requirement of solvents or residues (to be removed during the fabrication process) that improve the safety during the fabrication [15].

The principle of *solution spinning* techniques relies on solvent vaporization during the drawing process of a fiber [14]. The fabrication of fibers using this methodology has been previously reported among others by Persano [15]. Solution spinning has been carried out using different alternatives such as gels spinning [16], liquid crystal spinning [17], or wet spinning [18]. Solution spinning allows in comparison with melt spinning the fabrication of fibers from thermally unstable polymers [15].

Three different variations of solution spinning have been described, i.e., wet, dry, and flash solution spinning depending on the strategy employed to remove the solvent. In wet spinning, the dissolved polymer thread passes through a coagulation bath that contains a solvent that: must be miscible with the spinning solvent and immiscible with the polymer in order to assist in fiber solidification. The dry spinning is, in comparison to wet spinning, much faster and the fiber solidification is produced by simple evaporation that could eventually be improved using gas-assisted drying around the extruded filament. The third alternative uses a difference in pressure in order to evaporate the solvent.

Finally, *emulsion spinning* has been mainly employed to produce fibers from those polymers that are either insoluble or do not melt [14]. As a result, this method is an interesting alternative to process inorganic materials [19], high melting point fluorocarbons [20], and flame-retardant formulations [21].

7.2.2 Electrospinning

Elecrospinning is today one of the most extended approaches to fabricate micro- and nanometer size fibers [22]. Electrospinning is however an old technique. It was first studied in detail by Zeleny [23] in 1914 on electrospraying and patented by Formhals in 1934 [24]. This technique uses electrostatic forces to produce fine fibers from polymer solutions or melts and the fibers thus produced have a thinner diameter (from nanometer to micrometer) and a larger surface area than those obtained from conventional spinning processes [22].

Two important advantages of using electrospinning include that the fiber formation can be carried out at room temperature and using atmosphere conditions. The setup of typical electrospinning equipment is depicted in Fig. 7.1. The standard setup consists of three major components, i.e., a high voltage power supply, a spinneret (e.g., a pipette tip) and a grounded collecting plate (usually a metal screen, plate, or rotating mandrel). Using these components, a high voltage source is applied to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated toward a collector of opposite polarity [25, 26].

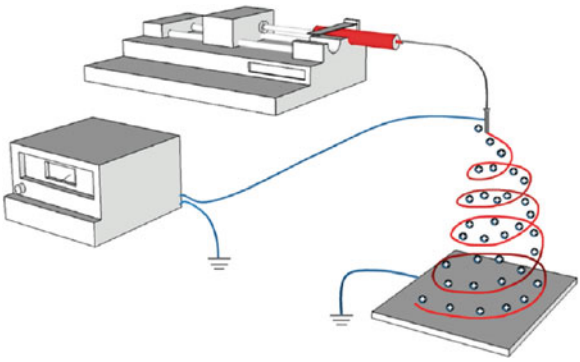

Fig. 7.1 Illustration of the electrospinning apparatus for the fabrication of fibers. Reproduced with permission from [27]

7.2.3 Melt Blowing

As has been depicted by Ellison et al. [28] during melt blowing, fibers are straightforwardly fabricated in a single step by extruding a polymer melt through an orifice die. The extruded polymer is then drawn down with a jet of hot air. This process does not require the use of solvents and has, therefore, important environmental advantages. This methodology was first developed in the 1950s at the Naval Research Laboratory with the goal of making submicron fibers to trap radioactive particles in the upper atmosphere [29]. Wente [30] first described the construction of a melt blowing die composed of a series of orifices and slots that enable the fabrication of superfine fibers. Later, the extension of this methodology at the commercial scale was carried out first by Exxon [29, 31] and later by a large number of companies including Vose, 3 M, Kimberly-Clark, Cummins, and Johns Manville that reported the use of this technology to fabricate commercial nonwoven products [29].

Today, a large number of polymers including poly(butylene terephthalate) (PBT) [32], poly(ethylene terephthalate) [33], polyethylene [30], polypropylene (PP) [33–35], poly(methyl methacrylate) [30], polyamides (e.g., nylon) [30, 36], and polystyrene (PS) [30] have been explored and successfully employed for producing blown fibers. In addition to the use of single polymers, this approach has been equally employed for the fabrication of bicomponent microfibers. For instance, Zhao et al. [33] investigated the fabrication of polypropylene (PP)/poly(ethylene terephthalate) (PET) bicomponent (bico) filaments by using the melt blowing (MB) process.

In Fig. 7.1 are summarized the most relevant technologies available for fiber manufacturing (Table 7.1).

7.3 Fibers Bearing Antimicrobial Molecules

The most extended strategy to fabricate fibers with antimicrobial properties involves the incorporation of antimicrobial molecules such as antibiotics within the fiber structure and their subsequent controlled release.

Table 7.1 Selection of fiber manufacturing processes and their advantages and disadvantages

	Fiber diameter	Advantages	Disadvantages
Melt electrospinning	<100 nm to 500 μm	Direct writing capability; solvent free; low cost; diameter is proportional to mass flow rate	Low output: device is time consuming to build. Limited number of polymers tested. Polymers require some thermal stability
Solution electrospinning	<50 nm to 10 μm	Simple to establish; low cost; suitable for many polymers; submicron diameters readily attained	Low output; direct writing is difficult; significant solvent is generated
Melt spinning	1–500 μm	High output; very consistent production; can be used in weaving technologies; industrially successful	Requires drawing onto a spool. Variable diameters at high stretching; difficult to attain submicron diameter fibers; significant cost to establish
Solution spinning	1–200 μm	Can process thermally unstable polymers; diversity in the number of configurations (e.g., flash, liquid crystal, gel spinning); industrially successful	Solvent requires removal. Complex coagulation baths needed for wet spinning. Dry spinning requires significant solvent removal systems
Melt blowing	<500 nm to 10 μm	High output: industrially successful	High cost to establish, therefore to perform research; difficult to control fiber architecture

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One of the pioneer studies using this approach was reported by Bucheńska [37]. She employed polyamide fibers (PA6) as supports to carry out a graft polymerization of acrylic acid (AA). The resultant fibers, containing carboxylic groups in their structure, were additionally modified with three different biocides, i.e., penicillin, neomycin, and gentamycin to obtain antimicrobial fibers. The activity was tested against *S. aureus*, *E. coli*, and *P. aeruginosa*, and the modified fibers showed strong biocidal effects on the Gram-positive microorganism *S. aureus* and the Gram-negative *E. coli*. The author evidenced a long-term activity since the release of antibiotics into solution proceeds for quite a long time after which there is still enough antibiotic on the fibers to provide them with antibacterial properties.

Another illustrative example of a controlled-release mechanism in the fiber with broad-spectrum antimicrobial properties based on poly(vinyl alcohol) (PVA) was described by Vigo et al. [38] (Fig. 7.2). Its strategy involves the modification of the alcohol groups (provided by the poly(vinyl alcohol)) by reaction with 5-nitrofurylacrolein in the presence of an acid catalyst. The presence of moisture leads to the slow release of the nitro compound thus producing the expected antimicrobial activity.

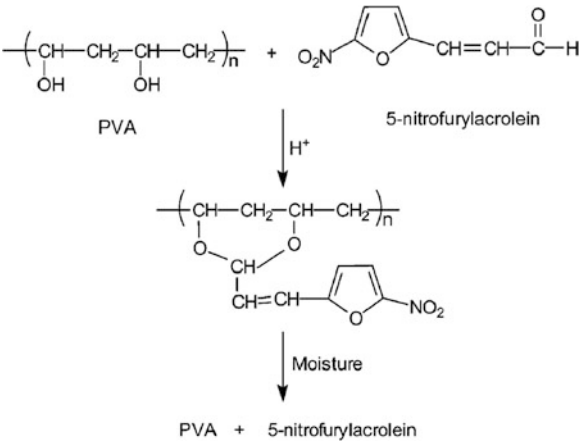

Fig. 7.2 Preparation of the broad-spectrum antimicrobial fiber based on PVA. Reproduced with permission from [8]

Another strategy has been reported recently by Ahire and Dicks [7] to prepare nanofibers containing 2,3-dihydroxybenzoic acid (DHBA). Electrospinning of DHBA into a blend of poly(D,L-lactide) (PDLLA) and PEO (24 %; 50:50) produced nanofibers of 400–450 nm in diameter. The principle behind their approach is based on the idea that free iron enhances biofilm formation, delays wound healing, and may even be responsible for persistent inflammation. They employed *Pseudomonas aeruginosa* (that readily forms biofilms in wounds, which often leads to chronic infections that are difficult to treat with antibiotics) as a model bacteria to prove that the presence of DHBA which is an iron chelator is able to reduce the bacterial contamination. The authors demonstrated that exposure of *P. aeruginosa* Xen 5 DHBA, electrospun into a nanofiber blend of poly(D,L-lactide) (PDLLA), and poly(ethylene oxide) (PEO), referred to as DF, for 8 h decreased biofilm formation by approximately 75 %. Moreover, their findings indicated that DHBA electrospun into nanofibers inhibits cell growth for at least 4 h, which is equivalent to the time required for all DHBA to diffuse from DF. This is the first indication that DF can be developed into a wound dressing to treat topical infections caused by *P. aeruginosa*.

