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NANOTECHNOLOGY FOR ANTIMICROBIAL FINISHING OF TEXTILES

Vhanbatte S.B., DKTES's Textile & Engineering Institute, Ichalkaranji, MS, India

Landage S.M., DKTES's Textile & Engineering Institute, Ichalkaranji, MS, India

Wasif A.I., DKTES's Textile & Engineering Institute, Ichalkaranji, MS, India

Dansena B., DKTES's Textile & Engineering Institute, Ichalkaranji, MS, India

Karche N.V., DKTES's Textile & Engineering Institute, Ichalkaranji, MS, India

Abstract: *Owing to its high surface area to mass ratio, nano-particles fascinate engineers for various applications. Surface modification is one of the interesting textile applications which enhance functionality like hydrophilicity, hydrophobicity, anti-bacterial, UPF improvement, self-cleaning etc. In the present review, application of nano-silver particles are on textile material for improving antimicrobial property has been discussed. Synthesis, properties, application and evaluation of nano-silver particles and treated textile substrate are reviewed. Amongst various options, application of nano-silver found to be effective and economical.*

Key Words*: Antimicrobial finish, chemical reduction method, Nanosilver, Nanotechnology, etc.*

WHAT IS NANOTECHNOLOGY

Nanotechnology is the science and technology of small things that are less than 100nm in size. For comparison, a human hair is about 60-80,000 nanometres wide. Scientists have discovered that materials at small dimensions small particles, thin films, etc. can have significantly different properties than the same materials at larger scale. There are thus endless possibilities for improved devices, structures, and materials if we can understand these differences, and learn how to control the assembly of small structures. There are many different views of precisely what is included in nanotechnology. In general, however, most agree that three things are important: Small size, measured in 100s of nanometres or less, unique properties because of the small size, Control the structure and composition on the nm scale in order to control the properties.

At the nanoscale, properties of materials behave differently, governed by atomic and molecular rules. Researchers are using the unique properties of materials at this small scale to create new and exciting tools and products in all areas of science and engineering. Nanotechnology combines solid-state physics, chemistry, electrical engineering, chemical engineering, biochemistry, biophysics, and materials science. It is thus a highly interdisciplinary area, integrating ideas and techniques from a wide array of traditional disciplines.

NANOTECHNOLOGY IN TEXTILES

The use of Nanomaterials and nanotechnology-based processes is growing at a tremendous rate in all fields of science and technology. Textile industry is also experiencing the benefits of nanotechnology in its diverse field of applications. Textile based nano-products starting from nanocompositefibres, nanofibres to intelligent high performance polymeric nanocoatings are getting their way not only in high performance advanced applications, but nanoparticles are also successfully being used in conventional textiles to impart new functionality and improved performance. Greater repeatability, reliability and robustness are the main advantages of nanotechnological advancements in textiles. Nanoparticle application during conventional textile processing techniques like finishing, coating and dyeing enhances the product performance manifold and imparts hitherto unachieved functionality.

New coating techniques like sol-gel, layer-by-layer, plasma polymerization, etc. can develop multi-functionality, intelligence, excellent durability and weather resistance to fabrics. The present article focuses on the development and potential applications of nanotechnology in developing multifunctional and smart nanocompositefibres, nanofibres and other new nanofinished and nanocoated textiles. The influence of nano-materials in textile finishing and processing to enhance product performance is discussed. Nanocoating is relatively a new technique in the textile field and currently under research and development. Polymeric nanocomposite coatings where nanoparticles are dispersed in polymeric media and used for coating applications is a promising route to develop multifunctional and intelligent high performance textiles. The most researched area to produce multifunctional, smart fibres is the preparation of nanocompositefibres where the exceptional properties of nanoparticles have been utilized to enhance and to impart several functionality on conventional textile grade fibres. Nanofibres, which are sub-micron size in diameter, are gaining popularity in some specialized technical applications such as filterfabric, antibacterial patches, tissue engineering and chemical protective suits.

NANOTECHNOLOGY BASED FINISHES

Nanotechnology has opened immense possibilities in textile finishing area resulting into innovative new finishes as well as new application techniques. Particular emphasis is on making chemical finishing more controllable, durable and significantly enhance the functionality by incorporating various nanoparticles or creating nanostructured surfaces. The unprecedented level of textile performances claimed for these nanofinishes such as stain resistance, antimicrobial, controlled hydrophilicity / hydrophobicity, antistatic, UV protective , wrinkle resistant and shrink proof abilities can be exploited for a range of technical textile applications such protective clothing, medical textiles, sportswear, automotive textiles etc. Nanofinishes are generally applied in nanoemulsion form, which enables a more thorough, even and precise application on textile surfaces. They are generally emulsified into nanomicelles, made into nanosols or wrapped in nanocapsules that can adhere to textile substrates easily and more uniformly. Since nanoparticles have a large surface area to volume ratio and high surface energy, they have better affinity for fabrics. Therefore these finishes are more durable, effective and do not adversely affect the original handle and breathability of the fabric. A range of different textile products and finishes based on nanotechnology has already been launched in the market.

