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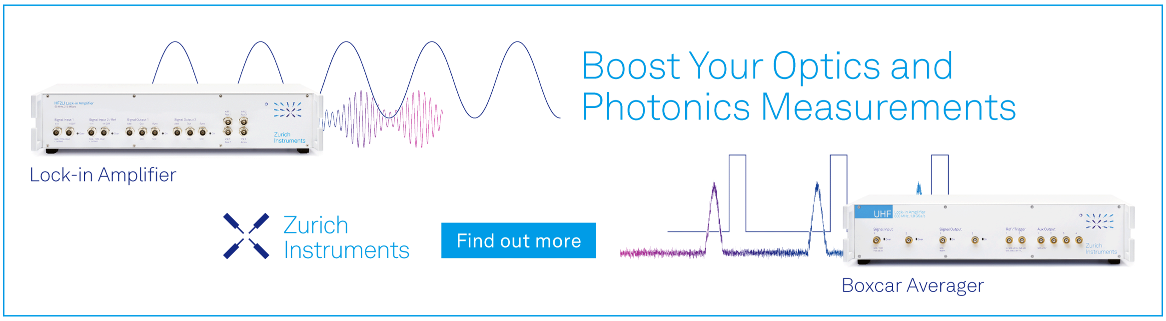

Recent Trends in Smart Textiles: Wearable Sensors and Drug Release Systems

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Abstract. Nowadays nanotechnology can provide high durability and high performances for textile materials. In particular, the uptake of opportune functional molecules into textile fabrics is a powerful approach towards the development of engineered functional surfaces such as the so-called "smart textiles", able for example to react and adapt to specific external environmental stimuli from their surroundings. Thanks to the large number of available sensing molecules and electronic devices, the introduction of the sensor technology in textiles can result in wearable sensors, useful for a wide range of daily life applications, such as medical and diagnostic, health care and telemedicine, fitness, sportswear and leisure, wellness, as well as military and emergency services equipment, and environmental. At the same time, in the last years there is a growing interest in textile-based drug release and delivery systems thanks to their potential innovative medical and well-being applications. In this way, the sol-gel technique or nanocomposites polymerization are promising methods exploited to better control the size and shape of the hosting nanostructured 3D network as textile coatings, and firmly bind to or include functional moieties, in order to obtain wearable sensors or controlled drug release textiles materials.

INTRODUCTION

Humans civilization development goes hand in hand with that of textile technology. Plant leaves or animal skins had been used by our ancestors to realize clothing, mainly to defend themselves from environmental conditions. Gradually, natural materials such as flax, silk and cotton were then woven into more comfortable clothing. Finally, more recently, a broad range of man-made polymers, such as nylon, polyester and acrylic, progressively appeared and greatly enhanced everyone lives over the last century. Giving for granted that protection and esthetics are the two main characteristics associated with clothing, technical performance is a third emerging feature required to satisfy the needs of today's consumers. In the last decade, textiles have been facing new challenges with the advancement of miniaturized electronics and new smart materials. Therefore, textiles are nowadays expected to exhibit additional functionalities besides the conventional ones. The traditional markets of apparel textiles is now influenced by both consumers' lifestyle and availability of novel materials [1] such as antimicrobial, self-extinguishing, water repellency, wrinkle resistance, UV protection, moisture management, soil release performances, to mention the most common functions [2]. The remarkable growth of engineered textiles can be justified by the excellent combination of textile properties (mechanical, thermal, electrical, etc.) with the surface finishing versatility. In this scenario "technical textiles" have emerged in high-tech fields, such as smart packaging, automotive, health care, sport. Textiles are ideal substrates for the integration of nanotechnology, electronics and optical devices, offering a platform able to respond to mechanical, chemical, electrical, thermal, optical or magnetic stimuli. Smart-textiles development is entering a new era thanks to the convergence of different disciplines, such as chemistry, engineering, polymer sciences and electronics. In the present paper, a review of the challenges in

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wearable sensors development and current trade-offs are firstly considered. Then, an overview of recent technological breakthroughs is provided with the aim of showing the potential of new enabling technologies to overcome technological barriers. Finally, new approaches for drug delivery systems with a focus on advancement of functional materials are described to reveal cutting-edge topics that will shape the future of textiles.

