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Intelligent Textiles and Clothing for Ballistic and NBC Protection

Technology at the Cutting Edge

edited by

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Preface

This Advanced Study Institute was organized to fill the need to bring together experts from several parts of the world to make a critical assessment of existing knowledge in the area of defense-related textiles and clothing for ballistic and NBC-protection and to identify the needs for future research into these materials and products.

The Advanced Study Institute brought together eminent scientists and engineers and gave young researchers the opportunity to closely interact with the invited experts. A remarkable fact was the rather high participation of industry in the ASI. It is indicative of the interest in this fast developing field, expected to lead to interesting collaborative research opportunities.

This book contains the papers of the most important speakers at the ASI. As can be seen, the variety of themes is interesting. It also shows the multidisciplinary nature of the ASI and areas in which future research will be performed. Protective clothing has appearance and performance characteristics which sharply contrast with those of about 10 years ago. For the next 10 years, cutting edge research will lead to even more changes that hardly anybody is able to foresee today. That change will be the result of the accelerated introduction of smart (electronic) technology in textiles and clothing, the application of nanotechnology including electrospinning and biotechnology, and the use of sophisticated testing by applying (physiological) mannequins and advanced modelling.

As co-directors, we would like to express our sincere thanks and appreciation to all who contributed to the success of the ASI: to NATO for the generous grant, to the fellow members of the organizing committee, viz., Prof. H.A.M. Daanen (TNO, the Netherlands), Dr. T. McLellan (Defense R&D, Canada) and Dr. S. Ramkumar (Texas Tech University, USA). Many thanks goes to Mrs Els Van der Burght (Ghent University, Department of Textiles) for the general logistics of the whole ASI and to Mrs Noëlla Van Reepingen, the wife of Prof. Kiekens (co-director) for playing a magnificent role as a host lady contributing to the overall friendly and enjoyable atmosphere of the ASI.

The organizers are very proud of having had the chance to welcome several distinguished guests during the opening session on Tuesday, April 6. The Ministry of Science and Education and the Ministry of Defense of Croatia were present. The Universities of Zagreb and Split sent their highest delegates. Also, the city of Split and Split-Dalmatian County sent their Excellencies. A word of thanks is expressed for the presence of Prof. Darko Ujevic, Dean (University of Zagreb) and to Prof. Paul Van Cauwenberge, Rector (Ghent University, Belgium) who opened the ASI. Thanks to many others who contributed, but who are not mentioned here.

Last but not least, we have to thank Prof. S. Jayaraman (Georgia Institute of Technology, USA) for preparing this book for publication.

Ghent University, Belgium Paul Kiekens
EMPA, St. Gallen, Switzerland René M. Rossi
University of Zagreb, Croatia Ana Marija Grancaric

Contents

Introduction

Technology is the key to combating terrorism and protecting ordinary citizens, first responders and soldiers from danger. The area of *intelligent* or *smart* textiles is an emerging discipline that is rapidly transforming defense-related textiles and clothing for ballistic and NBC protection. This book presents the fundamentals of defense-related protective clothing and addresses technology at the cutting edge in this field.

Park and Jayaraman lay the foundation for the engineering design of intelligent protective textiles and clothing. They define an intelligent individual protection system and illustrate the use of the structured methodology for designing a mass incident garment for chem-bio protection. They highlight the need for a transdisciplinary approach to the field of intelligent individual protection to realize the ultimate objective of cost-effective protection *anytime*, *anywhere* for *anyone*.

Lobnik presents a detailed analysis of one of the key building blocks for intelligent protection systems, viz., optical chemical sensors. These sensors can be embedded into textile structures by using conventional dyeing, printing processes and coatings, while fiber-optic chemical sensors and nanofiber sensors can be incorporated by weaving, knitting or laminating.

Freney and Renaud trace the emergence of biological warfare to historic times and discuss the role of textiles as potential vectors of infections in hospitals or communities. They describe the major characteristics of antimicrobial textiles and their role in protecting individuals from both involuntary infections that occur in hospitals and communities, and voluntary infections due to terrorist attacks.

Rossi and Psikuta present the complexity of assessing coupled heat and mass transfer in protective clothing since the layers of the system are a combination of fabric and air layers that constantly change with the movements of the wearer. The simulation of the human thermoregulatory mechanisms requires the combination of physical models representing the body (manikins) with physiological (mathematical) models. They discuss examples of advanced measurement methods to characterize the thermal properties of fabrics and garments.

McLellan and Daanen highlight the importance of sweat evaporation in promoting cooling and maintaining thermal homeostasis. Sweat evaporation is severely hampered in protective clothing and can lead to catastrophic consequences for the wearer.

They discuss several methods to reduce heat strain in protective clothing to enhance the safety and comfort for the wearer.

Langenhove et al., introduce the concept of smart textiles and explain how textile materials and structures can be used as sensors, actuators, communication devices, energy sources and storage tools, and even processors. They discuss the important role of smart textiles in thermoregulalation and present the details of a smart suit for rescue workers.

Maillet et al., present the need for protecting soldiers from ballistic and CBRNE threats. Currently, ballistic, CBRNE and tactical jackets are three different components, developed separately and worn on top of each other. They discuss the accomplishments on the EPIDARM project whose goal is to provide optimum protection while reducing cost and weight of the system.

Grancaric et al., discuss the importance of protective clothing against radioactive contamination and the need to make such clothing reusable, especially for use on the space station. They discuss research aimed at modifying cotton fabrics with natural zeolite nanoparticles for imparting the ability to protect from radioactive contamination.

Sata and Ramkumar discuss the importance of individual protection of warfighters, first responders and civilians to meet the current threat of toxic chemicals and chemical warfare (CW) agents. They discuss decontamination technologies such as adsorptive carbon and enzymes and other recent developments in the field. They highlight the importance of decontamination technologies as a countermeasures strategy for sustaining the operational capability of warfighters.

Turaga et al., provide an overview of the applications of nanomaterials such as nanofibers and nanoparticles in military and industrial sectors including the latest developments in the field. They highlight the need for research that focuses on functionalized stand-alone nanofiber webs and stress the importance of investigating the toxic and lethal effects of nanoparticles-based materials before bringing them into the defense arena.

Thus, the various chapters in the book complement each other and address the broad spectrum of defense-related protective textiles and clothing.

Sundaresan Jayaraman

Chapter 1
The Engineering Design of Intelligent Protective Textiles and Clothing

Sungmee Park and Sundaresan Jayaraman

Abstract Terrorism has been on the rise in the past decade and continues to disrupt everyday life in many parts of the world. Protection against such threats is therefore critical for preserving peace and security around the world. In particular, the safety of defense personnel engaged in confronting and responding to such threats must be ensured. Since textiles and clothing are pervasive and are always "on" the soldier, they can serve as an excellent infrastructure or platform for such individual protection systems.

In this chapter, we present an engineering design framework for the design and development of intelligent protective textile structures and clothing. We begin with an analysis of the various types of threats against which individuals must be protected. Using this taxonomy of threats, we develop a set of performance requirements – ranging from protection against the various threats to the comfort of the active user – for such textiles and clothing. We then discuss the translation of these requirements into the realization of structures through the optimal selection of materials, manufacturing and sensing technologies. We conclude the chapter by presenting the need for a transdisciplinary approach to the field of intelligent individual protection to realize the ultimate objective of cost-effective protection *anytime*, *anywhere* for *anyone*.

Keywords Engineering design framework • Intelligent individual protection system • Wearable motherboard • Smart textiles • Terrorism

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1.1 Introduction

Terrorism has been on the rise in the past decade and continues to disrupt everyday life in many parts of the world. Indeed, it has so dramatically altered people's perceptions that it is no longer thought of as an "if" but as a "when" and "where" the next terrorist act would occur. Consequently, the quality of life of individuals has been significantly transformed and a new *normal* has emerged in society. The answer to "how to protect" individuals – common citizens, first responders, law enforcement personnel and soldiers – lies in technology. The rapid advancements in technologies – materials, manufacturing, sensing, computing and communications – provide a rich array of solutions that can and should be harnessed to develop and deploy solutions to protect human life.

1.1.1 Risk Assessment: The Role of Ambient Intelligence

A detailed assessment of the risks from the various threats is the first essential step in the design and development of solutions. Unfortunately, casualties are associated with protection of citizens and preservation of national security – be they soldiers engaged in combat with the enemy or first responders saving the lives of innocent victims subjected to terrorist attacks. Consider a soldier in an urban warfare scene who is in constant communication with the remote command and control center. As shown in Fig. 1.1, the soldier must – in a very short period of time – go into "high-risk" environments about which there is no *a priori* knowledge, viz., the type of potential threat. Therefore, the second step is the detection and identification of the threat – explosive, chemical, biological, nuclear, etc. This should be carried out accurately and reliably. This analysis of the threat species must be thorough; it should result in a reliable diagnosis and the effective treatment of the individuals affected by the incident.

The next step is to contain the threat and limit its spread to minimize casualties. Then, the individuals (and the environment) must be decontaminated effectively

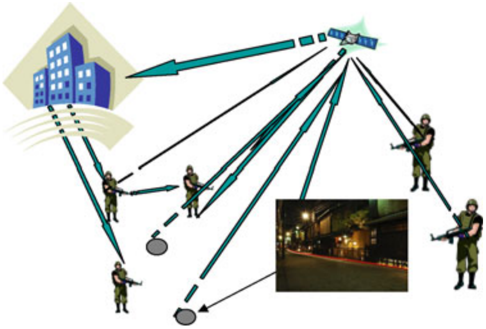


Fig. 1.1 An urban warfare environment: soldiers and first responders

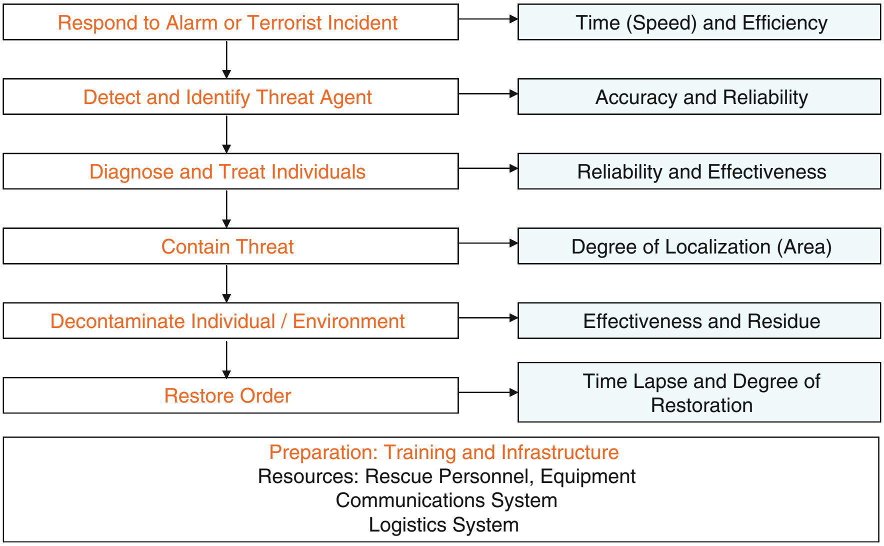


Fig. 1.2 A typical incident response scenario: events and metrics

and thoroughly with no residue on the individuals leaving the scene. The final step is to restore order (to the extent possible) in the incident response scenario. A successful response depends on the quality of preparation for such an event, i.e., availability of adequate resources including trained personnel, state-of-the-art equipment, a reliable and efficient communication system, and an effective logistics system in support of the operation. In Fig. 1.2, the sequence of steps is shown on the left with the corresponding performance metrics on the right [12].

Access to the information about the highly dynamic environment in a timely manner is important. This situational awareness or *ambient intelligence* is critical both for the soldier/first responder engaged in the hazardous operation and for the commanders who must *sense* and extract the information from the dynamic environment in real-time, *adapt* and *respond* appropriately to the potential threat; the response could include sending in reinforcement, asking the soldier/first responder to change course or return to the base, thereby minimizing their risk. For instance, if the soldier/first responder suddenly encounters hazardous gases, it is important to know the hazard type so that appropriate protection measures can be taken (e.g., using appropriate masks, respirators or administering antidotes) and to evacuate safely. In the event the soldier/first responder is shot, information about the individual's location, physical condition (e.g., heart rate and electrocardiogram) and location of the wound on the body will be critical in locating, reaching and attending to the soldier within the so-called "Golden Hour" to prevent a fatality [13]. Therefore, harnessing information intelligently and at the right time is critical to minimize the loss of human life.

The remainder of the chapter is organized as follows: In Sect. 1.2, the major types of threats are discussed and the concept of hazard vulnerability analysis is presented; in Sect. 1.3, the framework for an intelligent individual protection system (IIPS) is developed; the methodology for the design and development of an IIPS is presented and illustrated with a specific example of an IIPS for chem-bio protection in Sect. 1.4. Specific examples of IIPS developed using the engineering design paradigm are presented in Sect. 1.5; the need for a transdisciplinary approach to advance the field of intelligent individual protection is presented in Sect. 1.6 along with a few concluding remarks.

1.2 Threats, Hazard Vulnerability Analysis and Protection

Table 1.1 shows a set of major terrorist incidents and the threat agents involved in those attacks in recent years. As stated earlier, the critical first step in the design and development of an IIPS is an understanding of the major types of threats and an assessment of the vulnerability of the system or individual to the threats or hazards, viz., hazard vulnerability analysis.

In addition to the three types of threats listed in Table 1.1, viz., conventional, biological and chemical, there is a fourth one, which is nuclear. Fortunately, nuclear incidents are rather difficult to perpetrate. We will now discuss the nature of each of these threats and their potential impact, and this is known as hazard vulnerability analysis.

Conventional Weapons are typically explosives that are launched as bombs. When such weapons are used, dust and shrapnel cause injuries to individuals as shown in Table 1.2. The damage can be detected almost immediately. The explosive

Table 1.1 Major terrorist incidents and threat agents

Date	Location	Type	Delivery method
March 2010	Moscow Subway System	Conventional (explosive)	Suicide Bombers
July 2006	Mumbai Commuter Trains	Conventional (explosive)	Planted Bombs
2006	Iraq	Chemical	Chlorine with Vehicle-borne Explosive
July 2005	London Underground	Conventional (explosive)	Planted Bombs
March 2004	Madrid Commuter Trains	Conventional (explosive)	Planted Bombs
September 2001	World Trade Center, New York	Conventional (missile)	Aircraft
2001	United States	Biological	Anthrax spores through mail
1995	Tokyo Subway System	Biological	Sarin Gas (GB) released through subway system
1984	Oregon, US	Biological	Salmonella contamination of salad bars at restaurants

Table 1.2 Characteristics of threats

	Conventional	Nuclear	Biological	Chemical
Launch mechanism	Explosive, missile (aircraft)	Radioactive bombs	Pathogens and toxins	Nerve, blister, blood, choking and incapacitating agents
Damage occurs through	Dust, Shrapnel	Breathing and skin exposure	Skin, breathing and ingestion	Skin, eye, ingestion and injection (Shrapnel)
Detection time	Immediate	Immediate	Immediate and/ or delayed	Immediate
Damage type	Structural	Radiation: alpha, beta and gamma rays	Diseases (smallpox, pneumonia)	Chemical
Ease of launching	Easy	Difficult	Medium	Medium
Risk duration	Short-term	Short- and long-term	Short- and long-term	Short- and long-term
Containment	Easy	Difficult	Difficult	Difficult
Potential targets	Buildings, HVAC systems, bridges, tunnels, mass transit, water distribution systems, public places (sports stadiums), etc.			

generally causes structural damage, which, in turn, leads to the collapse of the structure. It is relatively easy to launch a conventional weapons attack as was evident during the Oklahoma City bombing in 1995. The attacks on September 11, 2001 in New York were unique in that aircraft were used as weapons for the first time. The duration of the risk from the damage due to conventional weapons tends to be short-term. The containment of the threat is relatively easy since the threat area is generally localized.

Nuclear Weapons are radioactive bombs. Damage to individuals occurs through breathing and skin exposure to the dust contaminated with radioactive materials. Radiation in the form of alpha, beta and gamma rays can have both short- and long-term impact on the individuals and the environment. Since all the three forms of radiation are odorless and colorless, they can be detected only with radioactive detectors, but the detection itself can be immediate. The containment of the threat would also be difficult; however, it is difficult to launch a nuclear weapons attack since access to radioactive materials and weapons is not easy.

Biological Weapons are pathogens and toxins. The former are disease-causing organisms, some of which can reproduce and cause damage long after the attack. Pathogens can be bacteria such as anthrax, viruses such as smallpox and dengue fever, and microplasms that can cause pneumonia. Toxins are poisonous substances produced by living things; even small doses of toxins can cause large-scale damage to lives. Potential toxin weapons include ricin and botulism toxin. Toxins are also considered to be chemical weapons. Biological weapons cause damage through

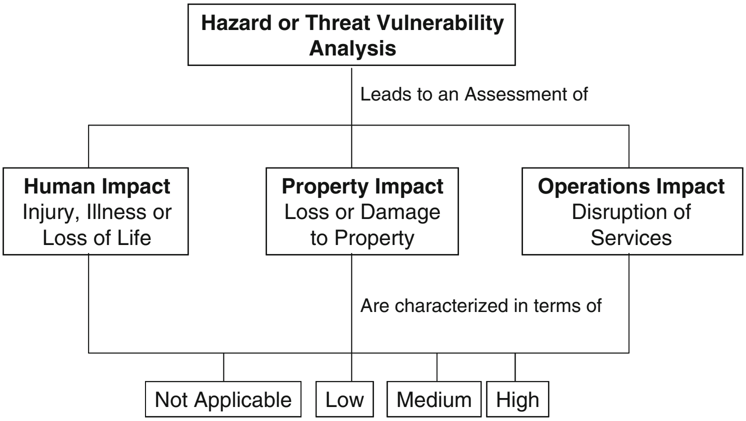


Fig. 1.3 A framework for hazard or threat vulnerability analysis

breathing, skin and ingestion and the reaction can be immediate and/or delayed depending on the nature of the weapon. Likewise, detection can be immediate and/or delayed. The duration of the risk is both short- and long-term as some of the pathogens can mutate and cause damage over time. However, launching a biological weapons attack is of medium difficulty because of restricted access to such materials. Containment of the threat would not be easy.

Chemical Weapons are chemical agents that can cause different types of damage depending on the particular agent. Nerve agents attack the individual's nervous system; blister agents attack the skin; blood agents attack the blood and impair its ability to hold and deliver oxygen; choking agents attack the lungs; and incapacitating agents irritate the mucous membranes, eyes, nose and mouth leading to the individual's incapacitation. These chemicals attack the individual through skin, eyes, ingestion and penetration or injection caused by shrapnel. The detection can be immediate; the duration of the risk from the chemical weapons attack can be both short- and long-term. It is easier to launch a chemical weapons attack than to launch a nuclear weapons attack. Since the likely method of delivery of chemical agents is in the form of gas, which can spread quickly and widely, containment of the threat due to a chemical weapons attack can be difficult.

Hazard or Threat Vulnerability Analysis: The next step in laying the foundation for the design of an IIPS is to carry out hazard vulnerability analysis or assessment of the potential impact of the hazard on humans, property, and operations or service. The hazard depends on the toxicity of the threat and the amount of exposure to it and is typically expressed as follows:

$$\text{Hazard} = \text{Toxicity} \times \text{Exposure}$$

Thus, a highly toxic threat can pose a significant hazard even if the exposure is short; likewise, prolonged exposure to a low-level threat can cause significant harm. As shown in Fig. 1.3, the human impact can be characterized in terms of injury, illness or loss of life; the property impact can be assessed in terms of damage to or loss of property; and operational impact can be determined in terms of disruption of services. The degree or extent of the impact can be characterized on a scale – Not applicable, Low, Moderate and High – as shown in the figure. The results of the analysis must provide the foundation for preparedness, which includes a protection system designed for that specific threat or group of threats.

Thus, an understanding of the nature of the threats along with the hazard vulnerability analysis provides the foundation for the design, development and deployment of protection systems in desired operating conditions. The protection must ideally encompass three facets: (1) advanced awareness and warning to help soldiers and responders better prepare for the dangers to be encountered; (2) personal protection and safety of personnel at the disaster scene; and (3) collective protection to minimize losses and contain the threat at the disaster scene. The focus of this chapter is on personal or individual protection and safety, which we will now explore.

1.3 An Intelligent Individual Protection System (IIPS)

An Intelligent Individual Protection System or IIPS must be *user-centric* and must provide *timely*, *efficient* and *comfortable protection* that is *effective* for the intended range of *threats* and *deployments* and is based on situational awareness or real-time assessment of the user's *condition*. This statement of purpose, much like the Institute of Medicine's statement of purpose for a healthcare system [2], must be treated as a "call to action" to design and deploy an IIPS that ensures cost-effective protection and safety *anytime*, *anywhere* for *anyone*. The statement also identifies the desired attributes of an IIPS that must be realized through design. Specifically, the IIPS must have the ability to *sense*, *feel, think*, *communicate* and *act* to protect the individual. It must enhance the individual's operational effectiveness through the seamless integration of form and function. It must build on a modular architecture and incorporate state-of-the-art technologies in sensing, materials, manufacturing, information processing and communications along with its own energy or power source. It must be intuitive and easy to use, upgradeable, and reconfigurable. While no "price" can be placed on the value that will be derived from the successful deployment of an IIPS (e.g., lives saved), it must nevertheless be affordable to facilitate its widespread use in the field. The IIPS must ultimately lead to better outcomes in the field in terms of fewer injuries and loss of lives.

The Driving Strategy: Users in hazardous environments such as defense personnel do not get the proverbial "second chance" and so, failure is not an option for the IIPS – it *cannot* fail. Failure could lead to loss of life, an undesirable outcome. Doing it right the first time calls for the adoption of the 'zero defects' paradigm, which should drive the realization of IIPS. It requires a structured approach in the design process and should result in flawless performance in the field. The soldier's uniform is always "on" the soldier and IIPS must be user-centric. Therefore, the uniform is the logical choice as the *infrastructure* or *platform* for IIPS.

1.3.1 The Lifecycle of an Intelligent Individual Protection System

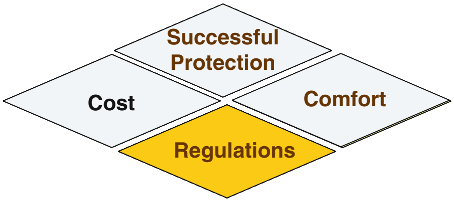
The ten-step process encompassing the lifecycle of an IIPS from concept to post-market surveillance is as follows:

1. Carry out in-depth hazard or threat vulnerability assessment
2. Define system performance requirements
3. Establish specifications and standards to meet performance requirements
4. Design robust system to meet specifications and standards – both industry and regulatory
5. Buy defect-free system components (e.g., materials, sensors, processors and devices)
6. Manufacture and build defect-free systems
7. Test and validate system performance
8. Verify conformity to specifications and standards
9. Facilitate deployment through training and system support
10. Conduct post-market surveillance to assess system performance in field

These steps can be viewed from three perspectives, viz., the end users, the manufacturers and the administrators responsible for procuring and supplying the IIPS to the end users. While successfully protecting the end user (soldier) is paramount from all three perspectives, comfort is an additional critical factor for the end user because an uncomfortable system, however efficacious, is not effective if it is not used. From the manufacturer's perspective, meeting the standards and cost are additional factors that must be considered in the design and delivery of IIPS; this cost includes the raw materials, manufacturing and logistics expenses associated with getting the product to the end user. And, from an administrator's perspective, end user acceptance and cost are important; in this case, the cost refers to the "total cost of ownership," which includes the product cost, the training cost, the maintenance cost and disposal cost. Thus, it is a delicate balancing act to match successful protection or degree of risk with cost, comfort and regulatory requirements as shown in Fig. 1.4.

Risk-Based Design of Protection Systems: An excellent example of this type of risk assessment leading to the definition of a tiered protection system can be found in the U.S. Environmental Protection Agency's (EPA) chemical protective ensemble. The EPA has defined four levels of protection (Levels A, B, C and D) for these ensembles based on an assessment of the impact of the threat in terms of the following factors: volume, composition and toxicity of the threat agent, the duration of exposure, and the physical environment [8]. Level A provides the highest degree of

Fig. 1.4 Design of an IIPS: a delicate balancing act



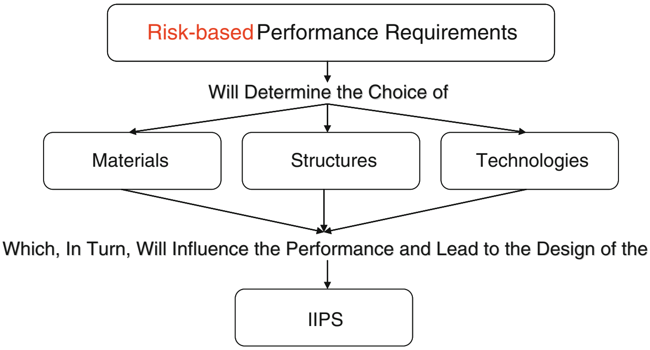


Fig. 1.5 The IIPS design engineer's toolkit

respiratory, skin, eye and mucous membrane protection from solid, liquid and gaseous chemicals, and is defined as a "totally encapsulating, single-piece chemically-resistant ensemble with gas-tight closures and interfaces between pants and boots, and sleeves and gloves." Level B provides the highest level of respiratory protection (same as Level A), but a lower level of skin and eye protection while Level C provides a diminished level of respiratory protection along with Level B degree of skin protection. Finally, Level D provides no respiratory protection and only minimal skin protection.

Thus the challenge in successfully realizing and deploying IIPS lies in balancing risk, performance, comfort and cost; herein lie the opportunities too. The engineer's toolkit for designing the system is shown in Fig. 1.5. The degree of risk will drive the performance requirements or specifications, which, in turn, will determine the choice of materials, structures and technologies, among others; and these parameters must be optimally balanced to realize the desired performance of IIPS in the field.

The Twin Catalysts: Innovation is at the heart of the realization of an IIPS and is also the catalyst that can trigger its development. As shown in Fig. 1.6, innovation is driven by inspiration and is born out of the necessity to devise an original solution that is valuable, novel, timely and outstanding, among others. Innovation is therefore critical for the realization of IIPS since it involves exploring hitherto unchartered territories and breaking new ground, especially given the complexities of the

Fig. 1.6 The characteristics of innovation

Inspiration
Necessity
Neat
Original
Valuable
Applicable
Timely
Intelligence
Outstanding
Novel

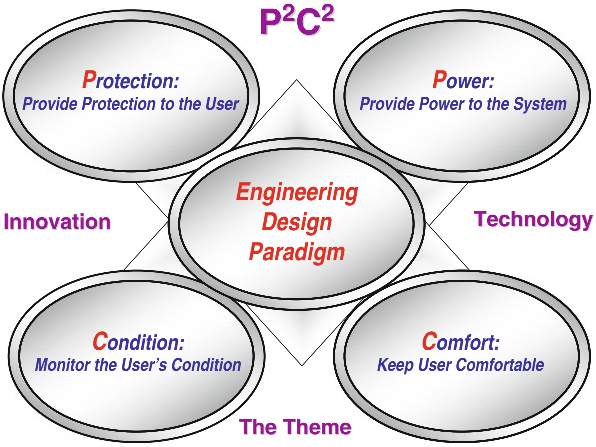


Fig. 1.7 The IIPS conceptual framework and the engineering design paradigm

requirements of such a system. A systems approach that incorporates the "soldier as a system" paradigm is the other key catalyst for the realization of IIPS. Such an integrative approach leads to the *science* of the engineering design of intelligent protective textiles and clothing.

1.3.2 The Key Facets of an Intelligent Individual Protection System

Figure 1.7 captures the thematic framework for an IIPS defined by the statement of purpose presented earlier in which Protection, Power, Condition and Comfort are shown as "P^2C^2" and innovation and technology are brought together through the adoption of the engineering design paradigm to realize IIPS. We will now discuss each of these facets in-depth.

Provide Protection to the User: The objective is to provide protection from the threat to the user and to minimize the time of exposure to the threat since the user (say, first responder) is required to be present in the threat zone The first step in protecting the user is to identify, locate and track the individual throughout the deployment zone. The protection must be designed based on the type of threat and potential modes or avenues of damage to the user. As mentioned earlier, the types of threats include conventional, nuclear, radiological, biological and chemical weapons. The routes of damage to the user include dermal, respiratory, ocular, ingestion and injection [12]. The class of personnel for which the IIPS is intended viz., first responders, soldiers, industrial workers and public safety personnel must be considered in its design since the specifications will vary with the profession.

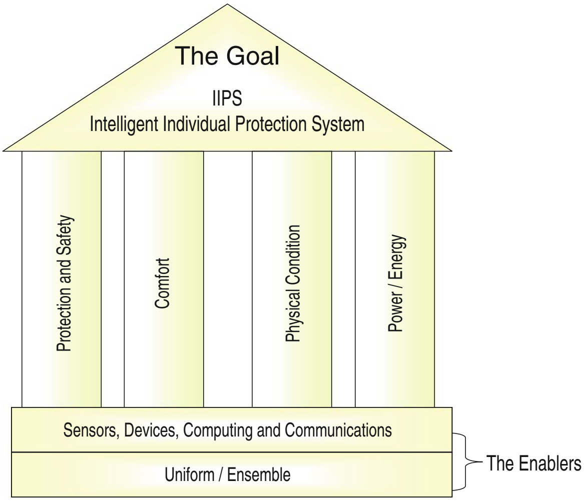
Monitor the User's Condition: The IIPS must monitor the physical condition of the user during deployment so that necessary remedial actions may be taken to keep the individual safe. These include monitoring the physiological parameters (e.g., heart rate, respiration rate, electrocardiogram, temperature, and blood oxygen content), the level of hydration and the degree of heat stress (due to the ambient conditions and/or the worn ensemble). In addition, the user's posture must be monitored to detect any abrupt changes, which might, but not in all cases, signal sudden falls due to getting hurt. Finally, if the user is physically hurt by penetration from shrapnel, bullets, etc., it must be detected. All the monitored parameters must be transmitted to a remote location so that appropriate action can be taken to ensure the safety of the user including providing medical care if needed.

Keep User Comfortable: The typical load carried by a combat soldier ranges from 35 to 45 kg. This load can result in a great deal of discomfort for the solider leading to fatigue, which is magnified with rough terrain and bad weather. Ultimately, it has the potential to impact the soldier's combat effectiveness. Therefore, one of the key goals articulated in the statement of purpose presented earlier is to keep the user comfortable. This can be accomplished by reducing the load carried by the user, mitigating the effects of extreme weather conditions by reducing heat exhaustion through hydration and proper ventilation, reducing hypothermia by keeping the user warm, and ensuring that the ensemble fits the user properly and size discrepancies are minimized or eliminated.

Provide Power to the System: The IIPS requires the incorporation of a plethora of sensors, communications and computing devices to realize its primary objective of serving as an intelligent protection system for the individual. These devices require power or energy to run and this power source must be portable and be an integrated part of the IIPS.

Thus, by adopting the paradigm of engineering design, the desired IIPS can be built by integrating state-of-the-art technologies in materials, manufacturing, sensing, computing and communications. As shown in Fig. 1.8, the uniform or ensemble serves as the foundation in which the sensors, devices, computing and communications technologies are built as enablers. The four pillars that signify the functionality of IIPS, viz., protection and safety, comfort, physical condition of the user, and

Fig. 1.8 The IIPS house



power to the system are shown in the figure. We will now discuss the design and development of an IIPS using the engineering design paradigm.

1.4 Design and Development of an IIPS: Application of the Engineering Design Paradigm

The major steps in the adoption of the engineering design paradigm for an IIPS are shown in Table 1.3.

These steps are an amplification of the ten-step process associated with the IIPS lifecycle presented earlier. The overall objective is to translate the "what" or requirements of a product to a "how" through a judicious selection of materials and fabrication technologies and applying the design parameters so that the resulting product meets the desired needs. This paradigm is represented in Fig. 1.9.

The underlying methodology is known as the "Design for X" or DFX methodology. We will now present the key concepts behind this engineering design methodology.

1.4.1 The DFX (or Design for X) Methodology

The DFX (*Design for X*) methodology is a structured engineering design approach to realizing the desired performance capabilities in a final product. In DFX, *X* represents the specific design or performance criterion as shown in Fig. 1.10. For instance, *X* can represent functionality, usability, manufacturability, maintainability,

Table 1.3 The key steps in the engineering design process

The activity	The significance
Understand the needs	What needs to be done (the goal)
Prioritize the needs	How important are the needs (scale 1–5 or % weight)
Map needs to measurable parameters	Define the metrics of performance
Assess the competition	What else is available (benchmarking)
Define the specifications	The goal or target values or specifications to be met
Realize the design	The how: make it happen through materials, technologies and manufacturing methods
Test, evaluate and refine the design	Iterative process to arrive at the final product

Fig. 1.9 From what to how: translating performance requirements into the real product

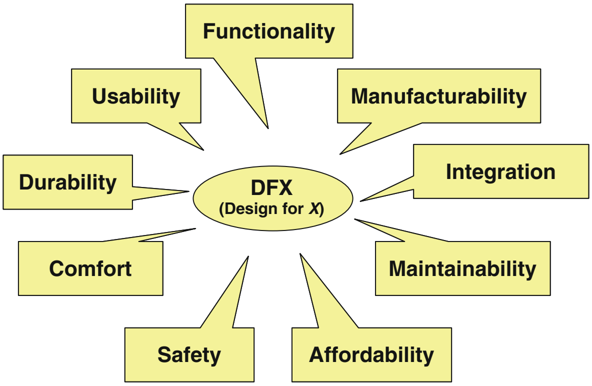


Fig. 1.10 The design for X (DFX) methodology for IIPS

safety, affordability, durability, and comfort, among others. Let's consider the MIGZ3® from Lion Apparel,[1] which is a "mass incident garment for law enforcement that provides chem-bio protection and mobility in perimeter control scenarios and counter-terrorism at high profile events" [6]. *Design for Functionality* would be the primary objective and in this case, the primary function of the system is to protect against the threats that are likely to be encountered at high profile events, viz.., chemical and biological.

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[1] The MIGZ3 is being used as a real-world product to illustrate the engineering design methodology for IIPS; the authors were not involved in the design of the MIGZ3.

From the viewpoint of *Design for Usability*, the system should be designed such that it does not impede the mobility or the effectiveness of the user in such perimeter-control situations; the ease-of-use of the system should promote compliance, which is critical for protecting the user because, in practice, a system that is difficult to use is more than likely not used. The *Design for Comfort* should similarly address factors such as breathability, weight, dimensional stability, and range of motion – factors that affect the comfort of the user in such high stress situations as protecting high profile targets. In exploring the *Design for Durability* or *Deployment* facet, factors related to the service life of the system, the frequency of usage, the training required for using the system, and storage between uses must be addressed.

As mentioned earlier, the user will not get the proverbial “second chance” and so, the *Design for Safety* facet is absolutely critical; the FMEA (failure modes and effects analysis) methodology should be adopted to anticipate the potential modes of failure and identify appropriate countermeasures that must be incorporated into the design. Finally, in *Design for Integration*, the various components that comprise the system must be designed to ensure seamless integration across the components and should address factors such as leakage at the interfaces, interoperability and modularity (to facilitate easy replacement of damaged components or upgrading of obsolete components). Thus, DFX is an effective paradigm for analyzing and utilizing the desired performance requirements to design and create the final product.

1.4.2 Application of the Engineering Design Methodology: Creating the IIPS for Chem-Bio Protection

As stated earlier, the purpose of the MIGZ3 is to provide chem-bio protection for law enforcement personnel at high profile events. We will now apply the DFX methodology to arrive at the final product specifications.

Ranking of Needs and Establishment of Metrics: As shown in Table 1.3, the next step in the design process is to prioritize or rank the needs specified by the end user. Such prioritization will guide the designer in channeling the scarce resources on features that are ranked high and valued by the user and so, *must* be included in the product. Following prioritization, the metrics of performance desired in the product are established. Metrics are typically “objective” measures associated with various characteristics of the product that can be measured in the laboratory. They can also be used for competitive benchmarking with other products and technologies.

The *needs-metrics* matrix relates the product *needs* with the corresponding *metrics*. The matrix associated with chemical protection needs for MIGZ3® is shown in Table 1.4. For each challenge chemical, the associated target value is established; for instance, the permeation for Acrolein should be less than 6 $\mu g/cm^2$ based on an hour of cumulative assessment; this means the proposed design should offer at least this level of protection against Acrolein. The value is also known as the target specification.

Table 1.4 Needs-metrics for chemical protection: barrier chemical permeation performance as per NFPA 1994, class 3 requirements

Need	Metric (target value)
Protect against challenge chemical	Requirement (based on 60 min cumulative results) (μg/cm^2)
Acrolein	<6.0
Acrylonitrile	<6.0
Ammonia	<6.0
Chlorine	<6.0
Dimethyl sulfate	<6.0
Mustard (HD)	<4.0
Soman (GD)	<1.25

Source: http://www.lionapparel.com/pdf/Lion_MIGZ3.pdf

Table 1.5 Materials selection for chemical protection: barrier chemical permeation performance as per NFPA 1994, class 3 requirements

Need	Metric (target value)	Material choice with associated performance
Protect against challenge chemical	Requirement (based on 60 min cumulative results) (μg/cm^2)	Gore® Chempak® selectively permeable fabric (μg/cm^2)
Acrolein	<6.0	<1.0
Acrylonitrile	<6.0	<1.0
Ammonia	<6.0	<1.0
Chlorine	<6.0	<1.0
Dimethyl sulfate	<6.0	<1.0
Mustard (HD)	<4.0	<0.5
Soman (GD)	<1.25	<0.5

Source: http://www.lionapparel.com/pdf/Lion_MIGZ3.pdf

Materials Selection: Now that the "what" has been established in the form of needs and corresponding performance metrics, the next step is to determine "how" the needs and metrics can be realized through the selection of materials and manufacturing technologies. Typically, no material is impervious to breakdown caused by chemicals nor is any material resistant to all chemicals. So, the material properties that are important for barrier protection must be specified. Using these properties, appropriate candidate materials can be identified and compared to select the best one that meets the requirements. In the present example, the properties related to barrier protection are permeation rate and breakthrough time. Permeation rate is defined as the rate at which the chemical moves through the material while breakthrough time is defined as the time taken to completely permeate through the materials. This type of a structured analysis must have led the designers to the choice of Gore Chempack® selectively permeable material for MIGZ3 shown in Table 1.5. For each of the chemicals, the penetration amount is significantly less than the allowable limit or target specification shown earlier in Table 1.4.

Table 1.6 Materials selection: barrier physical property performance as per NFPA 1994, class 3 requirements

Need	Metric (target value)	Material choice with associated performance
Material performance	Requirement	Gore® Chempak® selectively permeable fabric
Weight	Lightweight	250 gm/m^2
Ball burst strength	135 N	905 N
Puncture propagation tear	25 N	53 N in machine direction 43 N in transverse direction
Total heat loss	>200 W/m^2	>400 W/m^2
Dimensional stability	High	−1.5% in machine direction −1.0% in transverse direction

Source: http://www.lionapparel.com/pdf/Lion_MIGZ3.pdf

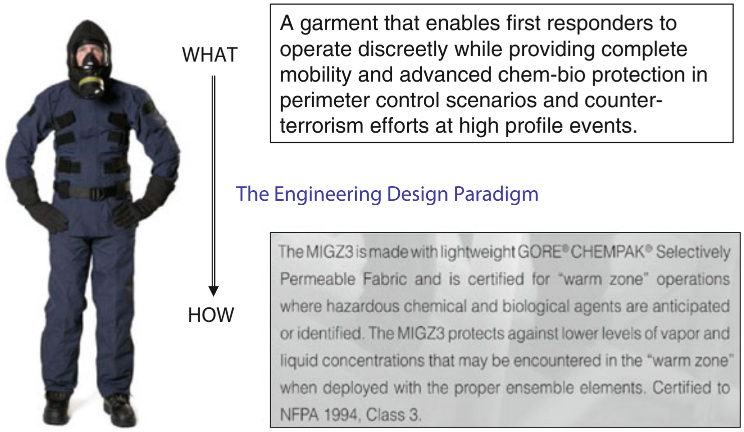
Table 1.7 The product specifications for MIGZ3®

Certification	NFPA 1994, class 3
Zone	Warm
Systemic physiological protective dosage factor (PPDF$_{sys}$)	4087 PPDF$_{sys}$ (average)
Garment design	Two-piece coat and pant
Respiratory system	Many options to choose from
Hand protection system	GORE™ G9492 glove system with GORE™ CHEMPAK® Ultra Barrier Fabric worn under Nomex® Outer Glove
Foot protection system	Lion chem.-bio sock with GORE™ CHEMPAK® selectively permeable fabric; leather lace-up tactical boot
Barrier technology	CHEMPAK® selectively permeable fabric
Storage life	Up to 10 years
Multi-use	Yes, if not damaged, exposed or contaminated
Training suit available	Yes

Source: http://www.lionapparel.com/pdf/Lion_MIGZ3.pdf

In a similar manner, Table 1.6 shows the needs-metrics matrix along with the material selected for meeting the physical barrier performance of MIGZ3.

The Final Production Specifications: By addressing each of the facets in Figs. 1.9 and 1.10, the final production specification is developed. Table 1.7 summarizes the specifications for the MIGZ3 ensemble shown in Fig. 1.11. One of the key factors in the successful deployment of IIPS is end-user training. As shown in the table, a training suit is made available for prospective users to learn to use the system. Thus, the MIGZ3 garment serves as an excellent example for exploring the successful application of the engineering design paradigm for the realization of an IIPS, i.e., the transition from "what" to "how."



A garment that enables first responders to operate discreetly while providing complete mobility and advanced chem-bio protection in perimeter control scenarios and counter-terrorism efforts at high profile events.

The MIGZ3 is made with lightweight GORE® CHEMPAK® Selectively Permeable Fabric and is certified for "warm zone" operations where hazardous chemical and biological agents are anticipated or identified. The MIGZ3 protects against lower levels of vapor and liquid concentrations that may be encountered in the "warm zone" when deployed with the proper ensemble elements. Certified to NFPA 1994, Class 3.

Fig. 1.11 The MIGZ3 – the mass incident CBRN garment (Source: http://www.lionprotects.com/law-enforcement-migz3-mass-incident-garment)

The success of IIPS in the field depends on its efficacy in protecting the user and the ease of deployment, which includes the ease of training and use. While no value can be put on the life of an individual saved from a threat, the cost of the product is an important factor in the successful acquisition and subsequent deployment of the technology. The proposed engineering design methodology provides an objective approach not only for realizing the desired performance of the product, but also for allocating and controlling costs that will impact its total cost of ownership.

1.5 Advancements in Intelligent Individual Protection Systems

We will now discuss the key advancements in IIPS utilizing the building block approach represented in Fig. 1.7. Depending on the need, these building blocks are integrated and engineered into successful intelligent individual protection systems.

1.5.1 The Protection, Condition and Comfort Building Blocks: The Wearable Motherboard

One of the early attempts to develop an IIPS was the research carried out at Georgia Tech (funded by DARPA through the US Department of the Navy) which led to the realization of the world's first Wearable Motherboard™ or the Smart Shirt [14]. The engineering design paradigm presented earlier was used to design and develop the Smart Shirt based on the user requirements (performance characteristics) shown in Table 1.8. The details of the framework can be found elsewhere [16].

Table 1.8 The wearable motherboard: user requirements analysis

Functionality	• Act as a Flexible Motherboard • Domain-specific: sensing, monitoring and processing capabilities dictated by the intended end-use
Usability	• Privacy • Security • Electrostatic charge decay • Resistance to EMI (electro-magnetic interference) • Hazard protection • Flame and directed energy retardant • Physiological thermal protection
Durability	• Flexural endurance • Mechanical strength ◦ Tear ◦ Tensile/shear ◦ Burst • Abrasion resistance • Corrosion resistance • Heat resistance • Electrical resistance
Shape conformability (dimensional stability)	• Conform to desired product shape • Dimensional stability during repeated use
Maintainability	• Ease of care • Ease of mending • Ease of diagnosing problems • Launderability
Manufacturability	• Ease of fabrication • Compatible with standard manufacturing machinery
Connectivity	• Sensors • Processors (computing, wireless communication) • Monitors and equipment • Power source (battery charging/changing) • Other *i*-Textile modules
Affordability	• Material cost • Manufacturing cost • Maintenance cost

Several versions of the Smart Shirt have been produced and with each succeeding version, the system was continually enhanced from all perspectives – functionality, capabilities, comfort, ease of use and aesthetics. This IIPS addresses the facets of Protection, Condition and Comfort shown in Fig. 1.7. Specifically, it detects the penetration of a projectile (e.g., bullets, shrapnel) and, for the first time, a very systematic and comfortable way of monitoring the vital signs of soldiers in an *unobtrusive* manner [3].

The Smart Shirt uses optical fibers to detect bullet wounds, and special sensors and interconnects to monitor the body vital signs (heart rate, respiration rate,

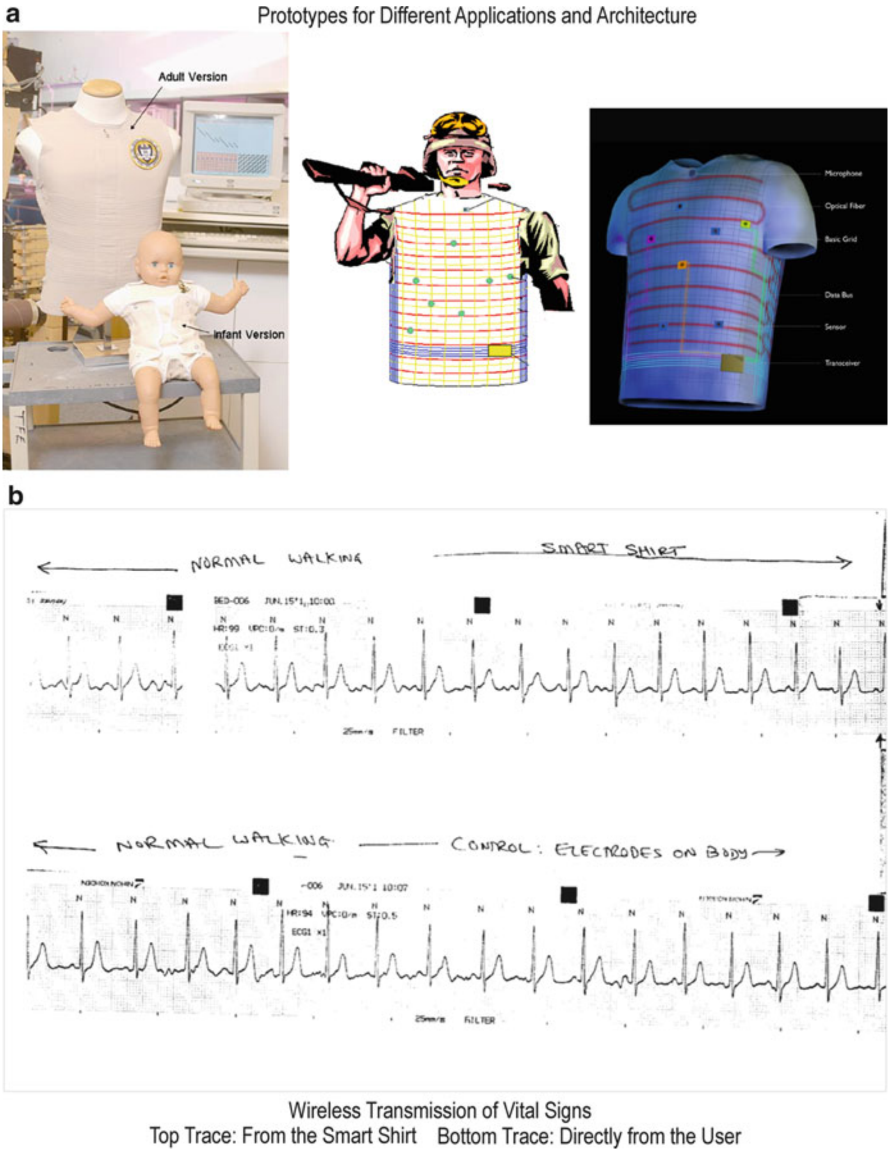


Fig. 1.12 The wearable motherboard or smart shirt

electrocardiogram, body temperature and pulse oxymetry or SpO_2) during combat conditions (see Fig. 1.12). Just as special purpose chips and processors can be plugged into a computer motherboard to obtain the desired information processing capability, the Smart Shirt provides an extremely versatile framework for the incorporation of sensing, monitoring and information processing devices. The sensors can be positioned in desired locations on the body and plug into the Smart Shirt. The flexible data *bus* integrated into the structure transmits the information from the suite of sensors to the multifunction processor known as the Smart Shirt controller or transceiver. This controller, in turn, processes the signals and transmits them wirelessly (using an appropriate communication protocol such as Bluetooth, 802.11b) to desired locations (e.g., battlefield triage station, field hospital). The *bus* also serves to transmit information *to* the sensors (and hence, the wearer) from external sources, thus making the Smart Shirt a valuable information infrastructure [9–11].

The motherboard or "plug and play" concept means other sensors can be easily integrated into the structure. For instance, a sensor to detect oxygen levels or hazardous gases can be integrated into a variation of the Smart Shirt for first responders. This information along with the vital signs can be transmitted to the incident command center where personnel can continuously monitor the first responder's condition and provide appropriate instructions including ordering evacuation, if necessary.

Thus, the Smart Shirt serves as yet another example of the realization of an IIPS using the engineering design paradigm.

1.5.2 The Comfort Building Block: Printed Electronics

History has shown repeatedly that cold weather can have a significant impact on the performance and welfare of soldiers in combat. For instance, the Chinese 26th Army recorded a casualty rate of over 90% from frostbite in the fall of 1950 in Korea [7]. In another study, the characteristics of cold weather combat – defined as combat in temperatures of −20°F and below with heavy accumulation of snow – were compared to combat in a chemical environment [1]. It addressed the role of fatigue, clothing, equipment maintenance, mobility and the time taken to complete specific tasks in cold weather conditions. It concluded that, "like the chemical environment, the cold-weather environment itself kills the unprotected soldier." Typically, the military knows the dangers of a chemical environment but it does not realize the potentially devastating impact of cold weather on combat effectiveness. Therefore, protecting soldiers against harsh cold weather is just as important as protecting them from CBRN (Chemical, Biological, Radiological and Nuclear) threats.

Keeping Warm: The Role of Printed Electronics: One of the common ways of keeping individuals warm and comfortable in cold weather is through the use of multiple layers of clothing. The air between the layers acts as an effective insulator; however, this will increase the bulk and add to the soldier's load and discomfort. Another approach is to embed metallic heating elements into clothing, but this again can impair the soldier's mobility because the elements tend to be rigid and heavy. A recent novel advancement – termed PrinTronix® – is the convergence of textiles, conductive materials, printing technology and information technology to create fabric-based intelligent flexible electronics [15]. PrinTronix transforms the traditional paradigm of "printing for design" to "printing for functionality." The embedded

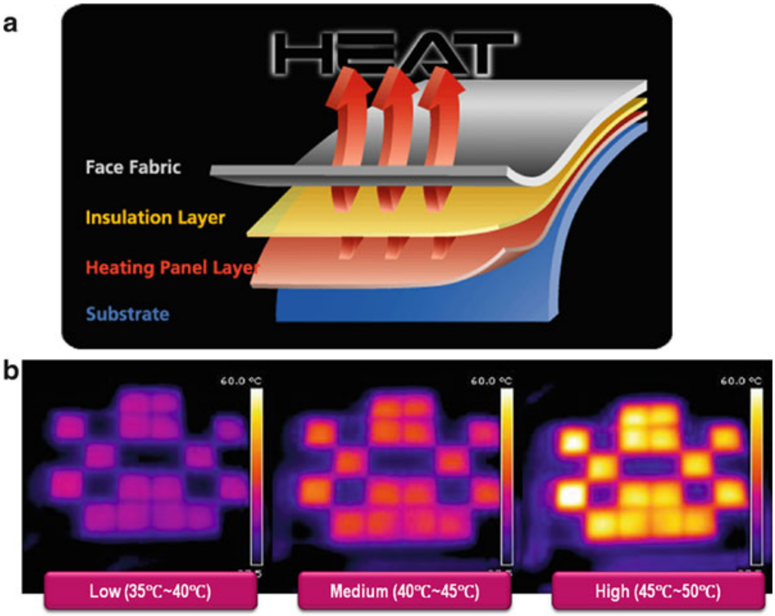


Fig. 1.13 The comfort building block: HeaTex (**a**) configuration (**b**) uniform heat distribution at different temperature settings (Courtesy: Kolon Glotech, Inc.)

conductive electrical circuits can then be utilized for a variety of applications including heating, signal transmission, information processing, and smart sensing with integrated sensors and connectors.

HeaTex® is a heating textile and represents the commercial realization of PrinTronix technology. HeaTex is composed of several layers of different ranges of electrically conductive materials as shown in Fig. 1.13. The power for the printed circuit comes from a 7.4 V rechargeable lithium-polymer battery. The user can regulate the warmth using the controller with three different temperature settings in the range 35–45°C and be comfortable. As seen in the figure, the heat distribution is uniform across the fabric surface at the three temperatures. Additionally, the temperature can be controlled remotely using the wireless HeaTex® Temperature Controller.

