Smart Textiles

Wearable Nanotechnology

Edited by

Nazire D. Yilmaz

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Preface

Originally, the need for textiles and clothing was related to protecting the human body from exposure to the elements of nature. A more comprehensive definition of conventional textiles also includes home textiles utilized in furnishings and the ones that have found use in bedrooms and bathrooms. Following these basic needs, aesthetics have become one of the main drivers of our selection of clothing and textiles. Recently, more functionality has started to be required, so functional/technical textiles, which can serve more sophisticated needs, have emerged. The last generation of textiles, smart textiles, remain one step ahead of the others by sensing and reacting to environmental stimuli.

Nanotechnology has carried the level of smart textiles one step further. Textile materials receive smart functionalities without deteriorating their characteristics via application of nanosized components. Consequently, functions conventionally presented by nonflexible bulk electronic products are achieved by "clothes."

Smart wearables should be capable of recognizing the state of the wearer and/or his/her surroundings and responding to them. Based on the received stimulus, the smart system processes the input and consequently adjusts its state/functionality or present predetermined properties. Smart textiles should also cater to requirements concerning wearability. Through the incorporation of nanotechnology, the clothing itself becomes the sensor, while maintaining a reasonable cost, durability, fashionability, and comfort.

This book provides a comprehensive presentation of recent advancements in the area of smart nanotextiles, with an emphasis on the specific importance of materials and their production processes. Different materials, production routes, performance characteristics, application areas, and functionalization mechanisms are referred to. Not only are mainstream materials, processes, and functionalization mechanisms covered, but also alternatives that do not enjoy a wide state-of-the-art use but have the potential to bring smart nanotextile applications one step forward.

The basics of smart nanotextiles are covered in the first chapter. Nanofibers, nanosols, responsive polymers, nanowires, nanogenerators, and nanocomposites, which are smart textile components, are investigated in Chapters 2 through 7, respectively. Nanocoating is investigated in Chapter 8, and nanofiber production procedures are examined in Chapter 9. Characterization techniques, which have uppermost importance in ensuring proper functioning of the advanced features of smart nanotextiles, are covered in the last chapter.

Nazire Yilmaz
Denizli, Turkey
September 2018

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Section 1

INTRODUCTION

1

Introduction to Smart Nanotextiles

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Abstract

This chapter provides a comprehensive presentation of recent advancements in the area of smart nanotextiles giving specific importance to materials and their production processes. Different materials, production routes, performance characteristics, application areas, and functionalization mechanisms are referred to. Not only the mainstream materials, processes, and functionalization mechanisms, but also alternatives that do not enjoy wide state-of-the-art use, but have the potential to bring the smart nanotextile applications one step forward, have been covered. Basics of smart nanotextiles, introduction to smart nanotextile components such as nanofibers, nanosols, responsive polymers, nanowires, nanocomposites, nanogenerators, as well as fundamentals of production procedures have been explained. In addition to materials and production technologies, characterization techniques, which have uppermost importance in ensuring proper functioning of the advanced features of smart nanotextiles, have also been investigated.

Keywords: Smart textiles, nanofibers, nanosols, nanowires, responsive polymers, nanocomposites, nanogenerators, characterization, fiber production, nanocoating

1.1 Introduction

Originally, textiles/clothing relates to catering the needs for protecting the human body from cold, heat, and sun. A more comprehensive definition of conventional textiles also include home textiles utilized in furnishing and the ones that find use in the bedroom and the bathroom [1, 2]. Following these basic needs, aesthetics have become one of the main drivers for people to use clothing and textiles [3]. Recently, more functionality has started

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to be required, so functional textiles/technical textiles, which can cater more sophisticated needs, have emerged. The last generation of textiles, smart textiles, is capable of one step ahead: sensing and reacting to environmental stimuli [2, 4, 5].

