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Nanotechnology applications in textiles

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Abstract: The advent of nanotechnology has invigorated many industries and textile industry is not an exception. The present status of nanotechnology use in textiles is reviewed, with an emphasis on improving various properties of textiles. The improvements on the application areas of nanotechnology in textile industry such as high-tech fibres, stay clean textiles, antibacterial textiles, antistatic textiles, textiles that can change colour, textiles protecting UV radiation, flame retardant textiles, textiles healing and nourishing human body are covered.

Keywords: Antibacterial, nanotechnology, nano-particle, photocatalysis, textile finishing.

Introduction

Nanotechnology is an emerging, highly interdisciplinary field, premised on the ability to manipulate structural materials on the level of individual atoms and molecules. Nanotechnology is an umbrella term covering a wide range of technologies concerned with structures and processes on the nanometer scale (nanometer = nm, one-billionth of a meter [10^{-9}m]). Nanoscience and nanotechnology can be considered as 'key' technologies and have revitalised material science and led to the development and evolution of a range of new improved materials through nano-structuring. It encompasses expertise spanning over traditional physics, chemistry, material science, computer simulation and electrical and mechanical engineering yet is not defined exclusively by any one of these disciplines. The unique and new properties of nano-materials have attracted not only scientists and researchers but also businesses, due to their huge economic potential. 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 (around 0.1-100 nm, one nanometer is one millionth of a meter). Nanotechnology brings new functions and properties to develop new products and applications in the industrial fields such as chemistry, medical technology, automobile, food industry, pharmacy, textile industry, environmental industry and biotechnology where nano-scale is so important. Nano technology is an interdisciplinary science which takes role in the material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, textiles, optical coatings, photovoltaics, antibacterial agents, physics, biology. Many nanotechnology based innovations have appeared in the literature (Scientific American, 2002; Gross, 1999), offering great promise for the future.

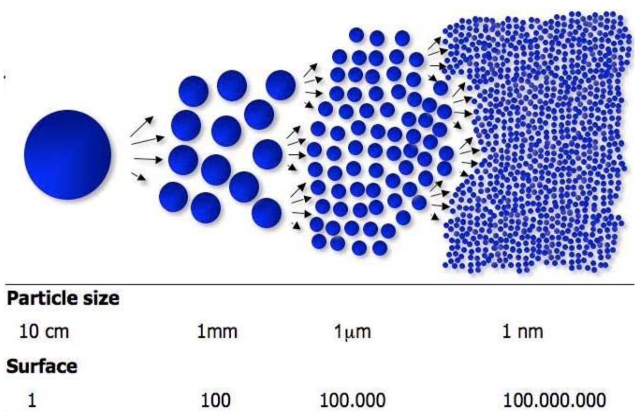
Size matters

Size effects constitute a fascinating aspect of nano-materials. In a pragmatic approach, we can use the following definition for nanotechnology: a) it deals with structures whose area is smaller than 100 nm at least in one dimension, b) it exploits characteristics and phenomena which occur in the transitional zone between the atomic and mesoscopic level and c) the technology describes deliberate manufacture and/or manipulation of individual nanostructures. Nanotechnology deals with the effect that properties of materials can change drastically when the particle size falls below approximately 100 nm. It may lead to novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size.

Materials in the nanometre size range exhibit fundamentally new behaviour, as their size falls below critical length associated with any given property. Intervention in the properties of materials at the nano-scale permits the creation of materials and devices with performance characteristics and functionality not previously thought possible. It marks a threshold where quantum physical effects increasingly play an important role and marks the interdisciplinary interaction of sciences (mostly chemistry and physics); therefore nanotechnology is called a convergent technology. Decreasing the size of particles to nano-scale dimensions fundamentally changes the properties of the material. For example, 50 kg of 1mm-size $SiO2$ particles, with a surface of 120 m2, when decreased to 1 nm would have a surface area of 120.000.000 m2. In addition, as the particle size decreases the number of molecules in the surface relative to the bulk increases, giving new and unexpected properties. This has been illustrated schematically in Fig. 1.There are two fundamental strategies for arriving at the nano-dimensions (Foster, 2005). The underlying efforts responsible for nanotechnology-based advances can be largely divided into two seemingly divergent approaches:

precision engineering (top-down) and structure-induced self-assembly (bottom-up).

Fig. 1. Schematic representation of particle size and surface at nano-scale.



The "top-down" approach

Starting from micro technology structures, the components are gradually miniaturised (primarily featured in physics and physical technology). Enlarging the surface and separation of the particles means an increase in free energy making the system less stable. Also some work is lost due to friction effects.