Finally, instead of using chemical reactions or including the antimicrobial molecules within the precursor solution, Choi et al. [39] explored the possibility to incorporate antibiotics within the fiber structure by sorption. In particular they used two antibiotics, doxycycline (Doxy) and ciprofloxacin (Cipro), that were applied under a variety of conditions to wool and to hydrolyzed wool at 40 °C and nylon (used as a control). The authors evidenced that depending on the antibiotic employed the sorption process differs. As a result, Doxy was much higher in wool than in nylon, whereas sorption of Cipro was similar in both fibers. More interestingly, a drastic increase in sorption of antibiotics by hydrolyzed wool was observed and could be attributed to an increase in polar functional groups by peptide scission and in oxidized sulfur groups by cystine oxidation. As a result, both sorption and zone of inhibition (ZOI) values were improved by hydrolysis of wool. In particular, wool hydrolyzed for 20 or 40 min at 40 °C and dyed with Doxy at 45 °C for 3.5 h maintained around 30 mm of

ZOI after 24 h of challenge by a simulated flow of blood. Wool hydrolyzed for 60 min at 40 °C and dyed with Cipro at 45 °C for 3.5 h also maintained its antibiotic activity for an extended time.

7.4 Hybrid Organic–Inorganic Nanofibers with Antimicrobial Properties

The incorporation of inorganic nanoparticles or their precursors, well known for their excellent antimicrobial activity, is an alternative to provide antimicrobial properties to micro/nanofibers [40, 41].

In this context, several strategies have been employed. On the one hand, preformed nanoparticles have been incorporated in the solution prior to the fiber formation. For instance, one-dimensional polymer nanostructures have been employed as templates for the preparation of inorganic nanofibers with antimicrobial properties [42]. An example of this strategy was reported by Hwang et al. [43] that described the preparation of ZnO/TiO_2 composite nanofibers by electrospinning. As depicted in Fig. 7.3, the resulting nanofibers showed better antimicrobial activity against both Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* under UV irradiation than in the absence of light. Interestingly, the combination of both ZnO and TiO_2 within the same fibers produced the best results.

Instead of incorporating nanoparticles formed in a separate step, several groups designed strategies to form the nanoparticles within the solution employed for the fiber construction. This alternative was employed by Abdelgawad et al. [44] that designed a green route to produce antibacterial nanofiber mats loaded with silver nanoparticles (Ag-NPs, 25 nm diameter) (Fig. 7.4). The first step for the fabrication of nanofiber mats is the preparation of colloidal dispersions of chitosan-based Ag-NPs blended with polyvinyl alcohol. Aqueous PVA solution was mixed with chitosan-based Ag-NPs at various weight ratios and electrospinned. As a result, nanofibers (150 nm average diameter and narrow size distribution) were obtained and cross-linked with glutaraldehyde. According to their findings, these fibers showed superior antimicrobial properties as a result of the synergistic combination of chitosan and Ag-NPs.

Instead of incorporating already formed nanoparticles several groups used nanoparticle precursors to, once impregnated in the fibers, fabricate the nanoparticles in situ [45, 46]. For instance, Pant et al. [47] fabricated silver-impregnated TiO_2/nylon-6 nanocomposite mats exhibit excellent characteristics as a filter media with good photocatalytic and antibacterial properties and durability for repeated use. More precisely, the strategy depicted by Pant et al. involves the incorporation of silver nanoparticles (NPs) in electrospun TiO_2/nylon-6 composite nanofibers. The silver NPs were obtained through the photocatalytic reduction of silver nitrate solution under UV-light irradiation. TiO_2 NPs present in nylon-6 solution were able to cause the formation of a high aspect ratio spider-wave-like structure during

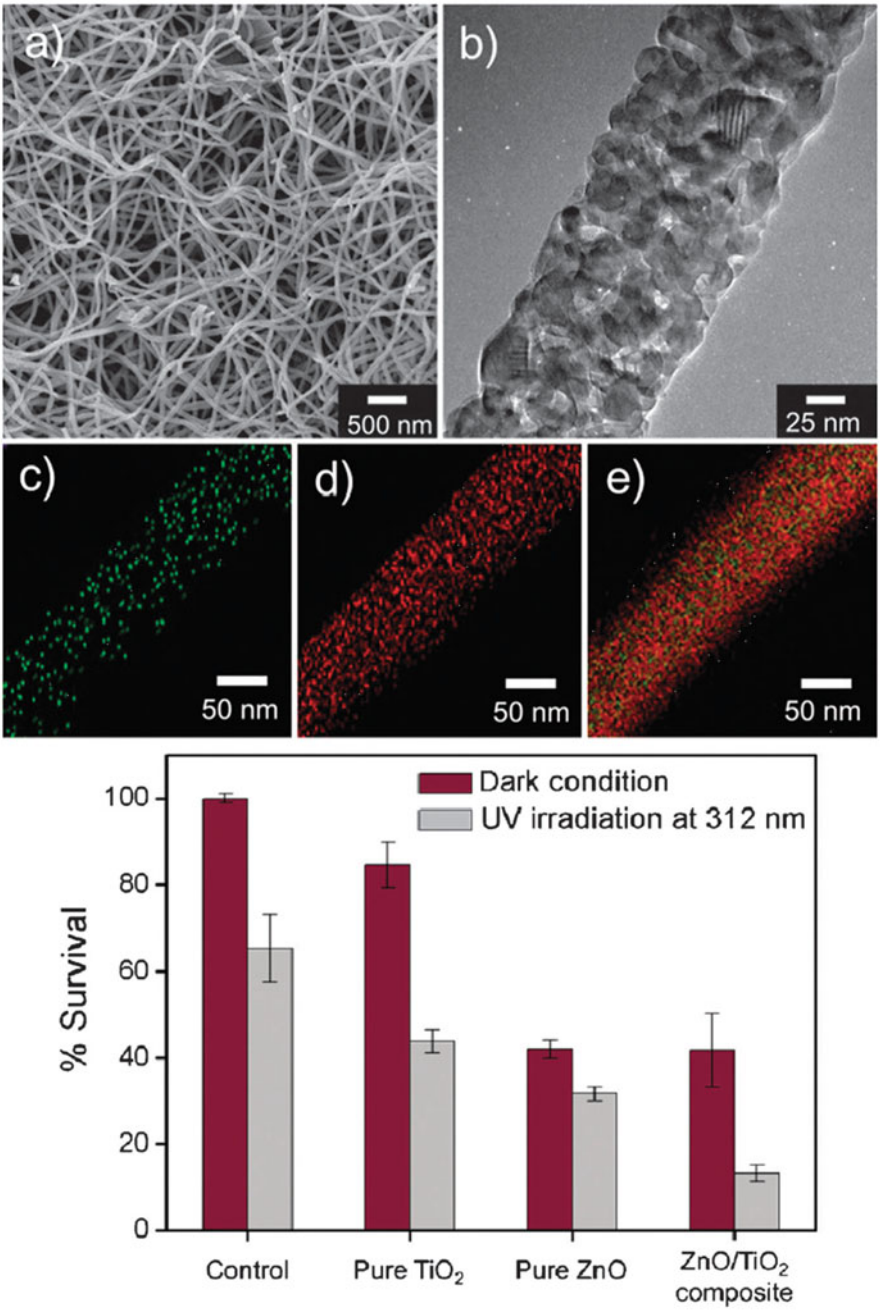

Fig. 7.3 *Above:* (**a**) FE-SEM and (**b**) TEM image of the fabricated ZnO/TiO_2 nanofibers. EDS mapping images of the composite nanofibers with (**c**) Zn element, (**d**) Ti element, and (**e**) Zn–Ti elements. *Below:* Graph of % survival of *S. aureus* after treatment with control, TiO_2 nanofibers, and ZnO/TiO_2 nanofibers in the absence and the presence of UV-light irradiation at 312 nm for 30 s. The number of bacterial colonies on the untreated Petri dish surface under the dark conditions was defined as 100 %. Reproduced with permission from [43]

