ADAPTIVE TEXTILES FOR THERMAL MANAGEMENT USING WOOL FIBERS

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Adaptive Textiles for Thermal Management Using Wool Fibers

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Certificate of Originality

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_________________________________(Signed)

IQBAL MOHAMMAD IRFAN (Name of Student)

Dedication

I dedicate this thesis to my Late Father, Prof. Md. Abdul Awal, who inspired me to learn science and engineering from my childhood and his passion towards science will always be my inspiration; to my mother Ms Sultana Razia, who always prayed for my triumph and gave me absolute love and support; to my two lovely brothers Mr Asif Iqbal and Mr Imran Iqbal, who provide me utmost support during my PhD tenure.

Abstract

Adaptive textiles are well recognized for responding to various environmental stimuli such as changes in humidity, temperature, pH, electrical field, solvents and light. These functions facilitate them for working as sensor, actuator, artificial muscle and functional material. Therefore, this can be classified as "Very smart textiles". The current commercial manufacturing method of developing adaptive textiles for clothing comfort utilizes phase change materials, various responsive synthetic materials, conductive materials, wearable attachment, coating application and artificial intelligent technologies which can sense and control environmental temperature and humidity in the microclimate of human body. However, this method generates high amount of carbon footprint along with processing complexity and the scientific merit of this practice is also questionable. However, up to now, it is rather hard to find publications reporting research and development using bio-based materials.

Wool fibers has stimuli-responsive shape memory ability. Upon water/sweat stimulation, they undergo shape change in length and width direction, making them ideal raw materials for developing adaptive textiles using natural fibres. Wool knitwear is generally considered as winter clothing materials for keeping the body warm. An investigation into water-gradient responsive wool knitwear for developing adaptive textiles and thermoregulation ability has excellent potential to rediscover the wool biopolymer as a clothing material all over the year. This study aims to explore the thermoregulatory performance of wool-based knitwear using the water-driven shape memory effect (SME) of wool biopolymer. In this study, a knitted structure has been prepared using 100% descaled wool yarn, and their thermal management property has been examined and compared under various water gradient levels. This study presents the findings that water actuation of wool knitwear enables pore size change effect significantly impacts body thermoregulation by the clothing.

Moreover, two commercially popular knitted structures, such as Single Jersey and Double Knit, have been prepared from 100% wool yarn. Their smart heat and moisture regulation behaviour due to SME have been investigated and compared to detect the fabric structural effect on SME and thermoregulation performance. This study presents the findings of SME of wool in the form of fibres, yarns, and fabrics stimulated with water using an optical camera and light microscope. It has been found that the water stimulated fabrics to exhibit 20% more area change compared to the dry sample. Moreover, the water gradient responsive, unique pore actuation behaviour of the fabrics has been noted for both structures. The thermal regulation performance of the samples at different water gradients such as 0,25,50,75 and a100 percentage of water absorption have been investigated by measuring air permeability, thermal conductivity values, water vapour transmission through the samples under different environmental temperatures and humidity and IR characterization using FLIR-IR camera and ATR-FTIR spectroscopy. The evidence suggests that SME, technical structure, and unique pore actuation ability of the fabrics plays a crucial role in improving fabric thermoregulation performance stimulated with water. The Single Jersey structure is the most suitable for maximum pore actuation, cool touch, and air permeability. Besides, in harmony with the air permeability values, the water vapour transmission for single jersey fabrics is increased significantly compared to double knit structure from the dry samples to wet samples of different water gradient for each set of ambient condition. Furthermore, Single Jersey demonstrates the lower surface temperature both in dry and wet conditions than the double knit in thermal images, indicating that the single jersey sample can provide a better radiative cooling effect than double knit samples. The quantitive analysis of the IR transmission of dry and wet samples also supports thermal images for single jersey fabric. However, the double-knit fabric shows the only better thermal property in terms of thermal conductivity measurement. These overall results illustrate that wool knitwear and a single jersey structure may offer a promising clothing material to the wearer all over the year.

This material can give a similar response upon contact with body sweat/water and the humid environment. Besides, woolen knitwear is established as textiles for both hot and cold because of their superior water-actuated shape-memory performance. Herein, a robust and sustainable bio-based woolen respirator with the superior ability of cooling management are demonstrated using simple knitting and melt-blown technology. The as-prepared respirators provide excellent protection from airborne particulate along with a high level of cooling, compared with a commercial mask. Moreover, it exhibits a high rating during wear trial. This provides a new insight to develop high quality sustainable respiratory mask with an excellent cooling performance from functional biomaterials.

Publications Arising from the Thesis

Journal Publications:

1. Hu, Jinlian*, **Mohammad Irfan Iqbal**, and Fengxin Sun. "Wool Can Be Cool: Water-Actuating Woolen Knitwear for Both Hot and Cold." Advanced Functional Materials 30.51 (2020): 2005033.
2. **Mohammad Irfan Iqbal,** Fengxin Sun, Bin Fei, Qingyou Xia, Xin Wang, and Hu, Jinlian*. "Knit Architecture for Water-Actuating Woolen Knitwear and Its Personalized Thermal Management." ACS Applied Materials & Interfaces 13.5 (2021): 6298-6308.
3. **Mohammad Irfan Iqbal,** Shi Shuo, Jiang Yuenzhang, Bin Fei, Qingyou Xia, Xin Wang, Wenbo Hu and Hu, Jinlian*."Woolen Respirators for Thermal Management" Advanced Materials Technologies 6.6 (2021): 2100201.

Conference Proceedings:

1. **Mohammad Irfan Iqbal** and Hu Jinlian* "Wearable wool knitwear with shape memory effect", The 9th International Conference on Advanced Fibers and Polymer Materials 19-22 November 2019, Donghua University, China; p274.

List of Patents:

1. Hu Jinlian* and **Mohammad Irfan Iqbal,** Water-Actuating Woolen Knit Pores for Thermoregulation, United States Provisional Patent Application No. 63/0093,365

Awards

1. **Outstanding Poster Presentation Award:** Wearable Wool Knitwear with Shape Memory Effect, The 9th International Conference on Advanced Fibers and Polymer Materials conference held in Donghua University, Shanghai, China.19 November 2019

Invited Talk

1. Adaptive Comfort Textiles for Healthcare, China Textile Engineering Society Youth Forum, Wuxi, October 16-18, 2020

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List of Abbreviations

SME	Shape Memory Effect
IR	Infrared Radiation
ASHRAE	American Society of Heating, Refrigeration And Air-Conditioning Engineers
COVID-19	Coronavirus Disease 2019
CAGR	Compound Annual Growth Rate
USD	U.S. Dollar
PCMs	Phase Change Materials
NPs	Nanoparticle
SMMs	Shape Memory Materials
SMP	Shape Memory Polymer
MWCNTs	Multiwalled carbon nanotubes
BNNSs	boron nitride nanosheets
PVA	poly (vinyl alcohol)
NASA	National Aeronautics and Space Administration
AgNW	Silver Nanowire
SEM	Scanning Electron Microscope
MMT	moisture management tester
HB	Hydrogen bond
DB	Disulfide bond
UV	Ultraviolet
CNT	Carbon Nanotube
ETPM	Extended Two-Phase Model
IFs	Intermediate Filaments

DSC	Differential scanning calorimetry
XRD	X-Ray Diffraction
SMPU	Shape Memory Polyurethane
DHMP	2,6-dihydroxymethyl pyridine
Tg	Glass Transition Temperature
PEG	Poly (Ethylene Glycol)
WVTR	Water Vapour Transmission
ASTM	American Society for Testing and Materials
AATCC	The American Association of Textile Chemists and Colorists
WKW	Woolen Knitwear
PTM	Personalized Thermal Management
PP	Polypropylene

Chapter 1 Introduction

1.1 Adaptive Textiles

Adaptive textiles are well recognized for responding to various environmental stimuli such as changes in humidity, temperature, pH, electrical field, solvents and light[1]. These functions facilitate them for working as sensor[2], the actuator[3], artificial muscles[4] and functional materials[5, 6] as shown in **Figure 1.** Therefore, this can be classified as “Very smart textiles”. The growing demands of this material have been observed in recent times, and it is expected to be continued to establish a sustainable, smart and functional clothing industry. The functional textiles market is broadly labelled based on their end uses such as fashion & entertainment, sports & fitness, medical and healthcare, transportation industry, defence & military sector, and design industry[7]. The smart fabrics market is growing rapidly amid sportswear & medical textiles [8], where thermoregulation or thermal management is the utmost priority for bringing comfortability to the wearer.

Adaptive textiles have gained growing attention in recent years. The performance in this field can be compared to research in electronics, many solar energy-based systems, self-cleaning, fire-retardant, quick-drying. Textiles can be categorized into the following groups based on their function: shape memory, chameleonic, water-resistant and vapour permeable, heat storage, thermoregulated, vapour absorbing, heat evolving fabric and electrically heated suits. The efficacy of adaptive textiles is still being studied. A remarkable group is involving to prepare microcapsule with bi-component structure. Shape changing textiles have been developed using unique polymer matrix materials. Shape memory polymer fibers could be produced by a different type of shape memory polymers. With shape-shifting polymers, it has become possible to fabricate novel fabrics which can reversibly change shapes by using moisture from the atmosphere depending on the humidity and temperature. Climate responsive textiles have been developed with materials and fabrics that can be altered with water vapour transmission or porosity to changing environmental conditions. A variety of items can be produced using such materials for apparel and technological applications. Adaptive textiles thus provide immense opportunities for fashion and functional clothing industries. Moreover, these solutions will come from the collaborative efforts of engineering, science, design, and process development.

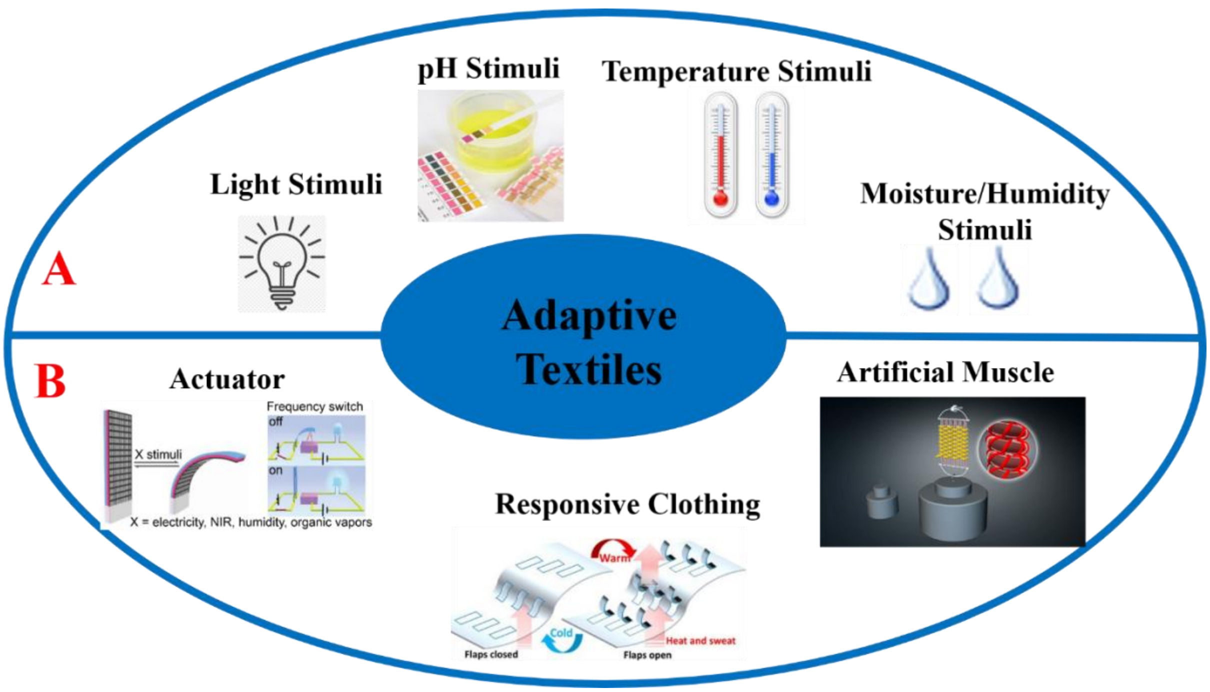


Figure 1 Concept of adaptive textiles (A) Stimuli (B) Applications

1.1.1 Adaptive Microfibers and Nanofibers

Nanotechnology has been very important to the development of adaptive polymeric materials during the past decades. The combination of appropriate fabrication methods, different nanofibers, adaptive polymers, nanofilms, and nanoparticles of adaptive polymers can be accomplished. For example, researchers have used self-assembly techniques to build nanofibers with a shape memory effect using electrospinning. If adaptive polymers are manufactured with nanostructures, several specific properties may be obtained due to the surface properties and orientation structure of nanomaterials. Some novel functions can now be obtained using nanotechnology. Hence, nanomaterials are used in many fields because of their performance. Electrospinning can be used to make continuous fibers with diameters varying from micro to nanometres. Electrospinning is useful for many kinds of polymers. Polymers can be chemically modified and tailored with additives of varying complexity. There are several parameters involved in the electrospinning process. Various polymer systems, including water-soluble polymers, biopolymers and their derivatives, and multiphase polymer systems, have been documented to obtain nanofibrous membranes by electrospinning. Preliminary investigations have shown that the electrospun nanofibers have limited water vapor diffusion resistance and extreme efficiency at trapping aerosol particles. The pore size of the nanofilm may be changed. Fabrics made from nanomaterials has demonstrated some unique properties. Electrospinning techniques may prepare protective clothing. Also, electrospinning is a good alternative to prepare lightweight and breathable fabrics. Nanofibers are able to adsorb chemical agents without compromising air and water vapor permeability. Nonwoven materials created by layering electrospun fibers have small pores with a porosity. Nanofibers and nanofilms can be used in tissue engineering, scaffolding, wound dressing, and many other practical applications. Also, some materials that create a mask can be obtained from nanofilms.

1.1.2 Shape Memory Fibers and Fabrics

Shape memory polymers and fabrics can be prepared from shape memory polymers and fibres, such as, shape memory polyurethanes, polyethylene terephthalate-polyethylene oxide copolymers, thermoplastic polynorbornenes, and other polymers that show shape memory effects by cross linking after spinning. Wet spinning, dry spinning, melting, electrostatic spinning, twisting etc can be used to get adaptive textiles. Shape memory fibers can be made of natural, modified polyurethane/rayon, or artificial fibers .The blended yarns can be fancy, core spun and friction yarns. Textile sewing threads can also be made of shape memory polymer fibres. Shape memory fabrics can be woven, knitted, braided and nonwoven. The fibres mentioned above, yarns and fabrics revert to their original form if heated above the shape memory temperature. Therefore, shape memory fibers can be used for anti-crease effects, dimensional stability, and many kinds of fancy purposes. The fabrics may be added to textiles depending on the uses and properties needed, including shirts, collars and cuffs. There are many applications for the elbows and knees of trousers, skirts, tops, and any other fabrics that need to be extended, sewn or moulded.

1.2 Comfort Management

Comfort management is a fundamental and essential need of a wearer. However, the definition of comfort is very complex and is varying with respect to different individuals. Comfort has been defined based on thermal and non-thermal factors and is deeply associated with the surrounding environment such as hot and cold, humid and non-humid conditions[9].It helps to function the human body smoothly and actively through bringing the physiological, neurophysiological and thermo-psychological balance to the wearer[10]. In contrast, discomfort can be easily described in such terms as irritation, ache, hot and cold. The discomfort may develop from extreme environmental conditions such as hot and cold feeling, dry and moist sensation. These unwanted feeling can only be regulated or control by wearable clothing with advanced structures or fibrous materials. Clothing comfort can broadly be classified as psychological, tactile, and thermal comfort[11]. Psychological comfort related to fashion sense rather than fabrics property[12]. Tactile comfort is defined as the amount of stress generated in body due to the fabric. Hence, this comfort property has been evaluated by the mechanical and surface characteristics of the fabric[13]. Thermal comfort is related to the wearer's ability to maintain core body temperature and transfer microclimatic heat, moisture, and sweat from the body due to extreme environmental conditions [14]. However, thermal comfort has been considered an essential element of overall comfort[15].

1.2.1 Thermal Management

The American Society of Heating introduced the term thermal comfort, Refrigeration and Air-Conditioning Engineers (ASHRAE) as that state of mind that shows satisfaction with the ambient temperature[16] and adapts with the thermo-regulation ability of the human body. The human body is a system that works best at a certain range of core temperature for instance, (37 ± 0.5) ^{o} C which is influenced by the clothing and surrounding environments. To maintain this core temperature, the balance between heat generation and heat loss to the environment is vital for survival. Changes in core temperature may have a severe effect on daily human life and can lead to sickness. It has been observed that the variation in ±7 °C core temperature could be a cause of death. The harmful consequences of variation in core temperature are presented in **Figure 2.**

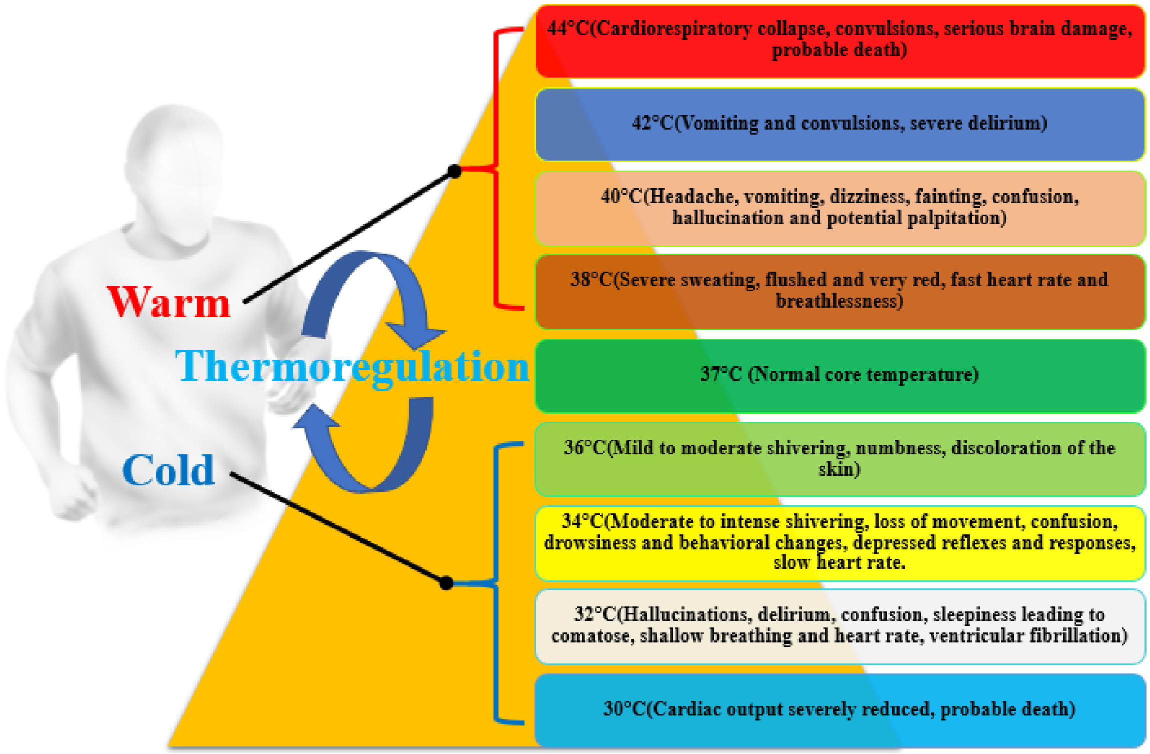


Figure 2 Adverse physiological reactions to a change in core temperature[17]

1.2.2 Mechanisms for Thermal Management

As reviewed above, maintaining the heat balance in human body is necessary in order to keep the core body temperature in steady state. Textiles and clothing contribute the best in this regard by heat exchange between the body surface and surrounding atmosphere. The key factors affecting the thermal management performance of textiles will include the heat insulation, mass transfer in the form of vapor and liquid through clothing, body heat exchange with surroundings by conduction, convection, radiation, evaporation and condensation, and so on**.** It is essential to illustrate the following terms to give a detailed theoretical background to the current research.

1.2.2.1 Conduction

Thermal conduction is defined as the spontaneous transfer of heat from high-temperature region to the low-temperature region between two adjacent materials with a temperature gradient[18]. In the extreme cold or warm condition, significant variation on the temperature has been noted between the outer and inner layers of the clothing. The larger heat loss occurred by conduction because of larger temperature difference between the two surfaces. In order to keep the core body temperature of human being constant and steady due to the temperature differences between body, clothing and surroundings, heat energy will dissipate from the high temperature area to the area of low temperature. This heat flow activity is known as conduction heat transfer, and is explained by Fourier's Law[19]

$$Q = -KA\frac{\partial T}{\partial x} ---------- (1)$$

Where Q is the heat flow rate, k is a constant and acknowledged as thermal conductivity of the studied material, A is the area of the contacted body, the minus sign denotes that heat transfers down the temperature difference, from the region of high temperature to low temperature one.

In the temperature tuneable garments, the heat is balanced by losing or gaining heat from the body to the environment, as well as from environment to the body through the clothing. From Equation 1, we can observe that when $\frac{\partial T}{\partial x}$ and K are constant, if A is larger, the absolute value of q is larger, and if A is smaller the absolute value of q is smaller. Therefore, in order to manufacture thermoregulated apparel, we need to engineer the types of material in which A value can be switchable with the environmental temperature changes. However, body heat loss by conduction is negligible, for instance at resting condition 3% heat loss has been observed via outerwear, footwear and undergarments[20]

1.2.2.2 Convection

Thermal Convection is the exchange of heat by the movement of a fluid mass (liquid or gas) due to the temperature difference of the environment[21]. The heat transfers from high temperature surface to the low temperature region. This heat exchange mechanism is called convection and can be characterised by Newton's law of cooling:

$$Q = hA\Delta T ---------- (1)$$

Where Q is the convective heat flow rate, h is a constant and acknowledged as heat convective constant, A is the surface area for heat transfer and ΔT is the temperature gradient. Heat convection may occur in two way namely natural and forced convection. Natural convection occurs due to the temperature and density difference of heated fluid. Forced convection occurs when heated fluid is circulated with the help of external devices such as fan or pump. Heat is exchange through the clothes by both natural and forced convection. However, the transfer of heat through convection depends on various factors such as movement of body, ventilation effect and air movement. During natural convection the atmospheric air layer of user is heated by conduction from the wearable clothing and hence generates lower density air because of adding of water vapor to the air consequently the air movement rises. In this state, the velocity of air is 0.05 m/s. It has been noted that forced convection occurred above 0.2 m/s[22]. Thus, the air velocity contributes significantly for bringing clothing comfort via heat convection.

1.2.2.3 Radiation

40% of heat exchange with the environment may occur via heat radiation [23]. Thermal radiation is an electromagnetic energy, which is generated due to the materials surface temperature. In contrast with convection and conduction, for radiative heat loss there is no need for contacted surface with temperature gradient and it can even occur through a vacuum media. The key factors for radiative heat loss included: surface area of the body, emissivity and reflectivity characteristics of the objects.