The "bottom-up" approach

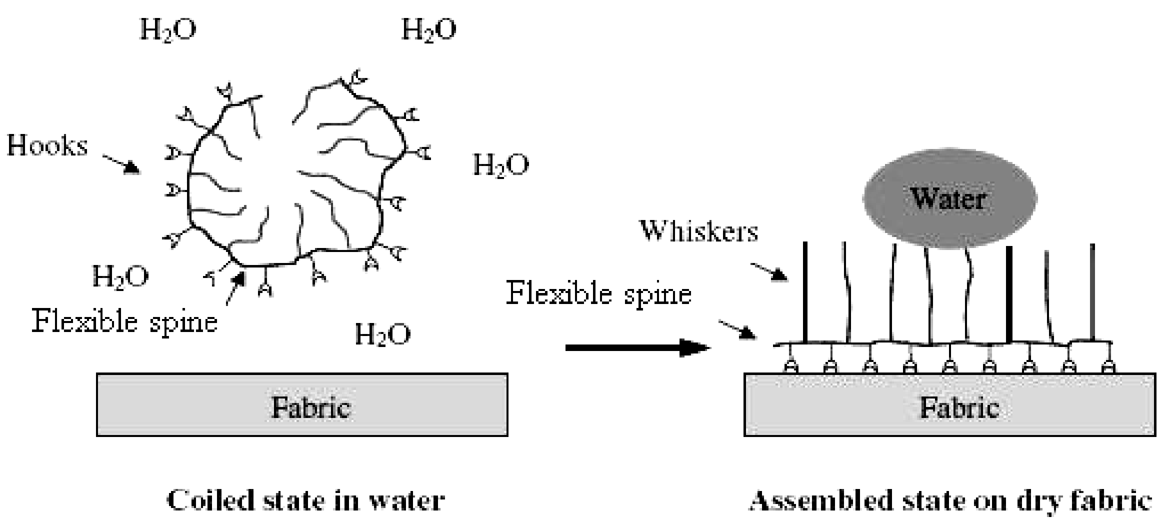
Increasingly complex structures are specifically assembled form atomic or molecular components. This approach is popular in chemistry and biology, where dealing with objects of the nanometer scale is a familiar practice. Colloidal particles can be produced by sol-gel technique. Stable colloids guarantee that the particle size will be nano and no work is necessary to enlarge surface.

Relevance to textiles

As in the other fields, nanotechnology has a great role in textile industry. Textile fabrics are one of the best platforms for deploying nanotechnology. Fibres 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 energetics experienced by macromolecules or supramolecular clusters in the vicinity of a fibre 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 nano-particles 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 (Wong *et al*., 2006). In addition, a coating of nano-particles on fabrics will not affect physical and mechanical properties such as hand, strength, air permeability and wetting, considerably (Carfagna, 2005; Cientifica, 2006; Xin, 2006). 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.

Therefore, the interest in using nanotechnologies in the textile industry is increasing. Current applications of the nanotechnology in the textile industry that have taken place in fibres, yarns, fabrics, nonwovens; finishing like dyeing and coating; electronic textiles,

Fig. 2. Schematic representation of the transition of **Nano-Whisker Architecture** *(Nano-Pel and Nano-Care Finishes).*



fibre modifications and value added applications are considered important and hence discussed here.

Applications in fibres, woven and knitted fabrics and dyeing

One of the applications of nanotechnology in textile industry is in polymeric materials for producing conventional fibres such as PES (Polyester), PA (Polyamide) and PP (Polypropylene) in nano scale. By nanotechnology, the electrical, thermal, mechanical and chemical properties of the fibres can be improved to enlarge the application fields of the fibres in the final use such as "breathable" laminates and super absorbency of fibres provided by the process of creating open-pore-structure in a variety of polymers. In medical textiles, high specific surface areas are required mostly. Polymeric nano-fibres are the right materials with nano-scaled diameters and long lengths. For example, decreasing the fibre diameter reduces the contact angle between fibres; so that the final product made using these fibres have an excellent wetting behaviour (Huang, 2005). In addition to these, the light weight fibres which are produced by nanotechnology gain phenomenal strength (*Aitex_interest paper* (2005) www.nanospain.org/ files/papers/ aitex%20interest .pdf). Nano-fibres have multifunctional properties like high surface area, a small fibre diameter, good filtration properties, thin layers and high permeability (Casey & Turney, 2006; Nyati, 2005; *Nanotechnology Foundation of Texas Newsletter* (2003) http://www.nanotechfoundation.org/ download/Update_June_2003.pdf). It's proven that the addition of carbon nano-tubes to a common commercial polymer, polypropylene, leads to eliminate "die swell" effect, causes in swelling of polymers when passing through the capillary tube in electro-spinning process. This improvement enhances the strength of the fibres against the high voltage between capillary tube and the collector. So, this composite polymer can be spun at high speed in production (www.azom.com). Polyester is a textile fibre with very poor water absorption characteristic. Its hygroscopic properties have been increased by a factor of 30 by coating it with a special film of tens of nano-meter thick (50-nano-metre film - made up of 20 layers - on outside of fibre). Quup is a nylon filament yarn with double the moisture uptake of conventional yarn (Cookson & Wang, 2007). In medical textiles, devices such as woven and knitted vascular grafts are used for replacing human arteries in by-pass surgery and in "scaffolding"-machine embroidered implants- for connecting nerves during reconstructive shoulder surgery. Dressings for wound healings are the most necessary health-care products for chronic wounds, warfare conflicts, traffic accidents etc. It facilitates the wound healing apart from covering the wounds from environmental infections These new developments are the results of innovative use nanotechnology (Extreme textiles: designing for high performance, Release pp.3, http://www.squid-labs.com/projects/tensegrity/ExTexRls_Web.pdf).