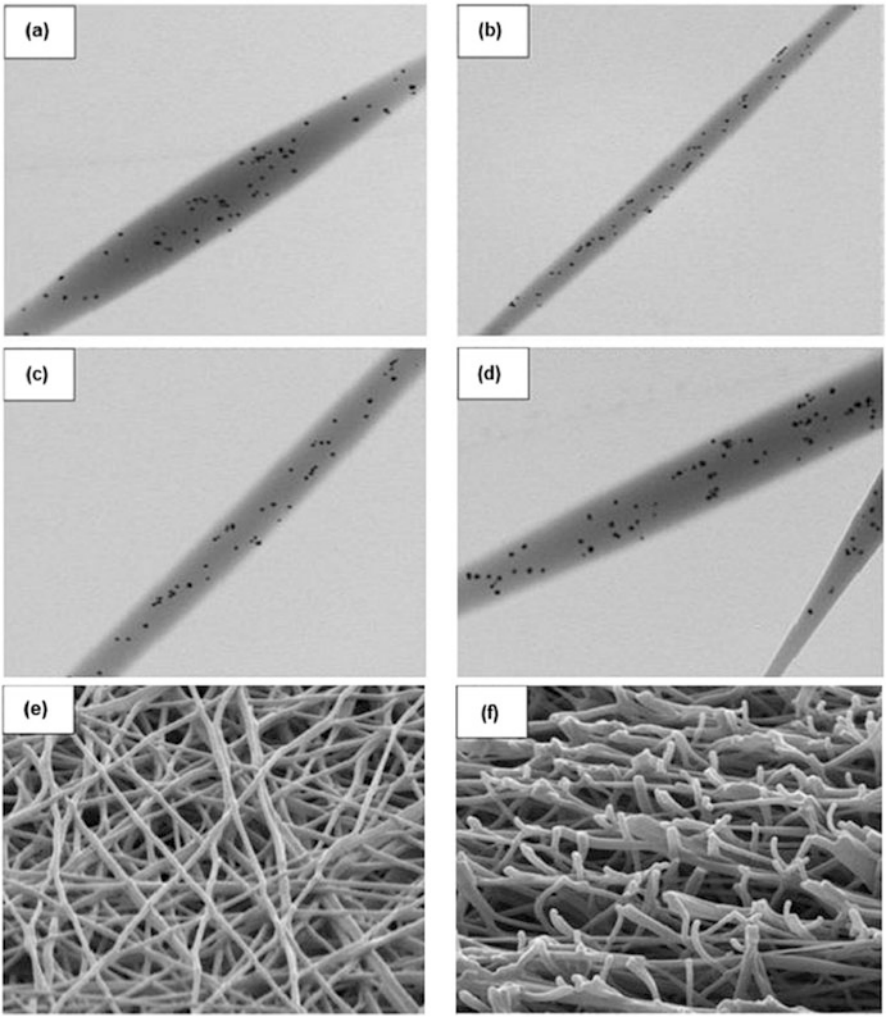

Fig. 7.4 TEM micrographs of e-spun fibers of 60/40 (weight ratio) PVA/CS-Ag-NPs, (**a**–**d**) micrographs show individual PVA/CS-Ag-NPs fibers loaded with Ag-NPs; (**e**) PVA/CSAg-NPs nanofiber mat top-view; and (**f**) cross-section of PVA/CS-Ag-NPs nanofiber mat. Reproduced with permission from [44]

electrospinning and facilitated the UV photoreduction of $AgNO_3$ to Ag. The antibacterial, efficacy tested against *Escherichia coli*, showed that TiO_2/nylon-6 nanocomposite mats loaded with Ag NPs are more effective than composite mats without Ag NPs.

A similar approach has been reported by Liu et al. [48] for the preparation of antimicrobial fibers. Their strategy involves three consecutive steps, i.e., prepolymerization, electrospinning, and finally photo-cross-linking process that leads

to water-stable cross-linked electrospun zwitterionic poly(sulfobetaine methacrylate) (PSBMA) fiber. The fibers were employed to construct a membrane that exhibited strong resistance to protein adsorption as well as cell attachment. Moreover, as depicted in Fig. 7.5, 3 h bacterial incubation results evidenced that the PSBMA electrospun membrane exhibited very little bacterial attachment for both P. aeruginosa and S. epidermidis in comparison with other electrospun fibers such as polycaprolactone (PCL) or using standard supports such as tissue culture polystyrene (TCPS) or glass. Equally, bacterial adhesion tests carried out during 24 h show that the PSBMA electrospun membranes still exhibited the lowest bacterial adhesion for both species. In addition to the antifouling properties observed in the PSBMA fibers, the authors explored the antimicrobial activity of the silver-incorporated electrospun PSBMA membrane. $AgNO_3$ was incorporated into the electrospun PSBMA membrane through ionic interactions and the antimicrobial activity of the Ag^+-impregnated membrane was determined using a zone-of-inhibition method. The authors found that the electrospun PSBMA membranes infused with silver nitrate inhibit the growth of both *P. aeruginosa* and *S. epidermidis*. The zone of inhibition was 6.3 mm for P. aeruginosa and 3.6 mm for S. epidermidis after 24 h of incubation. These membranes are promising materials among others for wound dressing purposes since they can prevent attachment and entry of the environmental pathogens to the wound. In addition to the protection capabilities, the dressing applied to the wound would not need an often replacement, which leaves less chance of introducing new bacteria with repeated exposure of the wound site to the environment.

Shi et al. [46] reported the synthesis in one-step approach of silver nanoparticle-filled nylon 6 nanofibers by electrospinning. They employed the electrospinning solvent (formic acid) as a reducing agent for in situ conversion of $AgNO_3$ into silver nanoparticles during the solution preparation. The resultant silver nanoparticle-filled nylon 6 hybrid nanofibers show a fibrous structure with diameter between 50 and 150 nm having narrow size 2–4 nm silver nanoparticles uniformly dispersed throughout the nylon 6 matrix. Interestingly, these silver nanoparticle filled nylon 6 nanofibers exhibit a steady and long-lasting silver ion release behavior, and robust antibacterial activity against both Gram-positive *B. cereus* and Gram-negative *E. coli* microorganisms.

Not only silver nanoparticles, also silver ions exhibited excellent antimicrobial properties when incorporated in nanofibers. An illustrative example of antimicrobial hybrid particles was reported by Bajpai et al. [49]. They focused on investigating the feasibility of using silver (I) ions loaded poly(acrylonitrile)-grafted silk fibers as antibacterial dressing material. The poly(acrylonitrile)-grafted silk fibers were loaded with silver(I) ions by equilibration method. The resulting fibers were investigated for their biocidal action against *E. coli*, by using zone inhibition and colonies counting method. The bacterial growth was suppressed to a great extent thus indicating that the fibers are very effective in killing bacterial cells.

Copper (II) oxide nanoparticles (CuO NPs) have also evidenced remarkable antimicrobial properties. Yalcinkaya et al. [50] employed these CuO NPs nanoparticles to test the antibacterial efficiency of nanofiber composite yarns. Instead of incorpo-

