



Application of Nanotechnology for high performance textiles

Lei Qian
Institute of Textile Technology
College of Textiles
North Carolina State University

Juan P. Hinestroza
TECS, College of Textiles
North Carolina State University

ABSTRACT

This paper summarizes the recent development of nanotechnology in textile areas including textile formation and textile finishing. Details on two major technical aspects, using nanosize entities and employing specific techniques to create nanosize structure inside textile materials, have been elucidated. A number of nanosize fillers and their resultant performances have been reviewed. Particularly, nanolayer assembly, a new concept of textile surface coating, has been introduced. At the end, perspectives regarding future development of nanotechnology for smart and intelligent textiles have been addressed.

Keywords: Nanotechnology, nanosize fillers, nanosize structure, nanoparticles, cellular structure

Introduction

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade, including materials science, mechanics, electronics, optics, medicine, plastics, energy, electronics, and aerospace. Its profound societal impact has been considered as the huge momentum to usher in a second industrial revolution.^{1,2}

The “nano” in nanotechnology comes from the Greek word “nanos” that means dwarf. Scientists use this prefix to indicate 10⁻⁹ or one-billionth. One nanometer is one-billionth meter that is about 100,000 times smaller than the diameter of a single human hair. Nanotechnology endeavors are aimed at manipulating atoms, molecules and

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nanosize particles in a precise and controlled manner in order to build materials with a fundamentally new organization and novel properties. The embryo of nanotechnology is “atomic assembly”, which was first publicly articulated in 1959 by physicist Richard Feynman. Nanotechnology is called a “bottom up” technology by which bulk materials can be built precisely in tiny building blocks, different from the traditional manufacture — “top down” technology. Therefore, resultant materials have fewer defects and higher quality.

The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range. When a bulk material is divided into small size particles with one or more dimension

(length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected properties, different from those of the bulk material. It is known that atoms and molecules possess totally different behaviors than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanics. Between these two distinct domains, the nanometer range is a murky threshold for the transition of a material's behavior. For example, ceramics, which normally are brittle, can easily be made deformable when their grain size is reduced to the low nanometer range. A gold particle of 1 nm across shows red color. Moreover, a small amount of nanosize species can interfere with matrix polymer that is usually in the similar size range, bringing up the performance of resultant system to an unprecedented level. These are the reasons why nanotechnology has attracted large amounts of federal funding, research activity and media attention.

The textile industry has already impacted by nanotechnology. Research involving nanotechnology to improve performances or to create unprecedented functions of textile materials are flourishing. These research endeavors are mainly focused on using nanosize substances and generating nanostructures during manufacturing and finishing processes.

Nanotechnology in Manufacturing Composite Fibers

Nano-structured composite fibers are in the area where we see the early blooming of nanotechnology, while many other applications are still way off future. Those composite fibers employ nanosize fillers such as nanoparticles (clay, metal oxides, carbon black), graphite nanofibers (GNF) and carbon nanotubes (CNT). Besides, nano-structured composite fibers can be generated through foam-forming process, other than using nanosize fillers.

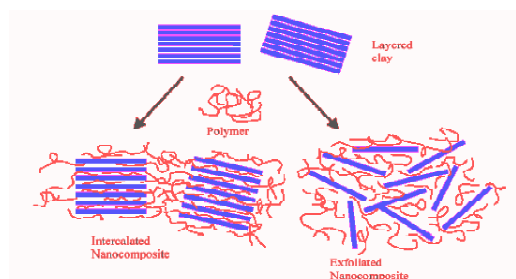
The main function of nanosize fillers is to increase the mechanical strength and improve the physical properties such as conductivity and antistatic behaviors. Due to their large surface area, these nanofillers have a better interaction with polymer matrices. Being in the nanometer range, the fillers might interfere with polymer chain movement and thus reduce the chain mobility. Being evenly distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; nanofibers can transfer stress away from polymer matrices and enhance tensile strength of composite fibers. Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nanofillers used. Distribution of nanofillers in polymer matrices through mechanical and chemical approaches is one of the important aspects leading to high quality of nanostructured composite fibers. Although some of the filler particles such as clay, metal oxides, carbon black have previously been used as microfillers in composite materials for decades, reducing their size into nanometer range have resulted in higher performances and generated new market interest.