The configuration of the HeaTex fabric – size, shape and heating temperature range – can be customized to suit the application; since it does not add any appreciable weight or volume to a typical fabric, the intrinsic properties of the base materials used for the clothing are not altered as seen in the jacket in Fig. 1.14. HeaTex can be washed in a typical washing machine without loss of performance. Additionally, studies have shown that the blood flow of the wearer improves due to the far infrared emission from the heating elements in HeaTex [15]; it also provides anti-bacterial properties with a bacteriostatic reduction rate of 99.9%. These additional capabilities further contribute to enhancing the comfort of the user in combat.

Fig. 1.14 The HeaTex jacket (Courtesy: Kolon Glotech, Inc.)

Thus, a HeaTex-integrated IIPS can keep the soldier comfortable in cold weather conditions and thereby maintain his operational effectiveness in the field. This comfort building block can be a valuable addition to the protection and condition building blocks discussed earlier.

Keeping the Processors and Devices Functional: The Role of Conductive Textiles: The traditional keyboard on devices and instruments in an IIPS is being replaced by touch-sensitive interfaces. These interfaces rely on conductivity (typically through the user's fingers) to operate and execute the various commands. When the user is wearing gloves – for protection against cold or handling hazardous materials – the touch interfaces will not work since the glove material typically acts as an electrical insulator. Doffing the gloves to use the device is not a feasible option since it can cause damage to the user's hands. One solution is to incorporate conductive materials at the finger tips of the gloves to create a conductive layer between the fingers and the device. This will achieve the twin objectives of protection for the soldier's hands and ensuring the functionality of the touch-based devices. A commercial example of such a gloves is the etip™ glove from The North Face® company shown in Fig. 1.15.

1.5.3 *The Power Source Building Block: Photovoltaics*

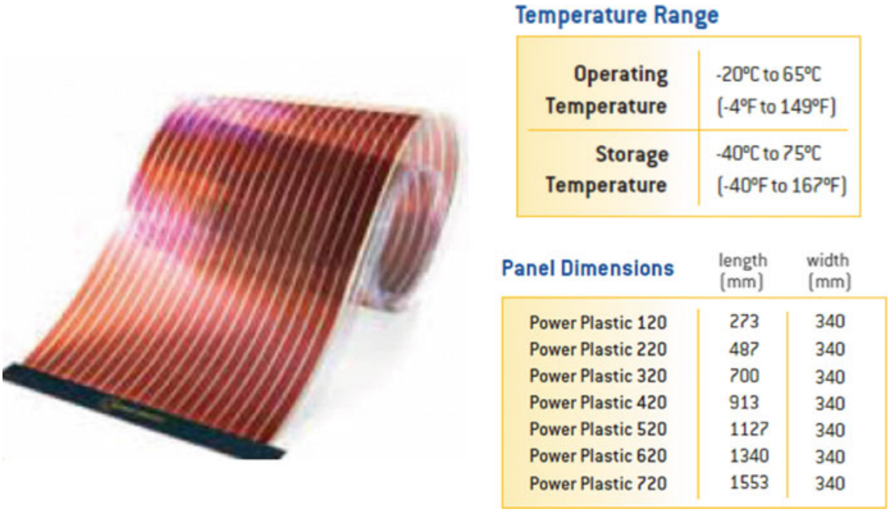
As the number of sensors and processors proliferate in the IIPS, there is a critical need for energy to power these devices. Carrying heavy batteries as the source of power is not a viable option since it can affect the soldier's mobility and effectiveness on the battlefield. Yet another option is to be "tethered" to the armored vehicle accompanying the soldier, which would also restrict his mobility especially in high

Fig. 1.15 The etip™ glove (Courtesy: The North Face)

risk combat zones such as the ones in Afghanistan. Recent developments in photovoltaics (PV) are promising and are opening up avenues for their incorporation into textile structures and serving as power sources for the sensors, processors and other devices in the IIPS. However, these PV devices must not adversely affect the flexibility of the textile material onto which they are incorporated. Therefore, traditional crystalline semiconductor-based PVs that are inherently rigid are not feasible candidates for incorporation into an IIPS.

Polymer-based PV technology is at the cutting edge and is resulting in solutions that can be integrated into textiles and clothing without significantly impairing their flexibility and other textile-like characteristics. One such commercially available technology is Konarka's Power Plastic®, which is a lightweight, thin-film photovoltaic material based on patented photo-reactive materials made from conductive polymers and organic nano-engineered materials [5]. Konarka claims that these materials can be printed or coated onto flexible plastic using an inexpensive, energy-efficient manufacturing process (Fig. 1.16). Power Plastic reacts with both indoor and outdoor light, which expands its potential applications (on and off the battlefield). By incorporating these panels into the IIPS, an on-board sustainable energy source that is unobtrusive and lightweight can be created. For instance, an IIPS with the penetration detection and vital signs monitoring capabilities of the wearable motherboard, together with the heating capabilities of HeaTex can be powered using an integrated power source exemplified by Konarka's Power Plastic. However, durability, cost and conversion efficiency are the key metrics in determining the success of polymer-based PV technology as a viable power source for IIPS.

Thus, these advancements illustrate the building blocks approach to the development of IIPS using the engineering design paradigm, which can lead to the realization of the capabilities defined earlier in the statement of purpose for IIPS.



Temperature Range

Operating Temperature	-20°C to 65°C (-4°F to 149°F)
Storage Temperature	-40°C to 75°C (-40°F to 167°F)

Panel Dimensions

	length (mm)	width (mm)
Power Plastic 120	273	340
Power Plastic 220	487	340
Power Plastic 320	700	340
Power Plastic 420	913	340
Power Plastic 520	1127	340
Power Plastic 620	1340	340
Power Plastic 720	1553	340

Fig. 1.16 PowerPlastic®: source of sustainable embedded energy (Courtesy: Konarka Technologies, Inc.)

1.6 Looking Ahead

The field of intelligent or smart textiles has seen a steady stream of advancements since the development of the wearable motherboard technology; it was the first ubiquitous textile-based platform for a personalized sensor network for the individual and paved the way for exciting opportunities to develop adaptive and responsive systems that can "think" and "act" based on the individual's condition, stimuli and environment [9].

1.6.1 Developing a Research Agenda: Application of the Engineering Design Paradigm

The engineering design paradigm can once again be applied to "design" the opportunities for advancements in the field of defense-related intelligent textiles and clothing. The overall objective is to use the soldier's uniform as the "interface" to the world – be it to the sensors and electronics on-board, the outside environment to detect any threats, or to the body inside that is being monitored and protected. The key capabilities desired in an IIPS – sense, feel, think, communicate and act – should be used as the "basis" for identifying "what" the requirements are from that particular facet so that the "how" can be executed using the structured methodology.

Thus, for instance, in the area of sensing, there are needs for advanced physiological sensors (to monitor the soldier's condition), environmental sensors (to monitor the operating environment for chemical, biological and radiological threats) and physical object sensors (to detect any objects or projectiles in the soldier's proximity). Routing of the information through the fabric infrastructure – to carry the data signals between all the electronics embedded in the fabric – requires interconnection technologies that can be rapidly scaled to large area surfaces. One such technology is known as textillography, which can lead to the rapid realization of junction architectures in textile structures [4]. On the "think" facet, smart algorithms and data fusion techniques for analyzing large amounts of sensory data must be developed. The rich data stream or ambient intelligence can be harnessed to design and implement real-time feedback mechanisms in the IIPS to "act" and thereby enhance the degree of protection for the user. For instance, certain individuals are susceptible to *anaphylaxis* reaction (an allergic reaction) when stung by a bee or spider and need a shot of *epinephrine* (adrenaline) immediately to prevent serious illness or even fatalities. Therefore, an exciting research opportunity is to explore the use of advancements in MEMS (micro-electro mechanical systems) technology to create a feedback system – including a drug delivery system – that can be integrated into the IIPS to administer the drug and prevent fatalities in combat situations. Actuators using shape memory polymers can be designed and integrated into IIPS. On the "energy" front, there are numerous opportunities including scavenging the energy generated by the soldier's movement using embedded sensors in the IIPS.

IIPS and Knowledge Banks: The ease with which personal data can be collected in real-time using the IIPS will result in the creation of "knowledge banks" of human performance. These knowledge banks can be mined to learn about the performance of soldiers in high stress situations and develop means to mitigate the dangers of operating in such environments through proper conditioning and training before deployment.

1.6.1.1 The Future of Intelligent Individual Protection: Need for a Transdisciplinary Approach

Figure 1.17 shows the need for a transdisciplinary approach towards intelligent individual protection, which means that it should be pursued as a *new* field of endeavor that brings together knowledge (both foundational and technological advancements) from other established fields such as materials/textile science and engineering, electronics, manufacturing and systems engineering, and computing and communications. Whether it is the development of sensors, manufacturing technologies or other elements associated with intelligent individual protection that are shown in the figure, a transdisciplinary approach will bring an innovative perspective leading to revolutionary advancements in IIPS. This is because a transdisciplinary inquiry focuses on *the* issue, viz., intelligent individual protection, rather than what each of the other disciplines can "contribute" to the issue or topic (IIPS).

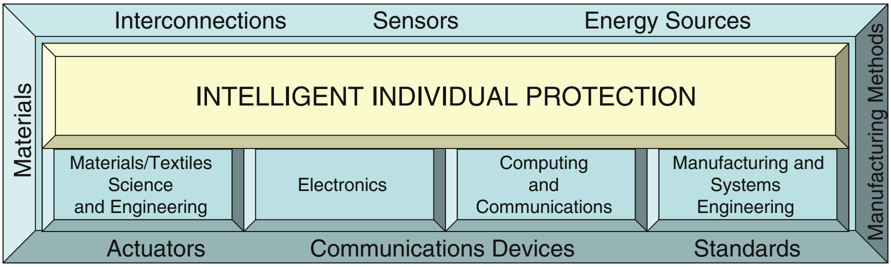


Fig. 1.17 Future of IIPS: need for a transdisciplinary approach

In closing, technological advancements have contributed significantly to enhancing the quality of life for the soldier. The pace of advancements is accelerating. The field of defense-related intelligent textiles and clothing is well-positioned to harnesses these advancements to transform individual protection and safety and realize the ultimate objective of cost-effective protection *anytime, anywhere* for *anyone*.

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Chapter 2
Wearable Optical Chemical Sensors

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Abstract Wearable sensors can be used to provide valuable information about the wearer's health and/or monitor the wearer's surroundings, identify safety concerns and detect threats, during the wearer's daily routine within his or her natural environment. The "sensor on a textile", an integrated sensor capable of analyzing data, would enable early many forms of detection. Moreover, a sensor connected with a smart delivery system could simultaneously provide comfort and monitoring (for safety and/or health), non-invasive measurements, no laboratory sampling, continuous monitoring during the daily activity of the person, and possible multi-parameter analysis and monitoring. However, in order for the technology to be accessible, it must remain innocuous and impose a minimal intrusion on the daily activities of the wearer. Therefore, such wearable technologies should be soft, flexible, and washable in order to meet the expectations of normal clothing. Optical chemical sensors (OCSs) could be used as wearable technology since they can be embedded into textile structures by using conventional dyeing, printing processes and coatings, while fiber-optic chemical sensors (FOCSs) as well as nanofiber sensors (NFSs) can be incorporated by weaving, knitting or laminating. The interest in small, robust and sensitive sensors that can be embedded into textile structures is increasing and the research activity on this topic is an important issue.

2.1 Introduction

Traditionally, our clothes function as a protective layer, offer comfort and aesthetic appeal, and serve for communication and cultural purposes. Moving beyond these functions, textiles provide a pervasive platform upon which to build sensor networks [1–3].

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Through the integration of novel technologies, clothing will be equipped with sensory functions, information and power transmission capabilities, and an infrastructure for embedded microsystems. This additional functionality has important applications in areas like threat detection, personalized healthcare, athletic performance and future fashion trends. Smart fabrics (in which the sensing capabilities are integrated into the textile) are capable of sensing body or environmental conditions arising from various sources (mechanical, thermal, photonic, chemical, electrical or magnetic). Conventional electronic components are hard and brittle, which leads to an inharmonious integration into a soft textile substrate. While electronic components are being continuously miniaturized, in order to preserve the inherent mechanical properties of the clothing, the ultimate objective is to directly integrate the sensing capability into the textiles themselves, i.e., the fabric becomes the sensor. As an intermediary interface, wearable sensors have the potential to monitor and respond to both the wearer's body conditions and his or her environment. Given the intimate connection with the wearer, garments may accommodate sensors placed in close proximity to the skin that look into the physiology of the body, e.g., breathing rate, body temperature and heart rate. Conversely, clothes act as our protective shield, and sensors may be configured to look outward to the environment and identify any potential hazards that may endanger the wearer.

2.2 Optical Chemical Sensors

An appropriate definition of chemical sensors is the so-called "Cambridge definition": "Chemical sensors are miniaturized devices that can deliver real-time and on-line information about the presence of specific compounds or ions, even in complex samples" [4–7]. Optical sensors, or *optrodes*, represent a group of chemical sensors in which electromagnetic radiation is used to generate the analytical signal in a transduction element. These sensors can be based on various optical principles (absorbance, reflectance, luminescence and fluorescence), covering different regions of the spectra (UV, visible, IR and NIR) and allowing the measurement, not only of the intensity of light, but also of other related properties, such as refractive index, scattering, diffraction and polarization, decay time and lifetime.

The usual aim of a chemical sensor is to produce a measurable signal that can be correlated with the concentration of a specific compound present in the immediate environment of the sensor [8]. Typically, a chemical sensor consists of a chemical recognition phase (sensing element or receptor) coupled with a transduction element (Fig. 2.1).

Chemical sensors may be classified according to the operating principle of the transducer element, as listed bellow [7].

- Optical sensors – based on absorbance, reflectance, luminescence, fluorescence, refractive index, optothermal effects and light scattering. Examples of transducers used: fiber optics connected to optoelectronic systems, photodiode. As an example, a luminescent sensor can be constructed by associating a sensing

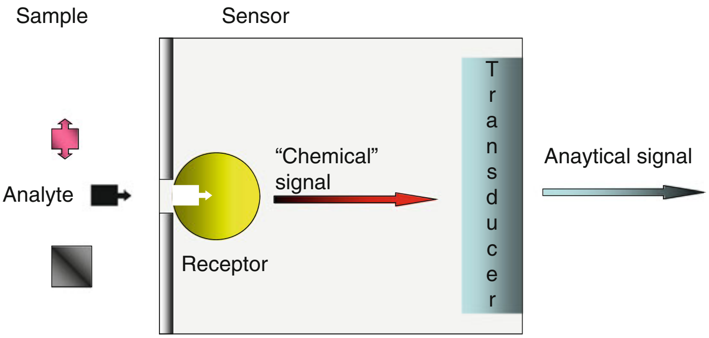

Fig. 2.1 Schematic representation of the composition and function of a chemical sensor

element, which emits light when in contact with a specific analyte, with a photodiode that converts the energy of the incident light into a measurable signal.
- Electrochemical sensors – including voltametric and potentiometric devices, chemically sensitized field-effect transistor (CHEMFET) and potentiometric solid electrolyte gas sensors. Examples of transducers used: amperometric and potentiometric detection-based electrodes and semiconductors.
- Electrical sensors – including those with metal-oxide and organic semiconductors as well as electrolytic conductivity sensors.
- Mass sensitive sensors – for example, piezoelectric devices and those based on surface acoustic waves.
- Magnetic sensors (mainly for oxygen) – based on paramagnetic gas properties.
- Thermometric sensors – based on the measurement of the heat effect of a specific chemical reaction or adsorption that involves the analyte. Example of transducer used: thermistor.

Alternative sensor-classification schemes follow the receptor principles [9]:

- Physical – here no chemical reaction takes place. Typical examples are sensors based on a measurement of the absorbance, refractive index, conductivity, temperature or mass change.
- Chemical – in which a chemical reaction with the participation of the analyte gives rise to the analytical signal.
- Biochemical – in which a biochemical process is the source of the analytical signal. The biochemical principle may be regarded as a subgroup of the chemical principle.

Sensors having a receptor part based on a biochemical principle are usually called biosensors. The selectivity and sensitivity provided by nature have been utilized in such sensors, frequently by immobilizing the biologically active compounds, such as enzymes and immunoglobulin, within a receptor part of the sensor. An effective way of obtaining the biological selectivity is a combination of cell cultures, tissue slices, organs and sometimes of whole living organisms with the transducer.

In general, optical chemical sensors may be categorized under the headings of direct sensors and indicator-mediated sensors. In a direct optical sensor, the analyte is detected directly via some intrinsic optical property such as, for example, absorption and luminescence. In an indicator-mediated sensing system, a change in the optical response of an intermediate agent, usually an analyte-sensitive dye molecule is used to monitor the analyte concentration. This latter technique is useful, particularly in the case where the analyte has no convenient intrinsic optical property, which is the case for many analytes. The purpose of the so-called indicator chemistry (dye in/on polymeric support) in optical sensing is to convert the concentration of a chemical analyte into a measurable optical signal. Indicator dyes are synthetic dyes that undergo a color change during an interaction with a chemical species. The indicators should be chosen by their sensitivity, selectivity, photo-stability characteristics and compatibility with simple and inexpensive optoelectronic measuring devices (LEDs, photodiodes, etc.). In most indicator-based optical sensors, the indicator is immobilized in a solid matrix. The polymers used as a solid matrix in optrodes can have one or more of the following functions: (a) may act as a rigid support onto which the indicator is immobilized, (b) may act as a solvent or cage for the material to be immobilized, (c) can provide selectivity for certain species by virtue of the permselectivity of most polymers, (d) polymers are frequently used as protective covers for sensitive working chemistries, and (e) can serve as optical isolation to prevent ambient light from entering the optical system of the optrode.

The choice of polymer is governed by the permeability of the polymer for the analyte, its stability and availability, its suitability for dye immobilization, its compatibility with other materials used in the fabrication of optrodes. In fact, the proper choice of the immobilization matrix is the most crucial step in the design of a sensor and can have a significant impact on whether a sensor works or not.

Following the choice of indicator and polymeric support, the next step in the sensor design will involve the immobilization of the indicator on the support. The three most common methods are adsorption by impregnation, entrapment by chemical doping and covalent bonding. With respect to the sensing application, the resulting materials are expected to be resistant to leaching and therefore the impregnation method is inconvenient. Chemical doping is accomplished by adding the indicators in organic polymers during the polymerization or the molding process. This concept is intermediate between the impregnation and covalent-bonding techniques and provides a general, inexpensive route for the immobilization of indicators. Its drawback, however, is a certain degree of leaching of the indicators. Covalent immobilization is accomplished by creating a covalent bond between the indicator and a polymer surface. The operational stability and shelf life is superior (no leaching, crystallization, evaporation of the components). However, obtaining the indicator chemistry and polymers with functional groups is inevitably linked with a significant synthetic effort.

Recent developments in the field of OCSs have been driven by such factors as the availability of low-cost, miniature, optoelectronic light sources and detectors, the need for multi-analyte array-based sensors, particularly in the area of chemical sensing, advances in microfluidics and imaging technology, and the trend toward sensor networks [1]. The changes should be reversible and applied in various formats, such as test strips and disposable tests, but preferably by making use of optical waveguides, including optical fibers, integrated optics, capillary devices, etc.

Micro-technology and micro-fabrication technology are key terms that continue to dominate discussions in all branches of sensor-miniaturization research and development. Micro-fabrication has reached the stage of serious application and is accepted as a good alternative to classical “macroscopic” technologies. It has provided us with the means to produce sensors characterized by high sensitivity, small size, enhanced optics and low cost. New developments in solid-state physics, the technological application of quantum effects, materials research and optical technology have opened the door to the world of nanoscience, which will probably gain in importance in all fields of sensor applications over the next 10–20 years. All the innovative production, characterization and modification methods suitable for nanotechnology are oriented consistently towards the idea of “engineering on the atomic and molecular level”. Nanoscience is the field related to knowledge of the properties of matter in the nanostate. The subject of nanoscience is the investigation of fundamental mechanisms of structure formation, structural organization and transformations at the nanolevel, and involves complex interdisciplinary investigations of the physical and chemical properties of nanoscale objects.

Nanoscience serves as a basis for nanotechnology. The main goal of the latter is to develop economically and environmentally efficient methods for the design of novel nanostructured materials and highly dispersed systems, the preparation of films and coatings, the fabrication of functional nanostructures and the elements of nano-electronic devices that are promising for applications in various fields, from information and telecommunication systems, sensors, optoelectronics and catalysis to medicine and bioengineering.

Nanostructured materials cross the boundary between nanoscience and nanotechnology and link the two areas together, so these definitions are very appropriate. Although nanotechnology is widely talked about, there is little consensus about where the nanodomain begins. It is recognized that the size range that provides the greatest potential and, hence, the greatest interest is that below 100 nm; however, there are still many applications for which larger particles can provide properties of great interest. To properly understand and appreciate the diversity of nanomaterials, the most common way of classifying nanomaterials is to identify them according to their dimensions. As shown in Fig. 2.2, nanomaterials can be classified as zero-dimensional (0-D) (nanoparticles), one-dimensional (1-D) (nanowires, nanorods, and nanotubes), two-dimensional (2-D), and three-dimensional (3-D). This classification is based on the number of dimensions that are not confined to the nanoscale range (<100 nm).

Materials at the nanoscale lie between the quantum effects of atoms and molecules and the bulk properties of materials, where many physical properties of materials are controlled by phenomena that have their critical dimensions at the nanoscale. A change from macro- and micro- to nanoscale qualitatively modifies most physicochemical properties of materials. When the sizes of materials are reduced in one or more dimensions, their physical and chemical properties can change dramatically

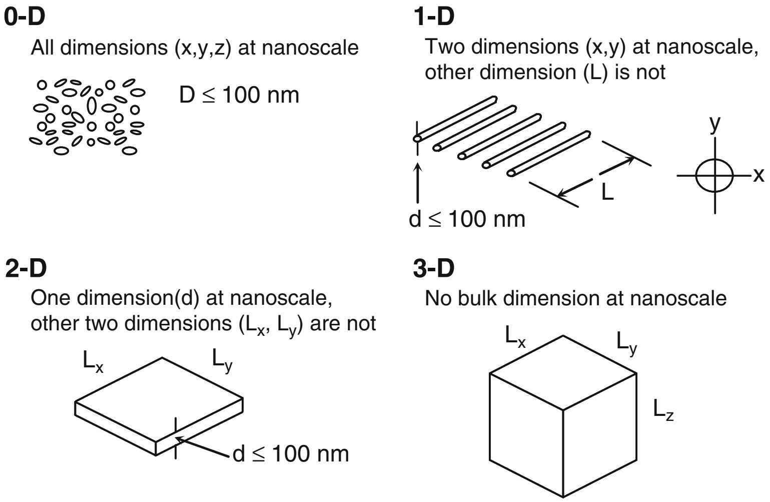

Fig. 2.2 Classification of nanomaterials according to their dimensions

due to the extraordinary increase in the surface-to-volume ratio. As a result, the larger surface area of the nanoparticles compared to their volume plays a significant role in dictating the important properties of these materials. These changes affect their optical properties (Stokes' shift, resonance, etc.), chemical properties (chemiluminescence, surface functionalization, etc.) electromagnetic (electronic, magnetic, dielectric, etc.), mechanical (lattice dynamics, mechanical strength, etc.), and thermal properties (Seebeck coefficient, thermal resistance, etc.).

The sensor characteristics can be tuned not only by the choice of the indicator and polymeric support but also by merely reducing the size (<100 nm). This is because materials that are smaller than the characteristic lengths associated with the specific phenomena often display new chemistry and new physics that lead to new properties that depend on the size. Perhaps one of the most intuitive effects is due to the change in the surface-to-volume ratio. When the size of a structure is decreased, this ratio increases considerably and the surface phenomena predominate over the chemistry and physics of the bulk. Therefore the sensor characteristics, such as sensitivity [10] and response time [11], can be dramatically improved. The literature [12, 13] defines an optical nanosensor as a device with dimensions smaller than 1 μm that is capable of detecting chemical or biological parameters by optically transforming the information into an analytically useful signal. However, nanotechnology deals with the study and application of structures of matter with at least one dimension of the order of less than 100 nm [14]. Here we will use the term nanosensors strictly for less-than 100-nm-sized particles that are used in sensing applications. This is also due to the fact that beads bigger than 100 nm behave similarly to bulk film optrodes. In contrast, sensing beads smaller than 100 nm show improved sensing characteristics [15]. The nanosensors consist of an inert, for intracellular measurements, biofriendly matrix in which a sensing component and/or an optical reporter are entrapped. The transduction method of choice is currently fluorescence, because of the high sensitivity and relative ease of the measurement. Most of the nanosensors reported so far have used fluorophores that are sensitive and selective to the chosen analyte as the sensing component. More recently, there have been signs that more complex sensing schemes are being developed; these utilize the capacity of the sensor matrix to accept the encapsulation of more than one component, thus allowing a synergistic approach to be employed [13]. Nanoparticles containing indicator dyes can either be used directly as nanosensors or as components of optical sensor materials. Most of the nanosensors known as PEBBLEs (Probes encapsulated by biologically localized embedding) have been designed for making quantitative measurements in the intracellular environment as they are small enough to be inserted into living cells with a minimum of physical perturbation [16, 17]. PEBBLEs have many advantages over widely used fluorescence-dye-based methods, such as: (a) an increased number of analytes that can be measured because nanosensors are not limited to using a single fluorophore and can utilize cooperative interactions between ionophores, enzymes, reporter dyes etc., (b) the matrix protects the intracellular environment from any potentially toxic effects of the sensing dye, (c) the matrix protects the sensing dye from potential interferences in the cellular environment, e.g., non-specific binding proteins and organelles, (d) no selective sequestration of nanosensors into cellular compartments or leaking from, or being pumped out of, cells, (e) an enhanced ability to carry out ratiometric measurements, and (f) the in-vitro calibration of nanosensors is valid for in-vivo measurements [13]. When the dyed nanoparticles are used as components of an optical sensor, multi-analyte sensing becomes possible, since several types of beads (e.g., pH-sensitive and oxygensensitive) can be incorporated into one polymer. Nanosensors possess some advantages, such as an improved sensitivity, response time, ability to perform in-vivo measurement as well as the possibility to incorporate them into textile materials. However, the dark side of using "free" nanosensors for in-vivo measurements needs to be considered. Nanoparticles are very different from their everyday counterparts, so their adverse effects cannot be derived from the known toxicity of the macro-sized material. The prime concern is the retention of these particles in the body and the harmful effects over the long term [18], since nanoparticles can be responsible for a number of material interactions that could lead to toxicological effects [19]. By being able to fabricate and control the size, morphology and surface characteristics of nanoparticles, it could be possible to influence the resulting properties and, ultimately, design materials to give the desired properties. The optical properties that can be controlled at the nanoscale are of great interest in the field of optical sensor design [20]. Some optical chemical nanosensors rely on quantum dots [21], metal beads [22] and other materials; however, most of the them make use of indicators embedded in polymer beads [23–30] and sol–gels [31–37].

2.2.1 Nanomaterials Used in Sensors

In optical chemical sensing it is desirable to employ appropriate nanomaterials to achieve highly sensitive and predictable responses over wide analyte concentration ranges within the shortest possible time. A fairly broad spectrum of nanomaterials is used in sensors. Some recent publications [22, 38–47] suggest that chemical sensors have utilized nanomaterials with different structures, which can be classified as follows:

- nanoparticles, nanoclusters, nanocrystals used in optical sensors (biochemical, immune sensors, electrochemical sensors) (0D).
- nanotubes, nanorods, nanotapes, and nanowires used mainly in electrochemical and in optical biochemical sensors (1D).
- nanosized assembled film structures (Langmuir–Blodgett films and self-assembled mono- and multi-layers) used mainly in optical sensors (2D).

Most frequently, nanosensors utilize the so-called 0D nanomaterials, i.e., nanoparticles, nanocrystals, nanoclusters, and quantum dots. These are ensembles of several hundreds or thousands of single-charged atoms or molecules, several nanometers in size, with discrete energy levels. Such nanoparticles are smaller than the de Broglie wave of an electron, this renders them capable of intensively absorbing the electromagnetic radiation in the visible or near-UV regions.

Nanosensors utilize nanoparticles with a different chemical nature and physical properties [22]:

- semiconducting materials (CdS, CdSe, CdTe, ZnS, ZnSe, ZnO, PbS, PbTe, etc.).
- semiconducting materials doped with lanthanides [Eu^{3+}, Sm^{3+}, Tb^{3+}, Gd^{3+}, etc.]
- noble metals (Au, Ag).
- magnetic materials (Fe_3O_4, Fe_3S_4, γ-Fe_2O_3, $MO{\cdot}Fe_2O_3$, where $M = Ni^{2+}$, Co^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}).
- polymer- and silicon-based particles doped with dyes or containing surface-grafted functional groups.

The high diversity of nanomaterials and sensor types differing in terms of operation and analytical signal-generation principles, coupled with the broad spectrum of media analyzed and analytes, complicate any systematization of the published data on nanosensors. Different authors classify nanosensors based on the nanomaterial geometry, in which case the sensing elements are represented by tubes, rods, tapes, wires [48], nanoparticles, nanotubes, and porous silicon [14, 49, 50], nanosized films [51, 52], spheres, rods, cubes, or prisms [53, 54], etc. Other authors emphasize the application of nanomaterials in the analysis of environmental objects [14] with the use of optical [52, 54, 55] sensors. Some authors concentrate on only one specific type, 368, of nanomaterials used in optical sensors, i.e., quantum dots [55] or dye-modified silicon-dioxide nanoparticles [56]. One brief review cannot cover all the types and applications of nanosensors, which forces us to restrict ourselves to the selected principal types of nanomaterials used in optical chemical sensors. The emphasis of this chapter will be on the properties and applications of recently developed optical chemical nanosensors based on semiconducting materials (quantum dots) and sensors based on polymers and sol-gel materials, all operating on the principle of photoluminecence.

2.3 Fiber-Optical Chemical Sensors (FOCS)

Fiber-optical chemical sensors (FOCSs) represent a subclass of chemical sensors. In general, they are divided into intrinsic- and extrinsic-type sensors [8, 57–60]. In the extrinsic type, optical fibers are commonly employed to transmit the electromagnetic radiation to and from a sensing region that is in direct contact with the sample. In the intrinsic fiber-optic sensors, the optical fiber structure is modified and the fiber itself plays an active role in the sensing function. An optical fiber is a cylindrical cable whose diameter can range from less than 1 μm to several hundred mm. The materials most commonly used in the fabrication of the fibers are plastics, glasses, and quartz. The most common are extrinsic sensors, in which the indicator chemistry is immobilized at the tip of a single or bifurcated optical fiber. Alternatively, the sensing chemistry can be immobilized along a section of the core of the optical fibers to make an evanescent field sensor. One of the advantages of optical sensors is the use of inexpensive optical fibers that allow the transmission of optical signals over large distances without complicating the optical systems. In addition, because of the small size and flexibility of the fibers, the acquisition of data can be performed in situ in environments that are not easily accessible by conventional methods of analysis. Furthermore, because the primary signal is optical, it is not subject to interferences caused by static electricity, strong magnetic fields or the surface potential. In addition to a number of advantages in comparison with other sensor types, optical sensors have some limitations: (a) ambient light interference, (b) limited long-term stability because of photobleaching and leaching of the immobilized indicator (c) and there are improvement to be made in the selectivity of the indicators and immobilization techniques.

2.3.1 Electrospinning and Nanofiber Sensors

The electrospinning technique has been used since 1934 for the synthesis of 1D nanomaterials [61]. It has been shown to be a simple and versatile process for synthesizing complex oxide nanofibers. The electrospinning process involves the application of a strong electrostatic field to a capillary connected with a reservoir containing a polymer solution or melt. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Taylor cone). If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet is ejected. The jet moves towards a ground plate acting as counter electrode. Due to the extensional viscosity of the polymer solution and the presence of entanglements, the jet remains stable and does not transform into spherical droplets, as would be expected for a liquid cylindrical thread. The solvent begins to evaporate immediately after the jet is formed. The result is the deposition of a thin polymer fiber on a substrate located above the counter electrode.

The design and development of electrospun polymer fibers with sub-micrometer diameters from various kinds of materials have gained considerable attention due to several amazing characteristics, such as very large surface-area-to-volume ratios, a flexibility in surface functionalities, and superior mechanical performance, which make the polymer nanofibers optimal candidates for many important applications, such as electronics, medicine, sensor, and controlled-release technology, etc. [61–64]. The polymer fibers with sub-micrometer diameters down to a few nanometers can be prepared by electrospinning, which is a quick and facile technique to create high-surface-area fiber membranes where the fibers are several orders of magnitude smaller than those produced by conventional spinning techniques [65]. Numerous polymer systems, including homopolymers, various kinds of copolymers, blends, and composites were successfully electrospun [66–68]. The combination of the sol–gel process and the electrospinning technique followed by high-temperature pyrolysis allows for the convenient development of various ceramic/metal nanofibers. Sol-gel techniques can be employed to prepare precursor solutions, which can also be used to deposit coatings with spinning and dipping processes [64]. In the past few years there have been efforts to extend the application of the sol-gel process, combining it with other methods to fabricate various kinds of optical materials, mainly luminescence and pigment materials in different forms (powder, core-shell structures, thin films, and patterning). 1D nanomaterials fabricated by a combination method of the sol-gel process and electrospinning have become important for their exceptionally long length, uniform diameter, diverse composition, and large surface, which can be applied in biomedical fields, reinforced composites, catalyst supports, electronic and optical devices, as well as sacrificial templates.

For nearly a decade of research, many studies have been conducted and it has been expected that the electrospinning technique could play an efficient role in the fabrication of sensor systems. The chemical, physical and biochemical interactions of the analyte with composite indicator-based materials need to be understood in order that we can predict the behavior and the nature of the sensors. The deep theoretical and experimental studies will provide the predetermination of the properties of the nanofibers. The core area in the sensor technology is to control the material properties and the efficient immobilization of the biocatalyst. A large number of sensor systems have been reported using numerous types of materials. The core difficulty for the commercialization of a sensor system is to develop a highly reliable, reproducible, sensitive, economical and easy-to-handle, easy-in-process, selective, stable sensing device. The identification of the problem and an efficient solution to this problem are the key to the development of any technology.

2.4 Wearable Sensors

The possible ways of incorporating optical chemical sensors into a fabric are shown in Fig. 2.3. The sensors can be placed removably into textile structures by using a zipper, velcome tape, and by sewing. Removable sensors do not need special requirements, such as washing, light, fastness and leaching properties. Sensors incorporated into fabrics by using fiber-optic chemical sensors (FOCs) can be knitted, woven or laminated. To design larger sensor areas on textiles, when the fabric becomes the sensor, the optical chemical sensors (OCs) are dyed, printed or coated. Absorbance-based sensors undergo a color change that is detectable with the "naked eye" and, more precisely, by spectrophotometer or colorimetric measurements. In the case of luminescence-based sensors, direct intensity detection has been replaced in many applications by lifetime-based sensing, often using sophisticated phase-based techniques. The fluorescence lifetime of an indicator is an intrinsic property and it is virtually independent of any fluctuations in the light-source intensity, the detector sensitivity, and the light throughput of the optical system, sensing layer thickness and indicator concentration. Hence, in contrast to the absorption methods, no reference measurement is necessary, and, in contrast to the fluorescence-intensity measurements, no compensation for a variation in the mentioned instrumental parameters is necessary [2, 69].

2.4.1 *Wearable Absorption-Based Optical Chemical Sensors*

In recent years, much progress has been made in the integration of physical transducers into clothing, e.g., breathing rate, heart rate and temperature. The integration of chemical sensing into textiles adds a new dimension to the field of smart clothing. Wearable chemical sensors may be used to provide valuable information about the wearer's health, as well as monitoring the wearer during the daily routine within his

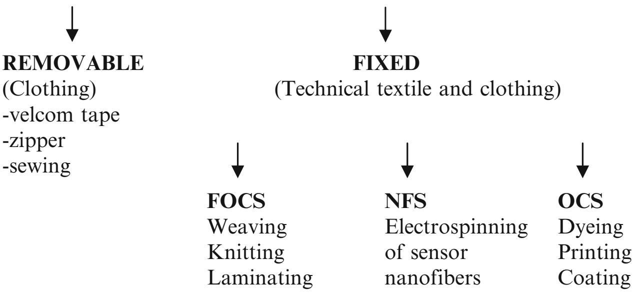

Fig. 2.3 Incorporation of sensors into fabrics

or her natural environment [1, 9, 69, 70]. In addition to physiological measurements, chemical sensors may also be used to monitor the wearer's surrounding environment, identifying safety concerns and detection threats. Whether the clothes are looking into the wearer's personal health status or looking out into the surroundings, chemical sensing calls for a novel approach to sensor and textile integration. In contrast to physical sensors, chemical sensors depend on selective reactions happening at an active surface, which must be directly exposed to a sample. Therefore, issues of fluid handling, calibration and safety must be considered. Some colorimetric as well as luminescence-based wearable sensors will be discussed in the following sections, and some of the potential applications of wearable chemical sensors will be discussed. Wearable sensors provide personalized monitoring, providing a far more realistic outlook than in a clinical setting. Wearable sensors for healthcare have been implemented by many research groups for various applications, including cardiovascular disease [71, 72] and ambulatory monitoring of the elderly [73]. Such applications typically monitor physiological signals, such as breathing rate, heart rate, ECG (electrocardiography) and temperature. These are all physical sensors, and they convert physical properties into electrical signals. Chemical sensing has not yet been implemented in these applications, although it has the potential offer to much information about the wearer's health. A major issue in monitoring chemical samples *in vivo* is sensor placement and sample delivery. As a wearable device, a non-invasive sensing device is essential. Urine, saliva, sweat, tears and breath are possible samples that may be acquired non-invasively [74]. Sweat is the most accessible specimen within the garment, and there are many developments within the textile industry to accommodate the movement of sweat through fabrics for various types of performance clothing. However, the integration of chemical sensors into textiles is not a straightforward task. It is necessary to consider the known problems of wearable physical sensors that are subject to physiological, environmental noise and motion effects. Chemical sensors are subject to similar problems, but there are additional constraints due to the nature of the sensing mechanisms. Chemical sensors respond to a particular analyte in a selective way through a chemical reaction. In order for this to happen, changes in the sensor surface or the bulk characteristics must occur to give rise to the signal. Therefore, the device surface must change and the analyte must be in contact with the sensor. The following issues must therefore be considered for integration:

2.4.1.1 Fluid Movement/Control

The garment must collect samples and deliver samples to the sensor. If the sensor is detecting the external environment, e.g., acidic gas plumes, the sample is likely to be volatile, whereas if the sensor is monitoring the body's physiology the sample, e.g., sweat, must be delivered to the sensor. In either case, there may be a need for reagent handling, fluid control, and waste storage, for which a dynamic control of the fluid is preferred.

2.4.1.2 Calibration

The regeneration of the original surface characteristics is extremely difficult and devices have to be constantly calibrated.

2.4.1.3 Wearability

The sensor itself must be robust, miniature, flexible, and washable in order to be integrally fixed into a textile. Materials that have similar mechanical properties to the textile are required.

2.4.1.4 Safety

The overall assembly of the sensor must be safe for the wearer's health. Toxic or hazardous chemicals must be avoided or well isolated from the wearer.

An optical approach is taken to develop textile-based sensors where already a change of color or a change in the other optical properties (absorbance, luminescence intensity, luminescence lifetime, etc.) indicates the presence of the analyte. Some problems connected to the instrumentation's incorporation into the textile materials can be neglected by using color-changed sensors that undergo a color change depending on the analyte used. As mentioned before, sensors can be deposited into textile materials by conventional dyeing, printing and coatings. The sensing area is large and the fabric becomes the sensor. Until now, not many papers have been published on this topic.

Grabchev et al. (2004) has studied different textile materials for solid-state sensor support [75]. Staneva et al. (2007) developed a colorimetric pH sensor on a viscose fabric used as a solid-state support [76]. The indicator dye was applied to the viscose fabric via a "conventional" dyeing process. The sensor showed good repeatability of colors appearing at consecutive pH changes, from 5.2 to 11.4 and vice versa. After a year, Staneva et al. (2007) reported the use of the pH benzo[de] antracen-7-one indicator dye immobilized on a viscose fabric for the detection of aliphatic amines [77]. It changes its color from yellow to orange and in the mean time decreases the fluorescence. They show that the immobilization on the textile matrix is an important factor that determines the properties of the sensor. It has been found that the viscose fabric changes the selectivity and sensitivity of the dye to a certain degree. H. Cao and coworkers published on the spectrophotometric detection of organophosphate diazinon using a porphyrine solution and porhyrine-dyed cotton fabrics [78]. The absorbance spectrum of the porphyrine meso-tetraphenylprphirine (TPP) shifts to shorter wavelengths when interacting with the organophosphates diazinon. This spectral shift in the presence of diazinon is more obvious in the difference spectra (TPP + diazinon)-TPP, and can be observed in a porphyrine-DMF solution and porphyrine-dyed cotton fabric. In solution, the difference spectrum has a peak at 412 nm and a through at 421 nm. For TPP dyed cotton fabric, the

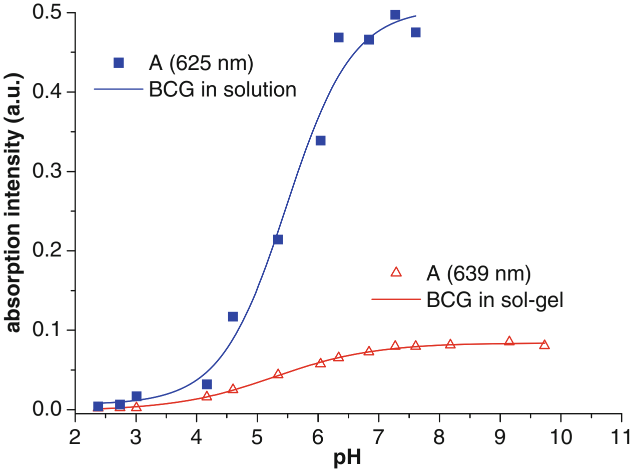

Fig. 2.4 Calibration curves of BCG in solution (squares) and of BCG immobilized in sol-gel (GPTMS:TEOS = 1:0) (triangles)

difference spectrum has a peak at 415 nm and a trough at 430 nm. Diazinon can be detected at a 0.5-ppm level by TPP in solution and at a 11-ppm level by TPP-dyed cotton fabric. The solid-state detection capability of TPP-dyed cotton fabric suggests that textiles can serve as the platform for chemical sensors. So far, authors have not reported about the leaching of an immobilized indicator. K. De Clerck et al. published a paper on the use of various pH indicator dyes for pH-sensitive textile materials [79]. After the first screening process in which different pH indicator dyes and textiles were tested, it was already clear that various pH-indicator-textile- systems are possible. They optimized the dyeing process and the water fastness, after the treatment with Perfixan, and reached acceptable values, with the color changes that happen in the neutral region being clearly visible. The best results were achieved by using Brilliant Yellow and Alizarin pH indicator dyes.

Novel real time-warning sensors based on a colour-change and triggered by hazardous chemical environmental changes, such as pH, were recently presented [80]. The sensors are optimized for a direct visual assessment of the colour change based on the use of absorption-based indicator dyes, such as Bromocresol Green (BCG) and Bromothymol Blue (BTB). The dyes were applied to commercial textiles, used for protecting clothing (cotton, viscose), via sol-gel coating. The sol-gel matrix was prepared using sol-gel precursors 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) in various ratios (1:0, 8:1, 5:1, 3:1, 1:1). Depending on the sol-gel matrix composition the colour change on the textiles upon exposure to various pHs was completed between 7 and 20 seconds.

Figure 2.4 shows the response of BCG in solution and of BCG immobilized in 100% GPTMS versus various pHs (from 2.3 to 9.7). The BCG pK_a value in solution is about 5.3, while upon BCG immobilization into sol-gel, the pK_a is not

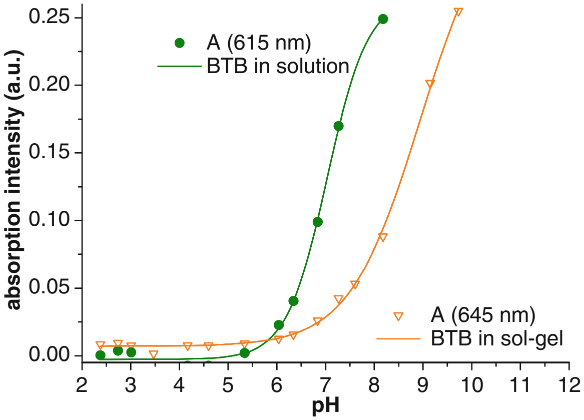

Fig. 2.5 Calibration curves of BTB in solution (circles) and of BTB immobilized in sol-gel (GPTMS:TEOS = 1:0) (triangles)

significantly different (pK_a 5.5). On the other hand it can be seen that the sensitivity of BCG incorporated into a sol-gel is reduced for approximately 5 times compared to that in solution. In the case of BTB, the pK_a in solution was about 6.8, while after immobilization it was shifted to 8.1. In contrast to immobilized BCG, here the sensitivity was not reduced, just the overall calibration plot was shifted to higher pHs for a pH difference of approximately 1.3 (Fig. 2.5).

Irrespective of the BCG and BTB sensitivity after immobilization, the visible colour change of BCG- and BTB-sol-gel-coated textiles was clearly observed after soaking the textiles in the solutions of pH range between 2.6 and 8 (Figs. 2.6A and B). Coatings with both indicators were evaluated also according to values a* and b* of the CIELAB system. We show here the examples for the colour position of the sol-gel coated BCG and BTB on cotton fibres and for the parameter a*, which defines the colour position on the CIELAB red-green axis. It was interesting to notice that the pK_a value of the BCG- and BTB-sol-gel coatings shifted also upon deposition to cotton textile material (to lower pHs). Not only the microenvironment but also the macro environment influenced the change in pK_a value. The coated cotton samples were additionally washed at 45°C in distilled water and showed satisfactory washing properties.

2.4.2 Wearable Fiber-Optic Chemical Sensors

The sensor in the case of body fluids should be incorporated within the layers of the garment. Coyle et al. developed a fabric-based fluid-handling platform for the collection of sweat [81]. The platform is composed of a fabric fluidic channel made from moisture-wicking material and super-absorbent material capable of absorbing high volumes of liquid. If the sensor is monitoring the external environment (gases),

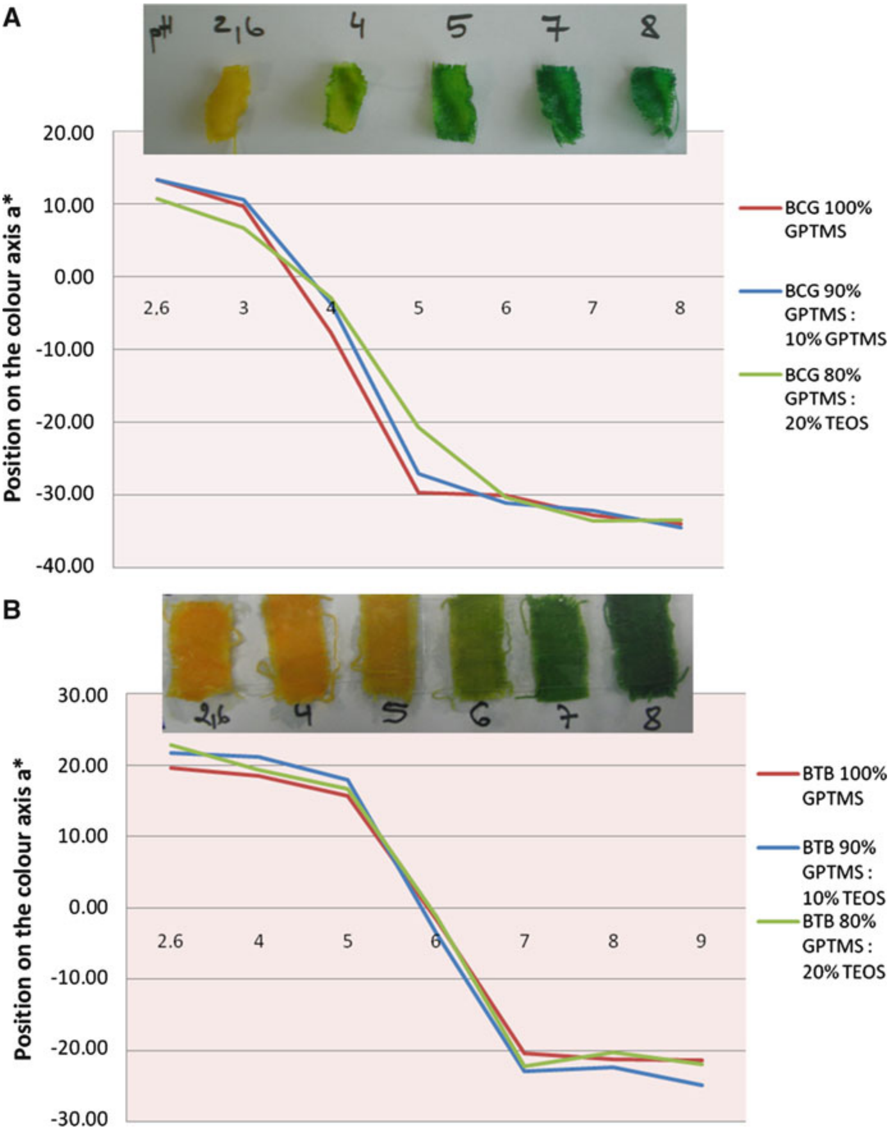

Fig. 2.6 BCG- (A) and BTB- (B) sol-gel coated cotton textiles of different precursors composition after soaking them in solutions of pH range between 2.6 and 8 versus the position on the CIELAB colour axis a*

the sensor should be positioned at the outer edge of the garment interface. Moreover, some toxic gases are heavier than air (Sarin, Tabun etc.), and therefore they move around at ground level. On the other hand, carbon monoxide is also a toxic gas that is lighter than air. Also, the position of the outer sensor on the garment (trouser leg, collar etc.) is important for the quick detection of the threat within the wearer's natural environment. Moreover, signal loss can occur when the fiber's optical

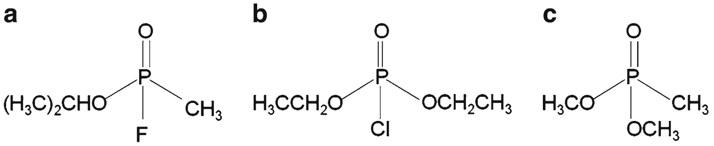

Fig. 2.7 Structures of the nerve agent and target compounds utilized in this study; (**a**) nerve agent Sarin, (**b**) reactive analog DCP, and (**c**) non-reactive simulant DMMP

chemical sensor is integrated into the part of the garment where it often bends (the sleeve around the elbow) since bending and mechanical damage can cause the light to escape. Textile materials possess a number of specific surfaces, as well as mechanical properties that can be very useful when applying them as solid-state carriers of different chemical sensors. Another option is to integrate fiber-optic chemical sensors into textile materials. As already mentioned, bending of the fiber and the mechanical damages cause light to escape and hence some degree of signal loss. Rothmaier et al. (2008) reported that plastic optical fibers are more resistant to the textile-manufacturing process, have a higher safety potential, higher flexibility and lower stiffness compared to glass fibers [82]. El-Sherif et al. (2000) presented a fiber-optic micro-sensor for the detection of chemical vapors (HCl and NH_4OH) integrated into textile structure [83]. The design of these fiber-optic sensors is based on a cladding-modification approach. The passive cladding of the optical fiber was removed from a small section and replaced by chemically sensitive material (polyaniline). The color changes of the polyaniline film were observed when it was exposed to HCl and NH_4OH chemical vapors.

Sensor materials, i.e., dyes, polymers, residual solvents and additives are the main cause for concern in terms of potential toxicity issues. One must ensure that during the time that the sensor is in contact with the skin, its components are not passing through the skin into the body or irritating the skin, and thus be a source of concern and a hazard to users.

In our laboratory, we have developed a nerve-agent-reactive fiber-optic chemical sensor system that is based on monitoring of the optical properties of a luminescence indicator. Actual nerve agents, such as Tabun, Sarin, Soman and VX, are not normally used in such studies in academic laboratories. Instead, surrogate compounds, such as analogs and simulants, that mimic the structural and electronic properties of actual CW agents are often utilized [76]. Because nerve agents possess reactive groups that inhibit acetylcholinesterase by covalent modification of its active site, our goal was to prepare nerve-agent sensors that respond only to the reactive molecules of analog diethyl chlorophosphate (DCP) (Fig. 2.7). DCP is an acetylcholinesterase inhibitor with effects that are similar to the nerve agents. On the other hand, the sensor is nonresponsive to less-harmful compounds that lack a reactive phosphoryl halide functionality (e.g., simulant dimethyl methylphosphonate (DMMP)).

A very important part of the prototype development was the instrumentation miniaturization, and the optical chemical sensor chip is part of a developed pocked-size portable sensor system that responds to the nerve-agent analog DCP in 3 s (Fig. 2.8).

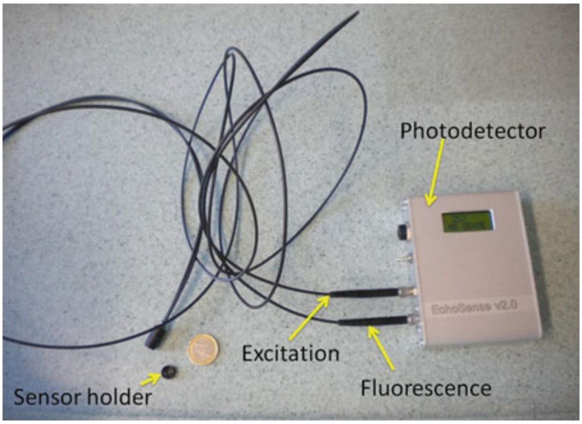

Fig. 2.8 Sensor-system prototype for organophosphate detection

The sensor system is easy to use and could be a part of a first responder's or soldier's equipment in order to ensure their safety.