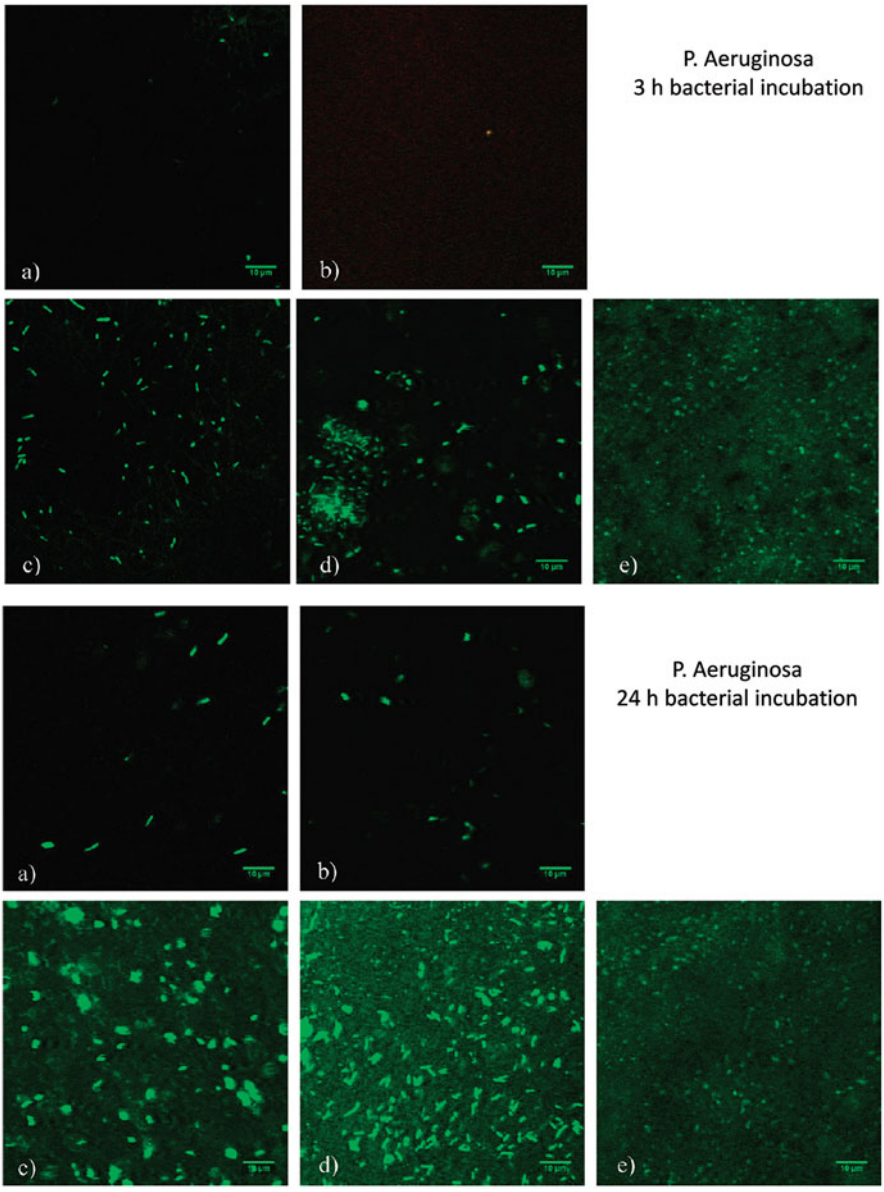

Fig. 7.5 Fluorescence microscopy images of *P. aeruginosa* attached onto electrospun PSBMA (**a**), PSBMA hydrogel (**b**), electrospun PCL (**c**), TCPS (**d**), and glass (**e**) at 3 and 24 h. Reproduced with permission from [48]

rating the NPs within the fibers, the resulting nanofibrous composite material combines the good mechanical properties of the core yarn with the high specific surface of the nanofiber shell to gain specific targeted qualities. Two polymers, polyvinyl butyral (PVB) and polyurethane (PU), were tested for the production of nanofiber composite yarns, and the antibacterial efficiency was evaluated against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus gallinarum* bacteria. According to the authors, PVB/nanofibers with a CuO antibacterial agent generally show significantly higher antibacterial efficiency compared to yarns covered with PU nanofibers. This can be directly related to the better uniformity of the antibacterial agent distribution caused by the reaction of CuO with acetic acid creating copper acetate.

7.5 Antibacterial Fibers with Covalently Bonded Biocides

While, as has been depicted above, most of the studies reported concern the release of a particular biocide to the environment, few works focused on the elaboration of "permanent" antimicrobial fibers by covalently immobilizing the biocide within the fiber structure. An interesting approach for the preparation of solvent-resistant antimicrobial fibers was described by Guo-Dong et al. [48]. The strategy reported is depicted in Fig. 7.6 and comprises a two-step synthetic approach by atom transfer radical polymerization (ATRP). The first step is the direct copolymerization of (2-dimethylamino)ethyl methacrylate) (DMAEMA) and glycidyl methacrylate (GMA) to fabricate an statistical copolymer poly[((2-dimethylamino)ethyl methacrylate)-co-(glycidyl methacrylate)] P(DMAEMA-c-GMA). This copolymer served as macroinitiator for the second polymerization step in which pentachlorophenyl acrylate (PPCPA) was employed as monomer to fabricate the second block. As a result, the authors fabricated a diblock copolymer having poly[((2-dimethylamino)

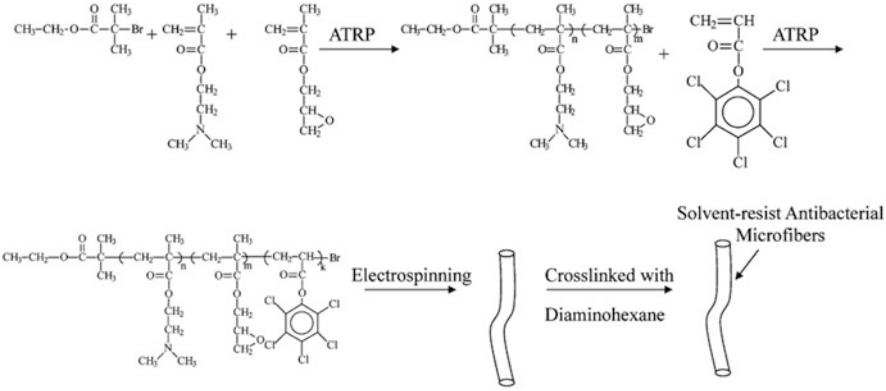

Fig. 7.6 Schematic illustration of the preparation of P(DMAEMA-c-GMA)-b-PPCPA microfibers via ATRP and electrospinning. Reproduced with permission from [48]

ethyl methacrylate)-co-(glycidyl methacrylate)] P(DMAEMA-c-GMA) block and a poly(pentachlorophenyl acrylate) (PPCPA) (P(DMAEMA-c-GMA)-b-PPCPA) block. Electrospinnning of P(DMAEMA-c-GMA)-b-PPCPA led microfibers with variable diameters 300 nm up to 1.3 μm. Taking advantage of the glycidyl groups, the authors improved the solvent stability the microfibers by reaction with 1,6-hexanediamine. In order to confer antimicrobial properties to these nanofibers, the authors carried out the modification of the tertiary amine groups of the P(DMAEMA-c-GMA) block and formation of quaternary ammonium salts (QASs). Upon evaluation of the antibacterial effect of the cross-linked microfibers against *E. coli* and *S. aureus* cultures, the authors concluded that 95 % *E. coli* and 97 % *S. aureus* were killed after 10 min contact with the P(DMAEMA-c-GMA)-b-PPCPA microfibers.

Another alternative explored involved the fabrication of fibers and their post-modification. For instance, Sun and coworkers attached *N*-halamine functional groups to cellulose to render textile materials biocidal [51, 52]. They fabricated a cyclic-amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) that could be grafted in the presence of acrylonitrile onto cotton cellulose. After chlorine bleach treatment, hydantoin units in the grafted copolymers were easily transformed into *N*-halamine structures. These grafted samples exhibited potent antibacterial activity against *Escherichia coli,* and the functional properties were shown to be durable and regenerable [51]. They extended this concept to other commercially available fibers such as Nomex®, Kevlar®, Kermel®, or PBI® [52]. The chemical structure of the different fibers employed and the strategy employed to modify them is depicted in Fig. 7.7.

7.6 Fibers with Responsive Antimicrobial Activity

The elaboration of antimicrobial systems able to act under particular environmental conditions has been intensively pursued during the last decade. As a result, different strategies mainly involving stimuli-responsive polymers have been reported. Among the most extended stimulus employed, pH [10] temperature [53] or photoinduced [54] changes will be considered in this section.

Ionic interactions were employed by Son et al. [10] in the finishing to produce antimicrobial fabrics. They utilize the ionic interactions between anionic carboxylic end groups of polyamides and cationic quaternary ammonium salts in the chemical finishing of nylon fabrics to achieve desired durable antimicrobial functions. They studied nylon 6.6 fabrics treated with 2 % on mass of fabric (omf) of each of the cetylpyridinium chloride (CPC) and benzyldimethylhexadecylammonium chloride (BDHAC), hexadecyltrimethylammonium bromide (HTAB), and dodecyltrimethylammonium bromide (DTAB) solutions. In particular, the pH of the finishing bath was very critical in affecting the ionic interactions, the effect on bacterial reduction and thus exhaustion of the salts on the fabrics. As depicted in the table below After ten Launder–Ometer washes, the fabrics treated under neutral and acidic conditions, specifically the BDHAC-treated ones, dramatically lost their

