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REVIEWON RECENT APPLICATIONS OF ANTIMICROBIAL AGENTS FOR POLYAMIDE AND POLYPROPYLENE

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Abstract

The growth of microbes on textiles during use and storage, will affects the wearer as well as the textile itself. The detrimental effects can be controlled by durable antimicrobial finishing of the textile using broad-spectrum biocides or by incorporating the biocide into synthetic fibers during extrusion. Consumers' attitude towards hygiene and active lifestyle has created a rapidly increasing market for antimicrobial textiles, which in turn has stimulated intensive research and development. This article is a review based on recent applications of antimicrobial agents to Polyamide (PA) and Polypropylene (PP) fabrics.

The requirements for antimicrobial polyamide and polypropylene fibers such as, qualitative and quantitative evaluations of antimicrobial efficacy, the application methods of antimicrobial agents and some of the most recent developments in antimicrobial treatments of these fibers using various active agents ie silver, quaternary ammonium salts, polyhexamethylene biguanide, triclosan, chitosan, *N*-halamine compounds and fixation of antibiotics are discussed.

Key word : Polyamide (PA) & Polypropylene (PP) Fabrics**,** antimicrobial agents**,** nano-silver, quaternary ammonium salts, polyhexamethylene biguanide, triclosan, chitosan, *N*-halamine**.**

Introduction

Biocidal textiles are antimicrobial modified ones, they kills or inhibit the growth of microorganisms such as bacteria molds, fungi and repel or kill crawling and flying insects that carry diseases and transfer them to humans in various form. These fabrics have important environmental impact in elimination or inhibition of such microorganisms and repelling diseases insects, thus providing protection against diseases.

Nowadays, biocidal textiles are very important and have a wide domain of applications for human demands due to the appearance of fatal diseases.

Biocidal fabrics are generally made from non-woven or woven,natural or synthetic fabrics or both of them by different industrial means.

Biocidal fabrics exist in the international market under different brand names, either in melt spinning fibers, e.g. Microsafe AM (produced by Hoechst-Celanese), Bactekiller (produced by Kanebo), Bolfurt (produced by Unitika), etc.; or in finished fabrics, e.g. Biochiton (produced by Asahi Chem. Ind.), Eosy (produced by Unitika),

Bio-Proof (produced by Morton), Kathon (produced by Rohm & Hass). They are based on specific biocidal agents as shown in Table 1.

Table 1. Antimicrobial agents added in melt spinning of fibers

Trade mark	Producer	Antimicrobial agent	Type of fiber
Mibrosafe AM	Hoechst-Celanese	Microban B	Polyacetate
Bactekiller	Kanebo	Zeolite & metallic ions	Polyester
Lilver fresh A	Kanebo	Zeolite & metallic ions	Polyacrylic
Bolfurt	Unitika	Copper sulfide	Polyester

This article will focus on the antimicrobial treatments of PA &PP.

Polypropylene (PP) fiber is one of the most widely used synthetic fibers because it is inexpensive and has outstanding mechanical properties. In addition, silver is unique in possessing high thermal stability, intense antimicrobial properties and little toxicity to mammalian cells and tissues.

Recent antimicrobial agents and improved polymer substances are included in this article, such as nano copper, zinc, silver compounds and triclosan which inhibit growth of micro-organisms by using an electro chemical mode of action to penetrate and disrupt their cell walls. When the cell walls are penetrated, leakage of metabolites occurs and other cell functions are disabled, thereby preventing the organism to function or reproduce. Triclosan when incorporated within a polymer migrates to the surface, where it is bound. Because, it is not water-soluble, it does not leach out, and it continuously inhibits the growth of bacteria in contact with the surface using barrier or blocking action.

Chitosan, triclosan, irgasan 300(2,4,4trichloro-2-hydroxy diphenyl- ether) , quaternary ammonium compounds, polymeric phosphonium salts, polymeric biguanides, N- halamin compounds and antibiotic drugs were investigated (1,2,3) . The textile fabric activity and the bioactive effect resistance depend on both binding type between the bactericidal product and fiber polymer and chemical nature of the used antibacterial agent.

Chitosan is an effective natural antimicrobial agent derived from chitin, a polysaccharide found in the exoskeleton of shellfish like shrimp or crabs. Chitosan is a naturally occurring substance that is chemically similar to cellulose with an NH_2 group in C_2 [Fig.1]. Coatings of chitosan on conventional fibers appear to be the more realistic prospect since; they do not produce an immunological response. The performance of chitosan in physics and chemistry is determined by the influence of two important structural parameters: degree of deacetylation (DD) and molecular

weight (MW), which affect solubility, enrichment ions, mechanics of the chitosan membrane and flocculation solubility and enrichment ions.

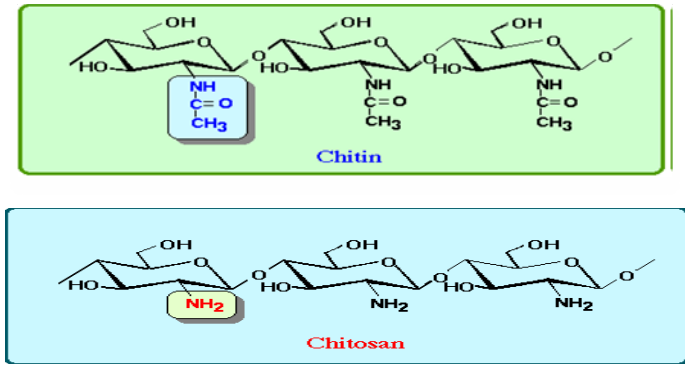


Fig.1 Structures of Chitin and Chitosan

Durability and performance of the new properties induced to the textile fabric are determined by several washings to evaluate the efficiency of the antimicrobial treatment and the capacity to increase the added value of the product.These microorganisms are found almost everywhere in the environment and can be multiplied quickly if the conditions are suitable, such as moisture, nutrients and temperature.

Most synthetic fibers, due to their high hydrophobicity, are more resistant to attacks by microorganisms compared to natural fibers. Proteins in keratinous fibers and carbohydrates in cotton can act as nutrients and energy sources under certain conditions. Soil, dust, solutes from sweat and some textile finishes can also be nutrient sources for microorganisms [4]. The growth of microorganisms on textiles produces 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 of the fabric and reduction in fabric mechanical strength.

Treatments of antimicrobial agents on textile

In order to obtain textile fabrics with antimicrobial performance, these can be applied by exhaustion, pad –dry cure, coating, spraying and foaming using the following methods:

- Impregnation of the fibrous material with a solution, suspension or emulsion of the bactericidal (fungicidal) agent.
- Padding of an antimicrobial agent, from its soluble state and converted if into an insoluble one on the fibrous material.

- Binding of an antimicrobial product on the fiber through chemical bonds (ionic, coordinativ and covalent).

Immersion of a bactericidal agent either in the spinning solution or the melt extrusion, during the spinning of the chemical fibers. For synthetic fibers, the antimicrobial active agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their finishing process.