2.4.3 Wearable Nanofiber-Optic Chemical Sensors (NFS)

Electrospun polymer fibers could be used in developing functional sensors, with the high surface area of nanofibers facilitating the sensitivity. Poly-Lactic Acid-co-Glycolic Acid (PLAGA) nanofiber films were employed as a new sensing interface for developing chemical and biochemical sensor applications [84, 85]. Highly sensitive optical sensors based on fluorescent electrospun polymer nanofiber films were also reported recently [86–88]. Preliminary results indicate the sensitivities of the nanofiber films when detecting ferric and mercury ions and a nitro compound (2,4-dinitrotoluen, DNT) are two or three orders of magnitude higher than that obtained from thin-film sensors.

Nanoscale tubes made from various materials, including carbon, ceramics, metals, and polymers are important in many industrial fields. Ultrafine fibers prepared from electrospinning can be used as templates to develop the various nanotubes [89, 90]. In general, the tube material is coated on the nanofiber template, and the nanotube is formed once the template is removed through thermal degradation or solvent extraction. For this purpose, the template nanofiber must be stable during the coating and be degradable or extractable without destroying the coating layer. By using PLA (poly(L-lactide)) nanofibers, Bognitzki et al. obtained polymer (PPX) and metal (aluminum), and metal (aluminum) nanotubes, respectively, through chemical vapor deposition (CVD) coating, and physical vapor deposition (PVD) coating and then thermal degradation. The wall thickness of the tubes was in the range of 0.1–1.0 μm [89]. Hou et al. employed a similar procedure. However, both PA (poly tetramethylene adipamide) and PLA nanofibers of smaller diameters were used as the templates and thinner nanotubes were achieved [90].

Electrospun nanofibrous membranes have received great attention for their sensor applications because of their unique large surface area, which is the most desirable property for improving the sensitivity of sensors, as a larger surface area will absorb more of a gas analyte and change the sensor's response more significantly. Silk fibroin-membranes-based sensors have been extensively used for analyzing various substances such as glucose, hydrogen peroxide and uric acid, etc. [91–93]. Apart from this, the literature shows the involvement of other electrospun polymers, such as polyaniline, polypyrole, polyamic acid, nylon-6, polyvinyl alcohol (PVA) and poly(acrylic acid)-poly (pyrene methanol), also as sensing interfaces [64, 94, 95]. Recently, efforts have been made to produce nanofibers for electrochemical sensors as well. Therefore, nanofibers that have a very large surface area would be ideal for sensor applications. Optical sensors are relatively new and not much work has been carried out in this field.

2.5 Future Trends

With respect to the integration of chemical optical sensors, it is an essential requirement for these devices to be completely self-sustaining in all respects if the promised massive scale up to true pervasive sensing is to be realized. However, in addition to the need for improvements in the engineering aspects of motes, there are very significant challenges for the chemical-sensor research community to deliver sensing platforms that are appropriate for an integration into scaled-up deployments in terms of sustainability, cost, reliability, etc. Examples of real deployments of chemical sensor networks are few and far between. Consequently, we are only beginning to understand how signals obtained from groups or communities of simple, low-cost sensors may provide a higher degree of certainty in event detection (e.g., through tracking the dynamics of response patterns to validate a decision) and to what extent this may compensate for the lack of sophisticated calibration procedures [96]. In general, there is speculation that in the medium term we will see a growth in the use of reagent-less and 'noncontact' approaches that can generate molecular or chemical information about a sample. For example, methods such as UV/VIS, IR, and Raman spectroscopies provide direct access to such information. While IR/Raman spectrometers are too expensive to be considered for scaled-up deployments, IR detectors tuned to the specific absorbance of target gases are available commercially, and the cost of these is likely to decrease rapidly [97, 98]. A direct UV measurement of the nitrate in wastewater, lakes, rivers, and marine environments is a good example of a reagent-less approach that has become increasingly employed in long-term monitoring applications [99]. Such nonselective measurements can be effective under very specific constraints (e.g., there are no co-absorbing species present in the sample) or where reagent-based approaches cannot be employed (e.g., the time scale is very long, months/years between servicing) [100].

Applications in wearable-sensors/body-sensor networks are certain to happen in the near future as the first commercial products are already appearing and a very significant user base is rapidly emerging, initially through consumer exercise/fitness products however, these will quickly evolve into personal-health applications and drive the demand for chemical sensing products capable of providing specific information on disease status that will complement the more generic health and environment information available from wearable sensors. However, the key to large-scale deployments of chemical sensors lies in the fundamental material science and device miniaturization. Accordingly, there is a wonderful opportunity to link research in molecular materials with microsystems engineering and developing new platforms capable of performing reliable chemical-sensor measurements in scaled-up deployments that will have a major impact on individuals and society.

2.6 Conclusions

Wearable sensors can be used to provide valuable information about the wearer's health and/or monitoring the wearer's surrounding environment, identifying safety concerns and detecting threats, during the wearer's daily routine within their natural environment. The development of wearable sensors/smart textiles can make great changes in the field of citizens' healthcare and safety. The application possibilities for optical chemical sensors integrated into textiles are limited by our imagination and creativity. Smart textiles open up a new market niche that can provide the textile industry with new products that have a high added value.

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Chapter 3
Textiles and Microbes

Jean Freney and François N.R. Renaud

Abstract Microbes can be carried by and even multiply on textiles. The first real, premeditated, microbiological warfare happened in 1763, during the Anglo-French wars in North America, when Native American emissaries were given blankets or handkerchiefs contaminated with smallpox. Thus, a small epidemic started and spread rapidly, causing considerable damage to the rank and file of the Native Americans. Nowadays, it could be said that textiles could be vectors of infections in hospitals or communities. The making of antimicrobial textiles could prevent them from becoming a reservoir of microbes in the transmission of infections and in cases of voluntary contamination in a terrorist threat for example. However, methods have to show that textiles are really active and do not attack the cutaneous flora they are in contact with. In this chapter, the role of textiles in the transmission of infections is summarized and the main characteristics of antimicrobial textiles are described.

3.1 Historical Background

Historically, the first use of a biological weapon to kill somebody was via the transmission of poison by way of clothing. For example, this was how Hercules was murdered. Nessos, a centaur, was killed by Hercules. Before dying, Nessos gave Hercules's wife, Deianeira, an elixir that was supposed to guarantee Deianeira that

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Hercules would not meet other women. Later, she gave Hercules a tunic on which she had added Nessos' blood given by the centaur. Thus Hercules died of burns and the symptoms he developed were those of anthrax [1].

Through the centuries, anthrax was also strongly related to another disease called black bane. People called it "black bane" because many cases involved the cutaneous or skin form of anthrax and its typical blackish sore. During the seventeenth and eighteenth centuries, more than 60–80,000 people, who were engaged in the wool industry such as shepherds, wool merchants and wool workers died of anthrax [1]. Industrial anthrax also known as woolsorter's disease was a serious threat in the nineteenth and early twentieth centuries, when the wool industry was flourishing [2].

Another example is during the wars between the French and the British in North America in the eighteenth century. The British gave the Native Americans of the Ohio valley blankets or handkerchiefs that were contaminated with smallpox. The Native Americans who were not immunized against that virus were killed in large numbers [3].

Sir John Pringle was one of the most prominent physicians of the eighteenth century. He invented the word antiseptics [4]. One of his observations was carried out in the London prisons. He demonstrated that typhus was able to spread from the prisoners to the lawyers and judges. He ordered the burning of the prisoners' clothes and this stopped the transmission of typhus. One hundred and fifty years later, Nobel Prize winner Charles Nicolle demonstrated that the responsible agent was the louse, since the sick were covered in lice. A similar case can be observed during the Moscow retreat where a great number of Napoleon's soldiers died of typhus.

Biological weapons were possibly used during the war in Rhodesia between 1976 and 1980. Guerillas claimed that uniforms and boots had been poisoned by Rhodesian agents and that anthrax and cholera had been introduced into specific areas [5].

In the interrelationships between microorganisms (bacteria, viruses, fungi) and textiles (clothes, sheets, etc.), two scenarios are possible; either the textile can transmit microorganisms and thus infections or, on the contrary, the textiles containing antimicrobial agents will prevent the transmission of infections. We will consider both these aspects in this chapter.

3.2 Textiles and Infections

3.2.1 Textiles as Infection Vectors

Textiles can contain infectious agents such as bacteria, viruses, fungi and therefore can act as reservoirs. Recently, Wattiau et al. [2] led a study on the occurrence of *Bacillus anthracis* strains isolated in an active wool-cleaning factory. This reservoir can be either passive in the case of viruses which are not able to multiply themselves outside living cells or active in the case of bacteria since they are able to multiply themselves mainly using cutaneous squames as the substrate.

A large number of hospital infections spread through clothing and textiles. Here are some of the most significant ones. In 1998, Takahashi et al. [6] described the contamination via vinyl undersheet by a *Streptococcus pyogenes* strain on 17 patients. In the same way, regular *S. pyogenes* infections occurred in a maternity hospital due to contaminated bras due to insufficient drying [7]. Some employees of the laundry department were infected with *Salmonella* and developed gastroenteritis due to contaminated sheets [8]. Barrie et al. [9] described *Bacillus cereus* post-operative meningitis caused by contaminated laundry. Gonzaga et al. [10] mentioned the case of newborns contaminated by laundry handled by staff infected with *Staphylococcus aureus*.

The risk of contamination is potentially very high during bed-making because of the spreading of bacteria through the atmosphere [11]. Perry et al. [12] showed that the same *S. aureus* strain was able to go from the sheet of the patient's bed to the nurse white-coat and that highly pathogenic *Clostridium difficile* and vancomycin resistant enterococci (VRE) can be found on white coats. Other types of hospital textiles can be contaminated such as curtains contaminated by MRSA (Methicillin-resistant *S. aureus*) [13, 14]. Doctors' ties are more often contaminated than bow ties [15]. Coronel et al. [16] showed that the sheets of hospitalized patients who are infected were more contaminated than those of non-infected patients.

3.2.2 Other Materials

Other materials or surfaces than textiles can also be reservoirs for microorganisms such as the case of pillows whose filling was contaminated with *Acinetobacter* [17]. Oie et al. [18] carried out a study on hospital door handles. They showed that 21% were contaminated by MSSA (Methicillin-susceptible *S. aureus*) strains, 8.7% by MRSA (Methicillin-resistant *S. aureus* strains) and 2.6% by both. Computer keyboards, electric blankets and TV remote controls are also microbe reservoirs [19–21].

3.2.3 Lifespan of Microorganisms on Supports

Several publications have put forward the lifespan of microorganisms outdoors. MRSA strains can survive several weeks on dry brooms and enterococci and staphylococci from 1 to 90 days on flasks, plastic bags and various textiles. In the case of microscopic fungi, survival can range from 1 day to several weeks even up to 5 months [22–24]. Viruses can resist several hours to several days in the case of CMV and HSV and up to 2 months in the case of poliovirus and rotavirus [25].

3.3 Textile and Bioterrorism

3.3.1 Bioterrorism Agents

Despite their differences, the types of biological agents that can be used in bioterrorism share common characteristics. The main source of infection or gateway comes through inhalation. Since biological agents are non-volatile (they cannot evaporate), they have to be dispersed using 1–5 μm aerosols which are able to stay in the atmosphere for a few hours whatever the climatic conditions. When the particles are inhaled, in order to transmit infection, they will have to get deep into the lungs and not remain at the level of the nostrils.

A list of critical agents can be found in Table 3.1 and has been defined on the basis of criteria such as the potential the agent has to cause a lot of casualties, the ability of the agents to be easily dispersed either via aerosols or via other means, the possibility of inter-human transmission, the correct or mistaken perception of people as well as the means of prevention for people (e.g., vaccines, improvement of monitoring or diagnosis). A more exhaustive list can be found in literature [26].

It is common to classify biological agents into three different categories A, B and C, A being the most dangerous ones (Table 3.1). Agents of the A category are able to cause mass destruction if they are disseminated among the populations and they require very high protective measures. B category biological agents (e.g., *Brucella* spp., *Burkholderia mallei*, *Burkholderia pseudomallei*, *Salmonella* spp., *Shigella dysenteriae*) can also be used on a large-scale but they are generally less powerful than those of the A category. The C category agents (e.g., yellow fever virus, Nipah and Hendra viruses, Hantavirus) are not usually considered as highly dangerous for the population but could become a threat in the future. One of the major problems could be the development of intentionally engineered biological weapons which would not be detected and would not be treatable by antibiotics or vaccines [27].

Table 3.1 Category A of biological agents

Agent	Disease
Variola major	Smallpox
Filovirus (e.g. Ebola et Marburg)	Hemorrhagic fever
Arenaviruses (e.g. Lassa and Junin)	Lassa fever, Argentine hemorrhagic fever
Bacillus anthracis	Anthrax
Francisella tularensis	Tularemia
Yersinia pestis	Plague
Clostridium botulinum neurotoxins	Botulism

Table 3.2 Epidemiological characteristics of some biological agents potentially used in bioterrorism

Biological agents				
Agent	Incubation	Lethality	Persistence	Dissemination
Bacteria				
Anthrax	1–5 days	3–5 days; fatal	Very stable	Aerosol
Plague	1–3 days	1–6 days; fatal	Extremely stable	Aerosol
Tularemia	1–10 days	2 weeks; moderate	Very stable	Aerosol
Viruses				
Smallpox	10–12 days	High	Very stable	Aerosol
Ebola	4–6 days	7–16 days; fatal	Unstable	Aerosol; direct contact
Biological toxins				
Botulinum toxins	Hours to days	High without treatment	Stable	Aerosol; sabotage
Ricin	Hours to days	10–12 days; fatal	Stable	Aerosol; sabotage

3.3.2 Epidemiology

Epidemiology can be defined as the study of the frequency, characteristics, location and means of spreading of an infection. Table 3.2 shows some epidemiological information of the main agents that can be used in bioterrorism [28].

3.3.3 Laboratory Diagnosis

Although they are considered the “gold standard,” the traditional methods of identification of bioterrorist agents such as culture, biochemical or immunological identification are not appropriate in case of an emergency. That is why a number of rapid diagnostic tests have been set up in order to detect and identify bioterrorist agents, particularly after the September 11, 2001 events. As one has a relatively short period of time to carry out prophylactic measures to reduce mortality and morbidity associated with bioterrorism, public health measures in response to such events have to be particularly quick in order to be efficient [29].

Contrary to chemical or nuclear attacks that can cause considerable human loss within minutes or hours, a biological weapon produces less visible effects that can be delayed a few days or weeks (Table 3.2). This factor may considerably complicate the detection of a biological attack. However, one of the advantages of biological weapons over chemical or nuclear weapons, for which immediate detection is indispensable, is that the detection of biological weapons may be slightly delayed by a few hours due to the incubation period of the pathological agent. One can imagine that in case of the detection of a biological agent, for example on a passenger on a flight, quarantine and therapeutic measures (e.g., antibiotics, vaccines, disinfection) could be rapidly carried out.

3.3.3.1 Sampling Methods

Most of the rapid diagnostic methods only work if there is a sufficient amount of biological agent and without interfering substances. In most cases, the methods of rapid detection require a certain number of steps to allow the growth or the concentration of biological agents and/or to purify the target agent of the sample before detection [30].

In the case of textiles (e.g., clothing, carpets), the sampling methods are mainly based on surface sampling [31, 32]. The sampling's objective is to determine qualitatively if a bulk material such as a visible powder or clothing is contaminated with a biological agent. Methods used for routine sampling of environmental surfaces include swabs, wipes, agar contact plates, surface rinses, and vacuums [2, 33]. The "Microbial-Vac" system (M-Vac, Microbial-Vac Systems, Inc., Jerome, ID) uses vacuum and centrifugation in order to recover and concentrate micro-organisms from various surfaces [34, 35].

Although significant research is being conducted, valid methods for collecting samples from porous and non-porous surfaces are needed [31, 32]. More information can be found in literature [36, 37].

3.3.3.2 Detection Methods

Discriminatory methods take into account the characteristics of any living cell. All microbes have a characteristic chemical structure on their surface that can be recognized by the immune system or these unique molecules are encoded via specific sequences of the DNA present in each cell [38]. All the methods used have advantages and disadvantages (Table 3.3).

Immunological Methods

Miniature hand-held assays (HHA) for the detection of biological agents have been on the market since the beginning of the 1990s. These systems such as the quick pregnancy diagnostic test were based on immunochromatographic techniques.

The biological detector of the "US Military's Biological Integrated Detection System (BIDS)" contains biosensors. Those tests have been set up for some biological agents such as *B. anthracis* or *Y. pestis* [38]. Techniques using antibodies are sometimes associated with the detection of mass modification. The SAW (Surface Acoustical Wave) systems use piezoelectric substances covered with antibodies. They produce an electrical signal when they undergo pressure or mechanical constraint and vice versa. When antibodies recognize the target particle, a change in the crystal piezoelectric mass occurs producing a variation of the crystal resonance frequency [39]. Such modification in frequency signals the presence of the biological agent. Additional information can be found in literature [40].

Table 3.3 Advantages and drawbacks of the detection methods [42]

Method	Advantages	Disadvantages
Non-DNA: indirect detection	Wide-spread use Large number of antibodies available Standard detection methods available Can be relatively inexpensive and portable. Do not necessitate cell lysis	Must have antibodies beforehand No information if antibodies do not bind to target False positive if antibody binds to the wrong target
Molecular (DNA or RNA)	Unique identification of species and strains of organisms	Must have target sequences beforehand Requires cell lysis and extraction before amplification Requires amplification (PCR or other method) Provides no information on growth or processing methods
Non-DNA: direct detection	Always provides information: does not depend on prior knowledge of target No antibody required No target amplification (copying) is required Measure intrinsic properties of target (shape, elemental composition, vibrations)	Requires high-sensitivity, high-resolution techniques Signatures libraries used for identification Instruments can be expensive and relatively nonportable

Molecular Methods

These methods based on the recognition of DNA and RNA have been in development for the last few years and have become the gold standard for the detection of bioterrorism [41]. The sensitivities and specificities found in literature approach 100% when compared to the culture or serological methods. Efficient methods of amplification of the signal or the target are indispensable since they need to detect fewer than 10 copies of nucleic acid per sample from a very small amount of the sample. In biological samples, the target amplification is more often used than that of the signal [38].

Physico-Chemical Methods

PCR (polymerase chain reaction) amplification and immunological methods present a major drawback which is the requirement of *a priori* knowledge of the target, i.e., “we only find what we are looking for!” If a terrorist uses a pathological agent which is not on the “official” list, it would be impossible to find [38].

Presently, there is a growing interest in the development of methods allowing analysis of molecules other than DNA via their intrinsic properties [42]. Through direct methods, a known target can be identified thanks to the data banks and unknown targets can be detected and kept for further analysis. Thus, all the detected components provide information whether they are identified or not. No information is lost.

Mass Spectrometry

Contrary to immunological or DNA-based tests, mass spectrometry can be used to identify various pathogens even if they are not suspected of being such [43]. The general principle consists in generating characteristic profiles (fingerprints) of the whole organism [44].

In the mass spectrometry technique, a sample is fragmented into charged small pieces which can be proteins, peptides, characteristic fragments of the cell wall or other molecules, all of different mass depending on their chemical composition. The masses are measured and compared to those of other particles. When a complex particle such as a bacterium is introduced into the spectrometer, it is separated into hundreds or thousands of fragments creating a complex profile made of different molecular weights. An automated system analyzes the profile and compares it to known profiles of bacteria, viruses and proteins already in the database. This technique also applies to sporulated bacteria [45]. For instance, Wilkes et al. [46] have used the pyrolysis MS technique for the rapid identification (7 min) of biological agents such as *Bacillus* spores from harmless powders (e.g., flour, methyl cellulose) but capable of causing terror in the context of a bioterrorist attack. A fully automated system called CBMS (Chemical Biological Mass Spectrometer) is able to identify the biological and chemical agents within 3 min directly on the spot [43]. Recently, a portable system (1.48 kg) for the detection of chemical weapons has been developed [47]. We can imagine that such application for the detection of biological weapons will be available in the near future.

Currently, there are many attempts to develop biosensors based on mass spectrometry [48–50]. The technique has been used to identify bacterial and viral proteins [51, 52] as well as whole bacteria and to differentiate aerosols of *Bacillus thuringiensis* and *Bacillus atrophaeus* spores [53]. The main principle of this method uses the MALDI-TOF technique (matrix assisted laser desorption/ionization-time of flight). These systems do not use any reagents and therefore are fast and only require a small amount of sample. The system associating mass spectrometry with MALDI-TOF is theoretically capable of identifying all types of biological agents (bacteria, viruses, spores and fungi). The drawbacks of the method are the necessity of obtaining a very strong concentration of the sample (10^5–10^7 cells/ml for full cellular analysis), the setting up of the complex spectral databases for each target cell and the possible loss of specificity in complex matrix [54, 55]. Additional details can be found in literature [56].

Other Direct Methods

In addition to mass spectrometry, other physical methods such as Raman spectrometry [57–59] and fluorescent techniques have been developed.

Hybrid Systems

As shown in Table 3.3, each method has its advantages and drawbacks and that is why hybrid systems using molecular and immunological approaches combined with mass spectrometry have been developed, so that the advantages of each technique are being utilized. For instance, the Lawrence Livermore National Laboratory (Livermore, CA) is offering a fully automated system (Autonomous Pathogen Detection System) using antibodies to collect the targets of a PCR amplification that considerably increases the sensitivity of the reaction [60, 61]. Hang et al. (2008) [62] have developed a rapid identification system of *Bacillus anthracis* spores combining a fast immunological method (less than 2 h) known as "Integrating Waveguide Biosensor" followed by a rapid germination of the spore, the vegetative form being identified via PCR. This method allowed the detection of a very small number of spores, around a 1,000.

The DNA-based methods have been combined with the MS (mass spectrometry) technology for the development of the TIGER system which can identify bacteria without having information on growth conditions [63]. Amplified DNA is introduced into the mass spectrometer in order to obtain a unique mass charge profile for every piece of DNA. The resulting profiles are calculated to determine the sequence and to compare it to the thousands of sequences contained in the databases so as to determine the origin of the DNA. This system does not require specific reagents for a specific organism, thus it is capable of identifying an unknown and unexpected organism in the sample as opposed to the conventional PCR. Moreover, since an organism does not modify the sequences of its DNA according to environmental conditions such as growth, this system avoids the drawbacks described previously with the conventional MS. Yet, contrary to the conventional MS, this system does not allow the identification of toxins which do not possess DNA and requires significant improvements to identify viruses [38]. Honisch et al. [64] introduced the use of comparative sequencing by MALDI-TOF MS for automated high-throughout microbial DNA sequence analysis.

Newer diagnostic platforms include acid nucleic microarrays ("labs on chips" containing hundreds to thousands of oligonucleotide probes for signature sequences) and mass spectrometry for sequence analysis [65–69]. Potential applications of such multiplexed detection technologies include the characterization of polymicrobial infections and the creation of "universal biosensors" to allow the simultaneous identification of a broad range of infectious agents in an environmental or clinical sample [70].

Following a similar technological progression from PCR to microarrays, the Pandora's box Project, based at Columbia University's Greene Infectious Disease

Laboratory, employs a staged strategy for molecular pathogen surveillance and discovery [71]. The first stage consist of MassTag PCR, a technique that attaches reporters "tags" of distinct masses to the amplified sequences, allowing the simultaneous, highly sensitive detection of more than 20 different pathogens [70]. This technology has been used to distinguish among various viral hemorrhagic fevers [72]. A second stage of diagnosis becomes necessary when the first stage fails, or when a larger number of sequences must be screened. For this purpose, the researchers first designed a pair of extensive microarrays, called Greenechips which are tools for discovery as well as for diagnosis. Because as many as 100 different regions of a genome may be represented on the chip, assays reveal enough sequence information to enable the rapid sequencing of novel pathogens.

The future for rapid infectious disease diagnosis is the "lab-on-a-chip" approach, where all sample processing, assay technologies, detection, and reporting are fully integrated into one unit.

3.4 Skin Microflora

Clothing and numerous textiles are generally in close contact with the skin and particularly with the skin microbial flora. It is important to know about these characteristics when we want to develop a textile with antimicrobial properties for example [73].

On the skin, bacteria form a structure known as a biofilm, i.e., a very resistant, specialized structure closely linked to the skin [74]. These bacteria have colonized the skin at birth and form a permanently involved dynamic system. The best proof is that this flora specific to an individual could dramatically change after a 24–48-h stay in a hospital. That flora fully fits the individual. The metabolism of the various species that compose the biofilm has selected the best ways to catch the energetic substrates and to avoid the action of the toxic substances generated [75].

To enter an organism, a potentially pathogenic bacterium first must attach itself to epithelial cells. Thus, it must penetrate the biofilm of the commensal flora that does not leave any free cellular space [74]. It is not competitive for the capture of substrates, cannot stand the toxic products of the bacteria, and finds a hostile physicochemical environment (pH, oxygenation, rH). Whenever it manages to bind, it is often eliminated along with epithelial cells during the desquamation process. That is why we must take care of the skin's commensal flora. That also shows that squames play a fundamental part in the dissemination of bacteria in the environment. The squames production of an individual is estimated at 3×10^8 squames per day, with a size ranging from 4 to 25 μm and containing an average of 100 bacterial cells [76, 77]. As soon as anyone is in a room, his own squames which are in suspension in the atmosphere are able to contaminate textiles and surfaces.

Basically, we can distinguish two types of microbial flora: resident and transitory (or transient) flora. The first one is composed of species that have settled in permanently whereas in the case of the second one, the bacterial species have a transitory

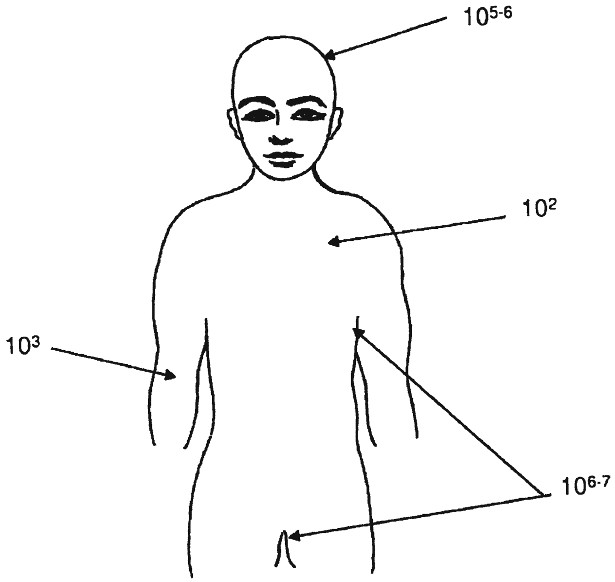

Fig. 3.1 Number of bacteria in CFU (Colony forming Unit) per cm^2 of skin following localizations

way of double origin: outdoor environment and intestinal tract. The study of the transitory flora is linked to most nosocomial infections.

3.4.1 Skin Resident Flora

Skin resident flora is stable. Usually 10^3–10^4 microorganisms per cm^2 are found on the skin. However, these figures can go up to $10^{6-7}/cm^2$ in wet areas such as the folds of the groin (Fig. 3.1).

3.4.1.1 Definition

The resident skin flora corresponds to bacterial and fungal species which are viable, commensal, and settled in permanently on the skin [78]. That flora is neither passive nor neutral and develops according to various parameters (e.g., climatic changes, hygrometry, site temperature, etc.). Those organisms develop on the skin in a stable way in regards to number and composition. They are able to survive as microcolonies on the surface of stratum corneum and on the outer coats of the epidermis. The flora which can be found on a specific part of the body cannot in any case be considered representative of the total skin flora since it varies considerably from one

Table 3.4 Regional diversity of the resident skin flora, frequency of isolation of the various microbial species

Cutaneous areas species	Face	Armpits	Hands	Perineum	Toe webs	Trunk
Staphylococcus epidermidis	+++	+++	+++	+++	+++	+++
P. acnes	+++	+++	+++	+++	+++	+++
Other coagulase negative staphylococci		++				
Staphylococcus aureus		++				
Aerobes corynebacteria	++		+		+	
Groupe A *Streptococcus*	+		++	++	++	
Other streptococci	++		+/−	++	+/−	+
Enterobacteria		++	+		+	++
Acinetobacter		++	+	+		
Fungi	+			+	++	
Anaerobes	+	+		++		

site to another (Table 3.4). Moreover, that permanent flora constitutes an efficient barrier against the colonization of exogenous species by bacterial antagonism. The microorganisms belonging to that flora are generally harmless except if they are introduced into the organism via a continuous breach. It is thus indispensable to respect that flora and not to modify or destroy it, particularly when in contact with textiles.

3.4.1.2 Description

Three major bacterial genera can be encountered: *Staphylococcus, Propionibacterium*, and *Corynebacterium.*

Genus *Staphylococcus*

Staphylococcus epidermidis is the most frequent species encountered all over the cutaneous zones (Table 3.4) and colonizes essentially the upper part of the body. It makes up for more than half of the cutaneous staphylococci. Its density can reach 10^4–10^6 CFU/cm^2 (colony forming unit) of skin in some hot and wet parts of the body (armpits, folds of the groin, perineum).

Genus *Propionibacterium*

It is composed of nonsporulated anaerobes Gram positive bacteria that are usual inhabitants of hair follicles and sebaceous glands [78, 79]. *Propionibacterium* bacteria are made of anaerobes bacteria, hence their higher presence in areas with low oxygen concentration (hair follicles for instance). There is a direct link between the number of *Propionibacterium acnes* strains present and the amount of sebum produced [80, 81]. These bacteria are directly responsible for teenage acne when the hair follicles widen following androgenic stimulation [82].

Genus *Corynebacterium*

The genus *Corynebacterium* is composed of pleiomorphic Gram positive bacteria. They are involved in the production of body odors especially from androgenic hormones spotted in sweat. This could explain that these body odors are more often produced by men than women [83]**.** *Corynebacterium jekeium* constitutes a particular case because it is frequently represented by bacteria which resist most antibiotics with the exception of vancomycine. They can be found on the skin of healthy people but much more frequently on that of immune-depressed or hospitalized people [84, 85].

Gram negative bacilli

They are unusual components of the resident flora especially because of the dryness of the skin. They are most often found in the transient flora following a gastrointestinal contamination. *Acinetobacter* bacteria are an exception since they can be found on the skin of more than 25% of healthy people. Men tend to be more colonized than women and colonization increases during the summer period because of perspiration [84].

3.4.1.3 Changes in the Resident Skin Flora

Although the composition of the resident flora seems to be relatively constant, several factors may interfere in the number and percentage of each of the resident microorganisms. Those factors can be endogenous and specific to individuals. They can also be due to exogenous factors such as environmental changes or to the influence of other microorganisms. Many studies have shown significant differences between the flora of healthy people and that of hospitalized patients. For example *Corynebacterium jekeium,* which is resistant to most antibiotics, can be found in higher proportions in hospitalized patients [85]. Contrary to non hospitalized people, Gram negative bacteria (*Proteus* and *Pseudomonas*) and fungi (*Candida albicans*) are most often encountered in hospitalized patients.

3.4.2 Transient Skin Flora

Transient skin flora is composed of bacteria, fungi and viruses that are on the skin and can be associated to nosocomial infections [86]. Those microorganisms do not usually multiply themselves on the skin but can survive and transmit infections [86]. They can originate from patients or inanimate surfaces. Brouwer and colleagues have shown that between 4% and 16% of the hand's surface can be contaminated by single contact and after 12 direct contacts this percentage was up to more than 40% [87]. The transmission of the transient flora depends on the type of species, the number of bacteria present on the hand, and their ability to survive on the skin as well as the degree of dermis humidity [88, 89, 90].

3.5 Antimicrobial Textiles

3.5.1 Biocides

3.5.1.1 Definition

Biocide is a general term to describe a chemical agent which inactivates microorganisms. The word biocide (which means "life killer") corresponds to a large family of chemical substances divided into four major groups: disinfectants (human or veterinary hygiene, for example), protective products (wood, leather, etc.), antiparasitic products (e.g., raticides, insecticides) and other products such as anti-stains. According to directive Biocide 98/8/EC, the term "biocide product" includes "active substances as well as preparations which contain one or more active substances meant to have a lethal effect on harmful organisms."

3.5.1.2 Mode of Action

Action mechanisms of components other than antibiotics are often difficult to handle as they offer multiple targets on surface components as well as on the inner structure of microorganisms contrary to antibiotics.

The action of a biocide agent may have either a lethal effect on microorganisms (bactericidal, sporicidal, fungicidal, virucidal), or a temporary inhibition of growth (bacteriostasis, fongistasis, inhibition of viral replication) [73]. As in the case of antibiotics, biocides may have several targets on microorganisms. Salton [91] described five steps:

- adsorption of the biocide on the cell followed by penetration into the cell wall;
- disorganization of the cytoplasmic membrane;
- leakage from the cytoplasm of small molecular weight components;
- degradation of proteins and nucleic acids;
- cell wall lysis by autolytic enzymes.

Additional information can be found in literature [92, 93].

3.5.1.3 Resistance

The fact that a bacterium is able to rapidly develop resistance to antibiotics is a well-known phenomenon. This is essentially due to a specific mechanism of action of those anti-infectious agents. In the case of biocides, the resistance mechanisms are not so well-mastered. If we take into account the lethal activity of biocides, resistance occurs very seldom. However, some intrinsic resistance mechanisms allow microorganisms to resist an aggression by these agents. They include stress responses, revival or dormancy phenomena, biofilms and sporulation development [93].

Acquired resistance mechanisms have been observed following mutations or acquisition of genetic materials (plasmids) encoding a specific resistance.

Generally speaking, microbial resistance to anti-infectious agents varies from one microorganism to another. The natural resistance of some microorganisms to biocides is a permanent and stable characteristic that allows definition of the spectrum of activity. Very often, it can be explained by a mechanism of impermeability to biocide from part of the cytoplasmic membrane. Among the factors that can explain this natural resistance are elements such as the outer membrane of Gram negative bacteria, the waxy cell wall of mycobacteria, slime, the biofilm or the exopolysaccharide surrounding some bacteria as well as the specific structure of the bacterial spore. Acquired resistance can be chromosomic or plasmidic. It concerns, for instance, the chlorhexidine and quaternary ammonium compounds groups.

The chromosomic acquired resistance occurs through mutation. It is observed on Gram negative bacteria such as *Serratia marcescens* or *Pseudomonas aeruginosa* through an outer membrane modification [94]. Plasmidic acquired resistance corresponds to the modification of the outer membrane within Gram negative bacteria. Among staphylococci, it can be explained by the presence of *qac* plasmidic genes [95] which are associated with an efflux mechanism towards cationic biocides (chlorhexidine and quaternary ammonium compounds) [96, 97]. This resistance corresponds to an increase in Minimal Inhibitory Concentrations (MIC) values. Other genes have been described such as *psk* gene which encodes resistance to chlorhexidine or the *mer* gene encoding resistance to mercurial components [98].

3.5.2 Antimicrobial Textiles

3.5.2.1 Definitions

It is not easy to define an antimicrobial textile, which commonly refers to textiles that act against bacteria. Due to recent developments, these must be differentiated from antiviral and antifungal textiles.

3.5.2.2 Main Applications

Hygiene

Antibacterial textiles were the first on the market- the first publication dating back to 1967 [99]. Their definition depends on their use.

If a textile is meant to be worn, it must respect the balance of the skin flora (discussed earlier) and not be aggressive. In this case, it will have to offer a bacteriostatic activity that prevents the development of bacteria instead of bactericidal activity which would destroy bacteria. As a matter of fact, the destruction of the skin flora could lead to a decrease in non-specific immune defenses which that flora represents.

However, as of now, no study has managed to compare the *in vitro* activity of a textile versus an *in situ* activity, or in real life conditions. Renaud et al. [100] have shown that a textile with a very high bactericidal activity in the laboratory killing practically more than 10^8 bacteria within 24 h corresponding to a 8 log reduction, had only a 50% efficiency in real life conditions. This finding shows that the temperature, humidity, and pH conditions as well as the behavior of bacterial strains can vary according to the situation (location). It is thus very difficult to apply the results obtained in a lab to real life experiments.

The aim of antibacterial textiles is to offer better hygiene by limiting the proliferation of bacteria. The applications concern mainly underwear, bed linens and carpets [101]. These textiles cannot in any way claim a medical action such as prevention of skin diseases, athlete's foot or venereal diseases for example. If it were the case, they would obey specific rules. Antibacterial textiles are designed to improve well-being. By stopping the development of bacteria, they limit the production of body odors by bacteria such as *Propionibacterium* or *Corynebacterium*. Presently, there is a growing interest in viral textiles which could be used as means of protection against all sorts of flu epidemics [102].

Textile Protection

Microbial attack is potentially one of the most insidious and destructive causes of damage to textiles [103]. Antifungal textiles have been mainly developed for the protection of the textile itself and a better preservation of the characteristics of the fiber. This covers generally outdoor-textiles such as Venetian blinds, swimming pool liners, shower curtains, tents, or parasols. Dampness favors the development of microscopic fungi which can damage the textile and cause permanent coloring [104]. Additional details can be found in literature [103].

Hospital Applications

The hospital is a particular place where multiresistant bacteria to antibiotics are encountered. As previously mentioned, textiles and passive surfaces can be reservoirs for infections. That is why one of the main goals of research in that field is to develop textiles which could be efficient against nosocomial infections [100, 105]. Present methods turn to nanotechnologies, particularly the use of plasmas [106, 107].

Other Applications

Some researchers focus on the development of very specific textiles for military purposes that could very rapidly destroy bacteria, fungi, viruses and even toxins as soon as they come in contact with the textile. As this textile would be very aggressive for the skin, it is thus essential to avoid any contact between the outer part of the garment and the skin [101].

Table 3.5 Biocides used in antimicrobial textiles

Organic	Inorganic	Others
Quaternary ammonium salts	AgCl	Extracts from marine brown algae
Oxydated cellulose	$AgNO_3$	Aloe extract
Chitosan	Apatite-coated titanium dioxide (TiO2)	Cypress oil
Cyanogen	Metal ions: Ag, Cu, Zn	
Iodine	Copper oxide	
Imidazole	Magnesium peroxde	
Aliphatic imide	Sulfur	
Isothioazolinone	Copper sulfide, silver sulfide	
N-halamine (Chlorine)	TiO_2	
Organosilane	Zeolites (with Cu, Zn, Ag)	
Phenols, polyphenols		
Polyethylene Glycol		
Polyhexamethylenebiguanide (PHMB)		
Sulfadiazine Silver		
Triclosan		

3.5.2.3 Main Active Components in Antimicrobial Textiles

The main active components are triclosan and quaternary ammonium compounds. Nowadays, the use of triclosan is very controversial since it has been demonstrated that even in minimal dose it could act as an antibiotic against a specific target and cause possible resistance [108]. Those minimal doses could be equivalent to those that can diffuse from a product, e.g., textile, which contains triclosan.

Triclosan is a preservative in a great number of household products, particularly toothpaste. It could represent a potential danger by developing a resistance to the antibiotics of the bacterial flora [109]. A recent study shows that almost three quarters of the population have triclosan present in their urine which means that the molecule is overused in a lot of daily life products [110]. Yet, it does not seem that the doses found in healthy persons present any toxicity [111].

Quaternary ammonium compounds are also very much in use because their antimicrobial spectrum is very wide. PHMB (polyhexamethylene biguanide) was successfully tested on hospital white coats [112]. Chitosan is a natural antimicrobial derived from the chitin of crustaceans. As shown in Table 3.5, there are several types whose antibacterial activities differ [113].

Mineral Substances

Zeolites (sodium aluminosilicates) can be used as supports for ions such as Ag+and Cu++ or Ag+et Zn++ and have been used for a very long time [100]. Other supports have been used such as ceramic or glass particles which contain silver. Silver and copper can also be directly fixed on textile fibers [114]. Their use in nanotechnology reduces their necessary amount and thus the production cost [115, 116]. Copper oxide is also used and presents interesting possibilities such as reducing the risk of skin pathologies in diabetics by using copper impregnated socks [117]. Apatite-coated titanium dioxide fixed to textiles is active but needs light to activate photocatalysis [118].

Natural Substances

Studies are being carried out on natural antimicrobial products for textile applications. Aloe extract, Cyprus oil, algae extract, essential oils have potential applications. Nevertheless, there are still some problems regarding reproducibility, traceability, and toxicity of the products [119].

3.5.2.4 Process for Making Antimicrobial Textiles [120]

Impregnation

Textiles are simply soaked in an active product. The process is easy but presents a major drawback: the product does not firmly adhere and easily detaches itself. That is why it cannot be used on the skin except for plasters. It does not resist washing.

Starching

An active agent is mixed with a binding agent (polymer) that adheres to the textile. Resistance to washing is five times better than single impregnation but it remains insufficient for long lasting applications. These two processes are often used with organic components that cannot stand high temperature.

Fiber Mass Treatment

An active component is mixed during the spinning process. If the antimicrobial substance cannot stand a high temperature, they are dissolved and cannot be incorporated into the fiber. This is the case for organic substances such as triclosan or chitosan microcrystallites. It is possible to use a fusion process only in the case of mineral products. Figure 3.2 shows zeolite included in a textile fiber.

Microencapsulation

Microcapsules containing an antimicrobial agent adhere to the textile using a binding agent. The textile becomes active only when the microcapsules are broken while wearing the garment. Resistance to washing is thus limited [121].

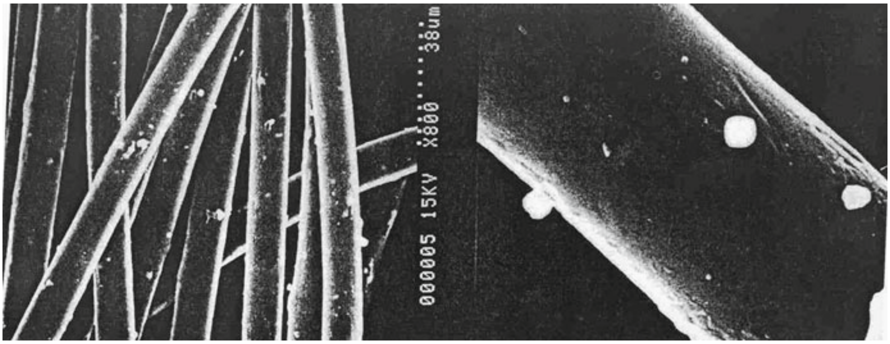

Fig. 3.2 Zeolites fixed on polyester fibers under electronic microscope [120]

Grafts

Molecular Graft

A beam of electrons produces radicals on to which active monomers bind themselves. Therefore, it is possible to graft antimicrobial substances to natural textiles. Real covalent bindings are produced and are very resistant to washing.

Chemical Graft

The active molecule is bound to the textile via a chemical method. This method is not in use very much at this time.

3.6 Methods of Textile Antimicrobial Activity Analysis

It is essential to be able to measure antibacterial activity of textiles *via* standardized methods before marketing them. Nowadays, a large number of methods coexist but they do not measure the same antibacterial ability of textiles [73]. All the standards generally use bacterial strains that are representative: *Staphylococcus aureus* (Gram positive coccus), *Klebsiella pneumoniae* or *Escherichia coli* (Gram negative bacilli).

3.6.1 Qualitative Methods (Agar Diffusion Test)

This method consists of putting a sample of textile on an agar medium that is inoculated with a bacterial suspension. Two possibilities present themselves: either the

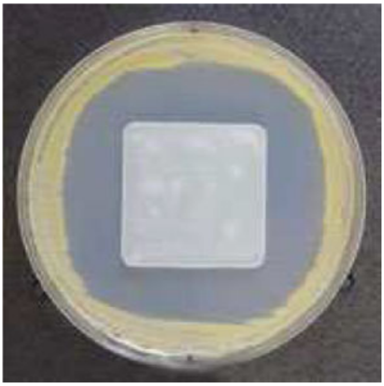

Fig. 3.3 Example of an agar diffusion test

antibacterial product can diffuse and can leave the sample, or it does not diffuse. If the antibacterial product diffuses into the agar solution after incubation (for example antimicrobial disposable wipes), there can be an inhibition zone (see Fig. 3.3) of the bacterial growth around the sample (principle of antibiogram). A certain number of standards are based on this principle: SN (Swiss Norm) 195920, AATCC (American Association of Textile Chemists and Colorists) 147, AATCC 90, NF EN ISO (International Organization for Standardization) 20745. Similar methods put forward the diffusion of antifungal products: SN 195921, AATCC 30.

That inhibition zone (Fig. 3.3) whose size is proportional to the diffusion of the active molecule means that the molecule leaves the sample. This could have two main consequences: (*i*) the possible toxic effect of the molecule when in contact with the skin could have harmful effects on the skin microbial flora or even pass on to blood; and (*ii*) the textile when losing its active molecules also loses its active principle.

In the case where the active agent is strongly bound to the textile or if it is not water-soluble, it won’t diffuse from the sample. Two cases present themselves in that situation: either the textile is active and when lifting the sample, no growth under the sample is visible, or the textile is inactive and when lifting the sample, bacterial growth will be present (Fig. 3.4).

3.6.2 *Quantitative Methods*

Those tests determine antibacterial activity of textile in a more efficient way. They are called challenge tests since a specific amount of bacteria are deposited on the sample then measured after an 18-hour incubation. Two methods are currently used.

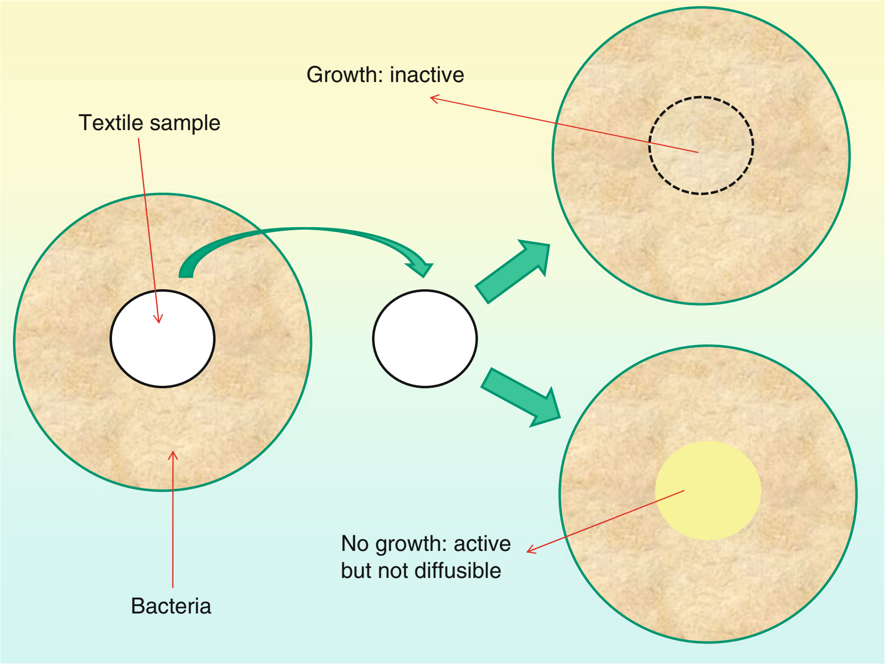

Fig. 3.4 Principle of agar diffusion test in a case of a non-diffusing agent

3.6.2.1 AATCC 100

It consists of depositing a bacterial suspension on a number of textile samples capable of absorbing such volume. After incubation at 37°C over 24 h, the bacteria are extracted either by shaking the sample by hand, or by a “stomacher” method and then counted. This number is compared to that of the bacteria introduced at the beginning and the reduction percentage is calculated. This method is only valid for textiles which are sufficiently hydrophilic and fully absorb the quantity of inoculum.

3.6.2.2 ISO 20743 Norm

This is the only ISO certified norm. It includes the former JIS (Japanese International Standard) L 1902 and XPG 39010. As it does not always have a control that corresponds exactly to the kind of the textile to be treated, one generally uses the “universal control” cotton to be the textile control (C). Samples of textile are inoculated with a bacterial suspension that differs according to the properties of the textile to

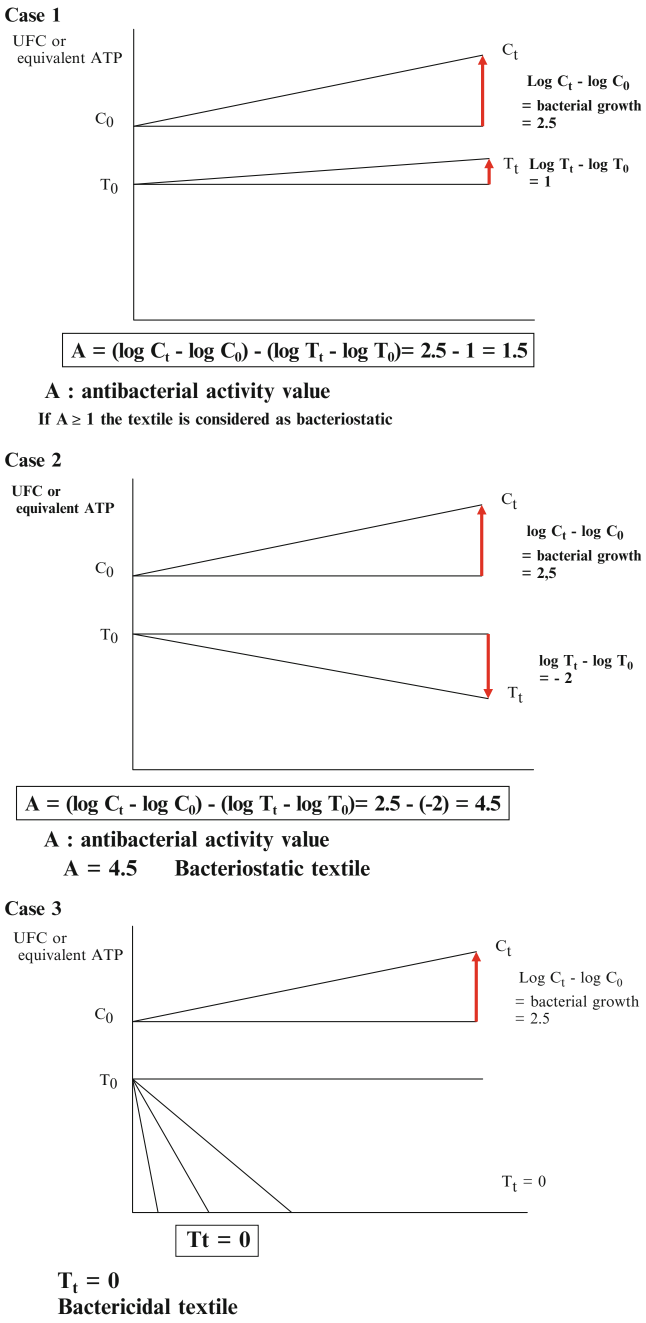

Fig. 3.5 ISO 20743 Standard for antimicrobial textiles: personal interpretation of the authors

be analyzed. If the textile is hydrophilic, the inoculation of the sample will be *via* the "absorption method." A control textile (C) without activity is inoculated in the same way. If the textile is hydrophobic or if we only want to test a side of the sample, the side to be tested will be laid on the agar previously inoculated with bacterial inoculum. A weight placed upon the textile allows for close contact between textile and bacteria to be transferred.

The bacteria are measured at time zero (T_0) and 24 h later (T_{24}) on the active and control textiles. The antibacterial activity is evaluated by calculating the difference between the value of the growth obtained on the control textile and that of the antibacterial textile (Fig. 3.5). This method has several advantages: (*i*) bacterial growth during the test is carried out on diluted growth medium which is very close to real life; (*ii*) the calculation process allows the use of the control textile whose physiochemical properties are different from those of the active textile; and (*iii*) this method is ISO-normalized. A similar quantitative ISO method for antifungal textiles is being set up. Other methods such as the "Shake Flask method" are used less often now.

3.6.2.3 Safety Control

Whenever antimicrobial textiles are in close contact with the skin, it is essential that the active agents remain totally harmless to the individuals. In France there are specific tests to control the absence of toxicity. They include a cytotoxicity (ISO 10993–5), a genotoxicity (ISO 10993–3), an irritation (ISO 10993–10) and a sensitization (ISO 10993–10) tests.

3.7 Conclusion

The bacteria present in the atmosphere settle on various surfaces – solid and/or textiles – on which they can multiply, or at least survive, sometimes for quite a long time. Those surfaces then become a potential reservoir of bacteria responsible for cross-contaminations between humans. This may be particularly dangerous in hospitals with immunosuppressed patients. At present, thanks to new technologies we can create bacteria-free surfaces and textiles, even fungi or viral-free surfaces. The use of such surfaces could lead to a better hygiene for people at large, limit the occurrence of nosocomial infections or play a protective part against possible biological weapons of microbial origin.

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Chapter 4
Assessment of the Coupled Heat and Mass Transfer Through Protective Garments Using Manikins and Other Advanced Measurement Devices

René M. Rossi and Agnes Psikuta

Abstract The assessment of the coupled heat and mass transfer in protective clothing is very complex as the layers of the system are a combination of fabric and air layers that constantly change with the movements of the wearer. The methods to measure these mechanisms become more and more sophisticated which increases the precision of models to predict the impact of heat and moisture fluxes on the human thermal physiology. The simulation of the human thermoregulatory mechanisms requires the combination of physical models representing the body (manikins) with physiological (mathematical) models. This chapter gives different examples of advanced measurement methods to characterize the thermal properties of fabrics and garments.