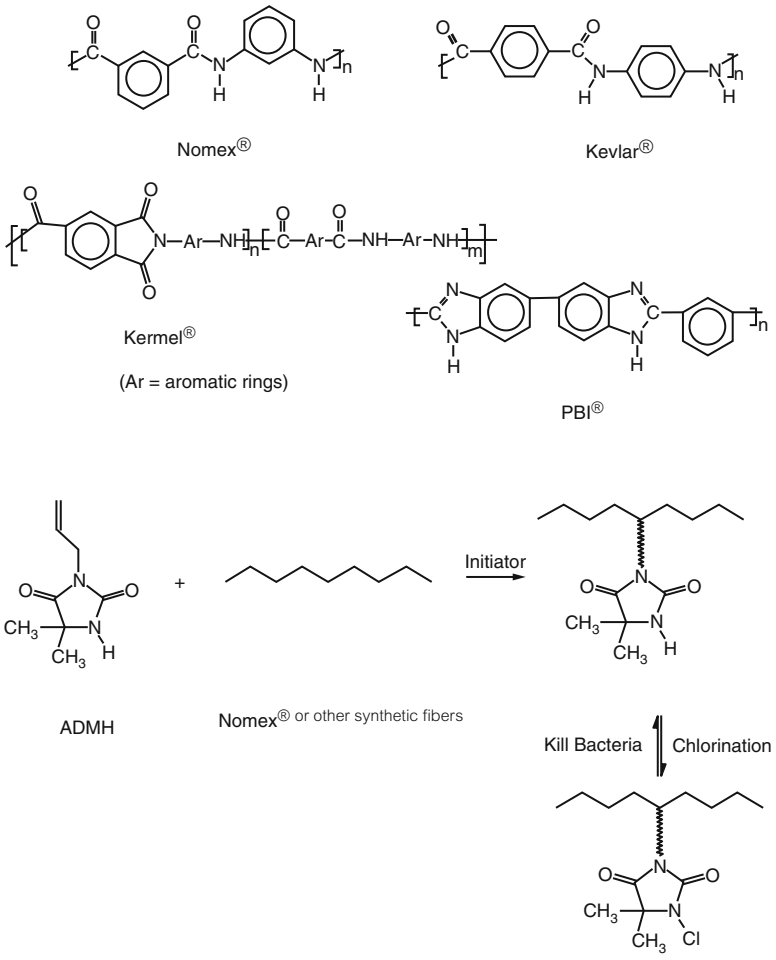

Fig. 7.7 *Above*: Chemical structures of the synthetic fibers. *Below*: ADMH grafting copolymerization and chlorination on the synthetic fibers. Reproduced with permission from [52]

biocidal properties. However, the finished products demonstrated excellent durability of antimicrobial functions at basic pH values (Table 7.2).

In addition to pH-sensitive antimicrobial fibers, temperature-responsive polymers have also been widely employed in the fabrication of antimicrobial fibers. Poly(*N*-isopropylacrylamide) is probably the most extensively employed thermoresponsive polymers with a phase transition at around 32 °C.

For instance, Liu et al. [53] studied the antibacterial activity of temperature-sensitive poly(*N*-isopropylacrylamide/polyurethane (PNIPAAm/PU) hydrogel grafted nonwoven fabrics with chitosan modification. They prepared series of temperature-sensitive hydrogel grafted nonwoven fabrics with different

Table 7.2 Effect of pH on bacterial reduction (%) to nylon 6.6. fabrics

	Bacterial reduction, *E. coli* (%)					
	CPC			BDHAC		
pH	1[a]	5	10	1	5	10
3.5	99.6	22.1	11.5	98.1	7.7	0
7	99.9	38.3	15.0	99.9	36.2	0
11	100	100	95.7	100	99.5	65.0

[a]After 1, 5, and 10 times Launder–Ometer washing; fabrics were treated with 2 % salt solution at 90 °C for 60 min; AATCC test method 100

N-isopropylacrylamide/polyurethane (NIPAAm/PU) feeding ratios. The resulting modified fibers were evaluated against *S. aureus* and *E. coli*. According to their findings, upon chitosan modification, the hydrogel grafted nonwoven cellulose fabrics demonstrate an antibacterial activity to *S. aureus* and *E. coli*, and the antibacterial efficiency is about 80 % within 1 h.

In another report, Chen et al. [55] fabricated chitosan wound dressings with temperature-responsive characteristics. Their strategy resort to the modification of polypropylene (PP) nonwoven fibers (NWF) by direct current pulsed oxygen plasma-induced grafting polymerization of acrylic acid (AAc). As a result, the hydrophilicity was improved due to the presence of carboxylic acid groups. These carboxylic acid groups were then employed to conjugate chitosan and poly(*N*-isopropylacrylamide) (PNIPAAm) using water-soluble carbodiimide as a coupling agent. The potential of these NWFs as wound dressings were evaluated using SD rat as the animal model. The authors evidenced that NWFs contained PNIPAAm were better than those contained only chitosan in wound-healing rates and the wound areas covered by PP-g-chitosan-g-PNIPAAm wound dressings healed completely in 17 days.

In those previous mentioned examples, the thermoresponsive characteristics of the polymer did not play any significant role. Some other approaches take advantage of the thermoresponsive PNIPAAm polymers to control the loading [56] or delivery [57] process of antimicrobial agents. An illustrative example was reported by Bajpai et al. [56] that employed the temperature induced alteration of the PNIPA swelling fabrics to induce the entrapment of silver nitrate [56, 57] (Fig. 7.8). In the first step, PNIPAAm fabrics are cooled below LCST allowed aqueous solution of silver ions to enter the swollen polymer network. Increasing the temperature forces entrapped water out of the matrix thus leaving only silver ions inside. These ions can be reduced to silver nanoparticles (AgNPs) using sodium borohydrate. Bajpai et al. [56] described the fabrication of modified cellulose fibers with PNIPAAm network produced in situ by photopolymerization using UV-radiation. Upon silver entrapment and nanoparticle formation the antimicrobial efficacy of the AgNP–PNIPAAm composites were evaluated against both Gram-positive and Gram-negative bacteria. The leaching of silver ions resulted in a clear zone of inhibition in the vicinity of the samples for both *E. coli* and *S. aureus* that depends on the amount of silver ions incorporated within the hydrogel (Fig. 7.9).

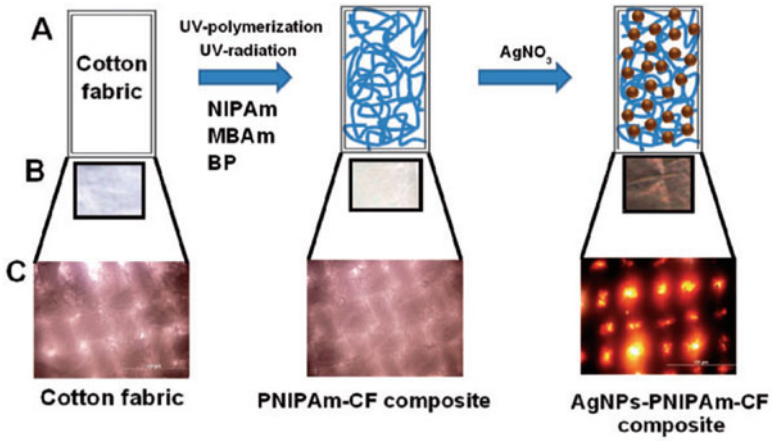

Fig. 7.8 Preparation of AgNPs loaded poly(*N*-isopropyl acrylamide) CF (AgNPs–PNIPAAm-CF) composite: (**a**) schematic representation of AgNPs–PNIPAAm-CF composite preparative route in two steps. Step 1 UV-radiation/photopolymerization of NIPAAm monomer in the presence of cross-linker and initiator on CF and Step 2 Silver nitrate entrapment using thermosensitive property of PNIPAAm and reduced with sodium borohydrate to embedded AgNPs on the CF via PNIPAAm chain attachment. (**b** and **c**) Photographs and optical microscope images of CF, PNIPAAm-CF composite, and AgNPs–PNIPAAm-CF composite, respectively. *AgNP* silver nanoparticle, *PNIPAAm* poly(*N*-isopropyl acrylamide), *CF* cotton fabric. Reproduced with permission from [56]

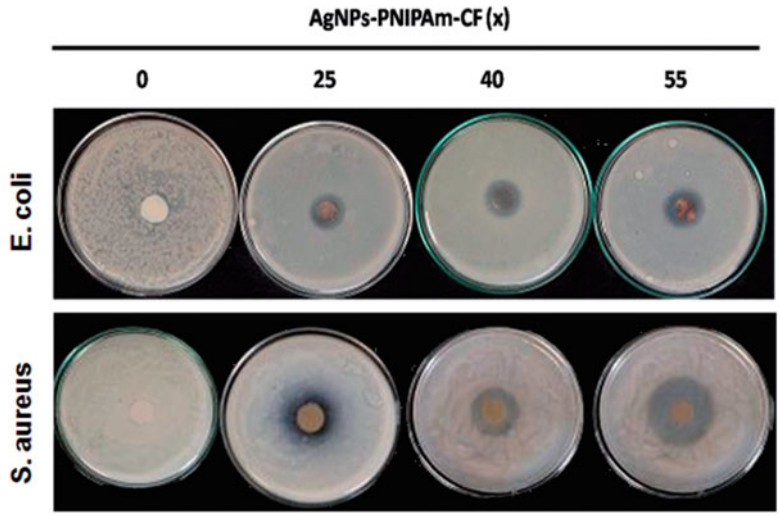

Fig. 7.9 Antibacterial activity of AgNPs–PNIPAAm-CF composites against *E. coli*. *AgNP* silver nanoparticle, *PNIPAAm* poly(*N*-isopropyl acrylamide), *CF* cotton fabric. Reproduced with permission from [56]

