Nanotechnology in Fibres and Textiles

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Abstract - Nanoscience and nanotechnology are considered to be the key technology for the recent era. Efforts are being worldwide to create smart and intelligent textiles by incorporating various nano particles or by creating nanostructured surfaces and nanofibres which lead to unprecedented level of textile performance such as stain resistant, self cleaning, antistatic, UV protective and various chemical and mechanical properties. The purpose of this paper is to examine the implications of nanotechnology for the fibre and textile industries in the world. The basics and impacts of nanotechnology are discussed in terms of various advanced products by different manufactured along with the properties of the products. With an appreciation of what nanotechnologies are emerging globally in the fibre and textile areas, the local industry will have the necessary background to ask the right questions and make informed decisions.

Keywords: Carbon nanotubes, Nanofibre, Electrospinning, Nanocomposites, Nanoparticles, Nanomaterial, Nanoemulsion, Plasma and Nanosphere.

I. INTRODUCTION

The prefix ‘nano’ is derived from the Greek word ‘nanos’, which means ‘dwarf’. In broad terms, nanotechnology refers to scientific and technological advances that rely on the properties of materials at a very, very small scale [1-4]. It involves many complex concepts that cannot be seen or understood easily. As nanoscience and nanotechnology cover such a wide range of fields (from chemistry, physics and biology, to medicine, engineering and electronics), they have been considered in four broad categories: nanomaterials, electronics, optoelectronics, biotechnology and nanomedicine [5]. The category of most relevance for textiles is nanomaterials.

II. FIBRES AND TEXTILES WITH NANOSCALE FEATURES

Nanoscale features may be built into fibres and textiles in different ways [4], 1) Production of fibres with diameters of nanoscale dimensions. These fibres are described as ‘nano fibres’, 2) Incorporation of nanomaterials into fibres to produce ‘nano composite fibres’, 3) Coating of fibres with films or related structures. The coating may have nanoscale dimensions or alternatively may simply be a ‘carrier’ for nano particles. Coatings would normally be applied to fibres in the form of yarn or fabric and Incorporation of membranes with nanoscale features into garment structures.

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III. NANOFIBRES

Normally nanofibres are produced by electrospinning process. The basic principle of electro spinning process is described in figure 1 [11]. A basic electrospinning system consists of a charged polymer solution (or melt) that is fed through a small opening or nozzle (usually a needle or pipette tip). Because of its charge, the solution is drawn toward a grounded collecting plate (usually a metal screen, plate, or rotating mandrel), typically 5-30 cm away, as a jet. During the jet’s travel, the solvent gradually evaporates, and a charged polymer fiber is left to accumulate on the grounded target. The charge on the fibres eventually dissipates into the surrounding environment. The resulting product is a nonwoven fiber mat that is composed of tiny fibres with diameters between 50 nanometres and 10 microns [12]. Potential uses for electro-spun fibres are in filtration, wound dressings, tissue engineering, nanocomposites, drug delivery devices and sensors [10]. Figure 2(a) shows nanofibres electrospun onto a polyester spun-bonded substrate; the substrate was chosen to provide the required mechanical, whilst the nanofibre web dominates filtration performance [13]. Figure 2(b) shows commercially-available nanofibres (fibre diameter approximately 250 nm) electrospun onto a cellulose substrate for air-filtration applications [14].
A significant hurdle [for the electrospinning process for nanofibre production] has remained for the nonwovens industry at large quantities of nanofibre webs from a scaled-up, commercially viable electrospinning process have not been available to explore new uses and applications [13]. As previously reported, nanofibre web composites have been used for several air filtration applications. Many of these air filters are made from webs of nanofibre filter media in widths exceeding 24 inches (610 mm). An example of this product is shown in Figure 3. A commercial facility manufacturing polyamide nanofibre web composites currently has production volumes in excess of 10,000 square meters per day [13].

