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ANTIBACTERIAL COATING OF FABRICS WITH NANOFIBERS

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IN
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BY

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Antibacterial Coating of Fabrics with Nanofibers

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Supervisor

Prof. Dr. Ali KİREÇCİ

by

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ABSTRACT

ANTIBACTERIAL COATING OF FABRICS WITH NANOFIBERS

ADEMOĞLU, Burcu
M. Sc. in Textile Engineering
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Textiles are in permanent contact with microorganisms, which can cause serious problems, including fabric rotting, staining, unpleasant odours and health concerns ranging from simple discomfort to physical irritation, allergic sensitization, toxic responses, infection and disease. Therefore, the control of undesirable effects of microbes on textiles is becoming an important issue in textile industry. Consumers' attitude towards hygiene and active lifestyle has created a rapidly increasing market for antibacterial textiles, which in turn has stimulated intensive research and development. Various active agents such as silvernitrate, silver nanoparticles and irgasan are used to gain antibacterial properties to fabrics. In this study, nanofibers and nanoparticles were physically bonded to the fabric surface by electrospin and electrospray coating processes. The nanofiber layer coated on fabric surface is invisible thin layer and it gives antibacterial property to the fabric. This method is more economical and ecological due to the less raw material usage and environmental friendly process (no air or water pollution). The results show that the treated fabrics, may have antibacterial activity even after several washing cycles. Electron microscopy was used to observe the antibacterial agents on the fabrics before and after washing process.

Key Words: nanofiber, electrospinning, electrospraying, antibacterial agent, washing resistance.

ÖZET

KUMAŞLARIN ANTİBAKTERİYEL NANOLİFLERLE KAPLANMASI

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Mikroorganizmalar ile sürekli temas halinde olan tekstil ürünleri, çürüyen kumaş, fiziksel tahriş, alerjik duyarlılık, toksik tepkiler, enfeksiyon, hoş olmayan koku ve sağlık sorunları gibi ciddi sorunlara neden olabilir. Bu nedenle, tekstilde mikropların istenmeyen etkilerinin kontrolü tekstil sektöründe önemli bir konu haline gelmekte ve tüketicilerin hijyen ve aktif yaşam tarzına olan tutumu yoğun araştırma ve gelişime teşvik ederek antibakteriyel tekstil için hızla artan bir pazar oluşturulmuştur. Antibakteriyel özellik sağlamak için gümüş, gümüş nano partiküller ve ırgasan gibi çeşitli aktif ajanlar kullanılmaktadır. Bu çalışmada, çeşitli antibakteriyel ajanların nanolif polimer çözeltilerine katılarak, elektrospin ve elektrospray yöntemiyle üretilen nanoliflerin ve nano partiküllerin, kumaş yüzeyine bağlanması amaçlanmıştır. Kumaş yüzeyini kaplayan nanolif tabakası çıplak gözle görülmeyecek kadar ince olup, kumaşlara antibakteriyel özellik kazandırmıştır. Klasik metotlara göre, bu yöntemle hammadde tasarrufu sağlanması, daha az çevre kirliliği ve kumaşların antibakteriyel özelliklerini yıkamalara karşı daha uzun süre muhafaza etmeleri amaçlanmıştır. Sonuçlar işlem görmüş kumaşların on yıkamaya kadar antibakteriyel özelliğe sahip olabileceğine göstermiştir. Yıkama öncesi ve sonrası kumaşların antibakteriyel ajanlarını gözlemlemek için elektron mikroskobu kullanılmıştır.

Anahtar Kelimeler: nanolif , elektrospinning, electrospraying antibakteriyel ajanlar, yıkama dayanımı.

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LIST OF ABREVIATIONS

$AgNO_3$	Silver nitrate
AgNp	Silver nanoparticle
CA	Cellulose acetate
CFU	Colony forming unit
CS	Chitosan
CuO	Copper oxide
DMF	Dimethylformamide
DBC	Dibutyryl chitin
E.Coli	Escherichia coli
MIC	Minimal Inhibitory Concentration
NSF	National Science Foundation
PA6	Polyamide 6
PAN	Polyacrylonitrile
PCL	Polycaprolactone
PLGA	Polylactidecoglycolide
PP	Poly propylene
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrolidone
PVC	Polyvinylchloride
QCS	Quaternized chitosan
QACs	Quaternary ammonium compounds
RR	Rib

SEM	Scanning electron microscopy
SF	Silk fibroin
S. Aureus	Staphylococcus aureus
ZnO	Zinc oxide

CHAPTER 1
INTRODUCTION

1.1. Introduction

Textiles have long been recognized as media to support the growth of microorganisms such as bacteria. These microorganisms are found almost everywhere in the environment and can multiply quickly when basic requirements, such as moisture, nutrients and temperature are met [1].

Most synthetic fibers, due to their high hydrophobicity, are more resistant to attacks by microorganisms than natural fibers. Chemically modify cotton to improve its resistance to rotting and improve other properties by acetylation of cotton. These treatments had limited industry acceptance because of relatively high cost and loss of fabric strength in processing. In addition, the growing use of man-made fibers such as nylon, acrylics and polyester which have inherent resistance to microbial decomposition came into wider use to replace cotton in many industrial fabrics [2]. Proteins in keratinous fibers and carbohydrates in cotton can act as nutrients and energy sources under certain conditions. Soil, dust and solutes from sweat and some textile finishes can also be nutrient sources for microorganisms. The growth of microorganisms on textiles inflicts a range of unwanted effects not only on the textile itself but also on the wearer. These effects include the generation of unpleasant odor, stains and discoloration in the fabric, a reduction in fabric mechanical strength and an increased likelihood of contamination. For these reasons, it is highly desirable that the growth of microbes on textiles be minimized during their use and storage. Consumers' demand for hygienic clothing and active wear has created a substantial market for antibacterial textile products. Estimations have shown that the production of antibacterial textiles was in the magnitude of 30,000 tones in Western Europe and 100,000 tones worldwide in 2000. Furthermore, it was estimated that the production increased by more than 15% a year in Western Europe between 2001 and 2005,

making it one of the fastest growing sectors of the textile market. Sportswear, socks, shoe linings and lingerie accounted for 85% of the total production. There is also a broader market for antibacterial fibers, for instance, in outdoor textiles, air filters, automotive textiles, domestic home furnishings and medical textiles [1].

1.2. Literature and Patent Reviews for Antibacterial Applications

The electrospinning process was employed by Xu and coworkers to prepare stabilized chitosan nanofibrous membrane as support for enzyme immobilization. Chitosan can provide an optimal micro environment for the immobilized enzyme to maintain relatively high biological activity and stability. CS (chitosan) nanofibrous membrane was directly fabricated from a mixed solution of CS with poly (vinyl alcohol) (PVA) and then treated in a NaOH solution to remove PVA and stabilize the morphologies of chitosan nanofibrous membrane in aqueous media [3].

Ignatova and coworkers proposes that the chitosan nanofibrous obtained by electrospun mats are promising for wound-healing applications as they could demonstrate the antibacterial activity of the photo-cross linked electrospun mats against Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli). The fibers were prepared by electrospinning of quaternized chitosan solutions mixed with poly (vinyl alcohol). Their group also prepared successfully nanofibers of the polyampholyte (N-carboxyethyl CS) by electrospinning adding a non-inorganic water-soluble polymer poly (acrylamide) to the spinning solution. The electrospun mats dissolved when put in contact with water or water vapor. To render the nanofibers insoluble, experiments on their cross-linking were performed by heat treatment. They could achieve the preparation of continuous defect-free fibers from quaternized CS (QCS) derivative by electrospinning of mixed aqueous solutions of QCS with poly(vinyl pyrolidone) (PVP). A scanning electronic microscopic study showed that electrospun CS fiber mats were indeed aligned and there was a slight crosslinking between the parent fibers. The electrospun mats have significantly higher elastic modulus (2.25MPa) than the cast films (1.19MPa). Viability of cells on electrospun chitosan mats indicated the potential to be processed into three dimensional scaffolds for cartilage tissue repair. In an interesting study based on cell

stain assay and SEM imaging, CS nanofibers produced by electrospinning were shown to exhibit cellular biocompatibility. It was found that the nanofibrous structure promoted the attachment of human osteoblasts and chondrocytes and maintained characteristic cell morphology and viability throughout the period of study. Bead formation was found to occur during electrospinning and could be controlled by controlling the molecular weight of CS and the solvent used for spinning [3].

Klossner et al. fabricated CS-based, defect-free nanofibers with average diameters ranging from 62 ± 9 nm to 129 ± 16 nm via electrospinning blended solutions of chitosan and polyethylene oxide PEO. They demonstrated using SEM imaging that as total polymer concentration (CS + PEO) increased, the number of beads decreased, and as CS concentration increased, fiber diameter decreased. As CS-PEO solutions phase separate over time, the solutions were stabilized using NaCl. They also showed that the degree of deacetylation was an extremely important parameter to consider when attempting to electrospun CS.

Subramanium et al. generated CS mat composed of oriented sub-micron fibers using the ectrospinning technique. Scanning electronic microscope images showed the fibers in the electrospun CS mats were indeed aligned and there was a slight cross-linking between the parent fibers. The electrospun mats have significantly higher elastic modulus (2.25 MPa) than the cast films (1.19 MPa). Viability of cells on the electrospun mat was 69% of the cells on tissue-culture polystyrene after three days in culture, which was slightly higher than that on the cast film [4].

Yao et al.and Yamamoto et al. has been reported recently electrospinning of chitosan solution. Both produced blend nanofiber of chitosan/poly(ethylenoxide) or poly(vinyl alcohol) from the chitosan solution mixed with PEO or PVA, the latter also reported that electrospinning of homogeneous chitosan nanofiber using trifluoroacetic acid/dichloromethane solvent, which requires additional extraction of the organic solvents. And it was also mentioned by the latter that chitosan solution dissolved in 0.2M acetic acid and its solvent mixtures with various volatile organic solvents or aprotic solvents cannot produce chitosan nanofiber via electrospinning. It is

considered that the surface tension depression produced by increasing acetic acid concentration in water is the most important solution factors in the electrospinning of chitosan [5].

Jing et al. and Youk et al. prepared nanofibers with AgNP's using dimethylformamide as the reducing agent. N,N-Dimethylacetamide (DMAc) was used as a reducing agent for the Ag+ ions in PLA solutions with ultrasonic treatment. The presence of AgNP's improves antibacterial activity significantly reduce the number of bacteria. Further, polymer nanofibers with AgNPs can be prepared using polymers with a strong interaction with AgNPs [6].

Wang et al. in omitted the precipitation stage with acetone. Their process was shorter and easier (three steps and 24 h of mixing), but because of presence of a high concentration of silver nitrate (437% on the basis of the polymer weight) in the electrospinning solution, this procedure may lead to in homogeneity in the distribution of AgNPs in the produced nanofibers. In addition, they showed that good antibacterial properties can be achieved with a very low concentration of silver ions. Youk et al. in 2005 also prepared Ag nanoparticles in situ in a PAN/DMF solution by using just DMF as the reducing agent. Their process was easy (two steps) but long (10 days) [7].

Spadaro et al. found that silver ion had a biocidal effect on as many as different kinds of bacteria, including Escherichia coli and Staphylococcus aureus. Feng et al. investigated the mechanism of the inhibition of silver ions on Gram-negative E. coli and Gram-positive S. aureus and showed that the interaction of Ag With thiol groups played an essential role in bacterial inactivation. In addition, AgNPs are small enough to pass through outer cell membranes and enter the cell's inner mechanism [8].

Son et al. prepared ultra-fine cellulose acetate (CA) fibers containing Ag nanoparticles by electrospinning a CA solution containing small amounts of silver nitrate ($AgNO_3$) and subsequent photo reduction. They revealed that very small amounts of $AgNO_3$ (>0.05 wt %) were needed to endow the ultra-fine CA fibers with

very strong antibacterial properties. It was also reported that poly (N-vinyl pyrrolidone) (PVP) containing Ag nanoparticles could be used to introduce Ag nanoparticles to other polymer nanofibers that are miscible with PVP. Poly (vinyl alcohol) (PVA) aqueous solutions with 5 % wt of the PVP containing Ag nanoparticles were successfully electrospun into PVA nanofibers containing Ag nanoparticles. In this study, antibacterial PVA nanofibers containing Ag nanoparticles were prepared by a simple heat treatment of electrospun PVA/$AgNO_3$ nanofiber webs for use in wound dressing applications, which has not been reported by other researchers. PVA has good hydrophilicity and biocompatibility. PVA is considered to be one of the best materials for the preparation of wound dressing nanofibers, because water can be used for its electrospinning. Furthermore, this process does not need any tedious processing such as precipitation– redissolution and long photo reduction [9].

Lin and Yang first reported the electrospinning of ultrafine polyacrylonitrile (PAN) fibers containing AgNPs. In their study, Lin and Yang prepared a PAN/silver nitrate ($AgNO_3$) solution in N, N-dimethyl formamide, reduced the Ag ions by adding hydrazine hydroxide, and then poured the solution into an excess of acetone to precipitate PAN protected AgNPs [10].

Xin et al. in addition, a coating of nanoparticles on fabrics will not affect physical and mechanical properties such as hand, strength, air permeability and wetting, considerably. The purposes of using nanotechnology in textile and apparel applications are low chemical usage; low energy costs. Thus, nanotechnology is today's most preferred solution for the textile industry because of the techno-economic advantages [11].

Yang et al. the average diameters of the PAN nanofibers and the Ag nanoparticles were 400 and 100 nm, respectively. Cellulose acetate (CA) nanofibers containing Ag nanoparticles were prepared by slow photo reduction of Ag+ ions within CA nanofibers for 20 days in a general laboratory environment, which can be used for antibacterial separation filters for submicron particles. In this study, for the commercial production of antibacterial separation filters, rapid photo reduction of

Ag+ ions within CA nanofibers were carried out by UV irradiation, and the photo reduction rate, distribution, and location of the resulting Ag nanoparticles were investigated. It is believed that the average size and location of the Ag nanoparticles have a great effect on the antibacterial activity of the CA nanofibers [12].

1.3. Objective of Thesis

The aim of the study is to produce durable antibacterial fabrics by coating the surface with a nanolayer which is not detectable to naked eyes and do not alter the properties of fabrics. Therefore, polyamide and polyacrilonitril polymer solutions with doped antibacterial agents were used to coat cotton fabrics by electrospin and electrospray techniques.

1.4. Structure of Thesis

The project is divided in five phases:

Chapter 2 is named as "Nanofiber". Nanotechnology in textiles is explained. The main purpose of this chapter is to give basic information about nanofibers. The term of nano is explained firstly. Then, nanofibers, production methods of nanofibers are mainly gives description about electrospin and electrospray process. Application areas of nanofibers are explained in detailed form.

Chapter 3 is named as "Antibacterial Textile, Finishing and Substances". This chapter gives detailed information about mechanism of antibacterial activity, antibacterial treatment and finishes, antibacterial finishing new and conventional methodologies, implications of antibacterial agents, quality control for antibacterial textiles.

Chapter 4, "Materials and Methods" includes the explanation of the apparatus and parts of the experimental set-up which were used in the experiments. The laboratory test equipments used in the characterization of nanofibers are presented and explained antibacterial test, laundering durability of antibacterial effect.

Experimental observations and results are given in Chapter 5 as “Results and Discussions”.

The conclusion of the thesis and recommendations for further studies are given in Chapter 6 as “Conclusions and Recommendations for Further Work”.

CHAPTER 2
NANOFIBER

2.1. Introduction

It is essential in the beginning of this study to firstly define what a ‘nanofiber’ is. To do so, we split the term into two parts, namely "nano" and "fiber. With the modern definition, we use "nano" to technically refer to physical quantities within the scale of a billionth of the reference unit - hence nanometer, nanosecond, nanogram and nanofarad for describing a billionth of a meter (length), second (time), gram (weight) and farad (charge) respectively. The latter term is more common. The term "fiber", or "fibre" in British English, comes from Latin "fibra". We define a "fiber" from a geometrical standpoint - a slender, elongated, threadlike object or structure [13].

2.2. Nanotechnology

The concept of nanotechnology is however not new, have been adopted by Taniguchi in 1974 when he defined the critical dimensions and tolerances be realized. Nanotechnology is part of the evolution of machining accuracy with no differences from traditional fields of science or engineering except in size [14].

Nanotechnology creates structures that have excellent properties by controlling atoms and molecules, functional materials, devices and systems on the nanometer scale by involving precise placement of individual atoms [15].

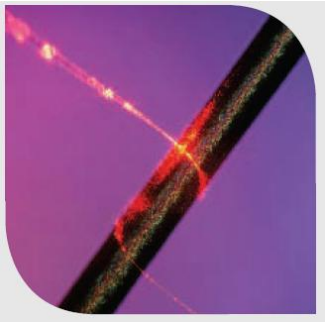


Figure 2.1.Human hair with nanofiber [15]

One nanometer (nm) is one thousandth of a micrometer (μm), one millionth of a millimeter (mm) and one billionth of a meter (m). To put the nanoscale into context: a strand of DNA is 2.5nm wide, a protein molecule is 5nm, a red blood cell 7,000 nm and a human hair is 80,000 nm wide (Figure 2.1). If one imagines that a nanometer is represented by a person, a red blood cell would be a massive 7 kilometers long [15].

Nano technology is an interdisciplinary science which takes role in the material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, textiles, optical coatings, photovoltaic, antibacterial agents, physics and biology [15]. Advantages of Nanotechnology;

i. Bottom-up, manufacturing approach-making materials and products from the bottom up, that is building them up from the atoms and molecules-would require less material and create less pollution [14].
ii. We could make very strong and very light materials according to the convenience [14].
iii. Energy-efficient, Molecular manufacturing can be energy-efficient because the key feature of its basis productive mechanisms-guiding the motion of the molecules using mechanical systems-impose no great energy cost. All a molecular the list beyond and on-almost any manufactured product could be vastly proved, often by orders of magnitude [14].
iv. Inexpensive-Molecular manufacturing will be inexpensive because it uses small amounts of material and energy and its costs of capital, land and labor will be low. The unique and new properties of nano-materials have attracted not only

scientists and researchers but also businesses, due to their huge economic potential [11].

2.3. Nanotechnology in Textiles

The technology can be used in engineering desired textile attributes, such as fabric softness, durability, and breathability and in developing advanced performance characteristics, namely, water repellency, fire retardancy, antibacterial resistance, etc. in fibers, yarns and fabrics.

Enhancement of textile materials by nanotechnology is expected to become a trillion dollar industry in the next decade, with tremendous technological, economic and ecologic benefits. Although, textile industry is a small part of the global research in the emerging areas of nanotechnology, the fibers and textiles industries in fact were the first to have successfully implemented these advances and demonstrated the applications of nanotechnology for consumer usage.

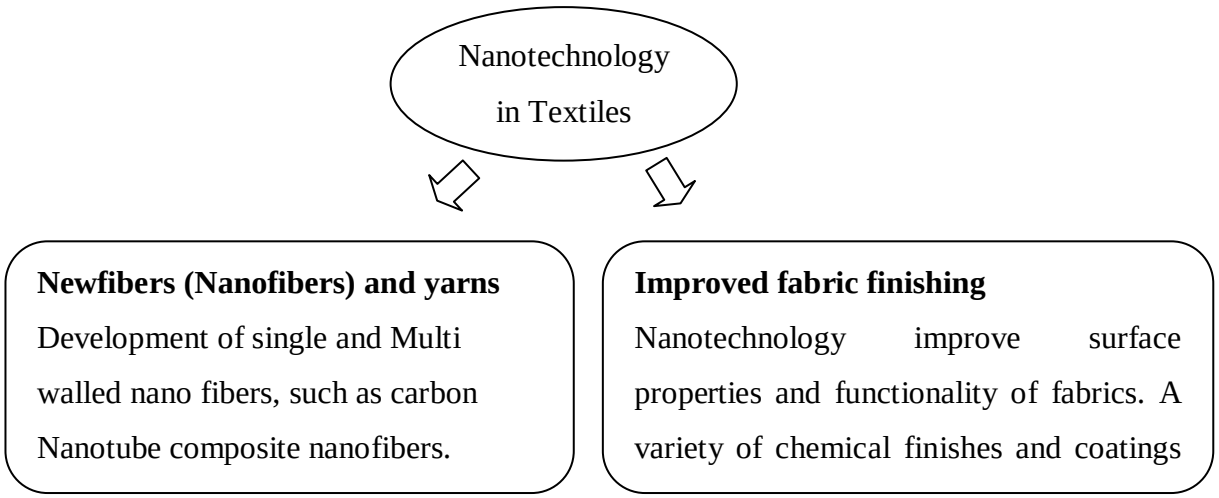


Figure 2.2.Nanotechnology in Fiber and Textile Manufacturing [16]

Nanotechnology in textiles have classified in two main areas of interest:

i. Applications of nanotechnology in fibers and yarn production and,
ii. Applications in fabric finishing. (Figure 2.2)

It is well known that the fabrics made of natural cotton fibers and those made of man-made synthetic fibers have their own advantages and limitations. For example, the cotton fabrics provide desirable comfort properties such as absorbency, breathability and softness. However, their applications often are limited due to their inferior strength, durability, crease resistance, dirt resistance, and flame resistance. Contrary to that, the fabrics made with synthetic fibers generally are very strong, crease resistant and dirt resistant, but they lack the comfort properties of cotton fabrics. The intention here is to demonstrate that the advancement of nanotechnology brings the possibility of developing next-generation cotton based fabrics that could complement the advantages of cotton and man-made fibers [16].