4.1 Introduction

The human body has to keep a thermal balance between heat production and heat loss in order to avoid either heat stress or hypothermia. However, as protective clothing is often bulky, thick and heavy, the heat and moisture exchange with the environment is limited. Therefore, the users of such clothing often face problems of increased core temperature and reduced working times. The analysis of the heat and mass transfer of single fabrics as well as multilayer clothing combinations is, therefore, important to predict the thermal status of the body for different activities and environmental conditions.

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Different mechanisms of heat and moisture transport occur in textile layers. They depend on several fabric parameters such as thickness, density, porosity, capillary sizes, or moisture absorption and adsorption properties. In ready-made clothing, the sizes and designs of the different layers determine the air layers as well as the contact area between the textiles. The thermodynamic processes of the coupled heat and mass transfer in these porous textile media are very complex, as the morphology of the textile/air layers combinations is continuously changing due to the movements of the wearer.

There are two distinct approaches to analysing the heat and moisture transfer from the body to the environment through multilayer textile combinations. The clothing can be described as a simple barrier to thermal transfer and to water vapour without considering the coupled phenomena of heat and mass transfer within the textile layers (evaporation and condensation of moisture with the associated change in the thermal state of the layer). This approach is mainly used to predict the impact of specific environmental conditions, clothing types and body activities on the heat balance of the body. On the other hand, the textiles can be analysed microscopically considering the thermal properties of the fiber-air-conglomerate in a one- or two-dimensional approach. Although some attempts were made to apply such a microscopic model to the transient heat and mass transfer mechanisms of whole clothing ensembles [21], the validation of such models remains limited.

4.2 Coupled Heat and Mass Transfer Through Textiles

From a physical point of view, textiles can be considered as porous media. In terms of heat and mass transfer, the fabric consists of three different fractions such as fibers, air and water, with defined thermal conductivity, heat capacity, diffusion constant, material absorbance and wicking properties. Different mechanisms define the thermal and moisture transport through fabric layers:

- Dry (conductive, convective and radiant) heat transfer, depending on the temperature gradient across the fabrics and the heat transfer coefficients.
- Thermal energy storage within the fabric.
- Diffusion of water vapour molecules through the pores of the textile. This water vapour transfer is determined by concentration or partial pressure parameters.
- Adsorption and migration of water vapour molecules and liquid water along the fibre surfaces, as well as transport of liquid through the capillaries between the fibres and the yarns. The driving forces of these phenomena are primarily the surface tension and the capillary forces.
- Absorption and desorption of water vapour, with the associated heat of sorption. This process is dependent on the hygroscopicity of the fibres.
- Evaporation of liquid with thermal energy consumption or condensation with thermal energy release.

These mechanisms of heat and moisture transport can be described by general conservation equations. By simplifying these equations (one dimension, steady-state conditions) and considering no interaction between heat and moisture within the layers, the heat and mass transfer can be described using basic materials characteristics like the thermal conductivity coefficient or the porosity. However, if an aggregate change of moisture takes place, the mechanisms become very complex and have to be described semi-empirically. This is the reason why efforts are made to develop human-like devices to study these phenomena in near-to-practice conditions.

4.3 Measurement of Fabric Parameters

4.3.1 Thermal and Water Vapour Resistances

The steady-state dry heat transfer through a single fabric layer occurs predominantly by thermal conduction. The thermal insulation of the textile is usually characterized by the thermal resistance R_{ct} [m^2K/W] which is dependent on the thickness and the thermal conductivity of the fabric. The thermal resistance is measured by determining the dry heat flux through the layer for a defined temperature gradient across the textile:

$$R_{ct} = A \cdot \frac{(T_s - T_a)}{Q} \tag{4.1}$$

with T_s: Temperature on the inner side of the textile layer [K]
T_a: Temperature on the outer surface of the textile layer [K]
A: surface area of the textile layer [m^2]
Q: heat delivered through the layer [W]

In air layers between single clothing layers, the dry heat transfer mechanisms depend on the air layer thickness. If the air layer is thinner than a critical thickness (around 8 mm [36]), the heat transfer will mostly occur through conduction. Above the critical thickness, natural convection will start and the dependency of the air insulation on the air layer thickness becomes non-linear.

Similarly, the steady-state water vapour transfer is described by the water vapour resistance Ret [m^2Pa/W], which is determined by measuring the heat used to evaporate moisture in relation to the water vapour partial pressure gradient across the sample:

$$R_{et} = A \cdot \frac{(p_s - p_a)}{Q} \tag{4.2}$$

with p_s: partial water vapour pressure on the inner side of the textile layer [Pa]
p_a: partial water vapour pressure on the outer surface of the textile layer [Pa]

A: surface area of the textile layer [m^2]
Q: evaporative heat loss [W]

There are many methods described in national and international standards to determine either the thermal resistance, or the water vapour resistance (respectively the water vapour permeability) of fabrics [33].

4.3.2 Liquid Transport

The third main parameter describing the transport properties of a textile layer is its ability to absorb and transport liquid moisture. This wicking effect of the fabric can either take place within the layer (in-plane or lateral wicking effect) or transport the liquid in the transverse direction to the surface, respectively between different layers in a multilayer combination (transplanar or vertical wicking effect). There are also different methods to measure the ability of the textile to wick moisture [33]. A new standard [1] based on the work by Hu et al. [15] describes the moisture management tester which is a method to determine the lateral wicking on both sides of a fabric. This method is designed especially to assess the non-uniform distribution of liquid in two-ply fabrics. However, it only assesses the distribution of water at the surface of a fabric, but give no information about the wicking properties within a material. In the past few years, different advanced (touchless) experimental techniques were used to characterize the transient liquid water transport in textiles without changing the microclimatic conditions during the measurements. Leisen, Beckham and their co-workers used Magnetic Resonance Imaging (MRI) to study the moisture transport in different textiles [5, 18–20]. Bencsik et al. [2] used Nuclear Magnetic Resonance (NMR) to quantify the liquid ingress of oil into fabric layers. Neutron Radiography was also used as another non-destructive and very fast method to qualitatively localize the presence of water in textiles [27, 38]. X-ray radiography and tomography was also used to analyze the water flow in porous materials [4, 30] and especially textiles [16, 34, 39].

4.3.3 An Example of Highly Coupled Heat and Mass Transfer: Hot Steam Flow

A particular example of the coupled heat and mass transfer is represented by the flow of hot steam due to high amounts of thermal energy that can be transferred by this form of mass transport. In a firefighter's working environment, steam can be present because of several factors. Nowadays, the fire attack tactics often consists in spraying very small water droplets onto the fire to reduce its temperature. This procedure leads to high amounts of evaporated water which create a very high water vapour partial pressure. As the water vapour pressure in proximity of the body is usually lower, a steam flow may occur towards the body. On the other hand, a firefighter on duty produces large amounts of sweat that mostly remain in the clothing layers due to their low overall water vapour permeability. When the firefighter approaches a fire, the high temperature may induce the evaporation of the moisture stored in the textile layers and thus the formation of hot steam. The analysis of the effect of steam on the human body therefore has to account for both cases such as a steam flow generated either from outside or inside the clothing layers.

It is very difficult to analyse the transfer of hot steam, as classical measurement devices have limited validity in this case. Humidity sensors usually have a too long response time and are sensitive to high moisture concentrations and temperatures. Therefore, steam flows are usually assessed with temperature sensors. However, with these sensors, the steam flow is actually not directly measured. They can only assess the heat released by the condensation of steam onto their surface. Thus, temperature sensors cannot differentiate between a dry heat flux and a steam flux, i.e. a moisture-assisted heat flux.

In different studies, the protection of fabric layers against external steam sources has been analysed. With different measurement methods, our group showed that the transfer of hot steam correlated well with the water vapour resistance of the material combination [31, 32]. This means that materials with high water vapour permeability are inclined to offer a reduced steam protection. Similar results were found by Desruelle and Schmid [6] who systematically analysed the heat flux through an aramid/viscose fabric in combination with a non-breathable polyethylene foil. The heat flux was analysed by placing a calorimeter behind the material combination and exposing the system to a steam flow produced by a generator set to a pressure of 3 bar. The highest heat flux was measured with the aramid/viscose fabric without the PE-foil. When the foil was placed behind the fabric (i.e., between fabric and sensor), the heat flux course was similar than without foil, but the intensity of heat transfer was reduced. The lowest heat flux was measured with the foil placed in front of the fabric. This result can easily be explained by the fact that the steam could not penetrate the foil and therefore, the heat transfer was reduced when the foil was placed in front of the fabric. When the foil was placed behind the fabric, steam could flow through the fabric and only condensed on the foil near the sensor. Therefore, the heat flux was much higher in this case. Similar experiments were conducted by Sati et al. [34] and here again, the water vapour impermeable material showed the best protection against a hot external heat flow.

The formation of steam under the action of an external heat source within clothing layers is very difficult to monitor due to the limitations of humidity sensors discussed previously. Therefore, we combined the use of temperature sensors and an X-ray radiography analysis to monitor steam formation and migration [17]. With this method, we were able to demonstrate that steam is formed in an outer layer of a firefighters' protective assembly previously wetted and that it flows towards the inner layers. This proves that large amounts of heat may be transferred by evaporation of moisture and re-condensation in skin proximity.

4.4 Cylindrical Model

4.4.1 The Sweating Torso

In order to analyse the coupled mechanisms of heat and mass transfer by considering both the evaporation of moisture with associated heat loss and the condensation of water vapour with release of heat, the dry heat, the water vapour as well as the liquid transport have to be combined into a single physical model. One method would be to try to replicate the thermal physiology of the human body by using a cylindrically-shaped apparatus. Such a device called torso was developed at Empa about 15 years ago. Its measuring cylinder with dimensions of the human trunk is heated from inside by heating foils and temperature sensors placed on its outer surface allow a regulation of the surface temperature. Sweating nozzles are distributed evenly over the surface of the torso and release moisture in liquid form to simulate sensible sweating. Fabrics or ready-made garments are placed around the torso. Usually air layers are avoided between the torso and the sample, but these can also be simulated by using spacers of a defined thickness.

Tests using the torso consist of three phases (Fig. 4.1). During the first phase, the surface temperature of the torso is regulated at 35°C. The heating power needed to maintain the surface temperature constant is measured and the thermal insulation (respectively the thermal resistance) can be calculated. During the second phase, a defined activity of the human body is simulated. This means that the heating power is fixed at a defined value (e.g. to correspond to 500 W for a human) and liquid is released through the sweating nozzles (e.g. to simulate a sweating rate of 1 l/h for a human). During this phase, the change of surface temperature is recorded. This reduction of temperature due to the evaporation of the released water is a measure of both the wicking efficiency of the sample and the evaporation rate. The decrease is also related to the dry thermal insulation of the fabric. In the third phase, a rest period is simulated by setting the heating power to correspond to the heat production of a man at rest (100 W), without water release. The remaining humidity in the textile layers induces a further reduction of the surface temperature until the moisture has completely evaporated. After this time, the surface temperature starts to increase again. The time at which the temperature is minimal is measured as the drying time and gives an indication of a possible “post-exercise chill”.

4.4.2 Development of the Winter Clothing Concept for the Swiss Army Using the Sweating Torso

In order to develop protective clothing with adequate thermal comfort properties, the expected range of environmental temperatures and the activities of the users have to be known. The three main clothing criteria for a balanced thermal comfort are the (dry) thermal insulation, the evaporative cooling efficiency during the activity,

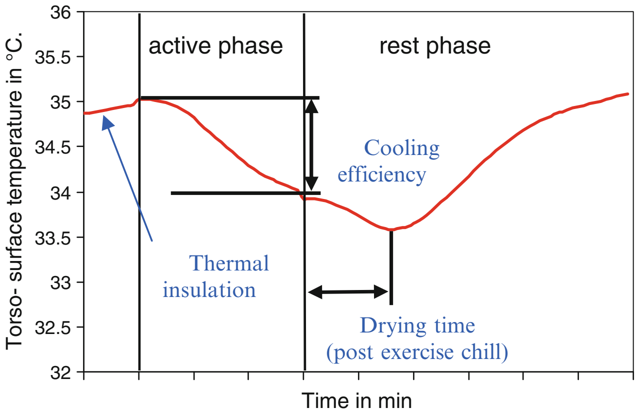

Fig. 4.1 Typical surface temperature of the torso during a three-phase measurement

as well as the drying time at rest. These three parameters can be measured simultaneously for instance using the sweating torso (Fig. 4.1).

The cooling efficiency not only determines how quickly the sweat produced by the body can evaporate, but also where this evaporation takes place. When several clothing layers are worn, sweat may be absorbed by the underwear and wicked further to outer clothing layers. Therefore, if the sweat does not evaporate directly on the skin, the cooling efficiency will be reduced. Nielsen et al. [24] showed that the evaporation of sweat in outer layers of a multilayer combination extracted only about 25% of thermal energy from the body compared to sweat evaporation near the skin. Havenith et al. [13] measured the evaporative cooling of multilayer protective clothing with a thermal manikin. They showed a discrepancy between the evaporative heat loss measured on the manikin and the expected heat loss due to liquid evaporation measured gravimetrically.

After an activity, the thermal insulation of the clothing should be restored very quickly to avoid a post-exercise chill. This means that the moisture remaining in the clothing layers after the effort has to be evacuated from the textiles as fast as possible.

Depending on the expected conditions of use, the three criteria may be more or less important. For the Swiss Army, three typical scenarios were developed:

- Marathon
  This scenario describes conditions where the metabolic heat production is very high. In order to avoid an increase of core temperature, the evaporative heat loss has to be maximized.
- Intermittent efforts
  In these conditions, the activity of the users change from high metabolic heat production followed by periods at rest. Therefore, on one hand, the cooling efficiency has to be high but on the other hand, the drying time of the clothing also has to be very short.

Table 4.1 Importance of the three thermal comfort criteria for three selected scenarios

	Marathon	Intermittent	Polar
Thermal insulation	Low	Medium	High
Cooling efficiency	High	High	Low
Drying time	Low	High	High

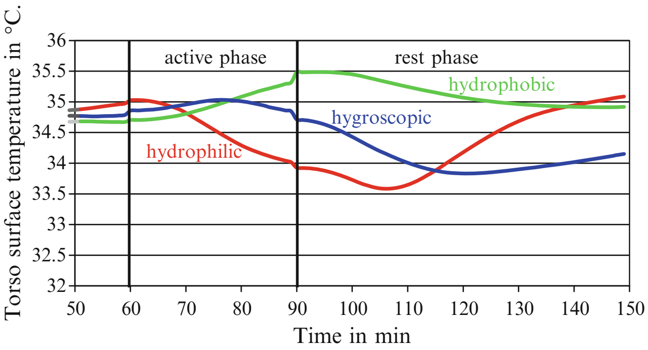

Fig. 4.2 Surface temperature course for three typical kinds of materials (hygrscopic cotton sample, hydrophilically treated PES sample, and hydrophobically treated PES sample)

- Polar conditions
  This scenario describes conditions with low metabolic heat production. Therefore, no liquid sweating is expected in these conditions. However, should the body still sweat, then the thermal insulation of the textile layers wetted by the sweat has to remain as near as possible to the dry thermal insulation and the drying time has to be very short.

For these reasons, the importance of the three thermal comfort criteria was defined according to Table 4.1 for the three different scenarios.

During the first phase of the project, a market screening was performed. The materials typically had three distinct behaviours depending on their bulk and surface properties (Fig. 4.2):

- hygroscopic materials first absorb the liquid and store it within the fibers. Therefore, at the beginning of the sweat phase (active phase), the surface temperature of the torso increases due to the higher heating power. Once the hygroscopic sample is saturated with water, the excess water evaporates, which leads to a decrease of temperature. The rate of temperature decrease is dependent on the dry thermal insulation and the evaporation rate from the fabric. At the end of the sweat phase, there is still a considerable amount of moisture stored in the sample and therefore, the temperature continues to decrease for a long time.
- a hydrophilic material usually has good lateral (in-plane) wicking properties. The sweat coming out of the nozzles can therefore quickly be distributed on a large surface, which leads to a high evaporation rate. The surface temperature thus starts decreasing shortly after the onset of sweating. On the other hand, the

remaining moisture at the end of the activity phase is low and therefore, the drying time in the rest phase is short.
- the hydrophobic material is not able to absorb the liquid and the lateral distribution is also poor. Therefore, the released liquid stays in the proximity of the sweating nozzle or drips off from the sample. As the evaporation only takes place from a limited surface, the cooling efficiency is very poor.

In the second phase of the project, new knits based on polyester were developed. The inter- and intra-yarn capillary transport was optimized by varying the number of filaments in the yarns, the knitting type and the surface treatment of the fibers. At the end of the project, a new technical specification was developed based on torso measurements and minimum requirements were set. It was decided that one of the key parameters was a delay of water evaporation in relation to the onset of sweating. Therefore, the temperature reduction after 10 min of sweat release was set at a minimum of 1.2°C and after 60 min at 2.0°C as a requirement for the underwear. The drying time should not exceed 5 min.

The complete clothing concept for the Swiss Army was conceived to be based on four different layers of clothing:

- a polyester underwear with hydrophilic treatment for high evaporation rate and quick drying time.
- a second layer made of polyester. This layer is also treated hydrophilically to allow excess sweat that might not be absorbed by the underwear to be buffered.
- the third layer is a polyester fleece. The outer side of the fabric is treated hydrophobically to prevent the wetting of this layer by possible condensation.
- the fourth layer is a highly water vapour permeable rainwear.

The clothing combination was then validated with human subjects in the lab and in the field. Most of these results are classified and can therefore not be published. However, the measurements clearly showed that the new layer concept had a much higher evaporation rate than the old combination made of hygroscopic fibers. Furthermore, the subjective thermal sensation was indicated as being less warm for the new combination during activities and less cold during a subsequent rest phase. The field tests confirmed these findings and the new concept was recently implemented in the troops.

4.5 SAM – Sweating Agile Manikin

4.5.1 Method Description

Thermal manikins are the most advanced devices for clothing research due to their anatomic shape and their ability to sweat and move. The first manikins were developed in the early 1940s, and the interest in using thermal manikins in research and product development has increased continuously over the past 20 years as indicated by the number of manikins being developed and manufactured. Currently, there are

Fig. 4.3 SAM – Sweating Agile Manikin

probably far over a 100 different manikins in use worldwide [14], but most of them simulate only the dry heat transfer from the body, without taking into account the production of sweat. Apart from clothing research, these evaluation instruments are nowadays implemented in a wide range of disciplines including automotive industry, environmental engineering, and the design of artificial microclimates for human occupancy.

In general, there are two different directions of thermal manikin development. One is represented by simple, yet accurate, reliable and rather inexpensive manikins [7, 8] which are meant to satisfy the needs of occupational hygienists or quality control officers of clothing manufacturers. The other direction of development takes a more sophisticated, multi-functional approach for research and advanced testing [9, 28]. These manikins are high-performance instruments, although they tend to be fragile and expensive. The system developed by Empa was named SAM (Sweating Agile thermal Manikin) and is one of the most advanced manikins today.

SAM's anatomically-formed body is divided into 30 separately-heated sectors, consisting of 26 shell parts and 4 heated joints (knees and elbows) (Fig. 4.3). Shell parts are moulded from a plastic mixed with aluminium powder, which increases the thermal conductivity of the relatively thin-walled shells and promotes temperature uniformity. The inner surface of each shell has a constantan wire wound onto it, which acts as a heating wire. A platinium wire wound on the outer surface of each shell part is used to measure its average surface temperature. Specially developed electronics and software enable each sector to be heated to a constant temperature or with a constant power, using just one power supply for all shell parts. The maximum total heating power is 1.2 kW, which relates to a very high level of human muscular activity.

SAM has 125 sweat outlets distributed over its surface. Although the human skin has millions of sweat glands, the outlets have been positioned to ensure a sweat distribution roughly similar to the human. Distilled water is used to simulate sweat, supplied through SAM's face to internal valves, which are used to regulate the flow. A very tightly fitting garment is used as a second skin which covers the outlets ensures that all the water evaporates at the surface (no immediate drip-off). Thanks to this second skin, SAM is suitable for simulation of both low sweat rates corresponding to insensible sweating and higher sweat rates corresponding to sensible sweating with vapour and liquid water as an output. The total sweat rate is controlled using a precision balance to measure the reduction in weight of water in the supply tank external to SAM. The total amount of moisture within the clothing is determined by monitoring SAM's weight. The sweat rate can be varied from 20 ml/h up to at least 4 l/h to simulate all possible activities and conditions.

SAM is also equipped with a walking system. The limbs are connected to 2-axis motors that allow SAM to perform realistic movements. Joints at the shoulders, elbows, hips and knees enable each limb to be moved in a vertical plane. The curves are defined with a series of points and spline interpolation is used to ensure a smooth curve of acceleration and deceleration. Thus, repetitive body movements such as walking and climbing can be performed during an active test phase.

SAM is positioned within an environmental chamber, which can be operated at temperatures between −30°C and 40°C and relative humidity between 30% and 95%. A wind generator which is usually positioned in front of SAM can simulate high wind speeds. Heating and sweating is supplied through the face of SAM. The control unit consisting of the computer, power supply, power switches and additional electronics is positioned on a trolley outside of the climatic chamber.

4.5.2 Measurements with SAM

Due to its ability to sweat and to move, SAM can be used for the realistic and reproducible assessment of the coupled heat and mass transfer through ready-made garments. SAM was, for instance, used in the frame of the European project "Thermprotect" to exactly quantify the different components of dry and wet heat loss for well defined materials tailored into identical garments [29]. In this project, three types of measurements using SAM were conducted. The dry heat loss was measured by heating the surface of the manikin to 34°C and to set the environmental climate in the climatic chamber to a defined temperature (e.g., 10°C), relative humidity and air velocity. A second type of measurement that was done using SAM was to assess the water vapour transfer (and the evaporative heat loss) in isothermal conditions (by setting the climatic chamber temperature to a surface temperature of the manikin, e.g., at 34°C) while SAM was sweating a defined amount of water. A third type of measurement was performed in non-isothermal conditions with sweat release to get the coupled dry and wet heat loss. For these measurements, the water vapour partial pressure at 10°C was set to be equal to the one during the isothermal measurement at 34°C. Therefore, the evaporative heat loss was assumed to be the same for the measurements at both temperatures. Thus, by measuring the total heat loss during the third measurement series and by subtracting the dry heat loss (first measurement series) as well as the evaporative heat loss (second measurement series), the heat loss component due to the higher conduction of the wet layers and condensation effects could be determined. Furthermore, the moisture collected in the different layers of the system could be assessed gravimetrically.

In general, the measurements using the manikin show less pronounced differentiations between materials as compared to material tests such as the sweating guarded hotplate or a cup method. This is mainly due to the presence of air layers in ready-made garments on the manikin which add significant thermal and water vapour resistances to the overall system. Furthermore, the presence of ventilation openings allowed parts of the dry heat and the moisture to by-pass the barriers created by the clothing layers.

Although manikins provide an efficient method to characterize the heat and moisture transfer through clothing, they have some limitations compared to the human body. The body is able to adapt greatly its heat loss by changing the skin blood flow. This vasomotor response of the blood vessels leads to a rapid change of the skin temperature. Furthermore, the sweat production of the body is not constant in time (as simulated by the manikin) but it develops gradually and is influenced by the evaporative cooling efficiency. The lack of vasomotor response in the manikin leads, for instance, to an overestimation of the cooling power of cooling garments [3]. Various attempts have been made to simulate the thermal response of a human more realistically, for example, by setting uniform heat fluxes to replicate different work loads, or non-uniform surface temperatures over the body, such as cooler hands and feet [22, 23], or uniform surface temperature changing over time [36].

4.6 Development of Human Simulators

Ideally, a manikin should sense and respond dynamically to the thermal environment as real humans do. This can be achieved by combining manikins with a mathematical model of human thermoregulatory system. With this mathematical model, the manikin control system regulating the local surface temperatures and the release of sweat is adjusted to react according to the onset of vasomotor reactions adequate to the conditions of exposure (e.g., cooler extremities and warmer trunk and head during vasoconstriction). For this purpose, we used Fiala's multi-node mathematical model of human thermal physiology and thermal sensation [10–12]. It consists of a passive system representing a virtual human body with the heat exchange mechanisms occurring in it, and an active system simulating physiological reactions such as shivering, sweating and vasomotor reactions. Consequently, the model is

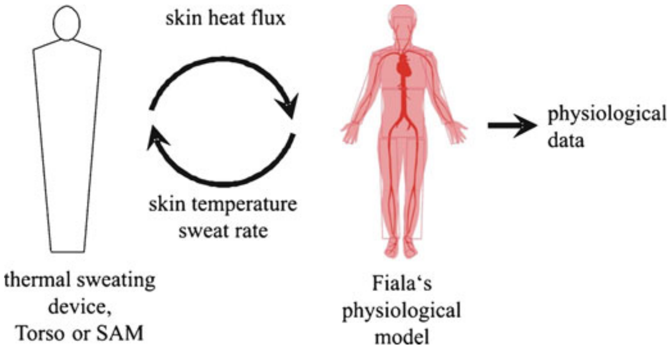

Fig. 4.4 Scheme of the data exchange in the thermophysiological human simulators

able to simulate human thermal responses under both steady-state and transient conditions.

The coupling method was first developed using the sweating torso to create a single-sector thermophysiological human simulator [25]. This work formed the basis for developing the coupling procedure for the multi-segmental thermal manikin. This procedure is based on real-time iterative exchange of the data such as the mean skin temperature and sweat rate predicted by the physiological model which are used as control parameters for the manikin and the heat loss from the manikin surface through the clothing to the environment which is used as the feedback signal (Fig. 4.4). In the course of such simulation, other physiological parameters like core temperature, skin blood flow or heart rate are also predicted.

The coupling of the multi-segmental manikin SAM is much more complex, as the 26 manikin segments should be controlled separately. Therefore, the coupling process was accomplished in two stages. First, a homogeneous surface temperature and sweat rate was set over the entire surface of the manikin. The area-weighted mean skin temperature and the sweat rates predicted by the physiological model were used as input parameters to the manikin control system for each shell part. The feedback signal from the manikin was the average heat flux from the entire manikin calculated from the power supplied to the shell parts divided by their surface area. Basically, this method was analogous to the coupling of the sweating torso. Its validation was made comparing the data with different human subject studies performed in cold and cool environments. The mean skin temperatures and the core temperatures obtained using the multi-sector thermophysiological human simulator with homogeneous surface temperatures showed good agreement with experimental data. Further details of this validation work can be found elsewhere [26].

In the second stage of the coupling process, the manikin was set up to produce heterogeneous surface temperatures and sweat rates at the various shell parts. Each shell part was controlled using an individual set-point temperature corresponding to the respective body part in the mathematical model. This time, the feedback signals from the manikin were local heat fluxes from individual shell parts.

The validation with human subject data proved to be unsatisfactory to date, as inter-segmental heat flows occurred due to the heterogeneous temperature distribution. Further work is therefore needed to quantify the heat flux occurring within the segments of the manikin in order to measure the individual heat loss of each segment precisely.

4.7 Conclusions

The prediction of the thermal comfort of the human body wearing protective clothing is very complex as it has to consider the three-dimensional geometry of the human body, the design of the clothing as well as the changing conditions due to the movements of the wearer. Therefore, the assessment of the coupled heat and mass transfer through multilayer protective clothing requires a simplification of real wearing conditions. However, advanced methods allow a more and more precise reproduction of reality. Manikins are a valuable tool to measure the heat and moisture transport through clothing in a repeatable way. By adapting the measurement parameters, the different mechanisms of heat loss can be studied and quantified separately. In the future, the use of physiological models to control the heat and sweat release of the manikins will further improve the precision of predictive comfort models.

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Chapter 5
Heat Strain in Personal Protective Clothing: Challenges and Intervention Strategies

T.M. McLellan and H.A.M. Daanen

Abstract Humans rely on sweat evaporation during exercise in the heat to promote cooling and to maintain thermal homeostasis. In protective clothing, however, sweat evaporation is severely hampered and this may lead to uncompensable heat strain, where core body temperature continues to rise leading to physical exhaustion and the cessation of work. The tolerance time depends on three main factors: (1) the initial core temperature that may be reduced by heat acclimation and pre-cooling, (2) the final core temperature, which can be increased due to physical training, and (3) the rate of change in body core temperature, which is dependent on the thermal environment, work rate and individual factors like body composition. Methods to reduce heat strain in protective clothing include: (1) increasing clothing permeability for air, (2) adjusting pacing strategy, including work/rest schedules, (3) physical training, and (4) cooling interventions.

5.1 Introduction

Humans are homeothermic creatures, and regulate their body temperature within a narrow range over the entire course of their lives [2]. When heat is generated by increased metabolic activity, humans are generally successful in maintaining a thermal steady state by activating heat-loss mechanisms to dissipate the excess heat. A hot and/or humid environment, however, imposes a major stress on the human

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body's ability to maintain physiological stability during exercise, due to a decrease in the thermal and water vapour pressure gradients between the body and the environment, thus impairing heat exchange [27]. Hyperthermia, and its attendant clinical symptoms of heat exhaustion and heat stroke, has become well recognised as a major risk encountered when exercising in hot environments [24].

In many occupational (e.g., firefighters, hazardous waste disposal, military) settings, protective clothing is required to shield the individual from environmental hazards or from injury. In these high-risk settings, any increase in psychological strain or impairment in mental functioning due to the clothing may also place the individual at an increased risk of an accident [21, 32]. Protective clothing, which is typically heavy, thick, multi-layered, and bulky, exacerbates the challenge of thermoregulation because of limited water vapour permeability across the clothing layers, further decreasing the rate of heat exchange [61].

Under certain conditions of high ambient temperature and/or relative humidity, or with the wearing of clothing ensembles that restrict evaporative heat loss, the evaporative heat loss required to maintain a thermal steady state (E_{req}) can exceed the maximal evaporative capacity of the environment ($E_{\max}$) during light exercise or even at rest. In these uncompensable heat stress (UHS) situations [26], the body constantly stores heat. This results in body temperature continuing to increase until either exhaustion (or death) occurs, or else the severity of the set of environmental conditions decreases (i.e., seeking shade or an air-conditioned room, removing clothing layers to promote greater evaporative heat loss, or being immersed in a cold water bath etc.).

While protective clothing is being continually improved and lightened, the requirement of adequate impact or environmental protection is generally contradictory to the desire for adequate ventilation. For example, the requirement to prevent hazardous liquid and/or gaseous chemicals from penetrating a chemical ensemble is often contradictory to the desire for the dissipation of metabolically generated heat. Scientific interest in the problems of exercise and heat exhaustion with protective clothing intensified following the 1990–1991 conflict in the Persian Gulf, where soldiers of the Allied coalition, faced with the threat of chemical weapons, were forced to wear nuclear, biological, and chemical (NBC) protective clothing that was originally intended for use in a temperate climate and not the hot desert environment. The major features of UHS, notably the biophysical interactions between clothing, the ambient environment, and physiology, are similar across military, occupational, and athletic protective clothing systems. In this chapter the impact of heat strain in protective clothing on performance is discussed as well as methods to reduce heat strain.

5.2 The Uncompensable Heat Stress (UHS) Environment

One approach to the problem of UHS is to explore the physiology of the human inside the clothing ensemble. Performance and heat tolerance are influenced by such individual factors as gender, age, and anthropometry. Furthermore, physiological manipulations such as hydration, training, fitness, or heat acclimation, may significantly affect individual responses to heat stress. A large body of research exists on the effects of these factors in situations where heat transfer is not impaired by clothing. However, these findings may not directly transfer over to situations where protective clothing is worn, due to the impact of clothing on heat exchange.

5.3 Heat Exchange

Mechanisms of heat transfer are grouped into two general categories consisting of dry (radiative, conductive and convective) and wet (evaporative) pathways. Dry heat exchange is dependent on the temperature gradients within the individual (e.g., core to periphery) and also between the individual and the environment. In addition, the rate of cutaneous blood flow to transport heat from the core to the periphery influences the degree of convective heat exchange. Wet heat loss arises from the evaporation of water, typically secreted by the sweat glands within the skin. The potential for evaporative heat loss is determined primarily by the water vapour pressure gradient between the body surface and the environment, which in turn may be modified both by the environment and clothing [52, 54].

When unclothed, the regulation of thermal energy exchanges between humans and the ambient environment can occur directly across the skin. When clothing is worn, however, an air layer is formed directly above the skin surface, and this microenvironment forms the initial environmental layer between the body and the environment. Multiple clothing layers form a successive series of microenvironments, each with its own thermal characteristics of temperature and humidity, through which metabolically generated heat must pass before being dissipated to the ambient environment [77]. Maximal evaporative heat dissipation from the body occurs when secreted sweat is vapourised at the skin [57]. When wearing protective clothing, much of the sweat may become absorbed into the clothing and trapped as water vapor in the intermediate air layers. The wetting or saturation of clothing by sweat may affect both the thermal or protective characteristics of the clothing and also influence the rate of heat transfer [17]. Rossi (chapter 4) shows that water vapor trapped in intermediate clothing layers may move towards the skin and lead to steam burns. In addition, the site of phase change may be raised above the skin due to the clothing microenvironment. In this scenario, a portion of the heat energy of vapourisation may come from the environment rather than the body, thus further decreasing the efficiency of evaporative heat loss [52, 61, 62].

Due to both the elevation in metabolic heat production and a decrease in evaporative efficiency, wearing protective clothing in the heat often results in an inability to dissipate generated heat which in turn leads to a continued storage of heat in the body. Due to the reduced permeability to water vapour and limited capacity for evaporative heat dissipation through protective clothing ensembles, even light exercise in a warm environment can produce a situation of uncompensable heat stress and continued heat storage in the body [43, 51, 68].

5.4 Heat Tolerance

Tolerance time is defined as the time required to reach one of several end-point criteria during the UHS exposure. The exact end-point criteria are typically driven by ethical considerations or by experimental design, and may therefore vary at different laboratories or even within the same laboratory from one experiment to another. Typically, ethical constraints revolve around the allowable increase in core temperature and heart rate; this increase in rectal temperature (T_{re}), for example, can vary by at least 1°C with typical ceilings reported between 39.0°C and 40.0°C for the use of protective clothing ensembles [3, 35, 53, 67, 71]. In addition, other factors such as nausea, ataxia, syncope, voluntary termination or a maximum length of exposure may define tolerance time. Tolerance time is influenced by three factors; the initial T_{re}, final T_{re}, and the rate of increase in T_{re} from the beginning to end of the heat stress exposure. Thus, tolerance time is determined by the heat capacity of the body ($C_{p,b}$), and the rate of heat storage ($\dot{S}$) as shown in the following equation;

$$Tolerance\ Time = \left(T_{re,Final} - T_{re,initial}\right) \cdot C_{p,b} \cdot mass \cdot \left(\dot{S} \cdot 60 \cdot A_D\right)^{-1},$$

where tolerance time is expressed in minutes, $C_{p,b}$ is in $J \cdot kg^{-1} \cdot {}^{\circ}C^{-1}$, and A_D represents the body surface area (m^2).

There is no consensus among thermal physiologists as to what limits tolerance time in the heat. Some researchers relate heat tolerance to the highest core temperature that can be tolerated prior to exhaustion [35, 54], whereas others relate heat tolerance to an increase in body heat storage (S) [84]. With the former definition, heat tolerance is affected only by those factors that alter the core temperature tolerated at exhaustion, while with the latter definition factors that influence both the initial and final core temperature, as well as the heat capacity of the body would affect heat tolerance.

5.5 Initial Core Temperature

Often overlooked in establishing heat stress tolerance time (TT) to UHS is the impact of the initial core temperature. For example, factors such as aerobic fitness [10], heat acclimation [5, 10, 59] and pre-exercise cooling [31, 36], which lower the initial core temperature, are associated with increased total heat storage and TT during UHS. Nielsen [59] examined the thermoregulatory and cardiovascular responses involved in a 12-day acclimation to a hot (35°C) and humid (87%RH) environment. Over the 12-day period, well-trained cyclists improved their cycle time to exhaustion by about 15%. Since both the rate of increase in core temperature during the exercise as well as the temperature tolerated at exhaustion (40°C) were unchanged from day 1–12, the 15% improvement was attributed entirely to the small but consistent decrease of 0.2°C decrease in initial T_c. Daanen et al. [19] observed that whole-body precooling caused a delay of about 15 min in reaching critical core temperatures. Similar findings have been reported for other hot and humid heat acclimation programs [5], including heat acclimation programs that involved wearing PPE [48], which created a hot and humid microenvironment close to the skin. Pre-cooling strategies (which are discussed below) also impact TT by lowering the initial T_c.

Conversely, factors such as hypohydration [10, 66], the post-ovulatory phase of the menstrual cycle [79] or prior immersion in warm water [31], which raise the initial core temperature, lower total heat storage and reduce TT. Cheung and McLellan [10, 11] have consistently reported that mild levels of hypohydration of about 2% of body mass increase resting T_c by approximately 0.2°C. These small changes decrease TT about 20% while wearing PPE and performing light exercise in a hot environment. Similarly, the increase in T_c of 0.3°C during the luteal phase of the menstrual phase decreased TT by 25% compared with the follicular phase when resting T_c was lower [79].

5.6 Final Core Temperature

Well-trained endurance athletes can tolerate high T_c, a phenomena that has led one group of scientists to advocate that reaching a critical internal brain T_c limited exercise performance in the heat [30, 31, 60, 63]. However, this concept has been challenged by others [40, 41, 58] and several recent studies have shown that individuals naturally slow their pace during exercise in the heat to prevent the attainment of critically damaging high internal T_c [7, 42].

Nonetheless, there are situations in the military and in some occupational settings where individuals cannot self-pace and must keep up with the rest of their peers. In such settings, it is clear that aerobic fitness is the most important individual factor for determining tolerance time during UHS. Well-trained endurance athletes can tolerate higher core temperatures compared with their less-fit counterparts [10–12, 56, 67, 71] and in some cases these differences may be as great as 1°C, translating into differences in TT of almost 100% [67]. A high level of aerobic fitness also protects the gut barrier integrity and reduces the leakage of endotoxin into the systemic circulation at any given level of thermal strain [71], and leads to cellular adaptation that reduces the pro-inflammatory response to the endotoxin and helps prevent cellular apoptosis [72].

More severe levels of hypohydration approaching 5% of body mass also have been reported to lower the T_c tolerated at exhaustion [66] and reduce TT. Closer examination of the results in this paper, however, revealed an increase in resting T_c, a finding consistent with the studies by Cheung and McLellan [10, 11] with milder levels of hypohydration. Thus, if the individual does not rehydrate properly from day to day and the state of hypohydration worsens, then heat tolerance while wearing PPE will deteriorate dramatically due to the reduction in heat storage capacity.

Simply transitioning from a low dress state to one of full encapsulation also lowers the T_c that can be tolerated at exhaustion [54], which will reduce TT. Having to wear an impermeable mask over the face and breathe through a canister can increase both physiological and psychological discomfort leading to the lower T_c tolerated at exhaustion.

5.7 Rate of Change in Core Temperature

5.7.1 Gender and Body Composition

Differences in heat tolerance between men and women while wearing PPE are largely attributed to differences in body composition [46]. In general, women have a higher proportion of body fatness compared with men. Since adipose tissue has a lower heat storage capacity, which is only about 50% of the value for lean tissue such as muscle, blood, bone and water [6], T_c will increase at a faster rate for women compared with men at any given rate of heat storage. Indeed, McLellan [46] demonstrated that the rate of increase in T_c was faster and the heat storage per unit of mass was lower for women compared with men. Additionally it was shown that only when men and women were matched for levels of body fatness did these differences disappear and tolerance times were similar between the sexes. These findings imply, therefore, that TT would be greater for lean women compared with obese men when PPE is worn in hot environments.

On average, the body surface area to mass ratio decreases from about 300 cm^2/kg at the equator to about 250 cm^2/kg in polar regions [37]. This means that people in tropic regions have a body composition that favors dry heat loss. However, this advantage is reduced when wearing protective clothing.

5.7.2 Environmental Influences

Indices of thermal strain, such as the rate of increase in rectal temperature, and cardiovascular strain, such as the rise in heart rate, reflect the increase in thermal and evaporative resistance in the progression from low to high states of protective posture (and concomitant encapsulation of the body). It is also evident that differences among the levels of protective posture become less evident as the rate of heat production, or metabolic rate, increases. The kinetics of evaporative heat loss are largely established by the characteristics of the clothing [17, 52]. High rates of activity whilst wearing protective clothing may result in situations where the rates of heat storage and heat tolerance are governed primarily by the rate of heat production and not by environmental conditions [43]. In these situations, variations in ambient water vapour pressure, which help to establish the gradient for evaporative heat loss, may have little impact on heat tolerance [43]. Craig et al. [18] and Shvartz

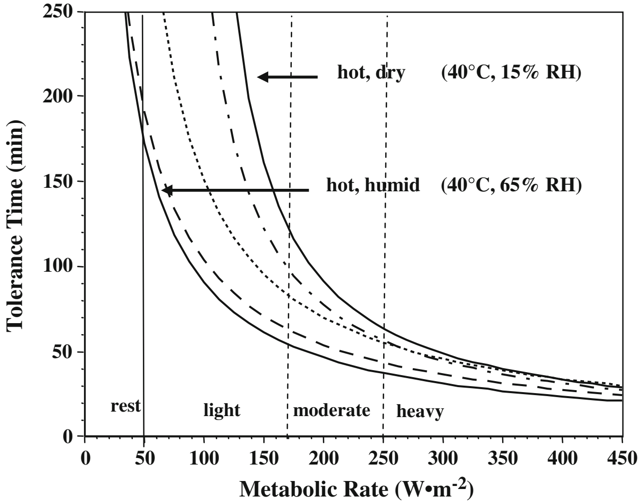


Fig. 5.1 Relationship between tolerance time and average oxygen consumption (VO_2) for the Canadian Cold War IPE worn at full protective posture. *Solid and dotted lines* represent data from various environmental conditions derived from McLellan [43] and McLellan et al. [50–52]

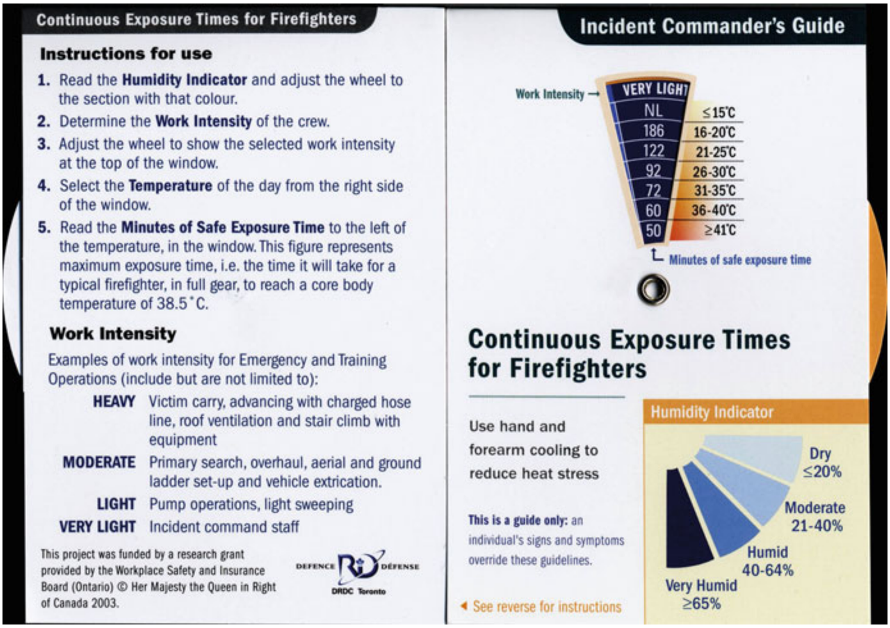
and Benor [73] first reported a hyperbolic relationship between voluntary tolerance time and the rate of heat storage. The curvilinear relationship between tolerance time and metabolic rate for different ambient temperatures and water vapour pressures while wearing NBC protective clothing is shown in Fig. 5.1. Each of these curves is accurately defined by a hyperbolic function where the vertical asymptote of the equation defines the metabolic rate that delineates compensable and uncompensable heat stress [43, 50–52]. As such, during UHS there is a continued increase in body heat storage and tolerance time is finite. Conversely, during compensable heat stress, where a thermal steady-state can be achieved, increases in body heat content, in theory, do not limit performance and tolerance times are infinite.

Figure 5.1 is also divided into work intensities classified as light (less than 170 $W m^{-2}$), moderate (between 170 and 250 $W m^{-2}$) and heavy (greater than 250 $W m^{-2}$) according to guidelines adopted for the U.S. military [28]. As the rate of heat production increases, it is apparent from Fig. 5.1 that variations in temperature and water vapour pressure have less of an impact on tolerance time. At work intensities above 250 $W m^{-2}$, tolerance times converge at approximately 50 min. Differences in tolerance time among different ambient conditions are more noticeable at lighter metabolic rates. This is because time is required for the sweat produced at the skin surface to evaporate and condense as it passes through the various clothing layers until it finally evaporates to the environment [8, 52] where the ambient vapour pressure establishes the gradient that drives evaporative heat transfer [29]. Clearly, in the dry desert conditions (40°C and 15% relative humidity) this vapour pressure gradient and resultant evaporative heat loss (and resultant cooling) will be much greater than in the humid environment of 40°C with 65% relative humidity. With lower rates of heat production these differences in the rate of evaporative cooling translate into marked differences in tolerance time. Conversely, at higher rates of heat production there is insufficient time for effective vapour pressure gradients to be established between the person inside the protective ensemble and the environment [52]. As a result, the rate of heat production becomes the primary factor determining the rate of heat storage and tolerance time.

5.7.3 Work and Rest Schedules

The curves shown in Fig. 5.1 can also be used to help explain whether implementing work and rest schedules while wearing this protective clothing is the correct strategy [44]. For example, the vertical asymptote for the desert condition (40°C and 15% relative humidity) occurs at a metabolic rate of 100 $\mathrm{W\,m^{-2}}$. At metabolic rates greater than this value there will be continued heat storage since the conditions represent UHS, whereas at metabolic rates below this asymptotic value cooling will occur since these conditions represent compensable heat stress. The reader should note that the metabolic heat production at rest is about 50 $\mathrm{W\,m^{-2}}$. If the soldier was performing a reconnaissance patrol moving at a slow speed the rate of heat production might approximate 175 $\mathrm{W\,m^{-2}}$. After 30 min of patrol core temperature might increase from 37.0°C to 38.0°C in the UHS conditions. If this were then followed by 15 min of rest, which would now represent compensable heat stress, core temperature might decrease to 37.5°C. The next 30 min of patrol would increase core temperature to 38.5°C followed again by another rest period which would lower core temperature again. A final 30-min patrol might then increase core temperature to 39.0°C where the soldier might begin to experience symptoms of exertional heat illness. Thus, in contrast to the 60 min of continuous work that would lead to core temperatures around 39°C, 90 min of total work are performed with this work and rest schedule. Therefore, in these dry desert conditions, implementing work and rest schedules is the correct strategy for increasing the total work output. However, the metabolic rate that defines the vertical asymptote for the hot and humid environment (40°C and 65% relative humidity) occurs at a non-physiological value of 10 $\mathrm{W\,m^{-2}}$ implying that even under resting conditions there will be continued body heat storage. Thus, during rest periods the soldier's core temperature will continue to increase and the next work bout will begin at an even higher core temperature than at the beginning of the previous rest period. As a result, less total work will be performed before symptoms of exertional heat illness are seen. In these very hot and humid environments, therefore, implementing work and rest schedules may not be the most prudent strategy if the objective is to move to a safer area where the protective clothing can be removed and the soldier can then cool more effectively.

Models can also be used to develop effective guidance for Commanders to predict continuous work times and provide work and rest schedules that could be adopted to



Continuous Exposure Times for Firefighters

Instructions for use

1. Read the **Humidity Indicator** and adjust the wheel to the section with that colour.
2. Determine the **Work Intensity** of the crew.
3. Adjust the wheel to show the selected work intensity at the top of the window.
4. Select the **Temperature** of the day from the right side of the window.
5. Read the **Minutes of Safe Exposure Time** to the left of the temperature, in the window. This figure represents maximum exposure time, i.e. the time it will take for a typical firefighter, in full gear, to reach a core body temperature of 38.5 °C.

Work Intensity

Examples of work intensity for Emergency and Training Operations (include but are not limited to):

HEAVY	Victim carry, advancing with charged hose line, roof ventilation and stair climb with equipment
MODERATE	Primary search, overhaul, aerial and ground ladder set-up and vehicle extrication.
LIGHT	Pump operations, light sweeping
VERY LIGHT	Incident command staff

This project was funded by a research grant provided by the Workplace Safety and Insurance Board (Ontario) © Her Majesty the Queen in Right of Canada 2003.

Incident Commander's Guide

Work Intensity → VERY LIGHT

VERY LIGHT	
NL	≤15°C
186	16-20°C
122	21-25°C
92	26-30°C
72	31-35°C
60	36-40°C
50	≥41°C

Minutes of safe exposure time

Continuous Exposure Times for Firefighters

Use hand and forearm cooling to reduce heat stress

This is a guide only: an individual's signs and symptoms override these guidelines.

◂ See reverse for instructions

Humidity Indicator

Dry ≤20%

Moderate 21-40%

Humid 40-64%

Very Humid ≥65%

Fig. 5.2 A schematic of the heat stress wheel developed for the Toronto fire service

help manage the heat strain of wearing protective clothing. If the models have been validated with human data in laboratory trials [26, 29], then there is greater confidence in their use for predicting heat strain responses in other sets of dress states, environmental conditions and rates of heat production. An example of a set of guidelines developed for the Toronto Fire Service is shown below in Fig. 5.2. In addition, software is available for download at http://www.toronto.drdc-rddc.gc.ca/CBRN for all NATO and PFP nations. This software provides guidance for all NATO dress states with the use of a tactical vest worn alone or in combination with a fragmentation vest and a host of environmental conditions and rates of heat production.

5.8 Intervention Strategies

5.8.1 New Chemical and Biological (CB) Uniforms

For the military, protective dress levels are defined that are intended to protect the soldier against the toxic hazards in the environment and safely ensure that sufficient time is available to transition from the lowest to the highest state of protection as required. Traditional CB protective ensembles employ an overgarment concept where the outer charcoal impregnated garment together with rubber gloves, overboots, mask and canister confer the desired level of protection. However, these ensembles have a high thermal resistance and low water vapour permeability and compromise soldier performance when worn in hot environments such as the Middle East [43, 54]. As a result several nations have incorporated new carbon sphere technology to develop protective garments that are designed to be worn as a stand-alone uniform and replace the need for the use of an overgarment concept [1, 22]. These stand-alone protective uniforms have a reduced thermal resistance and increased water vapour permeability when worn during full encapsulation but this is not necessarily the case when they are worn in their lowest state of protection. It is important to realize that the requirement to protect the individual against the hazards in the environment limits the extent of the improved heat transfer characteristics that can be expected in these stand-alone protective uniforms during full encapsulation with the incorporation of new carbon absorptive technology. Indeed, most of the improved heat transfer characteristics during full encapsulation for these new CB protective ensembles reflects the removal of the air and clothing layer represented by the normal combat clothing which is traditionally worn under the protective overgarment [45].

Since the requirement for protection constrains the extent of the improvement in heat transfer characteristics with these new uniforms during full encapsulation, it becomes critical to consider the impact of wearing these uniforms during a low dress state when operational conditions require the use of a lower level of protection for the majority of time and only occasional demands to transition to full encapsulation. Failure to consider this impact would generate misleading guidance about the potential benefit of these stand-alone CB uniforms. Further, if sweat rates and fluid losses are increased while wearing these new CB uniforms in hot environments during a low dress state, then fluid replacement guidelines [55] would need to be appropriately adjusted to ensure that soldiers were not becoming dehydrated prior to transitioning to full encapsulation. Improper fluid replacement can reduce heat stress tolerance during encapsulation due to a reduction in heat storage capacity [49] and a reduction in the core temperature that can be tolerated at exhaustion [66], and place individuals at a greater risk of orthostatic intolerance [9].

The incorporation of clothing vents into the design of these new CB uniforms may be one option to assist with heat transfer when the uniform is worn in a low dress state, especially if additional impermeable body armor needs to be worn to provide protection from blast and fragmentation particles. The low NATO dress state is a protective state that does not require filtration of the air exchange with the environment and would permit the opening of the vents. In this context, the use of clothing vents in the CB uniform may reduce the rise in core temperature during exercise in low dress states. If so, the initial core temperature upon transition to full encapsulation would likely be more similar to what is observed when the combat clothing or duty uniform is worn alone. Heat exposure tolerance time would then be able to more fully exploit the advantage of these new CB uniform designs in slowing the rate of heat storage and the operational effectiveness of the soldier would be maximally extended.