Bulk treatments are performed by embedding the active agents. Success of the treatment depends on the existing chemical compatibility of the active agent to both the polymer structure and the applied spinning procedure. In order to obtain a good distribution of the above-mentioned compounds into the core fibers, it is important to apply substances which can be dissolved or dispersed into the polymer [5].

Grafting is modification technique and functionalization of polymers, for improving their native characteristics or adding specific properties by using some biocides.

Specifications of the antimicrobial treatments

In order to obtain the greatest benefit, an ideal antimicrobial treatment of textiles should satisfy a number of requirements [2-6].

It should be effective against a broad spectrum of bacterial and fungal species, but at the same time it should exhibit low toxicity to consumers, e.g. not causing toxicity, allergy or irritation to the user. Antimicrobial-treated textiles have to meet some standards in compatibility tests (cytotoxicity, irritation and sensitization) before marketing.

- The finishing should be durable to laundering, dry cleaning and hot pressing. This is the greatest challenge as textile fabrics which are subjected to repeated washing during their life.
- The finishing should not negatively affect the quality (e.g. physical strength and handle) or appearance of the textile.
- 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.
- Also the antimicrobial finishing of textiles should not kill the resident flora of nonpathogenic bacteria on the skin of the wearer. The skin resident flora consists of several bacterial genera, which are important to the health of the skin as they lower skin surface pH and produce antibiotics to create an unfavorable environment for the growth of pathogenic bacteria

[7]. Also, antimicrobial agents on textiles may only reduce the density of the skin resident flora but do not completely eliminate them. To date, no evidence exists that the use of antimicrobial textiles changes the ecology of skin resident flora leading to the outgrowth of pathogenic bacteria [8].

Modes of Antimicrobial Action

A living microbe (e.g. bacteria or fungi) 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 semipermeable membrane which encloses intracellular cells and 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. Antimicrobial agents either inhibit the growth of microbes without much destruction (-static) or kill (-cidal) the microorganisms.

The antimicrobial products should have resistance to bacteria or pathogenic fungi. Such materials can be made by incorporation for this purpose nano silver (with large particles area) and silver substituted zeolite into polypropylene using melt spinning technique. These are non- toxic natural inorganic materials and are bactericidal agents, skin friendly and don't cause skin irritation against a broad spectrum of harmful microorganisms by combining with their cellular protein and inactivating them. High concentrations of heavy metal salts coagulate cytoplasm proteins resulting in damage of the cellular metabolism and the microorganism dies.

Metals and metal salts

Bulk treatments are performed by embedding the bioactive agent into the polyamide, before the Production of Antimicrobial Polyamide Fibers by Advanced Techniques

The manufacture of bioactive polyamide fibers can be accomplished through:

I- Physical fixation of the antimicrobial agent within the fine structure of polymers [6, 9].

II- Chemical bonding of the antimicrobial reagent by the preliminary modification of textile materials [7,10].

I-Physical fixation of the antimicrobial to the substrate

Physical fixation of the antimicrobial to the substrate can be carried out by the following processes:

1-Addition of bactericides to polymer chips before fiber formation:

Several approaches have been used to make antimicrobial fibers for use in clothing to eliminate odors and in carpeting to prevent fungal growth. In these products, the antimicrobial agent is incorporated into the fibers. This means that the agent must survive the high processing temperature (typically> 200ºC). In addition, the agent must diffuse out of the fibers to the microbe to kill it [5, 11].

For polyamide fibers, the antimicrobial active agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their spinning. Such processing provides the best durability as the bioactive agent is physically embedded into the spinning process.

Success of the treatment depends on the existing chemical compatibility of the active agent and both the polymer structure and the applied spinning procedure. In order to obtain a good distribution of the antimicrobial agent into the core fibers, it is important to apply substances which can be dispersed into the polyamide [7]. Since not all the bioactive molecules are compatible with the spinning process conditions, a selection of them according to the parameters of fibers manufacturing is required. In order to be active, a substance embedded in the fiber core should slowly migrate to the surface and should not modify the initial characteristics of the fiber [6].

Metals and metal salts are toxic to microbes at very low concentrations either in the free state or in compounds. They kill microbes by binding to intracellular proteins and inactivating them [12]. Silver is the most widely used with polyamide. Silver particles can be incorporated into polyamide by thermal reduction of silver acetate during melt processing of PA6 at 230 ° C [9] and in the extrusion step; the master batch was diluted with pure PA6 to vary the filler content.

Sliver nanoparticles have some advantages over silver salts because they are more stable against dissolution and diffusion to the surface of fabrics to be protected .Silver-nanocoated PA6,6 are produced by simple and effective manner with complete control of the silver loading level on the fabric [13]. During use, silver diffuses onto the surface of the fiber and forms silver ions in the presence of moisture. The rate of silver release can be influenced by the chemical and physical characteristics of the fiber and the amount of silver in the fiber (14).

The development of these composite fabrics is the purpose of fabricating them into a number of applications like vials, garments, fishnets, etc. For such

applications, the mechanical properties are to be studied having the same importance as the antimicrobial efficacy [15] .

PA6/Ag-nanocomposites can be prepared by the simple processing operation of mixing silver acetate into molten PA6 without the aid of a solvent or a carrier with the silver particles. The PA6/Ag nanocomposite was shown to be active against Escherichia Coli whereas the pure PA6 did not show any antimicrobial efficacy [16]. Furthermore, it was observed a relationship between the antibacterial properties and the total surface area of the nanoparticles. Smaller particles with a larger surface area were more efficient in the antibacterial activity tests.

Nylon 6,6 was prepared by interfacial synthesis technique and loaded with Ag nanoparticles to form Ag/nylon 6,6 nanocomposite and its antibacterial effects on E. coli was evaluated. Scanning Electron Microscope (SEM) image of synthesized nylon 6,6 fabric has smooth surface (Fig 2) , while (SEM) image of Ag/ Nylon 6,6 nanocomposites (Fig. 3) with Ag particles (70 nm) are formed on the surface[17].