2.4. Nanofibers

Nanofibers are solid state linear nano materials which cannot be seen without visual amplification. Considering the potential opportunities, being produced with simple equipments and requiring low powers provided by nanofibers are increasing interests in nanofiber technology. With regard to fibers, "nano" refers to the diameter of the fiber. According to the National Science Foundation (NSF), nano materials are matters that have at least one dimension equal to or less than 100 nanometers. However some scientists accept the nanofibers as less than 1 micron, while others describe them as less than 100 nanometers [17]. Advantages of nanofibers;

i. Materials in fiber form are of great practical and fundamental importance. The combination of high specific surface area, flexibility and superior directional strength makes fiber a preferred material form for many applications ranging from clothing to reinforcements for aerospace structures [17].
ii. One of the main goals for nanofibers has been to produce the strength they should theoretically possess. In conventional fibers produced today, there are fairly defined limitations to the percentage of crystalline that can be obtained in a fiber/yarn form. For example, the actual thickness of a carbon/carbon bond is approximately 1 nm. If a 5-nm-diameter fiber is produced, the molecular chains are effectively forced to align in a highly crystalline manner. Ideally, the

resultant strength of the fiber produced will be determined by the strength of the carbon/carbon bond in the molecular chains of the polymer [17].

iii. Another potential benefit of nanofiber technology is the tremendous increase in surface-area-to-weight or -volume ratios. The lure of nanotechnology stems from the possibility of redefining these limitations. If the fibers can be collected individually and aligned to specific orientations, it is possible to increase the maximum volume fraction of fibers in a matrix, thus increasing the material's strength. The increased surface-area-to-weight ratio also will allow for improved bonding with the matrix to help prevent failure due to pullout of the fibers [13].

iv. For fibers having diameters from 5 to 1000 nanometers, as shown in Figure 2.3., the surface area per unit mass is around 10 to 1000 m^2 per kilogram. In nanofibers that are three nanometers in diameter, and which include approximately 40 molecules; about half of the molecules are on the surface.

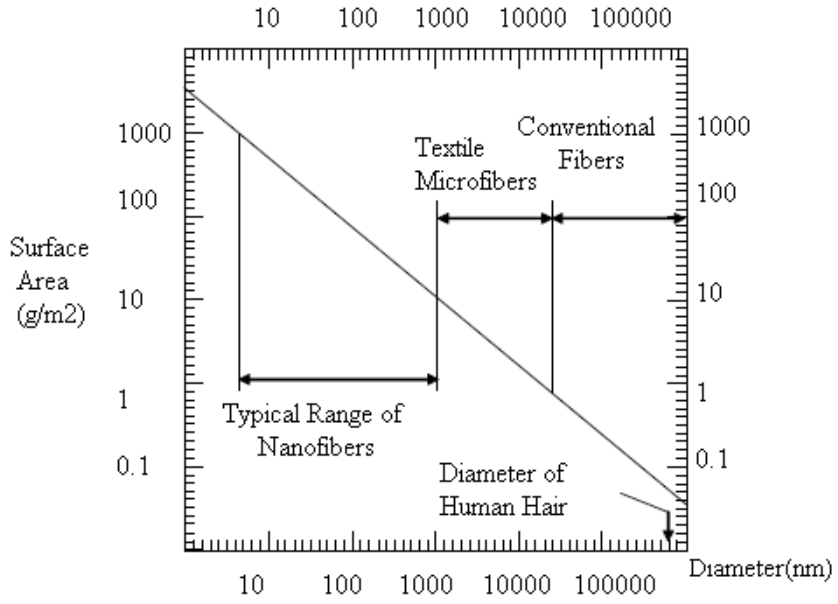


Figure 2.3.Effect of fiber diameter on surface area [18]

Other aspects of the nanofibres are given at below:

i. High performance in the filtration.

ii. In the properties of fabric performance such as water proofing, stain resistance, wrinkle resistance increase to great extent.

iii. The ability to control pore size.

iv. Good and soft handling.

2.5. Various Ways to Make Nanofibers

Polymeric nanofibers can be processed by a number of techniques such as drawing, template synthesis and electrospinning [13].

2.5.1. Drawing

Nanofibers have been fabricated with citrate molecules through the process of drawing. A micropipette with a diameter of a few micrometers was dipped into the droplet near the contact line using a micromanipulator. The micropipette was then withdrawn from the liquid and moved at a speed of approximately $1x10^{-4}ms^{-1}$, resulting in a nanofiber being pulled. The pulled fiber was deposited on the surface by touching it with the end of the micropipette (Figure 2.4.). The drawing of nanofibers was repeated several times on every droplet [13].

Drawing a fiber requires a viscous elastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pilling. The drawing process can be considered as dry spinning at a molecular level [13].

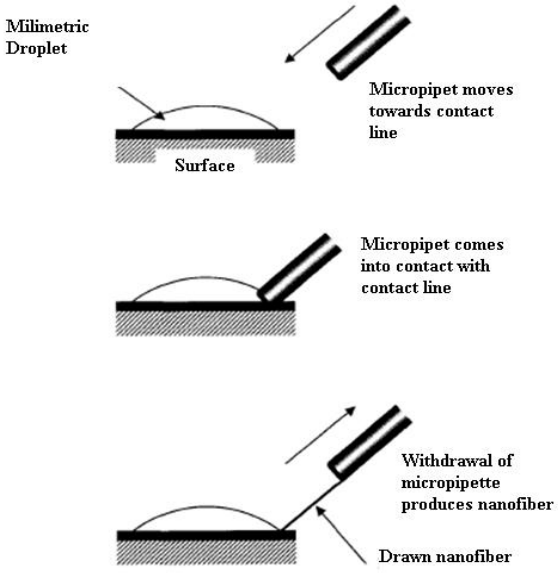


Figure 2.4.Obtaining nanofiber by drawing [13]

2.5.2. Template Synthesis

Template synthesis implies the use of a template or mold to obtain a desired material or structure (Figure 2.5). Under the application of water pressure on one side and restrain from the porous membrane causes extrusion of the polymer which, upon coming into contact with a solidifying solution, gives rise to nanofibers whose diameters are determined by the pores.

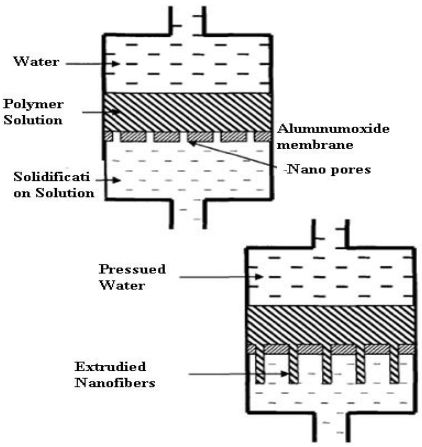


Figure 2.5.Obtaining nanofibers by template synthesis [13]

2.5.3. Electrospinning Process

Fibers have been conventionally produced by mechanically extruding polymer solutions or melts through spinnerets then drawing to reduce diameters sizes similar to natural fibers [19]. Typical fiber diameters produced by these methods range from 5 to 500 nm, with the lower. Limit of fiber diameter that is consistently achievable on the order of magnitude of a micron [20].

In recent decades electrostatic spinning or electrospin, however, remains the most convenient and scalable technique for nanofiber production. The process has been successfully scaled up and is already used in the production of industrial products such as air filter media. Electrospun nanofibers are orders of magnitude smaller in diameter compared to synthetic textile fibers and common natural fibers (Table 2.1).

Electrospun nanofibers with diameters as small as 3–5 nm however, these cannot be generated consistently in quantity, even at the laboratory scale. The smallest of the nanofibers, with diameters of only several nanometers, can be selected for imaging from an ensemble of nanofibers electrospun usually from dilute solutions of a high-molecular-weight polymer under carefully controlled conditions [21].

Table 2.1.Comparison of natural and textile fibers [21]

Fiber	Diameter(nm)	Coefficient of Varition(%)
Spider silk	3.57	14.8
Bombyx mori silk	12.9	24.8
Merino wool	25.5	25.6
Human hair	89.3	17.0
Cotton	10-27	2.5
Polyester	12-25	4-5
Nylon	16-24	3-6

Electrospin is a process for making extremely fine submicron fiber by a process of charging polymer solutions to thousands of volts [22]. Electrospin is the most advantageous and effective method for producing nanofibers. Long and continuous fibers can be produced with a wide range of polymer solutions and melts. By using this process to produce fibers is easy and cheap [13].

2.5.3.1. History of Electrospinning

The origin of electrospin as a viable fiber spinning technique can be traced back to the early 1930s. Formhals patented his first invention relating to the process and the apparatus for producing artificial filaments using electric charges. Though the method of producing artificial threads using an electric field had been experimented with for a long time, it had not gained importance until Formhals's invention due to some technical difficulties in earlier spinning methods, such as fiber drying and collection. Formhals's spinning process consists of a movable thread collecting device to collect the threads in a stretched condition, like that of a spinning drum in the conventional spinning. Formhals's process was capable of producing threads aligned parallel on to the receiving device in such a way that it can be unwound continuously. In his first patent, Formhals reported the spinning of cellulose acetate

fibers using acetone as the solvent. The first spin method adopted by Formhals had some technical disadvantages. It was difficult to completely dry the fibers after spinning due to the short distance between the spinning and collection zones, which resulted in a less aggregated web structure. In a subsequent patent, Formhals refined his earlier approach to overcome the aforementioned drawbacks. In the refined process, the distance between the feeding nozzle and the fiber collecting device was altered to give more drying time for the electrospun fibers.

In subsequent years, focus shifted to studying the structural morphology of nanofibers. Researchers were occupied with the structural characterization of fibers and the understanding of the relationships between the structural features and process parameters. Wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and differential scanning calorimeter (DSC) have been used by researchers to characterize electrospun nanofibers [23].

2.5.3.2. Electrospinning Theory and Process

Electrospinning uses the electrostatic force to spin fibers from a polymeric solution or melt, as illustrated schematically in Figure 2.6. The polymeric solution is initially ejected from the tip of a fine orifice or spinneret (such as a hypodermic needle) maintained at a positive potential up to several tens of kilovolts by a power supply. When the electrostatic repelling force of the positive charges overcomes the surface tension force of a polymer solution droplet at the tip of the liquid stream, the jet splits into two or more smaller streams. As additional charge builds up at the tips of these streams, they will subdivide, and this process continues until a large number of fine polymer filaments (the “splay”) are formed by evaporation of the carrier solvent. These filaments (nanofibers) are deposited on a target maintained at negative potentials up to several tens of kilovolts, where they bond together to form a nanofiber fabric. Depending on the polymeric material and the operating conditions, the fine fibers can range from ten to several thousand nanometers in diameter [24].

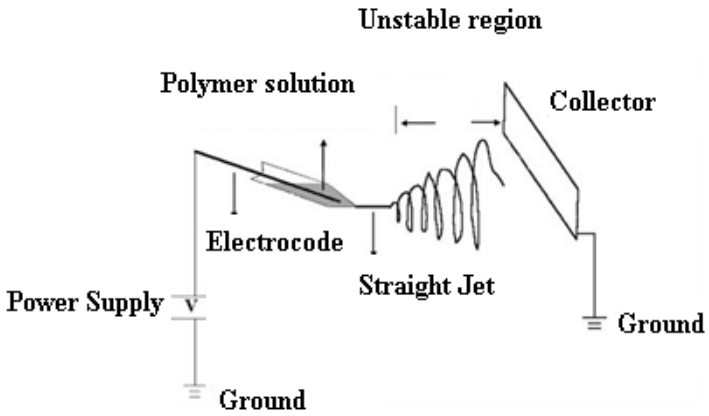


Figure 2.6.Electrospinning set-up [25]

Important features of electrospinning are:

i. Suitable solvent should be available for dissolving the polymer.
ii. The vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.
iii. The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.
iv. The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.
v. The gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form [13].

- **Effect of Processing Conditions**

Parameters for processing condition include the voltage, volume feed rate and collecting distance applied during electrospinning.

i. Voltage

To study voltage effect, the voltage was increased during electrospinning process from 20 kV to 35 kV while keeping a fixed polymer concentration, feed rate, collecting distance and the ratio of polymer to agent. It was observed that the diameter of fiber diameter did not dramatically vary with varied voltage. According to past works, higher voltage was reported to induce not only larger diameter but also smaller diameter. Applied voltage may affect some factors such as mass of polymer fed out from a tip of needle, elongation level of a jet by an electrical force, morphology of a jet (a single or multiple jets), and so forth. A balance among these factors may determine a final diameter of electrospun fibers. Increasing the applied voltage does increase the electrostatic force and create smaller diameter fibers, but it also draws more solution out of the spinneret.

ii. Feed Rate

The solution feed rate is another factor to influence electrospun fiber diameters. When the flow rate is increased, there is a corresponding increase in the fiber diameter simply because a greater volume of solution is drawn away from the spinneret.

iii. Collecting Distance

Relationship between the average fiber diameter and spinning distances, the fiber can be obtained within the collecting distance range and the diameters of fiber do not vary significantly with the difference of collecting distance. Collecting distance may affect some factors such as the evaporation of solvent, electric field strength, and so forth. A smaller collecting distance leads to greater jet stretching and elongation by increasing the electric field strength, which results in smaller fiber diameters. When adjusting collecting distance, it is very important to ensure the polymer solution jet has enough flight time for the solvents to evaporate.

iv. Effect of Polymer Solution Concentration

The average diameter of fibers increases significantly with the increase of polymer solution concentration. Beaded fibers were formed at too low polymer solution concentration (less than 4%) for any electric field and spinning distances. Surface tension effects could be dominant with decreased polymer concentration/solution viscosity and beaded fibers were consequently produced. Hence, despite the capability to shrink the size of the fibers by decreasing the polymer concentration, this success of obtaining finer fibers was compromised by the change of the fiber uniformity [25].

2.5.3.3. Structure and Morphology of Polymeric Nanofibers

In recent times, nanofibers have attracted the attention of researchers due to their pronounced micro and nano structural characteristics that enable the development of advanced materials that have sophisticated applications. More importantly, high surface area, small pore size, and the possibility of producing three dimensional structures have increased the interest in nanofibers.

The production of nanofibers by the electrospinning process is influenced both by the electrostatic forces and the viscoelastic behavior of the polymer. Process parameters, like solution feed rate, applied voltage, nozzle-collector distance, and spinning environment, and material properties, like solution concentration, viscosity, surface tension, conductivity, and solvent vapor pressure, influence the structure and properties of electrospun nanofibers. Significant work has been done to characterize the properties of fibers as a function of process and material parameters [23].

The electrospinning jet can be characterized by 3 regions (Figure 2.7)

i. Base, a region where the jet emerges from the polymer solution, typically the Taylor cone.

ii. Jet, the region beyond the base, where the electrical force stretches the jet and accelerates the polymer liquid. The diameter of the jet decreases and the length increases as the jet moves towards the collector.

iii. Splitting and Splaying region: Splitting refers to the breakup of the jet into two equal parts, while splaying occurs when a single jet divides into many charged jets with approximately equal diameters and charge per unit length [18].

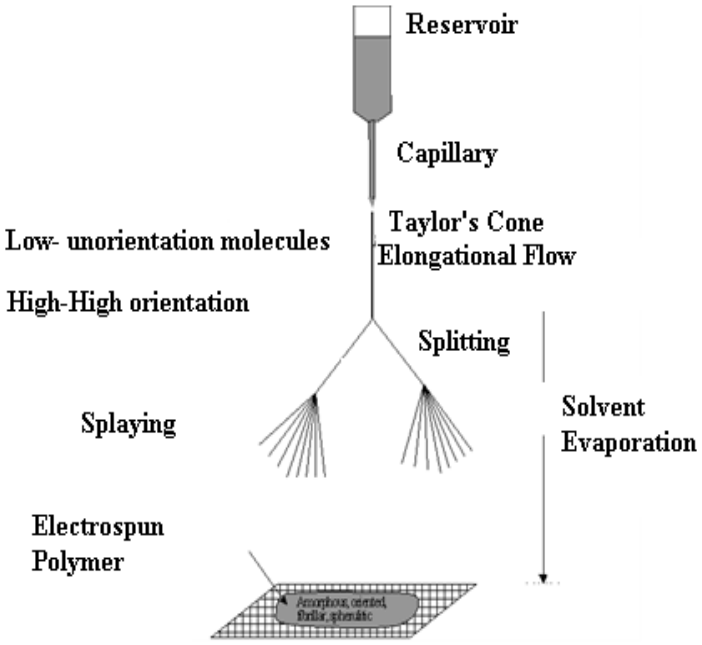


Figure 2.7.A schematic electrospinning a viscoelastic polymer [18]

2.5.4. Electrospraying Process

A variant of electrospinning is electrospray [26]. Electrospraying is similar to electrospinning as it employs a high voltage to disperse a solution. However, unlike electrospinning, the solution jet is broken into fine droplets which deposit as nanoparticles on the collector [27]. The basic difference between these two processes lies in the concentration of the solution. In electrospray the concentration is sufficiently low to destabilize the charged jet which then breaks down into small spherical droplets that solidify during the course and are deposited on the collector. In this case the polymer solution does not experience severe drawing and the formed film consists of small droplets instead of fibers [27].

2.5.4.1. Electrospray Background

It was Lord Rayleigh who, in 1882, wrote that an excessive charge on the droplets of liquid would lead to their disintegration as soon as the repulsive force between the charges on the droplet surface exceeds surface tension [28].

Droplets leaving the surface of the cone are charged and accelerated by the electric field towards a counter electrode (Figure 2.8). They lose some liquid due to evaporation which leads to the growth in surface charge density and consequent columbic explosions, which reduce even further the droplet sizes and form satellite droplets containing single ions. Recently, the process of electrospinning has attracted much attention because it can consistently produce polymer fibers that range from 5 to 500 nm in diameter. This process is a variation of the better known electrospray process, which produces small particles using electrical force. In this process, a polymer solution held by its surface tension at the end of a capillary tube is subject to an electrical field. Initially the polymer solution forms a droplet at the end of the capillary tube.

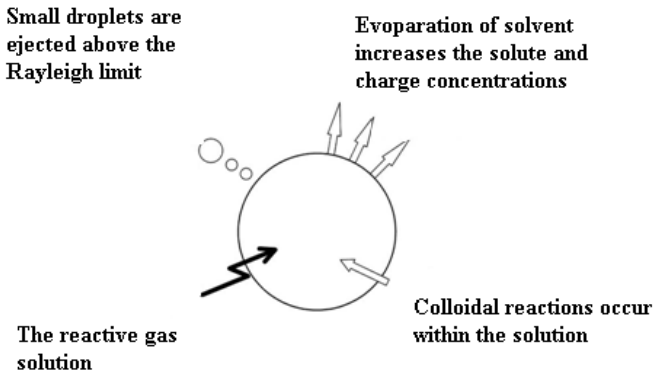


Figure 2.8.Fate of emitted droplets [28]

As the jet accelerates and thins in the electric fields, radical charge repulsion results in splitting of the primary jet into multiple filaments by splaying. By comparison, in the electrospray process, the jet is broken into small droplets and sub-micron beads are obtained (Figure 2.9). For high viscosity liquids, the jet does not break up, but travels as a jet to the grounded target. It undergoes thinning, splaying and bending as it travels, and the solvent evaporates leaving behind a charged fiber deposited on a grounded collector to form a nonwoven mesh.

The electrospun fibers may have a sizable static charge making it possible to manipulate them into three-dimensional (3-D) structures during their deposition with the help of electrical field. Depending on the solution viscosity, electrical field strength and other process parameters, porous structures of varying morphologies can be obtained. The viscoelastic behavior of the polymer solution keeps the elongated jet from breaking into beads and helps to maintain fibers with relatively uniform diameters [18].