Table 5.1 Estimated radiative and convective (R + C) dry heat transfer, the maximum evaporative potential of the environment (E_{max}) and total heat loss expressed in $W \cdot m^{-2}$ during a low level of protection for uniforms without and with zippered vents in the torso, arms and legs. A *positive value* indicates a source of heat gain whereas a *negative value* indicates heat loss. Also shown is the relative gain in heat loss that could be achieved with the use of the vents in the uniform

	R + C ($W \cdot m^{-2}$)		E_{max} ($W \cdot m^{-2}$)		Total heat loss ($W \cdot m^{-2}$)		%Gain [(Vents–No Vents)/No Vents]*100
	Uniform		Uniform		Uniform		
Environment	No vents	Vents	No vents	Vents	No vents	Vents	Vents vs no vents
Temperate (25°C, 80%RH)	−60.6	−66.3	−111.6	−139.1	−172.2	−205.4	+19.3
Tropical (35°C, 75%RH)	−5.5	−6.0	−56.5	−70.4	−62.0	−76.4	+23.3
Desert (50°C, 10%RH)	+77.2	+84.4	−154.2	−192.1	−77.0	−107.7	+39.9

McLellan [47] recently reported that the opening of zippered vents in the clothing reduced the thermal and cardiovascular strain experienced during a low dress state such that exposure time was increased after the transition to full encapsulation. The effectiveness of these vents for promoting heat loss from the body are influenced by their location, since the requirement to wear other protective equipment could reduce their utility, type of activity and wind speed [4], and the environmental temperature and humidity. Dry and wet heat transfer are affected by the thermal characteristics of clothing layers that cover the skin surface [29]. As environmental temperature increases above 35°C and begins to exceed skin temperature, a lower thermal resistance of the clothing actually promotes greater sensible heat gain. Thus the approximate 10% reduction in thermal resistance afforded by the opening of the vents in the uniform (Table 5.1) would, by itself, promote greater heat storage in hot environments. However, at any given wind speed, it is the ratio of the water vapour permeability coefficient (i_m) to the thermal resistance of the clothing ensemble together with the vapour pressure gradient between the skin and the environment that determines evaporative heat loss at the skin surface [29]. Thus the approximate 25% improvement in this ratio for the uniform with the vents compared with the uniform without vents (Table 5.1) would counter the negative effect of the lowered thermal resistance on sensible heat gain when exposed to hot environments. A summary of the impact of the open vents during a low dress state on the estimated sensible and insensible heat transfer in a temperate, humid (25°C and 80% relative humidity), tropical (35°C and 75% relative humidity) and desert (50°C and 10% relative humidity) environment is depicted in Table 5.1. It is clear that the extent of the advantage of incorporating open vents into the clothing to promote greater heat transfer away from the body will depend on the environmental conditions.

Details of the equations used to estimate sensible and insensible heat transfer were taken from Gonzalez et al. [29]. R + C was estimated as $(T_a - 36) \cdot I_T^{-1}$ where T_a represented the ambient temperature, 36 was the assumed mean skin temperature and I_T was the total insulative value of the uniform as represented in Table 5.1 but expressed in $m^2 \cdot °C \cdot W^{-1}$. E_{max} was estimated as $16.5 \cdot (i_m \cdot I_T^{-1}) \cdot (5.94 - P_a)$ where 16.5 is the Lewis relation expressed in $°C \cdot kPa^{-1}$, i_m is the Woodcock water vapor permeability coefficient from Table 5.1, 5.94 is the saturated skin vapor pressure at 36°C and P_a represents the ambient vapor pressure. Abbreviations for clothing uniforms are as in Table 5.1.

Similar findings have been observed with both passive [13] and active ambient ventilation systems [15] during exercise while wearing body armour in varied environmental conditions. Certainly when the environmental conditions favour evaporative heat loss then the benefits of the ventilation system are more evident [15, 47].

5.8.2 Pacing Strategies

The work pace during prolonged work in the heat is continuously regulated to prevent changes in physiological systems that may be limiting or detrimental to performance [81]. The physiological variables include the rate of body heat storage. Thermal sensors in the body are continuously informing the brain and the work pace is adapted. There is good evidence that the work pace is not only adapted with feedback mechanisms, but that anticipation also plays a major role [76, 82].

Several studies on pacing in the heat show that the initial pace is independent on ambient temperature. After several minutes, however, the pace starts to drop [75, 78, 80]. The metabolic heat production is reduced to compensate for the increase in body heat storage that results from the hampered dry heat loss in the heat. Therefore, it may be beneficial to start at a lower pace in the heat to reduce the initial speed of heat storage and thus override the tendency to slow down the metabolic rate later.

There is good evidence that the power decrement in the heat is not related to absolute core temperature thresholds. Similar core temperatures were observed in the heat and during cool circumstances despite differences in power output [80]. The electromyographic activity, however, was less in the heat, pointing at reduced neuromuscular recruitment in the heat. Recently, Duffield et al. [20] precooled subjects prior to performance in the heat. Precooling changed the pacing pattern in the heat; the drop in performance was almost absent. Again, neuromuscular recruitment was held responsible for the observed differences.

In summary, work pace seems to be adapted to heat stress by reducing muscular recruitment using feedforward and feedback control mechanisms. Precooling improves power output in the heat by selection of a more even work pace in the heat.

5.8.3 Cooling Strategies

The inability to evaporate sweat in impermeable protective garments, has led to the development of cooling systems between the skin and the protective garment layers.

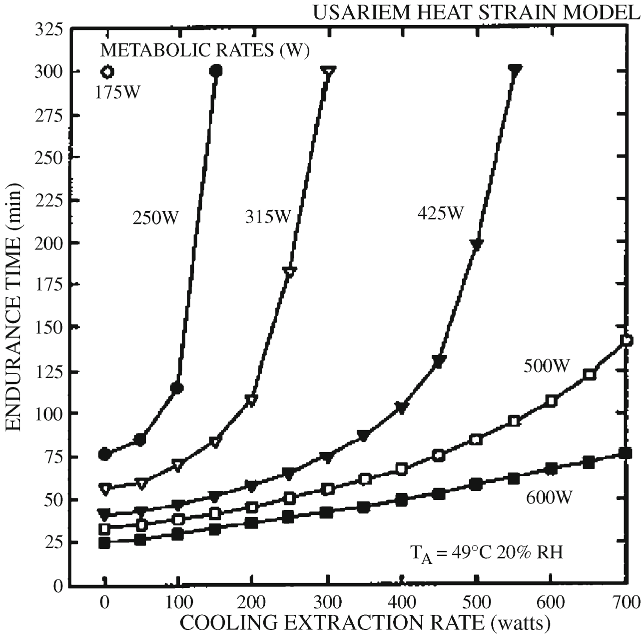


Fig. 5.3 The effect of cooling on tolerance time in protective equipment based on modeling studies [64]

Cooling can be performed prior to, during and after heat strain. Precooling is an effective means to lower the initial core temperature [19] and also benefits the pacing strategy in the heat [20]. Cooling during task performance is more challenging since the cooling system has to be carried or moved with the subject. In vehicles, where power sources are present, there are more possibilities for effective cooling than for the dismounted soldier or firemen.

Cooling after heat strain is mainly done in competitive sports with the aim to improve performance in the upcoming event. A recent overview showed that there are more studies showing no effect of aftercooling compared to positive effects regarding repeated performance, force delivery, pain, swelling, range of motion and inflammation markers [83].

Less cooling power is required to stay in thermal equilibrium during rest than during heavy exercise. Figure 5.3 shows the results of modeling studies regarding the relation between cooling extraction and endurance time at different metabolic rates [64]. Cooling extraction rates of about 100 W have almost no impact on tolerance time during heavy exercise (metabolism 600 W), but leads to increased performance during light work (metabolism 250 W). Therefore, the application of cooling systems should always be considered in relation to the task that is performed.

Prolonged cooling of the body can lead to skin vasoconstriction and thermogenesis. Both physiological responses are undesired since they counteract cooling efficiency.

Therefore, it is recommended to stop cooling when skin temperature drops below values of 33°C [14]. This value can be considered as the threshold below which vasoconstriction starts to increase.

Many types of commercial cooling systems are currently available in the market. Each vendor generally supplies a theoretical framework with the system. However, in practice most systems show limited applicability since they are only valuable for some specific tasks.

In general, one can distinguish between four main cooling methods: liquid cooling systems, air cooling systems, encapsulated phase change materials and external extremity cooling.

5.8.3.1 Liquid Cooling Systems

Liquid cooled systems have the advantage that body heat can be removed effectively, but a power supply, pump and heat exchanger are imperative. In a manikin-study Frim et al. [23] showed that a decreased inlet temperature and increased tubing length causes an almost linear increase in heat loss. The heat removal becomes essentially independent of flow rate at higher flows. The maximum heat removal is about 170 W under optimal conditions.

Generally, water is taken as the cooling fluid. It has the advantage that small leakages do not cause severe problems. However, other cooling fluids like glycol are known to have higher heat capacity and may thus be more effective in removing heat.

At this moment it is generally accepted that the disadvantages in terms of bulk and mass outweigh the benefits for dismounted soldiers and fire fighters.

5.8.3.2 Air Cooling Systems

The simplest version of air cooling is using ventilation only. In this case ambient air is blown in the air space between the skin and the inner clothing layer. Reffeltrath [65] blew 32°C ambient air in the immersion suit of a pilot and observed an increase in evaporation efficiency from 57% to 90%. The core temperature increase during the flight task was 0.5°C in 2 h as opposed to 1.0°C in 2 h without ventilation cooling.

For the dismounted soldier, systems are available that ventilate the air layer created by spacer materials under the ballistic vest. Evaluation of these systems by the armed forces generally shows that the small benefit due to increased evaporation efficiency is outweighed by the increased weight and mass of the system.

The cooling efficiency increases when the air is cooled or dried prior to entering the suit. Air can be cooled through several methods, such as adiabatic expansion and the use of a vortex pipe. However, this again causes an increase in weight and bulk that is undesired.

5.8.3.3 Phase Change Materials

Most materials absorb heat when they change from a solid to a liquid state. Ice vests are an example. In deep mines ice vests are used to extend working times in the heat. More recently, phase change materials based on paraffin were incorporated in clothing systems to function as a thermal buffer. However, large quantities of phase change materials are generally necessary to observe noticeable effects. Again, the weight of the system may outweigh the benefits.

5.8.3.4 External Extremity Cooling

Early work by Livingstone [38, 39] and House et al. [34] and House [33] revealed that the arteriovenous anastomoses, located in the palms of the hands and finger tips and soles of the feet and toes, are very effective when immersed in cold water for transferring heat from T_c. Indeed, House et al. [34] and House [33] showed that the rate of cooling from the immersed hands and forearms is dependent on the thermal gradient between T_c and the water bath, such that greater rates of cooling are evident when the hands were immersed in 10°C versus 20°C or 30°C water. Another important observation from this work by House et al. [34] and House [33] was that cooling continued until T_c returned to resting levels, implying that the regulation of the arteriovenous anastomoses were controlled centrally under conditions of heat strain rather than locally by the temperature of the surrounding skin temperature. These observations suggest, therefore, that the arteriovenous anastomoses would remain a very effective mechanism for transferring heat from T_c even if the hands were immersed in very cold ice water.

The use of hand and forearm immersion to assist with the management of heat strain for firefighters has been demonstrated by Selkirk et al. [69]. Fire services may require their personnel to go to a rehabilitation station after using one of two cylinders of air. During this rehabilitation period most of the firefighting PPE is removed and the 15–20 min of rest should be used to actively cool the firefighter. Selkirk et al. [69] revealed that tolerance time was increased 65% when the hands and forearms were immersed in cool water of 18°C, which was the in-line hose temperature available to the fire service. Certainly the immersion of the hands and forearms in colder water would promote greater heat loss [25] but colder water may not be available. Selkirk's study also demonstrated that 70% of the total cooling occurred during the first 10-min of immersion when the thermal gradient between T_c and the water bath was the greatest. Thus, very short cooling periods may still promote effective cooling to lower T_c prior to the start of the next work period. It is also noteworthy in these studies reported by Selkirk et al. [69, 70] that the combination of adequate fluid replacement and forearm and hand immersion in cool water was sufficient to increase tolerance time and work productivity 100% compared with the condition of fluid restriction and no cooling.

5.8.4 Fluid Replacement

Under conditions of UHS the benefits of fluid replacement on promoting and sustaining evaporative heat loss are far less evident ([10], [12]). Instead, the importance of fluid replacement on tolerance time during UHS is most evident on the initial T_c with the ingestion of cold water or ice slurry [36, 74] and on the core temperature tolerated at exhaustion [49, 70]. One of the very important aspects of fluid replacement during work in PPE is its impact on cardiovascular stability and the ability to attain higher T_c during weight-bearing activity with higher volumes of ingested fluid [70]. From a safety perspective, individuals carrying heavy equipment while wearing PPE are less likely to collapse from heat exhaustion if sufficient fluid is ingested before and/or during the heat stress exposure. Providing electrolyte and carbohydrate beverages will also promote greater volumes of fluid to be ingested, *ad libitum*, compared with water [16], which might also increase heat storage capacity when PPE is worn.

5.8.5 Summary

The wearing of PPE in warm or hot environments significantly increases thermal strain for the individual. The PPE creates a barrier to heat exchange between the body and the environment creating conditions of uncompensable heat stress where core body temperature continues to rise to dangerously high levels. This chapter has summarized the importance of individual factors, such as maintaining proper hydration levels and a high level of aerobic fitness, for improving tolerance times when the PPE is worn. In addition, other strategies such as microclimate cooling and use of pacing strategies and work and rest schedules were presented as options to extend tolerance when PPE must be worn.

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Chapter 6
Smart Textiles: An Overview

Lieva Van Langenhove, Carla Hertleer, and Anne Schwarz

Abstract This chapter introduces smart textiles and explains how textile materials and structures can be used as sensors, actuators, communication devices, energy sources and storage tools, and even processors. Conductive materials serve as the base for smart textiles. There are several advantages of using textiles as a substrate for smart functions; this chapter explains their important role in thermoregulation and highlights a smart suit for rescue workers.

Keywords Smart textiles • Protection • Monitoring • Communication • Textile integration

6.1 Introduction

Smart or intelligent textiles are a new generation of textiles that will actively contribute to our health and safety. They are expected to be one of the roads to a new sustainable textile industry. They are highly specialized high-tech products with a high added value and address specific target groups.

According to CEN's definition of smart textiles, there are several levels of smart functions [1]. In this chapter, we consider a textile to be smart when it has the capability to measure and/or to react. The reaction can be an intrinsic material property such as a color change, or it can be actively steered by electronics. The latter involves active data processing.

Smart textile products are stand-alone systems. The sensors provide information about the person, the environment or the textile itself. The smart suit may contain an

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electronics control device and energy supply. A smart textile system can have five basic components or functions:

- Sensor
- Actuator
- Data processing
- Communication
- Energy supply

Not all functions are foreseen in all applications of smart textiles. This chapter addresses examples of each of these functions.

6.2 Why Textiles?

Clothes are personal; they can be made to measure with a perfect fit and high level of comfort. Clothes make contact with a considerable part of the body. They also look nice and attractive, with the design and look being adapted to the actual consumer group. We all know how to use them. Maintaining textiles is a daily practice: domestic and industrial laundering is well-developed.

Textiles are extremely versatile in terms of products as well as processes. The building blocks of the textile material (*fibres* or *filaments*) are made of a broad range of materials, pure or in combination. Smart configurations and combinations of materials, advanced treatments and technologies lead to special properties such as hydrophilic/hydrophobic nature, antimicrobial, and selective permeability. Textile materials are able to combine advanced multifunctionality with traditional textile properties.

The objective of smart textile is to absorb a series of active components essentially without changing its characteristics of flexibility and comfort. Sensors, devices and wires should disappear into the textile. In a first phase, conventional components are being reshaped in order to fit in the textile, ultimately the fibres and textile structures themselves will become the active elements. And last, but not least, textiles and clothes can be produced on fast production machinery at reasonable costs. All this makes smart clothes an ideal vehicle for carrying active elements that permanently monitor our body and the environment, providing adequate reaction should something happen.

6.3 Interaction of Smart Textiles

Smart textiles interact with the human and the environment. A smart textile can be active in many fields. They can absorb or generate, reflect, shield, measure or affect a series of parameters such as:

- Temperature,
- Heat flux,
- Electrostatic and electromagnetic fields,

- Humidity,
- Chemicals in liquid or gaseous phase,
- Radiation,
- Movements,
- Forces,
- Odour,
- Biological activity.

Many body parameters can provide useful information on the health status of a person: temperature, biopotentials, sounds, movements, chemicals, mechanical parameters and many more. Research projects are being undertaken for measuring body parameters using textiles as a carrier of sensor systems or the textile itself as sensor [2–5]. Such suits commonly measure heart rate, temperature, respiration and gesture. Permanent monitoring combined with smart data processing strategies allows early detection of suspect conditions.

Protection is the second frame: the textile can react adequately on hazardous conditions that may have been detected. The reaction can consist of warning, prevention or active protection. After an event has happened, the smart textile is able to analyze the situation and to provide first aid.

On a longer term, the textile can support and follow up the healing process. Support to rehabilitation can be medical, chemical or physical. Textile materials can contribute to enhancing the rehabilitation process; they can actively remedy body deficiency or even takeover certain functions.

6.4 Conductive Textiles

6.4.1 Conductive Textile Materials

Electroconductive materials form the basis of smart textiles. Several conductive materials are in use. Metal fibres such as stainless steel and copper are readily available. They have fair to excellent conductivity. Since they are different from polymeric fibres, they may be hard to process and have problems of long term stability. Alternatively, as shown in Fig. 6.1, polymer fibres may be coated with a conductive layer such as polypyrrole, copper or gold [6]. The conductivity will be maintained as long as the layer is intact and adhering to the fibre. Nanoparticles can be added to the matrix for achieving conductivity. This will be discussed later.

6.4.2 Conductive Textile Sensors

One of the first applications where a conductive textile structure was used as a sensor is for electrocardiogram recordings. Such structures are called textrodes. They are true textile components, as they consist of 100% textile fibres. Simply

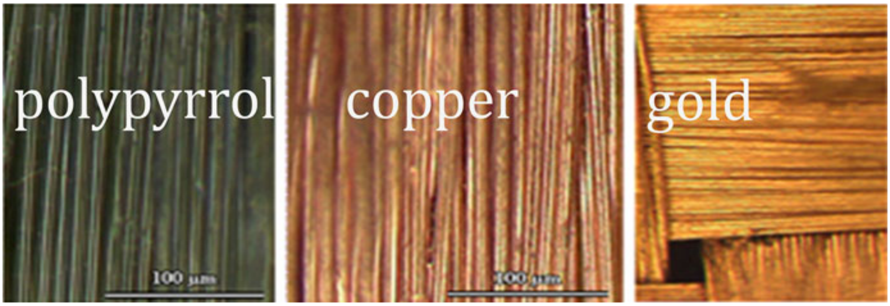

Fig. 6.1 Kevlar fibres coated with conductive materials

replacing conventional electrodes by such textrodes leads to a working smart textile system. Additional filtering considerably improves the quality of the signals.

A second application is the monitoring of respiration. Two major principles can be used to this end. Both are based on conductive yarns that are integrated in a belt (called respibelt) that is worn around the chest. When a staple fibre yarn is used, the current has to pass from one conductive fibre to another. In addition to the resistance of the fibres, the overall resistance is determined by the contact resistance at the fibre-to-fibre contacts. When the yarn is subjected to strain (for instance by stretching the fabric) it becomes more compact, causing the number of contact points to increase and the contact resistance to decrease. This leads to a reduction of the overall resistance of the yarn structure. Breathing induces a cyclic expansion and shrinkage of the chest and this leads to an increase/decrease of the length of the respibelt.

The second mechanism considers the conductive yarns in the belt as an electromagnetic coil whose inductance changes due to breathing. Figure 6.2 illustrates the signals acquired by such sensors.

The textrodes essentially measure the biopotential that is needed to make the heart muscle contract. Any muscle in the body is steered by a biopotential. So, textrodes can also be used for measuring muscle activity. However, the skin conductivity is low and due to the compressible nature of textile materials and the movements, the contact resistance is subjected to large variations. This phenomenon causes a lot of noise. Within the European project Context, a contactless sensor has been developed [7]. They use embroidery and lamination technology to produce EMG sensors for monitoring stress in professional situations (Figs. 6.3 and 6.4).

The conductivity of materials is often affected by several parameters which may be exploitable mechanisms for use as a sensor. Pouillet's law is a first example. This law describes how conductivity decreases due to material extension. Heating, wetting and absorption of chemical compounds in general may increase or decrease conductivity. Carbon nanotubes incorporated in fibres make the fibres conductive. Any mechanism that leads to swelling or shrinkage of the fibres alters the distance between the nanoparticles, causing the conductivity to change. Thermal expansion

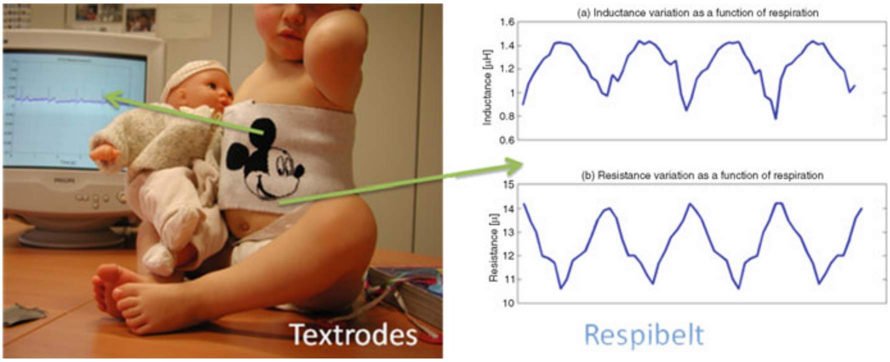

Fig. 6.2 Heart and respiration sensors based on conductive textiles

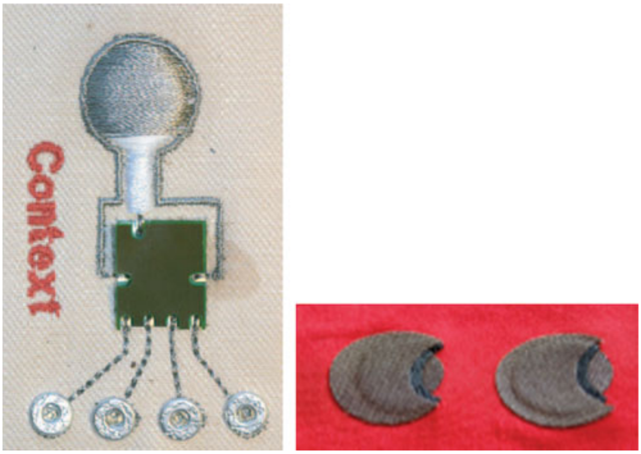

Fig. 6.3 Embroidered and laminated sensor for myography

in this respect is the base of thermoresistive fibres. Polymers that swell in the presence of water or chemical compounds in general can be used as sensors when carbon nanotubes are added. This has been the topic of the Inteltex project [8].

6.4.3 Conductive Textile Actuators

As previously described, conductive materials can be used in textile sensors in various ways. Textrodes designed for monitoring biopotentials are also be used as electrical actuators. Electro-stimulation has been shown to be effective for many purposes. Depending on the application, the impulse can vary from weak to strong. For

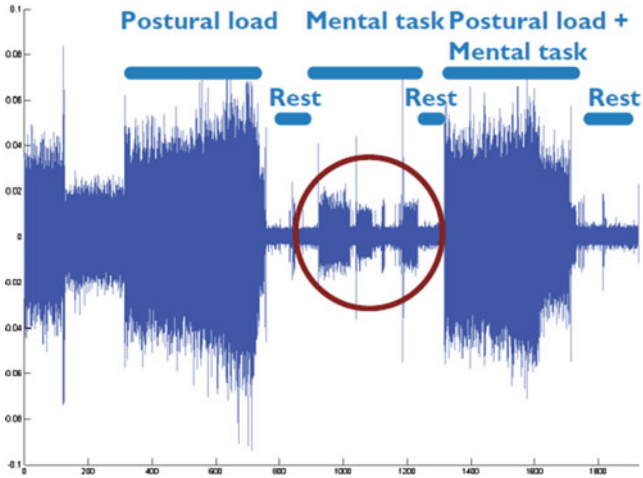

Fig. 6.4 Results of myographical recordings by textile sensors

instance, a tactile stimulus does not need a high current intensity. A higher level of stimulation is required for skin stimulation for reinforcing the tissue in order to prevent bed sores. Another application is the increase of skin permeability to enhance drug delivery. An additional electrical field can enhance drugs to pass through the skin. Real activation of the muscles requires the highest level of stimulation. Targeted effects are warming up or exercising the muscles.

Actual stimulation can only be achieved by higher current intensity. The current distribution in conductive electrodes being inhomogeneous, local peaks can occur [9]. Heat production is proportional to the square of current intensity, so current density peaks correspond to local hot spots. This possibly leads to burn injuries. Current concentration occurs at the edges of an electrode and particularly in the corners. A more homogeneous current density profile can be achieved by changing the local conductivity of the electrodes. Models have been established for calculating the current density distribution for electrodes with various conductivity profiles. As shown in Fig. 6.5, the peak current density can be reduced by more than half by using an electrode with concentric zones of conductivity (high in the middle, low at the outside) instead of a homogeneous electrode.

Several prototypes have been manufactured. They use several conductive fibres (stainless steel, copper coated, gold coated) and production methods (full insertion of conductive yarns, embroidery, lamination). In the framework of the European project Lidwine, clinical trials have been carried out using these electrodes (Fig. 6.6).

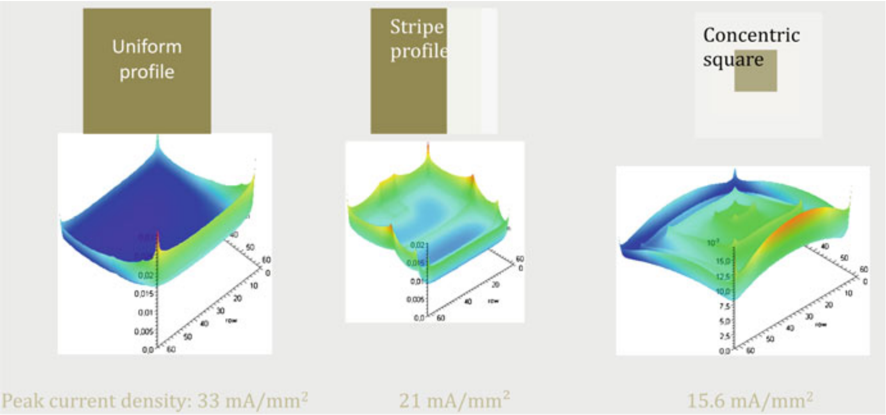

Fig. 6.5 Current density distribution for different electrode designs

Fig. 6.6 Textile products with embedded actuators

6.5 Textiles and Thermoregulation

As discussed earlier, conductive materials heat up when current flows through them. Polartec has presented a heating fleece [10]. It uses stainless steel fibres powered by regular batteries. Also Sefar commercialises woven heating elements [11].

Cooling is far more challenging than heating. The EU project Prospie considers several approaches for cooling. Ventilation is the first. Second, phase change materials are used. For some materials, wetting is an endothermal process. Such salts will be embedded in textile structures to generate a cooling effect initiated by wetting (due to sweating).

The Italian company Grado Zero has embedded ultrathin tubes in textile structures through which a cooling liquid can be circulated. An F1 pilot racer suit has been manufactured [12]. The liquid is cooled by a small Peltier element that is fixed on the back of the suit as shown in Fig. 6.7.

Fig. 6.7 F1 pilot cooling suit

As conditions (temperature, intensity of activity, etc.) change the need for insulation may vary. Adjustable insulation can be achieved by multilayer fabrics where the distance between the layers can be changed. An example of such a product is an inflatable jacket where air has to be blown into separate the layers. Another product consists of a comfortable cotton inner layer and a heat resistant aramid outer layer. Shape memory springs separate the layers by opening up when a transition temperature is exceeded. This product is thin and comfortable at low temperatures, whereas at elevated temperatures it automatically provides thermal protection. At present, the change is one-way.

Adaptable ventilation has been based on the structure of pineapples. They consist of multiple layers with large difference in hygral expansion coefficient. In the wet state, the leaves of the pineapple are closed. When the humidity decreases (in spring time) the leaves bend away from each other and the pineapple opens up allowing the seeds to get out. Similarly, several layers of coating have been applied to a fabric. U-shaped perforations are punched in the fabric and coating. When the material is wetted (simulating sweating) the blades of the perforations bend creating a large ventilation effect. The system is fully reversible.

Phase change materials have been developed by NASA in the ‘1990s for coping with large and rapid temperature variations in space cabins. They consist of micro-capsules with a hard shell filled with various paraffin waxes. They exploit melting heat which is much higher than the caloric value. As a result the material has a very high thermal buffer capacity. The melting temperature determines the temperature range of use.

Humidity control is very important in thermal comfort. Sweating is a natural mechanism of thermocontrol. Evaporation of sweat is an endothermal process. But sweat also gives an unpleasant feeling of wetness and cold. In firefighter suits, the

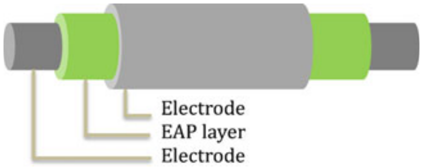

Fig. 6.8 Structure of an electroactive fibre

sweat cannot escape and migrates inside the suit. Local condensation may drastically reduce insulation and evaporation may lead to formation of steam. Both effects can give rise to burn injuries. Through an appropriate design consisting of selection and combination of proper materials and correct shape, it is possible to adequately evacuate humidity. Moisture can be transported for instance to a specific area where they are absorbed by hydrogels.

On the other hand, sweat is reflecting the health state of the body. In the Biotex project, devices have been developed for measuring several parameters of sweat such as pH, conductivity, sweating rate, concentration of K, Cl and Na ions. The latter give a good indication of dehydration of the body, which is very relevant for firefighters and sportspeople. Apart from sweat, pH is also a good indicator of the healing process of a wound. A textile compatible sensor has been designed within the Biotex project [13].

Thermal comfort is very important because thermal stress leads to increased fatigue. In extreme conditions, it may cause a person to faint. Full thermoregulating-textiles, however, are not yet within reach. It is a good example of what needs to be done in order to fully exploit the potential of smart textiles.

The first question is to measure the level of thermal comfort. A number of body parameters can be measured (e.g., skin temperature, humidity, conductivity), but true textile sensors are still under development. More work needs to be done for interpreting the data to quantify the level of thermal comfort. Secondly, adequate actuators are needed that can heat, cool, insulate, ventilate and regulate moisture. No effective textile actuators are available except for heating. Thirdly, thermal comfort is very personal and unique to the individual; so is the body response. Therefore, advanced self-learning modeling and control strategies are needed. A lot of work needs to be done before textile thermoregulation becomes a reality.

6.6 Electroactive Fibres

Electroactive fibres will play a major role in the future development of smart textiles. A generic structure is given in Fig. 6.8.

An electroactive fibre typically consists of a conductive core, an electroactive polymer (EAP) layer and an outer conductive coating. The inner and outer conductive layers act as the positive and negative electrodes, respectively. The electroactive layer determines the functioning of the fibre. A few examples of such fibres are discussed.

The first example is a mechanical fibre actuator based on an electrochemical process. A polymer is charged with anions and cations. Applying an electrical field causes one of the ions to be expelled or absorbed. This leads to shrinkage or swelling of the fibre. The system is fully reversible.

In electrostrictive systems, the electroactive layer is a dielectric material. An electrical field will cause opposite charges to concentrate at each of the contact surfaces. As a result, the surfaces will attract each other and the layer will become thinner. At the same time, the equal charges that have accumulated at each of the surfaces will repel each other, causing the surface to flatten. Both mechanisms lead to flattening and in-plane expansion of the electroactive layer. The contraction or expansion is very fast and fully reversible.

Energy consumption is very low but a high voltage is required (e.g., 400 V/μm for thickness strains up to 60–70% for acrylic polymers [14]). The required voltage can be reduced by decreasing the thickness of the electroactive polymer layer and by choosing a polymer with good dielectric properties. However, a minimum thickness is required (depending on the type of material, e.g., 0.1 mm for Teflon) in order to avoid breakages in current flow. Therefore a very homogeneous electroactive polymer layer is needed. If the electroactive layer is a piezoelectric material, the electroactive fibre can provide electricity.

Once electroactive fibres have been realized, the next challenge would be to integrate them in a fabric structure in an industrial production process. It requires the design of appropriate fabric structures to ensure the contacts are right and stable and that no false contacts arise.

6.7 Optical Textiles

Optical fibres can also be used as sensors and actuators. Three mechanisms can be applied, namely colour change, Snell's law or Bragg's law. The colour change of materials that are coated onto an optical fibre can be read out by a device. A major challenge is to fix such dyes in a polymeric material. Indeed the dye may bind on the polymer in a group that interferes with the colour-changing mechanism and this bond may cause the colour change to disappear. Colour change is not a new phenomenon. Alexander the Great already used a dyestuff extracted from snails that changes colour under UV light (Tyrian Purple).

At UGent, research is being carried out on pH-sensitive dyes. The goal is to use them in wound dressings in order to speed up the wound healing process. Here too a major challenge is to bind the dye on a textile substrate without losing the colour change.

Optical fibre actuators can be realized easily by damaging the cladding layer of the fibres as this causes the light to emerge. France Telecom has developed a shirt with embedded optical fibres in an 8*8 matrix. Each optical fibre is lit by a small LED. The shirt is meant as a visual communication tool when the noise of the environment does not allow communication by sound.

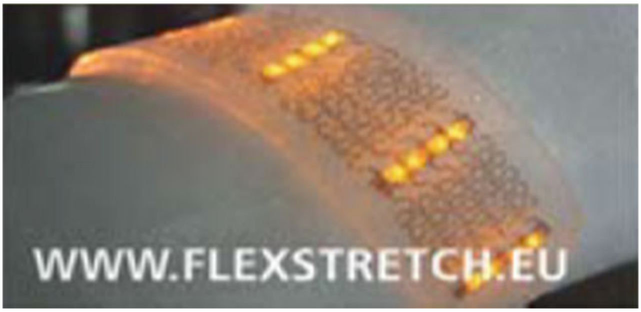

Fig. 6.9 Stretchable print with built-in LED

In the Lumalive project at Philips, miniaturised LEDs are built directly into the textile. In the Stella project, they have been embedded in a stretchable print [15] (Fig. 6.9).

Further progress can be made by printing the LED directly onto the textile substrate. The challenges include the low efficiency of organic active layers and so, the yield is low; and the material is very sensitive to oxidation.

6.8 Communication

Communication is very important so that action can be taken on the monitored information. First, all the active components in the smart textile – sensors, electronics and actuators – must be connected. Conductive fibres and optical fibres are used for this purpose. Communication with the wearer is handled by a textile keyboard or a textile display. A wireless connection can be made with the outside environment via an inductive link [16] and an ISM band textile antenna [17] as shown in Fig. 6.10. In the Proetex project, a GPS system embedded in a rescue suit allows the determination of a person's location.

Important criteria for selecting the optimal solution depend on the conditions of use of the system such as whether or not the wearer is moving, whether the user is located in a field or in a building.

6.9 Energy Supply

Energy is one of the key challenges in a smart textile system. Energy can be stored in the form of a battery and/or harvested from the environment. As for energy storage, two concepts are available namely, electrochemical batteries and capacitance-based batteries. Electrochemcial batteries are widely used. Today they exist in the form of

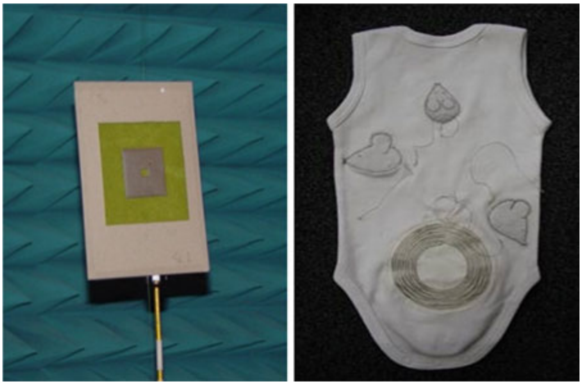

Fig. 6.10 Textile communication devices (ISM band antenna and inductive link)

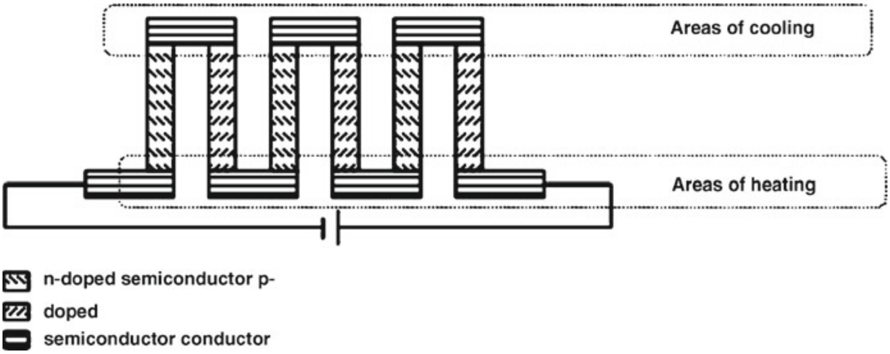

Fig. 6.11 Construction of a Seebeck-based thermoelectric generator

thin bendable foils. Unfortunately their capacity mainly depends on their volume, so that a reduction of the thickness must be compensated for by an expansion of the surface area. The battery is impermeable to moisture and this causes local discomfort due to sweat accumulation. As for capacitance-based batteries, carbon nanotubes have been reported to act as supercapacitors.

Energy is available in the environment in the form of heat, light and motion. Several mechanisms are known for harvesting them. Infineon has developed a device that harvests electricity from body heat. It is based on the Seebeck effect. It consists of a repetitive sequence of conductive, n-semiconductive, conductive, and p-semiconductive materials as illustrated in Fig. 6.11.

Electrons will rather move from n-semiconductive to p-semiconductive material than the other way around. This means they will speed up in the conductive areas between n and p semiconductive materials and slow down in the conductive areas between p and n semiconductive materials. Speeding up requires energy, slowing down releases energy, in this case in the form of heat. So some areas will cool down while others will heat up. When an appropriate configuration is chosen (an example is illustrated in the figure), a flat device is obtained that has a cooling and a warming surface.

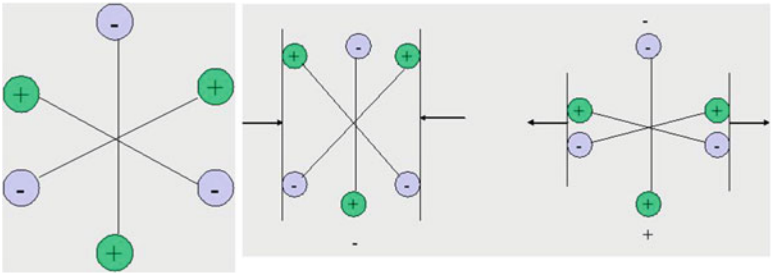

Fig. 6.12 Piezoelectric effect

As long as both surfaces are at different temperatures, an electrical current will be generated. The demonstration unit developed by Infineon has the dimensions of a Eurocoin and produces enough energy for a small sensor. This means that a stand-alone sensor can be achieved by integrating a local thermogenerator together with the sensor.

Piezoelectric materials allow the harvesting of electric energy from deformation. They are crystals with an asymmetric charge distribution. As illustrated in Fig. 6.12, extension or pressure leads to a net positive and negative center. These charges can be collected by two conductive layers that act as electrodes. Being a surface effect, the material thickness does not contribute to an increase of charge collection. The piezoelectric material is an electroactive material that can be applied in a manner similar to the electroactive fibre discussed in Sect. 6.6.

Challenges today are the material itself, the configuration of fibres, yarns and coatings to realize the required effect in the textile structure with decent yields, and adequate production technologies. In the case of piezoelectric materials, the challenges are to design the textile structure so that:

- a considerable amount of charges is being generated and
- the charges are being collected and taken to a battery

Considerable research is being carried out on organic photovoltaics. Photovoltaic fibres make use of these technologies. The Dephotex project aims at developing fibre-based photovoltaic structures [18].

6.10 Data Processing

Electronic components need to be integrated seamlessly in the textile structure. The Wearable Motherboard by Georgia Tech is the first development in this respect [19]. Optical and conductive fibres are integrated into woven or knitted structures; a variety of active components including sensors and processors can be integrated at desired points in the wearable motherboard to create a mobile and wearable information processing system that can be used in many applications.

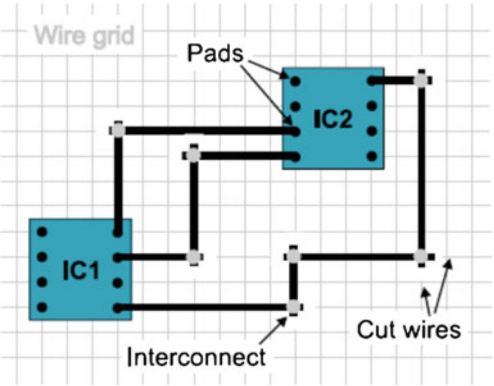

Fig. 6.13 Principle of woven motherboard by ETH

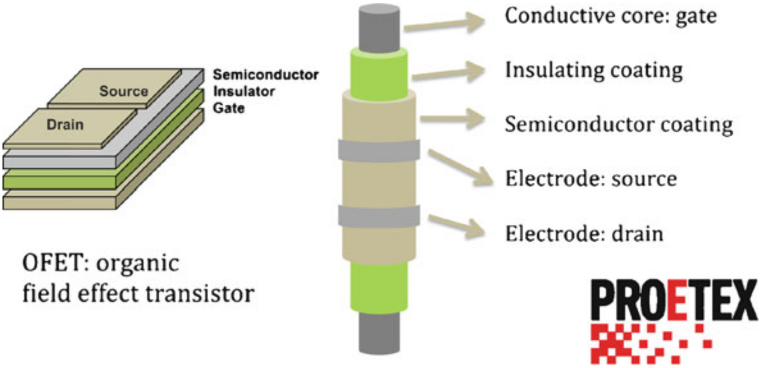

Fig. 6.14 Fibre transistor developed in the Proetex project

Based on the work of ETH Zurich [20], the Swiss company Sefar has designed a woven textile structure (Fig. 6.13) with a grid of electroconductive yarns onto which electronic components can be attached so that the appropriate connections are achieved with a good level of durability [21].

The next step in this evolution is to make the electronic components in the form of fibres. Within the EU project Proetex, a fibre transistor has been designed. The first generation started from a ribbon shape which can be woven into a fabric. A true fibre transistor requires further work in coating or other forms of deposition of subsequent active layers on a conductive fibre (Fig. 6.14).

Unfortunately the characteristics of such transistors are not very stable. They vary due to deformation caused by bending and stretching. On the other hand, this makes them suitable as a sensor. As mentioned earlier, organic semiconductors that are currently in use also suffer from oxidation.

6.11 Case Study in Smart Textiles: The Proetex Project

Today, one of the most advanced smart textile products is being developed in the framework of the Proetex project [22]. The Proetex smart suit protects rescue workers and allows fast follow-up of victims. The suit itself consists of an inner and outer garment and boots for the rescue worker and a victim patch for victims.

The inner garment contains textile sensors for measuring heart and respiration rate, temperature and sweat composition. These signals are used to trace whether the rescue worker is at risk (Fig. 6.15).

The outer garment illustrated in Fig. 6.16 is equipped with textile-compatible components such as accelerometers, temperature sensor, GPS module and visual alarm. An electronic box processes the data and controls the system. A flexible battery supplies energy. The results are communicated to a base station via a textile antenna.

Fig. 6.15 The evolution of the Proetex inner garment

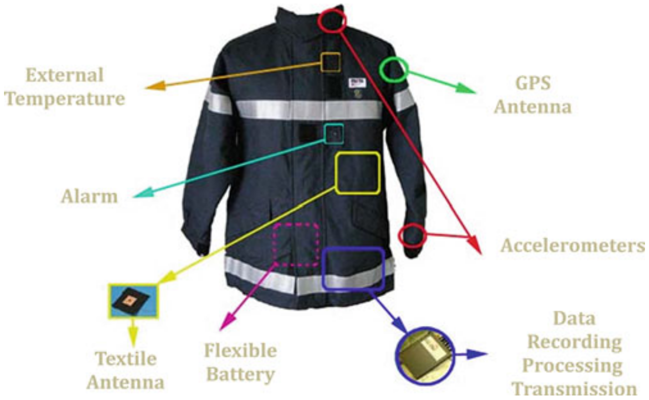

Fig. 6.16 The Proetex outer garment

Fig. 6.17 The Proetex victim patch

The victim patch shown in Fig. 6.17 contains the same technology as the inner garment. It can be applied easily on victims. It measures heart and respiration rate and body temperature enabling speedy evaluation for urgent care.

The key issues for the design of the system are:

- Comfort
- Working conditions – relevant parameters: only relevant information should be provided in order to avoid additional workload; this includes indication of danger and need for help.
- Effective alarm generation: the rescue worker or a responsible person should be informed adequately on what needs to be done.
- System maintenance: it must be possible to treat the suit using usual maintenance procedures.
- Ease of use: the use of the smart system should not require any additional effort
- Weight: the additional load should not reduce operation time of the rescue worker.
- Cost must be justified
- Robustness
- Energy constraints: energy requirements must be optimised
- Long range transmission: transmission range must be adjusted to the situation of use. Fighting a fire in a building is different from fighting one in an open field.

6.12 Conclusions

A smart textile is a powerful tool that can contribute to health and safety. It can monitor humans, the environment and itself. It can detect unusual conditions indicating potential problems; this allows prevention and early intervention. Protection could be provided without hindering comfort and ease of use. The smart textile system can monitor the impact an event might have had. It can identify measures to be taken such as treatment or calling for help. It can also support and follow- up rehabilitation.

Ultimately, the potential is endless. However, today, the developments are mainly at the level of embedding textile-compatible components. But research is being carried out to develop true fibre-based textile elements that can be active and be integrated seamlessly into a garment. Information on projects, people and products regarding smart textiles can be found at www.systex.org.

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Chapter 7
Innovative 3D Textile Structures for Soft Body Armor Protection: The EPIDARM Project

Jérôme Maillet, Marie Lefebvre, François Boussu, and Marc Pirlot

Abstract There is a real need for battlefield soldiers to be protected from ballistic and CBRNE threats and also to be in permanent contact and localization with the logistic support of the commander. Ballistic, CBRNE and tactical jackets are currently three different components, developed separately and worn on top of each other. One of the EPIDARM project's targets is to propose a personal protection demonstration for the optimal system configuration in order to reduce the cost and weight while improving protection. The systems approach used for the EPIDARM program considers the protective system inside its environment (threat, the wearer – generic soldier, task and climates). The latest emergent technologies in ballistic and CBRN protection, ergonomic effectiveness and financial cost are considered and help to select final solutions.

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7.1 Introduction

The French Ministry of Defense (MoD) requirements as regards the future combat suit can be represented using four main criteria: safety, operational capability, logistical footprint and integration modularity. The definition of the future combat suit must be balanced between these four opposing and complementary criteria (Fig. 7.1).

In the EPIDARM project, a survey has been conducted to better understand the future requirements for combat suits. One of the main results leads to the identification of three configuration systems including two levels of integration for each of them.

Description of the three configuration systems:

The three configurations are:

- Legacy protection, as defined by the current requirement documents and standards
- Raised protection level, targeted to cover the known new and foreseeable future threats
- Moderate protection, but optimal wearing comfort in all climatic conditions

Definition of the two integration levels as:

The two integration levels are:

- **I as highly integrated version**, for optimal simplicity and logistical footprint
- **M as highly modular version**, for optimal performance and wearability

To cope with the real condition of the soldier, various configuration systems coupled with their different integration levels have to be considered for different types of missions. Four main types of missions have been selected, which correspond to different soldier positions during a global campaign. These four missions are:

- Check Point
- Foot Patrol
- Vehicle Patrol
- Combat

Taking all these parameters into account, different types of soft protection have been proposed to address at least one or two main criteria of the MoD

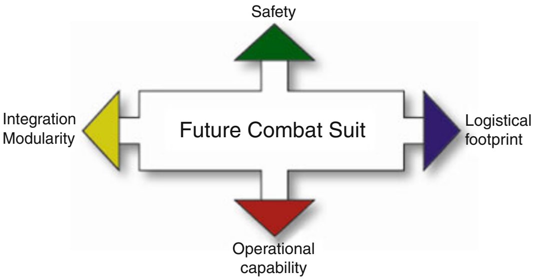

Fig. 7.1 The four parameters to define the future combat suit

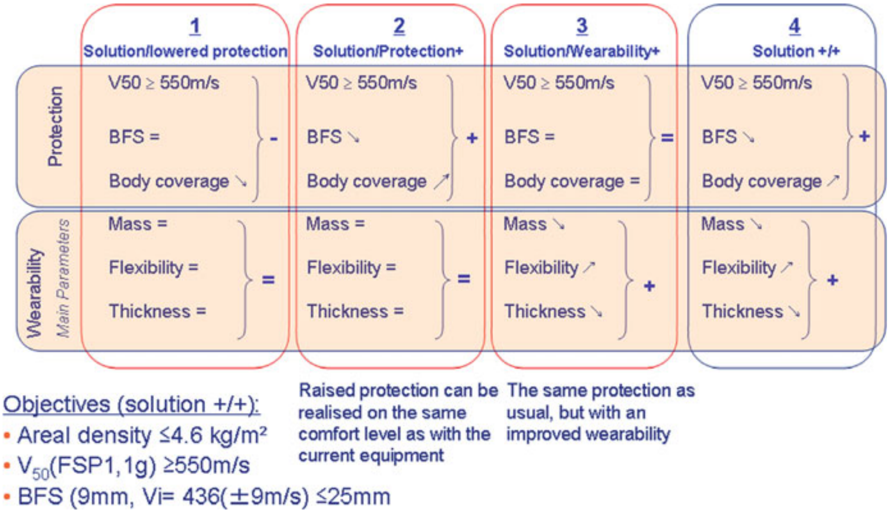

Fig. 7.2 Four main types of soft protection for combat suit

requirements. All the four main solutions have a V50 value equal or up to 550 m/s and are detailed as:

- A solution focused on lowered protection: Backface signature similar to what is obtained with current solutions, a lower body coverage and the same wearability as with the current solutions.
- A solution focused on an increased protection: Decrease of the back-face signature and increase of the body coverage with the same wearability as with the current solutions.
- A solution with increased wearability: Same protection with increased wearability.
- A solution with the best wearability and protection: Increased protection and wearability.

The following scheme sums up the different trends to follow in order to match with the definition of each of these protection solutions (Fig. 7.2).

For the soft protection, we will mainly focus on fibrous structures made of aramid fibers with different yarn counts. In fact, this fiber used in an adapted structure will permit us to reach our main objectives: develop cheaper solutions which stop high velocity fragments and 9 mm bullets with lower back-face signature.

7.2 Ballistic Testing of Individual Armor

7.2.1 Ballistic Threats

The basic ballistic threats against individual armor are handgun or rifle bullets and fragments (“shrapnel”) released by HE (High Explosive) ammunitions.

Fig. 7.3 9×19 mm cartridge

7.2.1.1 Bullets

A bullet is a projectile propelled by a firearm or air gun. It doesn't contain any explosive charge. In order to defeat the target, the bullet uses its kinetic energy. For this reason, it is called "kinetic energy projectile".

Some bullets are made of lead. This metal has a high density, thereby providing a high mass for a given volume. Moreover, lead is cheap and available. Another important property of lead is that it is a fairly soft material and therefore deforms easily under the minor resistance offered by the target even if the latter is "soft". Due to this deformation it can generate severe damage to the human body.

A full or partial metal jacket usually covers the lead core. Jacketed bullets are used for high-velocity (military) applications. The common jacket metals are copper, brass or steel. The mechanical properties of those metals offer sufficient strength and durability to the bullet. Moreover, the thin layer of harder copper protects the softer lead core when the bullet goes through the barrel and during flight, which allows delivering the bullet intact to the target (Fig. 7.3).

A partial metal-jacketed bullet is not covered up to the front, leaving the nose of the lead bullet exposed and allowing expansion. When the bullet hits a soft target, the pressure created in the front forces the material to expand outwards, increasing the axial diameter of the projectile. This phenomenon of expansion is called "mushrooming" because the resulting shape is typically like a mushroom.

"Hollow-point" bullets (HP) feature a cavity in the tip to cause the bullet to expand upon entering the target in order to decrease penetration depth. Despite the ban on military use, hollow-point bullets are one of the most common types of police ammunition, due to the reduced risk of ricochets and the increased chance of incapacitation.

For use against armored targets, penetration is the most important consideration. Focusing the largest amount of energy on the smallest possible area of the target provides the greatest penetration. For penetrating substances significantly harder than jacketed lead, the lead core is supplemented with or replaced by a harder material, such as hardened steel, tungsten carbide or depleted uranium. This type of ammunition is designed to penetrate armored targets and is thus designated "armor piercing" (AP).

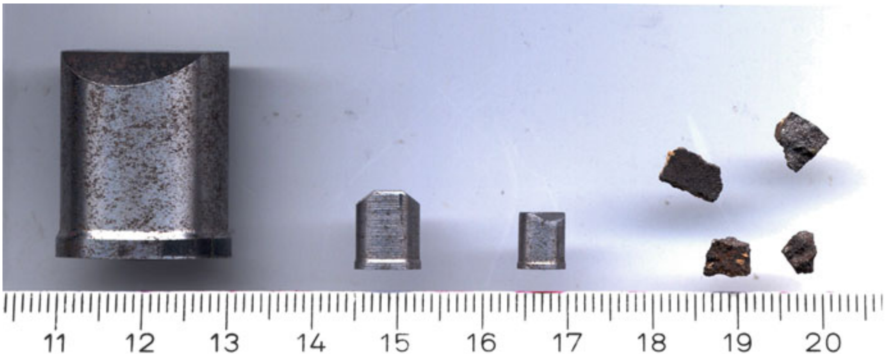

Fig. 7.4 Three FSP (20, 7.62 and 5.56 mm) and four real fragments

7.2.1.2 Fragments

Fragments are generated when a grenade, artillery shell or mine detonates. These explosive devices are made of hardened steel, the generated fragments have a variety of mass, shapes and sizes, and travel at different velocities. They may present very high initial velocities but are quickly slowed down. The extent of injury depends on several factors, such as the mass, velocity, shape, density and impact angle of the fragments.