WEARABLE SENSORS

Many wearable-tech items have been developed by integrating sensors and data transferring devices into textiles or fabrics. This new class of wearable electronic systems are designed to meet innovative applications in many consumers applications, such as fitness and healthcare, military, public safety and sports fields. A textile structure offers unique advantages over a conventionally bulk electronic device. In contrast to the latter, which is generally rigid, a smart textile is a fibre-based flexible system able to accommodate complex and severe deformations with high stability. Moreover, textiles are soft, light and breathable so that embedded-electronics can be shaped into curved surfaces and comfortably worn. Smart materials can be considered as a part of a complex system having the capability of responding to external stimuli and adapting their behaviour accordingly. Stimuli have very different origins, most of them are reported in Figure 1.

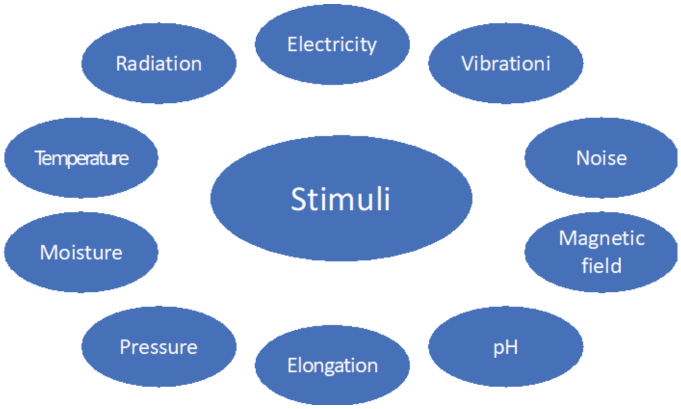

FIGURE 1. Origins of various stimuli for smart textiles.

Depending on the level of complexity, these materials can be divided into three categories: passive, active, and very smart textiles. Passive smart textiles can merely sense the environmental conditions or stimuli; active smart materials can sense and react to the conditions or stimuli; very smart materials can sense, react and adapt themselves accordingly. The latter category takes a step further in the development of intelligent materials thanks to the ability to adapt their behaviour to the circumstances (Figure 2). Indeed, further and higher level of intelligence can be achieved by those materials able to perform a function in a manual or programmed condition [3].

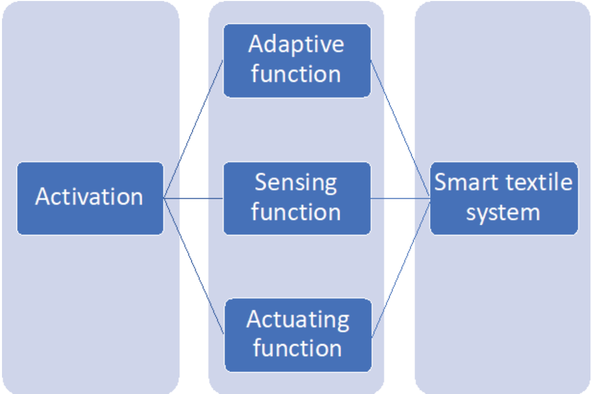

FIGURE 2. Schematic representation of a smart textile system, able to sense the environment, act upon it and adapt its behaviour.