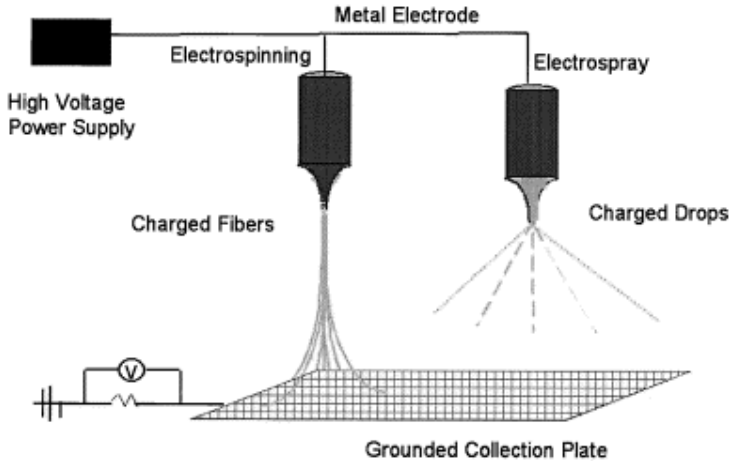


Figure 2.9.Electrospinning and electrospraying processes [18]

2.5.4.2. Spray modes

Different spray modes can be achieved by adjusting the potential difference between two electrodes in the electrospray process. These modes are characterized by the shape of the surface from which the liquid jet originates (Figure 2.10) [29].

These modes have significant effects on droplet size distribution. The spraying modes can be categorized into two groups:

i. Dripping modes, in which only fragments of liquid are ejected from the capillary outlet by the deformation and detaching of the liquid meniscus [19]. These modes are characteristic in that only fragments of liquid are ejected directly from the capillary nozzle; these fragments can be in the form of regular large drops (dripping mode), fine droplets (micro dripping mode), elongated spindles (spindle or multispindle modes), or sometimes irregular fragments of liquid. At

some distance from the nozzle outlet, however, these fragments contract into spherical droplets.

ii. Jetting modes by which the meniscus elongates into a long fine jet, The jet can be smooth and stable (cone-jet mode) or can move in any regular way: rotate around the capillary axis (precession mode) or oscillate in a plane (oscillating mode). Sometimes a few jets on the circumference of the capillary can be observed (multijetmode). The case when the jet branches are known as a ramified jet [30].

iii. The multi-jet mode made it possible to obtain simultaneously a large number of emission cones and droplets smaller than those obtainable from a single cone [32]. The most important mode of spraying is the cone-jet mode. In this mode, the liquid meniscus assumes the form of regular, ax symmetric cone with a thin jet (< 100 mm in diameter) at its apex, stretching along the capillary axis. The end of the jet undergoes instabilities of one of two types: varicose and kink [31].

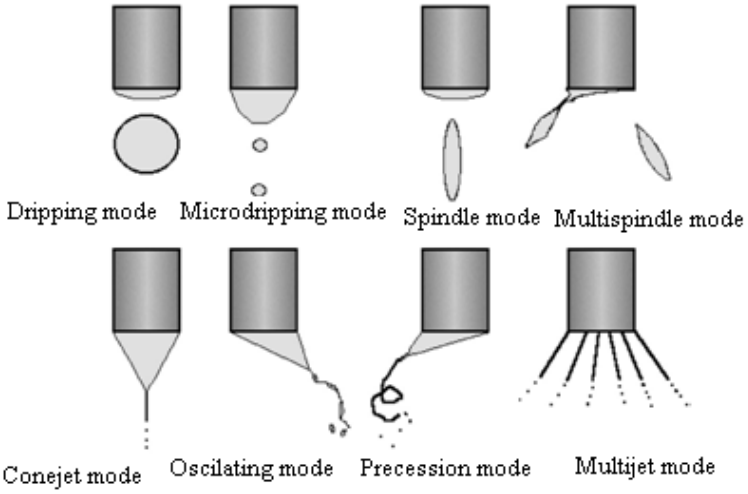


Figure 2.10.Various modes of electrospraying [31]

The aim of the electrospraying process is the formation of materials for protective technologies such as masks, garments, or respirators. The currently used materials are not very efficient in giving protection against small-sized biological agents or chemical compounds, and they are frequently heavy. The composite materials made from nanoparticles deposited onto nanofibers or sandwiched between two layers of fabric will provide light weight, low cost, and breathable structures with improved protection, duration and performance [30].

2.5.4.3. Processing Variables

Observations showed that solution flow rate is the predominant factor for determining the particle size, and also can fabricate smaller particles simply by decreasing the solution flow rate.

Rounder particles with smooth surface would have a relatively lower surface to volume ratio. It is concluded that high polymer concentration causes premature drying of the droplets at the orifice tip, whereas too low concentration causes solvent saturation at the collector. Furthermore, it is observed that higher polymer concentration results in larger particles possibly because there is more polymer mass in each droplet and thus after the solvent evaporation, more solid is left in each particle.

For a given voltage and liquid flow rate, an optimal concentration optimizes both the size and the structure of polymeric nanoparticles. Another important process variable is solution conductivity. Particle size increases with decreasing solution conductivity [31].

2.5.4.4. Applications of Electrospray in Nanotechnology

a) Fabrication of Inorganic Nanoparticles

A great deal of research has been done in the last decade by different groups in an attempt to manufacture and characterize nanoparticles with size-dependent physical properties intermediate between those of the bulk solid and molecules. This size dependence of energy levels allows one to control properties of nanomaterial that can be applied [28].

i. to control the average size of the particles;
ii. to obtain a very narrow distribution of sizes;
iii. to passivity the surface and eliminate surface states;
iv. to control the shape of the particles.

b) Nano Coatings and Composites

Recently, many researchers have tested the electrospray deposition technique of liquid-phase materials on various substrates. Electrospray deposition (Figure 2.11) is a process in which droplets produced by electrospraying from a solution or suspension of a material to be deposited are targeted to a substrate to form a tight surface layer. A solid layer is obtained after solvent evaporation. Evaporation can be sped-up by heating the substrate. To improve mechanical properties, the layer may be sintered at higher temperatures, if applicable. Usually, the material to be deposited is sprayed directly onto the substrate, but the layer can also be formed from a precursor. The precursor is a compound which is decomposed at high temperature or converted to another substance in chemical reactions with other compound sprayed simultaneously or delivered in the gaseous phase. The reactions usually take place on the substrate, and a new product is obtained (Figure 2.11).

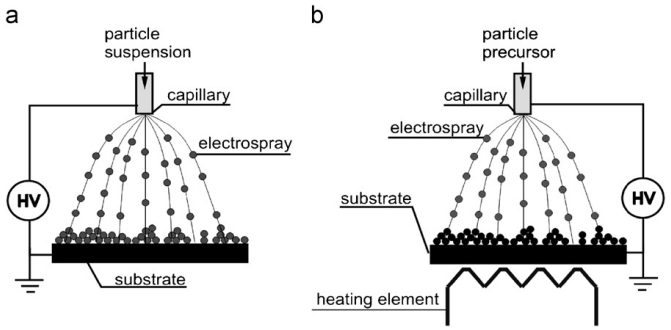


Figure 2.11.Scheme of electrospray deposition of micro- and nano-thin film: a) from a solution or suspension of particles to be deposited, b) from a precursor thermally decomposed on the substrate [21]

2.5.4.5. Advantages of Electrospraying

Electrospraying is a single-step, low-energy, and low-cost material processing technology, which can deliver products possessing unique properties. The substrate is not damaged after the spraying process. Optimization of the processing conditions will result in a low number of voids, flaws and cracks in the coating and give a sufficiently good homogeneity of the layer [30].

In addition to their, the electrospraying has other following advantages over conventional mechanical atomizers:

i. Droplet size is smaller than that available from conventional mechanical atomizers, and can be smaller than 1 μm.
ii. The size distribution of the droplets is usually narrow, with small standard deviation that allows production of particles of nearly uniform size.
iii. Charged droplets are self-dispersing in space (due to their mutual repulsion), resulting also in the absence of droplet coagulation.
iv. The motion of charged droplets can be easily controlled (including deflection or focusing) by electric fields.
v. The deposition efficiency of a charged spray on an object is order of magnitudes higher than for un-charged droplets.
vi. These characteristics characterize electrospraying as a versatile tool for micro- and nano-thin-film deposition, or micro- and nano-particle production [21].

2.6. Applications of Nanofibers

Nanofiber related publications and patents appear to have grown in number rapidly over recent years. An analysis of patent activity in particular allows an overall summary of the commercial potential of nanofibers and affords the identification of application areas where the technology might play a key role. A large majority of the patents issued on the technology are U.S. patents, with about two-thirds being related to biological or medical application of nanofibers. The second largest group deals with application of nanofibers in filtration, followed by other applications such as sensors, composites, and catalysis. Figure 2.12 illustrates the diversity of applications where nanofibers might be used [21].

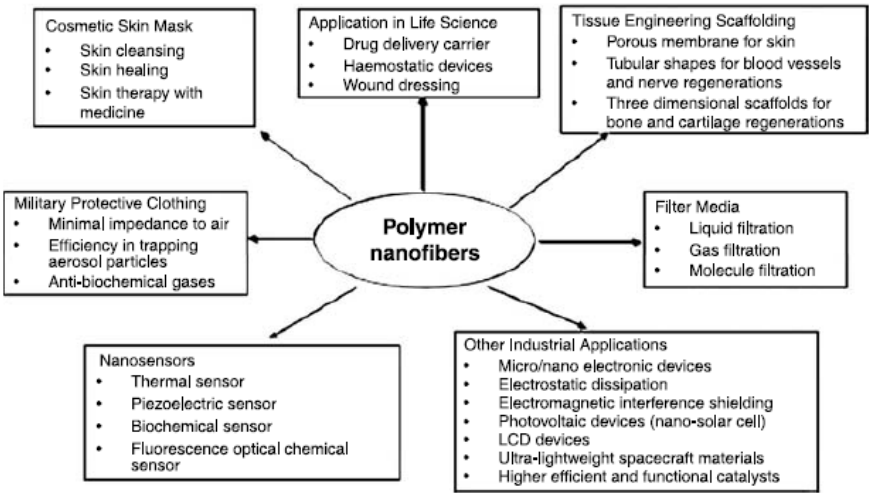


Figure 2.12.The diversity of applications proposed for polymer nanofibers [21]

CHAPTER 3
ANTIBACTERIAL TEXTILE, FINISHING AND SUBSTANCES

3.1. Antibacterial Textile

3.1.1. Introduction

Humans are often infected by pathogenic microorganisms in the living environment. During the daily usage of textile products, humid and warm environment aggravate appropriate living conditions for the microorganisms [32]. This leads to the development of new materials, which can provide quality and safety benefits to their users. Polymers and their antibacterial modifications belong in this topical field of scientific research as well as commercial interest due to their wide applicability [33].

Mold, mildew, fungus, yeast, and bacteria (microorganisms) are part of our everyday lives. There are both good and bad types of microorganisms. The thousands of species of microorganisms that exist are found everywhere in the environment and on our bodies. These organisms impact producers, retailers, and users of all kinds of products. Understanding microorganisms, which they are, where they come from, and why they grow on certain materials provides us a basis for controlling them and their negative effects. This control capability, with the right technology, can provide for a valuable feature on a wide range of textiles.

Value enhancing finish technologies can be developed around fads and fashion trends but the most enduring finish technologies are designed to improve fabric performance and function. Antibacterial finishes enhance apparel performance while meeting consumer led feature demands. Antibacterial treatment is rapidly becoming a standard finish in some textile categories and should be viewed as a finish with a future [34].

3.1.2. Microbes or Microorganisms

Microbiology, the study of microscopic organisms, derived its name from three Greek words: micros (“small”), bios (“life”), and logos (“science”). Taken together they mean the study of microorganisms which are very small and cannot be seen by unaided eye. They include a variety of micro-organisms like bacteria, fungi, algae and viruses [2].

Bacteria are unicellular organisms which grow very rapidly under warmth and moisture. Further, sub divisions in the bacteria family are Gram positive (S. aureus), Gram negative (E. coli), spore bearing or non spore bearing type. Some specific types of bacteria are pathogenic and cause cross infection. Fungi, molds or mildew are complex organisms with slow growth rate. They stain the fabric and deteriorate the performance properties of the fabrics. Fungi are active at a pH level of 6.5. Algae are typical micro organisms which are either fungal or bacterial. Algae require continuous sources of water and sun light to grow and develop darker stains on the fabrics. Algae are active in the ph range of 7.0-8.0 [2].

Dust mites are eight legged creatures and occupy the household textiles such as blankets bed linen, pillows, mattresses and carpets. The dust mites feed on human skin cells and liberated waste products can cause allergic reactions and respiratory disorders. Some harmful species of the bacteria and fungi are listed in Table 3.1 [35] and microbe types are listed in Table 3.2 [2].

Table 3.1.Some harmful species of microorganisms [35]

Bacteria	**Fungi**
Gram Positive Bacteria	**Cloth damaging fungi**
Staphyloccus aureus or pyogens Staphyloccus epidermis Corynebacterium	Aspergillus niger Aspergillus fumigatus Trichoderma viride
Gram Negative Bacteria	**Crop damaging fungi**
Escherichia coli Klebsiella pneumoniae Proteus vulgaris Pseudomonas pyocynans	Fusarium species Rhizoctonia solani Sclerotium rolfsii

Table 3.2.Microbe type [2]

Microbe type	Description	Causes	Treat with
Bacteria	Simple structure/Fast growing in warm and wet conditions	Unpleasant Odours (e.g.E. coli)	Antibacterial Agent
Fungal (moulds and mildews)	Complex structure/Slow growing	Staining and loss of performance skin infections	Antimycotic Agent

3.1.3. Mechanism of Antibacterial Activity

A living microbe (e.g. bacterium, fungus) typically has an outermost cell wall which is mainly composed of polysaccharides. This cell wall maintains the integrity of cellular components and shields the cell from the extracellular environment. Immediately beneath the cell wall is a semi permeable membrane which encloses intracellular organelles and a myriad of enzymes and nucleic acids. The enzymes are responsible for the chemical reactions that take place within the cell, and the nucleic acids store all of the genetic information of the organism.

The survival or growth of microorganisms depends on the integrity of the cell and the concerted action and proper state of all of these components. Almost all antibacterial agents used in commercial textiles are biocides. They damage the cell wall or alter cell membrane permeability, denature proteins, inhibit enzyme activity or inhibit lipid synthesis, all of which are essential for cell survival [1].

Negative effect on the vitality of the microorganisms is generally referred to as antibacterial. The antibacterial effect can be divided into two different categories: microbiostatic and microbicidal:

i. Microbiostatic effect: If an antibacterial agent leads to the inhibition of the proliferation of a microbial population and thus, hinders microbial growth it is called microbiostatic.

ii. Microbicidal effect: Antibacterial agents leading to the elimination or death of the cells are called microbicidal [36]. The differentiation of antibacterial activity is given in Figure 3.1.

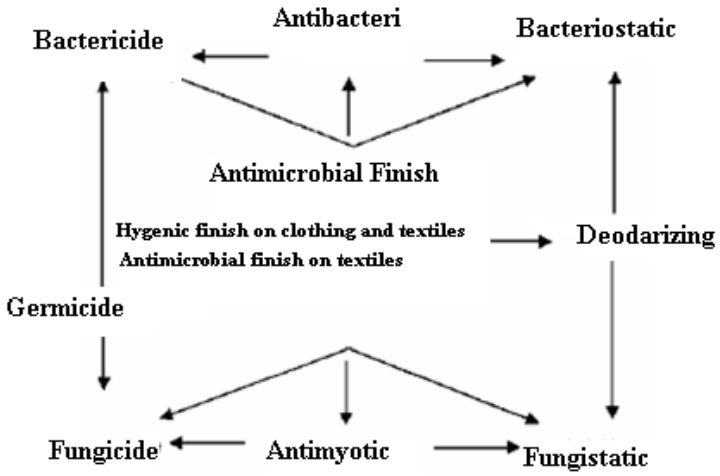


Figure 3.1.Differentation of antibacterial activity [37]

The activity, which affects the bacteria, is known as antibacterial and that of fungi is antimycotic. The antibacterial substances function in different ways. In the conventional leaching type of finish, the species diffuse and poison the microbes to kill. This type of finish shows poor durability and may cause health problems. The non-leaching type or bio-static finish shows good durability and may not provoke any health problems. A large number of textiles with antibacterial finish function by diffusion type. The rate of diffusion has a direct effect on the effectiveness of the finish. For example, in the ion exchange process, the release of the active substances is at a slower rate compared to direct diffusion and hence, has a weaker effect. They are active only when they come in contact with microorganisms. Considering the medical, toxicological and ecological principles has developed these so called new technologies [37].

In the broad spectrum of existing bacteria there are pathogenic and non-pathogenic organisms. Both of them can multiply abnormally on the textile surfaces with an accumulation that compromises the hygienic cleanliness [38]. Some examples of pathogenic and non pathogenic microorganism are listed in Table 3.3.

Table 3.3.Show examples of pathogenic and non pathogenic microorganism [38]

Microorganism	**Pathogenicity**	**Effects**
Bacillus subtilis	Generally non pathogenic	Food spoiling occosionally conjunctivitis
Escherichia coli	Low pathogenic	Food spoiling occosionally urinary bladder infection
Klebsiella pnuemoniae	Pathogenic	Pneumonia,urinary bladder infection
Proteus vulgaris	Low pathogenic	Inflammations
Staphyloccus epidermis	Low pathogenic	Surgical wound infections
Staphyloccus aureus	Low pathogenic	Toxic shock,purulence
Pseudomonas aeuroginosa	Pathogenic	Multi infections

The proliferation of pathogenic micro-organisms has to be fought for the physiologic impact to the human health, while non pathogenic microorganisms have to be controlled for the visual, olfactory and tactile effects produced by their metabolism. The textile materials, on which source of nutrients are present become a medium for a rapid multiplication of microorganisms [39].

3.1.4. Antibacterial Textile

An antibacterial textile is one that has been chemically treated to kill, or suppress the growth of harmful microorganisms. After treatment, common household products such as bedding, draperies, carpets, upholstery, socks, underwear, sportswear, children's wear and automobile textiles will be less likely to transmit bacteria, molds and fungi, thus reducing odors, mildew, stains and prolonging the useful life of the textile. The demand for antibacterial finishes in the textile industry continues to rise as new products and applications are introduced. Consumers identify antibacterial textiles with cleanliness and protection against microorganisms and have come to expect it in new textile products [39].

3.1.5. Future of Antibacterial Textiles

A wide range of antibacterial textile goods are now available to the consumer with increasing demand for expanding product lines. Once primarily used for tents, tarps and other soil-contact textiles, the market is now booming for more environmentally friendly and functional products for sports and leisure clothing, home furnishings,

outdoor use textiles, hotel industry products and particularly medical and healthcare applications.

The greatest challenge to antibacterial textiles is the durability of the antibacterial function. Essentially, repeated laundering can affect the properties of the fabric. There are processes that incorporate a longer-lasting antibacterial effect and technology is developing means to regenerate, or make permanent, that quality. It is expected that innovations will continue in the textile field, perhaps incorporating multifunctional properties such as antibacterial finishes [39].

Antibacterial fictionalization of textiles aims on the one hand to protect the material from microbe derived destruction, and on the other hand to protect human beings from contamination. On the garment sector it is the hygienic aspect that counts and for the technical textiles it is the material protecting aspect [36].

3.1.6. Benefits of Antibacterial Textiles

A wide range textile product is now available for the benefit of the consumer. Initially, the primary objective of the finish was to protect textiles from being affected by microbes particularly fungi. Uniforms, tents, defense textiles and technical textiles, such as, geotextiles have therefore all been finished using antibacterial agents. Later, the home textiles, such as, curtains coverings, and bath mats came with antibacterial finish. The application of the finish is now extended to textiles used for outdoor, healthcare sector, sports and leisure. Novel technologies in antibacterial finishing are successfully employed in non-woven sector especially in medical textiles [2].

When caring for clothing or linens that are treated with such anti-microbial chemicals, consumers should wash products without using chlorine bleach, as it will deactivate the treatment. The extension of antibacterial treatments into main stream apparel and home textiles adds to consumers overall comfort and well-being, in addition to enhancing the life cycle of textiles [40].

Antibacterial do not all work the same. The vast majority of antibacterial work by leaching or moving from the surface on which are applied. This is the mechanism used by leaching antibacterial to poison a microorganism. Besides affecting durability and useful life, leaching technologies have the potential to cause a variety of other problems when used in garments. These include their negative effects because; they can contact the skin and potentially affect the normal skin bacteria, cross the skin barrier, and/or have the potential to cause rashes and other skin irritations. A more serious problem with leaching technologies has to do with their allowing for the adaptation of microorganisms. An antibacterial with a completely different mode of action than the leaching technologies is a molecularly bonded unconventional technology. The bound unconventional antibacterial technology has a mode of action that relies on the technology remaining affixed to the substrate killing microorganisms as they contact the surface to which it is applied. Effective levels of this technology do not leach or diminish over time. When applied, the technology actually polymerizes with the substrate making the surface antibacterial. This type of antibacterial technology is used in textiles that are likely to have human contact or where durability is of value [34].