With regard to these variable characteristics of fragments, it is obvious that testing each shape and size of a fragment travelling at various velocities is practically impossible. It's the reason why NATO has introduced, and recommends, the fragment-simulating projectiles (FSP) (Fig. 7.4).

7.2.2 Ballistic Tests

The obvious challenge for body armor manufacturers is to develop products that will stop the projectiles, but it is also important that the energy is dissipated over a large area. The faster the energy can flow away from the point of impact, the more the energy is spread across a larger area; thus less energy density at impact point and less "shock" energy is transmitted through the fabric to cause back face deformation against the underlying woven structure.

The back face deformation corresponds to the amount of deformation that the rear surface of body armor will transmit when struck abruptly by a projectile. Although the bullet may not perforate the body armor, the part of the body directly behind the point of impact receives a "blow" as a result of the deformation of the armor. Non-penetrating injury resulting from the rapid deformation of armors covering the body is called "behind armor blunt trauma" (BABT). This trauma can induce relatively minor injuries such as bruising to more serious injuries where internal organs are damaged. In extreme circumstances, the BABT may result

Fig. 7.5 Back face signature

in death, even though the projectile has not perforated the armor. Armor designers attempt to minimize the weight and bulk of personal armor systems while taking into account the risk of blunt trauma. Indeed, the danger of BABT in military and security forces personnel increases with the constant increase of the bullet energy.

Each part of a complete body armor sample must be tested for resistance to penetration and deformation according to ballistic test standards. One of the widely used standards, especially for the evaluation of the blunt trauma, is the US National Institute of Justice (NIJ) standard 0101.04 [1]. The standard establishes the minimum performance requirements and test methods related to the ballistic resistance of personal body armors intended to protect the human torso against various types of bullets. The standard also lays down criteria for acceptance of the armor vest in terms of test sequence, workmanship, traceability and labeling.

The back face signature (BFS) is defined as the depth of the depression made in the backing material, created by a non-penetrating projectile impact. This test series requires the use of a plastically deforming witness media (clay backing material) held in direct contact with the back surface of the armor panel. This configuration is used to measure the depression produced in the backing material during non-perforating threat round impacts. The NIJ Standard recommends the use of Roma Plastilina #1 as backing material. A calibration of this backing material has to be realized before and after each firing sequence. Figure 7.5 represents a clay-based backing material used to determine the back face signatures.

It is important to note that the use of clay backing material does not reflect, represent, replicate, or duplicate the physical characteristics of the human (torso) or its physical response to this type of stimulus. However, the use of clay is intended to guarantee the inter laboratory reproducibility.

The resistance to deformation of body armor is thus determined by the measure of the back face signature indentation depth. For the different levels of armor, the acceptance criteria for penetration and BFS compliance are twofold.

First, there should not be perforation through the protection, either by the projectile or by any fragment (of the projectile or protection). Second, the measured BFS should not be greater than 44 mm.

An alternative method to determine the backing material deformation is to measure the volume rather than the depth of the depression. In some cases, the volume of the indentation created behind the ballistic protection can be determined directly by filling the cavity with water. The VPAM standard[1] describes this method of volume calculation in order to estimate the energy transferred.

7.2.3 Stochastic Behavior of the Projectile – Protection Interaction

The usual parameter describing the projectile-protection interaction is called V50, i.e., the velocity for which the probability of a given combination [projectile, protection] is 0.5. Thus V50 is a mathematical parameter, which is evaluated by means of different firings at variable impact velocities.

Originally the V50 parameter was established to evaluate protection against fragments. Because fragments are characterized by a variable distribution of mass, shape, size and velocities, the technique of V50 combined with FSP (Fragment Simulating Projectiles) was introduced. Today, this parameter is extended to the determination of ballistic performance of a protection against bullets.

The current standard to evaluate the efficiency of a material against ballistic fragmentation is the North Atlantic Treaty Organization Standardization Agreement 2920 (NATO STANAG 2920) [2]. The aim of this STANAG is the determination of the V50 performance of a given protection against a defined projectile.

The STANAG 2920 method for the evaluation of V50 consists of an even number of shots (at least six): half of the shots must perforate the protection and the other must not perforate. The highest recorded velocity of the group must not be more than 40 m/s higher than the lowest of the group of six. The V50 value is the average value of the six velocities.

The method recommended by the STANAG 2920, currently used by NATO, has however a great disadvantage: it does not offer any information about the dispersion of V50, e.g., the standard deviation.

The complete assessment of the ballistic performance of a target against a projectile is characterized by a phenomenon of dispersion, as it appears in Fig. 7.6.

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[1] Vereinigung der Prüfstellen für angriffshemmende Materialien und Konstruktionen (VPAM); "Allgemeine Richtlinie für ballistische Material-, Konstruktions- und Produktprüfungen", Apr 2006: 13.10.2006.

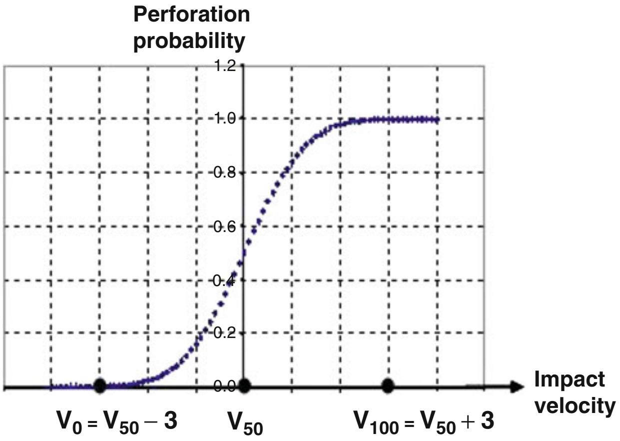


Fig. 7.6 Probability function versus impact velocity (at 99.7% confidence interval)

There is an uncertainty area in the perforation distribution that can be completely defined by V50 (average), and sd (standard deviation). The standard deviation characterizes the dispersion of the perforation velocities around their central value V50 or the slope of the curve at this central value.

It is important to note that V50 and sd are stochastic variables, their true values may never be known but can only be estimated. To estimate these two values, we need firing results. The values of V50 and sd can be calculated by different methods [3–8].

To evaluate the accuracy and the repeatability of each method, it is necessary to have a large sample of V50s and sds of which the average and the standard deviation can be calculated. The accuracy of a method is appreciated by the difference between the real value of V50 (or sd), which is obviously unknown, and the sample average of V50s (or sds) obtained from the tests. The smaller the difference is, the more accurate the method. The repeatability, or the precision, of a method is demonstrated by the sample standard deviation of V50s (S V50) or sds (S sd) from the tests. The smaller S V50 and S sd are, the more repeatable the method.

VPAM APR (Vereinigung der Prüfstellen für angriffshemmende Materialien und Konstruktionen Algemeine Prüfrichtlinie) is a norm that describes a test method for ballistic materials, design tests and product testing.

The VPAM test method has the advantage that every test shot can be assessed regardless of bullet velocity. For V50, an estimated value for the standard deviation will emerge, assuming that the possibility of penetration is a normally distributed function of hit velocity.

Besides V50, other certainty thresholds such as V95 can be elaborated. The innovation of VPAM method in comparison with the STANAG is the introduction of statistical risk evaluation. For a given penetration shot probability, a related critical velocity of the ballistic shot can be calculated. This allows the direct comparison of this critical velocity with the maximum impact velocity. Moreover, residual risks can be assessed by the determination of penetration probability for a given impact velocity. These advantages explain that the VPAM method is currently evaluated as a possible CEN norm.

7.3 Innovative 3D Textile Structure for Soft Body Armor Protection

The material aspect of personal ballistic protection is generally divided into two separate sub-systems: hard and soft. Indeed, the broad majority of threats can be defeated using two types of protections: soft materials and hard materials. Soft protections generally protect against fragments (up to a certain "velocity, mass, number" triplet) and hand guns (9 mm) threats whereas hard protections provide protection against "higher" threats like 5.56 mm or 7.62 mm caliber (armor piercing or not). However, the level of protection cannot be totally separated from other very important factors like the surface of protection, the ergonomic aspects (e.g., weight, flexibility) the logistical burden (number of pieces in the equipment) and the overall price of the ballistic protection system. Therefore, we chose to follow classical development lines for the individual blocks (soft and hard materials) but taking into account the possibility to think of the ballistic protection (and even the individual protection, including other aspects like CBRN protection, communications, energy source) as one system in which these individual blocks could be integrated much earlier than is done today in the development process, at least in certain areas of the individual protection system. The classical vision of the ballistic system (two sub-systems) is still valid from a material development point of view because all the technological blocks cannot be tackled together at the present time. It is our aim to try to propose some integrated solutions at the end of this project while keeping as a backup the classical two sub-system vision in case the integration is not possible from a process point of view or does not allow reaching any of the "performance targets."

Figure 7.7 describes the principal links between individual blocks/work packages. The first phase (green and orange straight lines) of the project was dedicated to evaluation of technologies (and associated processes) and the second phase (green and orange dashed lines) will be dedicated to selection of the best materials and processes as well as the evaluation of some routes of integration between these individual blocks.

7.3.1 Body Armor Protection Design

Armors can be designed to protect against a wide range of ballistic threats but, as the threat increases, the armor becomes heavier, stiffer and bulkier. Armor is good if it provides ballistic protection but also if it allows the wearer to operate easily a weapon system and to move quickly. Bulletproof vests are ranked according to their

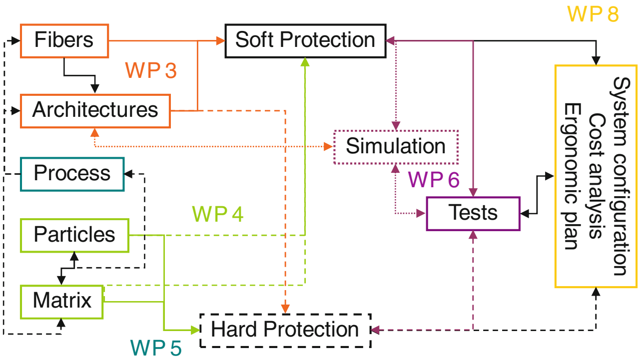


Fig. 7.7 Global interactions between the work packages and technological blocks

capability to defeat rounds. Soft body armor vests for law enforcement and civilian use consist of several layers of woven or UD fabrics made of para-aramid or polyethylene. They protect efficiently against handguns ammunitions (from Level I to Level III-A from NIJ Norm 0101.04) and also against fragments.

7.3.2 *Textile Material for Ballistic Protection*

Generally, the main disadvantages encountered with ballistic structures among the best known are the adverse effects of crossover points of fabrics and laminates delamination [9, 10]. This becomes a significant factor when shooting multi-impact because the integrity of the structure is no longer maintained. It would be interesting to use multiple technologies by taking advantage of their strong points while combining 3D textile fabrics.

Different kinds of 3D woven architecture can be chosen to take into account the tensile strength, the shear strength and the delaminating process according to the lifetime of different kinds of ballistic impact [11, 12].

7.4 Developments of High Performance Soft Ballistic Solutions Using Hybrid 3D-Fibrous Architectures and Classical Ballistic Protection Solutions

7.4.1 *3D Warp Interlock Fabrics*

The most used textile structures in technical application can be laminated, nonwovens, woven fabrics or knitted fabrics. In ballistic protection, we mostly find laminated or woven structure in soft protection or a combination of composite textile materials in

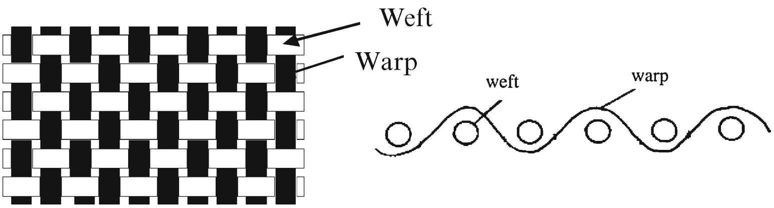


Fig. 7.8 Illustration of a plain weave fabric

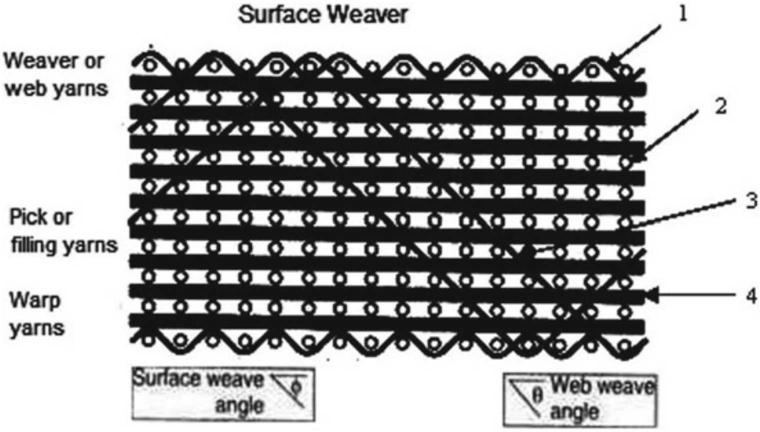


Fig. 7.9 Schematic representation of a warp interlock structure [13]

hard protection. Such kinds of materials have to be efficient and resistant against impact but also against the blast effect. Currently, the two dimensional plain weave structures represent effective ballistic protection. They offer a low cost method of producing large areas of material, with the same good mechanical resistance behavior that would have been obtained with laminates of unidirectional tape (Fig. 7.8).

These conventional fabrics are sufficient as existing solutions but can't help to reduce blunt trauma and weight ballistic protection. That's why, more and more textile structures are being developed and especially the three-dimensional structures as, for instance, the 3D warp interlock fabrics. Such structures are defined with a third yarn which goes through the structure in the thickness direction. These help to maintain the cohesion of the structure during an impact and thus reduce the effects caused by delamination in the laminates. The interlock structures exhibit good impact resistance. With this type of reinforcement, improved damage tolerance (within the meaning of ballistic term) is expected, which may be helpful in the case of multi-impact hits.

Figure 7.9 illustrates a 3D warp interlock fabric where we can find different yarns which have their own role. Indeed the first yarn (number 1) called "surface weaver" is used when the structure needs a smooth surface. This yarn doesn't influence the mechanical properties but is used for aesthetic aspect. The second yarn (number 2) is called "fill yarn or weft yarn", which gives the mechanical properties in the transverse direction.

The third yarn (number 3) called "warp yarn" is also used for the mechanical properties and undergoes undulations because it is working in the fabric thickness. The fourth yarn (number 4) called "longitudinal yarn" is also warp yarn and gives resistance and toughness in the longitudinal direction.

These advantages could be completed with these following specifications. Indeed Hu et al. [14] have mentioned that the 3D structures have an increase of compression (a) and flexural (b) strength after impact compared to a 2D laminate and a decrease of the area delaminated (c) (Fig. 7.10a–c).

Moreover, the shorter interlacing fibers in some architectures allow fabrics to bend easier and to shear better, which is unlike in 2D structures.

Three main types of such layer to layer, through the thickness and orthogonal interlock can be found in warp interlock fabrics. In the orthogonal warp interlock, the Z-yarns go through the whole fabric between only two columns of weft yarns. The main advantage is the presence of the column of longitudinal yarns which improves the mechanical properties of the fabric and limits the crimp inside the structure. On the other hand, the two yarns which go through the whole structure induce a weakness zone (Fig. 7.11).

In the layer to layer, the Z yarns connect separate layers of the fabric. This insertion allows the control of the crimp. Indeed the amount of Z yarn can be adjusted and many configurations can be possible to assemble layers together (Fig. 7.12).

In the through the thickness interlock, the Z yarn goes through the whole fabric across more than two columns of weft yarns. This configuration induces more thickness than the others, but it's possible to introduce a longitudinal yarn inside the structure which could compensate for the mechanical tensile loss (Figs. 7.13 and 7.14).

Regarding the advantages represented by the warp interlock, one of the proposed solutions to improve the ballistic protection and reduce the weight of body armor is to integrate 3D fibrous architectures such as warp interlock fabrics, at specific locations to absorb an estimated amount of energy.

7.5 Identification of the 3D Textile Material Solution for Impact Protection

A step-by-step procedure has been applied to find the best configuration of combining different type of textile materials to resist to different impact protections. To begin with, we propose to compare materials on their own taking into account the same density of fibers and weight (Table 7.1).

The 3D structure tested is a warp interlock layer to layer (LtL). The areal density value of the two solutions is approximately 4,600 g/m^2. A stack of plain weave

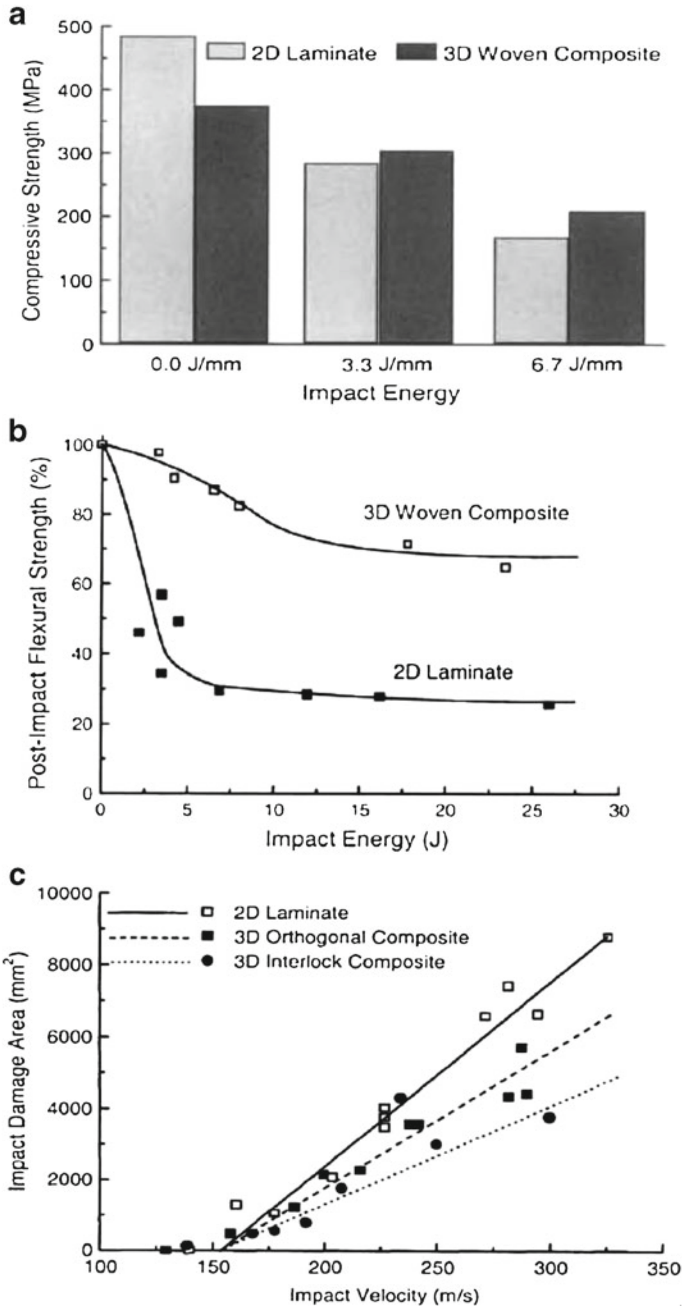


Fig. 7.10 (**a**) Effect of weaving on the compressive behavior; (**b**) Effect of weaving on the flexural strength; (**c**) Effect of weaving on the impact damage area

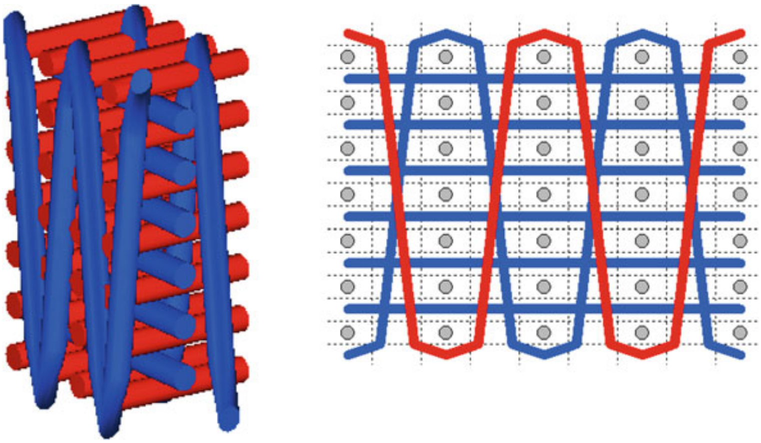


Fig. 7.11 Illustration of an orthogonal warp interlock (6 layers, 6 warp yarns) [13]

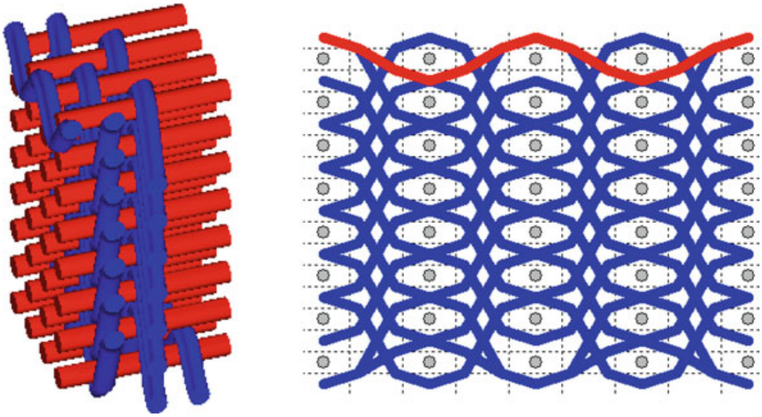


Fig. 7.12 Illustration of a layer to layer interlock (8 layers, 16 warp yarns) [13]

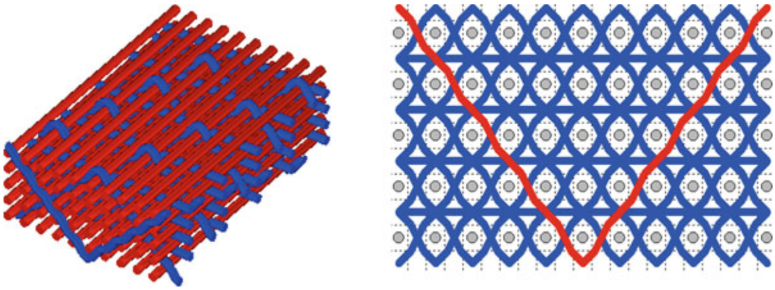


Fig. 7.13 Illustration of through the thickness interlock with longitudinal yarns (5 layers, 30 warp yarns) [13]

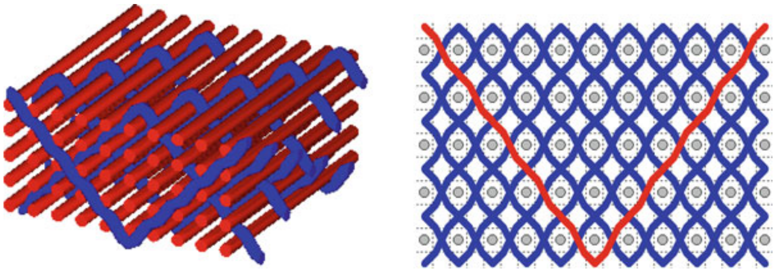


Fig. 7.14 Illustration of through the thickness interlock without longitudinal yarns (5 layers, 10 warp yarns) [15]

Table 7.1 Description of the multilayer fabric made with plain weave structure and the 3D warp interlock fabric (LtL)

Type of materials	Areal weight (kg/m²)	Assembling	Remarks
3D-fibrous structure (Layer to layer): 3D(LtL)	~4	Free	
Plain weave (PW)	~4	Stitching on PW	Diamond 5 × 5 cm

Fig. 7.15 Comparison of V50 values between Aramid Multi-Layer plain weave fabric and 3D warp interlock fabric (LtL)

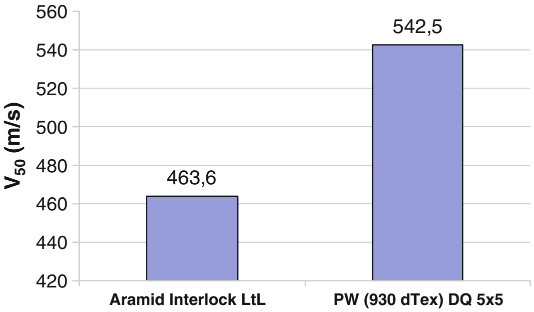


Table 7.2 Description of the multilayer fabric made with plain weave structure and the 3D warp interlock fabric (TtT)

Type of materials	Areal weight (kg/m²)	Assembling	Remarks
3D-fibrous structure (Through the Thickness): 3D(TtT)	~4	Free	
Plain weave (PW)	~4	Stitching on PW	Diamond 5×5 cm

fabrics has been stitched together using a diamond quilt of 5×5cm design. The results are shown in Fig. 7.15.

The 3D structure tested is a warp interlock through the thickness (TtT). The exact areal density of the 3D warp interlock is approximately 3,600 and 3,400 g/m^2 for the multi layer stitched plain weave fabrics (see Table 7.2).

Fig. 7.16 Comparison of V50 values between Aramid Multilayer plain weave fabric and 3D warp interlock fabric (TtT)

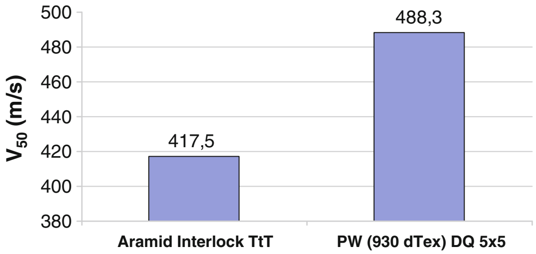
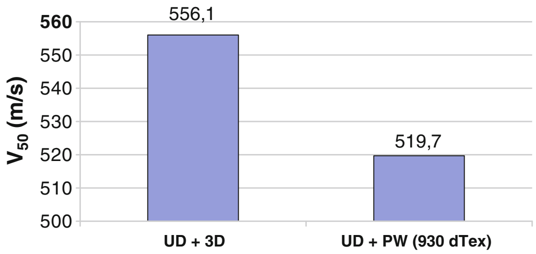


Table 7.3 Description of the different 3D hybrid solutions

Type of materials	Areal weight (kg/m²)	Assembling
UD + PW	~5	Free
UD + 3D(orthogonal)	~5	Free
UD + 3D(TtT)	~5	Free
UD + 3D(TtT)	~5	Free

Fig. 7.17 Comparison of V50 values submitted to FSP between 3D hybrid solutions



The test results are shown in Fig. 7.16.

For both cases, 100% – 3D fibrous structures are 17% less efficient versus fragments than 100% – 2D-PW at the same weight and with the same multi-filaments.

However, only one test has been carried out for each reference and it gives information but does not permit the drawing of a definitive conclusion.

At this stage of investigation, the obtained results suggest combining 3D warp interlock fabric with other textile materials to magnify the mechanical properties of resistance against different threats.

Considering a FSP projectile, different hybrid solutions (Table 7.3) have been tested using mainly a blend of unidirectional aramid material with textile solutions.

The areal density of all these solutions is approximately 5,460 g/m^2.

7.5.1 Case: FSP

The test results are shown in Fig. 7.17.

As shown in Fig. 7.17, the hybrid 'UD + 3D' (+7%) has a better performance than the 'UD + PW' combined.

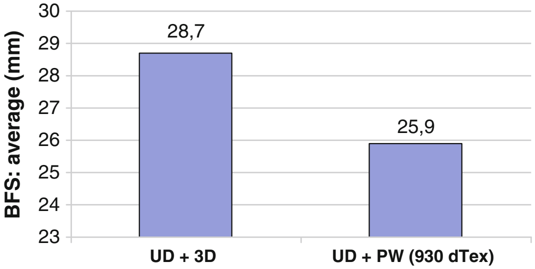


Fig. 7.18 Comparison of V50 values submitted to 9 mm between 3D hybrid solutions

Table 7.4 Description of different 3D hybrid solutions

Type of materials	Areal weight (kg/m²)	Assembling	Remarks
PW + Felt	~5	Stitching on PW	Best stitching
PW + 3D(LtL) + Felt	~5	Stitching on PW	Best stitching
3D(LtL) + PW + Felt	~5	Stitching on PW	Best stitching
PW + 3D(LtL) + Felt + PW	~5	Stitching on PW	Best stitching

7.5.2 Case: 9 mm

Considering a 9 mm projectile, the same hybrid solutions have also been tested.

As shown in Fig. 7.18, Hybrid ‘UD + 3D’ is less efficient (−10.8%) than the ‘UD + PW’ combination for the 9 mm shot.

Considering the V50 values for the hybrid solutions, a promising result is the use of 3D warp interlock fabric compared to the stitched multilayer plain weave fabric. But, considering the BFS values, the use of 3D fabric inside the hybrid solution leads to relatively lower performance corresponding to a difference value of 2.8 mm between the two solutions. Therefore, we investigated new hybrid solutions (Table 7.4) to maintain the same performance of the V50 value and decrease the BFS value.

The areal density of all these solutions is around 5,070 g/m^2.

7.5.3 Case: FSP

As shown in Fig. 7.19, the better performance of hybrid ‘3D + PW + F’ is than that of the ‘PW + F’ structure by 5.28%.

7.5.4 Case: 9 mm

As shown in Fig. 7.20, the hybrid structure ‘3D + PW + F’ has a small difference of 0.7% when compared to the ‘PW + F’ structure against a 9 mm shot. The difference of 0.2 in the BFS value cannot be considered to be significant and thus can be

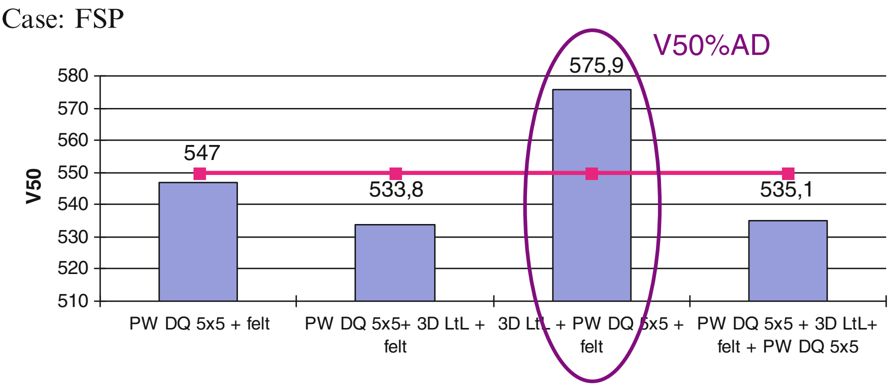


Fig. 7.19 Comparison of V50 values submitted to FSP between 3D hybrid solutions

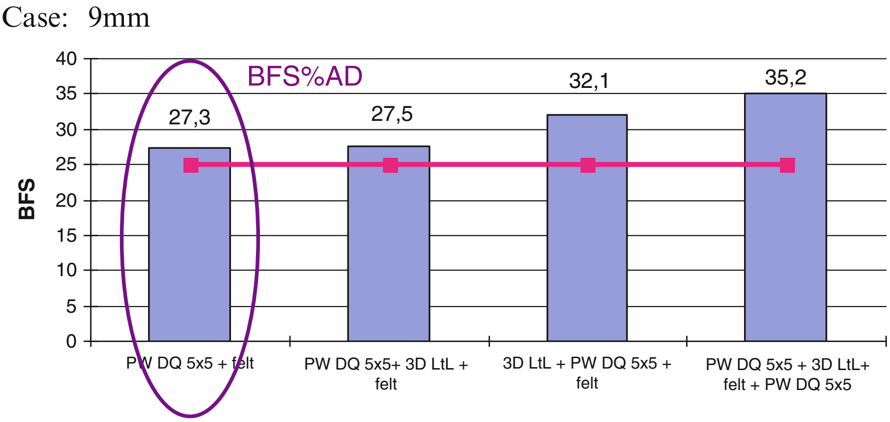


Fig. 7.20 Comparison of BFS values submitted to 9 mm between 3D hybrid solutions

assumed as equal. Thus, the hybrid solution '3D + PW + F', with an areal density of nearly 5,070 g/m^2 seems to be an efficient solution compared to the reference solution.

We chose the hybridization with the best protection against fragments as the ballistic protection necessary for the military.

7.6 Conclusion

Based on the military requirements for soft body armor protection for combat suits, new textile material solutions have been found by integrating weight, back-face deformation and cost reductions for the same degree of ballistic protection.

Ballistic tests have been performed on different configurations of textile material solutions using the STANAG 2920 norm. Main parameters have been identified and their potential effects on ballistic performances have been described. Interesting results are obtained when using different textile materials combined together inside the ballistic protection solution. The performance based on the V50 and BFS values with the same areal density of a given structure of 3D warp interlock fabric inside hybrid solutions has been compared to multilayer stitched plain weave fabrics.

It has been found that hybridizations containing 3D-fibrous structures allow:

- Close performances in fragment protection and trauma reduction when the 3D structure is in the middle of the ballistic pack.
- Better performances in fragment protection and lower for trauma reduction when the 3D structure is on top of the ballistic pack.

7.7 Looking Ahead

To attain the 25 mm backface signature, anti-trauma layers can be inserted in the best solution hybrid '3D+PW+F' with a minimum of extra mass per square meter. Additionally, investigations to reduce areal density must be carried out to find the optimal solution fulfilling all the required criteria.

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Chapter 8
Activated Natural Zeolites on Textiles: Protection from Radioactive Contamination

A.M. Grancaric, I. Prlic, A. Tarbuk, and G. Marovic

Abstract Clothing designed to protect against radioactive contamination was based on a simple principle. It was important not to inhale contaminated dust and air and to ensure that contaminated particles could not reach the skin. Therefore, the density of the textile was crucial. New developments, keeping in mind that textile should be lightweight, are focused on textiles which can chemically bind the contamination particles and not allow them either to diffuse to the skin or spread back into the environment. A great success would be if the clothing were made reusable (e.g., for use in the space station). Therefore, new methods (or chemical preparations) are being proposed for developing intelligent textiles.

Activated natural zeolite clinoptilolite is microporous hydrated aluminosilicates crystals with well-defined structures containing AlO_4 and SiO_4 tetrahedral linked through the common oxygen atoms. It is a nontoxic substance, excellent for adsorption of proteins and small molecules such as glucose. Due to its cation exchange ability, it has catalytic properties and has multiple uses in medicine, industry, agriculture, water purification and detergents. Applied on textiles it provides excellent UV-R and microbe protection. Therefore, the present chapter discusses attempts to modify cotton fabrics with natural zeolite nanoparticles for imparting the ability to protect from radioactive contamination.

Keywords Natural zeolite • Protective textiles • Cotton fabric • Natural radioactivity • Radioactive contamination

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8.1 Introduction

8.1.1 Zeolites

Zeolites are hydrated natural or synthetic microporous crystals with defined structures based on AlO_4 and SiO_4 tetrahedral building blocks connected through oxygen atoms. Zeolites have a variety of usages; they are employed as adsorbents, ion exchangers, catalysts and detergent builders in industry, agriculture, veterinary medicine, health care and environmental protection [1, 2].

Natural zeolites are rock-forming, microporous silicate minerals. A mineral of the natural zeolite, clinoptilolite, has a crystalline configuration, tetrahedron structure (Fig. 8.1). It has a lattice structure with long channels comprising water molecules and alkaline earth ions. As these do not occupy fixed positions, these ions may shift within the lattice. They can be easily released and exchanged without changing the character of crystal lattice, enabling clinoptilolite to have strong ion exchange properties, as example clinoptilolite bonds heavy metals. Many researchers report that clinoptilolite absorbs toxins and mold [3].

Clinoptilolite can be ground by a certain tribomechanical processing in a patented machine (Patent: PCT/1B99/00757) shown in Fig. 8.2 yielding particles on a submicron level (micro and nanoparticles).

The equipment for tribomechanical micronization and activation device (TMA equipment) shown in Fig. 8.2 consists of a box which is cooled by water and two rotor discs turned to each other. Each disc contains 3–7 concentric rings with specially designed elements of hard metal. The discs rotate in opposite directions

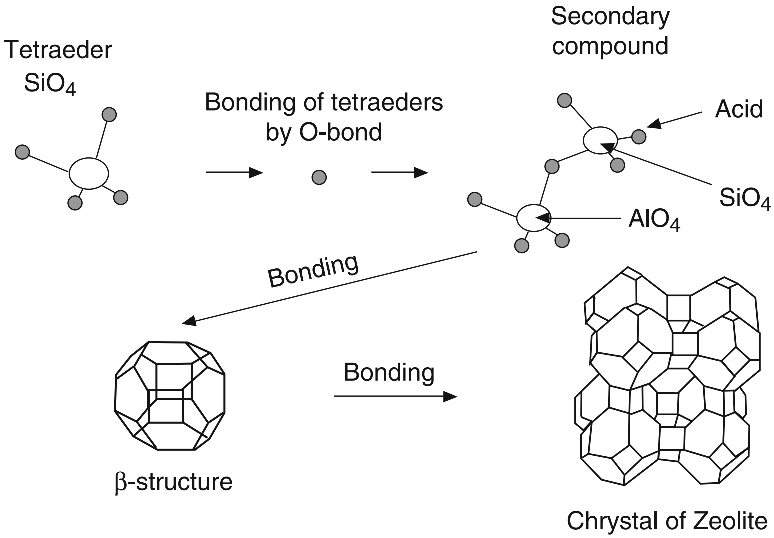


Fig. 8.1 Crystal of zeolite

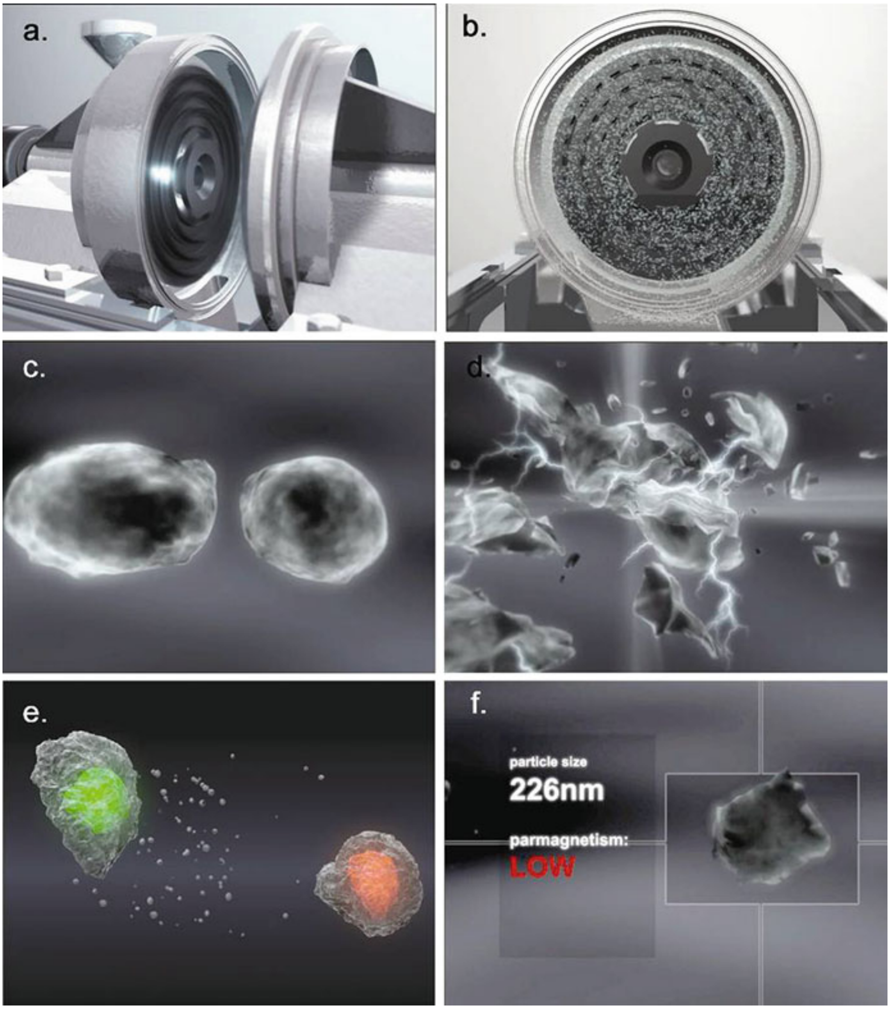
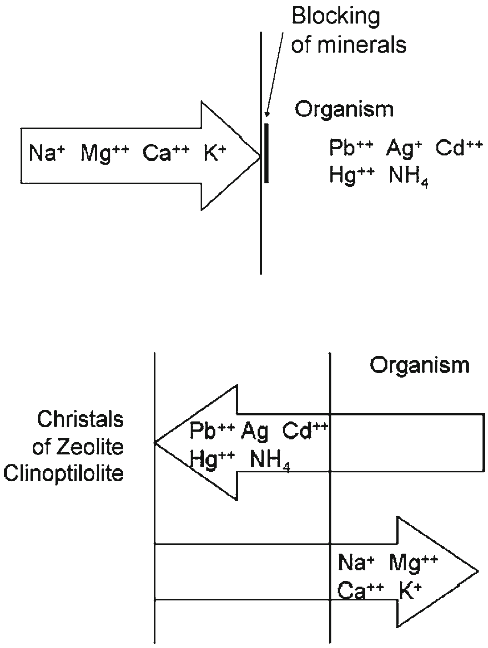


Fig. 8.2 Tribomechanical activation (TMA) – (**a**) TMA machine, (**b**) TMA machine with particles, (**c**) input of clinoptilolite particles, (**d**) crash of zeolite particles which results with micro and nanoparticles, (**e**) activated zeolite particles, (**f**) nanoparticles of clinoptilolite [4]

with the same angular velocity. Source material is fed into the equipment through the central section of the rotor system by a ventilating air stream. This is the reason particles are accelerated due to multiple changes in running direction; they collide and rub against each other in short time intervals – at least three times in one thousandth of a second at angles from 8° to 15°.

This does not change the chemical composition, but certain physical chemical properties are changed: increase in electrostatic charge, capacity of ion exchange, specific active surface and capacity of liquid absorption and water released from the

Fig. 8.3 Ion exchange by zeolite [1]



inside of the lattice. It is relevant to note that the crystal ball cracks on the surface during the activation process remain active in its inner layer. Nanoparticles in one gram of the micronized clinoptilolite have a total surface area of 50,000 m^2 and are interwoven with 50 million filter microchannels representing exceptionally powerful therapeutic microfilters. Well-known mechanisms of zeolite action and its action capacity are increased several times by this technological procedure [4, 5].

Due to the increased total surface area and excellent ion exchange (Fig. 8.3) as well as increased accessibility of the micro-channels, the activity of the zeolite is increased several hundred times. Activated natural zeolite has multiple uses in industry and agriculture and the broad spectrum of medical uses [1–9].

Composition and physical chemical properties of activated natural zeolite – clinoptilolite from Slovakia made by tribomechanical activation on the patented machine manufactured by Tribomin d.o.o. (Osijek, Croatia) according to the analysis of ISEGA Forschungs- und Untersuchungesellschaft mbH, Aschaffenburg, Germany are given in Table 8.1 [8].

8.1.2 Activated Zeolite in Diverse Biological Activities

Amongst other useful properties and applications, activated zeolite possesses diverse biological properties successfully used as vaccine adjuvant and for the treatment of diarrhea. Activated zeolite plays an important role in the regulation of an immune

Table 8.1 Composition and physicochemical properties of TMAZ analyzed by ISEGA Forschungs- und Untersuchungsgesellschaft GmbH, Aschaffenburg, Germany [8]

Chemical composition	
Component	%
SiO_2	65.0–71.3
Al_2O_3	11.5–13.1
CaO	2.7–5.2
K_2O	2.2–3.4
Fe_2O_3	0.7–1.9
MgO	0.6–1.2
Na_2O	0.2–1.3
TiO_2	0.1–0.3
Si/Al	4.8–5.4
Empirical formula	
$(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96} \times 24H_2O$	
Physicomechanical properties	
Specific mass	2.2–2.5 g/cm^2
Porosity	32–40%
Effective pore diameter	0.4 nm
Ion-exchanging capacity	mol/kg
Total	1.2–1.5
Ca^{2+}	0.64–0.98
Mg^{2+}	0.06–0.19
K^+	0.22–0.45
Na^+	0.01–0.19
Ion-exchanging selectivity	
$Cs > NH_4^+ > Pb^{2+} > K^+ > Na^+ > Mg^{2+} > Ba^{2+} > Cu^{2+} > Zn^{2+}$	
Chemicals absorbed	
NH_3, hydrocarbons $C_1 - C_4$, CO_2, H_2S, SO_2, NO_x, aldehydes	
Toxicity	
Nontoxic according to US Code of Federal Regulations (21 CFR 82, Subpart C)	

system containing high portion of silica; silicates and aluminosilicates act as non-specific immunostimulators like superantigens [2, 6].

Superantigens (SAG) are a class of immunostimulators and disease causing proteins of bacterial and viral origin with the ability to activate a relatively large fraction of T cell population. Where immunity is reduced, zeolite activates B and T cells populations. In the disease of autoimmune system, it lowers the cancer marker CD 56 [10].

It is well-known that protein kinase stimulates oncogenes which results in mutation of DNA and creation of malignant cells. Activated zeolite inhibits protein kinase B (c-Act) to other kinase included in the apoptosis process and that triggers cancer. In this way it prevents the creation of malignant cells [7].

Local application of such zeolite to animal skin cancers effectively reduced tumor formation and growth. It was shown that it might affect cancer growth by attenuating survival signals and inducing tumor suppressor genes in treated cells. Having antiviral properties on the skin that is activated locally by zeolite has

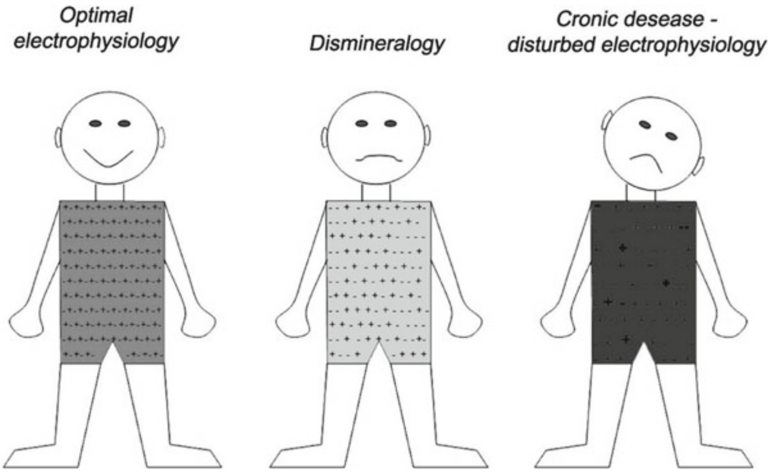


Fig. 8.4 Human body is electrically charged with examples of models for optimal electrolytic regulation and its disorders [1]

therapeutic applications against herpes virus infection or orally in the case of adenovirus or enterovirus infections.

Viruses are very small and on nosocomial level, from 65 to 80 nm for adenoviruses and enteroviruses to 100–200 nm for herpes viruses. Antiviral effects of activated zeolite can be explained by incorporation of virus particles into the pores of such crystals [11].

8.1.3 Antioxidative Effects

Activated zeolite has very strong antioxidative properties that could affect oxidative stress in cancer and diabetes patients. Free radicals are the main factors of many pathological changes in organisms. It was found that around 90% of various diseases are results of disturbances in cell function or cell damage caused directly or indirectly by the activity of oxygen free radicals. Oxygen free radicals have been implicated in numerous pathological processes including inflammation, reperfusion injury, autoimmune diseases, neurological disorders, *diabetes mellitus* and cancer [12]. It is confirmed that activated zeolite acts against disease *Psoriasis vulgaris* on the base of antioxidative activity [13].

Figure 8.4 is a schematic representation of the human body with examples of models for optimal electrolytic regulation and its disorders.

Total Antioxidant Status (TAS) measures the concentration of antioxidants in the organisms. Studies have shown that activated zeolite caused an increase in TAS value of more than 26% which is in comparison to known antioxidants (A, C, E vitamins, flavonoids, melatonin, etc.) that are ten times more effective [9].

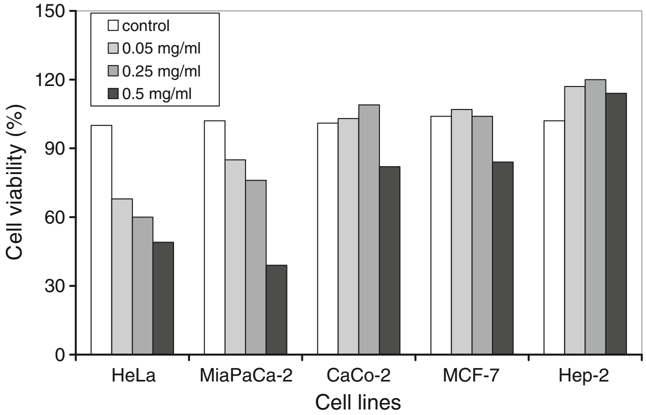


Fig. 8.5 The effect of activated zeolite treatment on growth of different human cell lines. The results are represented as a percentage of growth control cells. Legend: *HeLa* cervical carcinoma, *MiaPa-Ca-2* pancreatic carcinoma, *CaCo-2* colon carcinoma, *MCF-7* breast cancer, *Hep-2* laryngeal carcinoma [11]

Currently, various antioxidants are under clinical investigation as an adjunct to standard and experimental cancer therapies. Anticancer activity of antioxidants may not only be attributed to their radical scavenger properties, but also to direct modulation of cellular signal transduction pathways, resulting in growth arrest and apoptosis of cancer cells [7]. Recently, it has been shown that 4 weeks of oral supplementation with activated zeolite resulted in restoration of previously increased antioxidant levels (Randox Total Antioxidant Status) and decreases of free radicals (d-ROM-s Free Radical Analytical System) in plasma of cancer patients [9].

Besides its antioxidant property, activated zeolite demonstrated anticancer activity *in vitro* tissue cultures by inhibition of protein kinase B (c-Act) and induction of expression of tumor suppressor proteins, independently from p53 protein. Blockade of cell growth is shown in Fig. 8.5 through several cancer cell lines [11]. The effect of activated zeolite on cell proliferation *in vitro* was studied on several human cell lines. The cell viability was determined using MTT assay (from Sigma) which detects dehydrogenase activity in viable cells.

Figure 8.5 shows the effect of this zeolite on the growth of next human cell lines: HeLa-cervical carcinoma; MiaPaCa-2-pancreatic carcinoma; CaCo-2 – colon carcinoma; MCF-7 – breast cancer; Hep-2 – laryngeal carcinoma. The high inhibitory effects of zeolite are obtained with two cell lines, HeLa and MiaPaCa-2 which confirmed the recent results about zeolite inhibition of protein kinase B (c-Act).

Additionally, the combination of activated zeolite with doxorubicin for the treatment of mammary carcinoma-bearing mice was significantly more effective in reducing the number pulmonary metastases when compared to doxorubicin mono-therapy [7, 9, 14].

8.1.4 TMAZ in Healing Wounds

In wound healing, there are five important requirements: moist environment, antimicrobial, non-toxic to human cells, hypoallergenic and continuous debridement. Activated zeolite follows these requirements providing a favourable environment for the healing of superficial skin wounds [6, 11]:

Acute skin problems – mechanical skin damage, thermal burns, abrasions, insect bites, post-operative wound treatment, herpes simplex and herpes zoster.

Chronic skin problems – various skin infections, allergic reaction, degenerative diseases, neurodermitis, ulcus cruris, decubitus ulcus, etc.

8.1.5 Nanoparticles of a Natural Zeolite (Clinoptilolite) Applied on Textiles

Nanoparticles of a natural zeolite (clinoptilolite) applied on textiles are following the tendency for new textile applications as materials for human performance, such as medical, protective and sports applications. During the last few years, these developments led to rapid growth of different protective finishes, material modifications and applications of nanoparticles. Textile and clothing is a human's second skin; therefore, it is the most suitable interface between environment and human body. It is an ideal tool for personal protection and safety.

Cotton and polyester fabrics were modified and treated with nanoparticles of natural zeolite clinoptilolite. SEM micrographs of cotton fabrics at 2,500× magnification are shown in Fig. 8.6 [4] and of polyester fabrics in Fig. 8.7 [5].

From Fig. 8.6, it can be seen that some of zeolite nanoparticles entered into spaces between the cotton fibers, while other particles are incorporated into the surface and yet other particles remained on the surface.

The difference between the cotton fabric treated with zeolite during and after modification, in this case mercerization, is apparent. If the treatment were performed during mercerization, a portion of the nanoparticles remained incorporated within the fibers and it is not visible on the surface, while if it is done after mercerization, a larger number of zeolite nanoparticles remain in interspaces and on the fiber surface.

Similar effects are observed on polyester fabric shown in Fig. 8.7. The differences between untreated and modified fabric by alkaline hydrolysis are well known – the pits on surface results in silk-like polyester fabric. Treated with zeolite nanoparticles, unmodified polyester fabric has more zeolite particles on the surface, than an alkali-hydrolyzed one. In that case, the pits on the fabric's surface are filled with zeolite particles and only small amounts are deposited on the surface. It is assumed that part of the zeolite particles are trapped in the pits of the fiber surface.