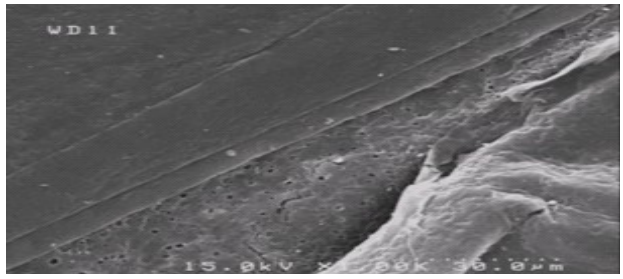


Fig.2. SEM image of blank Nylon 6,6 surface

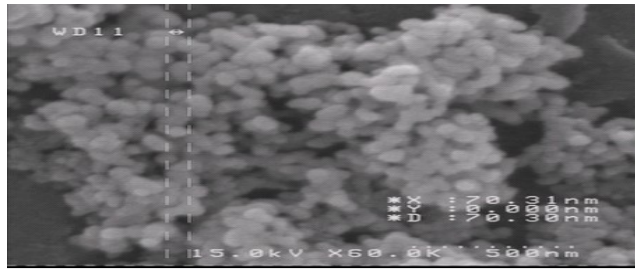


Fig. 3. SEM image of Ag/ Nylon 6,6 nanocomposites

Jeong et al. [18] used a conventional twin screw mixer to study the effect of additives and particle size of micro- and nanosized silver powders on the antibacterial properties of PP/Ag fiber. The analysis and characterization of the compounds were done by X-ray diffraction, DSC, SEM, mechanical properties and

antibacterial activity. The authors concluded that fibers containing silver nanoparticles exhibited superior antibacterial activity compared to samples containing micro-sized particles. The same authors prepared nano-composite PP/Ag fibers to create permanent antibacterial effects [19] using a conjugate (bicomponent) spinning machine. Antibacterial efficiency against Staphylococcus aureus and Klebsiella pneumonia was excellent when the master batch was used as the sheath and not as the core of the fibers. Dastjerdi et al. [20] have investigated the properties of bioactive continuous PP filament yarns containing Ag/TiO2 nanocomposites. The processing of the starting materials and the characteristics and microbio- logical activities of the resulting fabric was studied. Variation in a nano- filler content improved tenacity and modulus of as-spun and textured fibers. Biostatic efficiency had no distinct trend with increasing silver content. Optimum antibacterial activity was shown for 0.75% nanofiller, which corresponded to the minimum degree of crystallinity for that sample.

Chae et al.[21] determined the effects of silver nanoparticles on the dynamic crystallization and also the physical properties of syndiotactic polypropylene. Previous research work was done by Kotek and coworkers [22, 23] at NCSU to study the mechanical and structural properties of melt-spun PP/nylon 6 alloy filaments as well as those of poly(trimethylene terephthalate) (PTT) filaments containing silver.

Nano zinc oxide (ZnO)

Nano zinc oxide particles are one of the antibacterial agents content of the filament, which have not only ultraviolet absorbing and deodorizing actions, but also bactericidal actions. The bactericidal and antibacterial performances of nano zinc oxide particles are considered to develop due to one of the chemical characteristics of zinc oxide, that is, high affinity for sulfur. In particular, it is presumed that nano zinc oxide particles act on the thiol groups of enzymes existing in the cell membrane of bacteria in some way and thereby lowers the activity of bacteria [24].

There have been proposed a number of antibacterial fibers or yarns, comprising synthetic fibers, such as polyamide filaments including nylon 6, which contain powder substance having antibacterial properties. The technical problem is how to provide antimicrobial polyamide fibers which develops good antibacterial properties, it is less susceptible to color changes, deterioration of antibacterial properties and is excellent in washing resistance.

In order to solve this problem, production of antibacterial polyamide fiber includes the following steps: adjusting a moisture content of polyamide resin chips containing 0.1 to 5.0 mass% of nano zinc oxide particles to 0.05 to 2.0 mass%; melt –spinning the polyamide resin chips and discharging the undrawn fiber through a spinning nozzle; and solidifying the spun fiber at the position within 400 mm away from the nozzle face. In the fiber, nano zinc oxide particles content of polyamide resin is 0.1 to 5.0 mass% and preferably 0.3 to 3.5 mass %. If the content is less than 0.1 mass %, the filament does not show the satisfactory antibacterial performance. If the content is more than 5.0 mass % , operating efficiency is lowered in the production of the fibers because of frequent occurrence of end breakage during spinning or drawing or because of frequent occurrence of end breakage or fluff due to the wear of the guide, reed or heddle during weaving. Moreover, not only the antibacterial performance reaches saturation with which production cost rises, but also yarn performance as strength and elongation deteriorates.

In this production method, preferably the fine zinc oxide particles are coated with a coupling agent, due to the reaction induced by the photocatalytic activity of fine zinc oxide particles is occurred on the particle surface. Thus, there have been made attempts to suppress the photocatalytic activity by subjecting the particle surface to some treatment. For example, micro encapsulation surface treatment has been done to avoid contamination with oxygen and water .The nano zinc oxide particles which have been subjected to this treatment, have the problem of losing its chemical characteristics, though it still has optical characteristics of zinc oxide. In order to remain photocatalytic characteristics, preferably used are fine zinc oxide particles which are coated with a coupling agent. The use of a coupling agent for coating the surface of nano zinc oxide particles makes it possible to suppress the photocatalytic activity of nano zinc oxide particles satisfactorily using only small amount of agent and without waste of agent. Meanwhile it allows the ultraviolet absorbing action as well as bactericidal actions to remain the same as before. Thus in the fiber containing nano zinc oxide particles the surfaces are coated with such a coupling agent, its color change caused by ultraviolet rays can be effectively prevented and at the same time, its bactericidal effects are achieved [24].

Gawish et al.[25] studied the melt spinning of PP/nano- metals composite fibers, especially new PP/Zn biocidal composite fibers which produced and compared to PP/Ag fibers. These fibers were drawn fibers having permanent antibacterial and antistatic properties. They were prepared by using metal nanoparticles and melt spinning techniques. For this purpose, selected parameters

were chosen to attain the desired properties and maintain the bulk characteristic properties of the produced fibers. Such parameters included selecting a specific type of nanometal and also a low effective additive concentration. Tensile properties of the composite fibers including tensile strength, elongation at break, modulus and tenacity were evaluated. The antibacterial activity of the composite Ag and Zn fibers was compared to the control PP fibers against E. coli

2-Impregnation of polyamide fibers into a bactericidal solution of polyhexamethylene biguanide (PHMB)

Polyhexamethylene biguanide (PHMB), trade name Reputex Fig. 4 has broad spectrum of antimicrobial action with low toxicity. It has been successfully used with polyamide fibers to impart antimicrobial property by using exhaust or pad–dry–cure processes. PHMB containing 16 biguanide units provide more cationic sites per molecule for stronger binding possibly for polyamide fibers [26-28].

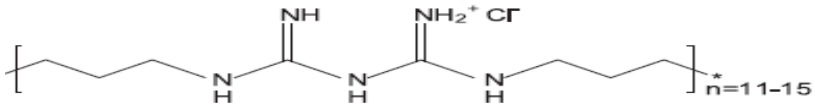


Fig. 4 Structure of polyhexamethylene biguanide (PHMB)

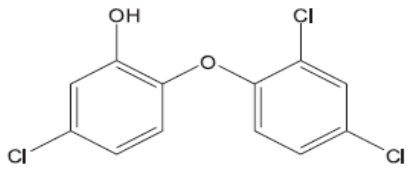


Fig.5 Structure of triclosan

Triclosan (2,4,4’-trichloro-2’-hydroxydiphenyl ether, Fig. 5) is a broad-spectrum antimicrobial agent with a minimal inhibitory concentration (MIC) of less than 10 ppm against many common bacterial species [29]. Unlike most other cationic biocides used on textiles, triclosan is not ionized in solution. It has been in use since the 1960s in a wide array of professional and consumer products including hand soaps, surgical scrubs, shower gels, deodorants, healthcare hand washes, toothpastes and mouthwashes [29, 30]. It inhibits microbial growth by blocking lipid biosynthesis [31]. Triclosan can also act like a disperse dye and can be used by exhaustion prior to dyeing, together with dyeing or after dyeing of polyester and nylon fibers at 5% owf ie. on the weight of the fiber [32]. During fabric use, the

agent migrates to the surfaces of the treated textiles at a slow rate to provide antimicrobial efficacy [32]. Triclosan products are used in the finishing treatment of woven or knitted fabric articles, such as hosiery, sportswear and most commonly through the addition of the triclosan additive product to a bath where the fabric to be treated are added. Triclosan can be exhausted at a very high exhaustion rate onto polyamide fibers when added to the dye bath. Additives containing triclosan are usually applied at rates ranging from 1-10% by weight on fabric [33, 34].