Carbon Nanofibers and Carbon Nanoparticles

Carbon nanofibers and carbon black nanoparticles are among the most commonly used nanosize filling materials^{3,4}. Carbon nanofibers can effectively increase the tensile strength of composite fibers due to its high aspect ratio, while carbon black nanoparticles can improve their abrasion resistance and toughness. Both of them have high chemical resistance and electric conductivity. Several fiber-forming polymers used as matrices have been investigated including polyester, nylon and polyethylene with the weight of the filler from 5% to 20%^{5,6}.

Clay Nanoparticles

Clay nanoparticles or nanoflakes are composed of several types of hydrous aluminosilicates. Each type differs in chemical composition and crystal structure. Clay nanoparticles possess electrical, heat and chemical resistance and an ability of blocking UV light. Therefore, composite fibers reinforced with clay nanoparticles exhibit flame retardant, anti-UV and anti-corrosive behaviors. For example, nanoparticles of montmorillonite, one of most commonly used clay, have been applied as UV blocker in nylon composite fiber. The mechanical properties with a clay mass fraction of only 5 % exhibits a 40% higher tensile strength, 68% greater tensile



Schematic of a nanosilicate composite

modulus, 60% higher flexural strength, and a 126% increased flexural modulus⁷. In addition, the heat distortion temperature (HDT) increased from 65°C to 152°C. Nanosize clay flakes are arranged densely and alternately than the therefore, the composite material has barrier performance to water, chemicals or other harmful species.^{7,8}

Another function of clay nanoparticles is to introduce dye-attracting sites and creating dye-holding space in polypropylene fibers, known as non-dyeable fiber due to its structural compactness and lack of dye-attracting sites. Nanoparticles of montmorillonite are modified with quaternary ammonium salt and then mixed

into polypropylene before it is extruded. As a result, polypropylene with clay nanoparticles by weight percentage of 5% can be colored by acid dyes and disperse dyes.⁹

Metal Oxide Nanoparticles

Nanosize particles of TiO₂, Al₂O₃, ZnO, and MgO are a group of metal oxides that possess photocatalytic ability, electrical conductivity, UV absorption and photo-oxidizing capacity against chemical and biological species. Intensive researches involving the nanoparticles of metal oxides have been focusing on antimicrobial, self-decontaminating and UV blocking functions for both military protection gears and civilian health products⁶. Nylon fiber filled with ZnO nanoparticles can provide UV shielding function and reducing static electricity of nylon fiber. A composite fiber with nanoparticle of TiO₂/MgO can provide self-sterilizing function¹⁸.

Carbon Nanotubes

Carbon nanotube (CNT) is one of the most promising building blocks existing. Its higher strength and high electrical conductivity are not comparable by carbon nanofibers. CNT consists of tiny shell(s) of graphite rolled up into a cylinder(s). With 100 times the tensile strength of steel at one-sixth weight, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, CNT seems to be a wonder material.

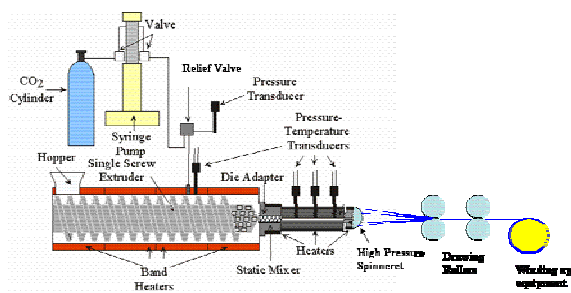
Generally, CNTs are classified into single-walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT). They are usually made by carbon-arc discharge, laser ablation of carbon, or chemical vapor deposition. The potential applications of CNTs include conductive and high-strength composite fibers, energy storage and energy conversion devices, sensors, and field emission displays.^{10,11}