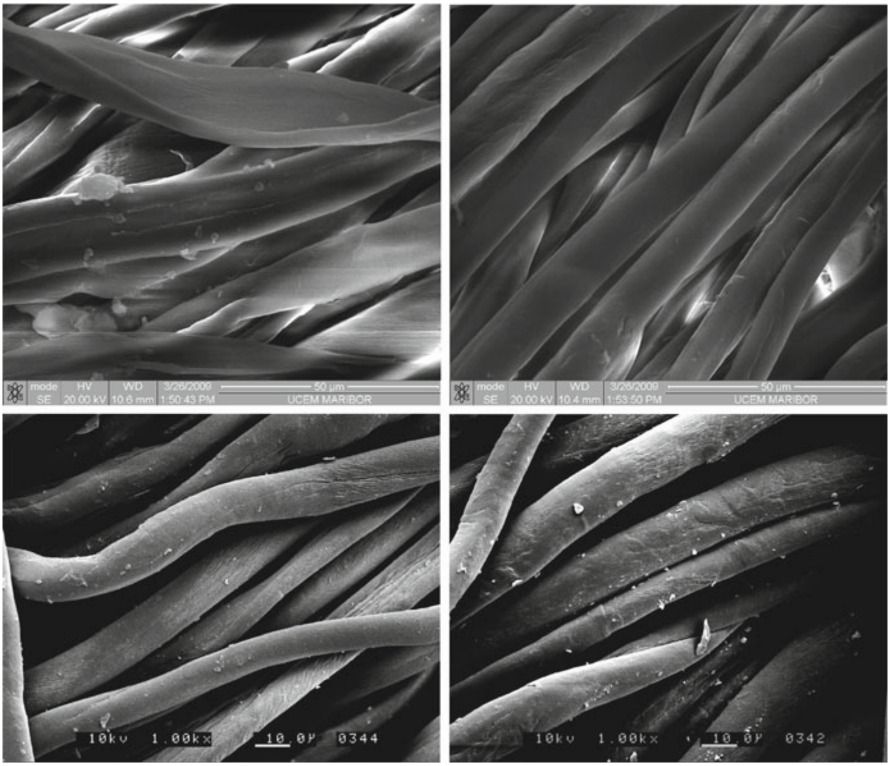


Fig. 8.6 SEM micrographs of cotton fabric, untreated and mercerized, and treated with zeolite nanoparticles during and after mercerization [4]

8.1.6 UV Protection

Good fabric UV protection is a guarantee that clothing will have the ability to protect the skin from incident solar energy.

While there are some beneficial effects of UV radiation (UV wavelengths from 100 to 400 nm) on the skin, it may cause skin damage such as sunburn, allergies, skin aging and even skin cancer especially during the summer time (UV-C). The UV-C radiation (from 100 to 280 nm) is absorbed by atmosphere, but UV-B (from 280 to 320 nm) and UV-A (from 320 to 400 nm) radiation reaches the earth and can cause known skin aging and the formation of skin malignant neoplasm. Diminishing of the earth's atmospheric ozone layer raises the UV exposure health risk. Therefore, more research and investigation of fabric UV protection has followed [15–17].

It is well-known that a garment provides some UV protection. Exposed fabric can reflect, absorb and/or scatter electromagnetic wavelengths in visible electromagnetic

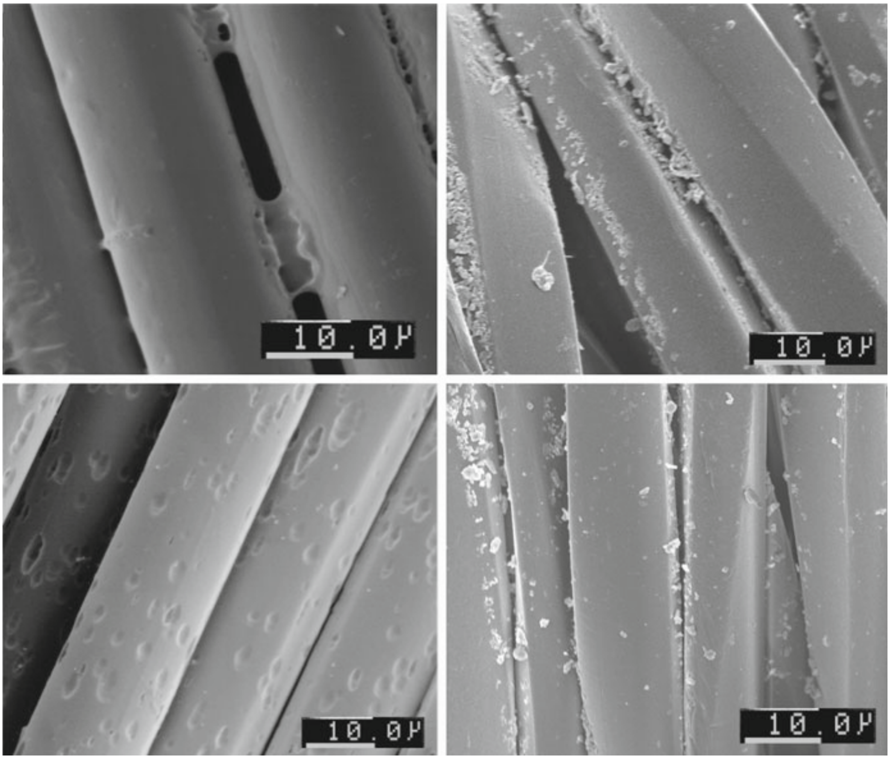


Fig. 8.7 SEM micrographs of unmodified polyester fabrics and treated with zeolite; alkaline modified polyester and treated with zeolite [5]

spectrum interval (Fig. 8.8), but in most cases it does not provide full protection properties. UV protection highly depends on a large number of factors, such as type of fiber, porosity, density, moisture content, type and concentration of dye, UV-B protective agents, and fluorescence whitening agents (FWA) in the case of white textiles, when applied [4, 5, 16–20].

In this chapter, UV protection of modified and zeolite treated cotton and polyester fabrics is expressed via *ultraviolet protection factor* (UPF) according to AS/NZS 4399:1996, indicating the ability of protection by textile materials to prevent erythema. The fabric labels and treatments are presented in Table 8.2 and the results in Fig. 8.9.

From the results shown in Fig. 8.9 it is evident that polyester fabric gives off better UV protection than cotton fabric after surface modification and treatment with nanoparticles of zeolite due to polyester chemical constitution. Polyester fiber has double bonds in polymer chain which can absorb small amounts of UV-R, and small amounts of UV-R are reflected from polyester multifilament.

Nanoparticles of zeolite on fabric surface are dispersed by scattering UV radiation resulting in better UV protection. Additionally, zeolite increases fabric surface area

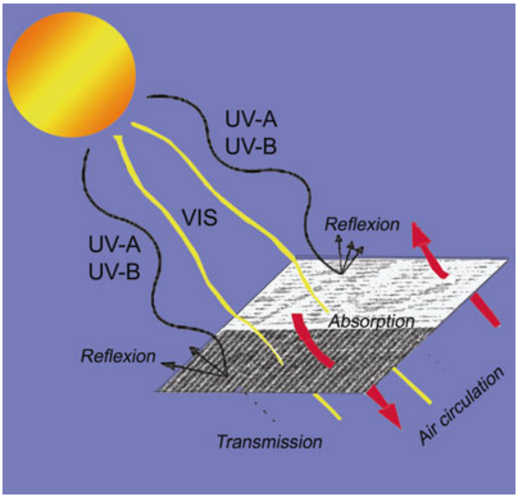


Fig. 8.8 UV radiation in contact with textile fabric

Table 8.2 Fabric labels and treatments

Label	Treatment
CB	Bleached cotton fabric
CBM	Bleached mercerized cotton fabric
CBZ	Bleached cotton fabric impregnated with zeolite
CBMZ	Bleached mercerized cotton fabric impregnated with zeolite
PET	Untreated polyester fabric
PETH	Hydrolyzed polyester fabric
PETZ	Polyester fabric impregnated with zeolite
PETHZ	Hydrolyzed polyester fabric impregnated with zeolite

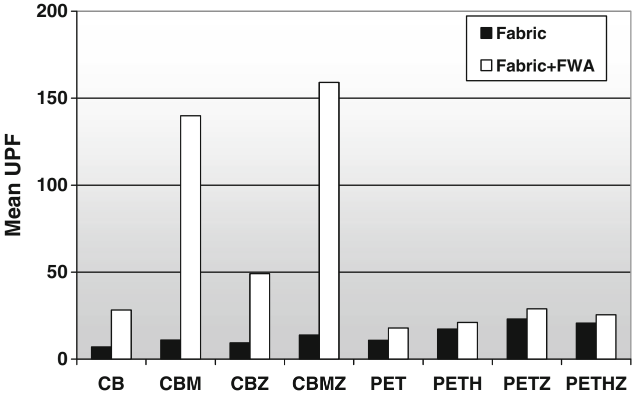


Fig. 8.9 Mean UPF values of cotton and polyester fabrics modified and treated with zeolite and FWA

resulting in higher adsorption of FWA. Therefore, mercerized and zeolite treated cotton fabrics give off excellent UV protection after FWA.

UPF values for polyester fabric have a behavior similar to that of cotton fabric. Modification of polyester fabric results in a little better UV protection, while treatment with nanoparticles of zeolite results in good UV protection. FWA treatment of polyester results in good protection as well. Meanwhile, FWA treatment to polyester fabric with zeolite results in very good UV protection.

To conclude, nanoparticles of a natural zeolite (clinoptilolite) applied on textile material scatter the light wavelengths of electromagnetic spectrum, resulting in enhanced UV protection.

8.1.7 Antimicrobial Protection

Clothing and textile materials are carriers of microorganisms such as pathogenic and odor-generating bacteria, and mold fungi because of the adhesion of these organisms on to the fabric surface. The need for a healthier and active lifestyle in the last few years has led to rapid growth of antimicrobial finishes for textiles to impart durable freshness and a feeling of safety and well-being for consumers [4, 6, 21, 22].

Therefore, it is of great interest to research antibacterial properties of textiles – nonwovens that can be used as protection masks and clothing in hospitals, woven for laundry and sheets in hotels and hospitals, and knits for summer clothing, socks and underwear [4, 6, 21, 22].

Since natural zeolite has antioxidant and anticancer activity and helps heal wounds, antimicrobial (antibacterial and antifungal) activity was determined with and without addition of antibiotics and antiseptics. Antimicrobial protection against Gram positive (*Staphylococcus aureus*) and Gram negative (*Klebsiella pneumoniae*) organisms was determined according to EN ISO 20645:2004. Antifungal protection against the fungus (*Candida albicans*) was determined according to EN 14119:2003.

Azithromycin, the most famous azalide with brand names Zithromax® (Pfizer) and Sumamed® (Pliva), was used as antibiotic, and Octenidine dihydrochloride brand name Octenisept® (Schülke & Mayer GmbH) as antiseptic.

Azithromycin has spectrum like other macrolide antibiotics, with extended activity to *Gram* positive and *Gram* negative organisms, as well as atypical pathogens [23].

Octenisept® is antiseptic which is effective against bacteria including *chlamydia* and *mycoplasma*, fungi and yeasts, protozoa (*trichomonads*), viruses (*Herpes simplex*, HBV, HCV and HIV) [24]. Antimicrobial treatments and the corresponding results are shown in Table 8.3 and Fig. 8.10, respectively.

Treatment of cotton fabrics with natural zeolite nanoparticles led to antimicrobial activity only for Gram positive *Staphylococcus aureus.*

Azalide treatment of cotton fabrics resulted in a high degree of antimicrobial protection to both Gram positive *Staphylococcus aureus* as well Gram negative *Klebsiella pneumoniae* bacteria. Applying the natural zeolite nanoparticles with

Table 8.3 The treatments and the antimicrobial activity of cotton fabrics

Fabric	Treatment	$S_{\mathit{taphylococcus\ aureus}}$ [mm]	$H_{\mathit{Klebsiella\ pneumoniae}}$ [mm]	$H_{\mathit{Candida\ albicans}}$ [mm]
B	Bleached cotton fabric	0	0	0
B-Z	Zeolite treated	0.25	0.25	0
B-AZI	Azithromycin treated	8.5	8.75	0
B-Z-AZI	Azithromycin and zeolite treated	10.0	10.25	0
B-OCT	Octenisept treated	3.0	2.5	3.25
B-Z-OCT	Octenisept and zeolite treated	3.0	3.25	3.0

Fig. 8.10 Antimicrobial and antifungal activity of cotton knitted fabrics treated with antiseptic and zeolite [24]

azalide has a synergistic effect. These fabrics give off the highest antibacterial protection. Antifungal activity did not occur.

The treatment of cotton fabrics with octenidine dihydrochloride (Fig. 8.10) leads to better antimicrobial protection. The antibacterial activity both on Gram positive *Staphylococcus aureus* as well Gram negative *Klebsiella pneumoniae* bacteria occurs, as well as good antifungal activity to microfungi *Candida albicans*. As with azalide, nanoparticles of natural zeolite and octenidine dihydrochloride show a distinctively synergistic effect in antimicrobial protection of textiles.

To summarize, the application of natural zeolite nanoparticles for antimicrobial protection has shown increased activity and synergism with some antimicrobial agents, e.g., azalide and antiseptics. On the other hand, azalides are not acceptable from dermatological or ethical viewpoints because of development of resistance.

8.1.8 Flame Retardancy

Most textiles consist of combustible fibers and so, it is very important to find the right treatment to impart flame protection properties to them. For most thermal protective applications, textiles comprising 100% synthetic and hence thermoplastic

Table 8.4 Labels and treatments for cotton and PES ribbons

Label	Treatment
PES	Untreated polyester
PES-A	Flame retardant finish – 220 g/l Apyrol PES (Bezema); 20 g/l Apyrol MH; 12 g/l H_3PO_4; 0.5 g/l Kemonecer WET (Kemo)
PES-A_Z	Flame retardant finish – 220 g/l Apyrol PES (Bezema); 20 g/l Apyrol MH; 12 g/l H_3PO_4; 0.5 g/l Kemonecer WET (Kemo); 5 g/l zeolite
PES-B	Flame retardant finish – 440 g/l Apyrol PES (Bezema); 20 g/l Apyrol MH; 24 g/l H_3PO_4; 1 g/l Kemonecer WET (Kemo)
PES-B_Z	Flame retardant finish – 440 g/l Apyrol PES (Bezema); 20 g/l Apyrol MH; 24 g/l H_3PO_4; 1 g/l Kemonecer WET (Kemo); 5 g/l zeolite
Cotton	Untreated cotton
Cot-C	Flame retardant finish – 220 g/l Apyrol CEP (Bezema); 20 g/l Apyrol MH; 12 g/l H_3PO_4; 0.5 g/l Kemonecer WET (Kemo)
Cot-C_Z	Flame retardant finish – 220 g/l Apyrol CEP (Bezema); 20 g/l Apyrol MH; 12 g/l H_3PO_4; 0.5 g/l Kemonecer WET (Kemo); 5 g/l zeolite
Cot-D	Flame retardant finish – 440 g/l Apyrol CEP (Bezema); 20 g/l Apyrol MH; 24 g/l H_3PO_4; 1 g/l Kemonecer WET (Kemo)
Cot-D_Z	Flame retardant finish – 440 g/l Apyrol CEP (Bezema); 20 g/l Apyrol MH; 24 g/l H_3PO_4; 1 g/l Kemonecer WET (Kemo); 5 g/l zeolite

fibers must be avoided. The only time they can be used is if they are part of a composite structure in which, for example, they are present as a component with a flame retardant/heat resistant majority fiber construction [25].

Cotton and other cellulose textiles are the most flammable materials used for protective clothing, accounting for more than 60% of the world annual consumption. Cotton and its blends are also used for temporary and permanent drapes, bed covers, mattress covers and furniture fabrics. By itself, cotton is readily ignited and burns rapidly. Therefore it is very important to protect cotton fabric against the flame [25, 26].

In most cases, flame retardant cottons are produced by chemically after-treating fabrics as a textile finishing process which, depending on chemical characteristics and cost, yields flame retardant properties having varying degrees of durability to various laundering processes [25]. Cellulose textiles are treated with those flame retardants that increase char or non-combustible products, usually organic phosphorous-based flame retardants.

Recently, the effect of natural zeolite on flame retardancy was investigated by Grancarić et al. [26–29]. Tables 8.4 and 8.5 show the results of treatments using organic phosphorous-based flame retardants with and without addition of natural zeolite to improve the flame retardancy of cotton [29] and PES [28] narrow fabrics.

From Table 8.5, it can be seen that the best flammability results were reached by using higher quantity of organic phosphorous-based flame retardant for both cotton and PES narrow fabrics. Zeolite has a positive effect on the flame retardancy achieved with organic phosphorous compounds.

Based on the Limiting Oxygen Index (LOI) values, it is evident that very good flammability results were reached for polyester fabrics, viz., lower than 5 s after-flame

Table 8.5 Burning behavior of vertically-oriented samples according to ISO 6940:2004 and Limiting Oxygen Index, LOI according to ISO 4589:1996 of treated cotton and PES ribbons [28, 29]

	ISO 6940:2004			ISO 4589:1996	
Label	$t_{afterflame}$ [s]	$t_{afterglow}$ [s]	l_{char} [mm]	$t_{100\ mm\ mark}$ [s]	LOI [%]
PES	62	–	170	91	20
PES-A	2	6	83	68	24
PES-A_Z	3	7	84	102	23
PES-B	3	6	78	111	23
PES-B_Z	3	5	81	97	23
Cotton	12	0	170	81	21
Cot-C	0	0	77	58	37
Cot-C_Z	0	0	108	46	37
Cot-D	0	0	100	[a]	>47
Cot-D_Z	0	0	77	[a]	>47

[a] Not possible to measure

time and 23–24 LOI. On the other hand, excellent flammability results were reached for cotton fabrics which means lower than 5 s after-flame time and high LOI (37–47).

The presence of alkyl phosphonate decreases the cellulose decomposition. The higher amount of flame retardant component causes lower decomposition temperature. The presence of alkyl phosphonate increases the residual weight of the final char product as well.

Nevertheless, despite its higher cost, the use of lower flame retardant concentration with zeolite for achieving very good flame retardancy is recommended.

8.1.9 Ability to Protect from Radioactive Contamination

As was shown earlier (Table 8.1), natural zeolite *clinoptilolite* is a microporous silicate mineral having a crystalline configuration and tetrahedron structure. Cesium (Cs) is in the first place of zeolite ion-exchanging selectivity, as follows:

$$Cs > NH_4^+ > Pb^{2+} > K^+ > Na^+ > Mg^{2+} > Ba^{2+} > Cu^{2+} > Zn^{2+}$$

Nanoparticles of a clinoptilolite are being applied to textiles used in medical, protective and sports applications affecting human performance. During the last few years, these trends have led to rapid growth of different protective finishes, material modification and application of nanoparticles. Textile and clothing acts as a human's second skin and serves as the most suitable interface between the environment and the human body. There is a need to investigate the use of zeolites in textiles as an ideal tool for personal protection and safety.

Research was carried out to investigate the behaviour of textiles processed with *clinoptilolite* zeolite with respect to radioactivity, specifically radioactive contamination, in order to be able to classify the processed textiles into the group of possibly radioactive-protective materials (personal and/or industrial textiles containing natural and/or artificial zeolites). The civil need for such textiles is obvious in the very fast growing field of nuclear medicine and PET/SPECT isotope production. Quantitative health risk for the persons wearing clothes made from these new fibres and impact on their health is to be evaluated for each purpose, military and security, and for common civil use [30].

As the physics of zeolite underscores its ability of adsorption, it is clear that the use of textiles processed with zeolite will be physically predisposed to be used in the field of radiation protection where liquid radioactive contamination is expected. Other dynamic physical properties such as capture of free dust particles are not possible or, are occurring too slowly to take place with respect to radioactivity and practical radiation protection. It is clear that zeolite can be used to hinder the radioactive alpha and beta contamination while the gamma (electromagnetic) component of ionizing radiation passing through textiles processed with natural zeolite cannot be prevented. However, the zeolite can adsorb a certain amount of contaminated liquid. The basic experiments validating the necessary input parameters to describe the natural radioactivity of fibres for further research regarding ionizing radiation contamination prevention using zeolite-processed textile were conducted.

Therefore, it is important to investigate the native radioactive characteristics of basic cotton fabrics (untreated and treated with zeolite) and basic zeolite compound used for processing the textile. A gammaspectrometric analysis of the afore-mentioned raw material and processed textile samples was performed.

8.2 Experimental Part

A 100% chemically bleached plain weave fabric with an areal density of 135 g/m^2 was used for the experiment. The fine powder of natural zeolite – clinoptilolite (micro and nanoparticles) from Slovakia was obtained by tribomechanical micronization. Activated natural zeolite (Z) is clinoptilolite particles made by tribomechanical activation on the patented instrument manufactured by Tribomin d.o.o. (Osijek, Croatia) shown in Fig. 8.2. The origin of clinoptilolite used in this study is Konica, Slovakia. By X-ray diffractometry it was found that the sample consists of about 80% clinoptilolite and the rest was clay minerals montmorillonite and mordenite. Moisture content was investigated by heating to 105°C; the maximum detected amount was 6% by weight. The particle size is around 200 nm. Composition and physical chemical properties are given in Table 8.1.

Three different samples were used in the experiment: Pure zeolite substance (Z); basic cotton fabric which was bleached and mercerized (BM); and treated with 10 g/l of activated natural zeolite.

The determination of possible radioactive contamination traces in any given textile sample requires the reference input radioactivity data. For the textile samples treated with *clinoptilolite,* the determination of NORM (Naturally Occurring Radioactive Material) radioactivity concentration of a pure zeolite and raw basic material

Table 8.6 The gammaspectrometrical analysis of natural zeolite and cotton samples

Activity concentration [Bq/kg]									
Radio nuclides	Zeolite (Z)			Bleached and mercerized (BM) cotton knitted fabric			Bleached and mercerized cotton knitted fabric (BZM) treated with 10 g/l zeolite		
^{238}U	125.82	±	32.32	13.86	±	5.52	35.33	±	10.04
^{232}Th	45.55	±	2.64	9.76	±	2.45	12.41	±	4.10
^{235}U	<4.99	±	0.27	0.69	±	0.52	<1.27	±	0.32
^{226}Ra	50.91	±	3.87	35.73	±	6.89	35.13	±	6.45
^{228}Ra	45.55	±	2.64	9.76	±	2.45	12.41	±	4.10
^{210}Pb	45.12	±	2.58	16.24	±	4.43	8.74	±	3.29
^{241}Am	1.22	±	0.32	3.49	±	0.52	2.82	±	0.36
^{40}K	938.53	±	7.80	172.07	±	10.40	150.96	±	11.19
K/gkg^{-1}	30.47	±	0.25	5.59	±	0.34	4.90	±	0.36
^{137}Cs	0.69	±	0.18	1.28	±	0.50	1.57	±	0.32
^{7}Be				5.02	±	3.50			

(cotton) is important. Special attention was paid to the samples with different concentrations of zeolite in the basic material. All textile samples were gammaspectrometrically analysed in the laboratory using HPGe and/or Ge(Li) detector (resolution 1.78 keV on 1.33 MeV ^{60}Co, relative efficiency 16.8%; resolution 1.56 keV on 1.33 MeV ^{60}Co, relative efficiency 18.7%) with electronic units and gammaspectrometrical software on a personal computer.

All samples were measured in Marinelli beaker, volume 1 L or volume 0.1 L. Measurement time was 80,000 s or higher. Dose rate measurement at 5 cm above the samples and 1 m above the laboratory ground in the absence of the samples was performed. This was needed to exclude the influence of natural radioactivity in the local environment on the measured data.

8.3 Results and Discussion

The gammaspectrometrical analysis of the given samples is presented in Table 8.6. The results are the NORM – activity concentrations of naturally occurring radionuclides in the samples of cotton textile, pure zeolite and cotton based textile treated with zeolite. The two artificial radionuclides found were expected.

The activity concentration of NORM radionuclides in pure zeolite samples leads to a conclusion that some impurities in the natural, pure zeolite material are present indicating that it is really a natural zeolite mineral because of the content of naturally occurring radionuclides.

Artificial zeolites can be prepared without any trace of radioactivity, natural or artificial, but on the other hand they can be contaminated with the trace radioactivity or other metal impurities during artificial man-made production processes.

Textiles, consisting of natural fibres like cotton, contain traces of naturally occurring radioactivity in various concentrations. This NORM concentration is highly dependent on the location where the natural fibres are grown. It is possible that natural fibres have a high content of radioactivity when a large amount of artificial phosphor fertilizer is used. If the concentration of ^{40}K is very high, ^{xxx}Cs is very likely to be found because it replaces the K in chemical bonds of food growth chain (^{xxx}Cs represents either the normal ^{56}Cs isotope or its radioactive sister ^{137}Cs). This fact is an obstacle for the precise gammasprectometrical analysis of the zeolite artificial radionuclide adsorption effect which is the main process for evaluation of the protectiveness grade of the textiles treated with zeolite.

All radionuclides listed in the Table 8.1 except anthropogenic ^{137}Cs are naturally occurring. The activity concentration of each of them is experimentally expected and leads to a conclusion that there is no anthropogenic radioactivity except for ^{137}Cs in these samples. From the viewpoint of "contamination," the samples were clean and ready for further investigation. Any artificial radioactive contamination to which the samples could be exposed and any adsorption process chemically fixing the contamination into the zeolite compound can be measured after the textile has been used for cleaning up contamination (decontamination) of preferably liquid radionuclides. In nuclear medicine, the contamination of a working area (hot spot where radionuclide dosage for diagnostic or therapeutic purposes) is highly possible. The radionuclides used in nuclear medicine are mostly liquid mixtures, applicable by needle into the patient. This is a possible working environment where the zeolite textiles can be applied (for cleaning the surfaces and "sucking" the contamination) [31].

Anthropogenic isotope ^{137}Cs is not a naturally occurring radionuclide and is not a generic ingredient of any natural zeolite mineral or textile. The natural textile ingredients like cotton incorporate the anthropogenic ^{137}Cs during growth. Activity concentration of the ^{137}Cs can tell us more about the fallout which took place at the location where natural textiles were grown or can tell us some details about the origin of the artificial textiles because every part of the world has a different and traceable local background radiation. It is not a compound of any natural zeolite but it can be present as an impurity in the artificial one.

The presence of the fission product ^{137}Cs in the natural zeolite and cotton fabric could be traced to the fallouts occasioned by the various nuclear tests all over the world, and probably, some due to the effect of the nuclear reactor accident at Chernobyl in 1986 [32, 33].

The test samples were clean and not contaminated. Any artificial radioactive contamination to which the samples could be exposed and any adsorption process fixing the contamination into the zeolite compound can be measured after the textile has been used for cleaning up contamination of preferably liquid radionuclides.

8.4 Conclusion

Further research involving the incorporation of natural or artificial zeolites into textiles to assess its ability to be used as radioactive contamination protective layers is needed. The physics of new material compounds can solve the chemical obstacle of binding the radioactive particles quickly and effectively into the zeolite. The technology of unbinding the contamination from zeolite-rich textile must be worked out to enable the reuse of the textile. The goal is to speed up the research on zeolites for use in smart textile compounds in the near future enabling us to use this textile for various protective purposes.

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Chapter 9
Developments in Decontamination Technologies of Military Personnel and Equipment

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Abstract Individual protection is important for warfighters, first responders and civilians to meet the current threat of toxic chemicals and chemical warfare (CW) agents. Within the realm of individual protection, decontamination of warfare agents is not only required on the battlefield but also in laboratory, pilot plants, production and agent destruction sites. It is of high importance to evaluate various decontaminants and decontamination techniques for implementing the best practices in varying scenarios such as decontamination of personnel, sites and sensitive equipment.

This chapter discusses decontamination technologies such as adsorptive carbon and enzymes, and highlights recent developments such as reactive skin decontamination lotion and Low-cost Personal Decontamination System (LPDS). Decontamination using solvent and non-solvent based systems is an important countermeasures strategy adopted by military, first responders and emergency personnel to sustain their operational capability and prevent additional contamination.

9.1 Introduction

The Chemical and Biological Defense Program of many nations utilize four key operational areas such as Sensing, Shielding, Sustaining and Shaping, into which the Chemical, Biological, Radiological and Nuclear (CBRN) countermeasures capabilities are categorized. In the United States, this division is defined as the operational capability of CBRN Defense Program. Decontaminating the soldiers and warzone equipment to minimize casualty, save lives, and to restore combating capacity, is the main priority of the sustaining operational capability of the military. Decontamination

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of Chemical and Biological (ChemBio) agents is an important military activity necessary to sustain combat capability and is an important requirement in the battlefield, laboratories, pilot plants and agent destruction sites [25]. A protective technology against ChemBio agents or a hazard mitigation strategy to counteract the threat and/or consequence of a ChemBio attack, implemented by the military, should serve as a tool to maximize the survivability, dexterity and overall performance of a warfighter while reducing the risk.

Advanced textiles-based protective systems, like many other essential military techniques and tactics, are one of the most important technological achievements which can determine the fate of a war or a rescue mission. Textile-fabric-based technologies have been known to serve the military as an important aid for camouflage, anti-ballistics, fire resistance and for individual/collective protection against chemical, biological, radiological and nuclear (CBRN) agents. Unlike the textile substrates which have activated carbon coated on their surface resulting in masking of the surface area of the carbon, and a heavier textile composite, fibrous carbon-based advanced textile substrates are lightweight and flexible and are highly efficient in adsorption of liquid chemicals and chemical vapors. Additives such as amines, copper and chromium salts, impart reactive and catalytic activity to adsorbent carbon fibers against toxic agents such as hydrogen cyanide, phosgene & cynogen chlorides [14]. Today, research and development in the area of military textiles tend to focus on incorporation of advanced technologies such as nanotechnology, membrane technology, reactive and sorbent decontamination technologies, anti-ballistic technologies, intelligent textile systems etc., which can enhance the efficiency and life expectancy of a soldier and provide excellent CBRN agent protection. Individual protection systems such as anti-ballistic jackets, ChemBio protective gear, personal protective equipment (PPE), CW agent decontamination kits, biological decontamination kits and collective protection systems such as tents, rapidly deployable structures, enclosed air filtration units and coated polymer liners are highly important tools to equip the military for prevention and mitigation of CBRN agent threat. In this chapter, we focus on existing and emerging technologies for individual protection.

Many ideas summarizing the recent advancements in the area of individual protection, in relation to the development and utilization of intelligent textile materials, have been reported [5]. Intelligent or smart textiles can be manufactured by incorporating electronic components with conventional textiles. Such textiles can be very useful in alerting the warfighter and the central command center for any abnormalities in normal physiological functions of the combatant. Also, penetration of a foreign material, chemical or biological, can be detected with use of intelligent textiles, thereby preventing casualty. To counteract the threat and harmful effects of chemical warfare (CW) agents and biological agents, strategic preventative and post-exposure approaches are needed. A preventative strategy to avoid any contact with the ChemBio agent can be very different from post-exposure decontamination and treatment strategies. A sensor-based system with high-end detection capabilities may not be of much use in a post-exposure scenario. Strategies for post-exposure decontamination involve removal of the ChemBio agent from the contaminated surface, prevention of spillage and off-gassing of toxic chemicals, rapid breakdown or destruction of the toxic agents to non-toxic compounds, rapid diagnostics and therapeutics. There is a need to develop a highly efficient and advanced decontamination system which can hinder or counteract the effects of the toxic ChemBio agents during a post-exposure event, facilitate the strategic tasks to restore combat capability and pose minimal logistic burden to the military personnel [24, 28–31, 33].

The threat of CW agents is real and complex in nature. In the case of chemical warfare, various classes of CW agents can attack the human body to compromise its normal physiological functioning by unique modes of action thereby causing stress, trauma, toxicity and lethality. Different classes of CW agents have varying physicochemical properties which affect their absorption through the skin, deposition on various surfaces, interactions with various organic and inorganic materials, and ultimately their fate in the environment. Therefore, the idea of developing a universal decontamination strategy which can counteract a majority of the CW agents is very challenging. Post-exposure strategies and characteristics of various decontamination systems for decontaminating human body and military equipment are discussed.

9.2 Decontamination: Emergency Response and Battlefield Scenario

In the battlefield, the CW agents may be delivered as fine aerosols in their purest forms, or mixed with additives (thickeners) which facilitate these highly toxic agents to persistently stick to a number of different surfaces. The surfaces which are susceptible to such an exposure in the warzone are the surfaces of weapons, equipment, vehicles, shelters, clothing and most importantly, the human skin. Neat CW agents that are mixed with polymeric thickening agents, readily adhere to all of these surfaces. These are particularly difficult to remove using aqueous (water-based) decontamination solutions, because, dissolution properties of many CW agents in conventional and readily available solvents (e.g., water and soap solutions) are adversely affected by the thickening agents [40]. Additionally, particulate matter arising from various environmental conditions and combat-related activities may also be present in the warzone; for example, dust, smoke, gunpowder, blowing sand, soot and exhaust. CW agents in aerosolized or vapor forms can adhere to such particulate matter that gets deposited on surfaces and crevices of military equipment, sensitive instruments and the human body. Furthermore, removal of CW agent contaminated dust particles from unreachable corners and surfaces of sensitive equipment which are frequently used in warzones can be very challenging [16].

Amidst an array of stressful tasks encountered by the warfighters and medical personnel in the battlefield, recognizing exposure to CW agents can be really tough. An individual can often misinterpret presence of foreign liquid droplets on their skin as their own sweat, especially while conducting military operations in a highly hostile environment. If military personnel were exposed to a CW agent, it could lead to devastating consequences within a matter of minutes. Rapid administration of appropriate (agent-specific) prophylactic, diagnostic and therapeutic protocols is very important to reduce such risks. Timely recognition of CW agent exposure, and the nature of the CW agent, is of utmost importance to make tactical decisions on personnel and equipment decontamination, diagnostics, detoxification and therapeutics to minimize casualty and mitigate the risk. Unfortunately, conventional agent detection systems may take a few minutes to confirm the presence of a CW agent in the battlefield. In many cases, such detection system may not be available during the time of an emergency. Therefore, military personnel or first-responders have to rely on prophylactic procedures, vaccines and PPE to avoid the effects of contamination. Furthermore, warfighters must rely on their intuition and treat the presence of any foreign material as a possible ChemBio agent threat, and take immediate measures to decontaminate themselves in order to mitigate the threat.

9.2.1 Individual Decontamination

Percutaneous (dermal), respiratory or ocular exposure to CW agents can result in severe detrimental effects to the health of a victim. Military gas masks can provide protection against respiratory and ocular exposure; however, a human body, which consists of approximately 1.8–2 m^2 of skin, is highly susceptible to liquid or vapor exposure via the dermal exposure route. Individual protection can be categorized into two main modes of action: (a) Contamination avoidance using prophylaxes, vaccines, protective garments, pre-treatments and PPE that may contain self-detoxifying and CW agent neutralizing materials, and (b) Post-exposure diagnostics and therapeutics strategies, and decontamination of skin and/or equipment using advanced technologies that contain self-detoxifying materials which can quickly sorb, retain and neutralize the toxic ChemBio agents within its structure [24, 33]. In the event of a sudden CW agent attack, the victim is caught by surprise and only has a few minutes time-window to mitigate the threat. Toxic dose of lethal nerve agents such as VX and G agents can be readily absorbed through the skin and the victim may still be asymptomatic; therefore, timely decontamination is the first key factor to reduce the toxic effects when it comes to taking counteractive measures against dermal exposure to CW agents [20]. The human skin is partly composed of intracellular lipids and therefore is hydrophobic in nature. Lipophilic compounds may readily penetrate the skin as compared to hydrophilic materials. Absorption through the skin is very rapid when the route of exposure is via the mucous membrane (eyes or mouth). Also, the toxic effects caused by a CW agent on intact skin depend on the length of time the agent is allowed to stay on the skin [34]. The longer the CW agents stay on the skin, the higher their absorption/penetration through the skin. Therefore, the most important aspect of a decontamination system is simply its ability to quickly and efficiently remove almost all of the toxic agents from the skin [18, 24].

Simplicity and speed of the decontamination procedure are the primary requirements for a warfighter who is exposed to toxic agents. Rapid removal of the CW agents from the skin should be the very first step taken during the decontamination process. The process of decontamination should be uncomplicated and should require minimal training. Upon suspicion of exposure, an individual should be capable of carrying out the decontamination procedure with relative ease. Use of soapy water immediately after exposure is the most basic method of decontamination [18]. However, water stations for immediate decontamination are often not accessible in a warzone. Therefore, alternate decontamination systems with fewer logistical requirements, which can be carried along by military personnel without any burden, are needed [23, 32]. Post-exposure detoxification can be achieved by immediate application of a suitable decontaminant to the skin and quick removal of the CW agents or agent-decontaminant mixtures from the skin. In case of non-availability of an advanced decontamination system, any strategy which helps in removal of agent from the skin may be practiced (e.g., absorption, scraping and washing with large amounts of water, soap solutions or non-toxic liquids) [19].

An ideal decontamination system should facilitate the immediate removal of the toxic agents from the skin upon application, and sorption (absorption and adsorption) and retention of toxic CW agent within the intricate structure of the decontaminant [27]. The decontamination device should not discharge vapors of the chemical agents or toxic chemicals during or after the decontamination procedure [24]. To avoid secondary contamination problems, an advanced decontamination system should be able to strongly hold the CW agents, mixture of reactive detoxifying compounds and CW agents, CW agent metabolites, other toxic chemicals and toxic vapors within its structure [23]. An ideal decontamination system should be portable, lightweight and easy to use, and should not only retain (hold) the sorbed CW agents but also render the chemical agents harmless or inert [23]. Additionally, the decontamination system itself should be non-toxic to the human body and must not irritate the eyes, skin or open wounds [24, 31]. The materials used in the decontamination system should not corrode or degrade sensitive equipment, weapons and tools used by the warfighter in the battlefield, and must not have any repulsive odor. The decontaminants should comply with medical and environmental safety guidelines. Thus, a highly efficient, self-detoxifying and advanced decontamination system should not only remove the CW agents instantaneously from the skin or equipment surfaces but also retain and neutralize the CW agent and toxic chemicals within its structure. The next generation ChemBio agent decontamination system for individual protection should not only demonstrate superior decontamination efficiency, but should also be skin-friendly and non-corrosive, and should overcome the challenges of feasibility, reliability, quality, supply chain logistics, and environmental compliance in all aspects of production, application, and disposal [28–31, 33].

Apart from CW agents, exposure to toxic volatile organic compounds and industrial chemicals can also lead to deleterious health consequences [7, 17]. The next generation of decontamination system should possess characteristics such as universal applicability towards a myriad of toxic chemicals, efficient and quick decontamination, non-toxic nature of the system itself, environmentally-benign composition, cost-effectiveness and ease of use [24].

9.2.2 Equipment Decontamination

Kaiser and Haraldsen have proposed an environmentally-friendly method for battlefield equipment decontamination, which involves use of organic solvents. This method is an important step towards improvement of surface decontamination technology by using environmentally- benign organic decontamination solutions. Technologies involving physical bombardment of particles on the contaminated surfaces do not effectively decontaminate the CW agents in unreachable and hidden corners of sensitive equipment. Since this technology uses liquid organic solvents, it is also useful for decontaminating equipment that gets smothered with dirt in warzone [16]. Kaiser and Haraldsen have reported observations on decontamination of known CW agents when the equipment was submerged in an ultrasonic bath filled with an organic decontamination solvents such as hydrofluoroethers (HFEs). It was found that nonpolar CW agents such as GB, GD, HD and VX were soluble in HFEs, mainly because HFEs are nonaqueous organic solvents [16, 37]. Moreover, HFEs are environmentally compliant and compatible with a number of sensitive equipment, including electronic equipment. HFEs have low surface tension, and therefore, can remove the neat CW agents from complex crevices of equipment. However, heavy ultrasonic agitation is needed to ensure complete removal of thick agents and agent-contaminated particulate matter [16]. It is highly important to utilize a simple marker which indicates that the CW agents and/or the CW-agent-contaminated particles are completely removed from the equipment surface. Use of ultraviolet (UV) light is an accurate technique which detects any traces of foreign contamination. A UV lamp can be used to visually confirm complete removal of any remnants of CW agents, toxic chemicals and agent laden particulate matter on surfaces of the equipment upon decontamination [16]. Recyclability of the contaminated solvent is an important factor to be taken into consideration while evaluating any solvent-based decontamination system. Adsorptive removal of the toxic CW agents from the agent solvent solution, can reduce the risk of secondary contamination. Also, subsequent recycling of the solvent is usually cost-effective.

Kaiser and Haraldsen have reported that removal of the CW agents from contaminated HFE solvent can be achieved by passing the CW agent laden solvent through a bed of activated carbon. Adsorption of the toxic CW agents onto removable/replaceable solid activated carbon cartridges reduces risk to the operator and renders the decontamination solvent suitable to be recycled [16].

9.3 Existing and New Decontamination Systems

All decontamination systems must safeguard military personnel from toxic consequences of ChemBio agent exposure, sustain their health, and serve towards enabling the combat efficiency quickly. Recently, new decontamination technologies such as Joint Service Transportable Decontamination System-Small Scale (JSTDS-SS), which involve use of high pressure liquids for equipment and facility decontamination, electrochemically activated (aqueous) chlorine dioxide technology for ChemBio decontamination and antimicrobial polyelectrolyte polymers to counteract biological agents, have been approved and validated by the US military. In the future, efforts geared towards development and evaluation of an intelligent decontamination system which has the capability to detect the agent, release agent-specific active decontaminant and confirm the detoxification of the CW agent shall contribute towards research and advancements in decontamination arena [33].

9.3.1 Technologies Mitigating Individual Threat

Lukey et al. have summarized the advantages and limitations of six skin decontaminants, including: (1) Reactive Skin Decontamination Lotion (RSDL), (2) M291 decontamination kit, (3) Hypochlorite bleach, (4) Diphoterine, (5) Sandia foam, and (6) Reactive sponge. Generally, a bleach solution is made of 0.5% sodium or calcium hypochlorite solution in water. Concentrated bleach solutions have been known to be effective in rapid decontamination of CW agents; however, the major limitation in the use of bleach solution lies in the fact that it exhibits dermal toxicity in the concentrated form (5% hypochlorite in water). On the other hand, dilute forms of bleach (< 0.5% conc.), which are relatively less toxic to the skin and eyes, are not efficient in counteracting the CW agents [18]. Chlorine is corrosive in nature and chlorine-based decontamination products such as bleach, can corrode equipment used in the warzone [24, 31].

Two decontamination foams: (1) MDF-100 and (2) DF-200, have been developed by Sandia National Laboratories [18]. MDF-100 is a two-component decontaminant. It consists of two compounds that generate foam to achieve decontamination, when mixed together. Anthrax spores have been reported to be neutralized using MDF-100. Furthermore, it has been reported that another formulation known as DF-200, neutralizes the agents faster than MDF-100, as it contains chemicals for enhancing the reaction rate for destruction of CW agents.

9.3.1.1 Decontamination of Well-Known CW Agents

Yang et al. have reviewed various mechanisms involved in reactive detoxification of four major CW agents; HD, VX, GB and GD. The most efficient detoxification mechanism is unique to each individual agent. Varying reaction conditions and different decontamination solutions are preferred for the most effective detoxification of each agent. How quickly an agent is neutralized into relatively less toxic or non-toxic compounds, depends on the rate of the detoxification reaction. Again, the rate of reaction is often dependent on the rate limiting steps such as dissolution of the CW agents in a decontaminant solution [40]. Polymer-based hydrophobic thickeners are often added to the neat CW agents to enhance their affinity to stick to the human skin and various other surfaces, making it difficult to wash them away. Dissolution of the CW agent in a decontamination solution is greatly affected if the applied agent is in a thickened (highly viscous) form. Presence of a polymeric thickening agent prevents the agent from dissolving in aqueous decontamination solutions. Therefore, in such cases, pure water may not be the best choice among the available decontaminants.

9.3.1.2 Sulfur Mustard (HD) and Nerve Agent Decontamination

Wormser et al. reported the toxic effects on guinea pig skin exposed to undiluted HD. After an hour of exposure only 0.3–0.6% of initial dose of HD was found on the animal's skin, because most of the agent had penetrated the skin. The absorption of the CW agents through the skin depends on lipohilicity (hydrophobicity), volatility and molecular size of the agent. However, the exact mechanism of uptake of HD through the skin is not clear. When guaze pads soaked in 0.5% hypochlorite (bleach) and water were used to wipe the skin, reduction in the HD content of the skin was found to be 68% and 64%, respectively. To significantly detoxify HD, relatively large decontaminant: HD ratios of the order 1000:1, and hypochlorite solution concentrations in the range of 0.5–4% are required [38].

Gold et al. investigated the decontamination efficiency of 0.5% and 2.5% sodium hypochlorite solution by visual observation of the guinea pig's skin wounds contaminated with HD. They found that unlike pure water, when hypochlorite solution was used as a wound decontaminant, it caused more damage to the HD-exposed lesions [9]. Therefore, using bleach as a universal decontaminant may not be the most efficient method for immediate decontamination, mainly because a highly concentrated solution of bleach may be required to neutralize all of the agents and this could be severely damaging to the wound lesions.

Another generic reactive decontaminant which is effective in a wide temperature range is called Decontamination Solution 2 (DS2). DS2 is comprised of 70% diethylenetriamine, 28% ethylene glycol monomethyl ether and 2% sodium hydroxide by weight. DS2 reacts quickly with the CW agents and is relatively less corrosive compared to bleach, however, it is toxic to the skin and damaging to coatings (e.g., paint) and surfaces made out of plastic [40].

Yang et al. have discussed some of the conventional reaction mechanisms involved in detoxification, including hydrolysis, nucleophile substitution and oxidation. It is interesting to note that major CW agents such as VX, HD, GD and GB react with water. Unlike GB and GD, solubilizing VX and HD in water is a challenge. VX initially dissolves in water resulting in a basic solution; however, these basic conditions leads to decreased solubility of VX. In case of HD, the agent's contact with water results in the formation of ionic products at the interface. This causes a reduced mass transfer rate of the agent into the aqueous solution, thereby, affecting its dissolution in the bulk water phase. Therefore, using aqueous solutions to carry out hydrolysis reaction may not be the most feasible or generic way to achieve significant decontamination [39, 40].

Another approach towards detoxifying the CW agents is facilitating the process for oxidation of the agents. In the case of oxidative neutralization of VX and HD, if the polarity of the aqueous solution is decreased by addition of an organic solvent to aid dissolution, then the rate of oxidation of the agents decreases. The rate of oxidation of VX can be particularly slow in pure anhydrous organic solvent and also in the case of acidic solutions. On the other hand, in basic solutions, VX may not be detoxified via oxidation because nitrogen is preferentially oxidized rather than sulfur [40].

Yang et al. also investigated the use of metal ions as catalysts to promote the hydrolysis of G type agents. Although Cu (II) ion is a very good catalyst for hydrolysis of GB, it was not as efficient in the case of HD and VX. In the case of metal ion catalyzed hydrolysis, reactions may be inhibited as Cu (II) may form complexes with sulfur in the case of HD and with diisopropylamino group in the case of VX [40].

Selection of an appropriate decontamination medium is critical in developing a solvent-based reactive decontamination system. Solubility of the agents in decontamination media is one of the primary governing factors in determining the efficacy of liquid-based decontamination. Organic solvents are often added to the aqueous decontamination solution to enhance dissolution of hydrophobic CW agents that may or may not contain thickeners, and are highly effective in solubilizing thickened agents which are otherwise insoluble in aqueous solutions. The decontamination media can be either aqueous (water-based), non-aqueous (organic) or a combination of both. Organic solvents have to be transported to the location and may pose some environmental hazards associated with their use. On the other hand, solid phase porous decontamination media can absorb, adsorb and retain significant amount of agents in their porous structure, but they are often compromised in their reactivity.

9.3.1.3 M291 Kit

One of the popular solid decontaminants which was fielded by the U.S. Dept. of Defense, the M291 Kit, consists of a free-flowing solid particulate resin mixture (XE-555) which is loosely packed in a fiber matrix. M291 Kit's particulate resin mixture consists of an adsorptive resin, anion-exchange resin and a cation-exchange resin. This resin mixture (XE-555) is designed to quickly absorb the bulk liquid CW agents from the skin and render them non-toxic by reactively neutralizing the agents, primarily via hydrolysis. However, some studies have reported that even after a period of 10 days, VX and $CH_3SCH_2CH_2Cl$, an HD stimulant, showed no signs of hydrolysis. However, GD did hydrolyze with a half-life of around 30 h [40]. One of the major disadvantages posed by the M291 Kit is that instead of immediately removing the bulk liquid chemicals away from the skin, this particulate decontamination system leaves dirty residue (dust) on the soldier's skin. Thus, the threat from the CW agents still stays imminent considering the fact that the solid particulate matter which has absorbed/adsorbed the agents is still on the skin, and the user is unsure whether the active agents have been rendered non-toxic.

9.3.1.4 Zeolites and Adsorptive Carbon Based Reactive Solutions

Bartram et al. have reported that solid decontaminating sorbents such as sodium zeolite (NaY) and silver exchanged zeolite (AgY), are quite reactive in nature [1]. To decontaminate surfaces contaminated with CW agents, such materials may be applied in the form of pellets, powder or in a suspension form (i.e., particles in solvent–polar or non-polar). These reactive zeolite sorbents may remove the CW agents from contaminated surfaces and render the agents non-toxic and relatively safe to handle after some time. Bartram et al. found that NaY was effective in reactively decontaminating HD. However, NaY just sorbed VX & O,S-diethyl phenylphosphonothioate (DEPPT) and did not reactively detoxify these agents. Degradation of the toxic chemical (parent compound) was not observed in the case of DEPPT or VX [1]. Therefore, NaY may be considered suitable for decontamination of HD but not for decontaminating most of the other agents that may be encountered in the warzone. On the other hand, AgY formed a silver alkoxide intermediate upon reacting with HD, and also rendered VX non-toxic, via silver catalyzed reaction. Steady-state half-life of VX was reported to be approximately 6.6 h when AgY was used as a decontaminant, and more than 5 days in the case of NaY decontamination. In the case of HD, the half-life was found to be 20 days for AgY decontamination versus 6.7 days in the case of NaY [1]. They did not provide information on CW agent removal efficiency of the zeolite-based decontaminants. As discussed earlier, an effective decontaminant should quickly remove all or most of the agent from the contaminated surface and quickly render it non-toxic. Further efforts are needed to conduct tests quantifying the amount of agent removed by such decontaminants from various surfaces.

Brown et al. have reported the use of dehydroxylated aluminum oxides and highly porous carbon containing reactive reagents. Such a decontamination system removes the bulk liquid CW agents by sorption and deactivates a portion of CW agent. To impart reactive properties to this solid decontamination system, 10–90% of the porous carbon's pore volume is filled by the reactive reagent. Preparation of freely flowing solid decontaminant particles involves impregnating the carbon with liquid reactive reagent and evaporating the excess reagent [3]. However, evaporation of excess reagent could lead to solvent losses and increase the cost of manufacturing. Moreover, the available pore volume of the porous carbon which facilitates the sorption of bulk liquid CW agents may be blocked by prior incorporation of the reactive reagents within the sorbent carbon's structure.

Highly porous materials are preferred in the case of reactive sorbent compositions which are made up of either dehydroxylated aluminum oxides, absorbent carbon or both. Highly porous carbon with surface area around 1,800 m^2/g is preferred for such applications. Dehydroxylation of Al_2O_3 is also preferred because such a treatment enhances its reactivity. The solid sorbent can be applied to contaminated surfaces in various ways: (1) dispersed in organic solvent; (2) as dry powder; and (3) in granular or pelleted form [3].

9.3.1.5 Acetylcholine and Nerve Agents

Nerve agents are highly toxic and lethal organophosphate compounds (OPs). Soldiers are often exposed to OPs in the combat zone. OPs inhibit acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) enzymes by binding to their active sites, thereby deactivating these enzymes. To ensure normal physiological functioning of the human body, the levels of neurotransmitter acetylcholine are regulated via enzymatic hydrolysis by AChEs present in the neuromuscular junctions and synapses in the central nervous system. Exposure to organophosphate nerve agents results in formation of a covalent bond between the agent and the active site of the AChE enzyme where acetylcholine is broken down by hydrolysis. This results in excess acetylcholine accumulation in the skeletal neuromuscular junction and cholinergic synapses. Consequently, there is continuous transfer of the nerve impulses in the body leading to cholinergic hyperactivity, which may include muscle contractions, drooling, lacrimation, twitching, seizures, flaccid paralysis, respiratory failure and death.

Use of enzymes to detoxify CW agents and their stimulants has been investigated since the 1950s. Hydrolysis of the OPs and nerve agents can be achieved by using appropriate enzymes such as organophosphorous hydrolases and organophosphorous acid (OPA) anhydrases, as biocatalysts [10, 40].

9.3.1.6 Immobilized Enzymes

Technologies which incorporate enzymes that can detoxify the OPs, have received much attention in the last few decades. Reactive cross-linking and immobilization of enzymes which can breakdown or scavenge the OPs on polymeric matrices, have been studied extensively and much work has resulted in considerable success [4, 10, 13, 15, 21]. As compared to conventional enzyme-based methods which involve incorporation of soluble enzymes that leach out from a decontamination sponge, techniques such as enzyme immobilization within the polymeric foam matrices offer many advantages. For example, enzymes immobilized or cross-linked to the polymeric matrix do not easily dissociate in the presence of aqueous solutions, and are resistant to harsh environmental conditions [11]. However, the issue of stability of the enzymes immobilized on foam structures has been of primary concern.