Nanotechnology has an important application area in dying process. Polypropylene is a wax like textile fibre and is the most difficult fibre to dye as it has no sites for the dye fixation. Nano-clays are used to create dye sites into PP fibres with modified quatemary ammonium salt. This lowers the cost of dyeing in apparel fibres. The nano-clay, montmorillonite, and some modified nano-clays can be used as sorbent for non-ionic, anionic, cationic dyes because nano-particles have small sizes that provide large surface area. To improve the dye sorption of polypropylene, the sorbent can be added physically into the polymer matrix for making a composite. Because of good dye sorption ability of the sorbent made from nano-clay, textiles made from that composite will have good dye ability, good colour fastness, less cost in dying and less problems in waste water treatment. Also they have functionality to improve the properties of the textile material such as strength, modulus, UV absorbance and fire resistance. In a melting or dissolving process by using heat, organic sorbent and/or mechanical blending nano-clays can be added to the polypropylene matrix. This gives the polymer structure thermal and chemical stability and good mechanical properties (Fan *et al.*, 2002; Yang *et al.*, 2005).

Applications in finishing process

The most interesting application area of nanotechnology in textile industry is the finishing process of textiles. The first work on nanotechnology in textiles was undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries (Russell, 2002). Later, more and more textile companies began to invest in the development of nanotechnologies. Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, a surfactant, ingredients and a carrier medium (Cramer, 2003). Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding. Of these methods, padding is the most commonly used (Anonymous, 2003; Xing, 2004; Yen *et al.*, 2003). The nano-particles are attached to the fabrics with the use of a padder 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.

As there are various potential applications of nanotechnology in the textile industry, only some of the well-known properties imparted by nano-treatments are critically highlighted in this paper. Focus has also been made on the finishes developed by Nano-Tex and the application of TiO2 nano-particles for textile finishing.

The Nano-Tex range of treatments was developed through nano processes which made it possible to design molecules with specific performance attributes, engineer the molecules to assemble on the surface of textile fibres with extreme precision, and ensure that they permanently attach to the fibres through the company's patented binding technology. Nano-care® fabric protection imparts a revolutionary, carefree quality to wrinkle resistant fabric that minimizes stains, offers superior liquid repellence and maintains wrinkle resistance. Nano-dry® indicates enhanced fabrics able to move perspiration away from the body while drying quickly. Nano-fresh® is designed to capture body odour and finally Nano-pel® is designated for fabrics that breathes, yet remaining liquid and stain-repellent (Abbas, 2007; Parsarpatet & Sonthisombat (2007), N.Jain, *Sticking to the core competency?* Nanotechnology applications in textiles, Nano-Tex –Fabrics to the nest, power point presentation; Nano-Tex –Intelligent Fabrics for better living, PowerPoint presentation).

The Concept of Nano-Whisker Architecture: Nano-Care™ and Nano-Pel™

Nano-Tex has developed two superior water- and oil-repellent products based on custom-designed fluorocarbon-containing polymers: Nano-Pel and Nano-Care. Nano-Pel is a water- and oil-repellent treatment that can be applied to all major apparel fabrics, including cotton, wool, polyester, nylon, rayon and blends. Nano- Care is a product for 100% cotton that imparts wrinkle resistance in addition to water and oil repellency. Nano-Pel and Nano-Care impart water and oil repellence to the substrates without adversely affecting other desirable properties of the substrate, such as soft hand (tactile feeling) and breathability. Since their introduction, Nano-Pel and Nano-Care have raised the bar on water- and stain-repellent performance.