Thermal radiation is considered as one of the electromagnetic radiations. It can transfer at the speed of light, 3×10^{8} m/s [48]. The relation between the wavelength and the frequency of thermal radiation can be described by the following equation.

$$C = \lambda\nu - - - - - - - - - - (2)$$

where C is the speed of light, λ is the wavelength of produced thermal radiation, ν is the frequency. Thermal radiation fits between the visible and microwave regions of the electromagnetic spectrum. The wavelength range is from about 0.1 to 100μm.

According to Wien's law, the higher the temperature of an object, the wavelength of peak emission will be shorter. The wavelength of the peak emission released by the human body is 9.35 μm, as the core temperature of the human body is 37°C.

1.2.2.4 Evaporation

Evaporation or water vapor transfer is the process through which heat exchange occurs by transforming liquids/sweat into gases. Significant amount of body heat can dissipate by this heat transfer process. The basic mechanism of water vapor transfer included following steps: water loss (600-800 mL day $^{-1}$) and released in the microclimate of the clothing due to the insensible perspiration. The evaporation rate solely depends on environmental vapor pressure. The higher the vapor pressure, lower the evaporation rate. Evaporation is also coupled with heat transfer. Personalized thermal management by clothing can achieve through evaporation (water vapor transfer)[24]. Evaporation through the clothing may occur in four different following ways[25]

1. Diffusion between fibre and air pockets
2. Absorption and transmission of water vapor by the clothing
3. Adsorption and migration of the water vapor along the cloth surface
4. Diffusion of the water vapor via the fibre or yarn capillaries

However, water vapor diffusion through the air pockets between the clothing is likely to be the major transport mechanism for evaporative heat loss of human body.

1.3 Shortcomings and Possible Solutions Being Addressed

From materials point of view the study on adaptive textiles for thermoregulation tends to exclude natural fibers, which are now a pivotal part of developing sustainable and green textile industry. Recent evidence suggests that many naturally occurring materials such as cotton, flax, silk and various animal hairs can be able to show stimuli responsive behavior due to their intrinsic structures or physical and chemical modifications of the materials. Since 18th century horse fibers have been widely used in hygrometers because of their length contraction ability upon contact with moisture. However, such fibers demonstrated negligible length contraction and slower response time, unable to utilize them for performance-based materials. Moreover, a recent study[4] revealed that wool, flax and cotton can be utilized as artificial muscles and actuators by introducing coil like special twist in the materials and hence can provide better response than the synthetic artificial muscles.

The available information suggests that wool fibers have unique shape memory properties This characteristic will give wool fibers significant potential as a new class of smart material in the adaptive comfort textile industry. However, those unique properties on end products may largely depend on the fabrication processes, the details of which might not have been discovered.

Although many researchers made claims for the shape memory properties of wool fibers, little evidence could be collected from scientific literatures regarding utilizing this characteristic for fabrication of personal thermal management clothing. Hence, there is a strong need for unbiased laboratory experiments to elucidate the origin and fundamentals of those unique properties of wool fibers and to develop the methods to effectively utilize the properties in the final products for thermoregulation. Having investigated the potential of wool fibers for smart materials, we report and suggest wool fibers for fabrication of thermoregulatory textiles, which have been used traditionally as safe and regular winter clothing materials.

From heat regulation point of view recent studies on adaptive textiles for thermoregulation usually consider either heat transfer or mass transfer, whereas for an efficient cooling and heating process both transfer mechanisms are utmost priority for bringing desired clothing comfort. However, authors generally place an emphasis on cooling fabrics rather than both heating and cooling. There is an urgent need for developing comfort textiles with synergistic heat transfer mechanism in order to get maximum effect and produce truly thermoregulatory textiles.

On the other hand, comfort management of respiratory masks along with excellent filtration performance is important and highly demandable in current COVID-19 situation. It has been used by all walks of life, not only by the common people to filter pathogen-based bacteria and virus but also by healthcare and sanitation workers in extreme atmospheric conditions. It has been noted that heat stress, sweating, and discomfort generated because of wearing respiratory face masks in hot and humid conditions. Moreover, the damp and warm micro-environments in face masks can turn as a hotbed for bacterial and viral growth within the mask, building an ultra-exposure risk to the consumers[26]. In commercial and traditional face masks, the thermal comfort properties are mainly resolute by the thickness and pore size of the nonwoven fibrous materials, while the thickness and pore size is tightly correlated to the filtration performance (prefers thick and small pore size) and, air permeability and conductivity (prefers thin fibers and big pore size). Hence, it is challenging to maintain thermal comfort in face masks without sacrificing the other filtration related performances.

1.4 Aims and Objectives

1. To develop an understanding of the adaptive mechanisms involved in stimuli-responsive wool fibrous materials by characterizing their physical and chemical functional properties.
2. To deepen the study on thermophysiological interactions of the human body and textiles with change in environmental conditions, with consideration of the personalized thermal management properties to establish the basic principles.
3. To validate the preliminary hypothesis by developing a testing method, setting up test instrument and conducting experiments.
4. To design and develop prototypes of comfort textiles using smart wool fibers.
5. To identify the roles of design factors and parameters such as fabric structural features, properties of functional fabrics, smart materials and distribution of adaptive fibers that will influence the comfort and functional performance of adaptive comfort textiles.
6. To carry out geometrical modeling to establish the relationships between produced functional materials and body thermoregulatory responses.

1.5 Significance and Value

1.5.1 Technological Significance

This work will bring development in the area of adaptive comfort textiles using responsive natural fibers, through the establishment of relationship between fabric pore actuation, the fiber and yarn shape change, the fabric structures and the shape memory behaviour. The study will be helpful for technologist and materials scientist to strengthen the fundamental understanding behind the various aspects of stimuli responsive shape memory ability and its association with clothing thermal management through a rigorous literature survey. It will also helpful for factory personals to fabricate such kind of comfort textiles using conventional natural fiber and machinery.

In order to search the published patents (Adaptive) OR (Smart) OR (Intelligent) OR (Responsive) OR (Moisture)) ((Comfort) OR (Thermoregulation) OR (Thermal management)) ((Textile*) OR (Fabric*) OR (Clothing*) was used as titles in Google Patent search engine and were counted and reported in **Figure 3.** It has been noted from the figure that the demand for personal thermal management through comfort textiles is growing in the research community, which signify the value added and fundamental research on this area.

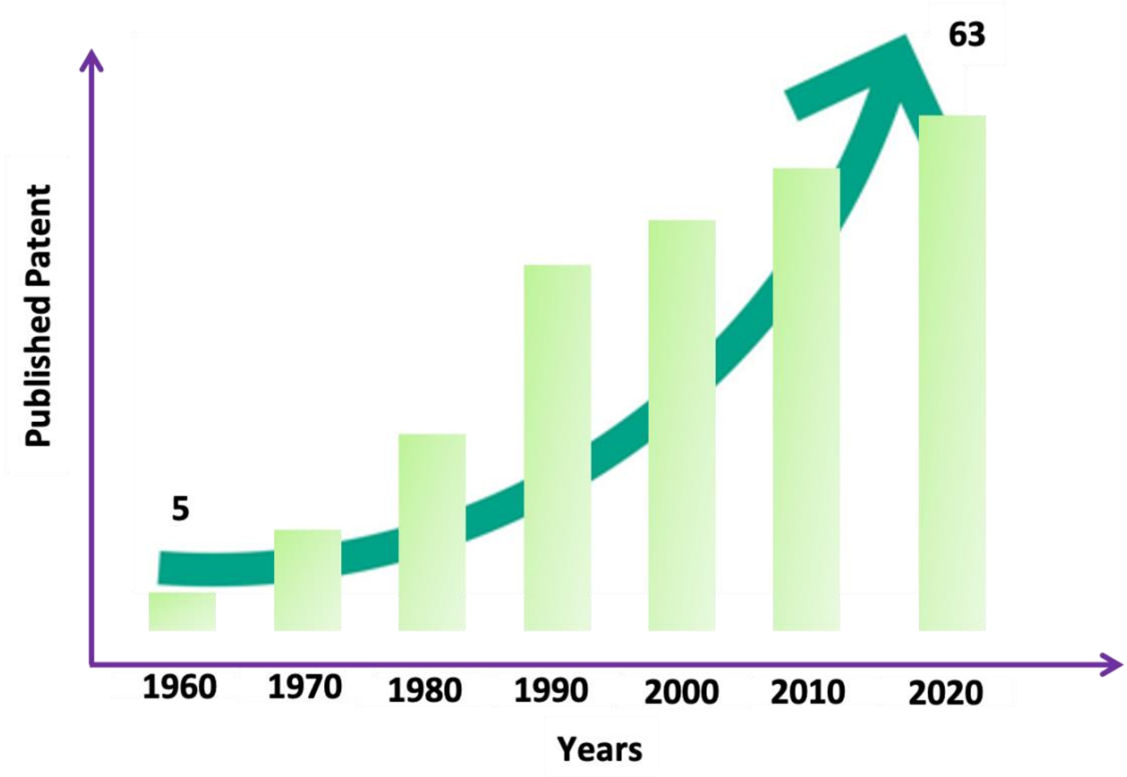


Figure 3 An overview on published patents based on adaptive comfort textiles. Source Google Patent database, November 2019

1.5.2 Commercial Significance

The market for wearables using smart textiles is expected to grow at a CAGR of 132% within 2016-2022 (represent $70 billion market)[27]. According to Grand View Research 2019, the market size of global smart textile was projected to be approximately USD 878.9 in 2018 and predicted to exceed at a CAGR of 30.4% from 2019 to 2025[28].Moreover, IDTechEx predicted that the smart textile industry will achieve around $3bn by 2026, where sports and fitness industry along with medical and healthcare industry will be dominating sectors[8]. It has been well acknowledged that the technology needs to boost up the smart textiles industry, should have sustainability and efficient thermal management performance with clothing comfort.

According to the report on cooling or thermoregulatory textiles, these market worth USD 1.25 billion in 2016 and is likely to record a CAGR of 11.1% by 2022[29]. There is a linear growth observed in such kind of products as it is emerging as an innovative and smart materials for garments and fashion manufacturers, which facilitates to fabricate dual mode textile by keeping the body cool, taking away sweat, and providing heat/wind insulation. Owing to have tremendous popularity of adaptive comfort clothing, is likely to influence overall smart textiles market demand over the next several years. North America, Europe, and Asia Pacific are actively participated to develop this rising market as sports and leisure activities becoming a part and parcel in everyone life in these regions.

The thermoregulatory textiles market has largely driven by the synthetic cooling fabrics because of their certain benefits such as higher availability and better thermal management performance in comparison to other natural fibers incorporated garments. However, the increase use of synthetic materials has great impact on our ecosystem and hence the use of natural materials and reengineer of conventional natural fibers are prime concern for many manufacturers. Moreover, cooling textiles having high price make them unaffordable to the end user. The fabrics become expensive due to the vast research and development and utilizing complex technology along with high end raw materials, for example nanotechnology and nonporous polyethylene. Here in our study, the technology can easily integrate into the finished products. This study conducts to facilitate easy and convenient Tech-to-Market approach as the raw materials and machinery involved to fabricate such fabrics are conventional and there is no requirement for additional arrangement or modifications in processing machineries.

1.6. Thesis Outline

- **Chapter 1:** In this chapter general introduction to the thesis is given. The objectives involved in producing adaptive textiles using natural fibers and the significance of this project are presented.
- **Chapter 2:** In Literature review the heat transfer property of the human body, and their mechanism are discussed. Smart natural fibers and various other adaptive materials for thermal management of the human body are highlighted here.
- **Chapter 3:** Methodology introduces the raw materials; fabrication methods and characterization systems used to prepare and analyze adaptive textiles for thermal management.
- **Chapter 4:** As a second skin of the human body, clothing offers protection, aesthetic quality, and courtesy. Because of the inability of materials to adapt to different weather conditions, different clothing is required for different seasons, namely, thin and open garments for summer, thick and closed ones for winter. Moreover, our body maintains its internal core temperature (37 °C) through sweating and shivering. Herein, we report a discovery that is contrary to available public and professional knowledge, that is, woolen knitwear can provide not only warmth, but also a cooling sensation when a body sweat. The fascinating water-responsive pore size change of the knit pores keeps the skin dry, thus helping to maintain a constant body temperature, providing comfort and safety.
- **Chapter 5:** Personalized thermal management using water-actuated woolen knitwear has great potential for smart textile production. However, woolen knitwear exists in a wide range of forms with different derivatives. Manufacturing of smart woolen structures with excellent cooling properties links to certain parameters such as a change in a loop formation, loop shape, and yarn arrangement

upon stimulation of body fluid. To address this issue, textile knit structures with different physical and mechanical properties have been prepared using water-responsive descaled wool fibers and their smart heat and moisture regulation behaviour have been investigated and compared to detect the fabric architectural effect on water-actuation and cooling performance of the woolen garment. The evidence suggests that the technical structure of the fabrics plays a crucial role in pore actuation and fabric cooling performance. The water-actuation and thermal management ability of single jersey were greatly enhanced because of unbalanced structures with lower mechanical stress among the loops and yarns. The experimental data is also in line with the theoretical analysis. Hence, unbalanced structure controls fast heat and mass transfer from the human body which may offer a promising year-round clothing material to the wearer. This material can give a similar response upon contact with body sweat and the humid environment and hence can act as a skin-like fabric. Their possible application can lie in different fields, such as thermoregulation, functional clothing, sportswear, and medical care.

- **Chapter 6:** COVID-19 pandemic recently has a great impact on personalized protection and healthcare, especially in the respiratory mask. However, due to the complex relationship between filtration performance and thermal management, there is a lack of investigation considering both characters in respirators. Keratin based biomaterials such as wool are recently well acknowledged as skin-like materials because of their superior moisture-actuation performance. To incorporate protective function against bacteria, virus, microdroplet and particulate matter, melt-blown polypropylene can be introduced as a barrier layer. Herein, a robust and sustainable bio-based woolen respirator with the superior ability of cooling management are prepared using simple knitting and melt-blown technology. The as-prepared respirators provide excellent protection from airborne particulate along with the high level of cooling, compared with a commercial mask. Moreover, it exhibits a high rating during wear trial. This provides a new insight to develop high quality sustainable respiratory mask with an excellent cooling performance from functional biomaterials.

- **Chapter 7:** This chapter summarizes the thesis and provide suggestions for future work to further explore the potential applications of spider silk inspired materials.

Chapter 2 Literature Review

2.1Comfort

2.1.1 The Thermal Balance

Comfort has a subjective sense that is changing all the time. Some researchers have described it as “an enhancement of physiology and psychology allowing the user to function without a sense of stress.” [30]. All aspects of comfort are matters of balance (thermal neutrality). Thermal state refers to a person's preference for a warm or cool climate. Thermal comfort is a priority for humans alongside other basic needs for human being[31]. Thermal comfort in the warm condition is linked to the heat and moisture release of the human body. To retain the equilibrium retained by the body, a microclimate is created around the body to help preserve this balance. A fabric assembly that was both high heat and moisture resistant at cold condition would foster and sustain a feeling of thermal comfort, maintaining the relationship between the amount of heat and energy.

2.1.2 Thermoregulation

The information about temperature is sent to the brain by a sensory nerve. They are spread all over the body. Temperature-sensitive nerve endings pick up temperature changes.

2.1.2.1 Thermoregulation of Human Body

It is important to understand the processes by which the human body controls body temperature in linked to specific factors and body activity. The aim of the thermoregulatory system is to maintain a steady body temperature of 37°C. It can be concluded that the human body would be in equilibrium for exposure to a constant (moderate) thermal condition with a constant metabolic rate. Since energy dissipation would equal energy output, there will be no significant energy storage inside the body. The heat balance equation for this condition is:

H - Ed - Sew - Ere - L = K = R + C -----[1]

where H = the internal heat production in the human body

Ed = the heat lost by water vapour diffusion through the skin

Sew = the heat lost by the evaporation of sweat from the surface of the skin

Ere - the latent respiration heat loss

L = the dry respiration heat loss

K = the heat transfer from the skin to the outer surface of the clothed body (conduction through clothing)

R = the heat loss by radiation from the outer surface of the clothed body

C = the heat loss by convection from the surface of the clothed body.

When a body's internal temperature is higher than the environment's temperature, the body causes a series of events to protect it. The body part that controls temperature send signals to the sweat glands and therefore more sweat is generated. When sweat evaporates from the skin, the skin cools, and the body's temperature is lowered to normal.

2.1.2.2 Physiological Thermoregulation

The sense of heat and cold is based on skin temperature receptors that are present in the superficial layers of the skin. Temperature sensors are sensitive to temperature or temperature change, these are also known as body’s thermometer. They can be seen over the entire body and can be found at places such as the extremities, fingers and toes, and hands and feet. Moreover, nipples, chest are most sensitive to heat. The hands and feet play an especially important role in controlling the body temperature. However, the hands and feet are only between 5 and 7 percent of the total skin area[32], 100-fold is the transition in vasoconstriction to vasodilation. Hands and feet can restrict or increase the amount of surface heat. The body develops a lot more sweat in the feet and hands than in other areas of the body because of the number of sweat glands is also higher in these areas. Temperature variations in the air or on the skin cause the nerve endings to activate the brain, sending impulses down the nerve to the spinal cord, and on to the brain. These impulses go to the hypothalamus, a key centre for temperature control. The nerves consist of two types, cold ends, and hot endings. These ends known as thermal receptors are responsive to temperature changes, Cooling triggers cold nerve endings and warming activates hot nerve endings. When we are in a thermal comfort zone, we are unaware of our own body temperatures. It is not said "my skin feels comfortable." The nerve endings are only signs of a transition, either a rise or a decrease in temperature. Temperature sensors are in the hypothalamus, but others are in the spinal cord. Researchers say the spinal cord can also control temperature when hypothalamus injured. Heat responsive neurones are in the anterior (preoptic) hypothalamus. The neurones respond to changes in the temperature of the blood circulating through this organ. Very slight changes in body temperature can cause the thermostatic mechanism. Sensors send signals to the hypothalamus that cause several different responses including blood vessels, sweat glands, and shivering. When heat is produced, it can also change due to modifications. A closed loop with a feedback mechanism would regulate the temperature automatically.

Activity can increase or decrease body temperature; however, skin temperature may be related to the climate. The regulating system controls heat output during exercise to allow a certain amount of temperature increase. At the same time, skin cooling happens when one raises their activity level. It varies from the pattern of a body at rest. The effect also varies from conditions where body temperature is affected by external means, such as air temperature.

The body temperature is regulated primarily by the hypothalamus (in the brain) with a few auxiliary centres of control in the cerebral cortex, medulla, and spinal cord. Thermal regulation relies on balance between heat loss and heat gain.

A control centre to avoid the overcooling lies in the Posterior Hypothalamus close to the "Corpora Mammillaria" and the other lies in the Anterior Hypothalamus in the Anterior Commissure. The Anterior (Preoptic) centre is responsible for the prevention of excessive heat. This area regulates evaporative cooling and movement in this area causes panting in animals and sweat in man. The anterior and posterior sites are thought to be related. Hence, the activity of one is depressed while the other is involved. When the two temperatures are balanced, a natural thermal sensation is achieved[33-35]

Adaptation is impaired if a person is overstressed If core body temperature increases due to insufficient heat loss, sweating lasts until it is exhausted, and body is heated subsequently.

The increase in temperature would have a two-fold reaction; vasodilation of the skin's blood vessels happens first, increasing blood flow increases the rate of heat loss by radiation. Secondly, sweating can be increased by increased blood flow to the skin and direct stimulation of the sweat glands by the parasympathetic nerves. Similarly, moderate-intensity exercise leads to a rise in body temperature, followed by a fall in skin temperature.

2.2 Role of the skin

The skin is the predominant tissue in the human body[36]. It is made up of approximately 1935400 mm^2 and is of varying thickness from 0.05 to 3.0 mm. The skin is made of two layers: the epidermis and dermis (inner layer). The skin's role is complex. Skin's function is to regulate body temperature[37], store organic and inorganic compounds, excrete water and salts, and obtain stimuli from the environment. The outer skin layer consists of epithelium and is rooted in the inner skin layer. The reticular area is in the dermis. This area contains fibers that allow it to travel in several directions. It includes blood vessels, collagenous and elastic fibers, and hair follicles between interlacing fibres[38-40]

2.2.1 Sweat Glands

Sweat glands are found in the entire body[41] and can be found in a large number in the soles and palms of the hands and feet. Density can exceed 7620 per cm^2 with other areas being higher concentrations such as the chest and forehead[42]. Each gland is a coil within the dermis and an outer membrane (mucosa) and secretions move through ducts to form the sweat pores[43]. A network of tiny blood vessels covers the sweat glands. The glands in the auxiliary area are simple branched. However, they are simple tubular glands elsewhere.

2.2.2 Insensible Perspiration

Under warm air conditions, about 26.5 degrees Celsius, the human body does not sweat at rest. However, the body can still lose heat via insensible perspiration. “Sweat” and “perspiration” are incorrectly thought to have the same meaning over the year[44]. Insensible perspiration doesn't really apply to liquid sweat, which occurs from the sweat glands. It refers to a gradual evaporation of moisture water vapor occurring all over the body surface, result of water vapour permeating the skin between both the cells of the epidermis[45].This can be considered heat loss by skin diffusion. Water vapor diffusion through the skin is a passive mechanism that is not regulated by thermoregulation. It is assumed that the intensity of vapor diffusion is proportional to the difference between the partial pressure of water vapour in the air Pa and the saturated water vapour pressure Ps. The key barrier to moisture vapor diffusion is provided by two layers within the skin: The Stratum Corneum and the Stratum Rucidum. In these layers, moisture vapor diffusion is thought to be fast in comparison to clothing vapor diffusion. An increase in skin or ambient temperature causes a rise in the production of insensible perspiration. However, the rate of perspiration will decrease as the temperature goes up[46]. It should be noted sweating should cease when insensible perspiration begins. This is because the pressure difference which drives the diffusion process is reduced once the skin becomes wet. Under normal indoor conditions one fifth of the heat lost by the body is from loss of insensible perspiration. Two thirds of 24 hours come from the skin and the remaining is at approximately 0.5 g/min from the respiratory tract. That equals a cumulative heat loss of 20W/24h. This associates to 0.032 l/h. of moisture as water vapour is liberated from the whole skin area per 60 min, which in turn is equivalent to a heat loss of around 18.5 kcal. /hour.

2.2.3 Function of Sweating

Sweating is part of the body's way of keeping a stable body temperature[47]. There are two ways of water transfer by perspiration, either as insensible or as sweating. Sweating is regulated by the autonomic nervous system with two separate parts. These are distinguished by the chemicals produced at different nerve endings. The sympathetic nervous system develops adrenaline. The parasympathetic mechanism makes acetylcholine. In the case of sweat glands, however, the nerves are originated from the sympathetic system, and not adrenaline.