Smart textiles can be also named as "intelligent," "stimuli-sensitive," or "environmentally responsive" [6]. Smart textiles have been described as "fibers and filaments, yarns together with woven, knitted or non-woven structures, which can interact with the environment/user" [7, p. 11958]. Smart textiles have broadened the functionality and, consequently, application areas of conventional textiles [7], as they show promise for use in various applications including biomedicine, protection and safety, defense, aerospace, energy storage and harvesting, fashion, sports, recreation, and wireless communication [4, 8–10].

Smart textile components perform various functions such as sensing, data processing, communicating, accumulating energy, and actuating as shown in Figure 1.1 [11]. In these fields, textile structures present some advantages such as conformability to human body at rest and in motion, comfort in close contact to skin, and suitability as substrates for smart components [8].

"Smartness" refers to the ability to sense and react to external stimuli [6]. The stimulus of interest can be electrical, mechanical, chemical, thermal,

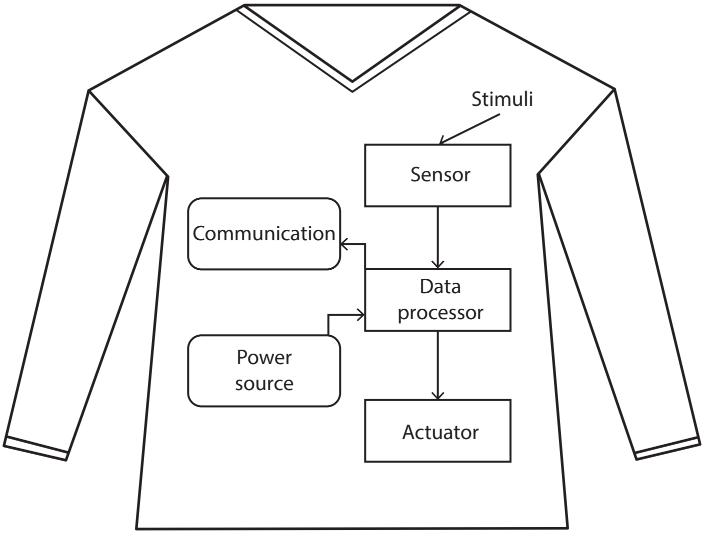

Figure 1.1. Smart textile components. (Reprinted from reference [11], with permission of Elsevier.)

magnetic, or light [4, 12]. Smart systems offer the capability of sensing and responding to environmental stimuli, preferably in a "reversible" manner, that is, they return to their original state once the stimulus is "off" [6].

Smart textiles can act in many ways for vast purposes including releasing medication in a predetermined way, monitoring health variables, following pregnancy parameters [13], aiding physical rehabilitation [14], regulating body temperature, promoting wound healing [15], facilitating tissue engineering applications [16], photocatalytic stain removing [17], preventing flame formation [18], absorbing microwaves [19], interfering with electromagnetic radiation [20], wireless communicating between persons, between person and device, and between devices (as in the case of IoT), and harvesting and storing energy [10]. In an everyday example, the smart textiles used for fashion, kids' toys, or entertainment can change color, illuminate, and display images and even animations [4, 10].

Smart textiles have attracted international research interest as reflected in the programs of the international funding bodies, for example, "Wear Sustain," a project funded by the European Commission. The Wear Sustain Project is directed by seven organizations, both public and private entities, across Europe, including universities, research centers, and short- and middle-scale enterprises (SMEs). This project has launched 2.4 million euros for funding teams to develop prototypes of next-generation smart textiles [21]. US-based National Science Foundation grants $218,000 to a career project titled Internet of Wearable E-Textiles for Telemedicine [22]. NSF of the USA has invested more than $30 million on projects studying smart wearables. The projects include belly bands tracking pregnancy variables, wearables alerting baby sleep apnea, and sutures that collect diagnostic data in real time wirelessly. NSF also supports the Nanosystems Engineering Research Center (NERC) for Advanced Systems for Integrated Sensors and Technologies (ASSIST) at North Carolina State University working on nanotechnological wearable sensors [23].