Generally, copolymers exhibiting water and oil repellence are comprised of a (meth)acrylate monomer containing a perfluoroalkyl group capable of directly giving water and oil repellence, a fluorine-free monomer capable of improving adhesiveness to fibres, and a monomer capable of ensuring durability through self cross- linking or reaction with reactive groups on the surface of the materials to be treated. Most commercial copolymers have N-methylol groups along the main chain, such as copolymers of perfluoroalkyl-containing (meth) acrylate and N-methylol acrylamide copolymers. However, when the fibrous substrate is treated with these copolymers, formaldehyde is produced, which is highly undesirable from an environmental and safety standpoint.

The architecture of the nano-whiskers is depicted in Fig. 2, where oligomeric or polymeric side branches (brushes) are attached to a flexible spine. Also attached are latent 'hooks' that can form covalent links with functional groups on the fibre surface upon drying and curing. In the aqueous state, the nanostructure coils up to shield the hydrophobic branches within a polar outer layer. Upon drying and exposure to heat, the coils unfurl, bringing the polar backbone and multiple hooks in close proximity to the fibre surface (which is generally polar). The brushes project outward from the surface, essentially forming a monomolecular layer to protect against future water or oil intrusion.

Nano-Tex has patented a formulation containing a novel water- and oil-repellent agent capable of binding to fibrous substrates and other materials without the production of formaldehyde. This formulation can impart formaldehyde-free wrinkle resistance and water and oil repellence when combined with a formaldehyde free resin such as dimethylurea glyoxal (DMUG) or butane tetra carboxylic acid (BTCA).

Chemical Synthesis and Additives: The key ingredient of Nano-Tex's patented water and oil repellents is a copolymer that comprises a) an agent containing a fluoro-aliphatic radical, b) stearyl (meth) acrylate, c) a chlorine-containing compound, such as vinylidene chloride, vinyl chloride, 2-chloroethylacrylate or 2-chloroethyl vinyl ether, and d) a monomer selected from those containing an anhydride functional group or capable of forming an anhydride functional group. This anhydride group can react with various nucleophiles on a fabric surface to form a durable ester bond. The composition can further comprise other additives such as poly (acrylic acid), which enhances performance and durability of the polymer by some mechanism, possibly by tacking the main ingredient to the surface of the fabric. Other optional additives include an antioxidant such as ethylenediamine tetra acetic acid (EDTA) to reduce substrate yellowing; a permanent softener/extender to improve the hand of the substrate and increase water repellency; a surfactant to emulsify the polymer in water; wetting agents; and/or a plasticizer.

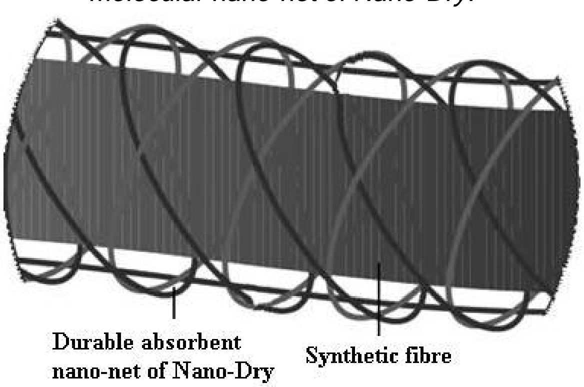
Process: The application of Nano-Pel and Nano-Care can be accomplished using typical textile mill finishing equipment. The composition can be applied to a fibrous substrate by many continuous finishing methods including dip/pad, spray, foam, knife coat and kiss roll, followed by drying and curing in an oven. Typically, the dip/pad method is used in which a fabric is immersed in a bath containing the composition followed by passing the fabric through two rollers that squeeze out excess solution. The treated substrate is then dried and cured to allow reaction of the polymer with the textile and with itself. One key step to ensure performance durability is to start out with a clean substrate. Since the durability depends directly on the covalent attachment of the polymers to the fabric substrate, it is imperative that the surface is not blocked by sizes, oils or contaminants. Therefore, substrates must receive a vigorous scour before to the application process.

The Concept of Nano-Dry™

A treatment that builds a three-dimensional molecular network surrounding a fibre (i.e. the Nano-Net architecture) is called Nano-Dry (Fig. 3). This hydrophilic, or moisture-loving, treatment is applied to polyester and nylon fabrics.

Synthetic textile materials, such as nylon and polyester, are uncomfortable to wear due to their poor permeability to water. In hot weather, sweat cannot easily penetrate (or wick) through these fabrics and evaporate. The poor wicking and permeability are due to the natural hydrophobicity of nylon and polyester polymers; water does not readily spread out over surfaces composed of these materials. Nylon and polyester also often exhibit static cling and stain retention due to their hydrophobic nature.

Fig. 3. The Schematic representation of the 3-D molecular nano-net of Nano-Dry.