Example of some nanoparticles:

There are numerous numbers of nanoparticles. Here just some nanoparticles are presented such as Clay nano particles, ZnO nanoparticles, TiO_2 nanoparticles, MgO nanoparticles, Silver nanoparticles, Fluorocarbon nanoparticles, Antimony pent oxide nanoparticles, Tourmaline nanoparticles.

Application area of Nanotechnology in Textile Finishing:

1. The functional water repellent, protection UV, absorption property, colourfastness, abrasion safety, fire retard, functional hygiene, antimicrobial functional protection self-cleaning.
2. Nano whiskers that make the fabric stained and water resistant. It also makes the fabric breathable rather than resin finishes.
3. The moreover whiskers give water and oil repellence, superior durability, breathable fabric remains soft and natural wrinkle resistance.
4. The nano net completely covers the core fibres and inject linen property in synthetic fibres i.e. the absorbency of linen in polyester fibres. It alters the synthetic fibres to

give a feel of cotton and linen that absorbs the body moisture and gives cooling effect.

5. "Wrap nano sheet" wraps the fibres completely to cover it and the property. It makes fabric strong and durable. It improves the colourfastness, crease retention and static resistance.
6. Clay nanoparticles are composed of various hydrous allumino-silicates that possess various properties like chemical, heat, electrical resistance that improve flame ret ardency and anti-corrosiveness of the fabric.
7. ZnO nano particles can impart UV shielding in fabrics that can also reduce static electricity of nylon fabric.
8. TiO2 and MgO have photo catalytic activity. These particles are able to break the toxic, harmful chemicals and biological agents. Hence, impart self-sterilizing functions to the fibres.
9. Silver nanoparticles possess antimicrobial and anti mould property. The particles are used to impart anti odour and ultra-fresh finishes to the undergarments and socks.

ANTIBACTERIAL FINISH

1. Necessity of antibacterial finishes

The growth of microorganisms on textiles, especially natural fibres-based textiles, could be discussed in terms of large receptive surface area along with availability of proper conditions for growing, i.e. temperature, oxygen, moisture and nutrients. The growth of microorganism has negative effects not only on textiles but also on the wearer (in case of clothes), since it results in biodegradation of textile materials along with their dissemination as a health risk.

2. Requirements for antibacterial finishes

An effective antimicrobial finish should be: quick acting to be effective, able to kill or stop the growth of microorganisms, it has to be durable to wash or dry cleaning, compatible with other ingredients in the finishing formulation, has minimal impacts on both the environment and the product quality, easy to apply for low cost and low toxicity criteria.

3. Mechanism of antibacterial finishes

Antimicrobial products can be classified into: i) bacteriostasis i.e. that stops the growth and spread of microbes, and ii) bactericides, i.e. that actually kill microbes. An effective biocide must reach and interact with its microbial target sites. The Bacteriostasic mechanisms of action of antimicrobial finishes are including preventing cell production, blocking of enzymes, damaging cell membrane, and/or destruction of the cell wall and poising of the cell from within. The antimicrobial efficiency of biocide formulations varies greatly between different types of microorganisms. Resistance to disinfection follows the decreasing order: Mycobacterium > Gram -ve bacteria > Gram +ve bacteria.

4. Antibacterial finishes and their effect

Chemistry of some antimicrobial finishes as well as their mode of action could be summarized as follows:

- Oxidizing agents such as aldehydes, halogens and peroxy compounds, these compounds can attack the cell membrane, arrive the cytoplasm and change/inactivate the microorganism's enzymes.
- Natural herbal products can be used for antimicrobial finishes.
- Chitosan is an effective natural antimicrobial agent derived from Chitin, an important component in crustacean shells.
- Radical formers like halogens, isothiazones and peroxo compounds; these are source risks to nucleic acids, since they are very reactive (also at low concentration level) due to the presence of free electrons.
- Complexing metallic compounds based on metals like cadmium, silver, copper and mercury cause inhibition of the metabolism.
- Triclosan 5-chloro-2-(2,4-dichloro phenoxyl) phenol products. Triclosaninhibits growth of microorganisms by penetrating and disturbing their cell.
- Quaternary ammonium compounds (polycationic properties). Fabrics finished with these substances lead finally to the breakdown of the cell.