II-Chemical bonding of the antimicrobial reagent

A more promising trend for imparting antimicrobial properties to polyamide fibers is the attachment of bioactive agent by chemical modification of the textile material with the objective of increasing its content or creating on the fiber new functional groups which are able to react with the antimicrobial agent. Along with other advantages, carrying out this method ensures a high biological activity of the fabrics at the least antimicrobial substance content as compared with the other methods.

Fixation of β- Cyclodextrin

New modification of synthetic fibers surface is done by fixation of supramolecular compounds like β – cyclodextrin (β-CD) or monochoro triazinyl β – cyclodextrine (MCT-βCD)which contain some biocidal and reactive groups such as triazinyl ring in addition to the presence of the chlorine atom which are very interesting [35]. Such host inner cavity CD compounds are able to form inclusion guest complexes with other chemical substances and thus, the treated fibers with CD will achieve new functional properties by selective inclusion of these chemical species in the fixed CD cavities, Also the complexed guest substances may be released from the fiber in a special rate depending on the surrounding conditions. Thus the inner CD cavity of molecules shows hydrophobic character, so that organic compounds containing nonpolar group may be included in the CD cavity. As a result of such inclusion, the physico-chemical properties of the included compounds is changed i.e. the vapor pressure of the volatile substances is reduced, the stability of the sensitive fibers against light and air is enhanced [36]. The complex compounds may be volatile perfumed extracts, odorous human sweat or specific active agents. This modification process is important for the production of antimicrobial and upholstery textiles.

Treatments of polyamide 6, Quiana and Nomex fabrics with β-Cyclodextrin(CD) or monochlorotriazinyl β- Cyclodextrin(MCT, β-CD) and quaternary ammonium salt 2gm/l were investigated.

The polyamide fabrics were immersed in a solution containing 10-50 g/l (o.w .f) of β-CD or monochlorotriazinyl β-cyclodextrin (MCT, CD) which is adjusted to pH 4 using acetic acid or citric acid at room temperature for 1h, then padded to pick up 100 %, dried at 80°C for 10 min. and then fixed at 160°C for 5 min. Finally the fabric is washed thoroughly with tap water and air dried [37].

The polyamide fabrics were treated with conventional exhaust and pad–dry–cure processes by using (β-CD), or (MCT, β-CD). The treatment with (β-CD) or (MCT, β-CD) improved resistance against Candida albicans. Also it was found that addition of quaternary ammonium salts increases antimicrobial activity as compared to all treatments [37].

S.Gawish etal [38] prepared novel fabrics by graftcopolymeriza- tion of glycidyl methacrylate (GMA) onto polyamide 6 fabric, using a chemical redox system $K_2S_2O_8/CuSO_4{\cdot}5H_2O$, followed by reaction of β-cyclodextrins (CD) or monochlorotriazinyl (MCT β-CD) with the GMA epoxy group. Some biocidal guests were complexed into CD cavity including p-hydroxy benzoic acid, $AgNO_3$–ethanolamine mixture, iodine, N,N diethyl toluamide (DETA), citronella, jasmine, and sweet basil. Characterization of the novel fabrics was done by Fourier Transform Infrared Spectroscopy (FTIR), Electron Scanning Microscopy(SEM), and Thermo Gravimetric Analysis (TGA). These modified fabrics were highly active against five strains of microorganisms [38] .

Quaternary ammonium salts

Quaternary ammonium compounds (QACs), particularly those containing chains of 11–16 carbon atoms, have been widely used as disinfectants [39]. These compounds carrying a positive charge at the N atom in solution and they cause a variety of detrimental effects on microbes, including damage cell membranes, denaturation of proteins and disruption of the cell structure [39]. During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antimicrobial ability as long as the compound is attached to textiles [40].The attachment of QAC to a textile substrate is believed to be predominantly effected by ionic interaction between the cationic QAC and anionic fiber surface [41].

Son etal. [42] discussed a new approach for employing the ionic interactions between anionic carboxylic end groups of polyamides and cationic quaternary ammonium salts in the chemical finishing of nylon fabrics to achieve desired durable antimicrobial functions. The finishing conditions such as pH, finishing temperature, and time were studied. The pH of the finishing bath was very critical in

affecting the ionic interactions and thus exhaustion of the salts on the fabrics. The finishing process should be carried out at a temperature above the glass transition temperature of nylon 66. The finished products demonstrated excellent durability of antimicrobial functions.

Nylon 6,6 contain fewer reactive sites which are quite resistant to chemical modification procedures, including antimicrobial finishing. Chemical modification of polyamide could be achieved by reacting carboxylic end groups with biocidal quaternary ammonium salts under alkaline conditions. The fabric was first dyed with acid dyes before QACs which were applied under alkaline conditions. The ionic interaction between the dye molecules and the QAC was sufficiently strong to provide a semi-durable antimicrobial finishing. Such a reaction could be implemented in the exhaustion treatment of nylon 66 fabrics with several quaternary ammonium salts (Fig.4). The interactions between carboxylic end groups and quaternary ammonium salts could provide improved durable antimicrobial functions over repeated washing tests [42].