**Figure 3 (Commercial air filtration cartridge using carbon nanotube nanofibres)**

Scientists at CSIRO Textile and Fibre Technology and The University of Texas at Dallas have recently processed multi-walled carbon nanotube nanofibres into yarns [15]. Some of the possible applications for the new yarns include:

1. Structural composites that is strong, tough and able to reduce mechanical vibrations.
2. Protective clothing that provides antiballistic and static-discharge protection, as well as radio and microwave frequency absorption.
3. Super capacitors, batteries and fuel cells in the form of yarn structures that is weaveable into textiles for storing or generating electrical energy.
4. Chemically or electrically powered artificial muscles for prosthetics and robots, morphing air vehicles and minimally invasive catheters with enhanced functionality for medical applications.
5. Electrical wiring and distributed sensors for electronic textiles.
6. Heat pipes that provide both structural reinforcement and heat dissipation.
7. High intensity source of field-emitted electrons for intense fluorescent lights and displays, as well as X-ray sources small enough to fit in a medical catheter.
8. Filaments for incandescent light sources with decreased susceptibility to mechanical damage because of yarn toughness and mechanical damping ability.

**IV. NYLON NANOFIBRES**

Toray has developed a nylon fibre with enhanced water-sorption properties [16, 17, 18, 19]. The new Nylon fibre has nothing special, it looks like any other nylon fibre with a diameter of 60 microns. But that one fibre is in fact a bundle of more than 1.4 million fibres, each just dozens of nanometers in diameter. Water seeps through the spaces between these fibers, which is what makes the material so absorbent. The fibre is spun using conventional spinning equipment, but the starting material is a precision mixture controlled at the molecular level. The new nylon fibre is just as strong and supple and easy to process as regular nylon, but with two to three times the ability to absorb moisture. And to cap it all, the material has the feel of a natural fibre, which is something synthetic fibre makers have never achieved before. The company plans to begin a business with the new fibre in two or three years, selling it for use in luxury apparel at a price that is more than 10 times that of the conventional nylon. Non-woven fabrics for medical applications are another possibility [19].

**V. NANOCOMPOSITE FIBRES**

In general, polymer nanocomposites with as little as 2 vol% addition exhibit large increases in tensile strength (>40%), tensile modulus (>70%), flexural strength (>60%), flexural modulus (>125%) and heat distortion temperature (from 65° to 150°C) without any significant loss of impact resistance (≥10%). They also lower water sensitivity, permeability to gases and thermal co-efficient of expansion values. By contrast, conventional polymer composites show poor ductility and mouldability with degradation and inferior surface smoothness and are difficult to process as films or fibres [20]. Nanomaterials that are most commonly incorporated into synthetic fibres are nanoparticles and carbon nanotubes. The particles may be spheres, fibrils or platelets, and by varying the amounts, their alignment, and distribution within the fibre, improvements in the mechanical, electrical, optical or biological properties may be obtained [4].

**VI. WITH CARBON NANOTUBES**

We are going to have dramatic developments in the textile materials field over the next 10 or 20 years because of nanotechnology, specifically carbon nanotubes [21], predicts Satish Kumar (Figure 4), a professor at Georgia Tech’s School of Polymer, Textile and Fiber Engineering. Using carbon nanotubes, we could make textile fibres that would have thermal and electrical conductivity, but with the touch and feel of a typical textile. You could have a shirt in which the electrically-conducting fibres allow cell [i.e. mobile] phone functionality to be built in without using metallic wires or optical fibres [21]. Researchers have developed a technique for producing composite fibres containing up to 10% of carbon nanotubes [21]. The strength of Zylon the strongest known polymeric fibre has been increased by 50% by incorporating 10% carbon nanotubes into the fibre. Single-walled nanotubes exist in bundles of more than 100 tubes measuring 30 nm in diameter.
The use of carbon nanotubes will have the greatest impact when researchers can learn how to break up the bundles to produce individual nanotubes, a process called exfoliation. If that can be done, the quantity of tubes required to improve the properties of fibres could be reduced from 10 percent to as little as 0.1% by weight. That could help make use of the nanotubes which now cost hundreds of dollars per gram feasible for commercial products [21].