Havens and Rase developed enzyme-immobilized polyurethane foams that can soak up liquids and detoxify the organophosphate pesticide agents. They developed wet and dry foams which may contain surfactants that affect the foam’s shape, cellular structure and water absorption capability. They recommended that after use, foams could be sealed in liquid bags. They also proposed that some foams be reused after the hydrolysis reaction has been completed. However, the hydrolysis reaction may take a long time to deactivate all of the active agents. Both wet foam, which was maintained in refrigerated condition and the dry foam, which was dried at normal room temperature, were tested for their loss of enzyme activity. Both showed significant retention of the enzyme activity [15]. Havens and Rase have not discussed the enzyme activity of wet foam maintained at room temperature and they have not provided information on duration of storage of the foam in a plastic bag for hydrolysis (detoxification) reaction to be completed.

Recently, there has been much attention directed towards development of new reactive decontamination formulations based on cholinesterase and oxidative oxime reactivity for sponges and wipes to be used in skin decontamination [23]. The U.S. Army Medical Research Institute of Chemical Defense has been involved in developing a polyurethane sponge with immobilized enzymes that not only absorb the CW agents but also destroy them by enzymatic activity. In this case, cholinesterases (AChEs) and other CW agent detoxifying enzymes are incorporated within the sponge's structure along with the oximes which restore the catalytic action of the OP-inhibited AChE enzymes [10, 11]. Such reactive sponges have been reported to maintain the stability of the enzymes for extended periods of times and at high temperatures. The sponges can be reused because of the presence of restorative oximes [10]. Although these sponges possess the capability to carry out detoxification of the agents and also prevent secondary contamination, attaining high decontamination efficiency is a challenge. The sponge's performance can be enhanced by incorporating highly adsorbent materials in its core [23]. Therefore, activated carbon was also incorporated in the foam structure to impart the necessary adsorptive properties to the reactive sponge [11]. The polyurethane sponges containing activated carbon core have been found to possess excellent adsorption properties that help in trapping organophosphorous vapors [18]. Gordon et al. have reported that in many cases the reactive-enzyme-immobilized sponges have performed as efficiently as some of the existing and new decontamination technologies. They evaluated the effectiveness of the decontamination sponges for protection against agents such as GD and VX, and found that in comparison with a new decontamination formulation known as reactive skin decontamination lotion RSDL, the reactive enzyme-immobilized sponge technology was equally effective for VX, and more effective in the case of GD [12]. Moreover, the reactive sponge outperformed the existing carbon power and reactive resin-based M291 kit in its decontamination capability for detoxifying GD and VX [12].

9.3.1.7 Reactive Skin Decontamination Lotion

Reactive Skin Decontamination Lotion (RSDL) is a new product which has been reported to be effective to protect against a number of CW agents. RSDL consists of 1.25 M potassium 2,3-butanedione monoximate in polytheylene glycol monoethyl ethers with 10% w/v water [18, 26]. The U.S. military has recently approved the procurement of RSDL for replacing the skin decontamination kit (M291 Kit) and equipment decontamination kit ([33]). RSDL was originally developed by the Canadian Defense Research Establishment and has been fielded by many of the world's military organizations [18]. RSDL is a patented broad spectrum, skin decontamination lotion used to detoxify CW agents and biological warfare agents such as trichothecene mycotoxin (T2 toxin) which can cause severe irritation to the eyes and the skin, and it is currently manufactured by E-Z-EM Inc., a Bracco company. Nerve agents such as VX, thickened form of VX and thickened mustard, can be effectively decontaminated by applying RSDL to skin with a cotton swab. Compared to application of RSDL on the skin with swabs or syringes, scrubbing the skin with an RSDL-soaked sponge decontaminates unthickened mustard more effectively [2, 18, 35]. RSDL, when used by itself, leaves an oily residue on the skin and can make the warfighters uncomfortable while performing critical military activities [18].

Although it has been confirmed that RSDL has demonstrated improved decontamination efficiency as compared to military's M291 kit, little is known about wound decontamination using RSDL. Walters et al. investigated the mechanical strength and collagen content during the healing process of a wound induced on the skin of Sprague Dawley rats treated with RSDL. They found that compared to control (untreated wounds), the tensile strength for RSDL treated wounds was 23% lower and the collagen content was 11% lower as well [36]. RSDL's applications are limited for wound decontamination because of the fact that it can only be applied to intact skin [33].

RSDL contains some water and is known to be highly effective in reducing the CW agent toxicity caused by highly toxic nerve agents such as soman (GD), sarin (GB), and VX and the less toxic blister agent sulfur mustard (HD), by detoxifying the agents. Presence of water may be undesirable in case of equipment decontamination, because water damages sensitive equipment, especially electronics. Therefore, new decontamination technologies that are nonaqueous, and can wipe away aqueous residues from surfaces, are needed for personal and equipment decontamination [23, 29].

Another formulation by Sandia National Laboratories is known as MDF-100 foam. Upon applying to the contaminated surface, the MDF-100 foam changes to a liquid in 30 min. It has been reported that the MDF-100 form is effective in case of dermal exposure to nerve agents such as GD (35-fold protective ratio) and VX (72-fold protective ratio) [18]. Here, the protective ratio is the ratio of the cutaneously-administered CW agent doses (LD50s) that caused lethality to 50% of the animal population, after and before decontamination. However, Lukey et al. have reported that in the case of nerve agents such as VX, other decontamination solutions were more effective and provided a protective ratio greater than 100-fold. Products such as diphoterine (slightly irritant to skin), soapy water and saline solution have been compared for their removal efficiencies, which were 50%, 37% and 32% respectively, in case of bulk CW agent (mustard) removal from the skin [18]. In the case of an in vitro skin test using diluted and undiluted bleach, mustard reduction was reported to be 67% and 79% [6, 8]. For agents such as VX, dilute bleach solution was ineffective. Although, undiluted bleach seems to be effective, it cannot be recommended for widespread use because it damages the skin and is a corrosive solution [23].

Efforts towards designing a highly efficient, nonparticulate, nonaqueous and universal decontamination system that is skin-friendly and can serve as a detoxification technique when used by itself, or in combination with other CW agent neutralization products, are necessary. The characteristics of an ideal decontamination system which addresses the requirements of the military personnel and civilian workers, can be summarized as shown in Figs. 9.1 and 9.2.

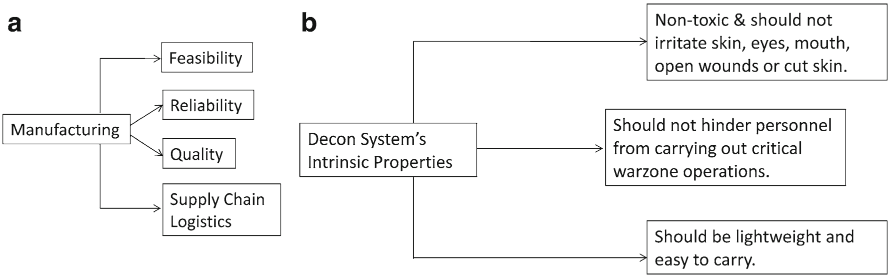

Fig. 9.1 (**a**) An ideal decontamination system's manufacturing criteria. (**b**) An ideal decontamination system's preferred intrinsic properties

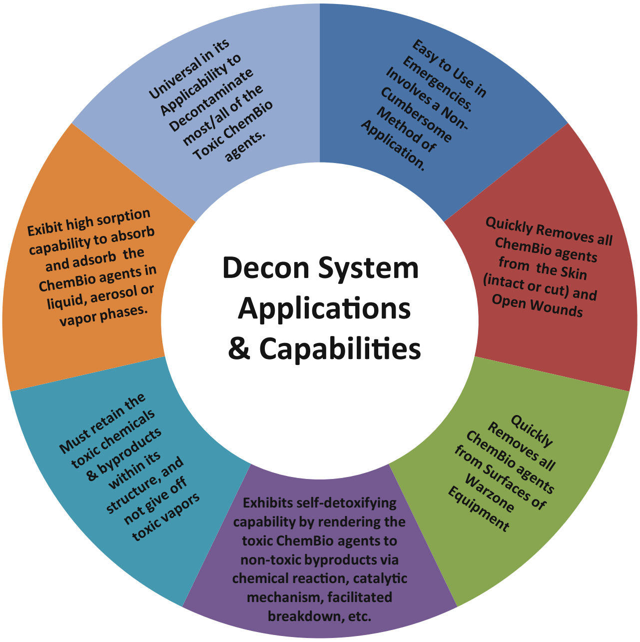

Fig. 9.2 Application criteria of an ideal decontamination system for countermeasures against chemBio agents and toxic chemicals

9.3.1.8 Dry Nonparticulate Decontamination Wipe

The development of non-aqueous decontamination technology that can be used both on human skin and military equipment over a broad range of environmental conditions is one of the priority areas of the Chemical and Biological Programs of the US military [28–31, 33]. Recent research at Texas Tech University has resulted in a needlepunched multi-layer substrate which has been proven to have vapor retention capability and bulk chemical absorption. The manufacturing of derivates of a

Fig. 9.3 Dry nonwoven decontamination wipe (Source: First Line Technology, LLC, Chantilly, VA)

Fig. 9.4 Dry nonwoven decontamination mitt (Source: First Line Technology, LLC, Chantilly, VA)

three-layered composite material varying in their weight, thickness and amount of natural/polymeric fibers was carried out using the contoured needle zone needleloom by Oerlikon Neumag Austria GmbH (formerly Fehrer AG) in the Nonwovens and Advanced Materials Laboratory at Texas Tech University's The Institute of Environmental and Human Health [22]. The composite wipe has been designed in a way that it exhibits high wiping efficiency, excellent toxic chemical/liquid absorption, superior toxic vapor adsorption and excellent toxic vapor retention capabilities. The evaluation by the Lawrence Livermore Laboratories has shown that the dry decon wipe is able to retain mustard vapors better than particulate carbon and the M291 sorbent decontamination technology [23]. The dry nonwoven pad is logistically better than the particulate decontamination technologies and can be formed into different shapes such as a wipe or a mitt. Figures 9.3 and 9.4 show the use of the nonwoven decontamination pad.

9.4 Conclusions

Decontamination of both warfighters and military equipment is an important tool to sustain the combat force. The next generation decontamination system should take into account a holistic picture of detoxifying chemical, biological and toxic industrial chemicals. This necessitates the need for a highly efficient decontamination system with improved logistics; however, there is no single solution to cater to multiple threat agents. A decontamination system which can have maximum detoxifying capability, reduce toxic effects and casualties, and enhance combat efficiency, will be the one which will be most sought after by military and first responder community. Fibrous materials can play an important role as a substrate to launch effective decontamination technologies such as catalytic particles, biocides and enzyme-based technologies. This challenge requires contributions from multiple disciplines such as chemistry, textile science, biotechnology, nanotechnology and materials engineering.

Glossary

AChE	Acetylcholinesterase
AgY	Silver Exchanged Zeolite
BChE	Butyrylcholinesterase
CBRN	Chemical, Biological, Radiological and Nuclear
ChemBio	Chemical and Biological
CW	Chemical Warfare
DEPPT	O,S-diethyl phenylphosphonothioate
DS2	Decontamination Solution 2
GB	Soman
GD	Sarin
HD	Sulfur Mustard
HFEs	Hydrofluoroethers
LPDS	Low-cost Personal Decontamination System
NaY	Sodium Zeolite
OPA	Organophosphorous Acid
OPs	Organophosphate compounds
PPE	Personal Protective Equipment
RSDL	Reactive Skin Decontamination Lotion
T2 toxin	Trichothecene Mycotoxin
UV	Ultraviolet

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Chapter 10
Nanomaterials for Defense Applications

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Paul Kiekens, and Seshadri S. Ramkumar**

Abstract Nanotechnology has found a number of applications in electronics and healthcare. Within the textile field, applications of nanotechnology have been limited to filters, protective liners for chemical and biological clothing and nanocoatings. This chapter presents an overview of the applications of nanomaterials such as nanofibers and nanoparticles that are of use to military and industrial sectors. An effort has been made to categorize nanofibers based on the method of production. This chapter particularly focuses on a few latest developments that have taken place with regard to the application of nanomaterials such as metal oxides in the defense arena.

10.1 Introduction

According to the National Science Foundation of the United States of America, nanotechnology involves research and technology development at the atomic, molecular and macromolecular levels, in the length scale of 1–100 nm [1]. Nanotechnology is aimed at understanding the phenomena and the properties of materials at the nanoscale, i.e., one-billionth of a meter, so as to create and use structures, devices and systems with novel properties and functions. In addition, nanotechnology is

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focused on manipulating nanoscale structures to facilitate their incorporation into larger material components and systems [1]. Nanotechnology is finding applications in a variety of fields such as defense, materials science, environmental, healthcare, electronics, optics and aerospace. The critical length scale for nanomaterials ranges between 1 nm or less and more than 100 nm depending on the need and the type of the field [1]. For example, in textile applications, the size of nanofiber materials used is generally 100 nm or more. When a bulk material is divided into a number of small sized particles with one or more dimensions in the nanometer range, nanosized particles exhibit novel properties that can be entirely different from that of the original bulk material. This is the fundamental aspect of nanotechnology that attracts a number of new applications in many different fields [2].

Nanotechnology has found limited applications in textiles such as chemical and biological filters, nanofiber-based biological scaffolds, nanoparticles-coated repellant textiles and nanofiber filters, which are relatively few compared to those in electronics and healthcare. Defense, healthcare and environmental sectors use nano-textiles and nanotechnology related textile products for improved functionality and performance. More importantly, nanofibers, due to their enhanced surface area and lightweight, can be used as effective filter and barrier media in chemical and biological defense clothing, face masks and filtration equipment [3, 4]. This chapter provides a brief summary of nanotechnology as it relates to textiles and highlights a few latest developments with regard to the applications of nano-textiles in the defense sector. In addition, a new, albeit simple, classification of nanofibers which has been recently developed [5] is highlighted in this chapter.

10.1.1 Classification of Nanotechnology

The field of nanotechnology can be broadly classified into three different types such as: (1) Incremental; (2) Evolutionary and (3) Radical [6].

Incremental nanotechnology is controlling and manipulating the basic nanoscale structure of materials so as to enhance their properties. Some of the examples include nanoceramic powder incorporated hulls of the ships with enhanced durability, polymer nanocomposites that have improved hardness and permeability and nanostructured plastics with superior strength [6, 7]. Evolutionary nanotechnology is devising nanoscale devices and materials which are a step above simple nanoproducts with high performance capabilities. Examples include carbon nanotube-based products for high-efficiency solar cells and thermoelectric conversion devices and medical diagnosis and treatment devices that use semiconductor nanowires [6, 7]. Radical nanotechnology deals with highly sophisticated products which are generally developed using multidisciplinary approaches involving nanotechnology, materials science, biotechnology, information technology and cognitive technology. Examples include nanomaterials for chemical and biological protection, nanoparticle incorporated antiballistic materials, improved communication tools and medical aids that are used in war theaters [6, 7].

10.1.2 Nanotechnology in Textiles

Since the advent of nanotechnology, the textile field has utilized the benefits of nanoscience to enhance fibers and finishes to textiles. However, important issues surrounding the commercialization and applications of nanofibers include productivity, performance-related characteristics, scale-up and cost [5].

A broad classification of nanotechnology-based textile materials includes: (a) non-functionalized textile products and (b) functionalized and finished textiles. Nano-textiles are basically fibrous structures with nanofibers, nanomaterials and nanofinishes incorporated into them. Nanomaterials serve as the foundation for developing higher order structures such as fabrics and composites. The high surface area and weight to volume ratio of nanomaterials and nanofibers at the building block level will be of immense use in the case of high performance, life and environment-related end-uses [5].

The advantages of nanotechnology that are of relevance to textiles are: (1) increased hardness with decrease in grain size; (2) increased wear resistance; and (3) lower melting and sintering temperature and improved transport kinetics [8]. Ramkumar and Singh have recently highlighted the advantages of incorporating nanotechnology into textiles, which can result in textile products with enhanced performance, functionality and smartness [5].

10.1.3 Nanofibers: Origin and New Classification

The process of dispersing fluids using electric charges which forms the basis for developing solution electrospun nanofibers dates back to 1902 with the granting of two separate and independent patents on dispersing fluids using electricity. Cooley was granted a patent for the apparatus for electrically dispersing fluids [9] and Morton was granted a patent for the method of dispersing fluids [10]. In 1940, Formhals was granted a patent for using electric charge to develop synthetic threads [11]. The technologies discussed in these patents basically contributed to the development of nanofibers.

The production of nanofibers involves the application of shear force to manipulate interfacial tensions and achieve phase separation that results from the rapid evaporation of the solvent. Nanofibers can be classified based on their production methods, processing techniques, functionalization, applications, etc. A simple method of classifying nanofibers based on the dispersion process by which they are produced is discussed in this section, as shown in Fig. 10.1. Dispersion of raw materials into its nano state is based on three basic methods: (1) Mechanical Dispersion; (2) Chemical Dispersion and (3) Electrical Dispersion. This categorization will help to determine how nanofibers are formed and can be further integrated into products produced via different process (i.e., wet laying and direct coating). The three basic methods given in Fig. 10.1 can be utilized in different production methods such as meltblowing, centrifugal spinning, sol-gel process, needle electrostatic spinning, needleless electrostatic spinning and electroblowing [5].

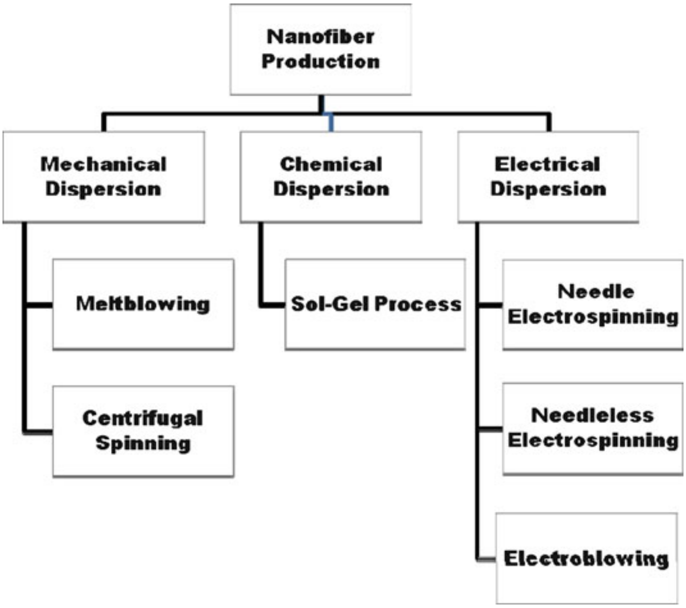

Fig. 10.1 Classification of nanofibers [5]

Techniques like electrospinning and meltblowing have been extensively discussed in the scientific literature [4, 12]. Hence, an attempt is being made in this chapter to present some recent developments in the field of nanofiber production.

10.1.3.1 Needleless Electrospinning

Nanofiber production via electrospinning has been widely exploited for the production of nanofibers on the commercial scale. Developing different types of nozzles and multiple head electrospinning are few notable incremental developments that have taken place in the last decade. Jirsak et al. [13] invented the needleless electrospinning method for the production of nanofiber webs [13]. In addition, these authors [14] have described the generation of multiple jets from a liquid impinging on a slowly rotating horizontal cylinder. In this electrospinning set-up, the rotating cylinder is immersed in a polymer solution which creates a layer on the surface of the cylinder. Due to the high voltage applied between the cylinder and the collector electrode, numerous Taylor cones are formed on the surface of the cylinder, resulting in a number of nanofiber jets. Nanofibers are collected on the textile backing layer which moves on the collector electrode. Thus, nanofiber layers are produced continuously and the production rate is dependent on the width of the machine, number of spinning rollers and the weight of the nanofiber layer. Wang et al. [15] have described a needleless electrospinning set-up using a cone-shaped metal coil as spinneret. According to Wang and co-workers, the conical coil surface can generate a large number of jets which results in enhanced fiber productivity. Furthermore, the average fiber diameter produced using coil as a nozzle resulted in fibers having finer diameter than those produced by the typical needle electrospinning. Niu et al. [16] have also demonstrated needleless electrospinning with a rotating disk and a cylinder and examined the effect of nozzle shape on the electrospinning process and resultant fiber morphology. Results from their study showed that the disk nozzle needs lower voltage to initiate fiber formation, and the fibers were mainly formed from the top edges of the disc. Whereas in the case of cylinder nozzles, the fibers are initiated from the edges and as the applied voltage increases, fiber formation spreads through the entire cylinder surface. According to the above work, with a given polymer solution, the critical voltage needed to generate nanofibers in the disk nozzle set-up was lower than that needed to generate nanofibers using the cylinder set-up. More importantly, fibers spun using disk nozzles were finer than those spun using cylinder nozzle. Subsequently, Tong et al. [17] patented a novel technique to produce nanofibers via needleless electrospinning. In this invention, electrospinning using rotating spiral coil has been described and the inventors claimed that the electric field intensity generated in the spiral coil set-up is uniformly distributed across the length of the spiral coil, which eventually addresses one of the disadvantages of electrospinning using cylinder set-up.

10.1.3.2 Electroblowing

Electroblowing involves injecting compressed air while applying a high voltage during spinning to develop nanofibers [18]. In this method, electrospinning apparatus is coupled with an air blowing unit. Electrical force and shear force generated by air are applied simultaneously to generate nanofibers from a liquid polymer. The air stream is used to provide the additional drag force on top of the electric force to the liquid polymer droplet. The compressed air stream is also used to control the evaporation rate of the solvent and the cooling rate of the fluid jet. Nanofibers produced are collected on a grounded collector. In this set-up, the collector is designed to recycle the air which flows through a high voltage region created between the nozzle and the collector [19].

10.1.3.3 Centrifugal Spinning

Most recently, researchers with The University of Texas-Pan American have come up with a novel method for producing nanofiber webs [20–23]. Sarkar et al. [24] have described the apparatus and the process of manufacturing nanofiber webs using centrifugal force. In this new method, termed as Forcespinning™, centrifugal forces are used instead of an electric field. According to the inventors, the simple combination of centrifugal forces with multiple configurations of easily interchangeable spinnerets gives tremendous flexibility in terms of materials that can be spun into nanofibers. The authors have claimed that by using the centrifugal method, nanofiber webs of both electric charge conducting and non-conducting solutions, metals and a number of solid materials such as bismuth can be melted and spun without chemical preparation.

10.2 Common Applications of Nanofibers

10.2.1 Healthcare Applications

Electrospun nanofibers have found a number of applications in the field of healthcare. The large surface area and the porosity of electrospun nanofibers make them ideal candidates for tissue engineering applications [25]. A few of those applications include tissue/organ repair and regeneration, vectors in the delivery of drugs and therapeutics, biocompatible and biodegradable medical implant devices, medical diagnostics and instrumentation, protective fabrics against infectious and environmental agents in hospitals and general surroundings, and cosmetic/dental applications [26]. Ultrafine powders like TiO_2 nanoparticles and coatings are used in sunscreens [27] and self-cleaning textiles for defense and healthcare applications [28].

The mixture of metal nanopowders and polymers has found many applications in the field of medicine. For example, polycaprolactone (PCL) is one such polymer with a history of proven biocompatibility. A nanofiber mat produced by the electrospinning of a mixture of PCL and titanium nanopowder has been found to activate the precipitation of hydroxyl apatite, when soaked in simulated body fluid solution, which is helpful in the regeneration of bones [25].

10.2.2 Biotechnology and Environmental Engineering Applications

The characteristics of electrospun nanofibers that enable their applications in biotechnology and environmental engineering sectors are a large surface-to-volume ratio, microscale interstitial space and high porosity. These properties are critical for developing nanofibers as membranes for biological and environmental applications. More importantly, electrospun nanofibers are particularly used as separation membranes for the removal of particulates from waste water [26].

10.2.3 Energy Generation Applications

Electrospun nanofibers are used in polymer batteries, photovoltaic cells and polymer electrolyte membrane fuel cells. Lithium batteries in personal computer notebooks and cell phones are being replaced by polymer batteries. Polymer batteries provide high dimension flexibility, are more resistant to electrolyte leakage and offer high

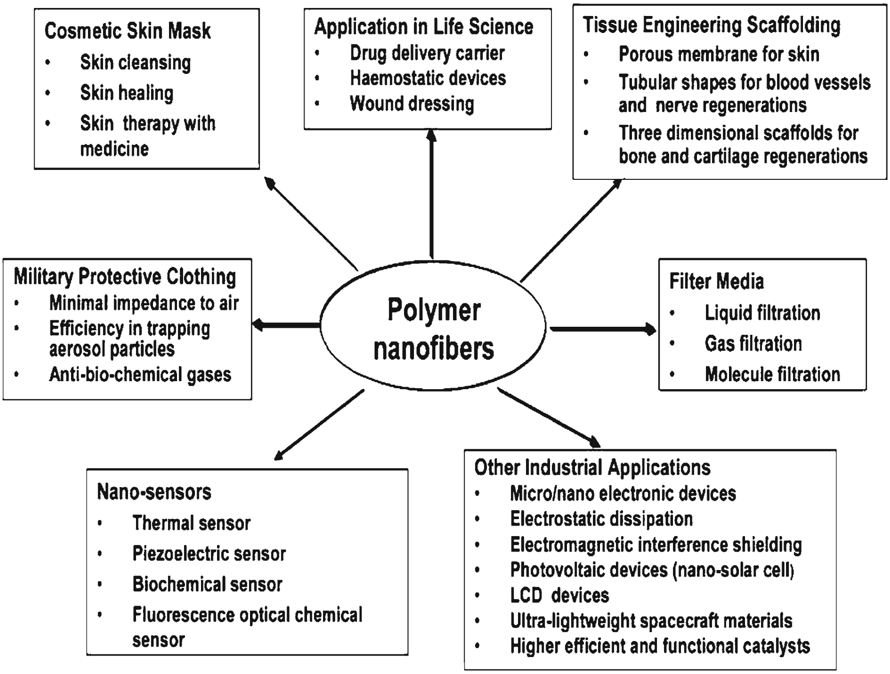

Fig. 10.2 Different applications of nanofibers [29]

energy density per weight [26]. These batteries can also be used in a number of defense applications for powering war fighting equipment.

A few applications of polymer nanofibers in different sectors are given in Fig. 10.2.

10.2.4 Defense and Security Applications

High-level protection is a must for military, firefighters, law enforcement and medical personnel as they need to deal with various kinds of biological, chemical and many different unknown threats. Chemical threats include nerve agents, mustard gas, and blood agents such as cyanides. Nanostructures have enabled the design of lighter and effective protective suits by virtue of their lightweight, high surface area and breathable porous nature [30]. Nanofibers, when functionalized, enhance the ability to detect chemical and biological warfare agents with higher sensitivity and selectivity. Nanofiber-enabled protective structures have taken personnel protection to the next level because of their ability to filter and destructively decompose harmful toxins [26]. These are known as self-cleaning/self-detoxifying personnel protective equipment.

Some of the applications of nanomaterials that are of interest to the defense and industrial communities are summarized in Table 10.1.

Table 10.1 Application of nanomaterials in the defense and industrial sectors

Nanomaterials	Application in military and industrial sectors	Reference
Chitosan nanofibers	Removal of heavy metals from contaminated waters	Haider and Park [31]
Polyacrlamidoxime/Polyacrylonitrile ($PANO_x$/PAN) nanofibers	Hydrolysis of p-nitrophenyl acetate, a simulant for organophosphates and nerve agents	Chen et al. [32]
Magnetite (Fe_3O_4) nanoparticles modified by oxime containing moieties	Hydrolysis of diisopropyl fluorophosphates	Bromberg and Hatton [33]
TNT-sensitive conjugated polymer TPA-PBPV(poly(triphenylamine-alt-biphenylene vinylen)) coated onto Polyacrylonitrile fibers	Sensors for explosives like trinitrotoluene	Deng et al. [34]
Carbon nanotubes	Carbon nanotube incorporated ballistic protection and bulletproof vests	Mylvaganam [35]
Alumina (Al_2O_3) nanofibers	Filter sterilization of biologically contaminated waters and water infested with heavy metals	Tepper and Kaledin [36]
Magnesium oxide (MgO) nanoparticles and its halogen adducts	Bactericidal activity (Gram positive and negative bacteria, spores and Bacillus cereus species)	Koper et al. [37], Stoimenov et al. [38] and Makhluf et al. [39]
MgO/CaO nanoparticles	Biocidal activity (Escherichia coli and Bacillus cereus)	Koper et al. [37]
Nanocrystalline zinc rods	Decontamination of sarin and mustard	Mahato et al. [40], Prasad et al. [41]
Chitosan/polyethylene oxide (PEO) nanofibers on a spunbonded nonwoven polypropylene substrate	Antimicrobial and metal ion binding activity	Sun and Li 2011 [42]
Zinc titanate nanofibers with polyvinylpyrrolidone as a binder	Sensor for nerve and mustard agents	Ramaseshan et al. [43]
Tin oxide nanowires	Sensor for dimethyl methyl phosphonate (DMMP), a simulant for sarin	Sberveglieri et al. [44]
Silver nanoparticles on cellulose fibers	Bactericidal activity (Escherichia coli and Enterococcus faecalis)	Dankovich and Gray. [45]
Zinc oxide (ZnO) nanoparticle containing formulations	Antibacterial agents in ointments, lotions and mouthwashes	Jones et al. [46]

Reactive nanoparticles and polyoxometalates	Skin exposure reduction Paste against chemical warfare agents	Hobson et al. [47] Koper et al. [48]
MgO nanoparticles	Hydrolysis of VX, GD and HD	Wagner et al. [49]
Al_2O_3 nanoparticles	Hydrolysis of VX, GB and GD	Wagner et al. [50]
Nanocomposite membrane from MgO nanoparticles and Polysulfone	Hydrolysis of paraoxon, a nerve agent stimulant	Sundarrajan et al. [51]
Carbon nanotubes dispersed in hexafluoroisopropanol functionalized polythiophene	Sensor for nerve agent stimulant, DMMP (dimethyl methyl phosphonate)	Wang et al. [52]
Aerogel Prepared (AP)-MgO nanoparticles	Dissociative chemisorption of paraoxon	Rajagopalan et al. [53]
Silver nanoparticles on cellulose acetate nanofibers	Bactericidal activity	Son et al. [54]
ZnO nanoparticles	Hydrolysis of sulfur mustard	Houskova et al. [55]
Cerium oxide nanoparticles	Growth inhibitory effects on Escherichia coli and Bacillus subtilis	Pelletier et al. [56]
Titanium dioxide nanoparticles	Photocatalytic inactivation of Bacillus anthracis	Prasad et al. [57]
Silver nanoparticles	Bactericidal effect on Escherichia coli	Sondi and Sondi [58]
Silver nanoparticles impregnated chitosan films	Antibacterial activity	Wei et al. [59]
Iron and titanium dioxide nanoparticles	Decomposition of mustard gas, soman and VX	Stengl et al. [60]
Alumina nanoparticles impregnated with polyoxometalates	Detoxification of sulfur mustard	Saxena et al. [61]
Manganese oxide nanosheets and nanotubes	Hydrolysis of 2-chloro ethyl ethyl sulfide, a simulant for sulfur mustard	Prasad et al. [62]

The efficacy of nanofibers and nanoparticles as tools to counteract various kinds of chemical and biological hazards has been well documented, as is evident from Table 10.1. However, Sundarrajan et al. [63] have reported that the use of nanoparticles in clothing and other applications is not feasible due to aggregation and containment within the clothing. The incorporation of various nanoparticles in a polymer solution and the electrospinning of the resulting solution may be a remedy to this problem. Nevertheless, the authors observed that the surface of nanoparticles is being covered by the polymer hindering the availability of the nanoparticles for reactivity. A possible solution would be the combination of the electrospraying technique with electrospinning. Nanofibers were electrospun and nanoparticles were electrosprayed in the approach followed by the authors. They have fabricated two types of membranes: (1) Simultaneously Processed Membranes (SIM) and (2) Layer-by-Layer membranes [63].

SIMs were synthesized by the combination of electrospinning of cellulose acetate and electrospraying of silver nanoparticles ($AgNO_3$). The resulting membrane was found to be effective against Gram-negative bacteria. Layer-by-layer membranes were fabricated by alternatively electrospinning a suitable polymer solution and electrospraying of nanoparticles [63].

10.2.5 Application of Nanomaterials in the Military Sector

Nanofiber-based filters and barrier materials are predominantly used as countermeasures to chemical and biological agents. Chemical warfare agents can find their way into the environment in two ways: (1) accidental release and (2) intentional release. Chemical warfare agents include nerve gases, mustard agents, blood agents and toxins such as arsine, chlorine and phosgene. Organophosphorous compounds, due to their acute neurotoxicity are of special interest to the military [64]. Nanofibers have been found to be sensitive towards warfare agents at concentration levels of parts per billion. This property makes them excellent candidates as sensing devices for chemical and biological toxins [26]. Nanofiber membranes are capable of providing protection against aerosols and toxic liquids. The functionalization of nanofibers adds another advantage and enables the nanofibers not only to adsorb biological/chemical agents, but also to decompose and detoxify them [65]. A face mask designed using functionalized nanofibers has been developed by Ramakrishna et al. 2006 [26]. The facemask used in chemical and biological warfare defense generally consists of two parts: (1) a high efficiency particulate air (HEPA) filtering layer and (2) an activated charcoal bed that adsorbs harmful gases and contaminants. The authors reported that nanofibers could be employed to replace the activated charcoal layer for the purpose of adsorbing toxins from contaminated environment. Chemical functionalization, post-spinning modification of nanofibers and nanoparticle polymer composites have been considered by the authors to embed active reagents into the nanofiber webs [26]. Metal oxide nanoparticles such as MgO are normally used for this purpose [51, 53, 62].

The increasing awareness about the use of nerve agents demands the need for suitable protective clothing and topical skin protectants. The various kinds of protective clothing used by the defense communities include: (1) HAZMAT (hazardous materials) suits; (2) JSLIST (Joint Service Lightweight Integrated Suit Technology); and (3) BDO (Battle Dress Over-garment). HAZMAT suits are impermeable, whereas JSLIST and BDO are permeable adsorptive protective over-garments [64]. A non-functionalized carbon adsorbent is generally used in JSLIST and is bonded to a substrate using an adhesive. This offers complete protection, but is bulky (weight of 2.6 kg) and possesses poor moisture retention characteristics, according to Ramaseshan et al. [64]. Most importantly, the disposal of used suits to prevent any further contamination by desorption is a potential threat in itself [64].

Nanofibers can be used to replace the activated carbon layer in the protection suits. The use of nanofibers in the protection suits offers a few advantages. For example, the use of nanofibers in breathing mask provides breathability and better comfort for the end user. Additionally, nanofibers are known to be capable of retaining small particles such as viruses. More importantly, nanofibers can be easily embedded in suits and face masks to provide better protection [66]. The high surface area of nanofibers and functionalization enable the effective binding and deactivation of chemical and biological agents of interest. In some instances, the need for external respirators in the battle dress over garment could be eliminated as the nanofibers are highly but selectively permeable. Multilayered nanofiber mats consisting of two or more distinct layers of fibers can be used as effective chemical and biological filter media. One class of fibers can have the ability to capture and decompose toxic gases. The other class of fibers will be able to oxidize and deactivate nerve agents. The small size of the pores serves the purpose of blocking the entry of bacterial spores resulting in multifunctional nanowebs for personal protection [67].

Figure 10.3 gives a general idea of different aspects of applications of nanomaterials in the military sector.

There are some new products emerging in the market involving nanomaterials that claim to have nuclear, biological and chemical (NBC) protection. For example, alumina nanofibers developed by a proprietary sol-gel reaction by Argonide Corporation, FL has been found to have applications in NBC protection such as: (1) filters for biologically contaminated water; (2) filters embedded into fabrics and nonwovens so as to enhance protection against biological agents and radiation; and (3) decontamination of surfaces. Additional applications of these nano aluminum oxide filters are: (1) high efficiency filters (>99.999%) for bacteria and viruses; (2) chemisorption of dissolved heavy metals; (3) sub-micron and nanoparticulate filtration, including radio isotopes; and (4) high flow capability filters that are several orders of magnitude higher in protection than equivalent membrane filters [36].

10.2.5.1 Decomposition of Organophosphorous Agents and the Use of Nanofibers

Functionalized nanofibers are effective media for decomposing organophosphorous agents such as nerve gases. There are several methods such as enzyme degradation,

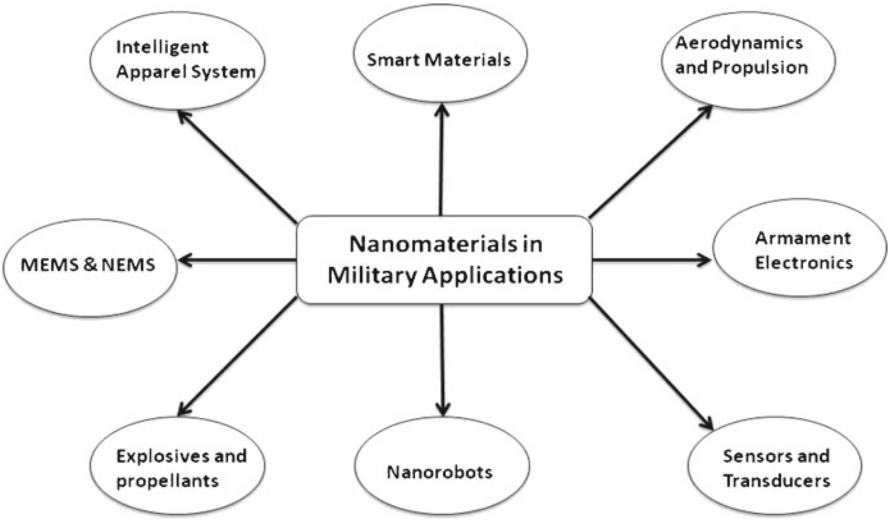

Fig. 10.3 Applications of nanotechnology in the military sector [68]

chemical degradation, photo-catalytic degradation and microbial (xenobiotic) degradation to decompose organophosphorous compounds. Although, enzyme degradation is the most sensitive, fast and simple approach, the process is associated with a number of limitations such as cost and enzyme stability. Therefore, a chemical method that utilizes functionalized fibrous products such as nanowebs can be a useful method from decontamination and logistics points of view [64].

Nucleophilic agents such as alkalis and oximes have been found to be capable of breaking the phosphorous-x bond in organophosphates resulting in phosphoric acid and other non-toxic byproducts. Metal oxide nanoparticles such as MgO, CaO, TiO_2, ZnO and Fe_2O_3 are known to hydrolyze organophosphates [64].

Mahato et al. [40] successfully employed nanocrystalline zinc rods in the decontamination of Sarin, a nerve agent that results in paralysis and mortality. Zinc oxide nanomaterials were developed by the sol-gel method and have been shown to hydrolytically decontaminate Sarin. The reaction also resulted in non-toxic products such as methyl phosphonic acid and isopropyl methyl phosphonic acid [40]. Prasad et al. [41] have investigated the ability of zinc oxide nanosized rods in the decontamination of Sulphur mustard. The zinc oxide nanorods were synthesized by the hydrothermal method. The authors observed that these nanorods successfully decontaminated Sulphur mustard by pseudo first order steady state reactions like hydrolysis and elimination [41]. These nanomaterials can be successfully added on to nanowebs and other fibrous materials to develop self-decontaminating protective products.

Nanofibers have also found their applications as sensors for use during combat. Deng et al. [34] developed a sensor for 2,4,6-trinitrotoluene (TNT) using a TNT-sensitive conjugated polymer TPA-PBPV (poly(triphenylamine-alt-biphenylene vinylene)). The polymer was coated onto electrospun PAN (polyacrylonitrile)

Table 10.2 Characteristics of different types of nonwoven fibers [70]

Fiber type	Fiber size (diameter in μm)	Fiber surface area per mass of different fibers (m^2/gm)
Nanofibers	0.05	80
Spunbond fibers	20	0.2
Meltblown fibers	2.0	2

nanofibers on a quartz plate. According to the authors, this assembly showed a higher sensitivity and faster response to TNT compared to a regular polymer (TPA-PBPV) film [34].

10.3 Nanofibers as Filters

Nanofibers are finding many applications in the field of filtration because of their high porous structure and high surface area [69]. The diameter of electrospun nanofibers has been found to be three times smaller than their meltblown counterparts, which plays a major role in an increase in their surface area and a significant decrease in their weight [70]. Table 10.2 summarizes the major differences in terms of fiber surface area per mass of the fiber for different fiber diameters.

According to Graham et al. [71], submicron size fibers provide better filtration efficiency when compared to their larger counterparts. They do so at the same pressure drop in the interception and inertial impaction regimes. The smaller sizes of the fibers generally lead to higher pressure drops. This however, according to the authors, is compensated by an increase in the interception and inertial impaction efficiencies [71].

Composite nonwoven structures that have been functionalized by electrospun nanofibers expanded the feasibility of the use of nanofibers in the filtration industry, according to Graham et al. [72]. The objective is to provide a highly permeable aerosol barrier in protective gear such as face masks and protective clothing. High air permeability provides comfort to the user and high aerosol efficiency provides suitable protection from aerosolized threat agents. Nanofibers are an ideal choice for these kinds of applications. The thickness of the nanofiber webs is often small, in the range of microns. This is because of the small diameters of the fibers themselves. The authors highlighted the fact that this limits the mechanical properties of the webs. A solution to this problem, as proposed by the authors, is to develop a layered composite structure by adding the nanofibers onto a substrate material. The substrate materials should be selected in such a way that they provide appropriate mechanical properties and complementary functionality to the nanofiber webs. The possibilities of including active chemistry in the nanofiber layer offer additional opportunities for functionality. The properties of these composites should include permeability specifications, resistance to penetration by specific liquids, flammability, laundering, mechanical durability, mechanical strength properties, and weather comfort [72].

Soldiers in war zones are frequently exposed to air contaminants because of their small size (<1 μm in diameter) and abundance. Some examples include volatile organic compounds (VOCs), microorganisms, allergens and tobacco smoke, which are known to be mutagens, carcinogens and irritants. In general, the exposure can occur through air, water and many other pathways. The filtration industry is under constant pressure to come up with new filter media that can create effective barriers for these minute particles [73]. Nanofiber composite webs are being used as barrier materials to trap submicron size particles. Although nanofiber webs are not prevalently used as standalone filters, they are effective components of multilayered filter media. Recent findings at Texas Tech University suggested that the aerosol filtration efficiency of cotton fabrics with nanofibers embedded in them is almost double that of the untreated cotton fabrics. However, the durability of these layered nanofibers is still an issue to be looked at and resolved [74].

10.3.1 Engine Filtration in Heavy Duty and Light Vehicle Engines

Air filters of a typical automobile are known to be ineffective in capturing particles smaller than 5 μm in size. Particles of 1–5 μm in size have been found to lead to engine wear which increases the emissions from the engine and shortens engine life [75].

Grafe et al. [75], showed that the use of nanofiber filter media extends the service life of vehicle engines in many off-road and on-road applications. Nanofiber filters significantly increased the life of the engine in applications involving sub-micron contaminants from engine exhausts and industrial processes [75]. Also, the life of nanofiber filters was found to be twice that of the conventional cellulose filters in the case of on-road applications [76]. The military communities can exploit the advantages of nanofiber filters as they use heavy duty vehicles in highly contaminated war theatres.

10.3.2 Nanofibers in Turbine Engines with Military and Multiple Applications

Harsh environmental conditions such as dusty desert climates have become common place these days in war theaters. In such climatic conditions, a combination of windy airflow and high dust necessitates the need for high barrier filters in turbines which has led to the development and use of self-cleaning pulse-jet systems involving nanofibers. Grafe et al. [75] observed that nanofilter layers enhance the ability of self-cleaning systems to dislodge dust from the filter surface, in addition to higher efficiency with minimal pressure drop. They do so when positioned on the upstream face of the filter, according to the authors. This is an important benefit of using nanofiber layers in self-cleaning filter applications. The combination of nanofiber media with pulse-jet cleaning system has found many applications in industrial filtration such as military vehicles [75].

10.3.3 Nanofiber Based Water Filter Systems for Military

Toxic metal ions in contaminated waters such as those in combat zones are a persistent problem. The removal of the metal ions and other contaminants is of critical importance for minimizing the exposure of soldiers to these contaminants. Haider and Park [31] successfully applied chitosan nanofibers prepared by electrospinning for the neutralization of toxic metal ions. The chitosan nanofibers were chemically neutralized (neutralization of the ammonium into amine group) in this process. The authors observed that chitosan retained its biocompatibility, hydrophilicity, bioactivity, non-antigenicity and non-toxicity in this process. The authors proposed that the advantages of the chitosan nanaofiber-based filter system over the current technologies include high surface area per unit mass due to the very fine diameter of the fibers, the porous structure in the swollen state and the environment friendly nature of chitosan [31]. Such nanofiber filters can be used in field deployable water purifiers, which can be used by the warfighters.

Removal of disinfection by-products (DBPs) from potable water is also an important issue for the military. DBPs are formed due to the reaction between chlorine and organics and are potential carcinogens. Approximately 20% removal of DBPs using hydrophobic-based nanofiber mats was reported by Thavasi et al. [65].

10.3.3.1 Ultrafiltration Media for Water Purification Using Nanofibers

A new 3-tier composite system involving the use of porous electrospun webs has been developed by Yoon et al. [77]. The authors have shown that the 3-tier system could be used as an effective nanofiltration media as it can exclude particles with sizes of few nanometers. The 3-tier composite system in Fig. 10.4 consists of three layers: (1) a "non-porous" hydrophilic top layer; (2) an electrospun nanofibrous substrate mid-layer (cross-linked PVA); and (3) a conventional non-woven microfibrous support which is a melt-blown polyethylene terephthalate (PET) mat [77]. The top layer is non-porous to particles but is porous to water. It is based on cross-linking polyvinyl alcohol (PVA), polyether-b-polyamide (Pebax) copolymer or their nanocomposites with surface-oxidized multi-walled carbon nanotubes [77].

Due to the weak mechanical stability of cross-linked PVA in aqueous conditions, the authors selected a more hydrophobic and mechanically stable polymer, polyacrylonitrile (PAN), as a nanofibrous support, which is an improvement to the above system. Chitosan has been selected as the top hydrophilic coating. This system exhibited an increase in the flux rate while keeping the same filtration efficiency over

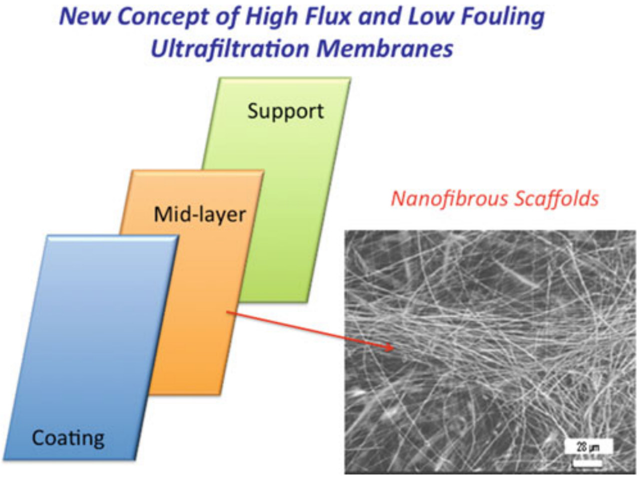

Fig. 10.4 Schematic representation of a three-tier system [77]

many of the best known existing filters. A decrease in the thickness of the coating layer resulted in an increase in the flux rate, according to the authors [77].

To increase the performance of the membrane by increasing the flux rate and decreasing the fouling, the same researchers proposed two strategies: (1) cross-linking of the chitosan layer with glutaraldehyde and (2) grafting of more hydrophilic polyethylene glycol molecules on to the chitosan chains [77].

Sun and Li [42] developed a nanofibrous composite filter by electrospinning a blend of chitosan and polyethylene oxide solution onto a spunbond nonwoven polypropylene substrate. Various diameters of the fibers were examined for their ability to be used in air and water filtration. The filter exhibited hexavalent chromium binding abilities of up to 35 mg per gram of chitosan. The filter also exhibited antimicrobial activity resulting in a 100-fold decrease in Escherichia *coli* colony forming units [42].

Similarly, nanofibers can be sandwiched between a range of other fibers and fabrics to enhance their performance characteristics. A variety of techniques could be employed to develop nanofilter membranes to meet specific requirements.

10.4 Nanoparticles in the Defense Sector

Nanoparticles, as the name suggests, are particles with any of its dimension in the nano range. A few examples of nanoparticles that are gaining increasing attention of late are the metal oxide nanopowders and magnetic nanoparticles. Their ability to destroy chemical agents and decontaminate personnel exposed to chemical agents will play a crucial role in designing novel protection strategies.

10.4.1 Metal Oxide Nanopowders

Rajagopalan et al. [53] have investigated the dissociative chemisorption of organophosphorous compounds by nanocrystalline metal oxides. They termed this phenomenon, destructive adsorption. The authors have evaluated the ability of aerogel-prepared magnesium oxide (AP-MgO) nanoparticles to destructively adsorb paraoxon. The MgO nanoparticles were found to be more efficient than their conventionally prepared and commercially available counterparts and other adsorbents like activated carbon. The reactive nature and high surface area of nanoparticles were found to be the reasons for the increased efficiency of nanoparticles in destructively adsorbing toxins like paraoxon. Similar results were found in the case of diisopropylfluorophosphate (DFP) [53].

10.4.2 Magnetic Nanoparticles

Magnetic Nanoparticles can be engineered to detoxify military personnel in case of a chemical attack [78]. This involves the functionalization of magnetic nanoparticles to bind to the toxin of interest. When injected into the body of suspected individuals, these magnetic nanoparticles could be drawn through the body using a strong magnetic field. When these nanoparticles have a very high magnetic moment, they could be pulled along with the bounded toxin molecules. Such an approach is termed as “tag and drag” approach. Gold coated iron, nickel and cobalt ferromagnetic particles are being investigated in the “tag and drag” approach [78].

10.5 Sensory Applications of Nanofibers

Semiconducting metal oxides are widely known for their application in gas sensors. Metal oxide nanofibers electrospun as nonwoven mats have been found to be advantageous in gas sensor applications [79]. Weng et al. [80] investigated the ability of one-dimensional polyaniline-polypyrrole (PANI-PPy) coaxial nanofibers (PPCF) to detect the presence of triethylamine (TEA), considered as a toxic compound by the food industry. The authors observed that the PPCF is more sensitive to the presence of TEA, compared to the individual abilities of PANI nanofibers and PPy [80]. Lim et al. [81] reported that mesoporous indium sesquioxide nanofibers were highly sensitive to the presence of carbon monoxide in air. Electrospinning has been successfully employed by these authors in the synthesis of metal oxides with high surface areas [81]. This could lead to the development of high response gas sensors, which can be of help to the military.

Moon et al. [79] attempted doping the metal oxide nanofibers to observe if it enhances the sensing capabilities of the metal oxide nanofibers. They compared the efficiencies of TiO_2 nanofibers and Pd-doped TiO_2 nanofibers. The doping with Pd enhanced the gas sensitivity of the TiO_2 compared to pristine TiO_2 nanofibers [79]. Song et al. [82] have developed a sensor for ethanol based on ZnO-SnO_2 electrospun nanofibers. The sensor exhibited good linearity at various concentrations of ethanol and was found to be reproducible and selective, with fast response and short recovery cycle, and cost effective [82].

10.6 Other Industrial Applications

Polymer nanofibers have the ability to alter the properties of the surface on which they are grown or coated. Chiou et al. [83] at Ohio State University have been successful in developing a variety of surfaces that are hydrophobic, hydrophilic and oleophobic in nature. More importantly, windows, safety glasses and protective shields that repel dirt can be synthesized with the help of this technology. The water attractive surfaces could be used to develop anti-fog coatings for military vehicle windshields and windows. Furthermore, this technique could be used to develop transparent plastic electronic devices. Polymers that conduct electricity could be used for this purpose. Researchers have developed a surface to charge organic light emitting diodes, which may eventually lead to the development of transparent plastic electronic devices [83].

Carbon nanotube (CNT)-embedded bulletproof materials are also being developed to harness the advantage of carbon nanotubes with regard to its light weight and material characteristics. According to Maharajan [84], carbon nanotubes possess a unique combination of high elastic modulus and high yield strain. These properties make them ideal candidates for use in bulletproof vests. Three different approaches have been proposed by the author to exploit the above advantages for using carbon nanotubes to enhance the ballistic performance of body armor: (1) Incorporation of carbon nanotubes into polymer matrix composites, metals and ceramics to improve the hardness, toughness and the erosion resistance of carbon nanotube composites; (2) Neat or composite carbon nanotubes that can be directly used in the form of woven or nonwoven fabrics; and (3) Reinenforcement of armor grade fibers with carbon nanotubes to increase their elastic modulus and energy absorption capacity [84].

10.7 Conclusions

Nanofibers in functionalized and non-functionalized forms are predominantly weak by themselves to serve as a stand-alone protective medium for defense applications. The high surface area characteristics play a critical part in using nanofibers as a filter/protective medium. High production methods which can also yield stronger nanofiber webs will be most sought after by the defense community. With the advent of new methods of nanofibers development, it may be possible to develop stand-alone nanofiber webs that can be used as effective personal protection medium. Research and development efforts are needed to focus on functionalized stand-alone nanofiber webs. In addition, toxic and environmental issues with regard to the use of nanofibers and nanomaterials have to be thoroughly investigated. For example, nanoparticles in blood can cross the blood-brain barrier and induce the production of free radicals resulting in serious cell damage. Nanoparticles can also be used in a negative way such as development of high energy bomb materials resulting in negative consequences [6]. The defense and research community should investigate the toxic and lethal effects of nanoparticles-based materials before bringing them into the defense arena.

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