ANTIMICROBIAL AGENTS

Natural Antimicrobial Agents:

Natural finishes are those in which various materials from plant or animal kingdom are used. In recent years, great attention has been devoted to biopolymers because of their biocompatibility and biological functions and consequently, they are used in textile, biomedical and pharmaceutical fields. Some marine animals such as prawns and fishes possess some compounds which exhibit antimicrobial activity. Chitosan is an effective natural antimicrobial agent derived from Chitin. Natural herbal products such as Neem, Tulsi, Pomegranate, Aloe Vera, Prickly Chaff Flower, Turmeric, Clove, etc. also exhibit antimicrobial activity. Studies reveal that some specific species of herbs having antimicrobial activity are suitable for textile application.

Synthetic Antimicrobial Agents:

The antimicrobial Dyes, Quaternary Ammonium Compounds, Polyhexamethylene Biguanides (PHMB), Triclosan (2, 4, 4'-trichloro-2'- hydroxydiphenyl ether), Regenerable N-halamine and peroxyacids and Metals and Metal salts such as Silver, Zinc, Copper. Their bactericidal activity goes on decreasing as they attach to the substrate. Furthermore, the biocide is gradually lost during the use and can be washed off the textile. For this purpose large amounts of these biocides are need to be applied to textiles for effectively control of bacterial growth and to sustain durability.

SILVER AS AN ANTIMICROBIAL AGENT

1. The History of Silver as an Antimicrobial Agent:

The use of elemental silver as an antimicrobial agent is nearly as old as the history of mankind. The ancient Egyptians mention the medicinal use of silver in their writings. Romans stored wine in silver urns to prevent spoilage. The courts of the Chinese emperors ate with silver chopsticks for better health. Druids used silver to preserve food. American settlers put silver dollars in milk to stop spoilage. Silver leaf was used during World War - I to combat infection in wounds.

2. Silver in Health Care:

Silver has a long and intriguing history as an antibiotic in human health care. It has been developed for use in water purification, wound care, bone prostheses, reconstructive orthopedic surgery, cardiac devices, catheters and surgical appliances. Advancing biotechnology has enabled incorporation of ionizable silver into fabrics for clinical use to reduce the risk of infections and for personal hygiene.

3. Biological Properties of Silver:

Silver is not a recognized trace metal but occurs in the human body at low concentrations ($<$ 2.3 μg/l) due to ingestion with food or drinking water, inhalation and occupational exposures. Clearly, occupational exposure or medicinal use of silver as an antibiotic in wound dressings, indwelling catheters, cardiac devices and in orthopedic surgery will be associated with higher than normal blood levels and may be a safety concern

4. Sustained Silver Release Wound Dressings:

Silver ion release will be sustained for the expected life-span of the dressing (up to 7 days). Three main forms of dressing are currently available:

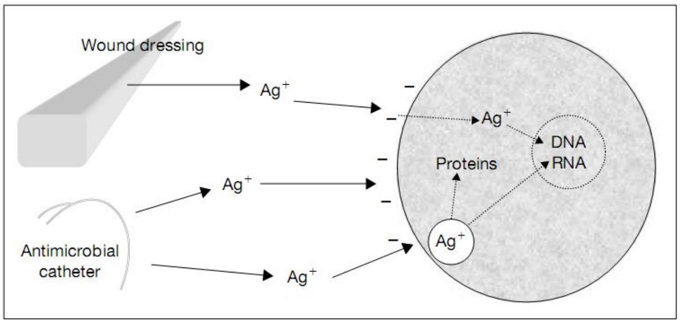
(1) Those releasing high levels of silver for rapid antimicrobial action.

(2) Dressings that absorb wound exudates and where silver ions released provide sustained antimicrobial action.

(3) Dressings that release silver sulphadiazine.

5. Antibiotic Action of Silver:

Silver is inert and exhibits no biocidal action. However, it ionizes in the presence of water or tissue fluids to release silver or other biologically active ions. This 'activated' ion shows a strong affinity for sulphydryl groups and protein residues on cell membranes.



6. Antimicrobial Action of Silver:

(1) Attachment to the bacterial cell membrane;

(2) Absorption/diffusion into the cell;

(3) Coagulation with bacterial proteins/enzymes.

The mechanism of action of silver is linked with its interaction with thiol group compounds found in the respiratory enzymes of bacterial cells. Silver binds to the bacterial cell wall and cell membrane and inhibits the respiration process. In case of *E-coli*, silver acts by inhibiting the uptake of phosphate and releasing phosphate, succinate, proline and glutamine from *E. coli* cells.