Sweating is a physiological reaction mediated by the adrenergic nerves. Sympathetic nerves supply the sweat glands in the hands and feet. Sweat glands can be involved in sweating responses to changes in temperature, However, they are still involved in emotional reactions, which appear to be secreted in the cold. In man, psychogenic sweating typically occurs on the hands, soles, and axillae in a cool setting, while on the whole-body surface in a warmer environment. Furthermore, as the body responds to thermal stimuli, as the sweat begins to increase on the skin itself, the sweat on the hands and shoes decreases or even vanishes.

The content of the sweat formed by these glands varies depending on the location in the body. The fragrance of sweat from the outer regions of the body is stronger than that from the rest of the body. The composition of the secretions can also differ with the cause of the secretions, sweat developed due to the heat is more acidic than the sweat created by exercise and the salinity and pH levels are also changed[48]. Sweat contains many waste products, such as urea, decomposition products from muscle action, such as creatinine and creatine, and most notably, salt[49].

Salt levels are unimportant in normal conditions, but in hot climates a loss of salt is significant. When the sweat glands overwork, the salt reabsorption process is compromised.

Sweat consists of salt (NaCl) and the effects of muscle activity, along with various minerals and amino acids. Due to presence of lactic acid along with other amino acids fresh sweat is acidic in nature. This is how amino acids bind together to form polypeptides and complete protein molecules. The below amino acids are reported in human sweat[50, 51]:

- Arginine
- Histidine
- Threonine
- Tyrosine
- Valine
- Isoleucine
- Phenylalanine
- Aspartic Acid
- Glutamic Acid
- Citrulline

Ammonia is also present. It is produced by decomposition of urea in stale sweat. Glucose, along with its related minerals such as potassium, calcium, magnesium, sulphates, phosphates and iron are present, with sodium chloride as the utmost significant mineral[52]

2.3 Heat Transfer in The Human Body

Human thermal control depends on heat transfer from the atmosphere to the body (Homeostasis). It depends on many factors including conduction, convection, radiation, and evaporation **(Figure 4)**. The heat transfer between the skin and the atmosphere is difficult to describe. Through evaporating sweat on the skin, heat is transmitted by the evaporation of sweat to the surface of the skin through the phase shift from sweat to water. It has been noted that the evaporation of insensible perspiration affects the heat and mass transfer process, even if the skin surface is not wet. If the skin is not in touch with another surface it can't conduct heat. Radiation is also permitted to radiate from the skin surface[53, 54].

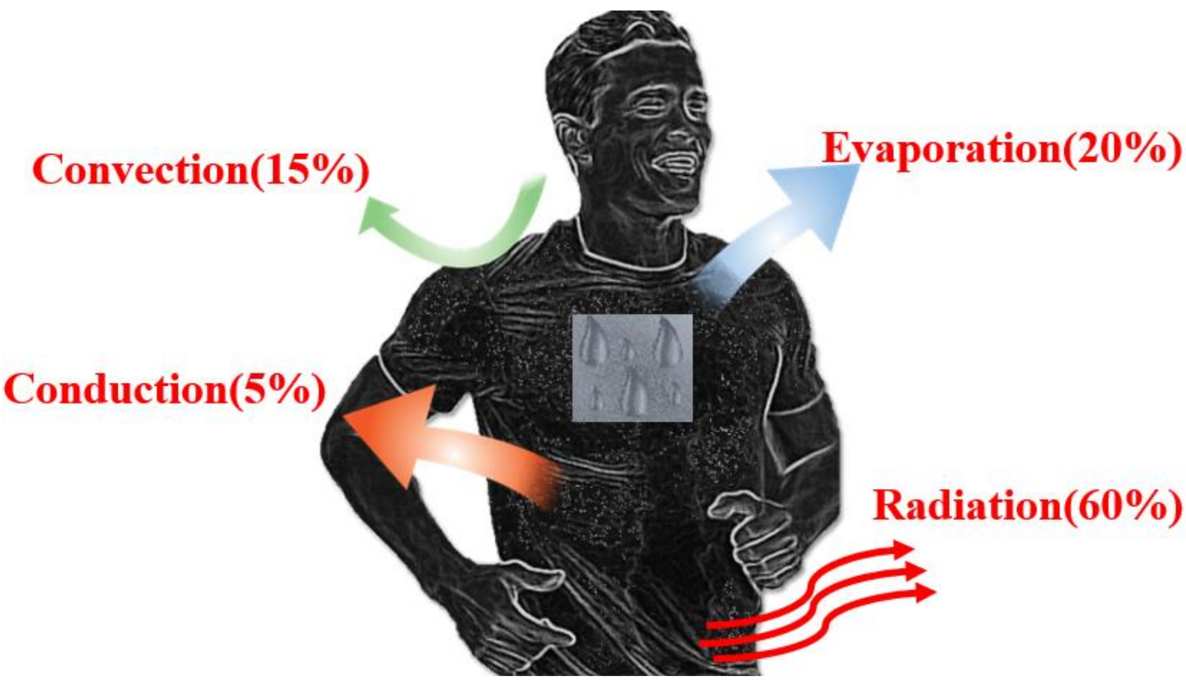


Figure 4 Mechanism of human body heat transfer[17]

2.3.1 Conduction

This is a mechanism for heat exchange between surfaces that are in contact. The amount of heat exchange in the human body accounts for less than 1 - 2% of the overall heat exchange, and it plays a minimal role in body heat exchange with its surroundings[33, 55]. However, it is assumed that conduction is happening at the ‘core' of the body. The central core is made up of primary organs such as the heart, lungs. The outer layer of this muscle contains skin, fat, and just a superficial layer of muscle. It will differ based on the heat transfer reaction kinetics at the skin surface with the atmosphere, and the metabolic rate in the body centre. Comfortable skin is characterized as a mean temperature of about 34°C. This is achieved by heat being transmitted from the core through the tissues of the shell to the surface. Clothing provides an intermediary layer between the skin and the environment. In thermodynamic equilibrium, body heat transfer can be divided into two separate parts. Firstly, there is a thermal exchange between the tissue and fabric, and secondly heat is lost by transmission from the surface of the textile to the surroundings.

2.3.2 Convection

Convection moves heat or energy between warm bodies or clothing and the atmospheric air[56]. It causes air to heat and become dense and rise as a natural convection boundary layer around the individual.

When air is static, convection can appear freely; or when body is moving, forced convection occurs. It is around 15% of body heat lost to the air and 3% lost to cooler items such as clothes.

Two factors influence how heat is transmitted between the body and the environment:

(i) the variation in temperature between the body surface and the surrounding air, which measures how much heat is given off or absorbed by a unit mass of air.

(ii) the rate air flow, which determines the volume of air striking in contact with textile

Convection is generally assumed to only occur in a fluid, and of course the body is not a fluid[57]. The circulatory system does contain fluid of high thermal ability that function as a controlled convection system. This helps to equalize, conserve, or dissipate heat from the body.

2.3.3 Radiation

This physical approach of heat transfer is also a significant mechanism[58]. Individual lose heat because of cooler objects around them. Around 60% of heat loss through the skin can be achieved through this process. However, radiation can escape from a freely exposed textiles, and it is not triggered by touch at the skin surface. The skin can act as a black body, but this feature is based on the colour of the skin. Its value diminishes once the body is in out of the sunlight[59].

All radiant heat emitted from the human body lies within the infrared wavelengths. This form of energy cannot be seen, and humans do not emit visible light.

Radiate heat from the man consists of two forms.

(i) the short wavelength, high temperature and ultraviolet radiation from the sun or from open furnaces.

(ii) the long wavelength radiation related with the individual's body.

Some objects, such as "grey bodies", reflect light equally in all wavelengths. Substances which are black or nearly black for some radiation and not for others are called coloured substances, and it is into this class that the human skin and maximum textile fall. The human skin is known to radiate for the spectrum of wavelengths[53]. However, the region of the body exposed to the air is effective in dissipating heat. The total heat loss is a minor amount due to the areas covered. between the fingers, between the legs and under the chin.

2.3.4 Evaporation

The critical process by which the human body controls body temperature is by evaporating the body's sweat in humid conditions[60]. Sweat diffuses through the boundary layer until the liquid sweat has been transferred into the vapor phase.

To prevent overheating, excess heat energy must be lost by the evaporation of sweat[60]. The loss of sweat is significant in controlling body temperature during strenuous exercise Sweat rates can be fine-tuned over a wide spectrum of energy output. The metabolic rate ranges from 100W at rest to l000W during exercise. The sweat rate can go up to 1.5 litres per hour to 4 litres per hour for people who are adaptable to heat. Maximum heat energy can be lost at these rates are lkW to 2.7kW[61, 62]. The heat is released from the body by evaporating water molecules is 0.58 Kcal. Evaporative cooling does not occur if sweat does not circulate without evaporating[63].

Evaporation of the body's heat is mainly dependent on the amount of sweat produced and the rate at which it can be carried away by the ambient air (RH). If the humidity is too high, it may not be possible for the air to absorb water vapour at the same rate at which the skin is generating it. Therefore, sweat will settle and roll off and not contribute to the evaporative process, and therefore the heat transfer will be insignificant.

However, more heat can be lost by less significant means. When the skin is not wet and active sweating is not present evaporation from the skin will still occur. The method is called evaporation and diffusion during expiration that leads to smaller amounts of heat loss[64]. This is known as insensible evaporation. The body also loses heat to warm food, air is taken in, and CO2 expired during respiration.

2.4 Environmental Effects on The Body Temperature

2.4.1 Effects of Environmental Heat

Environmental condition such as temperature and humidity can significantly influence the work efficiency of human being[65]. In hot weather the body can heat up and make the user feel uncomfortable from excessive sweating, and this can disturb the actual performance of many physical activity. Some users are exposed to extreme heat, usually because of radiation. High temperatures can be created in steel, ceramics, and glass factories. In the high-level sports service, all the forms of heat can be present. It has been noted that with high environmental temperatures, the rate of sweating decreases. Exposure to high temperatures induces fatigue in the sweat glands; maximum sweat rate is achieved as soon as body temperature has risen[66]. The sweat rate starts to decrease here. When work continues, the body's temperature increases, and work efficiency starts to decrease[67]. When a worker continues to work in a hot setting, they are at risk of a severe condition known as heat stroke. It has been noted that performance still fell even without an increase in body temperature; it is likely that the rise in temperature distracts the worker[68].

2.5 Adaptive Materials for Thermal Management

The heat and mass (liquid/gas) transfer properties of fabrics with sudden environmental changes are important for the manufacturing of adaptive thermoregulatory apparel. In the past, many intelligent and functional clothing with unique heat and moisture transfer properties have been established. In order to keep the human body under constant comfort level, the need for a constant microclimatic condition is necessary. Under this circumstances, adaptive and functional materials can be applied for keeping a constant temperature and humidity in the surrounding microclimate. Adaptive textiles can be defined as the materials that can adjust thermal balance of human body with sudden environmental changes by sensing and reacting to atmospheric conditions or stimuli, such humidity, temperature, P^H, light and so on[1]. With the evolution of state-of-the-art technology, currently many adaptive and functional materials are used and applied to the design of the adaptive comfort textiles.

2.5.1 Candidates for Adaptive Materials

Various candidates **(see Figure 5)** are well acknowledged for developing comfort textiles with adaptive in nature. This section reviews different approaches for fabrication of textiles with adaptive behaviour. The focus has been given to wearable electronic devices, conductive nanoparticle (NPs), shape memory materials(SMMs), IR responsive materials, Phase Change Materials (PCMs) and responsive textile fibres.

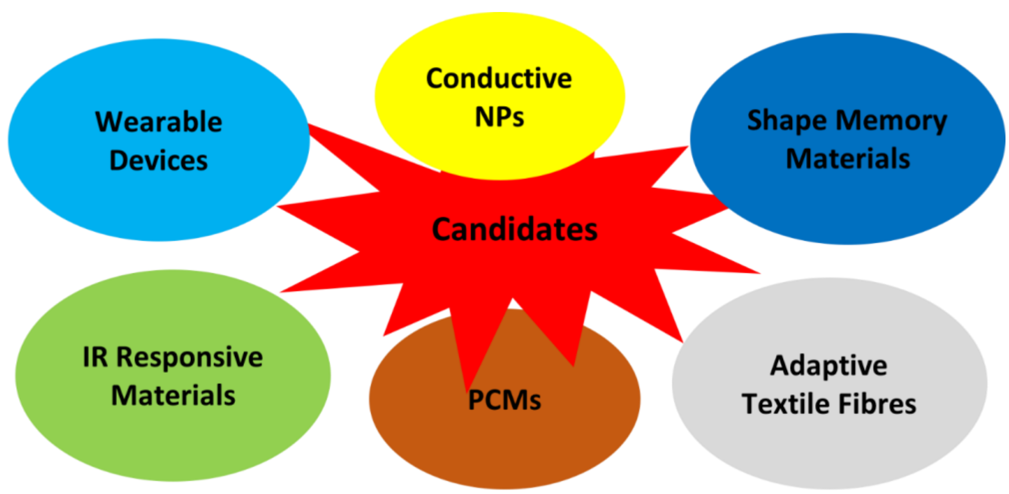


Figure 5 Candidates for adaptive comfort textiles

2.5.2 Phase Change Materials (PCM)

As an endotherm human being response to changes in environmental temperature. A human can feel cold, when a human enters a cold environment from a warm environment and there is a significant amount of heat loss occurs, because of decreasing microclimatic temperature. In contrast a human can feel warm, when a human enters a warm environment from a cold environment and there is a significant amount of heat gain occurs because of increasing microclimatic temperature. The human body is adapted to function within a narrow temperature range. Generally, the human body keeps its body temperature constant at 37 ± 0.5 °C under different climatic conditions.

Phase change materials are well acknowledged for the temperature regulation function. In order to enhance fabrics thermal comfort, in 20th century, first attempt has been made for integrating microencapsulated phase change materials (PCM) on clothing[69]. PCM typically has three states, solid, liquid, and gas along with four type of phase change: solid to liquid, liquid to gas, solid to gas, solid to solid. During the phase transformation process, heat is either absorbed or released as shown in **Figure 6** When heating the PCM, its temperature rises and reaches the melting point as well as absorbs heat subsequently changing the phase from solid to liquid state. The temperature is kept steady at the melting point until all material changes into liquid. When temperature lower and reaches the crystallization point, it changes from liquid to solid along with releasing of heat and during this process, the temperature is kept constant at the crystallization point.

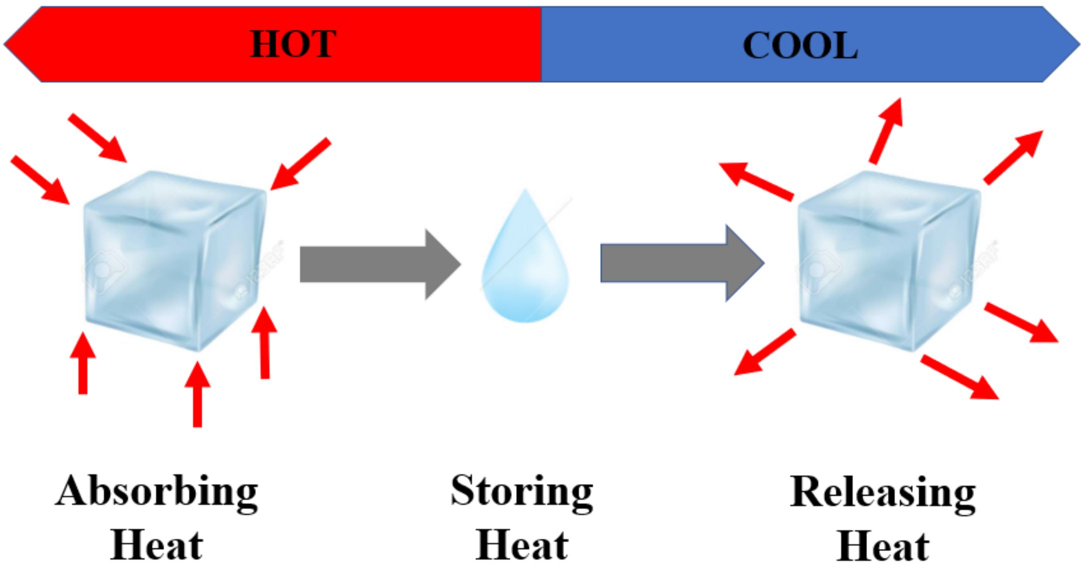


Figure 6 Mechanism for heat transfer of PCMs

Various PCMs have various switching temperatures and latent heat. The best PCM would have the following features[70]

1. High heat of fusion
2. Reversible solid-to-liquid transition
3. High thermal conductivity
4. High specific heat and volume change
5. Low vapor pressure

According to the phase change material handbook[70], paraffin is ideal PCM used in textiles because paraffins have: (1) a high heat of fusion per unit weight, (2) a wide range of melting points (-5 to 66 °C), and (3) they are flammable, nontoxic, noncorrosive, chemically inert, stable below 500 °C, as well as predictable. They also have negligible super cooling behaviour properties, low volume change on melting, low vapor pressure in the melt, reasonable cost, and high wetting ability. The density of paraffin ranges from 700 to770 kg/m3.

Since PCMs might be in liquid form during phase transition process, they applied in the textile substrate in the form of capsules in order to avoid drip off clothing during melting[71]. In order to achieve better thermal management, the capsule size needs to be small as much as possible. Microencapsulation is the technique of covering tiny droplets or particles in a shell material for the safeguard or regulated release during application and phase transition state[72]. In contrast to commercial insulation, which simply traps air, the encapsulated PCMs can trap materials in any physical state such as liquid, solid and both and significantly increases the capacity of materials to store energy. The PCMs can enhance clothing thermoregulation performance by absorbing, storing and releasing human body heat to help the body to remain in constant comfortable temperature. It can actively respond to temperature variation between the human body and surrounding environment. Thus, the PCMs facilitate the human body to retain its core body temperature across warm and cold weathering and across high and low levels of activity.

In order to manufacture different kinds of PCMs the mixing of PEG, eicosane, butane tetracarboxylic acid, hexanediol, stearic acid and noctadecane has been prepared[73-76] and then applied PCMs on textile substrates such as wool, cotton and artificial fibers to enhance their thermal regulation performance. The as-prepared PCMs apparel can absorb heat without a significant temperature change as its enthalpy is 219.37 J/g. However, the thermal regulation capacity of PCMs textiles using this method is not significant and only a negligible amount of PCMs can be incorporated to fabrics. Moreover, low-cost PCM-based thermoregulatory clothing has been introduced such as water impregnated cool apparel. The mechanism of these materials is dependent on heat absorption and dissipation that is propelled by water evaporation. Because of liquid evaporation, the heat will absorb from the environments to enhance the kinetic energy of water molecules. Therefore, the microclimate heat between the clothing and the human body lowers, providing the wearers with a cool feeling. However, PCMs based apparel has lower thermal conductivity and most suitable for indoor uses because of its limited capacity of thermal absorption[77]. Furthermore, the application of PCM to the textiles could increase water repellence and resistance[78]and the treated fabric becomes stiffer, less smooth and soft [79].The application of PCMs for comfort management has been demonstrated in **Figure 7.**

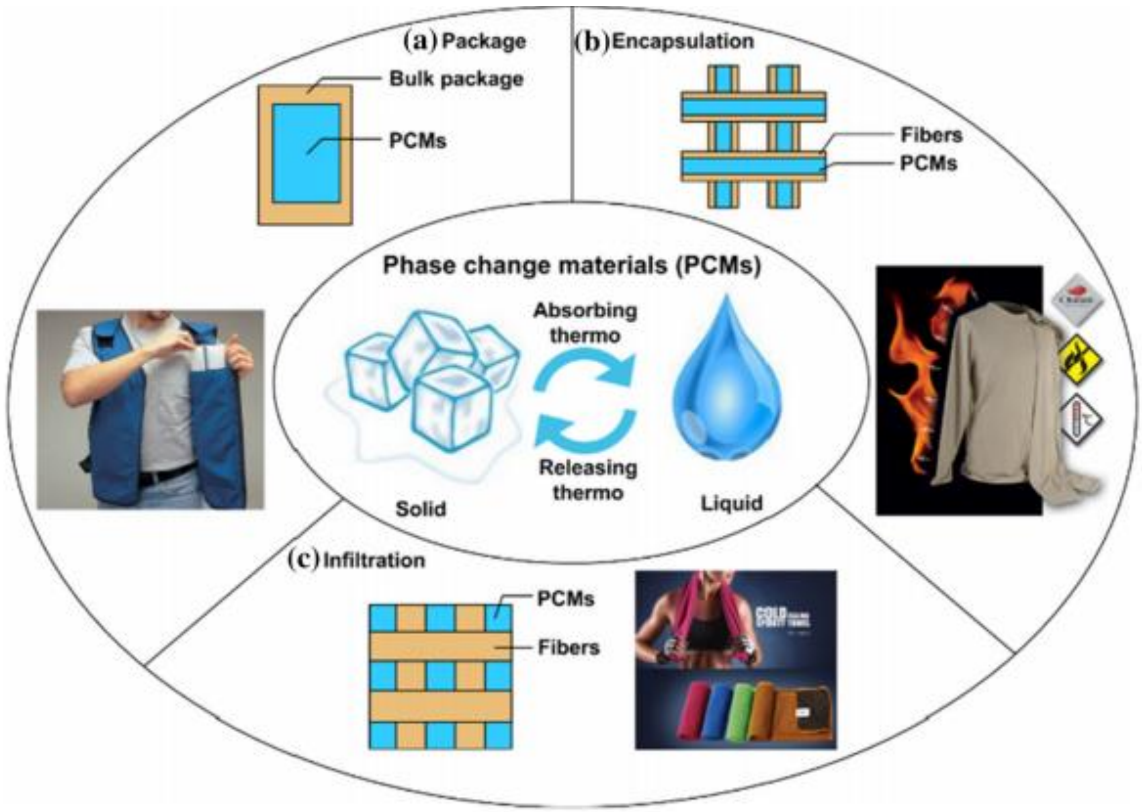


Figure 7 Application of PCMs (a) PCMs packaged and placed in the pockets of the vest lining, (b) PCMs encapsulated within the fibers and (c) Commercialized cooling textiles impregnated with water[80]

2.5.3 Shape Memory Materials

Shape memory materials (SMMs) are dual-shape materials along with environmental stimuli responsive ability. They can significantly change to the temporary shape from permanent shape and vice versa **(See Figure 8).** Temporary shape that is achieved by mechanical deformation and subsequent fixation of that deformation. They can return to their temporary shape from the permanent shape triggered by an external stimulus such as moisture, heat, pH, light, etc. Because of environmental responsiveness of shape changing materials, it has become possible to develop new clothing material with thermal regulation ability which can adapt with external environmental condition change such as temperature and humidity. Heat and moisture responsive textile production have become a reality with shape memory materials and fabrics so that alterations in heat and moisture transmission along with changes in environment conditions have been developed for comfort textiles applications.