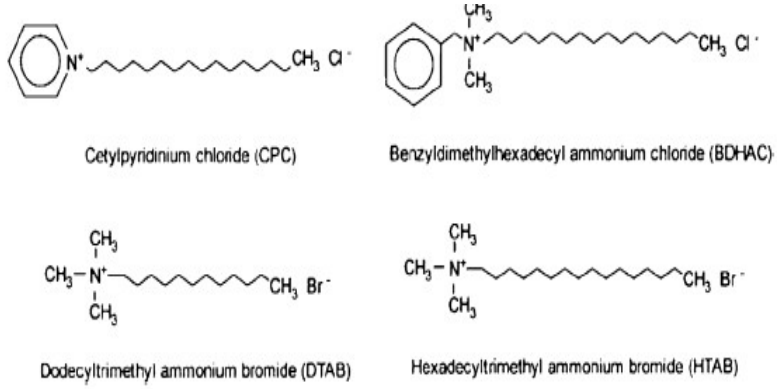
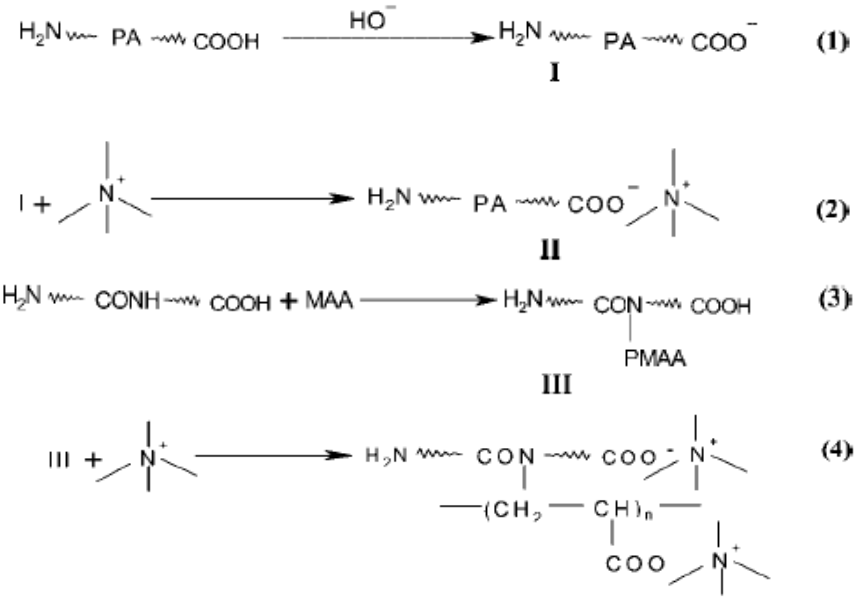


Fig 6. Structures of quaternary ammonium salts.

A simple, efficient, and practically applicable functional approach for improvement antimicrobial properties of nylon-6 fabrics and increase the washing durability of biofunctions was developed by Shalby etal [43]. This finishing approach is based on grafting the fabrics with methacrylic acid (MAA) to create additional carboxylic groups in nylon-6 macromolecules, followed by subsequent reaction with dimethyl -alklbenzyl ammonium chloride (DMABAC) solution under alkaline conditions. The carboxylic groups react with cationic agent through ionic interaction, which led to the immobilization of QAS on nylon-6 fabrics. The results can be explained by the following equations [43].



Saïhi etal used a graft copolymerization method to modify polyamide fibers. The fibers were grafted with monomers containing quaternary ammonium groups using sodium persulfate as initiator. Two monomers were used as vinyl monomers. The first monomer, called METAC, is methacryloyloxyethyl trimethyl- ammonium chloride [H2C = C (CH_3) - $CO_2CH_2CH_2N(CH_3)_3Cl$]. The second monomer, denoted CATAL, is a methacryloyloxyethyl dimethyldodecylammonium bromide

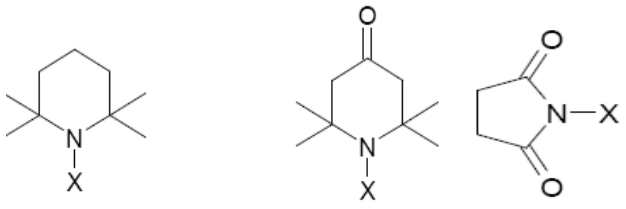
[$H_2C = C(CH_3)CONHCH_2CH_2CH_2N- (CH_3)_2(C1_2H_{25})Br$], Polyamide fibers grafted with the second monomer exhibit high antibacterial activity against *S. aureus*, but the fibers grafted with the methacryloyloxyethyl trimethylammonium chloride did not [44].

N-halamine

Among the currently investigated antimicrobial materials, only n-halamines have shown the capability of providing fast and total kill against a wide range of micro-organisms [45-48].

N-halamine structures have been incorporated into cellulose and nylon fabrics by a conventional finishing method in the presence of formaldehyede [49-50]

R, R' = H, Br, Cl, inorganic group, organic group



X= Cl, Br, H, Na

Fig.7 Structures of Cyclic Organic N-halamine Compounds

If one of R groups is an organic group, it is considered as an organic N-halamine, and major structures are amines, amides and imides. The type of organic N-halamine (Fig. 8) determines stability of halogen and biocidal efficacy.

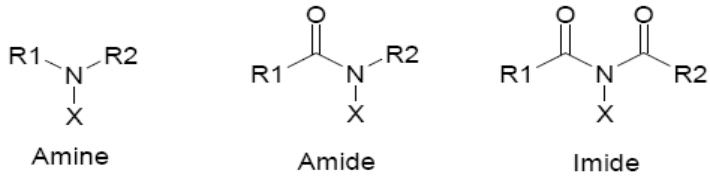


Fig.8 Organic N- halamine containing halogen

In general, N-halamine antimicrobial polymers or fibers have been prepared in three different ways.

Antimicrobial polymeric materials such as cellulose and m-aramid composite fibers were prepared by using N-halamine. An ionic liquid, 1-butyl-3-methylimidazolium chloride, has allowed the production of cellulose/m-aramid fibers. Stable and rechargeable cellulose/m-aramid composite fibers were prepared by dry-jet wet spinning of a composite polymer solution. Chlorination of the aramid nitrogen produced antimicrobial properties which were retained over 50 standard-washing cycles. Cellulose/m-aramid blends show a much higher chlorination level than the pure m-aramid fiber. The chlorinated fibers inactivated both Gram-negative *(E. coli)* and Gram-positive *(S. aureus)* bacteria, generally within 5 min with 6 log reductions [50] .

Preparation of an antimicrobial nylon fabric and its properties are discussed by Lin et.al [51] . Biocidal cyclic N-chloramine moieties were covalently bonded to Nylon 66. These moieties, which included hydantoins, oxazolidinones, and imidazolidinones, were stable during at least 3 months of dry storage, and their antimicrobial activities lost by reaction with reducing sodium thiosulfate and could be regenerated by exposure to free chlorine. Biocidal swatch tests showed that the nylon fabrics containing N-chlorinated hydantoin functional groups provided a 7.2 log reduction of *S. aureus* and a 7.1 log reduction of *E. coli* at a contact time of only 10 min.

Recently, a cyclic–amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH),was grafted onto various textile fabrics in a continuous finishing process to prepare durable and regenerable antibacterial textiles. Highly efficient radical grafting polymerization occurred inside or on the surfaces of fibers with the assistance of different initiators .In the finishing process, particular factors such as types and concentrations of radical initiators, drying and curing conditions were rather important in effecting the final grafts of ADMH on fabrics and were studied carefully. After exposure to chlorine, the grafted hydantoin structures in the samples could be transformed into N-halamine , which provided powerful durable and regenerable antibacterial activities. The influence of hydrophilic /hydrophobic properties of the fabrics on the antibacterial activities was discussed [52,53].