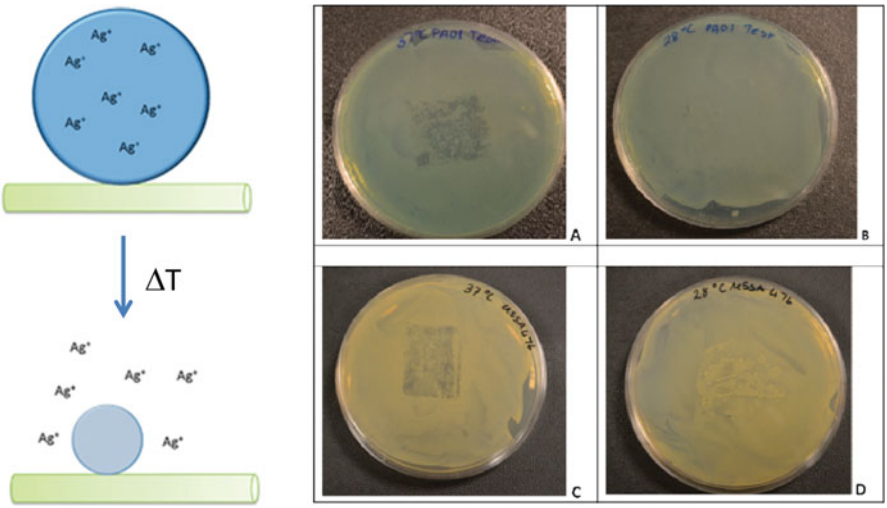

Fig. 7.10 Bacterial lawns of *P. aeruginosa* grown with silver nano-gel containing fabric at 37 °C (**a**) and 28 °C (**b**). *S. aureus* at 37 °C (**c**) and 28 °C (**d**). Reproduced with permission from [57]

Instead of using the changes induced by temperature to encapsulate the biocide, James et al. [57] fabricated nano-gels able to release the biocide at a particular range of temperatures. In their strategy, thermally responsive poly(*N*-isopropylacrylamide)-co-allylamine (PNIPAAm-co-ALA) nano-gels were synthesized and grafted onto nonwoven polypropylene (PP). The grafting process employed plasma reactions in the presence of maleic anhydride to functionalize the PP fibers. Immediately following formation of the maleic anhydride film (pp-MA) on fabric/polystyrene, the PNIPAM-ALA nano-gels containing silver nitrate were grafted to the pp-MA via amine nucleophilic attack from the ALA to the anhydride group on the film, forming amide linkages. Silver nitrate was incorporated into the nano-gels in their expanded state. The bacterial growth was measured before and after the lower critical solution temperature in order to evidence the role of the silver release on the antibacterial properties. As depicted in Fig. 7.10, below the LCST, the bacteria are able to grow while above the LCST bacterial growth was prevented or retarded.

Finally, several groups have been developed systems in which the antibacterial activity of the polymer fibers is regulated by the presence of UV-light [54]. It is well known that TiO_2 and ZnO nanoparticles [58–62] can effectively generate reactive oxygen species (ROS) on polymer surfaces under ultraviolet (UV) or day light exposure. The generated ROS can, in turn, provide light-induced antimicrobial properties employed in some cases to elaborate self-cleaning surfaces.

However, the presence of nanoparticles and the eventual possibility to come off from the surfaces of fibers and penetrate through skin and enter into the human body has raised several issues related to human safety. As an alternative to inorganic nanoparticles, different photoactive chemicals such as benzophenone derivatives have been incorporated onto cotton fabrics. These photoactive compounds can also

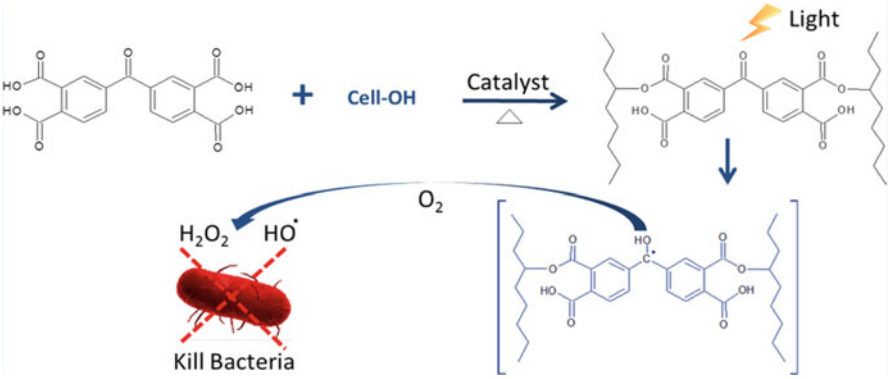

Fig. 7.11 Cross-linking reaction between cellulose and BPTCA and antibacterial activity in the presence of light. Reproduced with permission from [68]

generate ROS under UV irradiation, providing the fabrics with antibacterial activity [63]. The photoactive chemicals reported include porphyrin [64] and triazinyl porphyrin based [65], anthraquinone [66] and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BPTCD). For instance, the latter has been proven to be effective as a light-induced antimicrobial agent on cotton fabrics [67].

In a recent report, Hou et al. [68] investigated the photoactive functions of benzophenone tetracarboxylic acid (BPTCA) treated cotton fabrics and the mechanism of the light-induced mechanisms provided by the incorporated benzophenone group (Fig. 7.11). The generated ROS, including hydroxyl radical and hydrogen peroxide, by the fabrics were measured. More interestingly, the modified fibers exhibited excellent antimicrobial activities against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria strains. These results indicate that the photoactive compound, BPTCA, a derivative of benzophenone, retains its photoactive property even after being covalently incorporated to cellulose.

7.7 Biodegradable Fibers with Antimicrobial Properties

Biodegradable fibers with diameters ranging from several micrometers down to tens of nanometers have found an increasing interest as a soft porous scaffold for tissue regeneration and wound-healing applications. However, eventual infection control and tissue repair involve an inevitable dynamic interaction of the fibrous mat with the wound environment including bacteria. In order to prevent bacterial contamination and biofilm formation, several studies involved the use of biodegradable polymers for the fabrication of fibers incorporating different biocides.

Poly (lactide-co-glycolide) (PLGA), an FDA-approved biocompatible copolymer, chitosan, and poly(vinyl alcohol) (PVA) are the most extended biodegradable polymers employed for the fabrication of fibers.

For instance, Said et al. [69, 70] prepared fusidic acid (bacteriostatic antibiotic)-loaded ultrafine PLGA fibers for wound-healing applications. Degradation of PLGA within bacterial culture allows for the release of fusidic acid. As a result, an increase in the bacterial colonization within a wound increased the PLGA degradation and, in turn, the antibiotic release. Furthermore, Said et al. showed effective wound healing in an animal model of fusidic acid-loaded ultrafine PLGA fibers. This study demonstrated early and persistent bacteria eradication in wounds heavily infected with *S. aureus* and wounds lightly infected with native skin flora when treated with fusidic acid-loaded fibers.

In addition to PLGA, also fibers constructed from chitosan have been explored as antimicrobial scaffolds [41]. Chitosan well known as a sustainable, biocompatible, biodegradable, antimicrobial, and nontoxic polysaccharide has been employed in many fields of application. Due to its abundance in nature and biocompatibility, the cationic polysaccharide chitosan is an excellent candidate to fabricate functional nanofibers. Moreover, chitosan has shown excellent antibacterial and antifungal activities and inhibits the growth of different bacteria, algae, and fungi [41].

Chitosan nanofibers have been employed as support for other biocides or combined with other polymers in which the antimicrobial activity is provided by the chitosan. Pure chitosan electrospun nanofibers have employed as carriers of model drugs such as potassium 5-nitro-8-quinolinolate [71] or by incorporation of biocide silver nanoparticles which are at a later stage released into the solution [72].

Other authors fabricated fibers from blends of chitosan with polymers, such as poly(vinyl pyrrolidone) (PVP) [73, 74], polyurethane (PU), or poly(vinyl alcohol) (PVA) [75] and evaluated the biocide properties of the electrospun fibers. In these cases, the polycationic nature of chitosan establishes electrostatic interactions with the negatively charged residues of the macromolecules at the cell membrane surface, resulting in the death of bacteria and fungi.