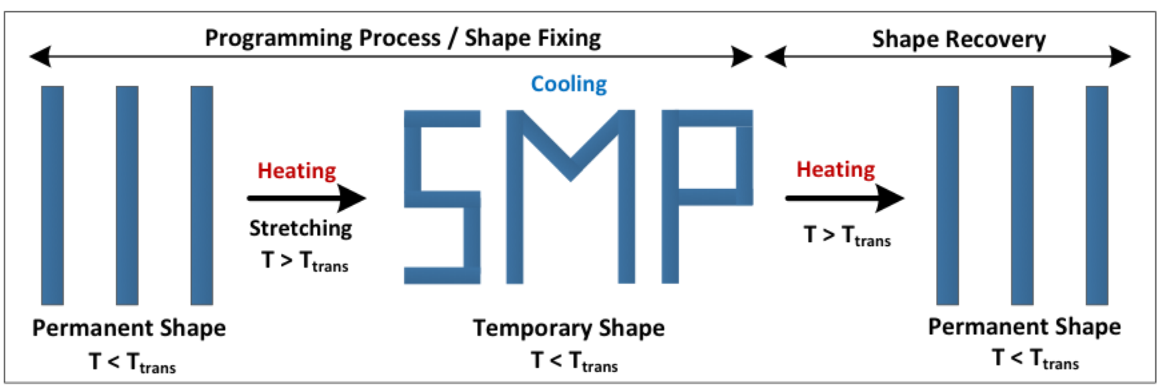


Figure 8 Mechanism of Shape Memory Polymer

Different approaches have been proposed in past decades for developing thermoregulating textiles based on shape memory effect. In1990s, for developing heat-protective clothing the DCTA R&TG (Defence Clothing & Textiles Agency), Colchester and UK have actively started research into the use of SMMs and their derivatives[81].The first attempt was to provide extreme protection from heat transfer. In the investigation, a thermo-responsive shape memory alloy (Nitinol) based springs were fabricated in cotton fabrics with bilayer structure. The springs were able to detect temperature change and shifting their shape accordingly. It has been reported that at ambient condition, the springs were in a flat shape and tightly packed between two layers of fabrics, generating a tiny air gap between the fabrics. On the other hand, when the ambient temperature increases significantly, the springs were expanded because their temperature is driven to shape memory ability. Hence, the gap between two layers of fabrics increased, consequently generating higher thermal insulation due to the trap of significant air between the two layers of fabrics. However, the repeatability of these springs was very poor as when the temperature dropped, they could not return to their initial shape without an external mechanical force. In addition, in a recent study, a humidity triggered thermoregulatory textiles based on heat transfer mechanism has been prepared **(See Figure 9)** [82]. It can reversibly regulate heat transfer based on the change in environmental condition. In the experiment, two bent SMM sheets (Nafion) were introduced between two fabrics to fine-tune the gap of the air layer. Because of the innate shape of the incorporated SMM sheets was curved, it can facilitate warm feeling by having thick air insulation layer between two layered structure of the fabrics. In contrast when the temperature of the air layer, or microclimate was increased, wearer would start to sweat, leading to the increase of humidity in the microclimate. Then, due to the humidity sensitivity of the smart SMM sheets, it would demonstrate shape shifting behaviour from curve to flat and thus, decrease the air layer between the two fabrics, leading to fast heat transfer from the human body to make wearers feel comfortable. These SMM-based thermoregulated textiles were capable to show quick response to the change of the ambient condition. It has been found that the responding time was just within five seconds, established their adjustment to the wide range of changeable environment. However, this kind of designed textile is not suitable for large scale production with low cost and hence the sustainability of this kind of textiles is questionable.

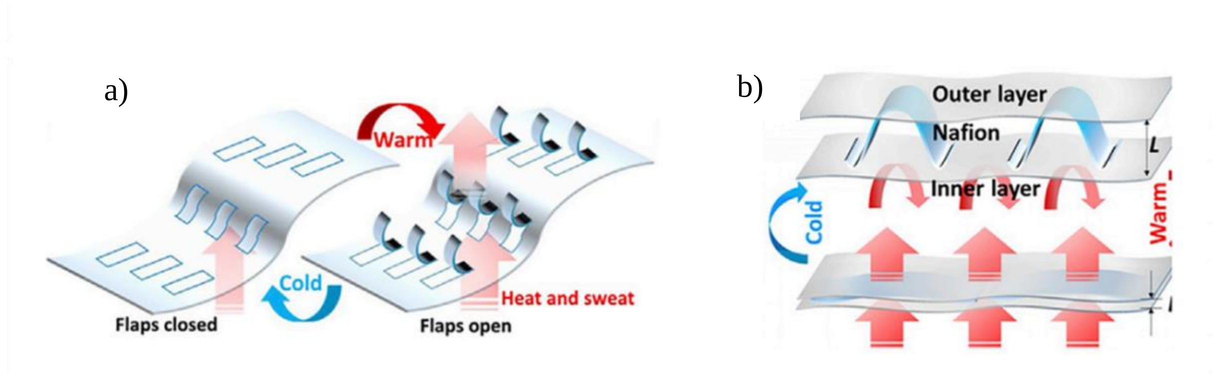


Figure 9 Humidity sensitive SMM based clothing (a) Nafion sheet schematics with openable flaps mimicking thermo-adaptive functionality of human skin and (b) The schematic of the thickness reversible structure using nafion as a thermally adaptive interlayer[82]

2.5.4 IR Responsive Materials

Heat transfer by radiation plays an important role in the thermal management of clothing. The wavelength of human body heat radiation is about 9.35 µm. The factors that contributes largely for heat loss by radiation are the temperature difference between human body and external environment, and the emissivity of the fabric. The radiation thermal resistance of an object can be described the following equation.

$$Ri = \frac{1-\epsilon}{\epsilon A} - - - - - - - - - - - (1)$$

where

A is sample area and $\boldsymbol{\epsilon}$ is the emissivity of the sample[83]

With the tuning of ϵ and A value, the value of the radiation thermal resistance can be altered. Therefore, it is very important to study the IR radiation properties of fabrics in order to fabricate thermoregulatory clothing by selecting appropriate materials.

During past decades, IR responsive textiles, as a group of the most applicable dynamic heat transfer materials, have established rapidly not only in academics, but also in the industry. In current developments of thermal regulation of textiles using IR responsive fabric, they are broadly classified into two types: IR reflective textiles and IR transparent textiles

IR reflective textiles can be developed using the following techniques:

1. Application of metal or non-metal coatings on the textile surface
2. Fabrication of pure metallic fabrics
3. Preparation of metal/polymer composite textiles

Coatings with different types of reflective materials, for instance, metal material Silver (Ag), Titanium (Ti), and Aluminium (Al), non-metallic compounds (e.g., titanium dioxide, antimony doped tin oxide, and azo pigments), and natural compounds (e.g., chlorophyll) has been used for manufacturing thermoregulatory textiles[84-87]. The presence of these materials enhances the sunlight reflection from the clothing and hence lowering the heat gain from external environment through radiation. However, particle size, shape, dispensability, concentration, and thickness of coating should be considered during preparation of metal coatings. Recently, metal nanoparticles such as copper, silver and titanium have been coated on polyester fabrics using electroless plating or vacuum deposition for thermal resistance purpose [88-92].The IR reflection rate of the coated fabrics increased from 8–10% to more than 30–90%. In addition to coating approach, the metallic fabric has been prepared using 100% metallic fibre yarn for fabricating IR reflective clothing and thus it exhibits excellent thermal reflection[93]. Though, this kind of fabric is heavy and stiff for next to skin wear and has lower tenacity. Therefore, to make the clothing comfortable and wearable a composite type metal-polymer core spun yarns have been introduced [94]. It can allow moisture absorption and better flexibility by altering polymer or metal fibre as core or shell parts. It has been observed that the mixing of the stainless steel/ copper filaments with PET yarns, increased 80% of the heat resistance of the blended composite fabrics compared with the pure polymer fabrics.

On the other hand, IR transparent textiles can be achieved through flexible textile structures. To develop cool clothing many researchers have attempted to employ this phenomenon[95, 96]. The cooling effect can be achieved by providing IR gating channel for human body heat dissipation. Traditional clothing prepared by wool, cotton, and polyester are mainly opaque to thermal radiation. Hence, the clothing absorbs the body heat, which is in mid-IR range. Subsequently, heat and discomfort will generate next to wearer skin. The opacity of textiles to the IR radiation usually occurs because of specific chemical bonds such as C−O, C−N, S=O, and C−H in the material structure. The absorption of wavelength peaks of these chemical bonds is in the same region as the human body's IR peak absorption (9.4 μm). In contrast, IR non-absorbing fibers such as polyethylene and nylon do not overlap with absorption peaks because of having unsimilar chemical bonds in the structure of these fibers. Having considered these unique features, the thermoregulatory apparel with radiative cooling effect can be achieved.

Recently, an innovative dual-mode textile based on IR reflection and transmission principle has been introduced using bilayer structures of carbon, copper and polyethylene with traditional cotton fabric **(See Figure 10 a-d)**[97]. They demonstrated that due to the different emissivity level of carbon (0.9) and copper (0.15) along with different thickness of IR transparent nanoPE, two different heat transfer coefficients can be obtained **(See Figure 10 d).** The fabrics provide heating and cooling by flipping out the low-emissivity layer and high emissivity layer towards the environment. Therefore, the dual-mode textile can maintain the body temperature within 32–36^0 C. However, these fabrics cannot switch automatically with environmental change and require an external source to flip out the surface.

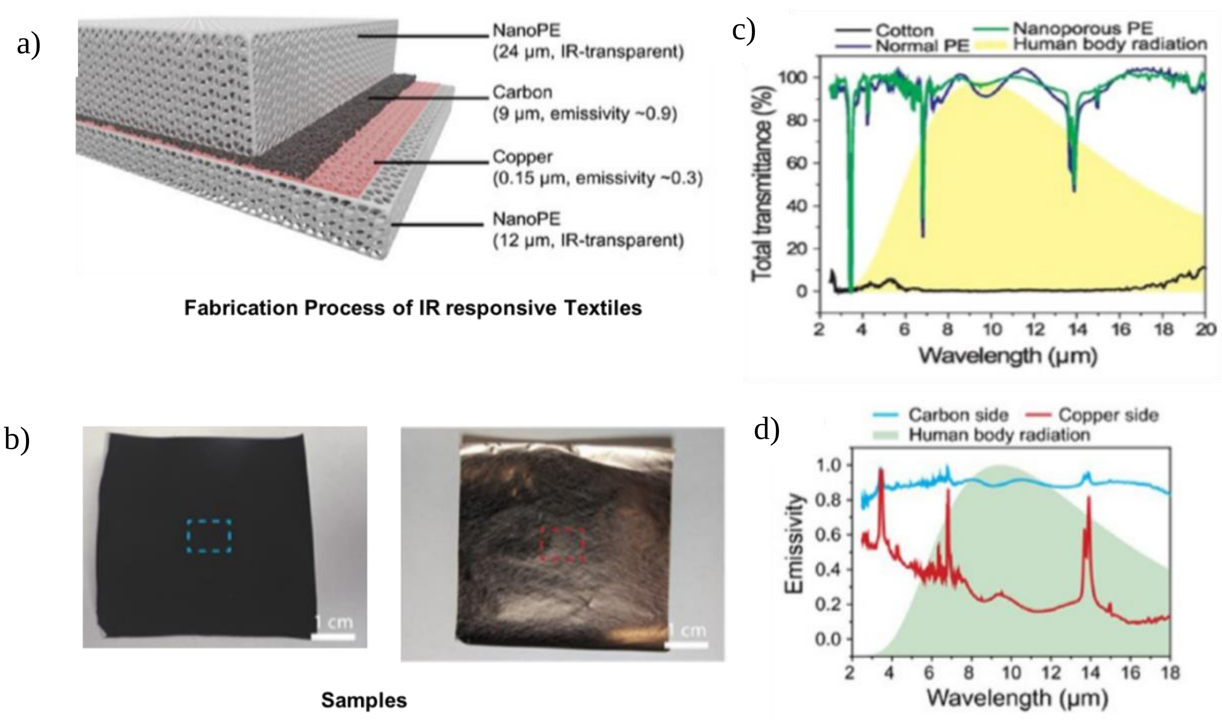


Figure 10 IR responsive dual-mode textiles (a) Fabrication process (b) As-prepared samples (c) IR transmittance of Cotton and as-prepared samples and (d) Emissivity of carbon and copper coating [98]

2.5.5 Thermo Conductive Materials

Thermal regulation of human body by clothing is generally driven in a complicated way by heat conduction, convection, radiation and evaporation. However, fabrication of personal cooling/heating textiles through heat transfer by conduction using low and high thermal conductive materials has gained a significant attention by researchers in a recent time. Using low-thermal-conductivity materials such as glass, ceramics, basalts, PCMs, polyimide fibers, polyphenylene sulfide fibers and polyaramid fibers are well-known for blocking the heat transfer by conduction between the human body and the environment. In contrast, high-thermal-conductivity materials are also used to fabricate personalized cooling textiles for indoor uses. Moreover, with multi layers of fabric or incorporation of feather fibers in clothing the heat transfer between the human body and the environment can block because of high level of air pocket existence, which is the best heat insulators in nature (0.023 W/mK). However, wearers comfort will be hampered by the thick and heavy clothing. Hence, to improve the comfort of users hollow fibers with different cross-sectional shape and shape-shifting fabrics based on stimuli responsive materials have been proposed instead of layered fabrics. These special structures of the fibers or the fabrics can trap more still air in the textiles, yielding the low thermal-conductivity clothing.

One of the techniques to apply conductive materials in the textile surface is coatings technology. Multiwalled carbon nanotubes (MWCNTs) are well-known conductive nanomaterials used in textiles through coating[99, 100]. Because of having high thermal conductivity and surface emissivity of MWCNTs the coated fabric demonstrated cooling effect and hence can use as personal thermal management of clothing[100]. It has been noted that the incorporation of 11.1% MWCNTs with resin coating formulation enhanced 78% of the thermal conductivity of cotton fabrics. Furthermore, the increasing of MWCNTs content to 50% boosted the thermal conductivity of fabrics by 1.5 times[100]

Instead of coating approach, the thermally conductive nanoparticles can be applied into the fibers structures[101]. The as prepared fibers can be woven or knitted as fabrics with enhanced thermoregulation effects **(See Figure 11).** In a comprehensive study, bicomponent structures composed of boron nitride nanosheets (BNNSs) and poly (vinyl alcohol) (PVA) were prepared through 3D printing method using hot stretching. The existence of well-oriented BNNSs in the structure of fibers has been noted. The well-aligned BNNSs contributed significantly as energy routes for thermal dissipation. In addition, mechanical properties were enhanced significantly, making the printed fibers suitable candidates for wearable applications. The main cooling mechanism of fabrics woven from a BN/PVA fibers was based on taking away the body heat through high thermal conductivity of fibers [101].However, the 3D printing technology is expensive and not suitable for large scale production. Therefore, its scope for mass scale thermoregulatory apparel production could be limited.

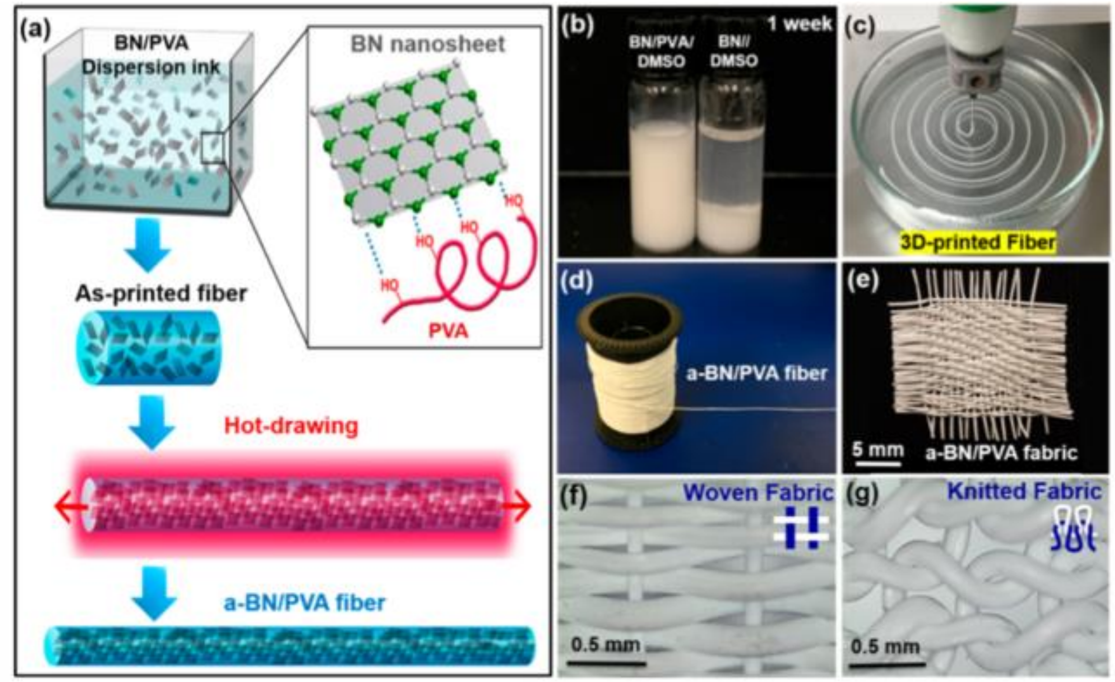


Figure 11 Highly thermally conductive textiles using BN/PVA Composite (a) BN/PVA Composite fibre fabrication process (b) DMSO/BNNS dispersion and PVA/DMSO/BNNS dispersion (c) The BN/PVA fibre was prepared through a 3Dprinting machine (d) BN/PVA fibre winding on a yarn bobbin (e) Textile woven by the a-BN/PVA composite fibers (f) Woven Structure and g) Knit Structure[101]

2.5.6 Wearable Electronic Devices

Generally, most of the clothing for thermoregulation are based on the physical and chemical properties of the materials without power supply. Moisture and air circulation through protective smart clothing is a complex phenomenon sometimes. This can cause discomfort next to body skin of the wearer by the accumulation and storing of metabolic heat, and condensation of moisture to water droplets in the microclimate. In order to avoid these problems many researchers introduced various external devices such as air-cooling fans and liquid cooling tube, which can improve thermal comfort of the users **(See Figure 12)**

Fresh air can be circulated next to the wearer skin by attaching lightweight and wearable electrically-powered fans at certain heat-sensitive positions of the garment [102]. Even though these clothes can enhance thermal regulation, they may cause some other serious issues regarding comfort such as heavyweight, complex in design and engineering, noise generation and nonuniform cooling effect around the body. These issues have limited the use of garments with a direct air convection strategy in regular life. Likewise, clothes with liquid cooling effect can achieve through distributing the liquid cooling substance in flexible tubes incorporated in the clothing around the body, which NASA developed to support astronauts with thermal comfort. The significant elements of this clothing system are a liquid reservoir, liquid cooling substance (water, propylene, and ethylene glycol) in a pump, sensors, and pipes attached to various parts of the garment. The primary strategy for cooling mechanism is established on transmitting body heat via conduction to cold fluid[103] However, this kind of tube arrangement with cloth for body heat transfer may cause some discomfort to the users. The potential challenges for these kinds of cloth manufacturing are product designing, low cost, and compact and movable structure. Moreover, for better cooling performance optimization in some factors such as the thickness of materials, the diameter of the tube, fluid temperature, and liquid circulation speed are required[104]

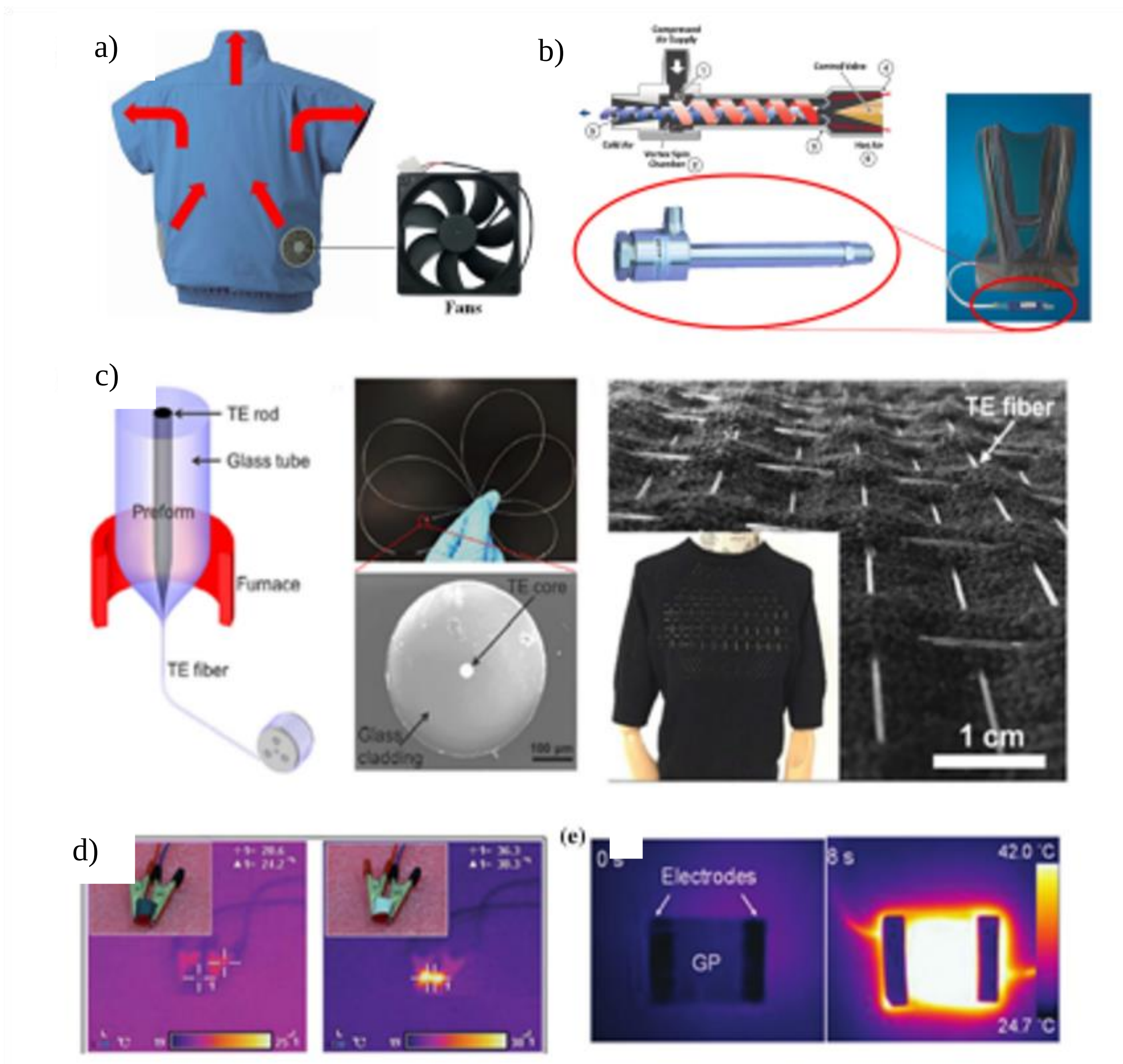


Figure 12 Thermal management clothing with supplied power (a) A normal T-shirt equipped with two fans at the waist; (b) Vortex tube equipped vest; (c)Schematic diagram of the thermal drawing process and its cross-sectional SEM image (d) IR camera images of AgNW/polydopamine nanocomposite cloth at an applied voltage of 0.7 V and IR images of graphene paper applied a voltage of 3.2 V

2.5.7 Moisture Management Fabric

The accumulation of sweat on the surface of the skin, a wearer feels discomfort. To keep the skin dry and comfortable, the sweat is needed to be transported away from the skin rapidly. When the clothing temperature reaches the dew point, the water vapor in the microclimate begins to condense into liquid water. The liquid water can cause discomfort because of transferring back to the inner surface of the fabric. The adaptive clothing requires to transfer the body sweat away from the skin and avoid the liquid water transfer back towards the inner surface of the clothing. Hence, moisture management fabric demands to be used. These kinds of fabric can transfer one-way liquid water. The backside of the moisture management garment can transfer away moisture into the face side. The key features of these fabric are:

(1) Fast absorption

(2) Fast drying

(3) Keeping the skin dry

Moisture management fabrics have special design structure on both surfaces through which the garments can keep the wearer skin dry by transferring sweat from inner surface to outer surface. It means that during sweating the liquid water can only transfer from one side to the other side and the process is irreversible. This kind clothes widely used as underwear, sportswear and outdoor activity. The moisture management tester (MMT) devised has been used for assessing the property of textile moisture management[105].