Beyond breaking up the nano tube bundles, researchers also face a challenge in uniformly dispersing the carbon nanotubes in polymers and properly orienting them. Producing conducting fibres would require boosting the nano tube percentage to as much as 20% [21]. The toughness, or capability to absorb energy, of composite fibres containing carbon nano tubes has been found to be more than four times that of spider silk and 17 times that of the Kevlar used in bullet proof vests making them what is believed to be the toughest known material. These fibres have twice the stiffness and strength, and 20 times the toughness, of the same weight and length steel wire [22].

VII. WITH SILVER NANOPARTICLES

The Korean company, Hyosung, is one of the world’s major nylon manufacturers [23]. Within its suite of ‘Mipan’ functional fibres, the company has developed ‘Nano Magic Silver’ nylon fibres containing silver nanoparticles to eliminate up to 99.9% of various harmful bacteria [24]. The developed ‘Mipan Nano-Magic Silver’ is a material proven to function far better in its antibiotic function than any other material used currently as antibiotic fibres. It excels in post-manufacture processes such as dyeing and is much more pleasant to the touch. In addition, as silver is mixed into the raw materials during the polymeric process, it maintains the powerful antibiotic effect and ultra-red ray emission even after repeated washings, and is more environmentally friendly as the antibiotic substance does not dissolve during washing [25]. It can be used in the following applications [24].
1) Daily activities and sport: sportswear, outdoor wear, sports bags, and running shoes.
2) Intimate freshness: lingerie, underwear, stockings and socks.
3) Clean and safe lifestyle: bedding, towels, dishcloths and personal sanitary goods.
4) Medical uses: hospital and laboratory gowns, clothes for patients, etc.

In addition to anti-microbial effects, the product exhibits anti-mould and UV-protective effects (Figure 5) [24].

UK-based company, JR Nanotech, has developed SoleFresh™ Nano-silver socks that are treated with silver nanoparticles [26]. The product is manufactured from 80% cotton and 20% elastic yarn, and contains 0.3% w/w nano-silver, with particle sizes ranging from 25 nm up to 250 nm. The following features are reported.
1) Foot odour is eliminated.
2) Athlete’s foot is eliminated.
3) Foot infection is prevented in patients with diabetes.
4) Feet are kept dry and fresh.

It is not stated how the silver is incorporated into the product [18], but it seems likely that the elastic fibre is produced as a composite containing the nanoparticles (Figure 6) [27].

VIII. WITH OTHER NANOMATERIALS

Carbon nano fibres (28) and carbon black nano particles are effective reinforcing materials for composite fibres [29]. Both nano materials also lead to high chemical resistance and electrical conductivity when used in composite fibres. Composite fibres with nano-sized clay particles or flakes (hydrated aluminosilicate) exhibit excellent flame retardance, UV blocking power and inertness to corrosive chemicals [29]. Inclusion of 5% nano clay in nylon 6 has been found to increase tensile strength by 40%, tensile modulus by 68%, flexural strength by 60%, and flexural modulus by 128% [29]. Nanoclays - used either alone or in conjunction with flame retardants - have potential to improve the flame retardance of synthetic polymers (such as nylon 6, 6) [10].

Figure 4 (nano composite fibre made with single-walled carbon nanotubes)

Figure 5 (Properties of Mipan Nano-Magic Silver)

Figure 6 (Nano-Silver powders are uniformly dispersed inside and on the surface of the material [polyester] unlike coatings on yarn)
Research on the use of nano-sized particles of the oxides of titanium (TiO$_2$), aluminium (Al$_2$O$_3$), zinc (ZnO) and magnesium (MgO) in composite fibres has focused on antimicrobial, self-decontaminating and UV-blocking functions for both military protection gear and civilian health products [29]. Incorporation of ZnO nano particles into nylon produces a UV protective effect and reduces static electricity [29]. A composite [nylon] fibre with nano particles of TiO$_2$ and MgO can provide a self-sterilizing function [29].