For instance, nanofibers containing quaternized chitosan (QCh) have been successfully prepared by electrospinning of QCh solutions mixed with poly(vinyl alcohol) (PVA) [75]. The average fiber diameter is in the range of 60–200 nm. UV irradiation of the composite electrospun nanofibrous mats containing triethylene glycol diacrylate as cross-linking agent has resulted in stabilizing of the nanofibers against disintegration in water or water vapors. Microbiological screening has demonstrated the antibacterial activity of the photo-cross-linked electrospun mats against *Staphylococcus aureus* and *Escherichia coli*. The obtained nanofibrous electrospun mats are promising for wound-healing applications.

Finally, also polyurethane–chitosan blended polymer was used by Shih et al. [76] to improve shrinkage and antimicrobial properties of woolen fabrics. The strategy involves, first the synthesis of polyurethane (PU) prepolymers from poly(ethylene glycol) (PEG) of different molecular weights. In the second step, the PU prepolymers were mixed with chitosan to form blended polymers. Shih et al. reported an improvement in both the shrink-proof and antimicrobial properties of the fabric with an increase in the temperature or duration of the heat treatment, as well as with an increase in the concentration of the processing agent.

7.8 Conclusions

This chapter describes the currently available strategies to fabricate micro- and nanometer size nanoparticles. Spinning techniques are among the most extended since permits the fabrication of continuous fibers from different polymers and blends. In particular, the possibility to incorporate biocide molecules or nanoparticles offers unique opportunities to produce fibers with antimicrobial properties. In this chapter, we summarized the alternatives reported to introduce antimicrobial moieties within fibers and the resulting activity against different bacterial strains.

More recently developed systems introduced the possibility to prepare active or nonactive antibacterial fibers that reversibly switch in response, for instance, to UV-light. Also nanofibers fabricated using pH or thermoresponsive polymers have been explored to direct the load and/or the release of the biocide in order to obtain materials able to precisely act in response to precise environmental changes.

Finally, some applications such as the use of fibers for wound dressing purposes require materials able to be reabsorbed. For this purpose, biodegradable polymers have been reported to be excellent candidates.

References

1. Sambaer W, Zatloukal M, Kimmer D. 3D modeling of filtration process via polyurethane nanofiber based nonwoven filters prepared by electrospinning process. Chem Eng Sci. 2011;66(4):613–23.
2. Lee S, Obendorf SK. Use of electrospun nanofiber web for protective textile materials as barriers to liquid penetration. Text Res J. 2007;77(9):696–702.
3. Jang B-H, Landau O, Choi S-J, Shin J, Rothschild A, Kim I-D. Selectivity enhancement of SnO_2 nanofiber gas sensors by functionalization with Pt nanocatalysts and manipulation of the operation temperature. Sensor Actuat B Chem. 2013;188:156–68.
4. Fathi-Azarbayjani A, Qun L, Chan YW, Chan SY. Novel vitamin and gold-loaded nanofiber facial mask for topical delivery. AAPS PharmSciTech. 2010;11(3):1164–70.
5. Vasita R, Katti DS. Nanofibers and their applications in tissue engineering. Int J Nanomed. 2006;1(1):15–30.
6. Zajicova A, Javorkova E, Trosan P, Krulova M, Holan V. Drug-loaded nanofiber scaffolds for a simultaneous delivery of stem cells and immunosuppressive drugs in cell-based therapy and regenerative medicine. J Tissue Eng Regen Med. 2014;8:277–8.
7. Ahire JJ, Dicks LMT. 2,3-Dihydroxybenzoic acid-containing nanofiber wound dressings inhibit biofilm formation by Pseudomonas aeruginosa. Antimicrob Agents Chemother. 2014;58(4):2098–104.
8. Kenawy E-R, Worley SD, Broughton R. The chemistry and applications of antimicrobial polymers: a state-of-the-art review. Biomacromolecules. 2007;8(5):1359–84.
9. Shin Y, Yoo DI, Jang J. Molecular weight effect on antimicrobial activity of chitosan treated cotton fabrics. J Appl Polym Sci. 2001;80(13):2495–501.
10. Son YA, Sun G. Durable antimicrobial nylon 66 fabrics: ionic interactions with quaternary ammonium salts. J Appl Polym Sci. 2003;90(8):2194–9.
11. Jang J, Lee KJ, Kim Y. Fabrication of polyimide nanotubes and carbon nanotubes containing magnetic iron oxide in confinement. Chem Commun. 2005;30:3847–9.

12. Ikegame M, Tajima K, Aida T. Template synthesis of polypyrrole nanofibers insulated within one-dimensional silicate channels: hexagonal versus lamellar for recombination of polarons into bipolarons. Angew Chem Int Ed Engl. 2003;42(19):2154–7.
13. Xie J, Li X, Xia Y. Putting electrospun nanofibers to work for biomedical research. Macromol Rapid Commun. 2008;29(22):1775–92.
14. Brown TD, Dalton PD, Hutmacher DW. Melt electrospinning today: an opportune time for an emerging polymer process. Prog Polym Sci. 2016;56:116.
15. Persano L, Camposeo A, Tekmen C, Pisignano D. Industrial upscaling of electrospinning and applications of polymer nanofibers: a review. Macromol Mater Eng. 2013;298(5):504–20.
16. Van Dingenen JLJ. Gel-spun high-performance polyethylene fibres. In: Hearle JWS, editor. High-performance fibres. Cambridge: Woodhead; 2001. p. 62–92.
17. Rey AD. Capillary models for liquid crystal fibers, membranes, films, and drops. Soft Matter. 2007;3(11):1349–68.
18. Hearle JWS, Woodings C. Fibres related to cellulose. In: Woodings C, editor. Regenerated cellulose fibres. Cambridge: Woodhead; 2001. p. 156–73.
19. Curran DJG. A method of making a composite ceramic fiber from pre-ceramic polymers. Google Patents; 1998.
20. Plunkett RJ. Tetrafluoroethylene polymers. Google Patents; 1941.
21. Tsuji T, Korematsu M. Highly flame-retardant shaped articles comprising a halogen containing polymer and polyvinyl alcohol. Google Patents; 1975.
22. Bhardwaj N, Kundu SC. Electrospinning: a fascinating fiber fabrication technique. Biotechnol Adv. 2010;28(3):325–47.
23. Zeleny J. The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces. Phys Rev. 1914;3(2):69–91.
24. Anton F. Process and apparatus for preparing artificial threads. Google Patents; 1934.
25. Sill TJ, von Recum HA. Electrospinning: applications in drug delivery and tissue engineering. Biomaterials. 2008;29(13):1989–2006.
26. Liang D, Hsiao BS, Chu B. Functional electrospun nanofibrous scaffolds for biomedical applications. Adv Drug Deliv Rev. 2007;59(14):1392–412.
27. Lalani R, Liu L. Electrospun zwitterionic poly(sulfobetaine methacrylate) for nonadherent, superabsorbent, and antimicrobial wound dressing applications. Biomacromolecules. 2012;13(6):1853–63.
28. Ellison CJ, Phatak A, Giles DW, Macosko CW, Bates FS. Melt blown nanofibers: fiber diameter distributions and onset of fiber breakup. Polymer. 2007;48(11):3306–16.
29. McCulloch WJG, Tappi T. The history of the development of melt blowing technology. In: Tappi Nonwovens Conference; 1999. p. 109–21.
30. Wente VA. Superfine thermoplastic fibers. Ind Eng Chem. 1956;48(8):1342–6.
31. Harding J, Keller J, Buntin R. Melt-blowing die for producing nonwoven mats. Google Patents; 1974.
32. Chen T, Li LQ, Huang XB. Fiber diameter of polybutylene terephthalate melt-blown nonwovens. J Appl Polym Sci. 2005;97(4):1750–2.
33. Zhao RG, Wadsworth LC. Attenuating PP/PET bicomponent melt blown microfibers. Polym Eng Sci. 2003;43(2):463–9.
34. Uyttendaele MAJ, Shambaugh RL. Melt blowing—general equation development and experimental verification. AIChE J. 1990;36(2):175–86.
35. Milligan MW, Haynes BD. Empirical models for melt blowing. J Appl Polym Sci. 1995;58(1):159–63.
36. Wang XM, Ke QF. Experimental investigation of adhesive meltblown web production using accessory air. Polym Eng Sci. 2006;46(1):1–7.
37. Buchenska J. Polyamide fibers (PA6) with antibacterial properties. J Appl Polym Sci. 1996;61(3):567–76.
38. Vigo TL. Advances in antimicrobial polymers and materials. In: Gebelein C, Carraher C, editors. Biotechnology and bioactive polymers. New York: Plenum Press; 1994. p. 225–37.