Three components should be present in such systems: sensors, actuators and controlling units. The sensors provide a "peripheral nervous" system to detect signals, thus in a passive smart material, the presence of sensors is essential. The actuators act upon the detected signal either directly or from a central control unit; sensors and actuators are essential elements for active smart materials. At the highest level, represented by very smart or intelligent systems, a central processing unit with cognition, reasoning, and activating capacities is needed. With the aim of building up a smart textile system, textiles can incorporate many functions, such as sensing, actuating, powering and communicating as well as data processing. However, garment capability to remain flexible, comfortable to wear, washable is a necessary condition that must be maintained. Wearable sensors can be introduced in many fields such as electrocardiogram (ECG), electromyography (EMG) and electroencephalography (EEG). Moreover, textile fabrics incorporating carbon nanotubes, thermocouples, luminescent elements or shape-sensitive materials can be used for many sensing applications or to detect specific environmental or bio- medical features such as moisture, oxygen or salinity [4]. Among the above-mentioned wearable systems, in the last decade, many papers investigated the ability of chemical textile sensors of responding to specific stimuli [5]. For instance, chromic materials change their optical properties due to many stimuli, with potential application in environmental pollution monitoring or in medical diagnosis [6]. In this scenario, halochromic pH sensors assume a certain importance for the determination of alkaline or acidic conditions in monitoring food quality, pollution levels and health conditions. For instance, variation of sweat pH is an index of body hydration and can affect the pathogenesis of skin diseases such as dermatitis, acne vulgaris and Candida albicans infections. The development of a wearable pH-meter can be realized by combining a fabric dyed with a halochromic molecule, working in the visible radiation range, with an optoelectronic circuit [7]. In order to develop optical pH sensors resisting laundry cycles, halochromic dyestuffs have been immobilized on textile fabrics by conventional dyeing methods or using nanotechnology conferring high durability to fabric functionalization due to nanoparticle high surface energy [8,9,10]. Sol-gel technique is a simple route for the fabrication of porous coating, without cytotoxic activity [11], widely used to produce hybrid films onto textile fabrics with stimuli-responsive properties [7,8,9,11] or technical performances, such as antibacterial [12], flame retardancy [13] or water repellency [14]. Results demonstrated that the treated fabrics show highly performing properties, still maintaining typical textile characteristics. Interesting results have been obtained by integration of electro-conductive carbon nanotubes (CNTs) tracks with an electronic device, developed for real-time monitoring of environmental relative humidity and temperature. Conductive tracks, as well as electrodes, produced by sol-gel synthesis, are able to transmit electrical signals thanks to the presence of CNTs. Variations in temperature and humidity produce changes of the conductive properties of the integrated tracks and potential conditions of high/low humidity can be detected [15]. Thanks to digital printing, deposition of conductive tracks (which maintains the flexibility of the treated fabric) can be easily obtained and, with the miniaturization of the integrated electronics, the obtained results could be used in the environmental field to monitor humidity parameters in humidity controlled environments.

DRUG RELEASE SYSTEMS

Textiles lie at the interface between human body and the environment and cover the majority of body surface for most of the day. This simple observation suggests that textiles can be used as comfortable systems for delivering active principles/drugs either towards the body or the surrounding environment. Skin surface can be as large as 2 m^2 and it is a potential route for drug delivery [16]. The ability of a substance to penetrate skin is related to molecular size: small molecules (<500 Da) can penetrate the stratum corneum or tranverse the epidermis through shunt pathways created by sweat glands and hair shafts, regardless of their lipophilic or hydrophilic nature. The mechanism of controlled release from textiles and fibres can be based on desorption from the fibre surface, diffusion from the fibres pores or degradation from the matrix, with each mechanism having different release kinetics. This observation implies that fibres and textiles offer opportunities for tuning drug release according to the user needs. Generally speaking, the finer the fibre the faster the drug release due to large surface-to-volume ratio. Functionalization of fabrics carried out with hosting cavities dispersed in a polymeric 3D matrix (either silane based), for controlled release of active molecule (either anti-oxidant, anti-microbial, drug, etc.) by stimuli towards skin can be classified according to the final aim of the product (Figure 3): many works describe the release of antimicrobial agents either from conventional fibres or nanofibres, which can be used for wound dressing [17,18] or vascular implants [19]. Microfibre and nanofibers offer ease of conformability to the actual wound shape and provide better coverage of the site of application [20] while vascular implants, frequently subjected to graft infection, can be loaded with antibiotics [21] to reduce cardiovascular surgical complications. Even sutures can be used for simultaneous wound healing and drug delivery, as recently reviewed by Blessy et. al [22]: sutures have been loaded with a variety of drugs, such as antimicrobials (synthetic or natural extracts), therapeutic protein and transcription factors or even stem cells. In our work [23], triclosan was used for functionalization of cotton for biomedical applications: it was complexed in β-cyclodextrin cavity, which was permanently grafted on cotton fibres. It was proved that preloading triclosan in β-cyclodextrin and subsequently grafting onto the fibre was much more effective than post-loading triclosan after β-cyclodextrin grafting, probably because of lower accessibility of the β-cyclodextrin cavity when it is grafted onto the fibre surface.