2.5.8 Smart Fibers

Many naturally occurring fibers have responsive behaviours towards environmental stimuli such as moisture, temperature, humidity and vapour that can be applied to develop adaptive comfort textiles. Till today, stimuli responsive natural fibers developed including animal hairs, protein fibers and cellulose fibres. For instance, hair fibre from horse have been utilized in hygrometers since 1700s because it can exhibit length contraction in response to moisture. However, the response time and length change showed by such natural fibers is too long and short for application in adaptive textiles. In this section, the natural fibers that can react and sense with environmental stimuli for developing adaptive comfort textiles are discussed briefly in terms of mechanism, processing condition and application.

Shape memory polymers (SMPs) can remember a shape when exposed to specific stimuli such as water, heat, radiation and P^H. These materials are well-acknowledged for their lightweight, flexible, stretchable, low cost, and easy processibility characteristics. Having looked at these properties, recently synthetic shape memory polymers have growing attention for industrialists and researchers [2]. In order to manufacture smart materials such as adaptive textiles, heat sensitives films and artificial medical devices etc.[106], SMPs are highly demandable. However, Petrochemical based shape memory polymers, mostly used so far for preparing smart materials, have recently become an issue of great concern from environmental and economic. The shift towards renewable and green smart materials has recently been prompted by their advantageous characteristics including non-toxicity, abundance, biocompatibility, biodegradability and sustainability. This can be fulfilled by the replacement of petrochemical based polymers with biopolymers like wool. Wool is a biopolymer animal hair fiber[107], which is mainly considered as a warm clothing material and thermal insulator. In the global context of fiber market, the percentage increase for use of wool is decreasing every year[108] due to the declining of wool demand for warm clothing materials. Hence, many researchers have shown an increased interest in rediscovering the wool as a potential smart materials as it's a highly absorbent fiber due to CO-NH and other groups which attract water[109] consequently showing the ability of SME. Chiefly, the α-keratin biopolymers play a significant role for shape memory behavior of wool; it is water responsive that the fiber can recover to the initial shape from a deformed shape without any external force[110].The wool fiber chemical constituents consist of crystals, hydrogen (HB) and disulfide (DB) bonds among its intra- and inter-macromolecules. Due to these structural features, wool fibers are able to show smart functions[107]. Furthermore, the SME of wool fibers has been discussed and analyzed extensively. Xiao et al. (2017) demonstrated that the wool has SME which can be stimulated by both heat, water, redox agent and UV-light [111].The dimensional changes of the hydrogel-coated wool yarns at wet and dry state has been studied. It has been reported that the length of hydrogel-coated wool yarns varied in the presence of water and, once dried, elongated again[112].

The use of natural fibers like wool, cotton and flax as moisture responsive actuators was also suggested and it was noted that these fibers had anisotropic property because of higher lateral expansion than longitudinally upon moisture stimulation. This anisotropic behavior can be applied to produce artificial muscle with contractile motion using a twisted coil structure. The developed artificial muscles were performed similar as like muscles produced from synthetic materials. Additionally, these natural fibers artificial muscles were applied in manufacturing smart textiles as shown in **Figure 13** as potential candidate in order to get adaptive textiles for body comfort[4].

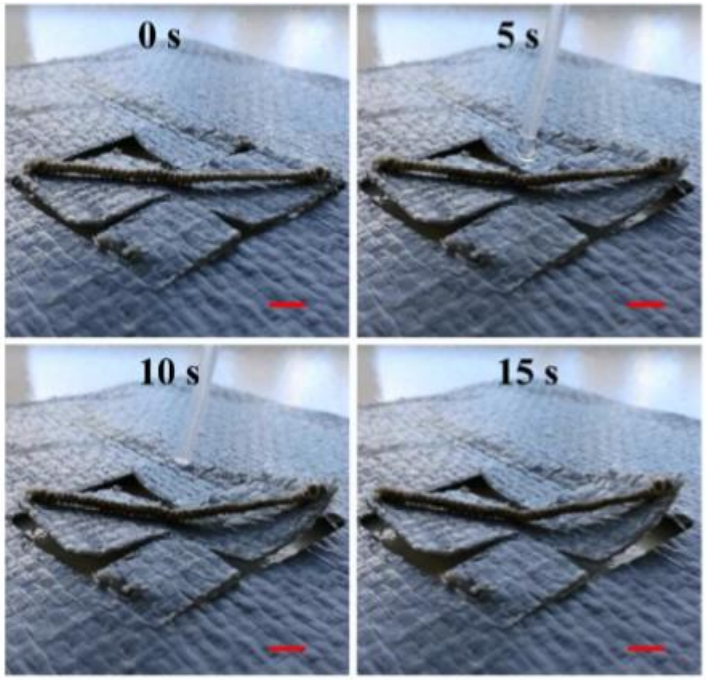


Figure 13 An examples of integrating natural fiber coils yarns into smart textiles: ventilation flaps that close when dry and open when wet[4]

Recently, torsional and tensile silk artificial muscles **(Figure 14a)** having water fog and humidity responsiveness has been developed and suggested to utilize in smart textiles and robotics application. The results for the produced silk muscles revealed that upon exposure to water fog, it can exhibit torsional stroke (547° mm^{-1}) like moisture stimulated graphene twisted fiber (588.6° mm^{-1}) and even can provide nine times higher torsional stroke than coiled water responsive carbon-nanotube fiber (61.3° mm^{-1}). Furthermore, the developed silk muscles showed **(Figure 14b and c)** significant contraction (70%) with the change in humidity from lower (20%) to higher (80%), which was higher than solvents driven coiled CNT yarn muscle (60%).[25] Artificial silk muscles were proposed for smart walking robot and moisture-sensitive adaptive textile.

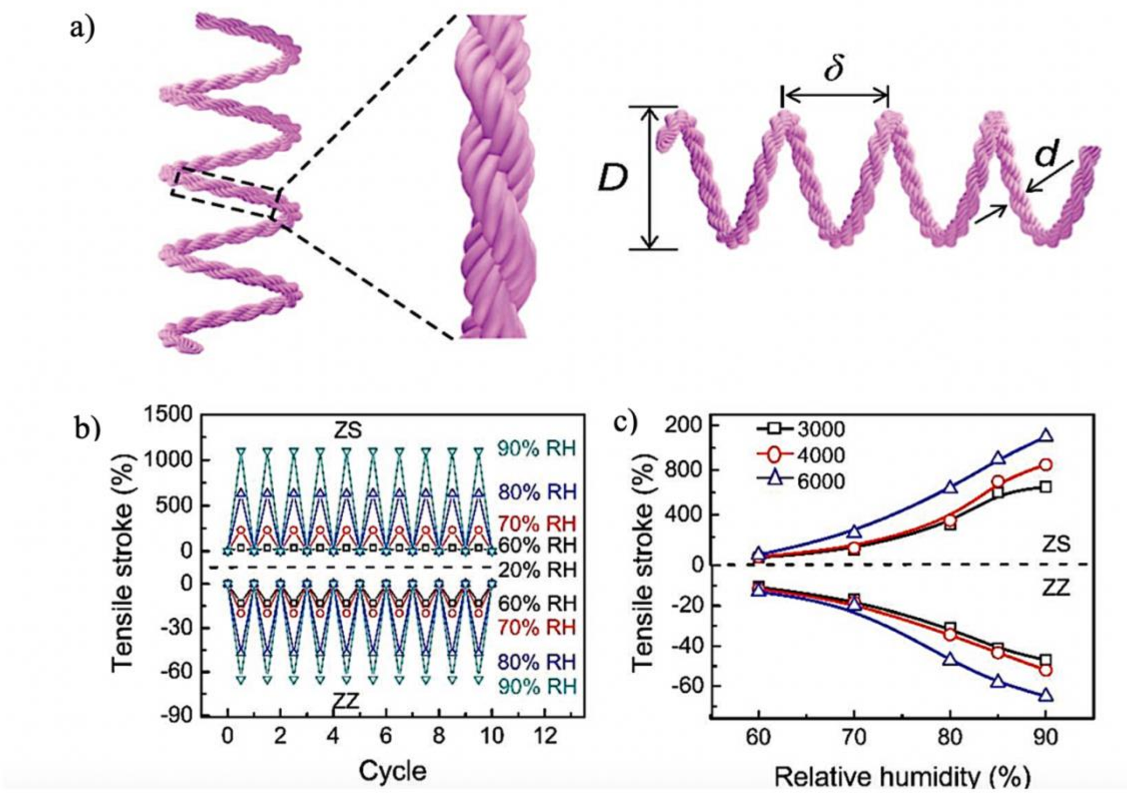


Figure 14 a) Schematic illustration of a coiled tensile silk muscle made from a two-ply torsional silk muscle and b) Tensile stroke change during selected cycles from 20% RH to various other humidifies for ZS and ZZ silk muscles c) Dependence of tensile stroke (relative to muscle length at RH 20%) on relative humidity for tensile silk muscles having different twist densities [113].

2.6 Smart Natural Fiber

Animal hairs such as wool and camel hair as well as fibroin fibers like spider silk are well recognized as protein fibers with excellent shape memory properties[106, 114-116]. Therefore, these fibers are known as smart fibres. In addition, they have significant mechanical properties with of high stress-strain ratio and elasticity which make those fibers equally important for both natural and commercial application.

2.6.1 Animal Hair Structure

Due to the scarcity and the luxurious feel of cashmere, it is more expensive in natural fibres[117]. Their specific characteristics like strength, brightness, warmth, and natural colours make them excellent fillers for textile products. These properties of wool are attributed to its excellent hierarchical structures. In late 1920, Speakman suggested that wool consists of various tissues[118]. Feughelman's model **(see Figure 15)** is a water-absorbing matrix(M) surrounded by a non-water-absorbing cylinder (C) which has a laterally embedded central fibre. With increase in humidity, the phase C matrix swells isotropically, but the moduli remain unchanged[119]. Heavy water (D2O) was used to test the hydrophobic property of phase C. The exchange of hydrogen to deuterium of the amide -NH was not seen at room temperature[120].Phase C grows in the same direction with fiber, its water absorbing capacity will burst upon in tension, it will uptakes water from the matrix. In 1957, Bendit showed that there is a phase change from α to β with the strain from 0 to 20%. His work showed the relationship between crystal and phase C and its ability to swell[121]. Astbury et al. in 1931 first discovered that the unextended α-keratin fibers are formed by well-arranged folded polypeptide chains using XRD[122]. In 1951, Pauling clarified that helices correlated with HBs binding and fold in terms of C-N-H interactions between helices. Then in the same year, Pauling also proposed the β-keratin structure[123, 124], also known as pleated sheet, as a new layer configuration of polypeptide chains. Regarding this, the structural transition from α-helices to β-sheet involves the distortion of HBs during tension. Chapman also proposed in 1969 that the α-crystalline lattice will change to β during microfibril stretching[125]. At the initial state, only α crystalline phase exists in microfibril. β phase begins to appear when some of microfibril starts to unfold at a critical stress. The stress will drop to equilibrium stress, balancing the thermodynamic equilibrium as soon as two-phase α and β coexist in microfibril. Then the stress begins to increase after the whole α phase is replaced by β phase and microfibril with pure β phase will experiences strain in further sample extension. This phase transition can be detected by X-ray analysis. In 1979, the inter-microfibrillar linkage in α-keratin fibers was proposed by Feughelman[126]. He used formic acid-water mixtures to treat wool and got its diametral swelling and longitudinal contraction of wool fibers, indicating the existence of linkages between intervals of microfibrils along the fiber direction. These linkages are a group of molecular chains and were proved part of nonhelical tails of the low sulphur protein. This low-sulphur protein indeed contains a helical part, appearing in microfibrils. The nonhelical component partially appears in the microfibrils and partially appears in the matrix. The DBs are gathering at nonhelical "tails", forming the crosslinks between the microfibrils. In 2001,

Feughelman developed his extended two-phase model (ETPM) with respect to detailed coverage of mechanical properties of α-keratin fibers[127]. With the help of electron microscope, the wool fibers are proved to consist of microfibrils, referred as intermediate filaments (IFs). IFs containing α-helices are detached by a sulphur-rich protein matrix. With decrease of humidity to 65% , the IFs become closer to each other and the globular matrix protein are squashed against the filaments. From the aspect of microscale, the camel hair is a heterogeneously composed semi-crystalline polymer of α-keratin. This composite architecture composes of regular aligned fibrils and amorphous matrix, which determine the hair mechanical properties. More accurately speaking, the α-keratin crystalline microfibrils embed in amorphous matrix. The covalent linkages mechanically connect the amorphous to microfibrils. Actually, the fibrils assume responsibility for crystalline phase in hair structure and the connected amorphous globules mainly support the matrix with disulfide bonds (DBs)[128]. Hierarchical structure with macro & microfibrils and helical coils wrapped by cortex and cuticles outside is shown in **Figure 16.** The cuticle cells are amorphous in structure and its function is preventing absorbing larger molecules. The outer cuticle has higher resistibility to chemical erosion than inter cortex. However, the cortex is the essential composition in any α-keratin fibres. Inside the cortex is cortical cells which are formed from long filaments, primarily known as microfibrils, and growing along the wool fibre. The similar units of other cell structure together with microfibrils are referred as intermediate filaments (IFs), which are in uniform structure and separated by a sulphur-rich protein matrix. Hierarchical structure of camel hair enables its high-water absorption ability. The mechanical and memory properties of camel hair have close relationship with inter- and intra-molecule interactions, that is, hydrogen bonds, salt linkages and disulphide bonds. Actually, a large concentration of sulphur-containing diamino acid cystine exits in hair fibers, which contributes a lot to the physical as well as chemical properties of fiber and keep the stability of the fiber at the same time. The DBs in hair keratin are controlled by oxidation and reduction reaction.

According to Feughelman in his 1997's book, two types of HBs exist in α-keratin structure: one appears between water molecules and hydroxyl groups and another one appears between the amide and the carbonyl group. The energy of HBs is in the range of 8-40 KJ/mol with the bond length in the range of 0.24-0.3 nm[129]. During the aqueous stimulating of camel hair, the polar -OH groups decomposed from water molecules will react with Amide N-H and C=O bonds, to form new hydrogen bonds. Viscoelastic tension and relaxation are another emphasis placed on animal hair extension and several structure models have been introduced to analyse these parameters[125, 130-132]. **Figure 17** illustrates Young's modulus with the combination of two phases in fiber structure. Spring A indicates the mechanical behaviour of phase C, the α-keratin fibers, in the Hookean region. In series with each other and parallel with A, Spring B and a dashpot correspond to the water-penetrable matrix. This also explains the time-dependent behaviour of wool fibers. During stretching, stress experiences linear Hookean region, yield. region and strain hardening region. The hair expresses a time-dependent relaxation behaviour and shares similar behaviours with cross-linked polymers due to the viscoelastic nature of its internal structures [133]. Water, thermal, and chemical processing (like Redox) are the leading causes influencing hair relaxation[134].The viscous and elastic analysis has been separated and quantitative determined by Nikiforidis et al.[135]

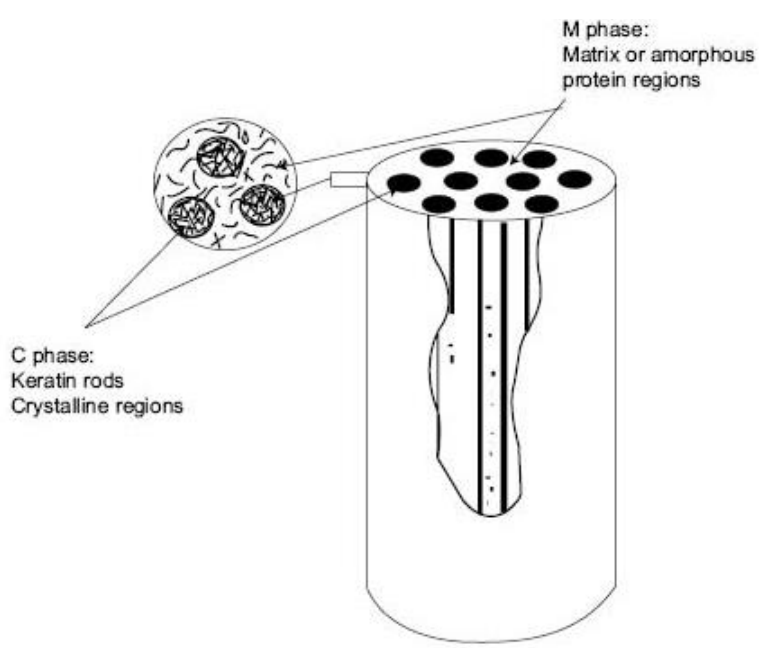


Figure 15 Cylindrical two-phase model of an α-keratin fiber [113]

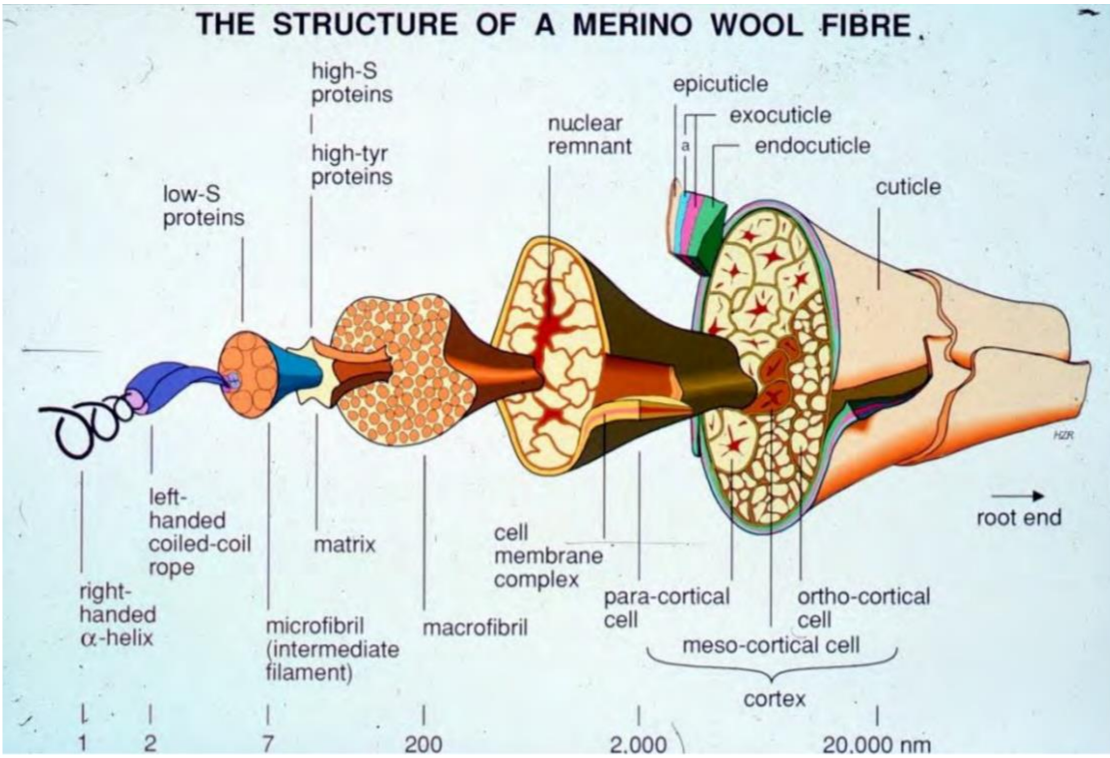


Figure 16 Schematic illustration of *wool* hair structure [Source: CSIRO, Photographer: Textile and Fibre Technology]

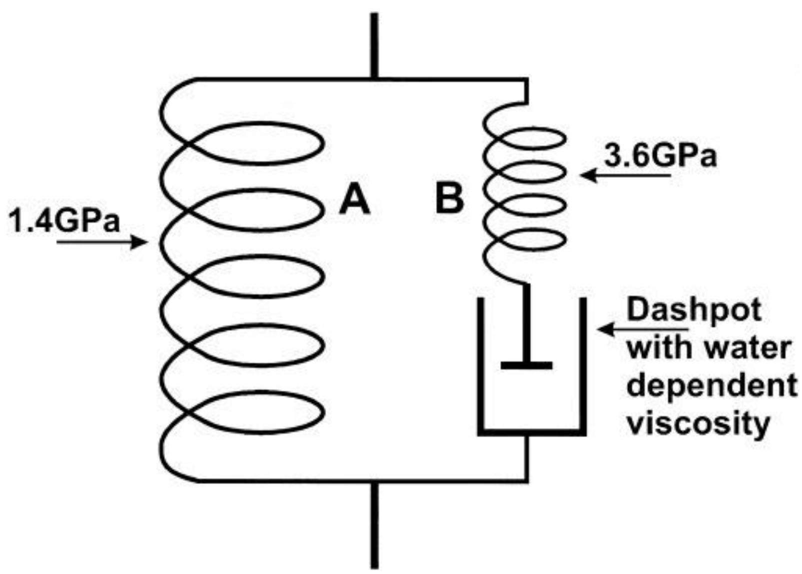


Figure 17 The spring dashpot model of the Hookean region mechanical behavior of wool and other αkeratin fibers at around 20°C [113]

2.6.2 Role of Water In Wool

In general, the hydrated water in a material such as a polymer or hair/fibre can be divided into three categories; they are: free water, freezing-bound water (intermediate water) and non-freezing-bound water. Freezing-bound water will express first-order phase transition including crystallization and melting and can be detected as endothermic/ exothermic peaks in DSC. However, it is difficult for non-freezing water to crystallize even in low temperature to -100^{o}C, which is firmly bonded to specific group of the polymer chains. Polymers containing the functional group such as hydroxyl group or amide and the carbonyl group that can react with water will own large amounts of non-freezing water. The water absorbed into wool is quite different with free water. Hiroshi Sakabe used DSC to examine the state of water absorbed on wool fibers and their histological components[136].He found that the wool samples with 3-hour 70^{o}C and 5-10 days treatment, the exothermic/endothermic peak of both free water and freezing-bound water would appear in DSC curves at about -15 and -35 ^{o}C, separately. However, wools with 1-day 20 ^{o}C and 3-hour 70^{o}C treatments both only showed peaks of free water in DSC at -20^o C and 0 ^{o}C. The results indicated that the longer treatment time is needed for wool to achieve a wool-water balance.