Different components are used for imparting smartness into textiles. These components include conductive fibers, conductive polymers, conductive inks/dyes, metallic alloys, optical fibers, environment-responsive hydrogels, phase change materials, and shape memory materials. These components are utilized in forming sensors as well as electrical conductors, and connection and data transmission elements [4]. Conductive materials added to fibers/yarns/fabrics include conductive polymers, carbon nanotubes, carbon nanofibers, or metallic nanoparticles [4, 24–26].

"Smartness" can be incorporated into textiles at different production/treatment steps including spinning weaving [27], knitting [28], braiding [29], nonwoven production [30], sewing [31], embroidering [3], coating/laminating [32], and printing [33] as shown in Figure 1.2.

Conventionally, conductive fibers and yarns are produced through adding conductive materials to fibers, or via incorporation of metallic wires/fibers such as stainless steel or other metal alloys [4, 25]. Another way to produce smart textiles is through incorporation of conductive yarns in fabrics, for example, by weaving. Drawbacks related with this method are the complexity, non-uniformity, as well as difficulty in maintaining comfortable textile properties [7].

Nanotechnology has carried the level of smart textiles one step further. Via application of nanosized components, textile materials receive smart functionalities without deteriorating textile characteristics [10, 34]. Consequently, functions conventionally presented by nonflexible rigid bulk electronic products are achieved by "clothes" [2].

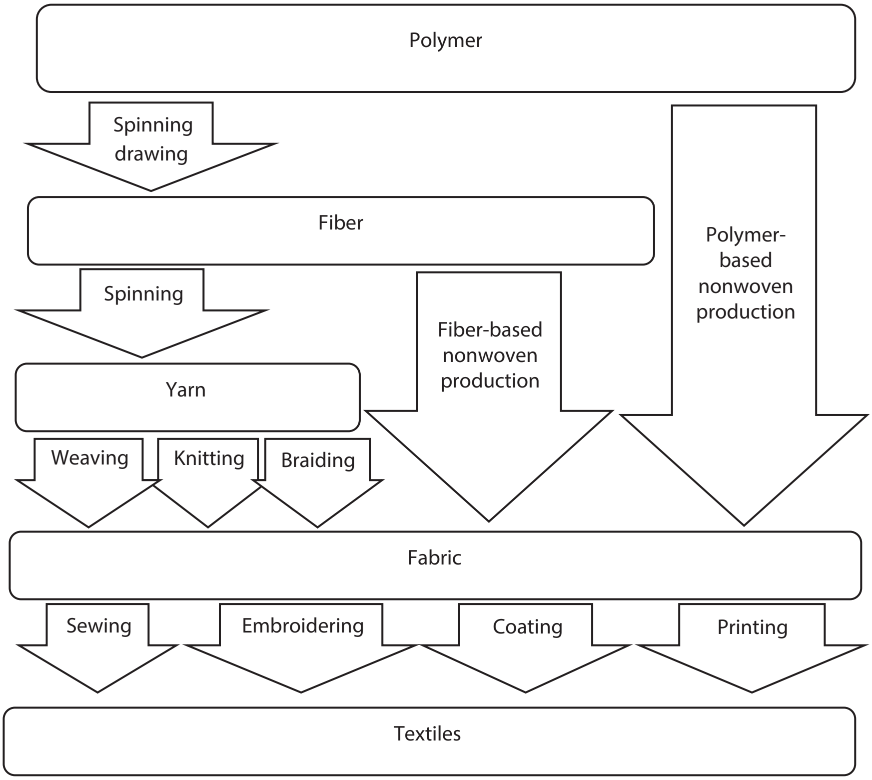

Figure 1.2. Production steps of textiles. (The image has been prepared by the author.)

Smart wearables should present capability of recognizing the state of the wearer and/or his/her surrounding. Based on the received stimulus, the smart system processes the input and consequently adjusts its state/functionality or present predetermined properties. Smart textiles should also cater needs regarding wearability [7]. Via incorporation of nanotechnology, the clothing itself becomes the sensor, while maintaining a reasonable cost, durability, fashionability, and comfort [35].