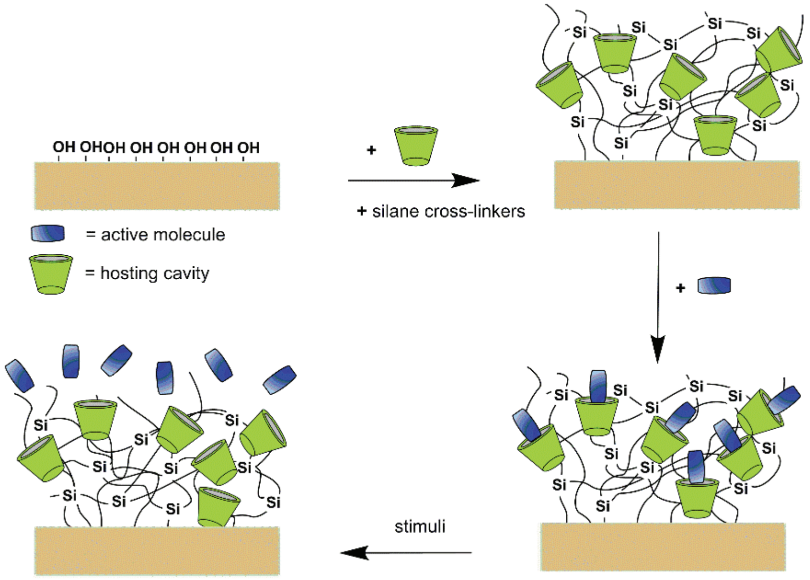

FIGURE 3. Application of active molecules on functionalized cotton surface and their controlled release from the functional hosting coated cotton by stimuli effect.

Use of textile substrates for topical delivery of cosmetic [24,25] or therapeutic agents for the treatment of skin diseases or localized inflammation and pain [26] has been reported in the literature. The majority of applications of cosmeto-textiles considers the delivery of vitamins and other antioxidant agents to the skin [27,28]. In our work [29], menthol-PCL micro- and nano-particles were produced and dispersed on a polyamide fabric with the aim of providing a refreshing effect to compressive socks, widely used by patients affected by chronic venous insufficiency. Patch tests on ten volunteers demonstrated effectiveness of menthol release without skin physiology alteration. In another work from our group [30], caffeine nanoparticles were produced by solvent displacement technique and used for functionalization of cotton, modal and micromodal single jersey fabric. Different release kinetics was observed depending on the type of fibre during Franz's cells in-vitro release tests. In general, it was observed that microfibres, with a greater surface-to volume ratio are more adapt for being used as substrate from drug delivery. The role of the textile substrate on drug release has been so far neglected: for instance, even though the type of weaving or knitting pattern alters surface topography and number of fabric-to-skin contact points, few works have been dedicated to understanding how fabric structure determines drug loading and, most importantly, drug release. Li et al. [31] demonstrated that honeycomb knitting pattern is capable of hosting more microparticles, increasing drug loading on the bio-functional fabric.