2.6.3 Smart Functions Inspired-Fibers

With the improvement of understanding to this natural material, animal hair is undoubtedly regarded as a kind of smart materials that are water/thermal dependent. It can alter its physical properties as well as appearance with proper stimuli. In 1931, Astbury found that the striking property of wool: the stretched sample can return to its original length in wet condition[122].The super contracted ability was also discovered in Merino wool by putting them in 8 M lithium bromide solution for 3 hours with 100 ^{o}C-heating[137]. Inspired by the marvelous characters of wools or silks, many researchers became interested in designing smart polymeric materials with similar structurally dynamic properties, that the polymers possess a kind of dynamic bonds such as HBs or DBs among molecular chains to respond to stimuli and achieve reversible transition. Hydrogen bonds (HBs, a kind of weak attractive bond) and disulphide bonds (DBs, a kind of strong chemical bond) are two main inter- and intra-molecular interactions to produce enthalpy transition and maintaining the integrity of structure in protein-based materials such as animal hair[138]. The hydrogen atoms are covalently attached to their oxygen atoms and attracted towards other nearby oxygen atoms. This attraction is the basis of the 'hydrogen' bonds. It is strong enough to be maintained during thermal fluctuations below their broken temperatures. The stronger the bonds, the more ordered and static is the resultant structure. Thus, the HB between polymer chains is stronger than those between polymer chains and water. The differences between two enthalpy levels produce excellent influence on shape fixity and recovery of animal hair. From the other aspect, the disulphide bond is the most frequent naturally occurring covalent cross-link in proteins, it can increase the enthalpy of the folded state by stabilizing local interactions[139].HBs and DBs also play key roles in crystal and amorphous regions. It is reported that both HBs and DBs in amorphous regions of wool can be reversible in special conditions such as Redox, humidity and thermal environment[140],which leads to the transformation between of temporary and permanent shapes[141].Chemo responsive SMPs which can also be called solvent-driven SMPs can find application in drug delivery, chemo-sensing techniques, chemo-responsive surfaces and so on. Based on water-absorbing capacity of Nano whiskers, water driven SME has been studied a lot[142].Cellulose Nano whiskers have high degree of crystallization and its molecular chains arrange compactly linked by strong hydrogen-bonding interactions. The switchable effect rather than the reinforcement effect of cellulose network has been applied on SMPs[143]. A HB is the electrostatic attraction between polar molecules that occurs when a hydrogen (H) atom bounds to a highly electronegative atom. It is not a real bond but an especially strong dipole-dipole attraction. It can be very strong and difficult to cleave in some circumstances such as in polymer or animal hair hard crystal phase proved by textile researchers using X-ray diffraction (XRD) [144-146]. HB based crystal can take responsibility of net-points in animal hairs as well as SMPUs to achieve shape recovery process. On the other hand, HBs in amorphous part is not as strong as those in crystals and they may be reversibly dissociated and regenerated under conditions like heat and water[147, 148], being widely used as switches in SMPs [149, 150].After realizing the close relationship existing between HBs and SME, since 2006, Hu's group designed a series of SMPUs using HBs as switch and implemented modelling of intra- and inter-molecular HBs among different PU segments. A supra-SMPU with pyridine derivatives was synthesized[151, 152]. In this SMPU, a strong single-HB is formed between pyridine-ring and N-H of the urethane groups as a switch-unit while the strong intermolecular interaction between N-H and C=O of urethane groups provides an elastic polymer network. This shape memory polyurethane has an excellent thermal and moisture sensitive SME. Through the systematic analyses with the FTIR technique, it is confirmed that the dissociation of HBs in a pyridine ring by increasing temperature results in thermally-induced SME, the adaptive replacement of the original HB in pyridine-ring by moisture molecules leads to a moisture-sensitive SME[153]. Meanwhile, another thermally induced shape memory polyurethane with self-complementary quadruple-HB in soft segments was achieved[154]. In addition, HBs were utilized in Nano-cellulose-whiskers to develop a rapid switch shape memory composite[155]. Both quantum chemistry and molecular dynamics were applied to study the hydrogen bonding interactions in shape memory polyurethanes including the HB strength and their relationship with thermal properties and modulus, competitive hydrogen bonding and phase interactions. In other recent work, they fabricated a series of polymeric thin films with different supra-molecular switches with 2,6-dihydroxymethyl pyridine (DHMP) as a hydrogen bonding acceptor and explored their potential application as moisture management material[156]. In Chen's work, when HBs between acrylic acid segments served as a reversible switch, a systematic increase in HB side group (HBG) concentration increased the Tg of the linear polymers[149]. Anthamatten et al. first used UPy in lightly crosslinked elastomers where the pedant pyridine ring formed hydrogen-bonded supramolecular switches with the NH urethane groups[157]. A controllable and straightforward triple-shape memory supramolecular composite was well synthesized through HB switches between polymer and mesogenic units. The HBs enable both broad and independent control of T_g[158]. It has been found in wool that the water content can effectively bring a drop to glass transition temperature because large amounts of HBs in the amorphous region can be destroyed by water molecules[159].It is also understood that the broken HBs in the amorphous region can be reformed after wool is dried again, indicating the generation of HBs can be reversible with or without water[160]. Jung et al. observed water-responsive SME in poly (ethylene glycol) (PEG)based PUs where the water could dissolve the PEG crystalline segment because of the disconnection of HBs [161]. Huang et al. found that water can lead to shape recovery in shape memory polyurethanes. With the increase of immersion time, an increase of water-to- SMP ratio has a linear relationship with the decrease of T_g[150]. The proposed mechanism was due to the weakened hydrogen bonding between N–H and C=O groups after immersing in water. Recently HBs have also been used as a switch for PH-sensitive SMPs[162]. Disulphide bonds (DBs) are strong chemical bonds that are either structural or catalytic and widely available within proteins. Study of DBs in SMPs as net point and switches have not been reported yet, but they are strong chemical bonds which are stable under some conditions and can be used as net points in SMPs as evidenced in wool which determines its elasticity under normal application environmental conditions[163, 164]. DBs are also a type of dynamic covalent bonds responsive to Redox and special light irritation that develops a premise for DB as switch in smart materials The Redox reaction is a powerful method to control DBs, the amount of cysteine will decrease, and methionine will increase in reducing reaction, leading to collapse of DBs. This is because DBs can be broken and then develop into two thiol groups in reducing solution. On the other hand, the broken DBs can be reversed by an oxidation reaction[165, 166]. This reversible change can be found in responsive polymer like capsules for applications such as drug delivery[167, 168]. Besides, the exchange reaction of DBs enables a polymer the healing ability stimulated by UV and visible lights[169, 170]. As an example of self-healing function, an epoxy polymer containing DBs could fully heal its tensile failure strain due to exchange reactions of DBs by UV-light and the healing process was dominated by the DB exchange reaction[171]. As far as SMPs concerned, there are only two reports in literature. A thermal responsive SMP was reported with a semi-crystalline and covalently cross-linked network where DBs were used only for self-healing function under UV-light. A semi-crystalline, dynamic network containing DBs was reported to have both shape memory (upon exposure to moderate heat) and scratch healing (upon exposure to high heat or UV light) capabilities. In Xu's study, a novel self-healing polyurethane material with DBs as switch has a SME[172].This healing is achieved by activating SMEs and the disulphide-thiol exchange reaction simultaneously. Thus, only one SMP reported in literature utilized DBs as switch responsive to redox treatment where cellulose derivatives with cross-linkable mercapto were used[173]. Strictly speaking, no DBs have been used in shape memory polyurethanes, but based on the above review, DBs could act as net points and reversible switches as well as self-healing capability when exchange reaction takes place among macromolecules under light, particularly UV-light conditions. Structural function stabilizes a protein while the catalytic nature mediates thiol-disulphide interchange for various functions[174]. Thus, DBS is proved to stabilize the properly folded conformation of the proteins under normal conditions and destabilize denatured conformations by decreasing conformational entropy [175].When catalytic, DBs are dynamic under a range of stimuli such as heat, light, redox and PH[176, 177].The formation and cleavage of DBs proceeding at a molecular level were also studied where inter and intramolecular DBs could be detected and modified[178]. This property has been used in responsive polymer capsules and micelles and gels for applications such as drug delivery. In Aoki's work, DBs were utilized as switch responsive to redox treatment where cellulose derivatives with cross-linkable mercapto units were used[173]. The well-built DBs among hair molecules act as cross-linkers, governing elasticity, and can be characterized by Raman [179]. The molecular structure of spider silk is different from camel or wool hair, the crystalline exists in β-pleated sheets those are in parallel direction to fibre axis. Hydrogen bonds still occupy an important role in linking amorphous chains and crystals neighbouring to each other. The amorphous part can be regarded as rubbery region that provide elasticity to the whole bulk. The strengthen action of β-pleated sheets in spider silk became an inspiration of fillings like carbon nanotube in artificial elastomers. In this method, different amounts of cellulose nanocrystals were covalently bonded to polyurethane chains and improve the crystallinity of hard segment, directly leading to the enhancement of shape fixity. The chemical structures of poly (butylene adipate) (PBA)-based polyurethane (PU) SMF has been studied, in which PBA serves as soft segments and the combination of 4'4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) act as hard segments. In another study the spider dragline silk is composed of amorphous soft chains filled by strong crystalline parts made by hydrophobic polyalanine sequences. The amorphous chains entangle with each other or linked by hydrogen bonds, granting the outstanding flexibility and extensibility. In contrast, the crystalline regions, which can be regarded as net points, are key factors to keep permanent shape and improve modulus. The addition of fillers in shape memory polymers to make polyurethane/cellulose nanocomposites still cannot have good improvement of recovery ratio. However, with the addition of cellulose nanocrystals, the shape recovery improves significantly due to the role of network points from cellulose nanocrystals. If hydrogen bonds reach a certain amount in polymer, the influence of water upon their mechanical properties increases. The water molecules can easily step between macromolecules in amorphous region and restrict the formation of hydrogen bonds between molecular chains, which can be viewed as plasticizing. This is crucial in fibre wet-spinning process because the modulus has largely been decreased, while the hydrogen bonds will reform in stretched state due to gradual dry condition.

2.7 Knowledge Gap

The current commercial manufacturing method of developing adaptive textiles for clothing comfort utilizes phase change materials, various responsive synthetic materials, thermo conductive materials, wearable attachment, coating application and artificial intelligent technologies which can sense and control environmental temperature and humidity in the microclimate of human body. However, this method generates high amount of carbon footprint along with processing complexity and the scientific merit of this practice is also questionable. Up to now, it is rather hard to find publications reporting research and development using water-responsive wool fibres. To utilize conventional wool fibers as raw materials for designing adaptive comfort textiles, we need to develop sound scientific understandings on the following issues:

(1) How does the adaptive function of wool fibers affect the dynamic moisture and temperature distributions?

(2) How do the stimuli responsive wool fibre based smart materials interact and influence the complex heat (conduction, convection and radiation) and moisture (vapor diffusion, liquid diffusion, moisture sorption/desorption and moisture evaporation/condensation) transfer processes?

(3) How can the distribution and concentration of these materials in the clothing composite structure be implemented in design and development?

(4) How would the structural design influence the thermoregulatory behaviour of the body and psychological sensory perceptions?

(5) How would the structural design influence the biological health of the body?

Therefore, there is a need for systematic academic research to establish intellectual understanding and develop enabling technologies. This project sets out to fulfil this need.

Chapter 3 Experimental Work

3.1 Highlights

This chapter is mainly focused on comprehensively describing the experimental materials, methodologies followed, and characterization techniques involved in the entire research work completed. The experimental work is divided and explained as 1) discovery of pore actuation ability of woolen knitwear using water responsive shape-memory phenomenon in descaled wool fibers and yarn, 2) revelation of knit structural effect on water-actuated pore on/off the ability of woolen knitwear, 3) Utilization of shape-memory wool fibers integrative respirators for personal protection, and its cooling performance

3.1. Materials and Equipment Utilized

The raw materials used for this research project and equipment for characterization/testing are summarized and tabulated in **Table 1** and **Table 2** respectively.

Table 1 Raw materials/chemicals used in the research project

Raw Material / Chemicals	Supplier
Wool Fibres	Mongolia Autonomous, China
Calcium Chloride (Nano Particles)	Aldrich Chemical Company, USA
Sodium Hypochlorite	Aldrich Chemical Company, USA
Hydrochloric Acid	Aldrich Chemical Company, USA
Polypropylene	Aldrich Chemical Company, USA
Distilled Water	In-House Prepared

Table 2 Major equipment used in the research project

Equipment/Software Name	Supplier
Ring Spinning Machine	ZINSER
Flat-bed automatic knitting machine	STOLL
Sample Dyeing Machine	Hong Kong MX DYEING MACHINE CO.LTD.
Melt-Blown Nonwoven Machine	Pure Living, Hong Kong
Light Microscope	LEICA
Scanning Electron Microscope	JEOL
Instron 4411for tensile	Instron Ltd, High Wycombe, England
Instron 5566 for tensile	Instron Ltd, High Wycombe, England
KES-FB1 for Fabric Shearing	Kato Tech
KES-FB2 for Fabric Bending	Kato Tech
KES-FB3-A for Fabric Compression	Kato Tech
KES-FB4-A for Fabric Surface	Kato Tech
KES-F7 for Thermal Conductivity	Kato Tech
Air Permeability for Fabric	SDL
Environmental Chamber	HAIDA
Moisture Management Tester	SDL
IR camera	FLIR
Water Contact Angle	SINDIN
Martindale abrasion tester	SDL
Filtration Efficiency Tester	TSI

3.2. Preparation of Water-Responsive Shape-Memory Wool Fibres, Yarns, and Fabrics

3.2.1. Preparation of Water-Responsive Shape-Memory Wool Fibres

Because of the presence of a protective grease layer and rigid scales on the surface of wool fibre, water molecules cannot interact easily with wool despite the presence of a large number of hydrophilic groups in its chemical structure. Therefore, 100% raw wool fibers (**Figure 18a**) were descaled (**Figure 18b**) using chlorine to enhance their water responsiveness. Chlorination, one of the most traditional and widely used approaches for wool descaling. An optimum process parameter was followed to control the degree of removal of scales with minimal damage of structure[180]. In brief, the scaled fibers were treated in an ultrasonic bath (35 kHz, 40 W) containing sodium hypochlorite (5 g/l), hydrochloric acid (1 g/l), and nano-calcium carbonate (10 g/l) at 37 °C for 45 min. The SEM images of the descaled and scaled fibers are shown in **Figure 18c** and **d** respectively. The breaking loads of the descaled and scaled Fibers were determined to evaluate the damage to the wool fibers by the descaling process. We found that the descaling treatment decreased the breaking load by approximately 8% **(Figure 19),** which is within the acceptable range.

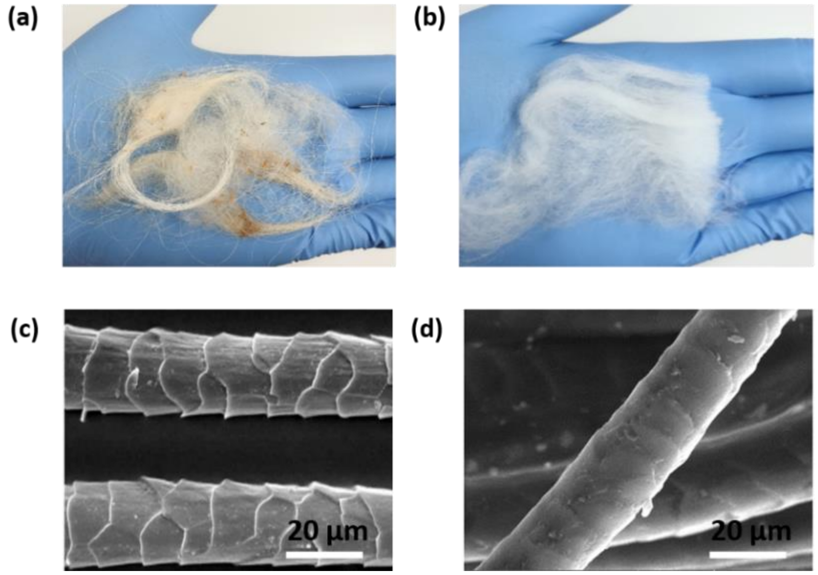


Figure 18 Surface morphologies of wool fibres: Digital images of (a) Pristine and (b) descaled wool fibres; SEM images of (c) Pristine and (d) descaled wool fibres

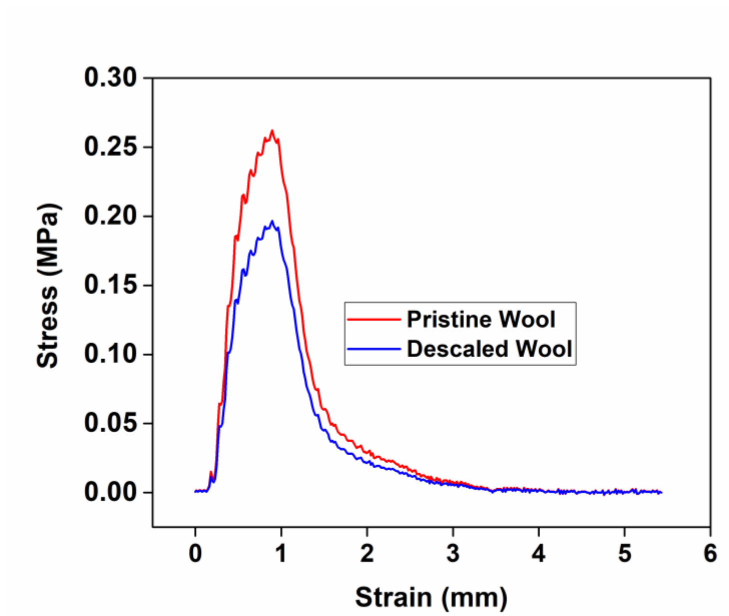


Figure 19 Tensile stress-strain behaviour of pristine and descaled wool

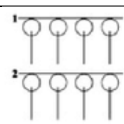
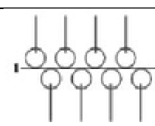
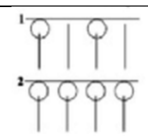
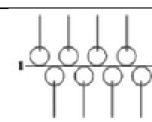
3.2.2. Preparation of Water-Responsive Shape-Memory Wool Yarns

The wool from which the surface and scales have been removed is spun by combing and ring spinning, with a twist of 280 twists per meter. The two single yarns obtained are combined with a twist of 500 twists per meter. The resulting double the stranded yarn was steam treated for 30 minutes to obtain a yarn with water-responsive shape memory effect. The tenacity, tensile modulus, and percentage elongation of the wool yarn were 6.91 N/tex, 1.52 N/tex, and 17.27%, respectively.

3.2.3. Preparation of Water-Responsive Shape-Memory Wool Fabrics

Knitted fabrics of four different commonly used structures for regular clothing namely single jersey, tuck, miss knit and double knit were prepared. A flat-bed automatic STOLL knitting machine (12-gauge) was used to fabricate the samples. To remove processing impurities and relax the yarn, the fabrics were further cleaned and tumble dried. The physical properties and morphology of the fabrics were given in **Table 3**

Table 3 Structural and physical properties of fabrics

Sample Code	S1	S2	S3	S4
Notation diagram				
Fabric Image				
Fabric Structure	Single Jersey	Knit and Tuck	Knit and Miss	Double Knit
Fabric Thickness (mm)	1.17	1.84	2.05	1.98
Fabric Weight (GSM)	208.33	275.71	374.93	408.78

3.2.4. Preparation of Electret Polypropylene Fabric

A horizontal melt-blowing machine **(Figure 20)** comprised of spinneret, hopper, host, web winding, electret treatment and air compressor was used to fabricate respiratory filter material. The machine is a pilot-scale production type machine with a dimension of $9\times3.5\times2.3$ m^3. The conventional production process for melt-blowing sample production was followed with slight modification. Briefly, the supplied PP particles of 50 Kg were at first fed into the hopper through which the materials transferred to the single screw extruder and subsequently extrusion of polymer melt through the spinneret holes were made. To fabricate the molten polymer into an ultrafine fibre a high velocity of hot air is provided at the exit of the holes from both sides of the row of holes. This air makes the molten polymer into a plastic sheet-like structure with filtering ability. A high voltage electricity was applied before collecting the web in the collector plate.

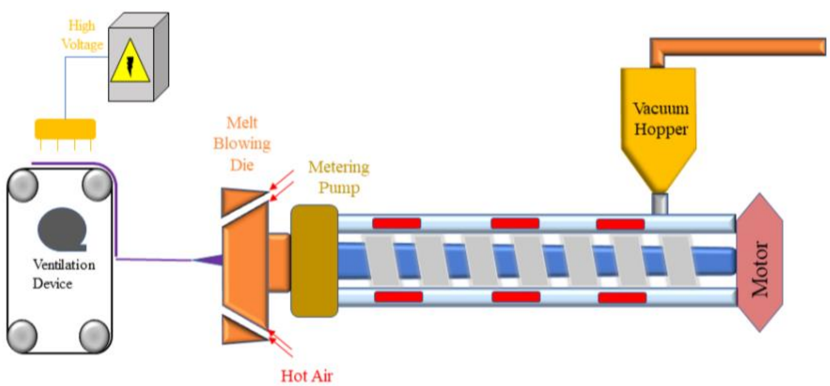


Figure 20 Schematic of Electret Melt-blown Scheme

3.2.5. Preparation of Woolen Respirators

Adult size woolen respirators were designed and in house fabricated using a process as presented in **Figure 21.** In Brief, two layers of woolen knitwear and one layer of polypropylene fabric were cut using a standard pattern size. After that, woolen fabrics were stitched together using a simple sewing technology at the edge with a simple pocket system between the two-layer. Then the ear loop stitched with the sample. Finally, the barrier polypropylene fabric was set in the pocket to complete the process.