One of the successful examples of CNT composite fiber is the SWNT- polyvinyl

alcohol fiber with fiber diameters in micrometer range produced by using a coagulation-based spinning process. The fiber exhibits twice the stiffness and strength, and 20 times the toughness of steel wire of the same weight and length. Moreover, the fiber toughness can be four times higher than that of spider silk and 17 times greater of Kevlar fibers used in bulletproof vests.¹⁰ Therefore, this type of fibers has potential applications in safety harnesses, explosion-proof blankets, and electromagnetic shielding. Continuing research activities on CNT fibers involve study of different fiber polymer matrices such as polymethylmethacrylate (PMMA) and polyacrylonitrile (PNA) as well as CNT dispersion and orientation in polymers. Processing approaches such as wet spinning, melt spinning and electron spinning were extensively explored.^{12,13,14}

Nanocellular Foam Structures

Using nanosize fillers is one of the most common approaches to create nanostructured composite fibers. Another approach is to generate nanosize cellular structures in polymer matrices.¹⁵



Schematic for Supercritical Fluid Extrusion of Nanocellular Fibers

A certain amount of nanosize porosity in material results in attributes such as lightweight, good thermal insulation, high cracking resistance without sacrificing in mechanical strength. A potential application of cellular structure is to encapsulate functional components inside of nanosize cells.

One of the approaches is to make use of thermodynamic instability to produce nanocellular materials. Controlled dosing of supercritical CO₂ is used to tailor the viscosity of a polymer melt. The domains of CO₂ embedded in the polymer melt expand in volume when the pressure applied to the system is suddenly reduced. These nanobubbles are then permanently entrapped in the polymer when the temperature falls below the solidifying temperature of the polymer matrix. The porosity of the final composite can be in the range of 10-20nm. In order to keep the pore size within nanometer range, a great effort is made in controlling the thermodynamics of the foam-forming process. The resultant nanocellular fibers can be used as high-performance composite fibers as well as for sporting and aerospace materials.

Nanotechnology in Textile Finishing

The impact of nanotechnology in the textile finishing area has brought up innovative finishes as well as new application technique. Particular attention has been paid in making chemical finishing more controllable and more thorough. Ideally, discrete molecules or nanoparticles of finishes can be brought individually to designated sites on textile materials in a specific orientation and trajectory through thermodynamic, electrostatic or other technical approaches.

Upgrade of Chemical Finishes and Resultant Functions

Nanotechnology not only has exerted its influence in making versatile fiber composites but also has had impact in making upgraded chemical finishes. One of the trends in synthesis process is to pursue a nanoscale emulsification, through which finishes can be applied to textile material in a more thorough, even and precise manner. Finishes can be emulsified into nanomicelles, made into nano-sols or wrapped in nanocapsules that can adhere to textile substrates more evenly. These advanced finishes set up an unprecedented level of textile performances of stain-resistant,

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hydrophilic, anti-static, wrinkle resistant and shrink proof abilities.¹⁶

Nanoparticles in Finishing

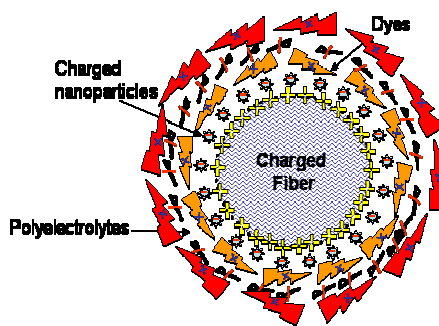
Nanoparticles such as metal oxides and ceramics are also used in textile finishing to alter surface properties and impart textile functions.¹⁷ Nanosize particles have a larger surface area and hence higher efficiency than larger size particles. Besides, nanosize particles are transparent, and do not blur color and brightness of the textile substrates. However, preventing nanoparticles from aggregation is the key to achieve a desired performance.