Based on their "smartness" level, smart textiles may be investigated under three categories [33]:

- Passive smart textiles
- Active smart textiles
- Very active smart textiles.

The first group can only detect environmental stimuli (sensor), whereas the second group senses and reacts to environmental stimuli (sensor plus actuator). On the other hand, the third group senses and reacts to environmental stimuli, and additionally adapts themselves based on the circumstances (sensor, actuator, and controlling unit) [2, 4].

1.1.1 Application Areas of Smart Nanotextiles

Potential application areas of smart textiles are innumerable. In terms of personal use, they can act for making us feel comfortable, warn and protect us against dangers, monitor biometric data, treat diseases and injuries, and improve athletic performance via use of sensor-embedded clothing. Furthermore, they can be used by military and other security staff for communication. Fashion and decoration are also irreplaceable applications for clothing, not excluding smart wearables. Related examples include color-changing, lighting-up, picture-video-displaying wearables [4, 33].

As textiles are in close contact with human body over a large surface area, sensors can be placed at different locations, which presents advantage for biomedical applications. This fact provides greater flexibility and closer self- and remote monitoring of health variables. Smart textile components responsive to pressure/strain can be used to measure heart rate, blood pressure, respiration, and other body motions. Accordingly, piezo-resistive fibers can be utilized as pressure/stress sensors [7, 13]. Smart textiles also show promise for sensing body temperature [2], movements of joints [14], blood pressure, cardiac variables [36], respiration [37], presence/concentration of saline, oxygen, and contamination or water. Thermocouples can be utilized in measuring temperature, whereas carbon electrodes are used for detecting concentrations of different biological fluids [38].

As expected, active smart functionality needs energy to act, which in turn necessitates generation or storage of power. Power generation may be attained via use of piezoelectric [5], photovoltaic [39], or triboelectric components [40], which can harvest energy from motion, light, or static electricity, respectively [10].

1.1.2 Incorporating Smartness into Textiles

Smart textile components include conductive polymers, conductive ink, conductive rubber, optical fibers, phase changing materials, thermochromic dyes, shape-memory substances, miniature electrical circuits, and so on. In terms of textile functionality, organic polymers pose advantages compared to stiff inorganic crystals. The former materials exhibit low weight, flexibility, resilience, cost efficiency, and easy processibility [33, 34].

As mentioned, these "smart" components can be included into the textile structure at different stages. At the fiber spinning stage, electrically conductive components may be added to the spinning dope. Smart components can be integrated into textiles in the course of fabric formation such as weaving or knitting. After fabric formation, the finishing stage provides practical solutions for adding active components on the fabric such as nanocoating procedures [3, 4, 33, 41].

Smart textiles present the capability of sensing, communicating, and interacting via use of sensors, connectors, and devices produced from environmental-responsive components [4]. Sensors may be considered as members of a nerve system that can detect signals. Based on the environmental stimulus, actuators react autonomously or as directed by a central control unit [7]. Conductive materials that exhibit property change based on environmental stimuli such as stretch, pressure, light, pH value, and so on can be used as sensors [7].

Smart activity can be achieved by incorporation of human interface components, power generation or capture, radio frequency (RF) functionality, or assisting techniques. By using these components, innumerable combinations can be obtained conventionally by introducing cables, electronics, and connectors. However, wearers prefer comfortable textiles rather than clothes resembling "Robocop" costumes. To achieve this, the smart functionality should be integrated into the textiles [3, 33]. This can be made possible by using nanotechnology.