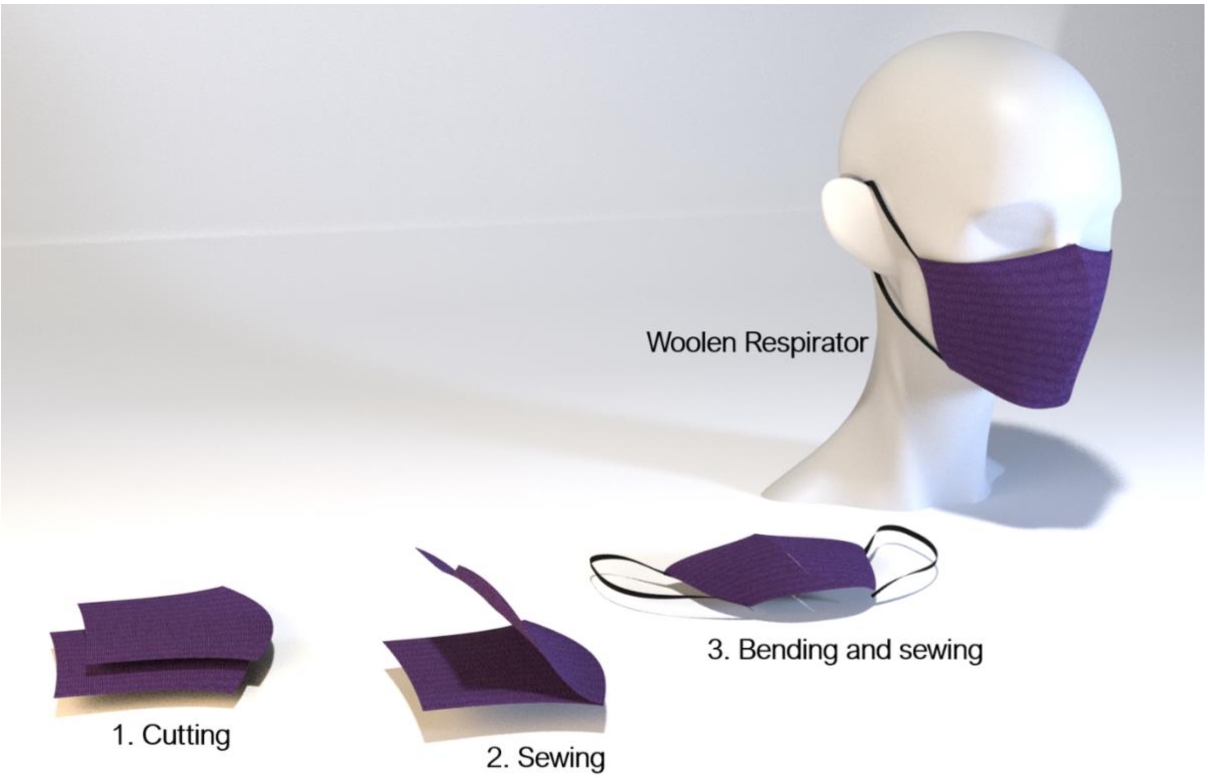


Figure 21 Schematic of fabrication process of woolen respirator

3.3. Characterization

3.3.1. Material Characterization

The mass per unit area and fabric thickness were determined according to ASTM D3776/D3776M-09ae2 (2009) and ASTM D1777-96e1 (2011), respectively. The sample thickness was measured using an SDL thickness gauge. The surface morphology of the fibres, yarns, and fabrics was analysed using a scanning electron microscope (JSM-6510LV, voltage: 20 kV) and a light microscope (LEICA M165 C).

3.3.2. ATR-FTIR analysis

The effect of water on molecular vibration due to a change in dipole moment was determined by ATR-FTIR spectroscopic (Bruker Vertex-70) analysis of the dry and wet samples. The test was conducted in the wavenumber range of 400–4000 cm^{-1} with a 16 scan number.

3.3.3. Mechanical Testing

The elastic modulus of single wool fibers was measured using an Instron 4411 universal testing machine. Briefly, the wool fibre sample was attached to a paper template with a 3 cm window. The tests were carried out under a standard testing environment (20 °C and 65% RH) with a crosshead speed of 10 mm/min. Twenty random samples were tested for dry and wet conditions, and their average elastic moduli are reported. Similarly, the breaking loads of scaled and descaled fibers were examined. Tensile tests of fabrics were performed according to the standard ASTM D 5035-95 using an Instron 5566 tensile testing machine (Instron Ltd, High Wycombe, England), in which the gauge length; crosshead speed; pre-tension and sample size were 150 mm, 50 mm/min, 0.2 N, 200 mm × 50 mm respectively. Three samples were tested with the same conditions and their mean were reported. The low-stress mechanical properties including bending, shearing, surface and compression were measured using popular fabric objective Kawabata Evaluation System of (KESF). In brief, the samples, 20 cm × 20 cm, were conditioned at 65% R.H. and 20℃ for 24 hrs before testing. For each fabric property, three replicates were tested. The physical and mechanical properties of weft knitted fabrics along the wale and course directions are different since the mechanism involved in deformation for the course and wale direction is distinct. Knit structure thus exhibits anisotropic mechanical properties. For this reason, the harmonic mean value of each corresponding fabric attribute was measured and statistically evaluated to get an overall estimate of bending, shearing, surface and compression properties. Tensile tests for respirators were performed according to the standard ASTM D 5035-95 using an Instron 5566 tensile testing machine (Instron Ltd, High Wycombe, England), in which the gauge length; crosshead speed; pre-tension and sample size were 20 mm, 50 mm/min, 0.2 N, 50 mm × 10 mm respectively. Three samples were tested with the same conditions and their mean were reported.

3.3.4. Shape Memory Evaluation

Shape memory performance of descaled wool fibers was analyzed, the single fibers were immersed in water at 20^0C for 1 hour for ensuring complete contact with water as depicted in **Figure 22**. A commercial camera recorded and observed the shapeshift and recovery performance of the studied fibres. The shape fixation (R_f) and shape recovery (R_r) were calculated respectively by the equation: $R_f = L_2/L_1$, $R_r = L_1\text{-}(L_3\text{-}L_O)/L_1$. Also, the fiber response to body sweat was examined using an artificial body fluid prepared by dissolving sodium chloride (8 g/l), carbamide (1 g/l), and lactic acid (2 g/l) in 100 mL of distilled water (pH 3)[181]. The shape memory ability of wool yarn has been measured in terms of length and diameter changes triggered by water. In detail, the conditioned yarn packages were converted by wrap reel technique to 1 lea of the skein (10 meters in length) to enhance accuracy in measurement of length and diameter change of the yarns stimulated with water and relaxation was done on the skein before marking. After that, the skein was dried at 105^0C for 1 hour. Thereafter, immediately the length and diameter of dried yarns were recorded by a light microscope and immersed in water at 20^0C for 1 hour to get the change in length and diameter of studied yarn stimulated with water. The yarns were eventually separated from the water and the hydroextractor separated the excess water. Finally, the yarn's shape changes such as length and diameter were recorded in a wet state using a light microscope and examined by image analysis software (Image J). Likewise, to characterize the fabric shape-shifting effect, the as-prepared fabrics were treated according to the procedure reported for yarns. However, in the case of fabrics, the conditioned fabric sample of four different structures with sample size 10 cm × 10 cm was considered and marked by a marker and measured the change of area during hydration and dehydration process**.** For each sample property, 50 cycles were performed to evaluate the repeatability.

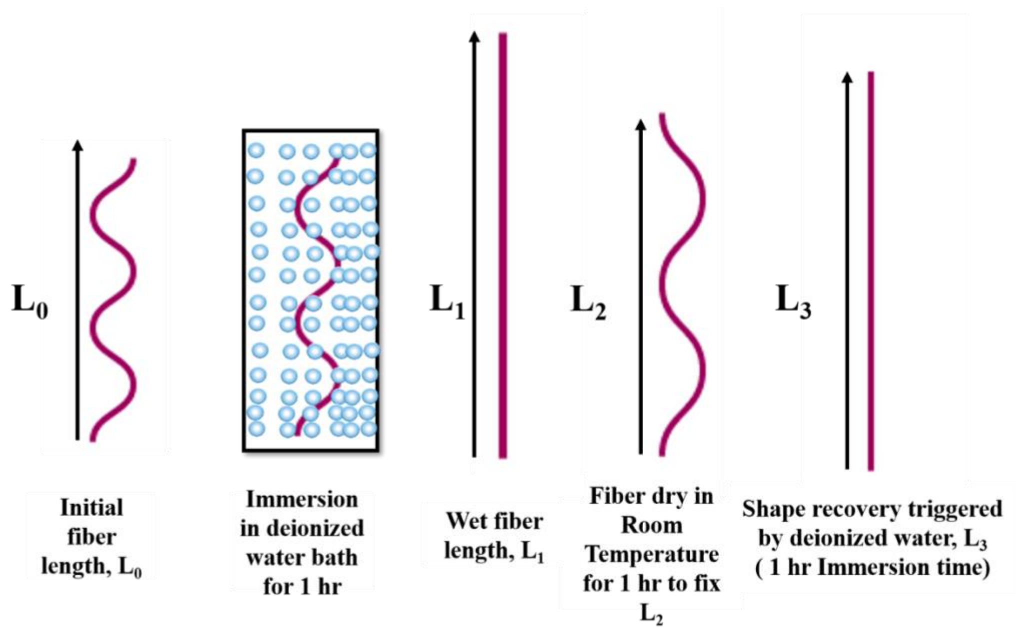


Figure 22 Schematic of water-induced strain deformation cycle of wool fibre to demonstrate the water-sensitive shape memory effect

3.3.5. Pore Actuation Measurement

To identify the water-driven pore actuation behaviour of the knitted woolen fabric because of the SME, the images of the back layers of the fabrics (attached to the body) with different water contents were captured using a light microscope, and the change in pore area (%) as a function of the water content of the fabric was measured and compared using Image J software. The water absorption was calculated as follows:

$$Water\ Absorption\ \% = \frac{W}{D} \times 100,$$

where W is the weight of water absorbed by the fabric and D is the weight of the dry fabric.

3.3.6. Thermal Testing

To assess the thermal comfort performance of the as-prepared water actuated fabrics, the air permeability; thermal conductivity; water vapour transmission (WVTR); wicking distance; drying rate and radiative heat loss were measured and compared. For air permeability and thermal conductivity investigation, the woolen knitwear with different degree of water absorption (0,25,50 and 100%) was considered and examined five times to get average values. However, during thermal conductivity measurement for accuracy purpose, the completely oven-dried samples with high surface temperature were avoided, which can be directly influenced by the experimental data of the thermal conductivity. Therefore, oven-dried fabrics were held in a silica gel sealed desiccator until the surface temperature of the fabrics becomes steady. SDL air permeability instrument at a pressure of 25 Pa with a head area of 1cm^2 was used. Thermal conductivity (k) was studied using a KES-F7 Thermo Labo instrument (Japan) as illustrated in **Figure 23.** Water vapour transmission properties of the fabrics were conducted according to ASTM E96-80B using a climatic chamber **Figure 24.** The WVTR was performed under different environmental temperature (20,25,30,35 and 40°C) with constant humidity of 80% RH. Likewise, WVTR with various relative humidity (20, 40, 60 and 80%) with a constant temperature of 25°C were tested. According to AATCC TM 197, the wicking height of as-prepared samples was measured. The samples were cut into strips (20 cm × 2.5 cm) and immersed in distilled water. Based on GB/T 21655.1−2008, the water evaporation rate was tested. During the test procedure, distilled water (0.2 g) was supplied on the fabrics (10 cm × 10 cm), and the weight was recorded every 5 min. For measuring radiative heat loss of studied fabric, oven-dried, and wet fabrics were considered. Thermal images were obtained for IR characterization using an IR camera (FLIR A655sc). In short, a closed chamber with a guard hot plate with a steady temperature of 380C was used and the thermal camera was placed in the air space with a constant angle and distance from the hot plate to provide uniform thermal radiation and mimic the human body temperature. Finally, pictures were taken every 5 seconds when the specimen was placed on the hot plate until the heat transfer reached an equilibrium state. The surface temperature was calculated using FLIR Tools software in which each pixel of the picture was allocated to one temperature value. The average was subsequently created based on all the values.

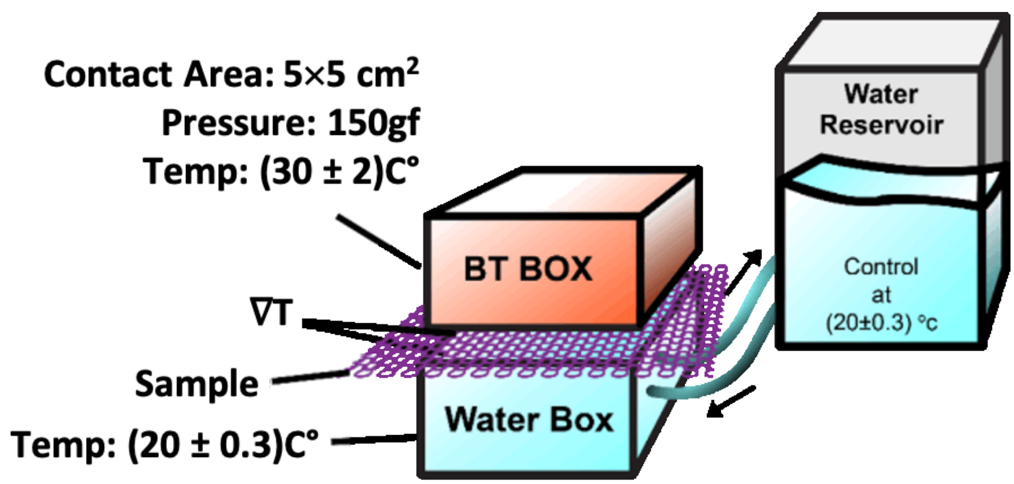


Figure 23 Schematic illustration of Thermo Labo II instrument

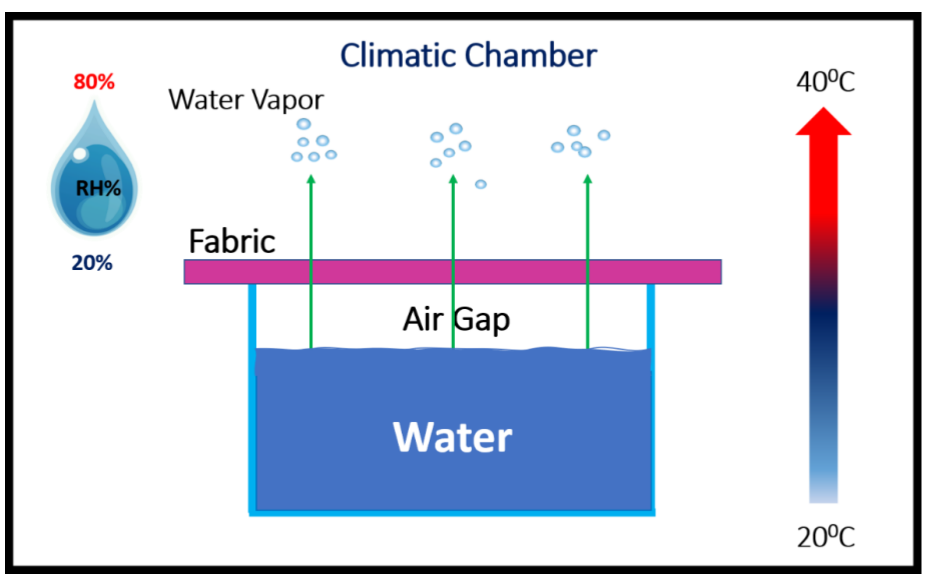


Figure 24 Schematic of water vapour transmission testing

3.3.7. Durability Testing

The abrasion test was carried following the British standard BS EN ISO 12947- 3:1998, which is the Martindale method for abrasion resistance in fabric for mass loss. The machine used was the Martindale machine and the test intervals used were as stated in the standard, test series up to 1000 rubs. After each series of rubs, the samples were removed and weighed to determine the amount of loss that occurred in that cycle.

3.3.8. Protective Performance Testing

The filtration efficiency and pressure drop were analysed using Standard TSI machine. The flow rate was maintained 85L/min with 0.3-micron sodium chloride particle. The conditioning of all fabric specimens was performed in controlled atmospheric condition (20 ± 2C° temperature and 65 ± 3% RH). The splash resistant was investigated with liquid transmission chamber. Briefly, the experiment was conducted after placing the specimen (80 mm 9 80 mm) between the top and bottom sensors in the test chamber of the machine (M 290, SDL Atlas Ltd). A predetermined amount of standard test solution (9.0 g L^{-1} NaCl) as sweat was dropped onto the top surface of the fabric (i.e., the skin or inner side of the apparel) for 20s and the absorption of the liquid from the inner to outer surfaces was observed for 120s. Moreover, the contact angle was measured to further verify the splash penetration efficiency of the samples. The water contact angle (WCA) was measured having an initial volume of about 10 μl was placed on a treated fabric fixed at observation stand. The static contact angle was measured for 60 s, with one frame taken every second, and the contact angle at 5 s was used for comparison. At least five independent observation for different droplets placed on different pieces of the same type of samples were performed.

3.3.9. Wear Trial Assessment

Because of the limited budget, the wear trial assessment conducted with 10 university research student who ranged in age from 30 to 33 and voluntarily participated in the test. We provided two samples that were woolen respirators and commercial mask. The participants were allowed to choose the sequence of wearing the masks randomly. The pictures and the instructions of wearing provided by the same researcher. The wear trial was conducted in controlled atmospheric condition (20 ± 2^0C temperature and 65 ± 3% RH). A wear trial evaluation questioner circulated to each participant **(see 3.3.10**) for subjective evaluation of the mask. Each trial lasted for 30 to 60 min. The subjects were allowed to adjust the scores at any time during the trial. All the subjects were encouraged to follow the social distancing measure during the test.

3.3.10. Wear Trial Evaluation Questionnaire

User No.: Sample No.: Date:

Please rate each item listed below using the following scale that best describes the given face mask quality in terms of wearing. This score must be between 1-5.

1: Poor

2: Average

3: Good

4: Very Good

5: Excellent

Characteristics	**1**	**2**	**3**	**4**	**5**
I. Product outlook (Design, Material and Hand-feel)					
II. Comfort when wearing (Phycological and Thermal)					
III. Comfort during face movement (Talking, Laughing and Freedom of face movement)					
IV. Overall wear trial rating					

Chapter 4 Water-Actuating Woolen Knit Pores for Thermoregulation

4.1 Research Highlights

- The fascinating water-responsive pore size change of the knit pores keeps the skin dry, thus helping to maintain a constant body temperature, providing comfort and safety.
- This work shows significant potential to rediscover natural fibers as smart materials and wool as an all-weather clothing material in all situations with or without exercising.
- Herein, we report a discovery that is contrary to available public and professional knowledge, that is, woolen knitwear can provide not only warmth, but also a cooling sensation when a body sweat.

Related Publication

- Hu, Jinlian*, **Mohammad Irfan Iqbal,** and Fengxin Sun. "Wool Can Be Cool: Water-Actuating Woolen Knitwear for Both Hot and Cold." Advanced Functional Materials 30.51 (2020): 2005033.

4.2 Introduction

The human body is sensitive to temperature and humidity and maintains its internal core temperature by the process of thermoregulation mainly through perspiration, i.e., the secretion of water-rich fluids by sweat glands, whose intensity depends on the ambient environment and physical activity **(Figure 25).** With the evolution of human civilization, various types of clothes made of different materials have been produced for protection, aesthetics, and civility, with limited consideration for thermoregulation. However, under certain conditions, garments must adapt to the inevitable switching between hot and cold environments[182]. To achieve reasonable comfort and maximal safety in such cases, for example, during heavy exercise in winter, several properties of the textile fabric need to be controlled such as water vapor permeability, thermal conductivity, air permeability, and infrared (IR) transmission **(Figure 26)**

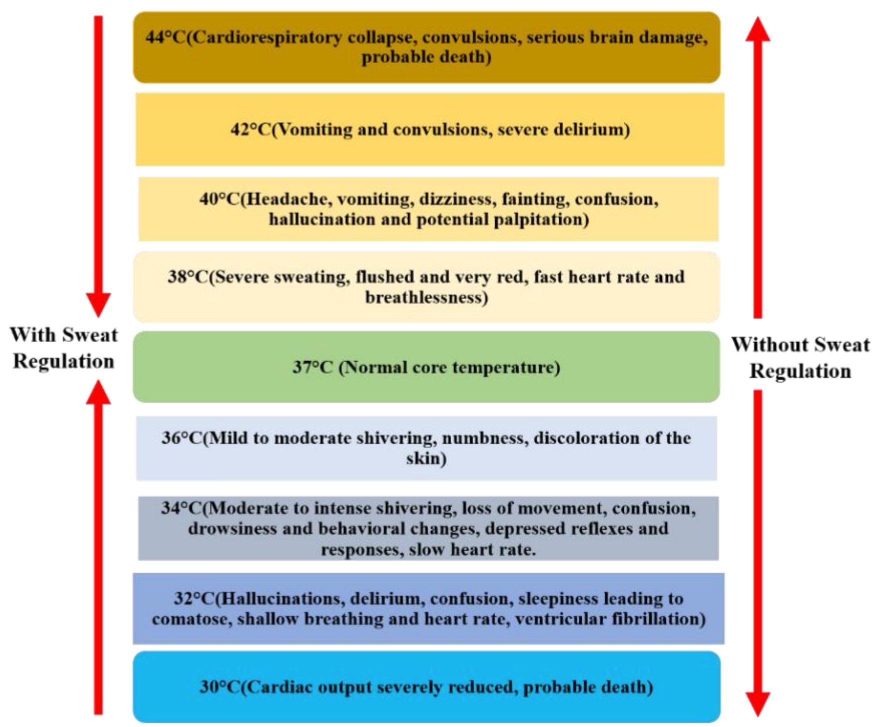


Figure 25 Importance of sweat management for thermoregulation

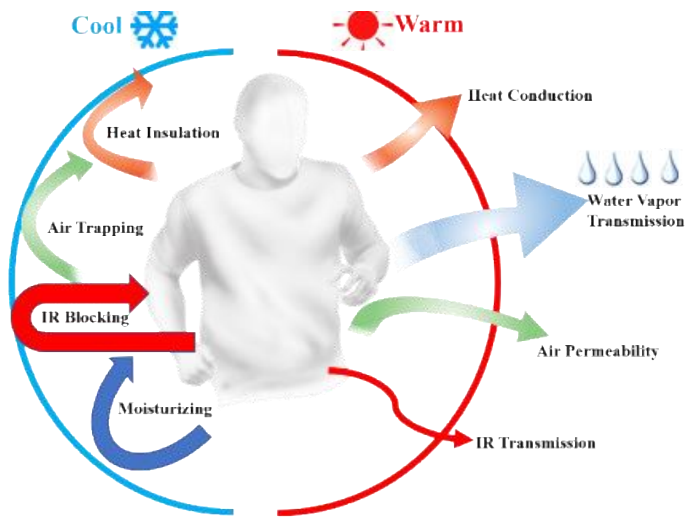


Figure 26 Schematic of human body heat transmission for comfort textiles

In response to the above demands**,** different approaches such as the use of phase change materials [183-186], IR-responsive materials[23, 97, 98, 187, 188], conductive materials[101], photonic structures[189-191], energy devices[103, 192, 193], moisture management fabric[194, 195] and others[196] have been proposed for developing thermoregulating textiles. However, most of these approaches are ineffective for the development of adaptive textiles for both hot and cold environments. Recently, the use of stimuli-responsive materials with shape-memory effect (SME) has opened a new horizon for the development of effective thermoregulatory apparel[113]. In the 1990s, the Defense Clothing & Textiles Agency of the UK Army used shape memory materials(SMMs) and their derivatives[197] to produce heat-protective clothing. For this, thermo-responsive shape memory alloy (Nitinol)-based springs were incorporated into cotton fabrics with a bilayer structure, whose thickness could be changed by the contraction and expansion of the conical spring (tunable air gap) with variation in ambient temperature, which offered a thermoregulatory effect. However, the mechanical action of these springs was very poor and sometimes an external mechanical force was required for their actuation. For another study, a humidity-sensitive SMM sheet (Nafion) was laminated into a fabric[82] that could quickly respond to the changes in the sweating intensity of a human body for heat and mass transfer. However, such approaches are not only unsuitable for large-scale production because of high cost, but also non-sustainable because of the toxicity of the chemicals. Temperature-sensitive hydrogels of poly-NiPAAm and chitosan were used for the surface modification of cotton fabrics for thermal management[198-200], which enabled the regulation of water vapor permeability or water uptake depending on the variation in ambient temperature by the contraction/expansion of the thermo-responsive hydrogels. In another study, a woven woolen fabric was coated with a shape-memory polyurethane solution[201] for thermal management. This type of coating and finishing surface modification has several issues related to processability, hand feel, washability, and sustainability. Moisture-sensitive natural cotton yarn smart muscles with expansion-contraction behavior have recently been proposed for the fabrication of thermoregulatory clothing[202]. However, the proposed techniques require a high degree of twist and plying approach, which makes the raw materials incompatible with conventional textile processing.