Several works have been published on the use of functional textiles for transdermal delivery [32,33], namely systems characterized by the drug reaching systemic circulation rather than being localized in the epidermis and dermis. In this case, the carrier formulation is more complex as the drug must cross the lipophilic barrier of the stratum corneum and the hydrophilic layers of the deeper tissues to reach blood circulation. Our group worked for transdermal release of melatonin from a textile substrate [34] with the aim of supplementing melatonin to the body gradually during use. Drug inclusion in electrospun nanofibres is an interesting trend of the recent years and a relevant number of research papers and perspective applications of functionalized nanofibres as drug delivery systems have been reviewed by Thekkar et al [35] in 2017. An interesting combination of electrospinning and cyclodextrin-based inclusion complex has been proposed by Celebioglu A. and Uyar T. [36]. Different electrospinning setups allow different drug distribution in the nanofibre, with core-shell arrangement being obtained by coaxial electrospinning, which has gained popularity because it reduces the unwanted initial burst effect and protects the therapeutic substance from external agent degradation.

Releasing active agents towards the environment is typical of protective textiles, for instance those acting as barrier against mosquitoes, ticks or other pathogens-hosting insects. As mosquitoes are still the most relevant route for transmission of infectious disease (malaria being the most widespread one with 445.000 death registered in 2016 [37]), any system providing cost-effective protection against insect bites is welcomed. Several authors have reported about development of mosquitoes-repellent textiles [38,39,40], especially concentrating their efforts for long-lasting effect, wash durability and controlled release. To achieve these goals, encapsulation of insect repellent agents is the most straightforward method. Sibanda et al. [38] developed a core-sheath bicomponent fibre prepared by melt-spinning of poly(ethylene-co-vinyl acetate) (EVA) as core and high density polyethylene (HDPE) as sheath. Before extrusion, EVA pellets were impregnated by N,N-Diethyl-m-toluamide (DEET) by a simple absorption process to a content up to 40% by weight. Pure liquid DEET, which is still the most successful insect repellent and gold standard, was heated to 80°C to facilitate EVA swelling and DEET absorption. Foot-in-cage test or arm-in-cage test, during which caged mosquitoes were offered dual-choice opportunity for feeding at treated/untreated body parts of human volunteers, demonstrated effectiveness of socks and gloves made of the extruded bicomponent fibres with durability up to 33 weeks or 20 cold washes.

For natural fibres, such as cotton and wool, which are not melt- or solution-extruded, different strategies have been proposed to add durable insect-repellent functionality: Teli et al [39] synthesized a new azo-dye by adding an amino group to DEET and coupling DEET-NH2 with naphtols in a diazotization process. By modifying DEET, the authors were able to simultaneously dye and add two functionalities (i.e. insect repellency and antibacterial activity) to cotton in one single process, with durable results. Other methods include microencapsulation of DEET in polymer shells and subsequent surface treatment of fabrics: in this regard, complex coacervation is a well-established technique based on emulsification of a hydrophobic substance with two oppositely charged polymers that complex and deposit on the surface of emulsions droplets. A variety of shells has been considered for encapsulating hydrophobic insect repellents: Place et al. [40] used bovine serum albumine (BSA) and the antimicrobial polymer PHMB for shell formation and DEET encapsulation, Abdul Aziz et al. [41] relied on the chitosan-gelatin complex formation for encapsulation of citronella oil. Generally, microcapsule shells have poor mechanical properties unless a crosslinking agent is used to permanently reinforce and stiffen the shell structure by chemically bonding the two oppositely charged polymers. Although no much appreciated by the scientific community and by the textile industry because it can release formaldehyde, gluteraldehyde is still one of the most used crosslinker [42]. As generally microcapsule emulsion is applied on the fabric by padding, the shell must have decent mechanical properties to stand the process without damage. However, durability of the treatment is poor and microcapsules are easily removed by washing if weak interactions occur between the microcapsule and the fabric.

To increase durability, microcapsules can be applied on the fabric by means of a binding resin [43]. In our work, DEET was encapsulated in β-cyclodextrin nanosponge network and applied permanently on the fabric in pad-dry-cure method by using an acrylic resin.

CONCLUSION

The goal of this paper was to focus on recent advances in the field of smart textiles and pay particular attention to the materials and their manufacturing process. Each technique shows advantages and disadvantages and the aim of this study was to improve the overall usability of smart clothing products by reviewing all developments, which have been done in this field in order to straighten the path for future investigations and researches in this field.

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