1.1.3 Properties of Smart Nanotextiles

The components of smart nanotextiles should provide some characteristics including mechanical strength, conductivity, flexibility, washability, and biocompatibility. These features, indeed, are not easy to achieve concurrently. Textile properties, such as drape, stretch, resilience, and hand, are especially important once the final use is taken into consideration. In order to achieve these characteristics, the structures should not be coarse and the resultant fabric should not be heavy (not exceeding 300 gsm). Of course, these requirements cannot be met via use of conventional electrical appliances, metal wires, and so on. The challenge is to maintain connectivity and integrity through the interconnections among the components and devices during deformation throughout the intended use. An approach to solve this problem is to use sinus-wave or horseshoe-shaped designs of the conductive components to minimize the effect of deforming in the flexible textile substrates. Another potential solution is to encapsulate the conductive component in a stretchable polymeric substrate [7]. Nanotechnology presents advantage in terms of mechanical flexibility. Thinness provides flexibility based on the nanosizes of the elements. Accordingly, a smart textile structure that preserves the extensibility of a conventional textile fabric can be achieved. Durability against washing and aging is also very important. This can be attained via effective bonding of smart components with the textile substrate through nanocoating procedures [41].

Besides, thinness and flexibility, transparency is another plus for smart components to be used in wearables, due to minimized interference with the designed appearance. As expected, at a very high thinness level, even opaque materials, such as metals, exhibit transparent optical property. Ultrathinness results in decreased optical absorption and increased light transmission [42]. Indeed, this level of thinness can be obtained from nanoscale materials via nanotechnological applications.

1.1.4 Nanotechnology

Nanotechnology, which is an emerging interdisciplinary field, is considered to provide various impacts in different science and technology areas including, but not limited to, electronics, biomedicine, materials science, and aerospace [43]. Nanotechnology shows promise for use in higher and higher number of applications in different arenas such as textiles and clothing to impart enhanced properties and performance [32].

In the last two decades, we have witnessed that nanotechnology has found use in textiles for improving and/or imparting properties including smart functionalization [32]. Nanotechnology enables certain functions including antibacterial, antistatic, self-cleaning, UV-protective, oil and water repellency, stain proof, improved moisture regain, and comfort performance in textiles while maintaining breathability, durability, and the hand [43]. Nanotechnology applications on textiles have succeeded in attracting great interest by both research and commercial communities [32]. The studies related to nanotechnological practices, that is, application of nanomaterials, on textiles cover *in situ* synthesis, cross-linking, and immobilization on textile substrates [32].

1.1.5 Nanomaterials

Nanomaterials refer to materials at least one dimension of which is in the nanometer order, that is, generally lower than 100 nm [32]. These materials show promise for use in functional and high-performance textiles based on their high specific characteristics stemming from great surface area-to-volume ratios [43].

Although there is a perception that the nanoscale materials are novel materials, they have been used since the early decades of the 20th century. An example to this is carbon black, a nanomaterial that has been used in automobile tires since the 1930s. Indeed, the capabilities of nanosized materials have increased drastically since then [44].

The use of nanoscale materials in the textiles field is increasing rapidly, and they have found use in various applications catering industrial, apparel, and technical needs. The main aims of incorporating nanomaterials in textiles include imparting functionalities such as electrical conductivity, flame retardancy, antibacterial, superhydrophobic, superhydrophilic, self-cleaning, and electromagnetic shielding [34, 45].

Most of the nanomaterial applications necessitate definite particle dimensions with narrow variation. By controlling production parameters, different characteristics of nanomaterials can be manipulated. These characteristics include particle dimensions, chemical composition, crystallinity, and geometrical shape. And the production parameters are pH, temperature, chemical concentration, used chemical types, etc. [44]. Various shapes are observed in nanoparticles such as nanorods, nanospheres, nanowires, nanocubes, nanostars, and nanoprisms. Via manipulation of synthesis variables, it is possible to attain different nanoparticle shapes [34].

A critical matter related to use of nanostructures is difficulty in dispersion as nanoparticles tend to agglomerate due to van der Waals and electrostatic double-layer attractions. In order to form stable dispersions, some precautions should be taken such as using dispersing agents including surfactants and functionalization of nanostructures using organic compounds and monomers [34].

Another major problem related to nanomaterials is their durability on textile substrates. Due to lack of surface functional sites, nanomaterials do not show affinity to textile fibers. In order to address this problem, surface functionalization via physical or chemical techniques has been suggested. Another solution is embedding nanoparticles in polymer matrices on textiles substrates [34].