To benefit from the consumer demand for antibacterial /antibacterial products and for the antibacterial and antifungal performance needs of the textile world, manufacturers have a choice. This selection should be done by considering:

i. Adopting an antibacterial technology with a proven history of use. This will help shorten the timelines in bringing products with an antibacterial/antifungal/odor-reducing, antibacterial feature to market.
ii. Adopting a non-leaching antibacterial that doesn't pose the risk of crossing the skin barrier. If it creates a "zone of inhibition" it leaches or moves and has the potential to cause problems.
iii. Adopting a non-leaching antibacterial that doesn’t pose the risk of creating adaptative resistant microorganisms.
iv. Adopting an antibacterial technology that can have its proper application tested for at the mill or at the retailers. A verifiable quality assurance program should be a key component of any application process.

v. Adopting an antibacterial technology that has technical and marketing support [37].

3.2. Antibacterial Treatment and Finishes

Textiles have always played a central role in the evolution of human culture by being at the forefront of both technological and artistic development. The protective aspects of textile have provided the most textile ground for innovative developments. Hygiene has acquired importance in recent years. The consumers are now increasingly aware of the hygienic life style and there is a necessity and expectation for a wide range of textile products finished with antibacterial properties [37].

3.2.1. Necessity of Antibacterial Finishes

Antibacterial treatment for textile materials is necessary to fulfill the following objectives:

i. To control spread of disease and danger of infection following injury
ii. To control the deterioration of textiles particularly fabrics made from natural fiber caused by mildew [37].
iii. To avoid cross infection by pathogenic micro organisms
iv. To control the infestation by microbes
v. To arrest metabolism in microbes in order to reduce the formation odor
vi. To safeguard the textile products from staining, discoloration and quality deterioration [2].

In order to obtain the greatest benefit, as mentioned above, an ideal antibacterial treatment of textiles should satisfy a number of requirements [1].

i. Firstly, it should be effective against a broad spectrum of bacterial and fungal species, but at the same time exhibit low toxicity to consumers, e.g. not cause toxicity, allergy or irritation to the user. Antibacterial -treated textiles have to

meet standards in compatibility tests (cytotoxicity, irritation and sensitization) before marketing.

ii. Secondly, the finishing should be durable to laundering, dry cleaning and hot pressing. This is the greatest challenge as textile products are subjected to repeated washing during their life.

iii. Thirdly, the finishing should not negatively affect the quality (e.g. physical strength and handle) or appearance of the textile. Finally, the finishing should preferably be compatible with textile chemical processes such as dyeing, be cost effective and not produce harmful substances to the manufacturer and the environment. One further consideration is that the antibacterial finishing of textiles should not kill the resident flora of nonpathogenic bacteria on the skin of the wearer. The skin resident flora consists of several bacterial genera, which are important to the health of the skin as they lower skin surface pH and produce antibiotics to create an unfavorable environment for the growth of pathogenic bacteria. Fortunately, antibacterial agents on textiles may only reduce the density of the skin resident flora but do not completely eliminate them. To date, no evidence exists that the use of antibacterial textiles changes the ecology of skin resident flora leading to the outgrowth of pathogenic bacteria [1].

3.2.2. Antibacterial Finishing New Methodologies

Textiles are a versatile material, combining very divergent properties, such as flexibility, strength, drapability, permeability, barrier properties, in one single and easy to process substrate. This is why an increasing number of different industrial sectors are applying textiles (construction & architecture, composites, transport, electronics). These new applications go hand in hand with a growing number of severe requirements. Hence, textiles are becoming an increasingly technical and complex product [41].

Hygienic fictionalization of fibers is performed either during melt spinning or in finishing processes. In the first method to be active the effective substances have to migrate to the fiber surface, in the latter fictionalization can be performed at the

fiber, yarn or fabric/fleece stage also in combination with other finishing processes [36].

Various methods, depending on the particular active agent and fiber type, have been developed or are under development to confer antibacterial activity to textiles [47].

i. For synthetic fibers, the antibacterial active agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their formation. Such processing provides the best durability as the active agent is physically embedded in the structure of the fiber and released slowly during use.
ii. The conventional exhaust and pad-dry-cure processes have been used for antibacterial finishing on natural as well as synthetic fibers for the biocides such as irgasan.
iii. Padding, spraying and foam finishing have been used for the silicone-based quaternary agents.
iv. Many other methods have been reported, such as the use of nanosized colloidal solutions, nanoscale shell-core particles, chemical modification of the biocide for covalent bond formation with the fiber, crosslinking of the active agent onto the fiber using a crosslinker and polymerization grafting [42].
v. In the field of textile finishing, new products as well as new techniques are being developed. Due to the rising energy costs and the enormous expenses related to waste removal, a lot of attention is being paid to water and energy savings during the development of new textile finishing techniques and products. In this respect, there is a growing use of water-based and solvent-free formulas and of solvent-free application techniques. In addition, energy saving coating and laminating techniques, such as hot melt, UV-curing and plasma are becoming increasingly important [41].

3.2.2.1. Plasma Treatment

Plasma treatment is a surface treatment that modifies the textile surface without altering the bulk properties (tear resistance, flexibility and density) of the textile material.

The drawing (Figure 3.2) below illustrates the working principle: by means of a plasma source, a plasma zone is generated with energetic and active particles (photons, electrons, ions). The textile material is guided through this zone and treated accordingly [41].

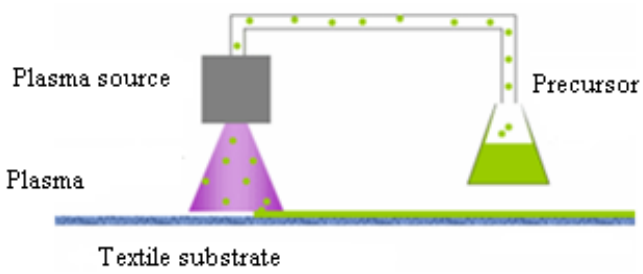


Figure 3.2.Plasma treatment [41]

The coating of a surface using the low pressure plasma method takes place in a vacuum chamber at a pressure of just a few thousandths of an atmosphere. The appropriate gas for the required process is allowed into the chamber and ionized by means of an electric field. The energy supplied to maintain the electric field causes the gas to become ionized – electrically charged – so creating the plasma, which depending on the process gas involved can be used for cleaning the surface (to improve wet ability) or to lend it a particular functionality (by modifying the surface chemistry). In the plasma coating technique, the energy of the charged gas molecules in the plasma is used to dislodge atoms from a metal plate which then deposit on the fibers to be coated, forming an extremely thin metallic film [43].

Figure 3.3.Textile fibers in the plasma coating plant [43]

In medical engineering, antibacterial and electrically conductive yarns are of great interest. Coating yarns with silver makes them highly suitable for obtaining both properties. But the quantity of silver applied as well as its adhesion to the yarns must

be controlled in order to prevent it from being washed out and from contaminating waste water. High-energy particles are accelerated from the plasma onto a silver plate, the target. In the process, silver atoms are ejected, which produces the coating on the yarns. In this so-called sputter process, the coatings build up one atom layer at a time, enabling control over the layers on a nanometer scale [44].

The most common applications of plasma treatments are;

i. Imparting hydrophilic properties
ii. Increasing adhesion
iii. Influence printability and dye ability
iv. Changing the electrical conductance
v. Imparting hydrophobic and oleo phobic properties
vi. Application of anti bacterial agents
vii. Application of fire retardant agents
viii. Antishrink treatment of wool
ix. Sterilization
x. Desizing of cotton [44].

Advantages of plasma treatment;

i. The new process allows the fiber or fabric coating to be significantly thinner than previously. Modify the wool fiber surface to a depth of nm without altering the bulk properties. Thus reducing both costs and material consumption while improving environmental friendliness and yet still maintaining the useful characteristics of the finished textile [43].
ii. Do not produce waste water or chemical effluents.
iii. The process is simple, clean, safe [45].

3.2.2.2. Sol-Gel Treatment

The sol–gel process is a versatile solution method for making tailor-made, composite advanced materials ranging from powders for thin film coatings or porous aerogels to dense ceramic materials [46].

The first experiments on sol-gel already took place in the fifties of the previous century. By their inorganic nature, sol-gel layers are extremely strong and wear resistant. Therefore, very thin 'nanometric' layers suffice to obtain the desired effects.

Since several years, there is an increasing interest in the application of the sol-gel technology for textile treatment. However, the formulas and methods used in other industrial branches have to be adapted to the raw materials and specific textile properties. The preparatory material (or precursor) used to produce the "sol" usually consists of inorganic metal salts or metal organic components, such as metal alkoxides. These precursors are submitted to a series of hydrolyze and polymerization reactions to create a colloidal suspension (or "sol") (Figure 3.4). By further processing this suspension, this solution is transformed into a ceramic material in different forms for different applications [41].

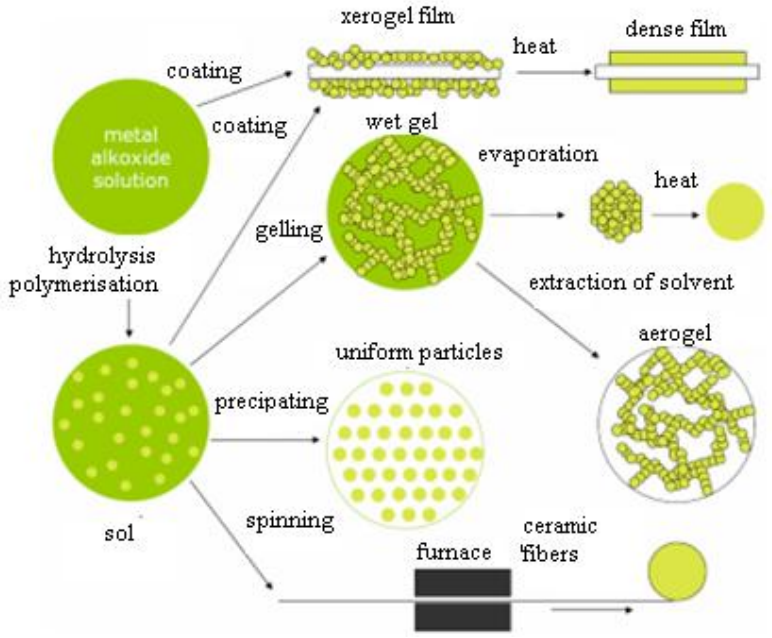


Figure 3.4.Sol-gel treatment [41]

3.2.2.3. Uv-Coating

UV-curing is a photochemical process to dry or "cure" inks, coating layers, glues, and other materials by using ultraviolet light. UV-curing represents about 4% of the actual industrial coating market.

Ultraviolet radiation is an electromagnetic radiation with wavelengths from 1 to 400 nanometre. For the treatment of surfaces radiation from all three ranges are being used. Besides oligomers and monomers, the UV formula also includes a photo-initiator. Under UV light, this compound is decomposed into two reactive parts (radicals) that will further initiate the polymerization and lead to the formation of a three-dimensional network. In this manner, it will take only seconds to cure the formula.

Figure 3.5.Uv-coating [41]

This technology is an interesting alternative to traditional water and solvent based processes by the use of 100% systems and aqueous formulas. Important advantages are energy efficiency production, efficiency application [41].

3.2.2.4. Fabrication of Electrospun Nanofibers Antibacterial Fabrics

Electrospinning, by which a high voltage is applied to the droplets of polymer solutions or melts to overcome the liquid surface tension and enable the formation of fibers, has been well recognized as a versatile and effective method capable of making fibers with diameters into the nano regime.

By controlling the process parameters, e.g. electric field strength and collecting distance, solvent, polymer, and solution properties, nanofibers with different morphology and properties can be achieved. The resultant nanofibers obtained through electrospinning can be easily engineered with desired pore size and porosity to enhance the barrier performance, and much more effective surface areas to carry functional agents with desirable properties.

In recent years, many functional nanofibers and composites have been developed through electrospinning by which well-selected functional agents have been added into the spinning dopes before they are incorporated into laminates to achieve many desirable properties, such as higher strength and modulus, better thermal stability and antibacterial properties.

Electrospinning is an attractive approach for generating nanofibers with diameters in the nanometer to micrometer range through the action of a strong electric field imposed on a polymer solution or melt. Besides the high production rate, low cost and simplicity of the setup, the unique ability of electrospinning is to efficiently form a well-defined three-dimensional nanofibrous membrane with a large surface area and a controlled pore structure (Figure 3.6). Several research groups have carried out some works using the electrospinning technique, but have focused on electrospun membranes with a single antibacterial agent [47].

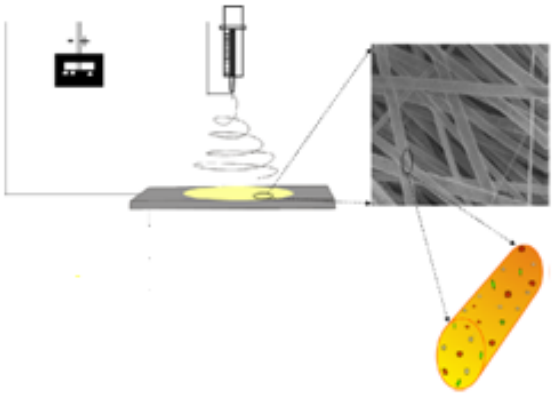


Figure 3.6.Schematic fibrous by using an electrospin technique [47]

3.2.3. Antibacterial Finishing Conventional Methodologies

A similar production process is used to create a wide array of different products in the fabric coatings industry. All products are composed of a fabric substrate to which a polymer coating is applied, giving the product characteristics of the coating and the fabric. The fabric gives the product strength, structure, and flexibility. The coating significantly enhances the fabric's performance capabilities and provides qualities such as water repellency, flame residence, chemical resistance, increased strength, and abrasion resistance. Coatings are composed of the polymer base, solvents,

pigments, plasticizers, lubricants, and fillers. These ingredients are prepared in mills and mixers to ready the material for application to the fabric. The coating is applied using a variety of techniques that dip, roll, or spread the coating onto the fabric material. The process must ensure that the fabric is not damaged during coating application. After application, the product passes through a flash-off area on its way to the drying and curing ovens. These ovens mark the final stage of the production process, where the coating is fused to the substrate [48].

The most common coating materials used in the industry is vinyl (PVC), polyurethane, and rubber compounds. Other compounds, such as acrylic and teflon, are also used to produce coated fabrics. There is no unique solution to polymer choice in coatings because different materials can be used to achieve similar results in the end product. The manufacturer's choice of polymer is affected by polymer properties, polymer availability, cost analysis, coating equipment to be used, tradition, and environmental protection [48].

PVC is the most commonly used polymer. It is inexpensive and resistant to combustion, chemicals, aging, and abrasion, and it can be applied to the substrate using a variety of techniques. With the use of plasticizers, PVC can be processed into a soft, manageable compound that can be easily applied to a fabric. PVC is used to produce coated products such as tarpaulins, tents, roofing materials, greenhouses, boat covers, boats, conveyor belts, pool covers, rainwear, luggage, automotive upholstery, and a variety of chemical protective clothing products [48].

Polyamide is another common coating type that can be used for a wide variety of products such as tents, life vests, evacuation slides, flexible fuel storage tanks, and apparel items. Inflatable boats, rainwear, luggage, automotive upholstery, water storage bags, food conveyor belts, and fuel hoses are also made with polyurethane coatings. Acrylic and Teflon are also used extensively as coating materials [48].

Acrylic resins are the most common material for a class of products known as geotextiles. These fabric products are used in earth structures [48].

3.2.3.1. Spraying

In disposable textiles such as bandage, gauze, tissue or some of the nonwoven textiles which after several washing do not need antibacterial stability, spraying colloidal solution with specified concentration, is both simple and efficient [49].

3.2.3.2. Spinning Process or Using Master batch

In order to cause antibacterial activities in synthetic fibers (by the use of melt spinning) nanocid can be added to melted polymer in the extruder, or nanocid master batch can be used. Not only adding nanocid (with Titan Base) to the fibers causes antibacterial activities in the fibers, but also increases fabric specific gravity which leads to improvement of fabric drape (Figure 3.7) [49].

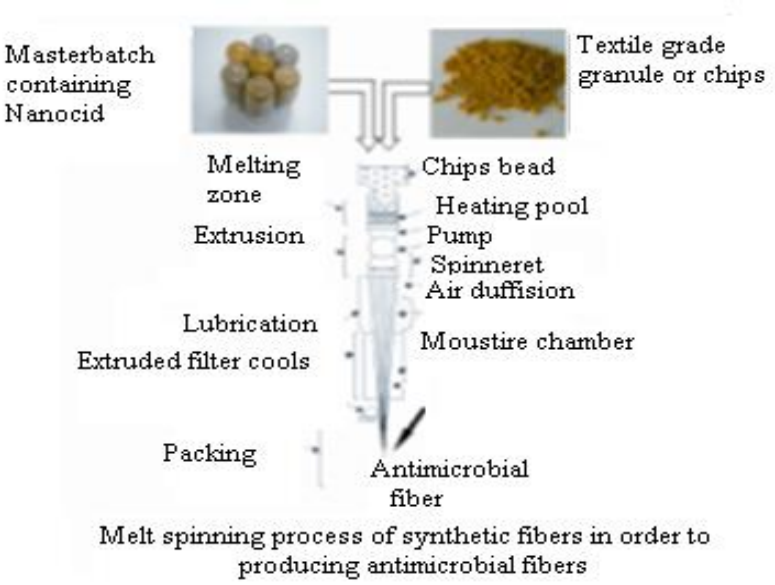


Figure 3.7.Spinning process [49]

3.2.3.3. Padding

In order to cause antibacterial activities in natural and synthetic textiles, depending on the production procedure, they can be padded. Period and temperature of the padding are effective in antibacterial stability and performance. Mixed textiles, clothes, bandages and all kinds of different textiles can be completed by this method.

By using this procedures, as it is shown in the picture below, nanoparticles are equally distributed on the textile surface; therefore, antibacterial activities are similar in all parts of the textile (Figure 3.8).

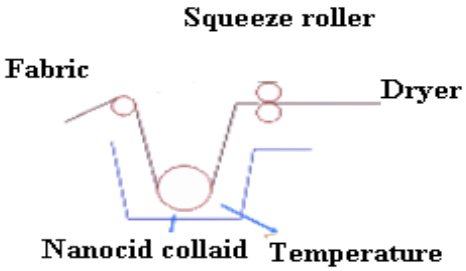


Figure 3.8.Padding [49]

3.2.4. Comparison between Conventional and New Technique

The most interesting application area of nanotechnology in textile industry is the finishing process of textiles. Coating is a common technique used to apply nanoparticles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nanoparticles, a surfactant, ingredients and a carrier medium. Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding. Of these methods, padding is the most commonly used. The nanoparticles are attached to the fabrics with the use of a paddler adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dye ability and so on [11].

Nanotechnology has a great role in textile industry. Textile fabrics are one of the best platforms for deploying nanotechnology. Fibers make for optimal substrates where a large surface area is present for a given weight or volume of fabric. The synergy between nanotechnology and the textile industry judiciously exploits this property of large interfacial area and the drastic change of energetic experienced by macromolecules or supra molecular clusters in the vicinity of a fiber when going from a wet state to a dry state. Nanotechnology also has real commercial potential for the textile industry. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will

lose their functions after laundering or wearing. In contrast, nanotechnology can provide high durability for fabrics, because nanoparticles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of nanoparticles on fabrics will not affect physical and mechanical properties such as hand, strength, air permeability and wetting [11].

3.2.5. Heat Setting for Coating Process

Heat setting of synthetic fabrics eliminates the internal tensions within the fiber generated during manufacture and the new state can be fixed by rapid cooling. This heat setting fixes the fabrics in the relaxed state. Setting of goods make it possible to use running properties of goods and also cross-linking by heating was adopted for stabilize the nanofibers to fabric [40].

3.3. Antibacterial Agents and Their Effect

Antibacterial agents are used to prevent three undesirable effects in textiles. The first includes the degradation phenomena like coloring, staining and deterioration of fibers. Because of their dye degradation potential, even some fungus can be used for removing dye from textile effluent. The second one produces unpleasant odor and the third effect is the increase of potential health risks. The conventional fibers and polymers not only show no resistance against micro-organisms and materials generated from their metabolism but also are most commonly prone to accumulation, multiplication and proliferation of micro-organisms into their surrounding environment. In fact, several factors such as suitable temperature and humidity, presence of dust, soil, spilled food and drink stains, skin dead cells, sweat and oil secretions of skin gland, also finishing materials on the textile surfaces can make textile optimal enrichment cultures for a rapid multiplication of micro-organisms. Therefore, many researchers have focused on the anti-bacterial modification of textiles. Recently, using natural material has been preferred for textile modification because of possible harmful or toxic effects of many chemical anti-microbial agents. Application of inorganic nanoparticles and their nanocomposites would be a good

alternative and consequently, they can open up a new opportunity for anti-microbial and multi-functional modification of textiles [50].