It is therefore desirable to find a way of imparting durable hydrophilic properties to nylon, polyester and other synthetic materials. This may be achieved by attaching hydrophilic materials to the hydrophobic fibres. Imparting hydrophilic properties to the hydrophobic substrate will also diminish or eliminate static cling and enable the release of stains during laundering.

The treatment durably attaches a hydrophilic network to a hydrophobic substrate without altering the other properties of the material, such as strength, colour fastness and hand (tactile feel).

The traditional treatments to impart hydrophilic properties for synthetic fabrics rely on film formation on the surface of the fabric and self-cross-linking properties of the chemical to achieve some level of durability to laundering. However, these treatments suffer from the conflicting refinements of moisture absorbance and adhesion to a synthetic and inherently hydrophobic substrate. A superficial or unattached hydrophilic film will absorb moisture in the wash, and upon abrasion it will tend to deteriorate and fall off after repeated washings. The more hydrophilic the film, then the resulting film the less durable. Conversely, the higher the durability, the less hydrophilic character the film will have. As a consequence, traditional commercially available hydrophilic treatments for polyester and nylon have durability only up to 5–10 home launderings. One approach employed to overcome the lack of durability is to increase the amount of chemical deposited on the surface. However, this technique quickly reaches diminishing returns on performance as the excess chemical begins to affect the hand of the fabric, it may affect the colour shade, and it will increase the cost.

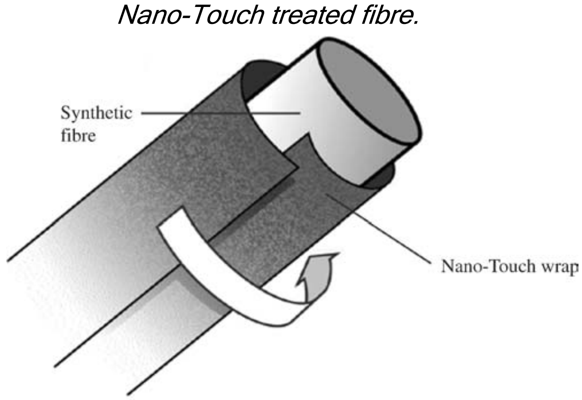
The Nano-Dry treatment achieves its durability not by film formation, but by the combination of covalent attachment to the fibre surface and the use of nano-molecules. Covalent bonding to the fibre surface allows attachment of large, highly hydrophilic, super-absorbent materials. Synthetic surfaces (e.g. polyester) often provide few reactive sites for chemical attachment. However, a large molecule that covers a significant portion of the fibre surface needs only a few attachment points to anchor durably. Large molecules are generally difficult to work with in textile processing due to their high viscosities in aqueous solutions.

However, specific process conditions can be optimized so that the molecules arrange themselves in a compacted conformation that minimizes viscosity. This, along with a clean fibre substrate and significant heat to help catalyse the attachment chemistry, results in a very efficient and durable treatment. A typical solids loading for Nano-Dry treatment onto the fabric surface is around 0.1–0.15% by weight of the fabric, compared to 0.8–4.0% by weight of fabric for conventional film-forming hydrophilic treatments.

The Concept of Nano-Touch

Use of blended textiles has decreased over recent years in favour of 100% cotton fabrics that offer good appearance and comfort. However, the use of 100% cotton yarn and fabrics has its disadvantages. Primarily, these fabrics tend to shrink and wrinkle. With the advent of synthetic textile fibres, the possibility arose for producing continuous filament yarns with greater strength and more durability than those formed of staple fibres. Furthermore, synthetics tend not to have wrinkling or shrinkage problems. Products made from synthetic yarn have excellent strength properties, dimensional stability and good colour fastness to washing, dry-cleaning and light exposure. However, 100% polyester and polyester-blended yarns and fabric made from these yarns have a shiny and synthetic appearance, they are clammy and prone to static build-up in low humidity, and they tend to be hot and sticky in high-humidity conditions. Additionally, because of its high tensile strength, polyester fibre is prone to pilling in staple form and picking in continuous filament form. Almost all the fibre materials can be classified as dielectric materials. This is especially true of synthetic fibres, e.g. nylon, polyester, polyolefins, and acrylics. Natural fibres such as cotton and wool can also have problems associated with static charge build-up. However, this problem tends only to occur at low relative humidity (typically less than 35%). In contrast, synthetic fibres will have static build-up problems even at much higher relative humidity (Adanur, 1995). Nano-Tex has launched a project to develop fabrics that exhibit the positive qualities of cotton and synthetics but without their negative qualities.

Fig. 4. Schematic representation of a Nano-Touch treated fibre.