Fixation of antibiotics

Another approach for imparting bioactive moieties to synthetic fibers consists of incorporating antibiotics. Such modification should result in bactericidal and bacteriostatic effects on a wide spectrum of Gram –positive and Gram-negative bacteria than in the case of modified fibers with furane derivatives. This type of modification requires functional group such as carboxylic groups, to be added to fibers prior to the treatment with appropriate antibiotics or anesthetic.

Carboxylic groups can be incorporated in polyamide fibers by grafting acrylic acid initiated chemically. If graft copolymerization is to be effective and suitable for commercial implementation, it should be characterized by the minimum quantity of homopolymer formed during the process or even better by its absence, short grafting time and a wasteless technology to avoid environmental pollution and to provide safe work conditions. These requirements, however, have not been met. The main problem consisted of the formation of a by product (homopolymer) in considerable quantities , which resulted difficulties such as the increase of grafting bath viscosity ,slowing down penetration of a free monomer into fibers , consequently , limited degrees of grafting and monomer utilization . In addition, it was necessary to remove the troublesome homopolymer by a time consuming extraction.

Buchenska [54] developed the conditions for the modification of PA6 fibers (grafting acrylic acid and postreatment with antibiotics) which would be suitable for implementing on a larger laboratory or commercial scale. Prior to the grafting process, the fibers were activated with a solution of benzoyl peroxide in benzene. The effects of the main process parameters and auxiliary additives on the degree of grafting, quantity of the homopolymer formed during grafting, effectiveness of grafting, extent of conversion, and grafting ratio were determined. The resultant fibers, containing carboxylic groups in their structure, were additionatly modified

with penicillin, neomycin, or gentamycin to obtain antibacterial fibers in relation to Gram-positive and Gram negative microorganisms (*Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aerruginosa*). This was confirmed in vitro by measuring the growth zones of the above-mentioned bacteria. The modified fibers show different activities in relation to the microorganisms, being dependent on the type and quantity of the added biocide. The kinetics of antibiotic release into water was examined and described by means of a mathematical equation. The release of antibiotics into solution proceeds for quite a long time after which there is still enough antibiotic on the fibers to provide them with antibacterial properties [54].

Protoporphyrins and metalloporphyrins

One class of biocide agents includes porphyrins and metalloporphyrins (MPS). The ability of porphyrins and MPS to kill a wide spectrum of pathogenic microorganisms has been extensively studied in recent years. A study by J.Sherrill etal. [55] examined the antibacterial activity of several types of MPS against mycobacterium, gram –negative and gram –positive bacteria. They found that MPS were effective against actively respiring bacteria, whereas anaerobic bacteria were fully resistant to the effects of MPS .Much of the previous research that has been performed with protoporphyrins IX (PPIX) was investigated. Antimicrobial effects in freely moving state, allowing molecules to be internalized by the microorganisms.

Porphyrins obtain their antimicrobial activity by producing reactive oxygen species (ROS) upon absorbing visible light. They absorb light in the visible and UV spectrum, with particularly strong absorption in the blue wavelength region. The ability of porphyrins to produce ROS on the absorption of light makes the use of porphyrins as antimicrobial agents grafted to polymeric surfaces a feasible biocide agent for use in biomedical applications.

Protoporphyrins IX and zinc proporphyrin IX were grafted to the surface of nylon6,6 films via an ethylene diamine bridge and polyacrylic acid (PAA). X-ray photoelectron spectroscopy showed that approximately 57%of nylon surface was covered by PAA and approximately 6% of carboxylic acid groups in PAA were grafted to ethylene diamine derivative of protoporphyrins IX or its zinc salt [55].

Surface modification of polymers

1. Radio Frequency RF plasma-treated polymers

The choice of polymers for various biomedical applications depends on their surface properties. All polymers do not possess the surface properties required for biomedical applications.

Surface properties of the materials like surface free energy, hydrophilicity and surface morphology, which influence in the polymer interaction, decide the choice of the polymer. Radio frequency RF plasma offers a unique route for surface modification of polymers without affecting their bulk properties. This process results in a smooth, pinhole-free ultrathin film. Plasma treatment of polymers can render the material surface either hydrophilic or hydrophobic through the use of the respective plasma gases. It has found various applications in automobile, electronic, biomedical and chemical industries [56].

2. Effects of plasma on a polymer surface

Plasma generated in a vacuum environment influences the surface of the polymer to make it suitable for a specific application. It has sufficiently high energy to break the covalent bonds of polymers exposed to the plasma. Plasma treatment can improve wettability, oxidize the surface. Various effects of plasma on a polymer surface may be summarized as : surface modification, grafting and film deposition [57].

Surface modification by plasma treatment is achieved using gases such as air, O_2, N_2, argon and helium. The objectives of plasma surface modification in biomedical applications are adhesion promotion, enhanced surface wettability and spreading and reduced surface friction. Factors that contribute to improved adhesion are removal of surface contaminants and weakly bound polymer layers, etching and substitution of chemical groups on the surface that permit covalent bonding.

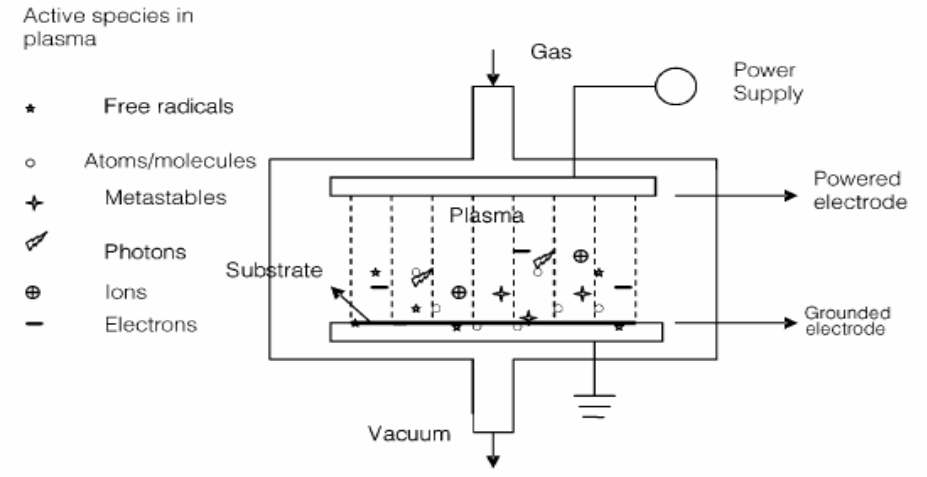


Fig. 9 Schematic diagram of plasma reactor

- **Removal of surface contaminants**

Low-pressure plasma is used for cleaning polymer surfaces of contaminants such as air pollutants, fingerprints, oxide layers, weakly bonded surface layers and other surface additives. It is possible to remove contaminations by simple plasma sputtering with the help of noble gases, by oxidation of organic contaminants with oxygen plasma or by reduction of oxides or sulphides by hydrogen plasma [58].