3.3.1. Requirements for Antibacterial Agents on Textiles

Requirements for antibacterial agents on textiles concern safety (producer and user), simple mode of application, wash and heat fastness and applicability without negative effects on the textile properties [36].

Several major classes of antibacterial agents are used in the textile industry. These agents are potent in their bactericidal activity, as indicated by their Minimal Inhibitory Concentration (MIC) values. However, their attachment to a textile surface or incorporation within the fiber substantially reduces their activity and limits their availability. Furthermore, the biocide can be gradually lost during the use and washing of the textile. For these reasons, large amounts of these biocides need to be applied to textiles to effectively control bacterial growth and to sustain durability [1]. Antibacterial agents are of relevance to a number of industrial sectors including environmental, food, synthetic textiles, packaging, healthcare, medical care, as well as construction and decoration. They can be broadly classified into two types, organic and inorganic [51].

i. Organic antibacterial materials are often less stable particularly at high temperatures and/or pressures compared to inorganic antibacterial agents. This presents a potential obstacle for the product formulation [51].
ii. Inorganic materials such as metal and metal oxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions. Of the inorganic materials, metal oxides such as TiO_2, ZnO, MgO are of particular interest as they are not only stable under harsh process conditions but also generally regarded as safe materials to human beings and animals. Some of the metal oxides e.g. MgO and CaO are essential minerals for human health. Other metal oxides such as TiO_2 and ZnO have been used extensively in the formulation of personal care products [51].

There are many compounds being used as antibacterial agents on textiles each with their own special properties and benefits and some are durable to washing [52].

3.3.2. Effect of Size and Shape on the Antibacterial Activity of Nanoparticles

The use of nanotechnology in the textile industry has increased rapidly, mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects and will lose their functions after laundering or wearing. Nanoparticles can provide higher durability for treated fabrics, with respect to conventional materials, because they possess large surface area and high surface energy that ensure better affinity for fabrics, which lead to increase in durability of the textile functions. Wash fastness is a particular requirement for textile and it is strongly correlated with the nanoparticles adhesion to the fibers. In order to increase the wash fastness, the nanoparticles can be applied by dipping the fabrics in a solution containing specific binder. Wash fastness can be further improved with the formation of covalent bonding between nanoparticles and the fabrics surface [53].

Nanoparticles possess a very high surface to volume ratio. This can be utilized in areas where high surface areas are critical for success. This could for example be in the catalytic industry; some nanoparticles actually have proven to be good catalysts. Some nanoparticles also show bactericidal effects and here a high surface to volume ratio is also important. In biology and biochemistry nanoparticles have attracted much attention. Nanoparticles are often in the range 10-100 nm and this is the size as that of human proteins [54].

3.3.3. Metals and Their Nano Composites

- **Tio_2 Nanoparticles**

Currently, TiO_2 nanoparticles have created a new approach for remarkable applications as an attractive multi-functional material. TiO_2 nanoparticles have unique properties such as higher stability, long lasting, safe and broad-spectrum

antibiosis. TiO_2 nanoparticles have been especially the center of attention for their photo-catalytic activities. This makes TiO_2 nanoparticles applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent, environmental purification, water and air purifier, gas sensors, and high efficient solar cell. The photo-activity property is strongly related to the structure, micro-structure and the powder purification [50].

- **Silver Nitrate and Silver Nanoparticles**

Silver nitrate is the most used antibacterial agent with a number of advantages. Among them, it is worth to note an excellent resistance to sterilization conditions, antibacterial properties with respect to different bacteria associated with a long-term of antibacterial efficiency. However, there are only a few antibacterial fibers available, mainly synthetic with high production cost and limited effectiveness. Advantages and disadvantages of AgNPs are given in Table 3.4.

Table 3.4.Advantages and disadvantages of silver applications [55]

Application	**Advantages**	**Disadvantages**
After treatment	Easy metallization, flexible costs	Bactericidal impact, not permanent, migration into skin possible (allergenic).
Silver coating	Permanent, no migration	High costs(up to 10 % Ag)
Antibacterial yarns	Antibacterial, no migration, permanent, multifilament, no environmental influences	Effect only given by contact with the skin and the release of silver ions.

Cotton yarns with antibacterial properties are most suitable for wound healing applications and other medical treatments thanks to their excellent moisture absorbance while synthetic based fibers are most suitable for industrial applications such as automotive tapestry and air filters. The silver-coated fibers were developed applying an innovative and low cost silver deposition technique for natural and synthetic fibers or yarns [56].

Silver ions and silver compounds have been extensively studied in various fields like antibacterial filters, wound dressing material, water disinfection, sensors, chemical

and gas filtration, protective cloth and air filtration, etc. Silver being a non-toxic metal has enjoyed reputation for antibacterial properties. It is considered to be the most toxic element to microorganisms in the following sequence: Ag>Hg>Cu>Cd>Cr>Pb>Co>Au>Zn> Fe> Mn [57].

As applications of silver have been known to possess strong antibacterial properties both in its metallic and nanoparticle forms hence, it has found variety of application in different fields.

Silver impregnated medical devices like surgical masks and implantable devices show significant antibacterial efficacy. Antibacterial properties of AgNPs;

- Broad-band effects against bacteria.
- Temperature-regulating properties.
- High heat conductivity, change of moisture (evaporation).
- Antistatic effect.
- Odor control [55].
- Environmental-friendly antibacterial nanopaint can be developed.
- Inorganic composites are used as preservatives in various products.
- Silica gel micro-spheres mixed with silica thio-sulfate are used for long lasting antibacterial activity.
- Treatment of burns and various infections [58].

There are concerns about the narrowness of the size distribution of the nanoparticles, and the degree of agglomeration. Baglioni et al., with respect to agglomeration, nanoparticles have a high ratio of surface area to volume, and it is much more energetically favorable for them to reduce their surface area by coalescing together. Thus, materials that melt at high temperatures if they are in bulk form may fuse together at much lower temperatures if they are nanoparticles. Before a process can be considered commercially viable, there are additional economic concerns. Many processes for nanoparticles have been developed at the laboratory scale, but they are not yet commercialized because of constraints, including scalability considerations and precursor costs [11].

- **ZnO Nanoparticles**

Zinc oxide (ZnO) is widely used in different areas because of its unique photo-catalytic, electrical, electronic, optical, dermatological, and antibacterial properties. For these applications, the nanoparticles need to be dispersed homogeneously in the different matrices, and a number of new synthetic strategies have been developed in order to prevent particles agglomeration, and increase the stability of ZnO nanoparticles dispersions. This is possible as ZnO has three key advantages.

i. It is a semiconductor. It is an important functional oxide, exhibiting excellent photo-catalytic activity.
ii. ZnO is bio-safe and biocompatible, and can be used for biomedical applications without coating.
iii. ZnO could be one of the most important nanomaterials in future research and applications. The application of nanoparticles in textile materials is the objective of several studies aimed at producing finished fabrics with different performances. For example, nano-Ag has been used for imparting antibacterial properties, nano-TiO_2 for antibacterial and UV-blocking properties.

Metal oxide nanoparticles are more preferable than nano silver due to cost effectiveness. In fact, zinc oxide and titanium dioxide are non-toxic and chemically stable under exposure to both high temperature and capable of photo-catalytic oxidation. Furthermore, nanoparticles have a large surface area to-volume ratio that results in significant increase of the effectiveness in photo- catalytic oxidation activity when compared to bulk materials [53].

- **Copper Nanoparticles**

Copper nanoparticles are submicron particles with antibacterial properties. The observation results are confirmed that copper nanoparticles anti-bacterial activity is clearly less than that of silver nanoparticles and deposition of Cu nanoparticles on the poly propylene (PP) nonwoven is used for the improvement of UV protection properties [50].

The antibacterial and antifungal properties of copper are effective in reducing the growth of various microorganisms. The antibacterial efficacy of technologically appealing materials containing copper based active powders or pigments in fabrics, paints or as coatings, aqueous copper solutions, complex copper species or copper-containing polymers has led to their use as antifungal compounds. Copper oxide (CuO) containing phosphate-based glass fibers (PGF) have been developed for potential use in wound healing applications [59].

- **Gold Nanoparticles**

Gold nanoparticles are known as a novel biomedical application. Their potent antibacterial effectiveness against acne or scurf and no tolerance to the antibiotic have caused their commercial usage in soap and cosmetic industries.

Gold nanoparticles is proposed the inhibit growth and multiplications of different microbes with Au nanoparticles efficiently against gram positive, gram negative and fungi [52]. Characteristics of inorganic nano structured materials on textiles are given in Table 3.5.

Table 3.5.Characteristics of inorganic nano structured materials on textiles [53]

Inorganic nano structured materials	Characteristics
TiO_2	Anti-bacterial, self-cleaning, UV-protecting, super hydrophobic
Silver	Anti-microbial, disinfectant, anti-fungal, UV-protection
ZO_2	Anti-bacterial, super hydrophobic
Copper	Anti-bacterial, , UV-protection
Clay	Anti-bacterial, UV absorber
Gold	Anti-bacterial, anti-fungal

3.3.4. Non-Material Antibacterial Materials

- **Quaternary Ammonium Compounds**

Quaternary ammonium compounds (QACs), particularly those containing chains of 12–18 carbon atoms, have been widely used as disinfectants. These compounds carry

a positive charge at the N atom in solution and inflict a variety of detrimental effects on microbes, including damage to cell membranes, denaturation of proteins and disruption of the cell structure. During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antibacterial ability as long as the compound is attached to textiles [1].

The attachment of QAC to a textile substrate is believed to be predominantly by ionic interaction between the cationic QAC and anionic fiber surface. Quaternary ammonium compounds (QACs) have a large variety of usage areas from cosmetics to clothes softeners, but especially they are known to be good disinfectants. In proper concentrations, they are very effective against fungal attack. The antibacterial action of the QACs is based on their damaging surfactant-like interaction with the membrane of bacteria resulting the loss of the membrane permeability. At convenient concentrations, they can cause cell leakage and the death of the cell. Quaternary structures are effective on both gram positive and gram negative bacteria, but they have a stronger antibacterial effect on gram positive ones, since gram negatives have an extra protective membrane [1].

- **Irgasan**

As an antibacterial, irgasan, it is commonly found in detergents, kitchen sponges, cosmetics, antibacterial creams, paint, textiles, curtains, sandal foot beds. During fabric use, the agent migrates to the surfaces of the treated textiles at a slow yet sustained rate to provide antibacterial efficacy. To achieve a more durable finishing, irgasan has been inserted into the hydrophobic cavity to form an inclusion complex which was then embedded in a polymer film or fiber, or encapsulated in microspheres which were subsequently attached to viscose. Irgasan can also be directly incorporated into synthetic polymers through melt-mixing or suspension polymerization [60].

- **Chitosan**

Chitosan is one of the most abundant natural antibacterial agents. Different from most other natural polymers, chitosan has high reactivity and process ability for its

specific molecular structure and polycationic nature. The antibacterial activity of chitosan was observed against a wide variety of microorganisms including fungi, algae, and some bacteria. Chitosan has several advantages over other type of disinfectants because it possesses a higher antibacterial activity, a broader spectrum of activity, a higher killing rate. Many attempts have been taken up to improve the antibacterial activity of chitosan, such as structural modification, adjustment of molecular factors, and forming complexes with other antibacterial materials. [61].

3.4. Implications of Antibacterial Agents

Inorganic and metallic-based nano structured materials have created a new interesting field in all sciences for the continuous investigations due to their undeniably unique properties. Their applications have already led to the development of new practical productions. Considering the indubitable role of textiles in human life, these new fields in textile industry have been increasingly welcomed. However, designing new applicable and affordable techniques for manufacturing scale-up production will not only create a new field of study, but meet the expanding human requirements [50].

3.4.1. Health and Environmental Risks of Silver Nitrate and Silver Nanoparticles

Recently, with increasing the public knowledge about health care in the world, people are increasingly concerned about the rise of possible subsequent diseases caused by new technologies including nanotechnology and application of nano materials especially inhalation during manufacturing or usage. It seems that the absorption of nano silver for various routes of exposure has been identified. However, it remains unclear whether nano silver particles or silver ions, released from nano silver at the side of application, were absorbed into the body. Silver nitrate is not a trace metal and serves no physiological role in the human body. Silver absorbed into human tissues from antiseptic respiratory sprays, implanted medical devices, wound dressings or dwelling catheters can be expected to reach the systemic circulation, mostly as a protein complex. Theoretically, silver can be deposited in any

tissue in the human body but the skin, brain, liver, kidneys, eyes and bone marrow have received greatest attention [62]. Selected textile biocides are given in Table 3.6.

Table 3.6.Tolerance to selected textile biocides [63]

Agent	Dermal resorption	Toxicity	Allergenicity
Irgasan	Yes	Little	low
Silver	No	Little	no
Quaternary ammonium salt	Yes	Moderate to highly toxic	moderate
Chitosan	No data	No hint(biologically deduced)	no
Copper compounds	No	Essential trace element, dose-dependent toxicity	no

3.4.2. Human and Environmental Risk Assessment of Irgasan

Irgasan is class of chemicals suspected of causing cancer in humans. There have been reports of individuals developing contact dermatitis (skin irritation). There has been some evidence also that irgasan cause photo allergic contact dermatitis, which occurs when skin exposed to irgasan has also been exposed to sunlight. A rash may result on the face, neck, back of hands, or sun-exposed areas of the arms. Irgasan can interfere with the body's thyroid hormone metabolism, lowering body temperature and causing a "nonspecific depressant effect on the central nervous system" of mice.

Symptoms of internal exposure, even in small amounts, may include cold sweats, circulatory collapse, convulsions, coma, and death. Long-term and repeated exposure to many pesticide products can damage the liver, kidneys, heart, and lungs and cause paralysis, sterility, brain hemorrhages, hormonal disruption, and immune suppression [64].

3.4.3. Human and Environmental Risk Assessment of Chitosan

Chitosan is biodegradable and biocompatible. Chitosan has lower toxicity toward mammalian cells. The antibacterial action of chitosan is influenced by both intrinsic factors and the environmental conditions, such as the type of chitosan and

microorganisms, the degree of polymerization, the degree of deacetylation, and the pH of medium [61].

3.4.4. Human and Environmental Risk Assessment of Quaternary Ammonium Compounds

Quaternary ammonium compounds can cause toxic effects by all routes of exposure including inhalation, ingestion, dermal application and irrigation of body cavities. Exposure to diluted solutions can cause mild and self-limited irritation. Concentrated solutions of quaternary ammonium compounds are corrosive and can cause burns to the skin and the mucous membranes. They can produce systemic toxicity due to their curare-like properties. They can also cause allergic reactions [65].

3.4.5. Human and Environmental Risk Assessment of Metal Oxide

The primary human health concern for the extremely small size of nano materials is that they may be introduced into and affect the body in ways completely different than their bulkier macro cousins. Nanosized particles were found to traverse through lung tissue in unexpected ways, gaining access to blood and lymphatic systems. The potential for different human health related characteristics such as enhanced adhesion, reactivity and absorption means that current methodologies for risk assessment simply are not applicable and safety data drawn from non-nano counterpart materials may be irrelevant. For example, when inhaled, nanoparticles are deposited more efficiently and deeply into the respiratory tract than non-nano materials, and these nano materials may evade human body defense mechanisms that trap larger particles [66].

Using commercially available raw nanoparticles to test toxicity is essential to understand human health risk and environmental impact, as this addresses unintended exposure. It is equally important to test surface modified nanoparticles, as these modified nanoparticles have different kinetics and bioavailability than the native nanoparticles, and they are frequently applied directly on human body for purposes such as disease diagnostics, treatment, and prognostics.

The toxicological reveals a trend among these transition metal oxides. TiO_2 is less toxic than CuO and ZnO in human cell lines. It was investigated the toxicity of oxides of Cr, Mn, Fe, Co, Ni, Cu, and Zn, each of which is widely used in industry and is in the same period as Ti. Toxicity increased with atomic number [67].

Gold nanoparticles were below detection limits in the brain tissue, gills and musculoskeletal samples. Gold nanoparticles were only detected in the combined organ and gut content samples, suggesting it was not moving through the circulatory system of the animal or being absorbed through skin or gill contact [68].

3.5. Evaluating the Effectiveness of Antibacterial Textiles

To record the quantitative reduction of bacteria by antibacterial textiles, test systems have become established which specifically record this process. In Table 3.7 is show compare that all of the most important recognized international test methods for antibacterial textiles.

Table 3.7.Overview of the most popular standards to test the performance of textiles, fibres, yarns and polymers for antibacterial effectiveness [55]

Designation	Title	Principle
SN195920-1992	Textile fabrics: determination of the antibacterial activity	Agar diffusion test
SN 195921-1992	Textile fabrics: determination of the antimycotic activity	Agar diffusion test
EN14119:2003-12	Textiles-evaluation of the action of microfungi	Agar diffusion test
ASTM E 2149-01	Standard test method for determining the antibacterial agents under dynamic contact conditions	Challenge test
JIS Z 2801	Antimicrobial products-test for antibacterial activity and efficacy	Challenge test
JIS L 1902-2002	Testing for antibacterial activity and efficacy on textile products	Challenge test

3.5.1. Qualitative tests

3.5.1.1. Agar diffusion method

Bacteriostasis agar is dispensed in sterile petriplates. 24 hours broth cultures of the test organisms (E. coli and S. aureus) should be used as inoculums. Using sterile cotton swab the test organisms were swabbed over the surface of the agar plates. The test fabrics (fabrics treated antibacterial agents) & Control (fabrics treated without agents) can be gently pressed in the center of the mat culture. The plates should be incubated at 37°C for 18-24 hours (Figure 3.9 – 3.10).

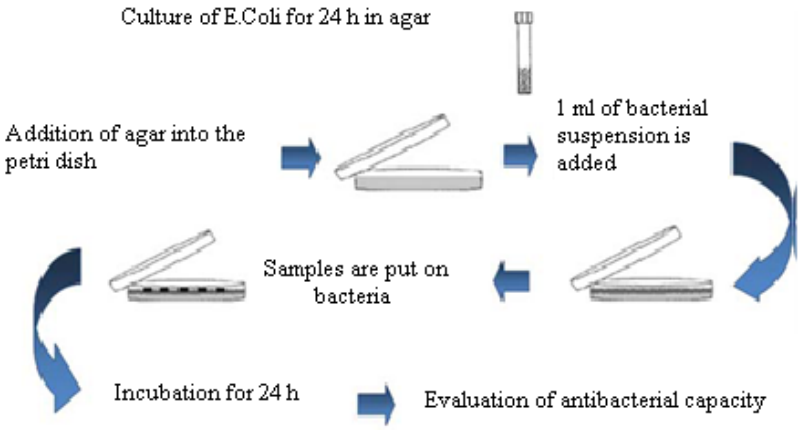


Figure 3.9.Method of antibacterial activity through diffusion test in Agar [56]

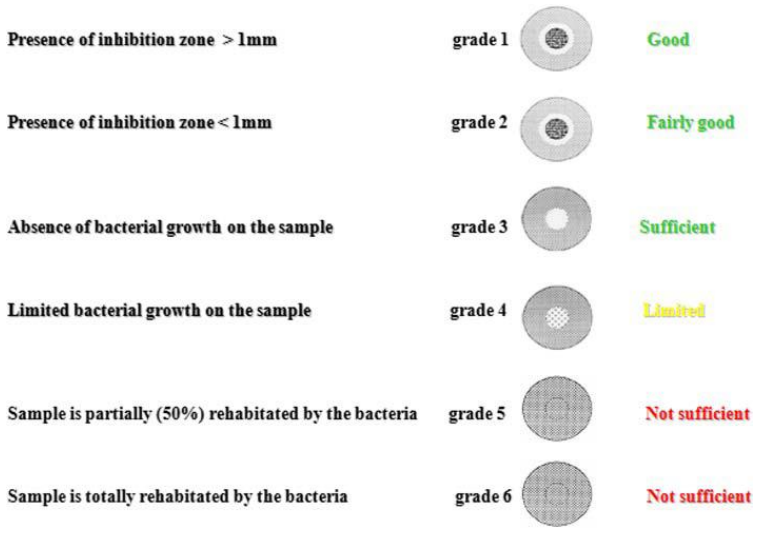
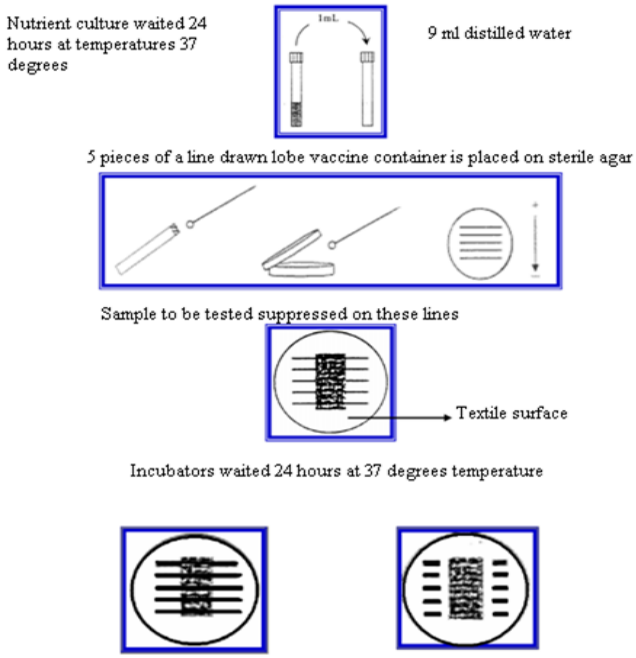


Figure 3.10.Different levels of antibacterial capacity as a function of the presence and size of inhibition growth area around the sample [56]

3.5.1.2. Parallel streak method (AATCC Test Method 147)

Using a 4 mm inoculating loop, one loopful of the diluted inoculums was transferred to the surface of TSA plates by making five streaks approximately 60 mm in length, spaced 10 mm apart covering the central area of a standard petri plates without a refilling of loop. Test specimens were cut with a rectangular die (25x50 mm) and were placed to inoculate TSA transversely across the five inoculums streaks. Petri plates were incubated for 18-24 h at 37 ^{0}C. Incubated plates were examined for interruption of growth along the streaks of inoculums beneath the specimen and for a clean zone of inhibition beyond its edge [64].



a) Non- antibacterial fabric b) Antibacterial fabric

Figure 3.11. Construction of the parallel streak method[64]

3.5.2. Quantitative Tests

3.5.2.1. Percentage Reduction Test

Specimens of the test material are shaken in a known concentration of bacterial suspension and the reduction in bacterial activity in standard time is measured. The efficiency of the antibacterial treatment is determined by comparing the reduction in

bacterial concentration of the treated sample with that of control sample expressed as a percentage reduction in standard time.