Basic Approach: The Nano-Touch treatment has been developed to create a permanently attached carbohydrate sheath (carbohydrates have the desired properties of cotton, which is itself considered a carbohydrate) around each synthetic fibre of the web. This treatment endows the treated web with the most desirable characteristics of the synthetic core and most desirable characteristics of the natural, carbohydrate sheath.

Process: The polyester or nylon core material, in fabric form, is passed through a bath containing an aqueous solution of water-soluble carbohydrate and cross-linker and, if necessary, a suitable cross-linker catalyst. The fabric is padded to remove excess liquor and heated to dryness to form a thin film of carbohydrate on the surface of the synthetic core. The fabric is then cured at a temperature high enough to cause reaction between the cross-linker, synthetic core and carbohydrate to form covalent bonds between the core material and the carbohydrate. Simultaneously, cross-links are formed between the carbohydrate molecules themselves, forming the sheath. Fig.4. is the schematic diagram of the resulting architecture.

By the nature of the wrap architecture, the enhanced properties of the finished fabric are surface related. Surface-related attributes such as feel (hand), moisture absorbency, matte finish and reduced static build-up are enhanced and the best properties of the synthetic fibre are retained at the core level, including strength, colour fastness and crease retention. The increased moisture regain improves the ‘natural’ feel of the fabric. Another attribute of the carbohydrate sheath wrapping the fibre is improved moisture wickability. Since the wrap layer has been designed to be ‘cotton-like’, the sheath is naturally hydrophilic and will wick moisture in a similar manner to the Nano-Dry treatment. The Nano-Wrap architecture creates a permanent attachment of the carbohydrate sheath (Nano-Touch). Additionally, the hydrophilic nature of the wrap, the increased moisture regain, and the fact that this additional moisture content is localized to the surface of the fibre all cause Nano-Touch treatment to exhibit durable anti-static performance.

Applications of nanoTiO2 in textile finishing

The application of nano-particles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances. For example nano-Ag has been used for imparting antibacterial properties and ZnO nano-particles for antibacterial and UV-blocking properties. Zinc oxide and titanium dioxide are non-toxic and chemically stable under exposure to both high temperatures and UV. Furthermore, nano-particles have a large surface area to-volume ratio that results in a significant increasing of the effectiveness in blocking UV radiation when compared to bulk materials. In this part, it will be relevant to discuss about Titania and functional mechanisms. TiO2 is one of the most popular and promising materials in photocatalytic application due to its strong oxidizing power of its holes, high photo-stability and redox selectivity. TiO2 is commercially available and easy to prepare in the laboratory. Titania (TiO2) has three main polymorphs viz. anatase, rutile and brookite. Among the three kinds of crystal structure of TiO2, commercially available anatase TiO2 fine particles are the most active for photocatalysis (Three Bond Technical News, 1st Jan., 2004,No: 62).

Production of Nano-particles

Production methods for nano-particles can be loosely classified into three general categories: wet synthesis, dry synthesis, and milling. In both wet and dry synthesis, nano-particles are generally produced in a bottom-up way from atomic precursors, whereas in the milling approach, nano-particles are produced from the top down by mechanically breaking down larger particles. Wet approaches include sol-gel and precipitation methods, whereas dry approaches encompass combustion, furnace, and plasma synthesis of nano-particles.

In all cases, there are concerns about the narrowness of the size distribution of the nano-particles, and the degree of agglomeration. All processes for making nano-particles lead to some spread in the particle size. The size distribution can be modified somewhat by adjusting the process parameters, or the size distribution can be tailored by removing the tails of the distribution through additional separation steps. This typically leads to lower process yield. With respect to agglomeration, nano-particles have a high ratio of surface area to volume, and it is much more energetically favourable 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 nano-particles.

Before a process can be considered commercially viable, there are additional economic concerns. Many processes for nano-particles have been developed at the laboratory scale, but they are not yet commercialized because of constraints, including scalability considerations and precursor costs (Baglioni *et al.*, 2003).

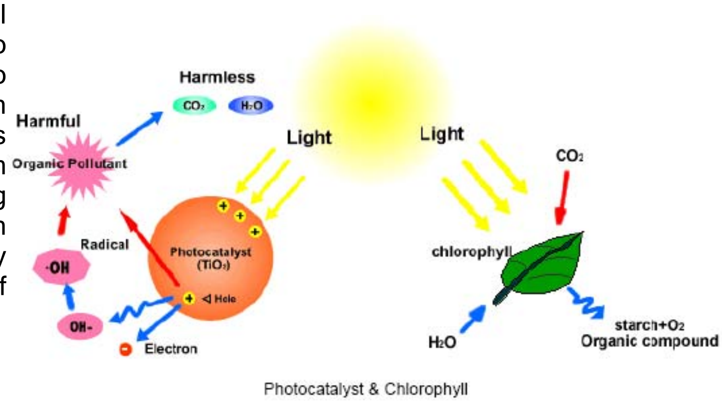
Fundamental concepts of photocatalysis

The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. The prefix “photo” means pertaining to light. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Generally speaking, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself.