- **Substitution of chemical groups**

Alteration of surface characteristics is also possible by substitution of chemical groups present on the polymer chain being modified. Different gases can incorporate large varieties of chemical groups such as hydroxyl, carbonyl, carboxylic, amino or peroxyl groups. Oxidation, nitration, hydrolization and amination processes induced by plasma are used to improve the surface energy of the substrate. Substituting the functional groups increases the surface energy and reactivity. Plasma-induced grafting is a two-step process for incorporation of functional groups and reactive sites to the polymer surface. Free-radical formation using inert gas plasma is followed by the introduction of an unsaturated monomer into the reaction chamber. The monomer reacts with the free radical to yield a grafted polymer. This process differs from activation in a way that it adds the material to the polymer backbone instead of functionally modifying the surface polymer chains [59-60].

- **Plasma polymerization**

The plasma polymerization process, which can produce thin films with unique chemical and physical properties, has found various biomedical applications [61]. In this process, gases in the plasma undergo polymerization through a free-radical initiation process. Methane, ethylene, propylene, fluorocarbon monomers and organosilicon compounds can be polymerized by this method. When the process gas mixture contains hydrocarbons, the hydrocarbon molecules are fractured into free-radical fragments. These free radicals initiate polymerization. As the molecular weight of the polymer increases, it is deposited on the surface of the substrate. Polymerization at an atomic level is also possible when sufficient energy is supplied to break all the bonds on the monomer. The plasma-polymerized thin films are generally pinhole-free, highly cross-linked and strongly bound to the surface, a list of gases used in plasma processing; including polymerization is shown in Table 2.

Table 2. Plasma gases and their applications

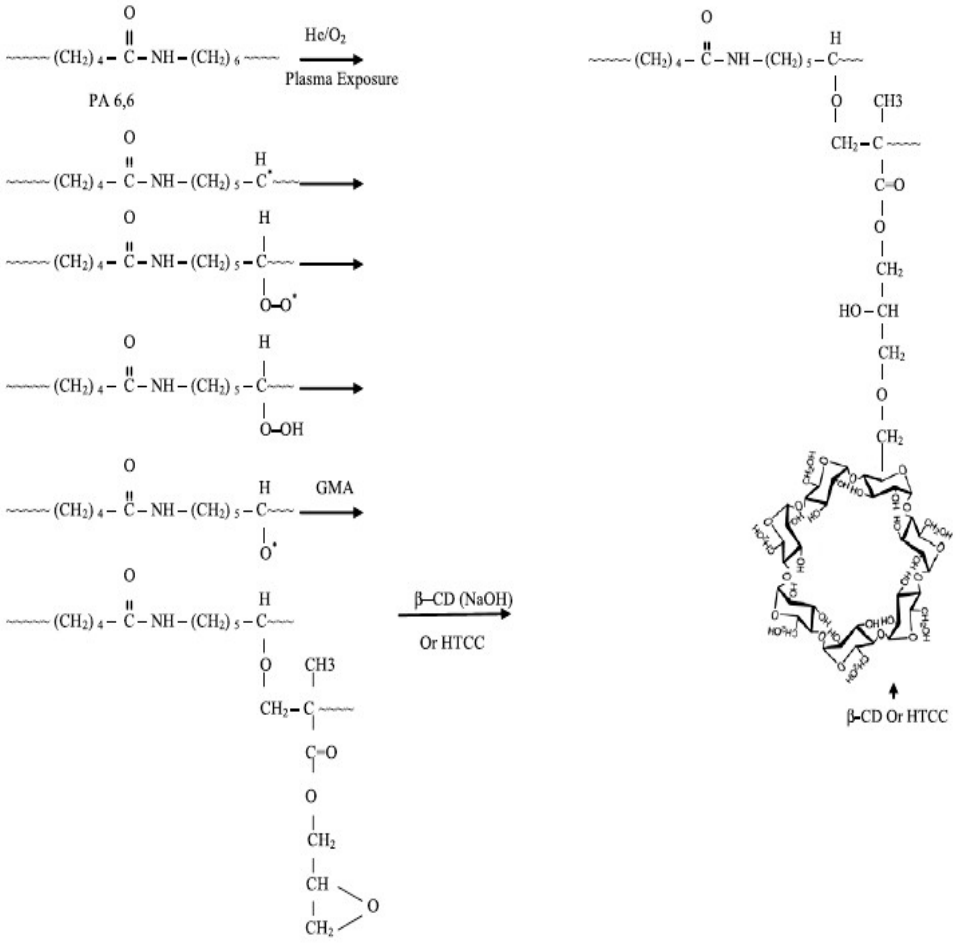
Plasma gas	Application
Oxidizing gases (O_2, air, H_2O, N_2O)	Removal of organics by oxidation and to leave oxygen species in the polymer surface
Reducing gases (H_2, mixtures of H_2)	Replacement of F or O in surfaces, removal of oxidation-sensitive materials, conversion of contaminants to low molecular weight species that do not polymerize or re-deposit on adjacent surfaces
Noble gases (Ar, He)	To generate free radicals in surfaces to cause cross-linking or to generate active sites for further reaction
Active gases (NH_3)	To generate amino groups
Fluorinated gases (CF_4, SF_6 and other perfluorinated gases)	To make the surface inert and hydrophobic
Polymerizing gases (monomer gases for direct polymerization, Ar or He pretreated)	Polymerization of layers onto substrates by direct polymerization or by grafting on Ar or He pretreated polymer surface

Atmospheric pressure plasma has several advantages over vacuum plasma techniques since operation is at ambient conditions, can easily be adopted for continuous on-line surface modifications of textiles, and do not require vacuum equipment. Atmospheric pressure plasma has been applied for numerous functionalities such as increased hydrophilicity, antistatic and enhanced dyeing properties, fire retardant and permanent fixation of biocidal agents into fibers. Biocidal fabrics kill or inhibit the growth of microorganisms such as bacteria, molds and fungi and repel or kill crawling and flying insects. An important feature of atmospheric plasma is its ability to modify the surface without affecting the bulk properties of the treated fabrics. several studies have been conducted using plasmas either under vacuum or at atmospheric conditions for surface modification and graft copolymerization of textiles such as cotton, nylon, polypropylene, polyethylene terephthalate (PET) and polyvinyl alcohol (PVA) and their blends, in which surface modifications have successfully been achieved [62-64].

Plasma surface modification

Several studies have been conducted using plasmas either under vacuum or at atmospheric conditions for surface modification and graft copolymerization of nylon in which surface modifications have successfully been achieved [65-67].

Oxidative atmospheric pressure plasma was utilized to activate surface of PA 6,6 fabrics followed by graft copolymerization of glycidylmethacrylate (GMA) and further reacted with triethylene- tetramine (TETA), quaternary ammonium chitosan (HTCC) or β-cyclo- dextrin (β-CD). The inner CD cavity was complexed with some insecticidal perfumes as illustrated below.