One of the novel abilities of nanoscale materials is "smartness," which shows promise for use in smart textile applications. Smart textiles include nanotechnological components such as nanofibers, nanowires, nanogenerators, nanocomposites, and nanostructured polymers. Smart nanotextiles are investigated for use in biomedical, aerospace, and defense applications, among others [43]. Development of smart nanotextiles requires knowledge on nanotechnological components, their properties, production techniques, and nanotechnical characterization methods.

This chapter provides a comprehensive presentation of recent advancements in the area of smart nanotextiles giving specific importance to materials and their production processes. Different materials, production routes, performance characteristics, application areas, and functionalization mechanisms are referred to. Not only the mainstream materials, processes, and functionalization mechanisms but also alternatives that do not enjoy wide state-of-the-art use, but have the potential to bring the smart nanotextile applications one step forward, have been covered. Basics of smart nanotextiles, introduction to smart nanotextile components such as nanofibers, nanosols, responsive polymers, nanowires, nanocomposites, nanogenerators, as well as fundamentals of production procedures have been explained. In addition to materials and production technologies, characterization techniques, which have uppermost importance in ensuring proper functioning of the advanced features of smart nanotextiles, have also been investigated.

1.2 Nanofibers

Among various forms that nanomaterials can take such as nanorods, nanospheres, and so on, the fiber form comes to the forefront due to its superior characteristics. The advantageous properties of this material form include flexibility, high specific surface area, and superior directional performance. These merits allow many uses from conventional clothing to reinforcement applications in aerospace vehicles. Nanofibers refer to solid state linear nanomaterials, which are flexible and have aspect ratios exceeding 1000:1. Nanomaterials are characterized by their dimensions at least one of which should be equal to or less than 100 nm. A million times increase in flexibility can be achieved via reduction of the fiber diameter from 10 μm to 10 nm, which also leads to increases in specific surface area, and in turn surface reactivity [46].

Numerous functionalizations can be attained by use of nanofibers produced from various polymers including polypyrrole, polyaniline [7, 47], polyacetylene [4], polyvinylidene fluoride, poly N-isopropylacrylamide (PNIPAAm), polyethylene glycol, and so on, and incorporation of different functional components such as carbon nanotube, graphene, azobenzene, and montmorillonite nanoclay [10, 34, 48, 49]. More of these polymers and functional components can be found in the following chapter [46]. Via use of these nanofibers, it is possible to achieve smart functionalities as follows.

1.2.1 Moisture Management

Moisture behavior of materials is determined not only by the chemical but also the topographical properties [50]. Nanofibers can be utilized for smart moisture management functions of textiles such as superhydrophobicity and switchable hydrophilicity–hydrophobicity. Superhydrophobicity can be obtained via mimicking the microstructure of various plant leaves, known as the “Lotus effect.” This function is provided by two characteristics: a hybrid rough microstructure and a hydrophobic surface [51]. Nanofibrous membranes of polyurethane, polystyrene, and polyvinylidene fluoride have been studied for producing superhydrophobic structures. The nanofibrous structure emphasizes both hydrophilic and hydrophobic characteristics. The rough microstructure of superhydrophobic materials can be improved by incorporating beads, rods, microgrooves, or pores/dents in the nanofibrous structures during electrospinning procedures. By varying electrospinning, dope parameters fibers in bead-on-string form can be obtained [46, 52, 53].

Nanoscale bumps and dents can be formed by incorporating nanoparticles onto nanofibers and sonicating these nanoparticles away. In this way, superhydrophobic effect can be provided. By introducing fluorinated polymers with low surface energy on the nanofibrous membranes, hydrophobicity can be further improved. A study showed that hierarchical roughness positively affected amphiphobicity (hydrophobic and oleophobic at the same time). Another material popularly used for hydrophobicity is the hydrophobic SiO_2 nanoparticle, which allows enhanced surface roughness [9, 50].