**IX. COATING BY NANO EMULSION**

Amino functional, polysiloxane finishes in macro emulsion and micro emulsion form can be used to enhance the softness of textiles [10]. The fine particle size of silicone softener microemulsions enables the emulsion to penetrate into the closely packed yarn structures of microfilament fabrics, imparting enhanced internal lubrication and softening through the improved distribution of the softening agent over the high surface area of the microfilaments [30]. A novel cationic silicone softener, Sandoperm SE1 oil liquid, has been developed by Clariant [30]. The novelty lies in the fact that, for the first time, the emulsifiers are linked to a covalent bond to the silicone chain, to produce a self-emulsifying amino functional silicone fluid. By this special chemical engineering of the molecule, Sandoperm SE1 oil liquid is emulsified for its applications by stirring it in water. The process creates nano emulsions wherein the particle size is extremely small and the silicone fluid is hydrophilic. Compared with typical macro emulsions (>150 nm particles) and micro emulsions (50-150 nm), Sandoperm SE1 oil liquid produces nano emulsions (10 nm), which impart an inner softness with a unique cool, natural and dry handle to woven and knitted fabrics [30].

**X. PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION (CVD)**

A plasma generated by electrical discharge through a gas consists of a mixture of positive and negative ions, electrons, free radicals, ultraviolet radiation, and many different electronically-excited molecules. By varying the conditions of the gas or gases present, a variety of surface treatments can be produced that change the chemical or physical nature of the fibre surface, thereby radically altering all treatments that depend upon fibre adhesion, e.g. coating, lamination and bonding [10].

Vacuum polymer coating enables very thin polymer films to be deposited onto fibre surfaces. This can be achieved through the condensation of monomer onto the fibre after the plasma treatment. This process is illustrated by the DryFab™ process commercialized by Sigma Technologies International Inc. [32-35]. The core of Sigma’s technology is the eposition of multifunctional acrylate polymers in conjunction with plasma activation and other inorganic layers on moving webs (Figure 7). Acrylate monomers are flash evaporated outside the vacuum chamber. Monomer vapor is guided into the vacuum and deposited onto the moving substrate with a linear nozzle. The vapor forms a thin liquid film, which is cured with an electron beam curtain. Additional metal or ceramic coatings may be deposited in various combinations to produce a variety of products [33].

**Figure 7 (DryFab™ Nano layer process)**

Thin film radiation cured acrylate coatings can be used to functionalize the surface of a variety of substrates. These include fabrics, polymer films, metal coated films, fibers, paper and metal sheets. The combination of in-line plasma treatment of the substrate for cleaning and adhesion promoting, with ultra thin polymer coatings (20 nm to 1 micron) [35] with unique functional properties, creates opportunities for new, high value added products. This versatile technology does not involve solvents or water based coatings, it is environmentally friendly, and the high process speed and low cost monomer materials make it highly cost competitive [33].

Conventional wet processes that are used to functionalize fabrics impart the same properties on both sides of the material. For example an anti-stain coating is water and oil repelling. Apparel in contact with the body with an anti-stain coating will feel very uncomfortable due to its inability to absorb moisture. The DryFab™ process can produce different functionalities on each side of a single fabric layer (Figure 8). For example an absorbing cotton fabric can be made anti-stain only on the outside surface, allowing the cotton against the body to absorb moisture [34].

**Figure 8 (Different functionalities on each side of a single fabric layer)**

The DryFab™ technology has numerous textile applications, including sports, leisure and casual apparel, medical, apparel, filter media, linen and upholstery, industrial membranes, packaging and building insulation [35].
XI. COATING BY SUPER HYDROPHOBIC POLYMER

Swiss company, Schoeller, has developed the ‘NanoSphere®’ technology for making fabrics naturally self-cleaning [36,37]. The technology involves a normal finishing process that can be applied to every fabric after coloration [37] it centers on the use of proven silicon based nano particles which are firmly anchored in a coating mix [38]. In order to transfer the non-stick and self-cleaning process from nature to textiles, the surface is altered through nanoparticles. On the basis of the ‘guest-host system’ and in combination with what is known as ‘sol-gel engineering’, Schoeller has developed a finishing technology which leads to the formation of a structured surface. The result is NanoSphere® [39]. Atomic force micrographs showing the surface of a Lotus leaf in comparison with the surface of a fabric treated with NanoSphere® are presented in Figure 9 [37].