7. Mechanism of Action of Silver Nanoparticles:

The silver nanoparticles shows efficient antimicrobial property compared to other salts due to their extremely large surface area, which provides better contact with microorganisms. The nanoparticles are attached to the cell membrane and also penetrate inside the bacteria. The bacterial membrane contains sulphur containing proteins and the silver nanoparticles interact with these proteins in the cell as well as with the phosphorus containing compounds like DNA. When silver nanoparticles enter the bacterial cell it forms a low molecular weight region in the centre of the bacteria to which the bacteria conglomerates thus, protecting the DNA from the silver ions. The nanoparticles preferably attack the respiratory chain, cell division finally leading to cell death. The nanoparticles release silver ions in the bacterial cells, which enhance their bactericidal activity.

Synthesis of Nanosilver using chemical reduction Method:

In recent years, noble metal nanoparticles have been the subjects of focused researches due to their unique electronic, optical, mechanical, magnetic and chemical properties that are significantly different from those of bulk materials. These special and unique properties could be attributed. For these reasons, metallic nanoparticles have found uses in many applications in different fields as catalysis, electronics, and photonics. A variety of preparation routes have been reported for the preparation of metallic nanoparticles; notable examples include, reverse micelles process, salt reduction, microwave dielectric heating reduction, ultrasonic irradiation, radiolysis, solvo-thermalsynthesis, electrochemical synthesis, etc.

Presently, the investigation of this phenomenon has regained importance due to the increase of bacterial resistance to antibiotics, caused by their overuse. Antibacterial activity of the silver-containing materials can be used, for example, in medicine to reduce infections as well as to prevent bacteria colonization on prostheses, catheters, vascular grafts, dental materials, stainless steel materials and human skin. The use of silver nanoparticles as antibacterial agent is relatively new. Because of their high reactivity due to the large surface to volume ratio, nanoparticles play a crucial role in inhibiting bacterial growth in aqueous and solid media.

Silver containing materials can be employed to eliminate microorganisms on textile fabrics or they can be used for water treatment. Contrary to bactericide effects of ionic silver, the antimicrobial activity of colloid silver particles are influenced by the dimensions of the particles the smaller the particles, the greater antimicrobial effect. Therefore, in developing routes of synthesis, an emphasis was made to control the size of silver nanoparticles. Silver nanoparticles have been produced using different methods: electrochemical method, thermal decomposition, laser ablation, microwave irradiation and sono-chemical synthesis.

The simplest and the most commonly used bulk-solution synthetic method for metal nanoparticles is the chemical reduction of metal salts. In fact, production of nanosized metal silver particles with different morphologies and sizes using chemical reduction of silver salts has been reported. This synthetic method involves reduction of an ionic salt in an appropriate medium in the presence of surfactant using various reducing agents. The dispersions of silver nanoparticles display intense colours due to the plasmonresonance absorption. The surface of a metal is like plasma, having free electrons in the conduction band and positively charged nuclei. Antimicrobial susceptibility testing methods are divided into types based on the principle applied in each system. They include: Diffusion (Kirby-Bauer and Stokes), Dilution (Minimum Inhibitory Concentration) and Diffusion & Dilution (E-Test method).

Antimicrobial susceptibility testing in the clinical laboratory is most often performed using the disc diffusion method. The Kirby-Bauer and Stokes' methods are usually used for antimicrobial susceptibility testing, with the Kirby-Bauer method being recommended by the National Committee for Clinical Laboratory Standards (NCCLS) (NCCLS, 03). The Kirby-Bauer method was originally standardized by Bauer et al. (the so called Kirby-Bauer method). This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. The antibacterial characteristics of silver nanoparticles produced have been demonstrating by directly exposing bacteria to colloid silver particles solution. In the present work on the preparation of nanosized silver nanoparticles from aqueous solution of silver nitrate, we employed as reductant a mixture of hydrazine hydrate and citrate of sodium; sodium dodecyl sulphate was employed as a stabilizer.

Silver nanoparticles were synthesized according to the method described in the previous section, the colloidal solution turned pale brown, pale yellow and pale red indicating that the silver nanoparticles were formed.

EVALUATION OF ANTIBACTERIAL ACTIVITY

Various tests have been used to determine the effectiveness of the antibacterial activity of textiles. Some of these tests are follows:

- Zone of inhibition test: Rapid qualitative method for determining antibacterial activity of treated textile materials against both Gram-positive and Gram-negative bacteria. In this test, by showing the inhibition zone around the tested sample, it can be shown if a tested finishing agent is protecting the textile from microorganisms or not.

- AATTC Test Method 100-2004: It is quantitative method for determining the degree of antibacterial activity of treated textiles. The bacterial growth amount in inoculated and incubated textiles is determined by using serial dilute ions which followed by inoculations in sterile agar plate.
- Tetrazolium/formazan test (TTC): TTC- test method is considered a rapid method for evaluating the antibacterial activity of the finished fabrics. The redformazan obtained indicates the activity and viability of the cells. Since, in the presence of bacteria, tetrazolium salts (TTC) is reduced to red formazan.

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