The evaluation of modified test is made on the basis of the percentage reduction of bacteria by the sample. Percentage reduction is calculated using the following formula.

$$R = (A-B) / A$$

Where R is percentage reduction, A is the number of bacteria in the broth inoculated with treated test fabric sample immediately after inoculation i.e., at zero contact time and B is the number of bacteria recovered from the broth inoculated with treated test fabric sample after the desired contact period (18 hours) [64].

3.5.3. Washing Tests

There are different test methods to check the durability fastness to washing. The selection of the test method depends on; customer's requirements process type (dyed, print, white or coating) quality construction, some most commonly used methods are:

- ISO-105-C01
- ISO-105-C02
- ISO-105-C03
- ISO-105-C04
- ISO-105-C05
- ISO-105-C06

The test methods from C01 to C05 are established to check the color fastness to washing of color textiles and cover the range from mild to severe. These test methods are not intended to reflect the comprehensive laundering procedures. The selection of washing test method depends on; construction of the fabric, type of printing or dyeing and use of the fabric [69].

3.5.4. Antibacterial Textiles

The product groups with possible applications for antibacterial textiles include apparel, interior trim and upholstery, sports and leisure, automotive interiors, protective clothing, medical textiles and cosmetics. In apparel-, interior trim- and automotive applications, these functional textiles could be used to produce "self-cleaning" or "anti-odor" clothes, furniture textiles or automotive interiors.

In household products, antibacterial textiles could possibly be incorporated into kitchen clothes, sponges or towels. In the medical sector, possible products include antibacterial wound dressings, patient dresses, bed lines or reusable surgical gloves and masks. Further thinkable applications are protective face masks and suits against biohazards or cosmetic products as antibacterial face masks or toothbrushes.

Various companies furthermore offer their industrial clients textile treatment technologies, additives or fabrics with antibacterial properties offers an antibacterial textile treatment which is used on a wide range of products including antibacterial underwear, kitchen sponges or clothes, bed sheets, towels, carpets or sport helmet padding and both offer antibacterial coating technologies, while antibacterial polymer master batches are available from (Table 3.8). Antibacterial fabrics which can be processed into outdoor clothing or household products were developed by [70].

Table 3.8.Antibacterial textiles and their fields of application [31]

Medicine	**Sport and leisure**	**Outdoor**	**Technology**	**Domestic**
Support stockings	Shoes	Jackets	Wall hangings	Curtains
Antidecubitus mattress	Socks	Tents	Roof coverings	Coverings
Incontinence liners	T-shirt	Uniforms	Facade linings	Cloths
Encasings	Cycle wear	Personal protective	Air filters	Bath mats
Bedding filling	Team kit	Astro turf	Automotive	Sanitizers
Pillows	Jogging suits	Sunshades	Geotextiles	Underwear
Implants		Awnings		Carpets

Together with the increase in new antibacterial fiber technologies and possibilities in the hygienic and medical applications, the demand for proper test systems to evaluate the effectiveness and safety of antibacterial textiles rose [55].

Textile fibers as well as clothing treated with specific chemicals are available, so that clothes can provide antibacterial properties. The function of antibacterial treatment of clothing is to avoid malodor created by bacterial degradation of sweat. Thus, the clothing can remain fresher for a longer period. Antibacterial treatment of clothing belongs to two groups:

i. The antibacterial chemicals are built-in the textile fibers during their manufacture. It is claimed that the antibacterial property of clothing, manufactured using such fibers, lasts during the whole life of the product.
ii. The clothing is coated with some antibacterial compound using various techniques.

- **Antibacterial Wound Dressings**

Presently silver containing wound dressings represent the state of the art. Wound dressings which do not release antibacterial agents into the tissues are preferable especially to prevent disturbance of the healing process [55]. New types of dressing should not only help to reduce costs in the health care sector; they should also help to accelerate the healing process, promote improved mobility, minimize pain when changing dressings and generally improve quality of life for the patient. This is only possible if specialists from the textile and medical sectors work closely together during the development of this type of innovative system for dressing wounds (Figure 3.12) [71].

Figure 3.12.Wound dressing [71]

Antibacterial agents in the fabric of socks eliminate the bacteria which cause smelly feet and fungal infections. People have known about the anti-bacterial properties of silver for centuries even the Romans used it to dress wounds.

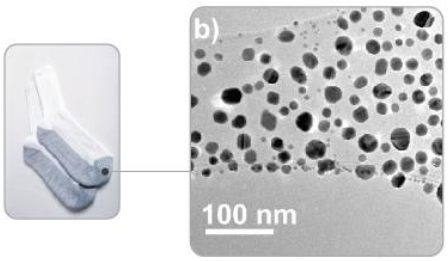


Figure 3.13.Antibacterial socks containing AgNPs [72]

Nowadays thanks to nanotechnology AgNPs can be invisibly embedded in many materials, including fabrics, where they perform their anti-bacterial effect. Silver ions released from the nanoparticles are poisonous to the bacteria that can thrive in the warmth and moisture of your feet and socks, so the bacteria in these socks are removed and the socks remain cleaner. Since AgNPs are not toxic to humans, many more consumable products have been developed that use this technology [72].

Statistics estimate a number of approximately 1.25 million patients with the possibility of ulcerations and the risk of an amputation. The diabetic foot syndrome is a long-term consequence. The feet and lower legs belong to the most sensitive body parts of a diabetic regarding the sensor motor and autonomous neuropathy. 40–70% of all non-traumatic amputations of the lower extremities are carried out on patients with diabetes mellitus. In the therapy of diabetic foot syndrome, local pressure release of lesions takes priority and therefore the supply with dimensionally accurate shoes [55].

- **Antibacterial Effect of Surgical Masks Coated with Nanoparticles**

A facemask is essential for protection of healthcare workers against some infections. However, there are certain factors that may compromise the protective effect of a facemask. In order to minimize the risk of transmission of infectious agents by contaminated protective equipment like masks, an antibacterial nanoparticle coating

has been developed. These chemical agents were pulverized into particles less than 100 nm in size so as to increase their surface area, and to improve their bacterial action. Silver or its compounds have been recognized for their broad-spectrum antibacterial activities [73].

- **Filtration**

Filtration media have been found to foul as a result of microbial slimes coating the surface causing a reduction of filtration capacity, we have noted. Filtrate quality can also be negatively affected by the presence of microorganisms on the filter media. Swimming pool and aquarium filters can be plugged by large amounts of algae or bacteria. Treatment of the filter media with antibacterial agent has been found to both preserve the life of the filter media and purify the filtrate. Degrees of effectiveness vary considerably depending on the substrate and the fluids being filtered. Evaluation of this technology to filtration of metalworking fluids, cosmetics, paints and foods is currently in progress [73].

- **Carpet**

Carpet is the first choice for covering the floor; it is a very suitable substrate for growing pathogenic microbes. Carpet is a famous textile, it is a very suitable substrate for growth of microorganisms such as pathogenic microbes, due to direct contact with human body, long washing periods and laying on the floor. The silken carpet in comparison with other carpets has a special position, for this reason it needs some special methods to maintain the quality of these goods, and protect from the action of microorganisms. Many antibacterial agents have been used as antibacterial agent for hygiene finish or antibacterial protection finish. Between these antibacterial agents quaternary ammonium salts exhibit marked antibacterial activity against a wide range of bacteria. These compounds have a central nitrogen atom which is joined by four organic radicals and one acid radical. Quaternary ammonium halide cationic surfactants are widely used for antibacterial surface-active and detergent properties [73].

- **Civil Engineering**

Proper design and choice of materials, we can state, have minimized the effects of microorganisms in most civil engineering applications. In most cases a variety of polypropylene fabrics are available for applications including roadbed stabilization, drainage ditch liners, pond liners and erosion control. Actual microbial degradation of the polypropylene fabrics is minimal. Yet, microorganisms (bacteria and fungi) have been shown to live on the surface of these materials and could affect water transport and/or degrade susceptible binders. The potential to improve value and performance of nonwovens used in civil engineering applications has been demonstrated but reduction to "real world" practice has not yet been done [74].

CHAPTER 4
MATERIALS AND METHODS

4.1. Introduction

In this chapter, the materials and their properties used in the experiments are given. The apparatus used in electrospin setups and experimental parameters applied on these systems are also given. Finally, experimental devices for the characterization of the material are explained.

Within the scope of this research, we designed fabrics which have antibacterial effect. For this purpose, the surface of fabrics was covered with an invisible layer by electrospin and electrospray methods. Silvernanoparticles, silver nitrate and irgasan were added to PAN and PA6 solutions to make the solution antibacterial. The antibacterial activity of nanofibers were evaluated against S. aureus (Staphylococcus aureus, gram positive) and E. coli (Escherichia coli, gram negative) with a parallel streak method. The surface properties of the nanofibers and the influence of agents on the textural properties were also studied by scanning electron microscopy (SEM).

4.2. Materials

4.2.1. Polyacrilonitril (PAN) and Dimethylformamide (DMF)

Polyacrilonitril was used as a main polymer. It was supplied from AKSA and N, N-Dimethylformamide purchased by SIGMA was used as a solvent for PAN. DMF is used as the common solvent which helps to undergo spontaneous slow reduction at room temperature to form antibacterial agents.

Table 4.1 shows all the concentration values which were tested to obtain the most suitable concentrations. Experimental all these values were examined and 5% concentration was determined as the most suitable value for electrospin application. However, bets results were obtained at 2% concentration for electrospray applications. Attachments of nanofibers or nanoparticles to the surface of sample fabrics were examined by means of rubbing test at each concentration. Then those samples were examined by trinocular microscope and SEM. As a result, these concentrations provide stronger bonding between fabric and antibacterial agents. Thus, the concentrations of solutions were decided as 5 % (wt) and 2 % (wt) for electrospin and electrospray processes, respectively.

Table 4.1.Concentration values of methods

Type of Method	**Range of Concentration**
Electrospin Method	12 % - 10% - 8% - 6% - 5% - 4% - 3%
Electrospray Method	0.1% - 0.5% - 1% - 1.5% - 2%

Figure 4.1 and Figure 4.2 show microscopic image of nanofibers obtained from electrospin method and electrospray method.

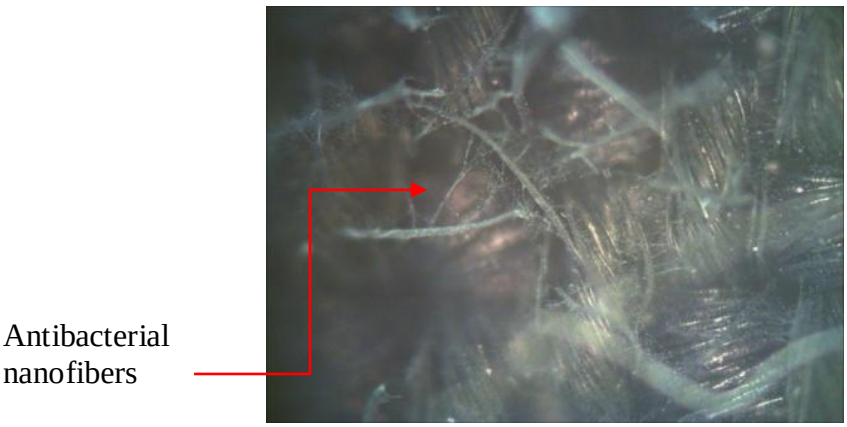


Figure 4.1.Microscopic image of nanofibers obtained by electrospin method

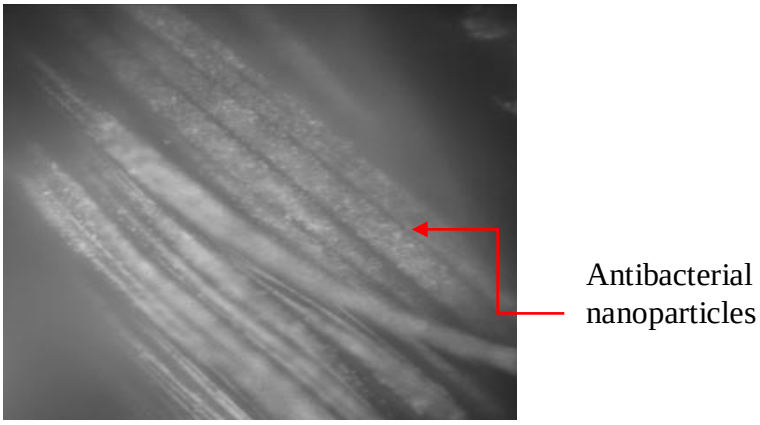


Figure 4.2.Microscopic image of nanoparticles obtained by electrospray method

4.2.2. Polyamide (PA6) and Formic Acid

Polyamide polymer was also used as an alternative polymer for this study in order to improve the bonding property of antibacterial material to cotton fibers by means of thermo fixing process. PA6 was supplied from SENTEFIL (Gaziantep) and Formic acid was purchased by SIGMA. The most suitable concentration was determined by systematic experimental study as 6 % for electrospin and 1.5 % for electrospray process. Table 4.1 shows the concentration values examined experimentally according to the methods. These concentrations provide stronger bonding between fabric and antibacterial agents.

4.2.3. Antibacterial Agents

Silver nitrate, AgNPs and irgasan agents have been studied as antibacterial agents, which have shown antibacterial reactions against microorganisms. Each of antibacterial agents was purchased by Sigma Aldrich.

4.2.4. Knitted Cotton Fabric

100% cotton fabric (rib weave, 143 g/m^2) was used for the application purpose. Characteristics of the cotton fiber, mechanical and physical properties of yarn are given in Table 4.2.

Table 4.2.Characteristics of cotton fiber and yarn

Cotton fiber data	
Cotton type	**Upland cotton**
Fineness (Micronaire)	4,5
Upper half mean length(mm)	29,17
Yarn Data	
Yarn Type	**Combed Ring**
Yarn Kind	100% Cotton
Yarn Count (Ne)	30/1
Yarn Twist (RPM)	776
Strength (cN/Tex)	18,82
Unevenness (%U)	9,3
Thin Places -50% (1km)	0
Thick Places +50% (1km)	10

Fabric samples were generously produced and dyed with three reactive dyes by Sanko Textile. Table 4.3 shows the knitted fabric properties.

Table 4.3.Construction properties of the knitted fabrics

Fabric Type	**Thickness (mm)**	**Courses/cm**	**Wales/cm**	**Fabric weight (g/m^2)**
Rib fabric (RR)	0,64	19	12	143

Before dying, fabric samples were bleached at 95°C and 60 minutes, according to the bleaching recipe given in Table 4.4. Bleaching and dyeing processes were carried out in industrial scale. The dyes which were reactive azo dyes were applied by using the dyestuff manufacturer's recommendations as given in Table 4.4.

Table 4.4.Process conditions

Bleaching Recipe		**Washing conditions after bleaching**
Peroxide	1,5 g/L	80°C rinsing (10 minutes) 50°C neutralization (peroxide enzyme) (10 minutes)
Caustic Soda	2 g/L	
Wetting agent (MepzowetH)	1 g/L	
Sequestering agent (Mepzoiyon KS)	1 g/L	
Liquor ratio	1/8	
Temperature, Time	95 °C, 60min.	
Reactive Dyeing		**Washing conditions after reactive dyeing**
Iyozol Dyes	Blue BRX	50°C rinsing (10 minutes) 50°C neutralization (acetic acid-1g/L) (10 minutes) 95°C soaping (10 minutes) 90°C soaping (10 minutes) 80°C soaping (10 minutes) 50°C rinsing (10 minutes) Cold rinsing (10 minutes)
% omf	1%	
Salt	40g/L	
Sodium Carbonate	8g/L	
Liquor ratio	1/8	
Temperature	60 °C	
Time	55 min.	

To enhance the barrier property while maintaining sufficient comfort, antibacterial polyamide and polyakrilonitril nanofibers were fabricated with additives through electrospin and electrospray. The cotton fabrics, cut to the size of collector dimensions, were coated with antibacterial nanofibers by electrospin (90second) and electrospray (90second) methods. The fabrics, coated PA6 antibacterial nanofiber, were treated for 90 seconds at 215°C for thermo fixation. Then the fabric was washed up to 20 washing cycles, later the fabric was air-dried.

4.3. Methods

4.3.1. Electrospin Apparatus

A detailed literature survey has been carried out prior to the establishment of an electrospin set up. The electrospin set up was designed and manufactured for this study by the support of University of Gaziantep (BAPYB under Grant No. MF.08.04). The experimental set up is seen in Figure 4.3. Experiments reported in this thesis have all been done using this set up at.

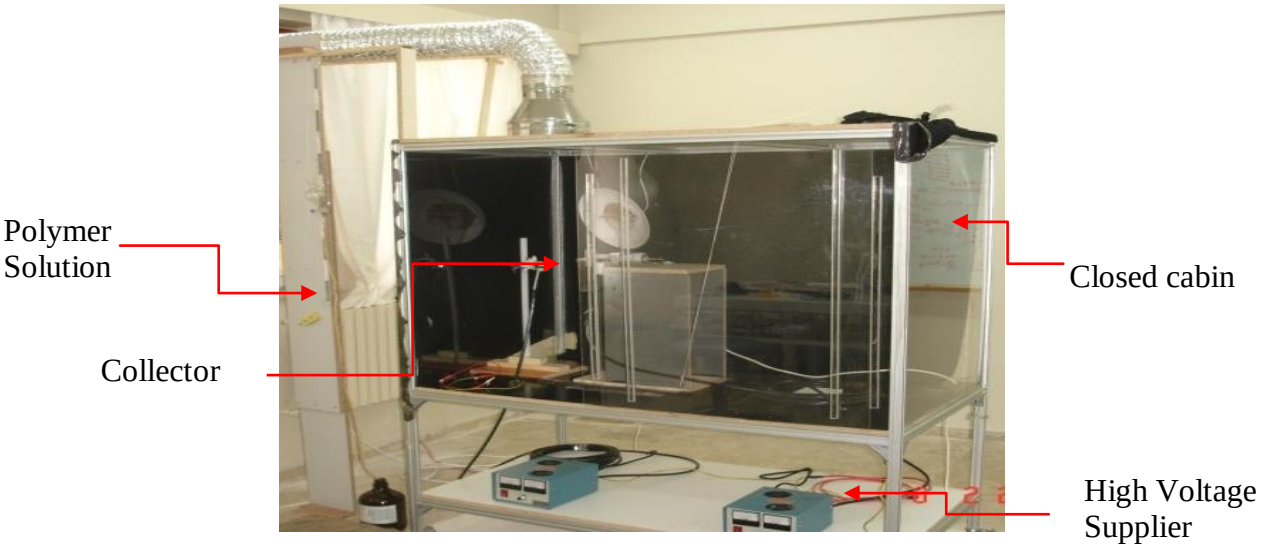


Figure 4.3.Electrospin set up

In the current work, a medical serum set was used to adjust the flow rate. Polymer solution was filled in it by the help of syringes. The flow was adjusted manually by changing the level of the polymer solution bottle with respect to spinning jets. Finally, desired flow could be provided.