The properties of fabric treated with NanoSphere® are given below:

1) NanoSphere® provides optimum impregnation of textiles. The waterproofing is excellent and the oil and grease repelling properties at a level never achieved before. Ketchup, honey, coffee, red wine and many other substances simply run off the nano-structured surface. And even if they fail to run off of their own accord, the stain can easily be rinsed off under running water.

2) NanoSphere® also benefits the environment. These textiles need less frequent washing and can be washed at lower temperatures. This offers a considerable saving in the consumption of energy, detergent and water.

3) NanoSphere® makes textiles robust, abrasion-proof and long-lasting. The washing permanency is many times higher than is the case with conventional impregnation. NanoSphere® resists pressure and friction and has no influence on the comfort of wear, appearance, feel, breathability or elasticity.

4) NanoSphere® is suitable for use in many areas of clothing. Further applications, for example in the home furnishing area or in the medical sector are definitely conceivable.

The US company, Nano-Tex [40], has developed a technology to make fabrics repellent to water and stains. This technology would appear to be similar to the NanoSphere® process developed by Schoeller, in that its effectiveness is attributed to its ability to reproduce the Lotus effect on fibre surfaces in fabrics. Nano-Tex-treatments have been used in men’s, women’s and children’s trousers, active wear, as well as uniform, shirtting and business attire. Nano-Tex also has product represented in the residential and interior furnishings industries, e.g. mattress fabrics and stadium seating. Nano-Tex uses the same, stain-resistant fluorinated particles as Teflon® [41]. These particles are about 500 times smaller than a human hair scientists combine three molecular ingredients. One has hooks that bind to fabric. A second has whiskers that repel oil and water. A third is water soluble. When something called an ‘initiator’ is added to the ‘nanostew’, it starts a chain reaction, binding the molecules together into chains that then curl into balls with hooks on the outside, whiskers on the inside. [See Figure 10.] When applied to the fabric, the polymer chains open up, reverting to their linear states. Heating then cures the polymer and binds it to the fabric, making the water and oil repellency permanent. Whiskers point away from the surface, forming an air layer between the water droplets and fabric surface, and this inhibits wetting of the fabric. Nano-Tex-treated garments will wet out by adding detergent when washing [42]. The whiskers fold over in the presence of detergent, allowing water to penetrate into the fabric and clean out any dirt.

Product attributes encompassed by the Nano-Tex treatments include

1) Spill resistant fabric enhancement for many types of fibers (cotton, synthetics, wool, silk, rayon, polypropylene) that repels a range of liquids (e.g. beverages, salad dressings, etc.).

2) Quick-absorbing fabric enhancement providing superior wicking properties, which pulls perspiration away from the body and dries it quickly to keep the body cool and comfortable.

3) In this dual-acting treatment, the first line of defense is Nano-Tex’s superior repellency technology which causes liquids to bead up and rolls off the fabric. For stains that get ground into the fabric, Nano-Tex’s patented release technology frees stains from fibers during a normal wash cycle.

4) The first permanent anti-static treatment reduces static cling and repels statically-attractive substances - such as dog hair, lint and dust - to improve the overall appearance and comfort of garments.
Garments should be washed in the normal way [42]. Tumble-drying with heat is required. For optimal performance, steam ironing will enhance performance. The use of liquid softeners is not advised. Dry cleaning is not recommended. The chemicals found in typical dry cleaning solutions contaminate the fabric and can negatively affect performance and mask the technology. Nano-Tex enhancements were consciously engineered to run on industry-standard fabric and garment production equipment, with minimal modification or capital investment required by licensees. Nano-Tex enhancements can be pad-applied in fabric form or can be dipped or spray-applied in garment form. This process is followed by a normal curing procedure.

A. Coatings incorporating silver

Scientists at Clemson and Clarkson Universities have developed a multilayer approach to the problem of making textile fibres “ultra hydrophobic” in an attempt to mimic the Lotus effect [43, 44]. Polyester fabric was treated with plasma discharge before being dip-coated with a mixture of poly(glycidylmethacrylate) (PGMA) and poly(2-vinylpyridine) and annealed [44]. The fabric was then treated with ethanol, followed by a suspension of silver nano particles (110-130 nm). Treatment with a second layer of PGMA entrapped the silver nano particles between the two polymer layers. Finally, carboxy-terminated polystyrene was grafted to the unreacted epoxy functionalities of the top layer. Water contact angles demonstrated the greater hydrophobicity of this approach in comparison with treatment with polystyrene alone.

