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ELECTROCONDUCTIVE NANOFIBERS FOR TEXTILE-BASED SENSORS AND ACTUATORS

STROE Cristina Elena[1], AILENI Raluca Maria[1], SÂRBU Teodor[1]

[1]National R&D Institute for Textiles and Leather, 16 Lucretiu Patrascanu Street, Bucharest 030508, Romania
E-Mail: office@incdtp.ro

Corresponding author: Stroe, Cristina Elena, E-mail: cristina.stroe@incdtp.ro

Abstract: *Smart textiles reach a remarkable potential for use in people's lives by adding new and multiple functions and properties, overcoming the barriers of conventional textiles. They consist of built-in mechanical, thermal, magnetic, chemical, and/or electrical sensing and processing technologies to monitor stimuli, collect and convert data and—sometimes—perform an action, thus being able not only to track and communicate environmental and user data but also to manage and alleviate potential health risks or to give people friendly ways to enjoy life. Many industries are utilizing these smart materials from defencemen to fashion designers, casual shoppers, sportive people, doctors and caregivers, to the occupied business-people.*
With the advancement of nanotechnology, electrospinning has made its presence felt lately due to its reduced complexity and the potential to obtain functionalized continuous fibres with micro and nanometer ordinal dimensions. Electroconductive nanofibers obtained by electrospinning due to their unique structural and electrical properties are very good candidates to obtain sensing and actuation devices. Compared to conventional materials, electroconductive nanofibers possess numerous benefits which can meet the desired requirements for developing such smart applications.
This paper discusses approaches to the manufacture of electroconductive nanofibers by electrospinning technology, their advantages and their use as nanofiber-based sensors and actuators for various applications.

Keywords: *smart textiles, electrospinning, stimuli sensitivity, wearable devices, artificial muscles*

1. INTRODUCTION

Smart textiles are becoming more and more present in our everyday life as they can help us to control and improve the quality of our lives and possess the ability to unlock human potential. The practical applications of these new materials involve different areas, different age groups and different functions, many of these are aimed at uses within the health care industry.

Sensors and actuators are essential elements for active smart textiles that can sense the external stimuli activity and further perform an action. These advanced textile materials can bring significant improvements in textiles performance in terms of functionality and adaptiveness and thus providing a series of services to consumers: knowledge service, communication service, healthcare and safety service and emotional service [1].

Over the last decade, electrospinning, a nanotechnology based on the action of an external electric field to extract from a syringe and a needle various polymeric solutions or melts in the form of nanofibers, has gained increasing attention in the scientific research community, being one of the most emergent routes to the synthesis of electrospun nanofibers with many interesting properties and possibilities to be used in the field of sensors and actuators. Electrically conductive nanofiber mats obtained this way could be highly suitable for sensors and actuators because of many advantages (Fig. 1).

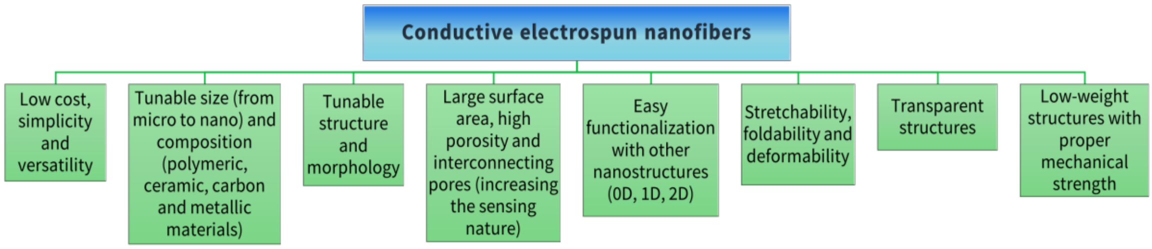

Fig. 1: *Benefits of conductive electrospun nanofibers*

The morphology and the diameter of the electrospun nanofibers play a key role in their final physical and chemical properties. Therefore, to make nanofibers with controlled structures and orientation but also with the desired functions, certain parameters of the technology should be adjusted accordingly (solution parameters, process parameters and ambient parameters). In addition, the different configurations of the equipment, contribute to the change in the composition, orientation, and architecture of the fibres. For example, coaxial electrospinning uses two or more separate syringes with capillaries of different sizes, the smaller capillary being incorporated into the larger one, forming multilayer core-sheath fibres of different materials in just one step. Some technologies exclude the use of capillaries (needles) to obtain nanofibers.

2. ELECTROCONDUCTIVE ELECTROSPUN NANOFIBERS PRODUCTION

Conductive polymers. One usual method for the manufacturing of conductive nanofibers by electrospinning involves the use of conductive polymers such as polyaniline (PANI), polyacetylene, polypyrrole (PPy), polythiophene (PTs), poly(3,4-ethylenedioxythiophene) (PEDOT), polyvinylidene fluoride (PVDF), etc. These polymers are known as electroactive polymers (EAP). They offer thermal, electrochemical, and environmental stability but also high conductivity. However, the processability of these polymers is a challenge [2]. They cannot be processed by melting and are insoluble in most solvents. Therefore, in most cases, they are used to produce coatings on the surface of nanofibers obtained from ordinary non-conductive polymers.