There are several collector types used in the electrospin process. Their main functions are to provide grounding and to collect fibers. In this study, a rectangular shaped galvanized thin metal plate coated with aluminum foil was used as collector. The dimension of the plate was 150 x 100 mm.

The closed cabin that was used for the purpose of realizing the electrospin process in it. This cabin helps to avoid any electrical discharge. Furthermore, the cabin was used as protector against the unwanted exterior effects, while electrospin process was taking place.

Two high voltage power suppliers, which are able to apply voltage between +50kV and -50kV, were used in all experiments. Voltage can be gradually regulated. It has a high voltage output wire for connecting to electrode with a mini alligator jaw clipped to collector or feeding unit. The output voltage can both be adjusted before or during the electrospin process.

Electrospin was conducted on a moving plate onto which sample fabrics were wrapped around. A positive voltage ranging from 20 to 35 kV was applied at the needle tip with respect to a grounded metal collector, which was placed at a distance of 10 cm from the spinning nozzle. The time required for coating of antibacterial nanofibers in the present work for electrospin and electrospray 90 second was sufficient to show good antibacterial activity. The electrospin process is given in Figure 4.4.

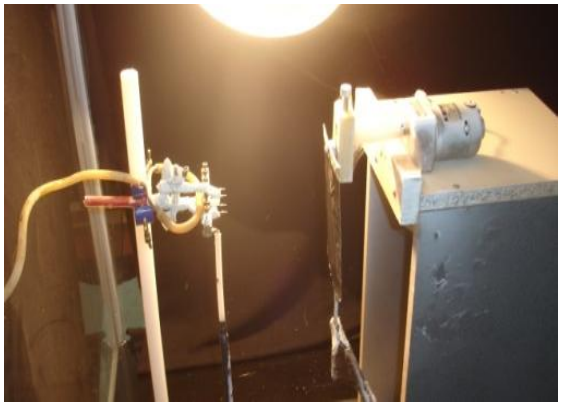


Figure 4.4.Solution electrospin set up

4.3.2. Experimental Parameters of Electrospin and Electrospray

Temperature, distance, humidity and voltage parameters were studied experimentally to obtain durable nanolayer on fabric. Emphasized values in Table 4.5are the best durable values.

In the electrospin process, the solutions of PA6 with formic acid and PAN with dimethylformamide were used. Table 4.6 summarizes the experimental parameters used in obtaining nanofibers from PAN and PA6 polymer solutions and Table 4.7 shows antibacterial agents and concentration.

Table 4.5.Experimentally examined values according to the methods

Parameter	**Value**
Temperature(ºC)	28- **25**-21-18-15-12-9-6-3
Distance (cm)	15-12-**10**-8-6
Humidity (%)	60-55-50-**45**-40-35-30-25-20
Voltage (kV)	40-**35**-30-25-**20**-15

Table 4.6.List of experimental variables in electrospin and electrospray

Material	**Antibacterial Solution of PA6 with Formic Acid**		**Antibacterial Solution of PAN with DMF**	
	Electrospray Method	Electrospin Method	Electrospray Method	Electrospin Method
Polymer Concentrations	wt.1.5 %	wt. 6 %	wt. 2 %	wt. 5%
Applied Voltages	35 kV/cm	20 kV/cm	35 kV/cm	20 kV/cm
Distances	10 cm	10 cm	10 cm	10 cm
Time	90 second	90 second	90 second	90 second
Temperature	25 ± 5^0 C (room temperature)	25 ± 5^0 C (room temperature)	25 ± 5^0 C (room temperature)	25 ± 5^0 C (room temperature)
Humidity	%45±5 RH	%45±5 RH	%45±5 RH	%45±5 RH
Flow Rate	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.5 ml/h

Table 4.7.Percantage of antibacterial agents

Antibacterial Agents	**Concentration (%)**
$AgNO_3$	0.5- **3** (interval 0,5)
AgNP	0.5- **3** (interval 0,5)
Irgasan	1 - **3** (interval 1)

In order to prepare the spinning solution, firstly antibacterial agents was dissolved/ (mixed) in DMF solvent within beakers. Later PAN powder was added into solvent under stirring. The solution was stirred for 3 h at 80 ^{0}C until all powders had been dissolved completely. In this way, a clear, homogeneous, and viscous solution was

obtained and used as the feeding solution for electrospin. Then, the antibacterial solutions were used for fabrication of nanofibers by electrospin.

Three different antibacterial agents were used to in PAN polymer solutions. Dimethylformamide was used as a solvent. The concentrations of solutions were 2 % and 5 % for electrospray and electrospin processes, respectively.

Similarly, the concentration of PA6 solution was 1.5 % for electrospray and 6 % for electrospin process. Unlike the PAN antibacterial solution, PA6 solution was prepared at room temperature. PA6 granule and formic acid was stirred for 3 hours with antibacterial agents. The color was turned from colorless to yellow–brown due to AgNPs. The prepared solutions were then subjected to the electrospin experiments.

The polymer solution was placed into a 10 mL glass syringe fitted with a needle and with an inner diameter of 0.4 mm. The polymer solutions were electrospun with a fixed mass flow rate of 0.5 mL/h. The applied voltage differences were 20 kV for electrospin and 35 kV for electrospray applications**.**

4.3.3. Bacterial Strains and Culture Condition

Gram-negative (Escherichia coli ATCC 25922) and Gram-positive (Staphylococcus aureus ATCC 6538) bacteria were used in the study for antibacterial susceptibility testing. The strains were cultured on nutrient agar and incubated aerobically at 37 ^{0}C overnight [64].

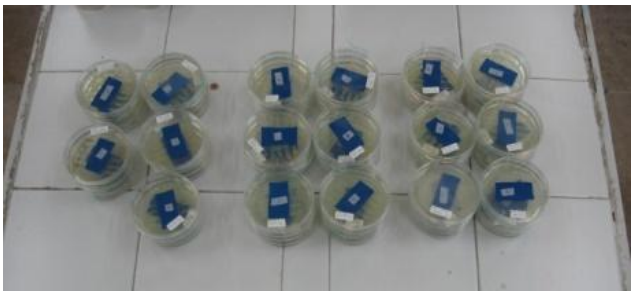


Figure 4.5.Experimental S. aureus samples

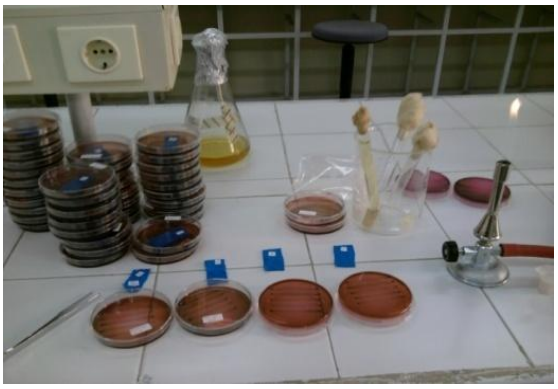


Figure 4.6.Experimental E. coli bacteria samples and strains

4.3.4. Thermo-fixation of Nanofibers

Thermo-fixation process was applied to some sample fabrics which have been coated by antibacterial PA6 nanofibers in order to improve the bonding between cotton fibers and antibacterial agents. Therefore, cotton fabric samples were treated for at 215^0C for 90 seconds in an oven.

4.3.5. Washing Operations

In this study, 1, 5, 10 and 20 washing cycles are applied to the fabrics treated by electrospin and electrospray methods according to TS EN ISO 105-C 06: Textiles - Tests for color fastness part C02: Color fastness to domestic and commercial laundering. A2S was chosen [75].

4.3.6. Characterization of Nanofibers by Scanning Electron Microscope (SEM)

The morphological appearance of the PAN and PA6 nanofiber mats and that of the individual fibers were investigated by JEOL scanning electron microscope (SEM) in Gaziantep University, operating at an acceleration voltage of 10 kV and 20 kV.

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1. Introduction

In this work, E. coli and S. aureus were chosen to evaluate the antibacterial activity of the sample fabrics. Because, those are responsible for more than 80 % of all infections. Qualitative evaluations were carried out and antibacterial activity tests were performed to ensure antibacterial resistance.

The purpose of the study was to determine the antibacterial activity of fabrics functionalized with irgasan, silver nitrate and AgNPs against Staphylococcus aureus and Escherichia coli bacteria. Usually, antibacterial properties can be acquired to textile materials by chemically or physically incorporating functional agents onto fibers or fabric. The antibacterial properties of such textile materials can be durable or temporary. Antibacterial properties of fabrics are easily achieved by finishing operations but the durability to washing is low. Addition to this, it has been known that antibacterial activity of fabrics during washing cycles and the dosage of antibacterial compound may be reduced or increased according to customer's request. However, the antibacterial agents will vanish completely if they are impregnated in materials without covalent bond linkages.

The study aims to provide a durable antibacterial activity for knitted fabrics by means of nano coating. This nano coating is fine that it cannot visible to human eyes and may not affect the fabric properties such as handling, strength, elongation and etc.

5.2. Antibacterial Test Results

The cultured bacteria were inoculated with sample fabrics incorporating the silver nitrate, AgNP and irgasan agents. The experimental results can be analyzed in four groups;

a) Fabrics treated by electrospin method with PAN based solution.
b) Fabrics treated by electrospray method with PAN based solution.
c) Fabrics treated by electrospin method with PA6 based solution.
d) Fabrics treated by electrospray method with PA6 based solution.

a) Fabrics treated by electrospin method with PAN based solution

Table 5.1 shows antibacterial test results of the fabrics for electrospin method with PAN based polymer. Experiments show that the antibacterial coating has no effect on S. aureus bacterium when the polymer solution was treated by irgasan and AgNPs. However, the coating can provide a strong resistance to S. aureus when the solution was treated by silver nitrate (Figure 5.1.). However, this sample loses its antibacterial activity after a washing cycle. On the other hand, all the samples resist to E. coli, but the sample treated with AgNPs exhibits higher resistance (++) then the others. This sample also shows strong resistance to E. coli after one washing cycle (Figure 5.2.). Figure 5.3 and 5.4 show resistance to E. coli of fabric treated with $AgNO_3$ and irgasan by electrospin method, respectively. SEM micrographs of the fabrics treated with irgasan and AgNP are given in Figure 5.5 and Figure 5.6, respectively.

Table 5.1.Antibacterial fabric with PAN based polymer test results

Fabric Treated (PAN Based Polymer) Electrospin Method	**Bacterium**	**Washing Cycles**				
		Cycle 0	**Cycle 1**	**Cycle 5**	**Cycle 10**	**Cycle 20**
Fabric treated with $AgNO_3$	S. aureus	++	-	-	-	-
	E. coli	+	-	-	-	-
Fabric treated with AgNP	S. aureus	-	-	-	-	-
	E. coli	++	++	-	-	-
Fabric treated with irgasan	S. aureus	-	-	-	-	-
	E. coli	+	-	-	-	-

* ++ : strong antibacterial activity

\+ : acceptable antibacterial activity

\- : no effect

Antibacterial activity of fabrics against E. coli and S. aureus was completely reduced to zero after five washing cycles. Generally resistance of fabrics to E. coli is higher than that of S. aureus by electrospin method with PAN based polymer.

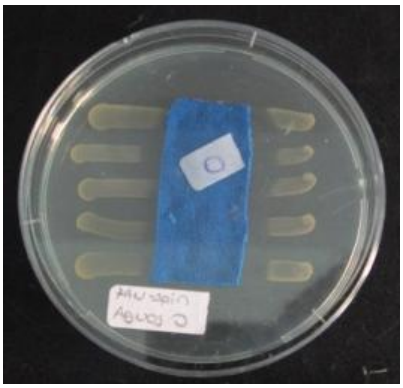
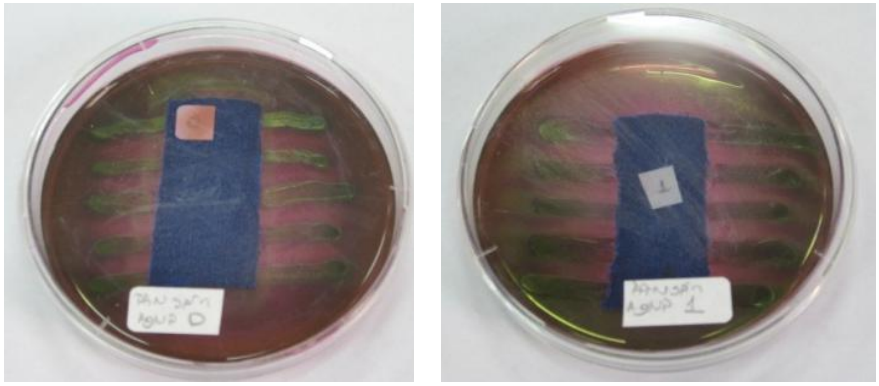


Figure 5.1.PAN Electrospin $AgNO_3$- 0 washing cycle (S. aureus)



a) 0 washing cycle b) 1 washing cycle

Figure 5.2.PAN Electrospin AgNP (E. coli)

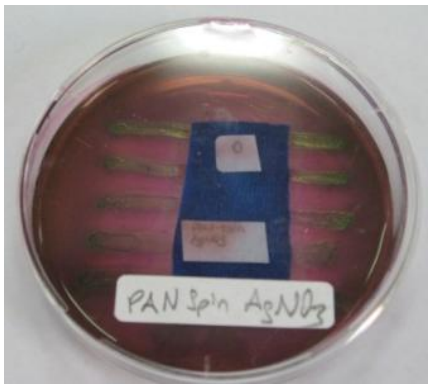


Figure 5.3.PAN Electrospin $AgNO_3$ 0 washing cycle (E. coli)

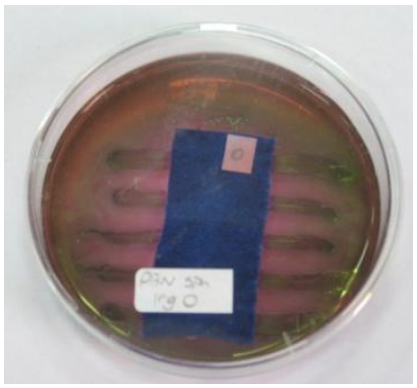


Figure 5.4.PAN Electrospin Irgasan 0 washing cycle (E. coli)

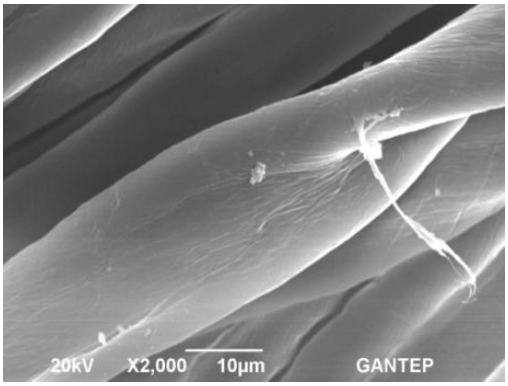


Figure 5.5.PAN Electrospin Irgasan 2000 X 0 washing cycle

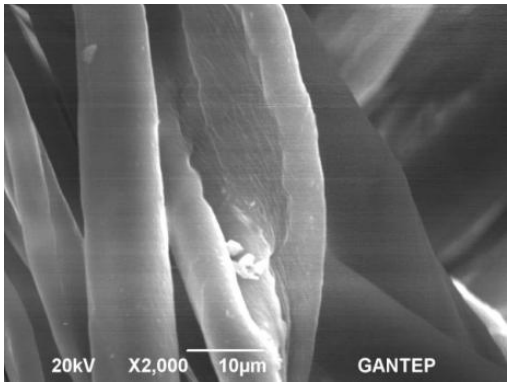


Figure 5.6.PAN Electrospin AgNP 2.000 X 0 washing cycle

b) Fabrics treated by electrospray method with PAN based solution

Table 5.2 shows antibacterial test results of the fabrics for electrospray method with PAN based polymer. The fabric treated with $AgNO_3$ shows no resistance to S. aureus but show resistance to E. coli before washing cycles. The fabric treated with AgNP shows no resistance to S. aureus, however it shows resistance to E. coli up to 5 washing cycles. On the other hand, when the fabric samples were treated with irgasan show strong resistance resistant to S. aureus up to 10 washing cycles, but it is antibacterial effect completely vanish within 5 washing cycles against E. coli. The other samples which were treated with AgNP produce less resistance bacterium. The antibacterial effect was lost after 5 washing cycles against E. coli.

Table 5.2.Antibacterial fabric with PAN based polymer test results

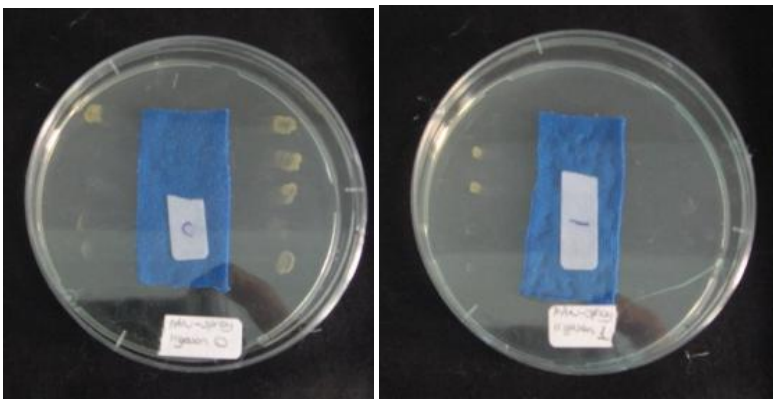
Fabric Treated (PAN Based Polymer) Electrospray Method	**Bacterium**	**Washing Cycles**				
		Cycle 0	**Cycle 1**	**Cycle 5**	**Cycle 10**	**Cycle 20**
Fabric treated with $AgNO_3$	S. aureus	-	-	-	-	-
	E. coli	++	-	-	-	-
Fabric treated with AgNP	S. aureus	-	-	-	-	-
	E. coli	++	+	+	-	-
Fabric treated with irgasan	S. aureus	++	++	++	++	-
	E. coli	++	++	++	-	-

* ++ : strong antibacterial activity

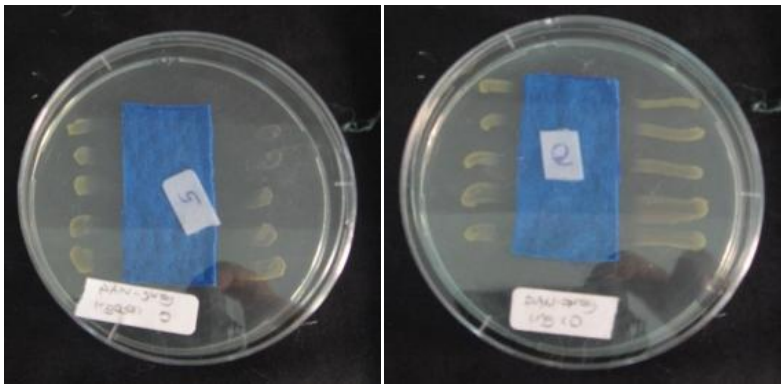
\+ : acceptable antibacterial activity

\- : no effect

As a general observation, irgasan looks as the most effective antibacterial agent against S. aureus and E. coli among the three antibacterial agents. In Figure 5.7 digital photographs of S. aureus antibacterial test of the fabric treated with irgasan by electrospray method for different washing cycles are shown.