As an example, the fabric treated with nanoparticles TiO₂ and MgO replaces fabrics with active carbon, previously used as chemical and biological protective materials. The photocatalytic activity of TiO₂ and MgO nanoparticles can break harmful and toxic chemicals and biological agents. These nanoparticles can be pre-engineered to adhere to textile substrates by using spray coating or electrostatic methods.¹⁸ Finishing with nanoparticles can convert fabrics into sensor-based materials. If nanocrystalline piezoceramic particles are incorporated into fabrics, the finished fabric can convert exerted mechanical forces into electrical signals enabling the monitoring of bodily functions such as heart rhythm and pulse if they are worn next to skin.¹⁹

Self assembled Nanolayers

Self-assembled nanolayer (SAN) coating is a challenge to traditional textile coating. Research in this area is still in embryo stage. In self-assembled nanolayer (SAN) coating, target chemical molecules form a layer of thickness less than nanometer on the surface of textile materials. Additional layers can be added on the top of the existing ones creating a nanolayered structure. Different SAN approaches are being explored to confer special functions to textile materials.

One of the technical approaches is to use electrostatic attraction to self-assemble nanolayer coatings on textile materials for protective and self-healing function. The electrostatic approach is particularly appealing as the thickness, homogeneity and sequence of these nanolayers can be precisely controlled by control of molecular architecture, self-assembly and electrostatic interactions.²⁰⁻²³ In addition, the self-healing capability makes this technique particularly tolerant to defects.²⁴



Schematic of the Electrostatic Self-assembly of Nanolayers on Charged Textile Fibers

The self-assembly process begins by exposing a charged surface to a solution of an oppositely charged polyelectrolyte. The amount of adsorbed material is self-limiting by the charge density of the substrate²¹. Surplus polymer solution adhering to the support is removed by simply washing it in a neutral solution. Under the proper conditions, the polyion is adsorbed with more than the stoichiometric number of charges relative to the substrate, reversing the sign of the surface charge. In consequence, when the substrate is exposed to a second solution containing a polyion of opposite charge, an additional polyion layer is adsorbed reversing in this way the sign of the surface charge once again. Consecutive cycles with alternating adsorption of polyanions and polycations result in step-wise growth in total thickness of polymer films²⁵.

The fundamentals of the electrostatic self-assembly are more complicated than they appeared to be.²⁶ Although this technique is based on the electrostatic

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attraction between positively and negatively charged species, the interaction between these charged species is specific to the nature of the substrate and that of the polyelectrolytes.^{23,27} Polyelectrolyte adsorption is nearly irreversible, so the built-up films do not represent equilibrium structures. This behavior adds to the versatility of the method, but implies that a close kinetic control of the adsorption process is required in order to control film thickness and growth. The electrostatic self-assembly may depend on factors controlling the entropy of the polymer chains, such as molar mass, flexibility of the chains, ion exchange capacity as well as the hydrophobic interactions, charge transfer interactions, π - π stacking forces, and hydrogen bonding.²⁸ No single theory is available that can provide a complete description of the self-assembly process; moreover, deeper understanding of the specificity of ion-ion and ion-substrate interactions on surface of textile materials with complicated contour remains a challenge.^{29,30,31,32}

Future Prospect

Future developments of nanotechnologies in textiles will have a two-fold focus: 1) upgrading existing functions and performances of textile materials; 2) developing smart and intelligent textiles with unprecedented functions. The latter is more urgent from the standpoint of homeland security and advancement of technology. The new functions with textiles to be developed include 1) wearable solar cell and energy storage; 2) sensors and information acquisition and transfer; 3) multiple and sophisticated protection and detection; 4) health-care and wound healing functions; 5) self-cleaning and repairing functions.

Undoubtedly, Nanotechnology holds an enormously promising future for textiles. It is estimated that nanotechnology will bring about hundreds of billions dollars of market impact on new materials within a decade; textile certainly has an important share in this material market. We expect to see a new

horizon of textile materials under this irresistible technology wave.

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