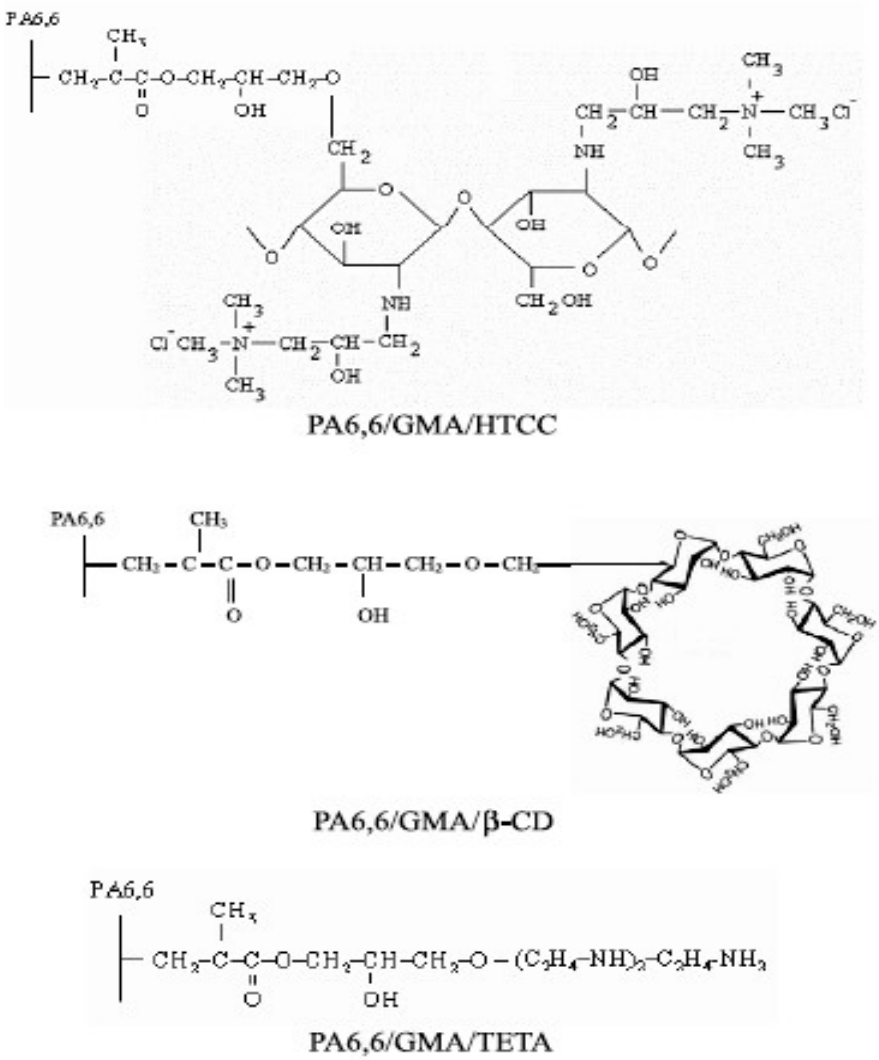


Fig. 8 Chemical structure of biocidal grafted PA6,6 fabrics.

Modified PA6,6 fabrics were analyzed by differential scanning calorimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. Antimicrobial activity and insect repelling assay were conducted and showed efficient antimicrobial and insect repelling properties [69].

Polyamide 6 fabric has been treated using low temperature plasma with both oxygen and argon gases followed by using some metal salts solutions such as copper sulfate, nickel sulfate, and silver nitrate. Oxygen plasma was found to be more

effective in enhancing some properties of polyamide 6 fabric. Exposure of polyamide 6 fabric to low temperature oxygen plasma caused changes in surface roughness. A rougher surface fabric is a good padding cloth and is important in conventional aqueous textile finishing and dyeing processing because of the higher rate of liquid uptake. Both density and crystallinity percentage of oxygen plasma-treated fabric slightly increased. The antibacterial properties of oxygen plasma/metal salts-treated polyamide 6 fabrics were markedly improved even after ten washings. The dyeability of the fabric was improved and the washing fastness properties [69].

Novel biocidal fabrics were synthesized by the graft copolymerization of glycidyl methacrylate (GMA) onto plasma-treated nonwoven polypropylene (PP) to produce PP/ GMA grafts. Atmospheric oxygenated helium plasma was used to enhance the PP fabrics' initiation before GMA grafting. The grafted PP/GMA epoxide group was reacted with

β-cyclodextrin, monochlorotrizynyl- β -cyclodextrins, or a quaternary

ammonium chitosan derivative [N-(2 hydroxy propyl)3-trimethyl -ammonium chitosan chloride]. Some interesting biocidal agents were complexed into the cyclodextrin (CD) cavity of PP/ GMA/ CD grafted fabrics. Fourier, Thermo gravimetric analysis,differential scanning calori-metry, and optical and scanning electron microscopies were used to characterize the grafted completed fabrics. These synthesized biocidal fabrics proved to be antistatic, antimicrobial, and insect-repelling

Uses of antimicrobial PA and PP fibers

Novel technologies in antimicrobial polyamide fibers are successfully employed especially in medical filed. Textile fibers with antimicrobial properties are given alone or in blends with other fibers. The field of application of the bioactive fibers includes sanitary materials, dressing materials, surgical threads, materials for filtration of gases and liquids, air conditioning and ventilation, constructional materials, pharmaceutical industry, footwear industry, clothing industry, automotive industry, marine, military and space etc… [70]. PP is used in different fields for hygienic and medical uses such as surgical masks, diapers[1], filters; burn wound dressings[2], hygienic bands and others including carpets, automotive fabrics, manufacturing clothing, underwear, socks, technical textiles, sport and military uniforms.

Conclusion

In health-related field, protection from pathogens is a growing concern, and textiles with antimicrobial properties are important. Nylon-6, Nylon6,6 and Polypropylene fabrics are of considerable use in the textile industry. The modification of polyamide to acquire antimicrobial properties is a very important task for a wide range of industrial applications, including clothing, bedding and interior fabrics and medical field.

The manufacture of bioactive PA and PP fibers can be accomplished by the addition of bactericides to the chips before fibers extrusion. Practice has shown that modification of synthetic fibers or addition of the necessary functional additives during spinning of the fibers is the simplest, most reliable, and effective methods. Manufacturing of modified chemical fibers by these methods are effective if large-tonnage are done.

Treatment of textiles in finishing is a relatively simple operation.

It is usually conducted with padding machines that allow measuring the applied substances without any marked excess of the reagents. This is followed by drying and heat treatment for stabilizing the applied reagent. When this method is used, the necessity of recycling the reagents and formation of waste waters are eliminated.

Creation of blended antimicrobial textiles is an important direction. Addition of antimicrobial fibers to blends will protect the components of the textile from biodegradation.

Treatment with electrophysical or plasma methods (eco-friendly method) has the advantage of reducing usage of chemicals, water and energy. They also offer the possibility to obtain multi-finishing textiles (e.g. hydrophilic, hydrophobic, and antibacterial) without changing the bulk textile properties (hand, softness, flexibility, etc.). This explains why plasma treatment has already been investigated extensively. Plasma processes should be studied at different stages of the production process (sliver, yarn level, or on fabric), for a whole range of different textile applications.

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