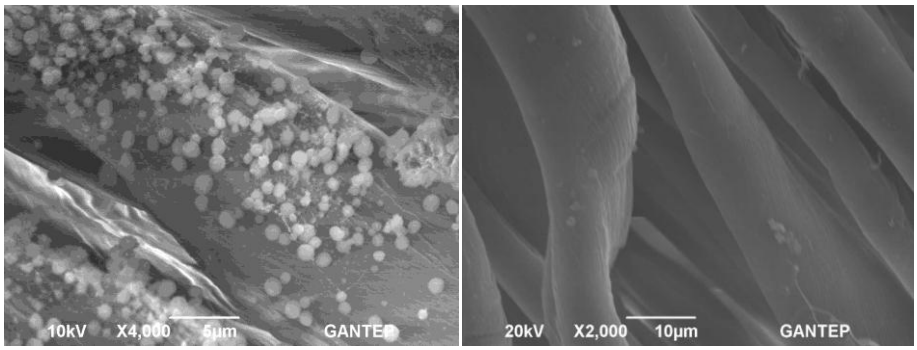
a) 0 washing cycle b) 1 washing cycle



c) 5 washing cycle d) 10 washing cycle

Figure 5.7.PAN Electrospray Irgasan (S. aureus)

SEM micrographs of the fabrics treated with irgasan for 0 and 10 washing cycles are given in Figure 5.8. It is seen that there is a dense nanoparticles on unwashed fabric surface, but a little amount of nanoparticles remains on the fabric surface after 10 washing cycles.



a) 0 Washing Cycle b) 10 Washing Cycle

Figure 5.8.PAN Electrospray Irgasan- 4.000X and 2.000X

c) Fabrics treated by electrospin method with PA6 based solution

Table 5.3.Antibacterial fabric with PA6 based polymer test results

Fabric Treated (PA6 Based Polymer) Electrospin Method	**Thermo Fixing**	**Bacterium**	**Washing Cycles**				
			Cycle 0	**Cycle 1**	**Cycle 5**	**Cycle 10**	**Cycle 20**
Fabric Treated with $AgNO_3$	✓	S. aureus	-	-	-	-	-
	x	S. aureus	-	-	-	-	-
	✓	E. coli	+	+	+	-	-
	x	E. coli	+	+	-	-	-
Fabric Treated with AgNP	✓	S. aureus	-	-	-	-	-
	x	S. aureus	-	-	-	-	-
	✓	E. coli	++	+	+	-	-
	x	E. coli	+	-	-	-	-
Fabric Treated with irgasan	✓	S. aureus	++	++	+	-	-
	x	S. aureus	++	++	++	+	-
	✓	E. coli	++	+	-	-	-
	x	E. coli	++	+	-	-	-

* ++ : strong antibacterial activity,

\+ : acceptable antibacterial activity,

\- : no effect

✓ : thermo fixation was applied x : thermo fixation was not applied

Table 5.3 shows antibacterial test results of the fabrics for electrospin method with PA6 based polymer. Firstly, it is seen that there is no antibacterial resistance of the fabrics to S. aureus and E. coli up to 20 washing cycles. However, the fabric treated with irgasan is only one sample resistant only to S. aureus up to 10 washing cycles.

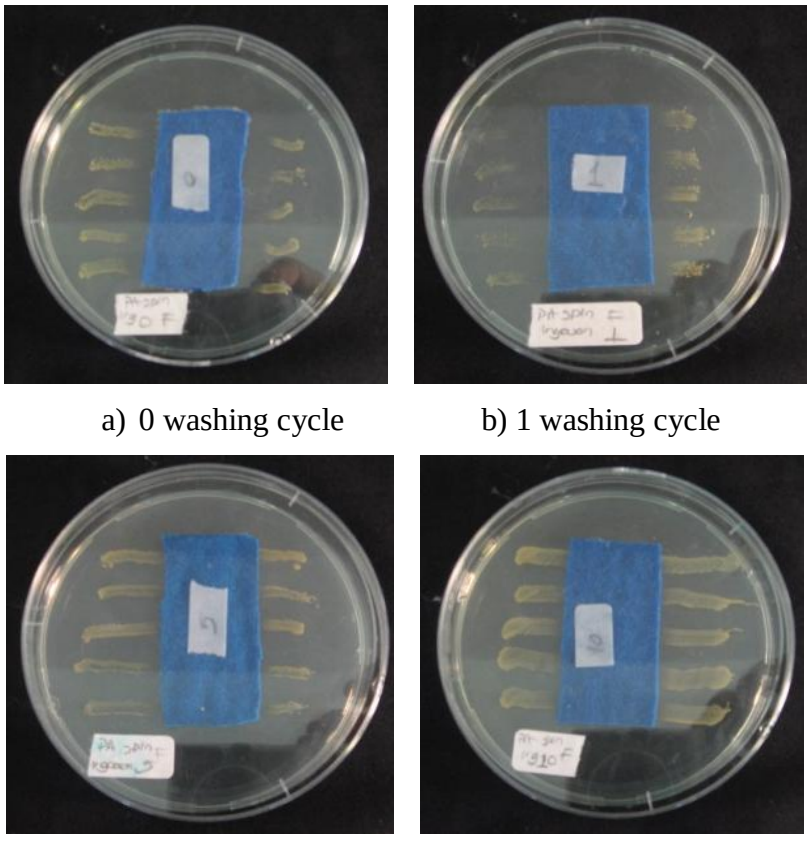
The fabric treated with $AgNO_3$ and AgNP are not resistant to S. aureus at all for both thermo fixed and not thermo fixed applications. However the fabric treated with irgasan is resistant to S. aureus up to 10 washing cycles for both thermo fixed and not thermo fixed options, respectively.

Fabrics treated with $AgNO_3$ is resistant to E. coli up to 5 and 1 washing cycles for thermo fixed and non thermo fixed, respectively. Thermo fixed fabrics are more

resistant to E. coli than the non thermo fixed ones when threaten by $AgNO_3$. Fabric treated with AgNP and thermo fixed is resistant to E. coli for up to 5 washing cycles but, the fabric without thermo fixing process is resistant to E. coli for only unwashed form. On the other side, the fabrics treated with irgasan are resistant to E. coli for one washing cycle for both thermo fixed and non thermo fixed conditions. Generally thermo fixation process improves antibacterial resistance of fabrics against E. coli.

The reason of different effects of thermo fixation process on antibacterial resistance may be structural difference of antibacterial chemicals. $AgNO_3$ and AgNPs are metallic chemicals but irgasan is organic compound. Heat treatment may enhance physical bonding of nanofibers on surface of fabrics for $AgNO_3$ and AgNPs, however, it may cause decomposition of irgasan.

Figure 5.9 show antibacterial test results of the fabrics, which is heat treated and covered with irgasan nanofibers, by electrospin method, for different washing cycles.



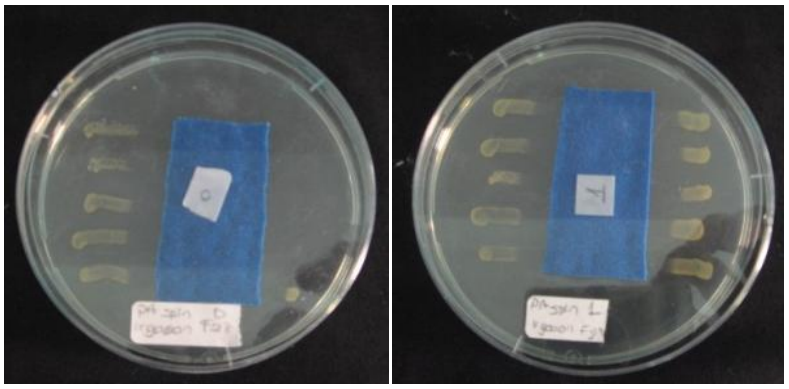
a) 0 washing cycle b) 1 washing cycle

c) 5 washing cycle d) 10 washing cycle

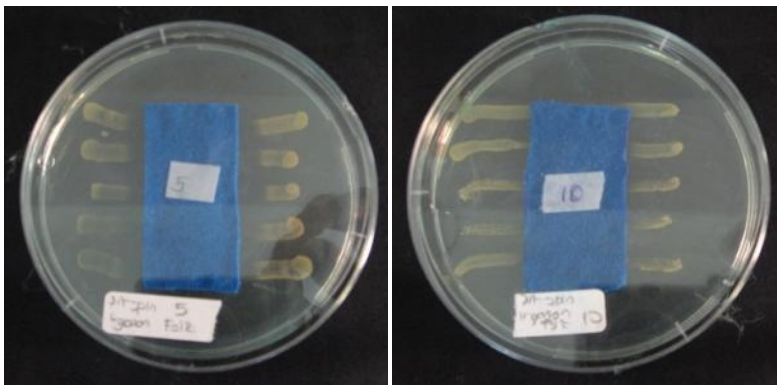
Figure 5.9.Antibacterial test results of thermo fixed fabrics for different washing cycles

The bacterium is S. aureus. It is obviously seen that the length of the inhibition zone is decreased when number of washing cycles is increased. Eventually there is no inhibition zone after 10 washing cycles.

The digital photographs antibacterial test of the fabric treated with irgasan without thermo fixing process for different washing cycles are shown in Figure 5.10. It is obviously seen that the length of the inhibition zone is decreased when number of washing cycles is increased. The fabrics without thermo fixation show acceptable antibacterial activity up to 10 washing cycles. However, generally, inhibition zone lengths of the fabrics become smaller when thermo fixing process was applied.



a) 0 washing cycle b) 1 washing cycle



c) 5 washing cycles d)10 washing cycles

Figure 5.10.Antibacterial test results of fabrics without thermo fixing for different washing cycles

d) Fabrics treated by electrospray method with PA6 based solution

Table 5.4.Antibacterial fabric with PA6 based polymer test results

Fabric Treated (PA6 Based Polymer) Electrospray Method	Thermo Fixing	Bacterium	Washing Cycles				
			Cycle 0	Cycle 1	Cycle 5	Cycle 10	Cycle 20
Fabric treated with $AgNO_3$	✓	S. aureus	-	-	-	-	-
	x	S. aureus	-	-	-	-	-
	✓	E. coli	++	++	++	-	-
	x	E. coli	++	++	++	-	-
Fabric treated with AgNP	✓	S. aureus	-	-	-	-	-
	x	S. aureus	-	-	-	-	-
	✓	E. coli	++	++	++	-	-
	x	E. coli	++	++	+	-	-
Fabric treated with irgasan	✓	S. aureus	+	-	-	-	-
	x	S. aureus	++	++	++	-	-
	✓	E. coli	+	+	+	-	-
	x	E. coli	+	+	+	-	-

* ++ : strong antibacterial activity,

\+ : acceptable antibacterial activity,

\- : no effect

✓ : thermo fixation was applied x : thermo fixation was not applied

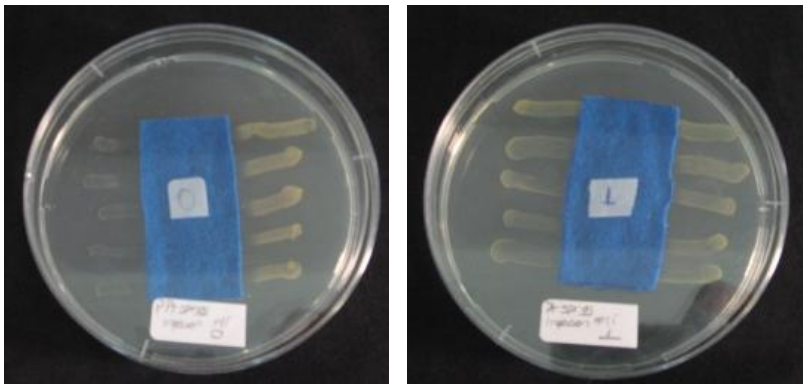
Table 5.4 shows antibacterial test results of the fabrics for electrospray of PA6 based polymer. $AgNO_3$ treatment shows no antibacterial resistance to S. aureus for any washing cycles with and without thermo fixing process. However, this treatment shows antibacterial resistance to E. coli up to five washing cycles. Thermo fixing process seems not affective on the antibacterial resistivity of the fabrics.

The sample fabrics treated with AgNP are not resistant to S. aureus at all for both thermo fixed and non thermo fixed conditions. However, the same fabrics show a strong antibacterial resistance to E. coli bacterium for both thermo fixed and non thermo fixed conditions.

The treatment of the solution with irgasan gives better antibacterial resistivity than the other antibacterial agents both S. aureus and E. coli. However, thermo fixing

process does reduce the antibacterial resistivity; the reasons may be organic structure of irgasan and high degree homogeneous solubility of irgasan in polymer solution.

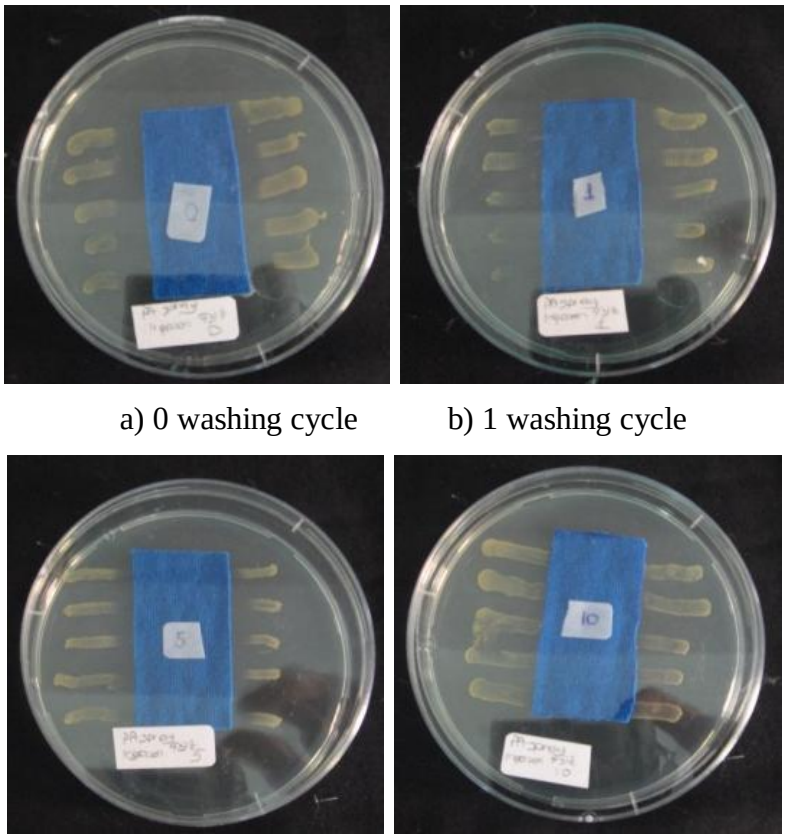
In Figure 5.11 digital photographs of S. aureus antibacterial test of the fabric treated with irgasan by electrospray method and thermo fixed for 0 and 1 washing cycles are shown.



a) 0 washing cycle b) 1 washing cycle

Figure 5.11.PA6 Electrospray Irgasan – Thermo-fixation (S. aureus)

The digital photographs of S. aureus antibacterial test of the fabric treated with irgasan by electrospray method for different washing cycles are shown in Figure 5.12 (without thermo fixing process). It is obviously seen that the length of the inhibition zone is decreased when number of washing cycles is increased. Eventually there is no inhibition zone for 10 washing cycles.

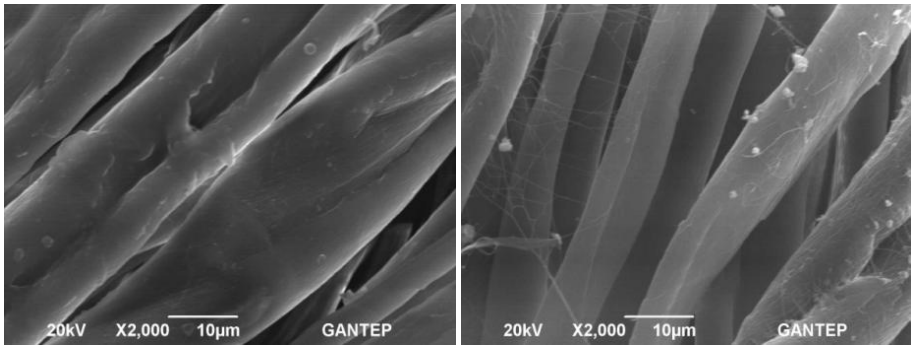


a) 0 washing cycle b) 1 washing cycle

c) 5 washing cycle d) 10 washing cycle

Figure 5.12.PA6 Electrospray Irgasan Not thermo-fixation (S. aureus)

SEM micrographs of the unwashed fabrics treated with irgasan for both thermo fixed and non thermo fixed conditions are given in Figure 5.13. It is seen that there is a structural difference on the surface of the fabrics. For the fabric applied thermo fixation, the nanoparticles are integrated on the surface.



a) Thermo-fixation b) Not thermo-fixation

Figure 5.13.PA6 Electrospray Irgasan 2.000 X - 0 washing cycle

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

Molds, yeasts and bacteria can cause discoloration, quality deterioration and formation of odor, by growing on textiles. As much as is the need to protect textile fabrics from microbial attack, antibacterial treatment for textile materials is also necessary to avoid cross infection by pathogenic microorganisms. To this end, the antibacterial agents can be applied to the textile substrates by conventional methods such as exhaust, pad-dry-cure, coating, spray and foam techniques or new methods such as electrospin and electrospray methods. Conventional surface modification processes are generally causes pollution of water and may be harmful for humans.

Electrospin is emerging as a promising and highly versatile method to process solutions, mainly of polymers, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. Application of this method has provided antibacterial nanofibers with improved properties. Parameters such as type of solvent, pH, concentration of antibacterial agent, charge density, applied voltage, solution flow rate, distance from nozzle tip to collector surface and time play a role in the characteristics of the obtained nanofibrous structures. It was shown that for longer production time, the nanofibers split and form short side arms on the main fiber possibly due to distortion of the electrical field during fiber deposition. The proposed method is a new method which may be used for the same purpose without causing water and pollution. Additionally, this method uses considerably less chemical materials are bonded to the textile structure physically, the surface properties will have longer permanence.

One of the newest methods for producing antibacterial textiles is adding antibacterial agents to textiles through electrospin and electrospray processes. The advantages of such an application are high productivity and relatively low processing costs. The antibacterial fabrics were successfully obtained by electrospin technique being a new

type of technique for coating with antibacterial agents (AgNP, $AgNO_3$ and irgasan). However, antibacterial textiles obtained by these methods exhibit low durability against repeated laundering. The washing durability of antibacterial fabrics depends on the amount of the agents imparted to the textiles and interactions between the agents and the fibers.

This experimental study shows that each of antibacterial agents shows different resistance. It is observed that irgasan is the most effective antibacterial agent than others. The fabrics coated with nanofibers and nanoparticles containing irgasan exhibit a considerable resistance to both E. coli and S. aureus for both electrospin and electrospray applications. The washing durability tests show that the significant antibacterial activity of fabrics treated with irgasan is actively remained for up to 10 washing cycles. However there is no antibacterial activity of the fabrics for 20 washing cycles. Consequently, it is seen that the usage of irgasan is more effective for long durability of the antibacterial activity against laundering.

Examinations on PAN and PA6 based antibacterial coverings showed that polymer types do not create clear difference in terms of bonding of naonofibers to the fabric surface.

The antibacterial action of electrospun nanofibers and electrosprayed nanoparticles has different influence. Generally the fabrics treated by electrospray method show more washing durability because of high monodispersity of nanoparticles. The main difference between these two processes is different percentage of the solution concentration. In electrospray method the concentration is sufficiently low to destabilize the charged jet which then breaks down into small spherical droplets that solidify during the course and are deposited on the collector. In this case the polymer solution does not experience severe drawing and the formed film consists of small droplets instead of fibers.

Generally thermo fixation process does not affect antibacterial resistance of fabrics to S. aureus for $AgNO_3$ and AgNP however; it affects adversely the resistance for irgasan. The reason of different effects of thermo fixation process on antibacterial resistance may be structural difference of antibacterial chemicals. $AgNO_3$ and

AgNPs are metallic chemicals but irgasan is organic compound. Thermo fixation may enhance physical bonding of nanofibers on surface of fabrics for $AgNO_3$ and AgNPs but decompose the irgasan due to its organic structure.

Future works

Different polymer types can be used for future studies. Some adhesive chemicals can be tested for binding of antibacterial agents to fabric surface without affecting fabric characteristics. The antibacterial activity of polymers as carrier of antibacterial agents, for instance PVP, is significant because the polymer is most effective in stabilizing antibacterial metal oxide nanoparticles against aggregation. There are concerns about the narrowness of the size distribution of the nanoparticles, and the degree of agglomeration.

The studies about covalent bonding can be performed. If covalent bonds are achieved between agents in nanostructures and fiber, the washing durability will improved more. For example, chemical modification of the biocide for covalent bond formation with the fiber, crosslinking of the active agent onto the fiber using a crosslinker and polymerization grafting.

The performance of different antibacterial chemicals by this method can be investigated. Many other compounds are used as antibacterial agents on textiles each with their own special properties and benefits and some are durable to washing. Such as, quaternary ammonium salt, titanium dioxide, chitosan etc. Metal oxide nanoparticles are more preferable than nanosilver due to cost effectiveness and bio-safe and biocompatible, and can be used for biomedical applications. For instance, zinc oxide and titanium dioxide are non-toxic and chemically stable under exposure to both high temperatures. ZnO could be one of the most important nanomaterials in future research and applications. The application of nanoparticles in textile materials is the objective of several studies aimed at producing finished fabrics with more effective performances. The attachment of quaternary ammonium compounds (QACs) to a textile substrate is believed to be predominantly by ionic interaction between the cationic QAC and anionic fiber surface. At convenient concentrations,

they can cause cell leakage and the death of the cell. They have a stronger antibacterial effect bacterium.

Lastly, knitted fabrics are used as substrate in this study. Woven and nonwoven fabrics in different constructions and fiber type can be used as substrates for other studies.

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