39. Choi HM, Bide M, Phaneuf M, Quist W, LoGerfo F. Dyeing of wool with antibiotics to develop novel infection resistance materials for extracorporeal end use. J Appl Polym Sci. 2004;92(5):3343–54.
40. Kriegel C, Kit KA, McClements DJ, Weiss J. Nanofibers as carrier systems for antimicrobial microemulsions. Part I: fabrication and characterization. Langmuir. 2009;25(2):1154–61.
41. Torres-Giner S, Ocio MJ, Lagaron JM. Development of active antimicrobial fiber based chitosan polysaccharide nanostructures using electrospinning. Eng Life Sci. 2008;8(3):303–14.
42. Wu J, Hou S, Ren D, Mather PT. Antimicrobial properties of nanostructured hydrogel webs containing silver. Biomacromolecules. 2009;10(9):2686–93.
43. Hwang SH, Song J, Jung Y, Kweon OY, Song H, Jang J. Electrospun ZnO/TiO_2 composite nanofibers as a bactericidal agent. Chem Commun. 2011;47(32):9164–6.
44. Abdelgawad AM, Hudson SM, Rojas OJ. Antimicrobial wound dressing nanofiber mats from multicomponent (chitosan/silver-NPs/polyvinyl alcohol) systems. Carbohydr Polym. 2014;100:166–78.
45. Saquing CD, Manasco JL, Khan SA. Electrospun nanoparticle-nanofiber composites via a one-step synthesis. Small. 2009;5(8):944–51.
46. Shi Q, Vitchuli N, Nowak J, Noar J, Caldwell JM, Breidt F, Bourham M, McCord M, Zhang X. One-step synthesis of silver nanoparticle-filled nylon 6 nanofibers and their antibacterial properties. J Mater Chem. 2011;21(28):10330–5.
47. Pant HR, Pandeya DR, Nam KT, Baek W-I, Hong ST, Kim HY. Photocatalytic and antibacterial properties of a TiO_2/nylon-6 electrospun nanocomposite mat containing silver nanoparticles. J Hazard Mater. 2011;189(1–2):465–71.
48. Guo-Dong F, Fang Y, Zhigang L, Xinsong L. Solvent-resistant antibacterial microfibers of self-quaternized block copolymers from atom transfer radical polymerization and electrospinning. J Mater Chem. 2008;18(8):859–67.
49. Bajpai SK, Chand N, Mary G. Preparation of poly(acrylonitrile)-grafted silk fibers with antibacterial properties. Fiber Polym. 2010;11(3):338–45.
50. Yalcinkaya F, Komarek M, Lubasova D, Sanetrnik F, Maryska J. Preparation of antibacterial nanofibre/nanoparticle covered composite yarns. J Nanomater. 2016, 7565972.
51. Sun YY, Sun G. Novel regenerable N-halamine polymeric biocides. II. Crafting hydantoin-containing monomers onto cotton cellulose. J Appl Polym Sci. 2001;81(3):617–24.
52. Sun YY, Sun G. Novel refreshable N-halamine polymeric biocides: grafting hydantoin-containing monomers onto high performance fibers by a continuous process. J Appl Polym Sci. 2003;88(4):1032–9.
53. Liu B, Hu J, Meng Q. Nonwoven supported temperature-sensitive poly(N-isopropylacrylamide)/polyurethane copolymer hydrogel with antibacterial activity. J Biomed Mater Res Part B Appl Biomater. 2009;89B(1):1–8.
54. Sun G, Hong KH. Photo-induced antimicrobial and decontaminating agents: recent progresses in polymer and textile applications. Text Res J. 2013;83(5):532–42.
55. Chen J-P, Kuo C-Y, Lee W-L. Thermo-responsive wound dressings by grafting chitosan and poly(N-isopropylacrylamide) to plasma-induced graft polymerization modified non-woven fabrics. Appl Surf Sci. 2012;262:95–101.
56. Bajpai SK, Bajpai M, Sharma L, Yallapu MM. Silver nanoparticles loaded thermosensitive cotton fabric for antibacterial application. J Ind Text. 2014;44(1):58–69.
57. James C, Johnson AL, Jenkins ATA. Antimicrobial surface grafted thermally responsive PNIPAM-co-ALA nano-gels. Chem Commun. 2011;47(48):12777–9.
58. Wu D, Long M, Zhou J, Cai W, Zhu X, Chen C, Wu Y. Synthesis and characterization of self-cleaning cotton fabrics modified by TiO_2 through a facile approach. Surf Coating Technol. 2009;203(24):3728–33.
59. Hizal F, Zhuk I, Sukhishvili S, Busscher HJ, van der Mei HC, Choi C-H. Impact of 3D hierarchical nanostructures on the antibacterial efficacy of a bacteria-triggered self-defensive antibiotic coating. ACS Appl Mater Interfaces. 2015;7(36):20304–13.

60. Qi K, Wang X, Xin JH. Photocatalytic self-cleaning textiles based on nanocrystalline titanium dioxide. Text Res J. 2011;81(1):101–10.
61. Milowska K, Rybczynska A, Mosiolek J, Durdyn J, Szewczyk EM, Katir N, Brahmi Y, Majoral J-P, Bousmina M, Bryszewska M, El Kadib A. Biological activity of mesoporous dendrimer-coated titanium dioxide: insight on the role of the surface-interface composition and the framework crystallinity. ACS Appl Mater Interfaces. 2015;7(36):19994–20003.
62. Zhong Z, Xu Z, Sheng T, Yao J, Xing W, Wang Y. Unusual air filters with ultrahigh efficiency and antibacterial functionality enabled by ZnO nanorods. ACS Appl Mater Interfaces. 2015;7(38):21538–44.
63. Hong KH, Sun G. Antimicrobial and chemical detoxifying functions of cotton fabrics containing different benzophenone derivatives. Carbohydr Polym. 2008;71(4):598–605.
64. Feese E, Sadeghifar H, Gracz HS, Argyropoulos DS, Ghiladi RA. Photobactericidal porphyrin-cellulose nanocrystals: synthesis, characterization, and antimicrobial properties. Biomacromolecules. 2011;12(10):3528–39.
65. Ringot C, Sol V, Barriere M, Saad N, Bressollier P, Granet R, Couleaud P, Frochot C, Krausz P. Triazinyl porphyrin-based photoactive cotton fabrics: preparation, characterization, and antibacterial activity. Biomacromolecules. 2011;12(5):1716–23.
66. Zhuo J, Sun G. Antimicrobial functions on cellulose materials introduced by anthraquinone vat dyes. ACS Appl Mater Interfaces. 2013;5(21):10830–5.
67. Hong KH, Sun G. Photoactive antibacterial cotton fabrics treated by 3,3′,4,4′-benzophenone-tetracarboxylic dianhydride. Carbohydr Polym. 2011;84(3):1027–32.
68. Hou A, Feng G, Zhuo J, Sun G. UV light-induced generation of reactive oxygen species and antimicrobial properties of cellulose fabric modified by 3,3′,4,4′-benzophenone tetracarboxylic acid. ACS Appl Mater Interfaces. 2015;7(50):27918–24.
69. Said SS, El-Halfawy OM, El-Gowelli HM, Aloufy AK, Boraei NA, El-Khordagui LK. Bioburden-responsive antimicrobial PLGA ultrafine fibers for wound healing. Eur J Pharm Biopharm. 2012;80(1):85–94.
70. Said SS, Aloufy AK, El-Halfawy OM, Boraei NA, El-Khordagui LK. Antimicrobial PLGA ultrafine fibers: interaction with wound bacteria. Eur J Pharm Biopharm. 2011;79(1):108–18.
71. Spasova M, Manolova N, Paneva D, Rashkov I. Preparation of chitosan-containing nanofibres by electrospinning of chitosan/poly(ethylene oxide) blend solutions. E-Polymers. 2004;56:1–12.
72. Qin YM, Zhu CJ, Chen J, Chen YZ, Zhang C. The absorption and release of silver and zinc ions by chitosan fibers. J Appl Polym Sci. 2006;101(1):766–71.
73. Yeh JT, Chen CL, Huang KS, Nien YH, Chen JL, Huang PZ. Synthesis, characterization, and application of PVP/chitosan blended polymers. J Appl Polym Sci. 2006;101(2):885–91.
74. Ignatova M, Manolova N, Rashkov I. Novel antibacterial fibers of quaternized chitosan and poly(vinyl pyrrolidone) prepared by electrospinning. Eur Polym J. 2007;43(4):1112–22.
75. Ignatova M, Starbova K, Markova N, Manolova N, Rashkov I. Electrospun nano-fibre mats with antibacterial properties from quaternised chitosan and poly(vinyl alcohol). Carbohydr Res. 2006;341(12):2098–107.
76. Shih CY, Huang KS. Synthesis of a polyurethane-chitosan blended polymer and a compound process for shrink-proof and antimicrobial woolen fabrics. J Appl Polym Sci. 2003;88(9):2356–63.