Thus, the photocatalyst is the substance which can modify the rate of chemical reaction using light irradiation with out being altered or consumed in the end. The process of photocatalysis can be better explained with the help of a schematic diagram comparing the actions of a man-made photocatalyst (Nano-TiO2) with a natural one (chlorophyll) in Fig. 5 (Mechanism of photocatalyst, Nippon Jitsugyo Publishing Co., Ltd.Japan).

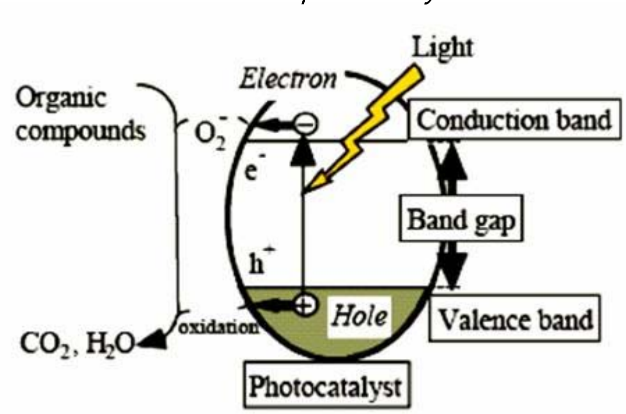
Chlorophyll of plants is a typical natural photocatalyst. The difference between chlorophyll photocatalyst to man-made nano TiO2 photocatalyst (here below mentioned as photocatalyst) is, usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, but on the contrary photocatalyst creates strong oxidation agent and electronic holes to breakdown the organic matter to carbon dioxide and water in the presence of

Fig.5. Schematic diagram comparing the actions of a man-made photocatalyst (Nano-TiO2) with a natural one (chlorophyll).



photocatalyst, light and water.

Fig. 6. The schematic representation of the mechanism of photocatalysis.



Photocatalysis Mechanism of TiO2

When photocatalyst titanium dioxide (TiO2) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e-) and positive-hole (h+) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is: 1240 (Planck's constant, h) / 3.2 eV (band gap energy) = 388 nm.

The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. The mechanism of photocatalysis TiO2 can be easily understood with the help of a schematic diagram (Fig.6) which is showing the actions of a man-made photocatalyst (Nano-TiO2) on exposure to light.

There are three types of crystal structures in natural titanium oxide: the rutile type, the anatase type, and the brookite type. All three of these types are expressed using the same chemical formula (TiO2); however, their crystal structures are different (Fig.7). Titanium oxide absorbs light having an energy level higher than that of the band gap, and causes electrons to jump to the conduction band to create positive holes in the valence band. Despite the fact that the band gap value is 3.0 eV for the rutile type and 3.2 eV for the anatase type, they both absorb only ultraviolet rays. However, the rutile type can absorb the rays that are slightly closer to visible light rays.

As the rutile type can absorb light of a wider range, it seems logical to assume that the rutile type is more suitable for use as a photocatalyst. However, in reality, the anatase type exhibits higher photocatalytic activity. One of the reasons for this is the difference in the energy structure between the two types. In both types, the position of the valence band is deep, and the resulting positive holes show sufficient oxidative power. However, the conduction band is positioned near the oxidation-reduction potential of the hydrogen, indicating that both types are relatively weak in terms of reducing power. It is known that the conduction band in the anatase type is closer to the negative position than in the rutile type; therefore, the reducing power of the anatase type is stronger than that of the rutile type. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photocatalytic activity than the rutile type (Bozzi *et al.*, 2005).

Photo-catalytic self-cleaning theory

Nano-sized silver, titanium dioxide and zinc oxide are used for imparting self-cleaning and anti-bacterial properties. Metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by a catalyst containing the metallic ion, thereby destroying the organic substance to create a sterilizing effect. Nano-materials possess enhanced catalytic abilities due to their highly stressed surface atoms which are very reactive. With the use of nano-sized particles, the number of particles per unit area is enormously increased.

Titanium dioxide is a photocatalyst; when it is illuminated by light of energy higher than its band

Fig.7. The schematic representation of the crystal structures of three polymorphs of TiO2.