Conductive additives in the spinning solution. The addition of a conductive material, such as carbon black nanoparticles, silver nanoparticles, carbon nanotubes/nanoparticles, graphene nanosheets or an ionic liquid, to the spinning solution is an efficient method of producing electroconductive nanofibers. Recently, the incorporation of ionic liquids into polymeric solutions has gained interest due to their extremely low volatility and their ability to significantly improve conductivity and promote electron transfer [2]. Ionic liquids are organic salts essentially found in the liquid state at room temperature [3]. Some ionic liquids explored as additives for electrospinning solution are 1-butyl-3-methylimidazolium chloride (C_4MIMCl), 1-dodecyl-3-methylimidazolium chloride ($C_{12}MIMCl$), 1-ethyl-3-methylimidazolium bromide (C_2MIMBr), and 1-ethyl-3-methylimidazolium phosphate $(C_2MIM)_3PO_4$ [4].

Graphene is also a suitable nano-additive candidate both for natural polymers and synthetic polymers for electrospinning because it possesses several excellent properties, such as thermal stability, hydrophobicity, conductivity, and mechanical strength. However, a very tough task remains the loading of graphene solution in the electrospinning setup and in general, two methods were addressed: one is based on in situ polymerization technique and the other one is the formation of rGO nanofibers in the presence of high temperature or chemical reduction methods [5].

Heat treatment of the nanofiber mat (carbonization). Electroconductive properties of nanofibers can be obtained by heat treatment of electrospun precursor fibres. The manufacture of carbon nanofibers is a method that involves heat treatment at high temperatures. For example, polyacrylonitrile (PAN) or polyvinylpyrrolidone (PVP) precursor nanofibers are converted to carbon nanofibers due to their easy carbonization process, resulting in one-dimensional structures that possess high mechanical strength, high rigidity, excellent electrical and thermal conductivity, good fatigue resistance corrosion [2].

Surface coatings. The last method involves coating the non-conductive nanofiber structure with a conductive material such as metals (e.g. copper, silver, nickel, gold), electroplating being a widely used technique for depositing metals on the surface of nanofibers [2].

3. ELECTROSPUN SENSORS AND ACTUATORS APPLICATIONS

SENSORS

The signals transmitted by the sensors are mainly in electrical form, so for the realization of a textile sensor, the most used and efficient method is the use of electroconductive materials.

Two essential properties are vital for the high sensitivity and fast response of a sensor: a large specific surface area and a very porous structure, characteristics that are fulfilled by nanofibers obtained by electrospinning. In addition, compared to conventional sensors, electrospun nanostructured sensors show faster adsorption and minimised bulk effects [6].

Conductive electrospun nanofibers can be used to create a variety of sensors like gas sensors, optical sensors (colorimetric and fluorescent), mechanical sensors, electrochemical sensors, and photo-electric sensors. They can be used in areas such as medicine and medical diagnosis, environmental monitoring, food monitoring, industrial processes, biodefence and military, agriculture and plant biology.

Among them, electrochemical sensors stand out, with applicability in the bio-medical field for fast and reliable monitoring of glucose and carbohydrates levels present in the body fluids like saliva, tear, interstitial fluid, sweat, or blood for the treatment and control of metabolic diseases like diabetes [7]. Most importantly, electrospun nanofibers as biosensors are a promising base for the early detection of cancer-related electrochemical biomarkers. For example, imunosensing with electroconductive electrospun nanofibers (immunosensors performing immunoassays on account of antigen and antibody recognition for detection of cancerous molecules in body fluids, especially in serum because of the inherent specificity and accuracy) is an encouraging applicable method for detection of cancer [8].

Gas sensors based on electrically conductive nanofibers have been shown to be suitable for the detection of various diseases (intestinal diseases, lung cancer, asthma, halitosis, diabetes, chronic kidney disease) by analyzing volatile organic compounds in human respiration [9]. Gas-sensing materials formed from nanofibers usually have a porosity of ~70–90%. The presence of large pores along with small pores, that facilitate gas diffusion can also be attributed to the advantages of these materials [10]. Moreover, sensors made of such materials are effectively used to detect a wide range of gaseous substances in the atmosphere, including pollutants, exhaust fumes or industrial gases: methane (mining), hydrocarbons (refineries), ammonia (fertilizers), etc.

Mechanical sensors are another category of sensors that can be developed using nanofibers. They have a high potential to be used in interactive portable/wearable devices, military applications, intelligent soft robots and health monitoring. Pressure and strain sensors are two types of mechanical sensors, the two most studied using electrospun nanofibers. A special advantage is that the electrospun nanofiber mats manifest high tolerance for repetitive external pressing [11].