XII. COATED POLYESTER FIBRES

Kanebo has increased the hygroscopic properties of polyester fibres by a factor of 30 through a coating with a special, multi-layered film whose thickness is measured in tens of nanometres [22, 23, 26]. The company plans to market the fibre for use in underwear and dress shirts [26].

A. Luminescent polyester

Teijin Fibers Ltd. has been the first in the world to trial the production of luminescent polyester. The polyester core is covered with approximately 60 layers of nylon and polyester that have different refractive indices for light, with provisions made for red, green, blue and violet. In the case of violet, the thickness of one layer measures only 69 nanometers. This creates a mystical hue that changes according to both how light strike the fabric and the angle from which the fabric is viewed [22].

B. Plasma

Plasma treatment of textiles offers potential for the enhancement of the properties of textile substrates. The DryFab™ Nanolayer process (32, 35) from Sigma Technologies International Inc. is one such example of a plasma technology that can be adapted to textiles. Deakin University has carried out trials at Sigma in order to examine the impacts of the technology on textiles. Four fabrics (100% cotton woven, 65:35 polyester/cotton interlock, 100% cotton single jersey and 65:35 polyester/cotton woven) were subjected to treatment by the DryFab™ Nanolayer process. Each fabric was quite hydrophilic to begin with, and treatment with the plasma/monomer system rendered the fabrics extremely hydrophobic (Figure 11) (32, 35). In comparison with the Nano-Tex procedure, the DryFab™ Nanolayer process has an advantage in that fabric functionality can be purpose-engineered through the choice of monomer(s). A disadvantage of the latter process is that expensive equipment is required, and currently most of the applications for the vacuum technology are not textile-related. However, Sigma is looking to act as a commission converter for textiles. This would allow companies to access the expensive vacuum technology without the capital outlay for the processing equipment. As a commission converter, Sigma would convert unfinished fabric into finished fabric using vacuum monomer deposition on a Sigma-owned and run machine.

Figure 11 (Polyester woven fabric treated with water; untreated fabric on left, and DryFab™ treated fabric on right.)

Sigma has also developed an atmospheric plasma treater, which operates at atmospheric pressure and does not incur the relatively high costs associated with the vacuum system. There is essentially no difference between the atmospheric and vacuum plasma treatment systems in the plasma component of the equipment; high surface energies and surface grafting can be achieved to similar levels with both. The major difference between the systems is in the application of coatings after the plasma treatment. The atmospheric treater achieves coating by bubbling helium gas through a bath of monomer before it is fed to the plasma head; polymer deposition can, at the present time, utilize only monomers with a relatively high vapour pressures, leading to levels of polymer that are considerably lower than achievable through the vacuum system. The advantages or disadvantages of this for textiles are unknown. Although metallization is possible only under high vacuum, the inability to access this in the atmospheric system is unlikely to be of any significant disadvantage for textiles. Longer term, Sigma intends to develop the atmospheric technology, as it is a lot cheaper, and there is considerable scope for the development of more efficient polymer coating systems. Trials carried out by Deakin University using the atmospheric plasma treater in the surface grafting mode, i.e. without any liquid monomer evaporation followed by polymer deposition, have revealed significant changes to the surface properties of fibres and fabrics.

XIII. CONCLUSIONS

The current trend of R & D activities in advanced materials, polymers and textiles clearly indicates a shift to nanomaterials as the new tool to improve properties and gain newer multifunctionalities. However, challenges and the success of the every individuals working in this area would depend to a large extent on the performance of the various techniques described in this paper.
As far as textile materials are concerned, the dispersion, impregnation or immobilization of nanoparticles of textile surfaces can be studied. Thus it can be summarized that nanotechnology research in textiles and fibres has a lot of potentials as a future scope of approach but would be largely governed by simultaneous progress in the newer, faster, simpler and more efficient techniques for nano materials, nanocoatings and nanocomposites used for in fibre and textiles.

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