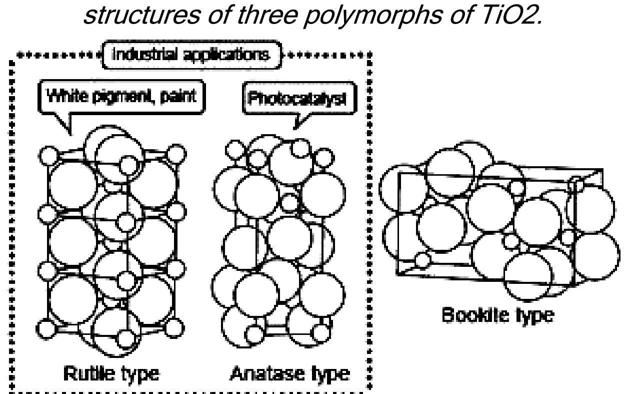
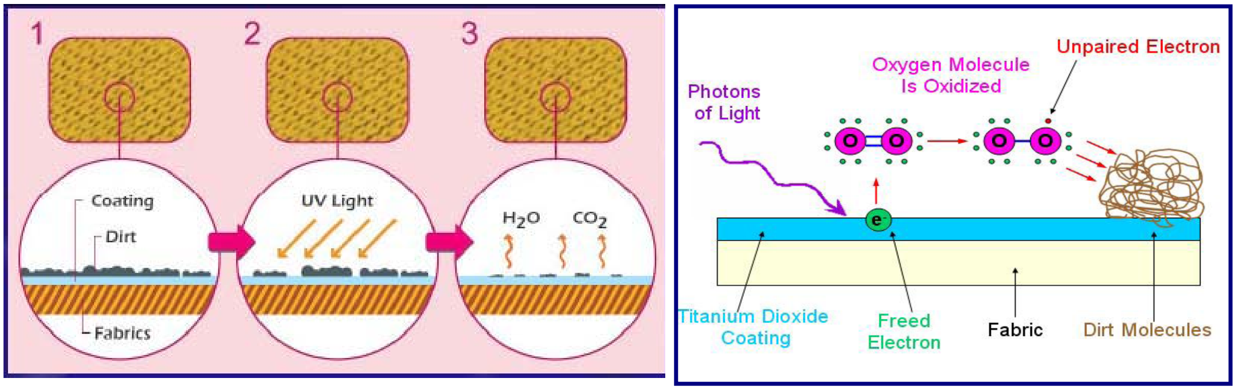


Fig. 8. The Schematic representation of self cleaning action of photocatalytic action of TiO2.



gap, electrons in TiO2 will jump from the valence band to the conduction band, and the electron (e-) and electric hole (h+) pairs will form on the surface of the photocatalyst. The negative electrons and oxygen will combine to form O2-. radical ions, whereas the positive electric holes and water will generate hydroxyl radicals OH. Since both products are unstable chemical entities, when the organic compound falls on the surface of the photocatalyst it will combine with O2 - and OH- and turn into carbon dioxide (CO2) and water (H2O). This cascade reaction belongs to the oxidation-reduction class and its action is schematically illustrated in Fig. 8. During the reaction, photocatalyst is able to decompose common organic matter in the air, such as molecules causing odour, bacteria and viruses or organic stain and dirt. Furthermore, when photocatalytic titanium dioxide is exposed to sunlight, it exhibits super-hydrophilic behaviour, which allows partially-decomposed stain/dirt residues on the surface to be washed away easily.

Conclusion

There is a significant potential for profitable applications of nanotechnology in cotton and other textiles. Several applications of nanotechnology can be extended to attain the performance enhancement of textile manufacturing machines & processes. The important properties imparted to textile materials using nanotechnology have been highlighted in this paper along with their mechanisms. In particular, the majority of the Nano-Tex products have been reviewed and analysed in depth and detail. In addition to that, the applications of nano-TiO2 have also been reviewed and analysed to a good extent. As mentioned, nanotechnology overcomes the limitations of applying conventional methods to impart certain properties to textile materials. There is no doubt that in the next few years, nanotechnology will penetrate into every area of textile industry. However, still there are a lot of items to be taken in consideration before industrial commercialisation of the nano-products. First there is the issue of costs, which in some cases is hampering the development of smart coatings and makes mass production economically less viable. Besides cost, a key point is the question of the impacts of uncontrolled release of nano-particles. Generally, the state of research into the health and environmental issues can be summed up as suggesting that the current results of studies on the impact are limited. In future, interdisciplinary research collaborations will lead to significant advancements in the desirable attributes of cotton and cotton blend textile applications. As the textile industry has the biggest customer base in the world, there will be more focus for the future advances in the customer-oriented products with nanotechnology applications. The future research may be targeted on developing improved dirt-, crease- and shrink-resistant properties in fabrics, temperature adaptable clothing and odourless undergarments.

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