Obviously, certain critical factors must be considered for the successful development of textile sensors. Abrasion, bending, stretching, confidentiality security, and the gap between laboratory and practical life are the main challenges facing conductive textiles. For the development of sensors made of such materials, it is necessary to ensure that they are durable in the long term, that they have sufficient robustness and dimensional stability, that they withstand frequent washing, dust, sweat or heat cycle over time, especially when intended for use in wearable devices or electronics. In addition, economic aspects are essential for the development of appropriate sensors [12].

ACTUATORS

Conventional actuators are rigid, have robust, heavy and noisy operating systems, features that make them unsuitable for assembly in smart textiles. With the advancement of wearable devices, actuators that overcome these limitations are needed. Thus, polymeric materials are a good solution for making actuators because they are soft, light and can produce flexible movements. However, low-voltage polymer-based actuators can only be used in a solution, while those operating in the atmosphere require high voltages, so it is difficult to extend their scope [13].

Actuators obtained using nanofibers resulting from electrospinning have several advantages, including the ability to be used a wide variety of polymers, good dispersion, increased flexibility, low weight, and the ability to produce different shapes, varying the essential factors. Besides, nanofiber structures have attracted attention for application as actuators due to their ultra-high surface-to-volume ratio, which improves their controllability by the excitation of different stimuli. The driving behaviour of an actuator is influenced by the type of material, physical properties and the thickness of nanofibers.

Thus, depending on the external stimulus used to activate and implement the actuator function, there are photo-sensitive actuators, electrochemical actuators, electrothermal actuators, pneumatic actuators, humidity/water sensitive actuators, magneto-thermal actuators, etc.

To date, several studies have been reported on nanofiber-based actuators using the electrospinning method, and such actuators can be divided into two types: single-nanofiber-based actuators and nanofiber mat-based actuators (table 1). However, only a few works involve the production of individual fibre-based actuators, mainly due to difficult testing procedures depending on the size of the fibres and the infinitesimal forces to be measured (from nN to a few µN) [14]. Also, nanofibers can be incorporated into the actuator component either as electrode layers or as electrolyte layers [15].

Most applications are based on the use of electrospun nanofibers to make artificial muscles because they can form bundles by their parallel arrangement, a configuration that is very similar to the structure of natural muscle fibres made of myofibers with diameters of about 1-2 µm [16]. Artificial muscles studied for a long time since 1950 [17] are very useful today in several applications such as humanoid robots, prosthetic limbs, exoskeletons, for controlling valves and stirring liquids in microfluidic circuits and medical catheters [18].

In this context, conductive polymers (CPs) are suitable candidates for such applications, given their biocompatibility, low actuation potentials and high mechanical properties, but they are mainly used as coatings using in situ chemical polymerization of conductive polymers on the surface of electrospun fibres or electrochemical polymerization [13] in particular to perform bending movements under the action of the electric field and/or oxidation/reduction reactions, so that they may experience changes in shape or volume.

Table 1: *Electrically stimulated actuators manufactured by electrospinning technology*

Actuation mechanism	Materials	Structure	Motion	Application	Ref.
Electro-thermal	PU and $FeCl_3$ powder	Single nanofiber	Bending	Artificial muscle tissue or a filter for a driver	[13]
Electro-chemical	PMMA fibres coated with gold and PANI	Strips of aligned nanofibers	Bending	Artificial muscle	[16]
Electro-chemical	Silk fibroin nanofibers coated with PPy and PEDOT	Bundle (rolling the nanofiber mat)	Elongation and contraction	Tissue engineering	[19]
Electro-chemical	PVDF-graphene nanofiber membrane dipped into an ionic liquid ($EMIMBF_4$) and two deposited PEDOT: PSS layers	Sandwich structure	Bending	Artificial muscles, biomimetic robots, and disposable biomedical devices	[20]
Piezo-electric	PVDF	Single nanofiber	Contraction	NEMS/MEMS	[21]
Electro-mechanical	PE film and PEDOT/PSS film with PVP/ PMMA nanofiber	By-layer structure	Bending	Flexible ambient devices with anisotropic actuation propertie	[22]

4. CONCLUSIONS

Electrospinning technology is a promising solution for the development of advanced materials that will bring a special contribution in improving our comfort, providing us with greater protection and improving our quality of life. Due to recent developments, sensors and actuators based on electrospun conductive nanofibers are gaining interest to be used in many applications such as soft electronics, biomimetic robots, haptic devices, medical diagnostics and treatment, global environmental monitoring, etc. Further improvements should be made to the operational characteristics of these devices. Sensors still need improved detection limits and actuators need enhanced actuation strain to obtain highly efficient devices. Also, some actuation materials need efforts to reduce the driven electric field strength, to improve the response time and to eliminate the surrounding electrolyte medium, so they can be applied in everyday applications. Moreover, it is necessary to reduce the production cost of some nanomaterials and increase the production rate, with repeatability and quality maintained over time to ensure long end-user functionality.

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