Wool, a keratinous protein fiber (animal hair)[107] is mainly considered a natural thermal insulator, and therefore, only used for winter clothing. With increasing global warming, the demand for wool in the fiber market is steadily decreasing[203]. Recently, researchers investigated the effect of water on the shape memory of animal hairs, such as that of sheep, goats, and camels, and on the variations of the crystal, disulfide, and hydrogen bonds in the macromolecules and reported that the wool fibers exhibit water-responsive SME[110, 204]. Clothing materials generally have a hierarchical structure because of the twisting of fibers into yarns and the knitting or weaving of yarns into fabrics. Besides wool fiber, the water responsiveness of a hydrogel-coated wool yarn was investigated[112]; however, the materials exhibited a poor response time because of slow water diffusion[205].

To overcome the drawbacks of the currently used thermoregulatory textiles and meet the demands for sustainable thermoregulatory textiles for practical applications, we designed a yarn with descaled pure wool fibers and prepared a knit fabric. In addition, we examined its adaptive thermoregulation in terms of water vapor permeability, thermal conductivity, air permeability, and IR transmission under various sweat levels. Contrary to intuition and worldwide public and professional knowledge, it is intriguing to see that wool can offer a cooling sensation during sweating. The SME of the woolen knitwear enables the pore size change of the knit pores upon water stimulation, and thus the wearer feels warm during no or less sweating and cool during sweating such as during exercising and in summer **(Figure 27).** This work can foster new ideas of rediscovering natural fibers as smart materials and wool as an all-weather clothing material in all situations with or without exercising**.**

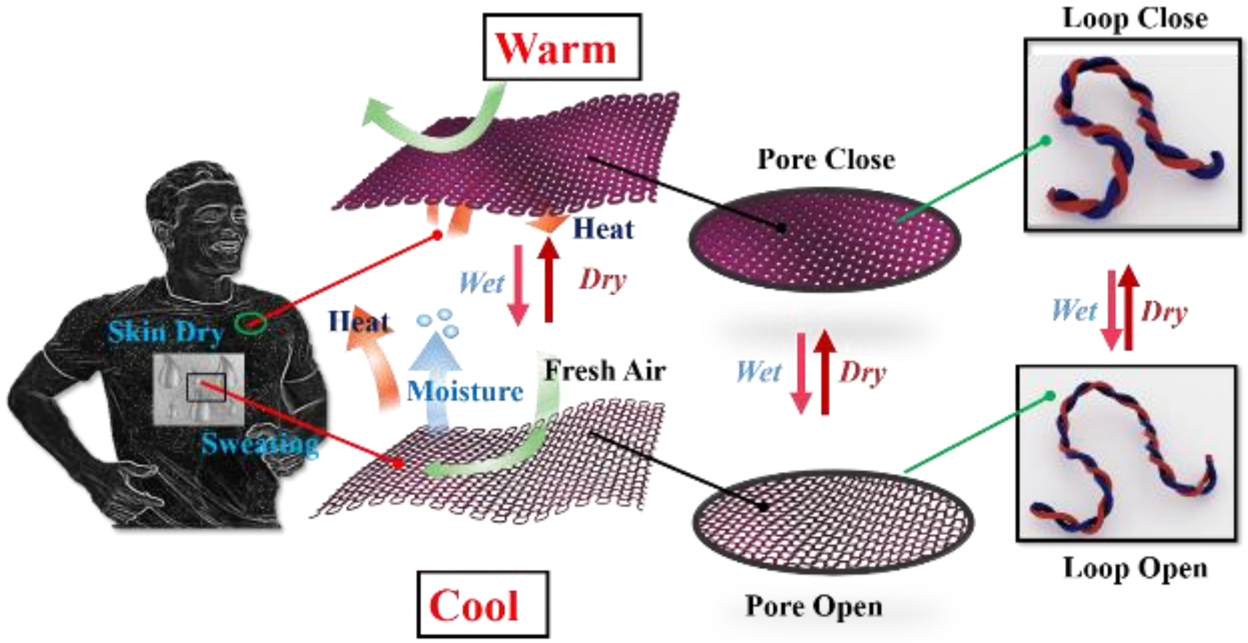


Figure 27 Water-actuating woolen knitwear for thermoregulation: Provides cooling sensation during sweating and warmth when the skin is dry

4.3. Results and Discussion

4.3.1 Two-Way Shape Memory of Wool Yarns

Wool fibers with a surface scale layer exhibited a slow and inconsistent response **(Figure 28)**, which is inappropriate for smart textiles. Herein, we report the two-way SME of wool yarns with descaled fibers achieved through a special treatment and design **(Figure 29).**

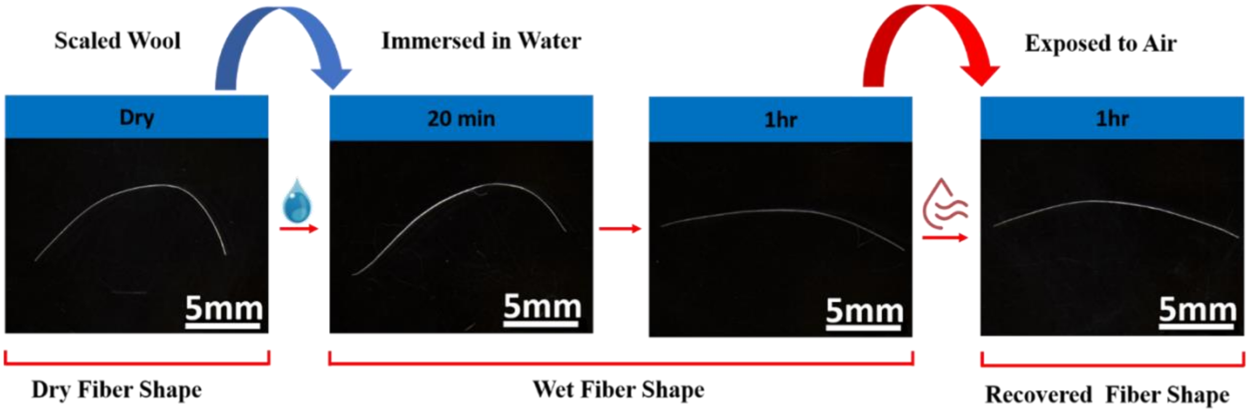


Figure 28 Light microscopic images of changes in the shape of scaled wool fiber stimulated with water

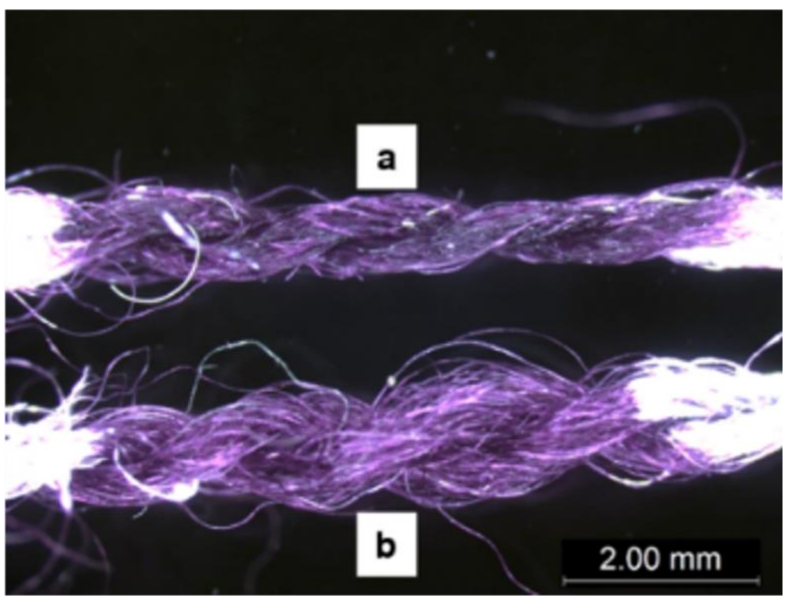


Figure 29 Light microscopy images of (a) wet wool yarn and **(b)** dry wool yarn

As shown in **Figure 30b**, the wool yarn exhibits a shape-memory behavior in response to water for fifty consecutive cycles. The reversible changes in length and diameter are because of the SME of the wool fiber (**Figure 30a and Figure 31)**. The fibers straightened upon wetting and recovered their original shape upon drying, where a strong relationship between dipole moment and peak intensity[206]. Moreover, to determine the response of the wool fiber to simulated body fluid, artificial acidic sweat was used. The response of the wool fiber to artificial sweat **(Figure 32)** was similar to its response to water, which confirmed that the shape-memory behavior of wool is the same for both sweat and water.

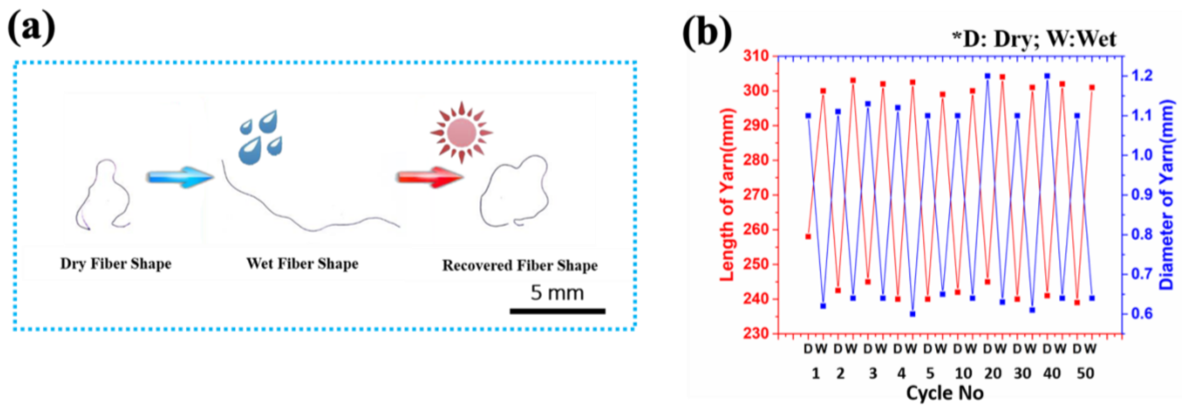


Figure 30 Two-way shape memory of wool yarn: (a) Light microscopic images of the fiber shape change stimulated by water (b) Reversible changes in length and diameter of wool yarn over fifty cycles

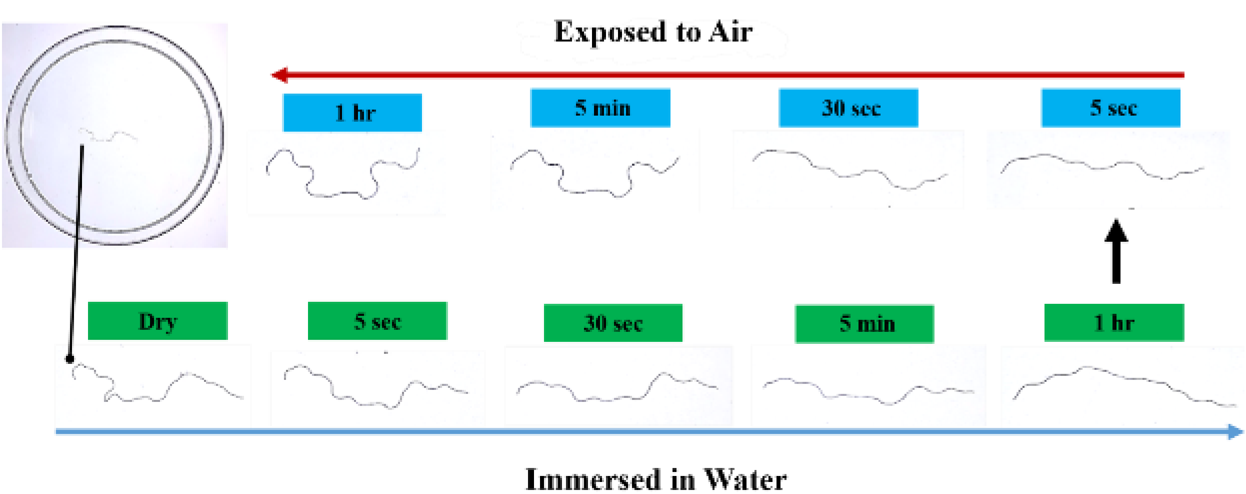


Figure 31 Photo images of changes in the shape of the wool fiber stimulated with water

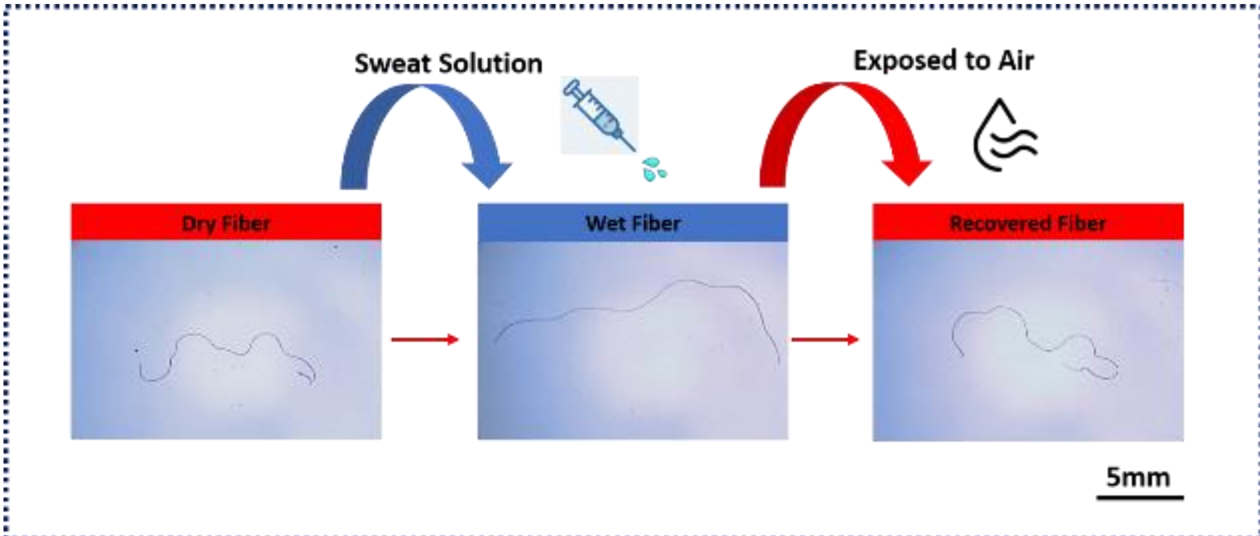


Figure 32 Light microscopic images of changes in the shape of the wool fiber stimulated with artificial sweat

Figure 33a shows the FTIR spectra of the dry and wet wool samples. As can be seen, the overall absorption band for the wet sample is much higher than that of the dry sample, especially in the ranges of 3050–3650 cm^{-1} and 1250–1850 cm^{-1}. This indicates that the absorption of water by dry wool causes higher molecular vibration along the chain, which leads to a significant expansion of the molecular chain during hydration; thus, the fiber straightened in the wet state because of a lower tensile modulus **(Figure 33b).** This confirms that the shape memory behavior of the wool yarn is associated with the shape change of the fibers during hydration and dehydration, which mainly depends on bond vibration and the mechanical properties of the fiber. It is noteworthy that unlike the previously reported wool fibers that exhibited a one-way SME, our wool fibers and yarns demonstrate a two-way SME.

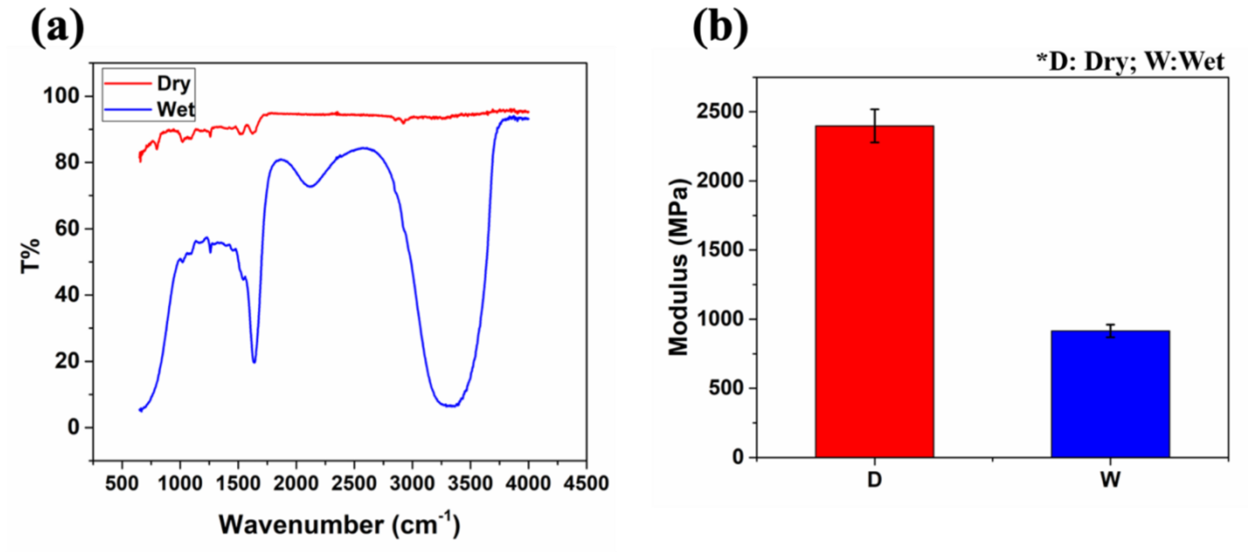


Figure 33 Two-way shape memory of wool yarn: (a) FTIR spectra of dry and wet wool fibers, and **(b)** Elastic moduli of dry and wet wool fibers

4.3.2 Water Actuation of Wool Knit Pores

A schematic of the pore actuation mechanism of the knitted woolen fabric stimulated by water is shown in **Figure 34.** The as-prepared knitted woolen fabric exhibited a reversible significantly large change in its area upon hydration and dehydration **(Figure 35)**, which can be attributed to the synergistic SME shown by the fibers and yarns in the fabric. The absorption of water by the wool fiber increases the yarn length and decreases the yarn diameter **(Figure 29a and b,)**, which leads to an increase in loop width and a decrease in loop height of the wet fibre **(Figure 36**).

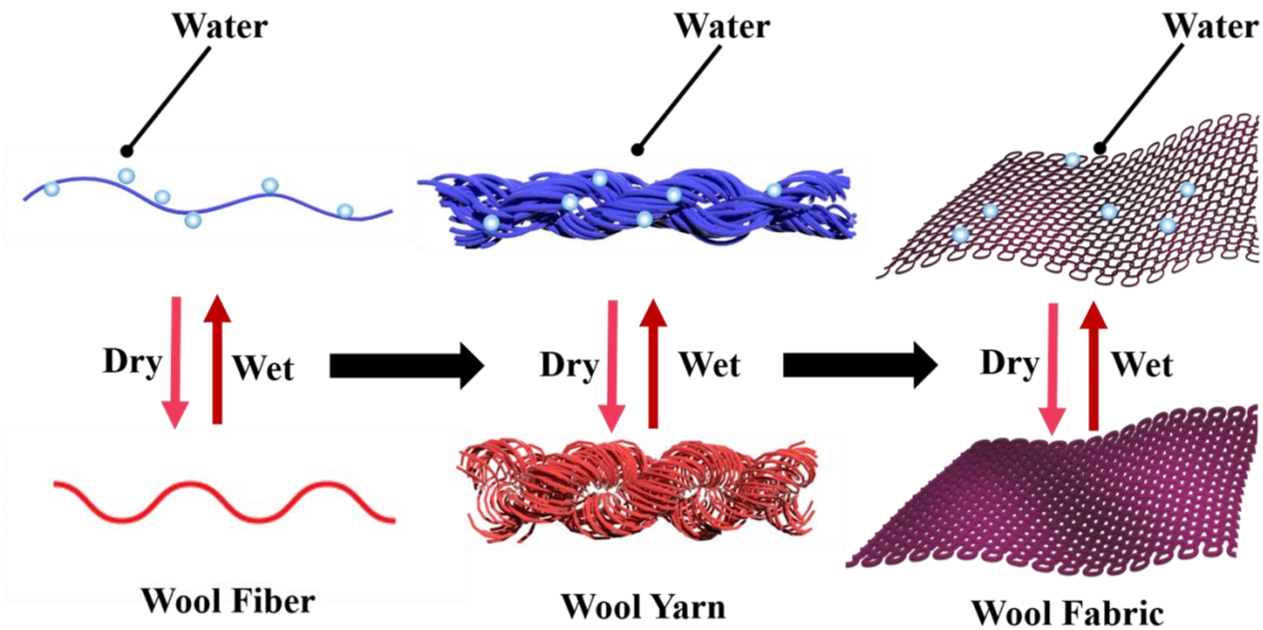


Figure 34 Schematic of water-responsive pore actuation of wool fiber, yarn, and fabric

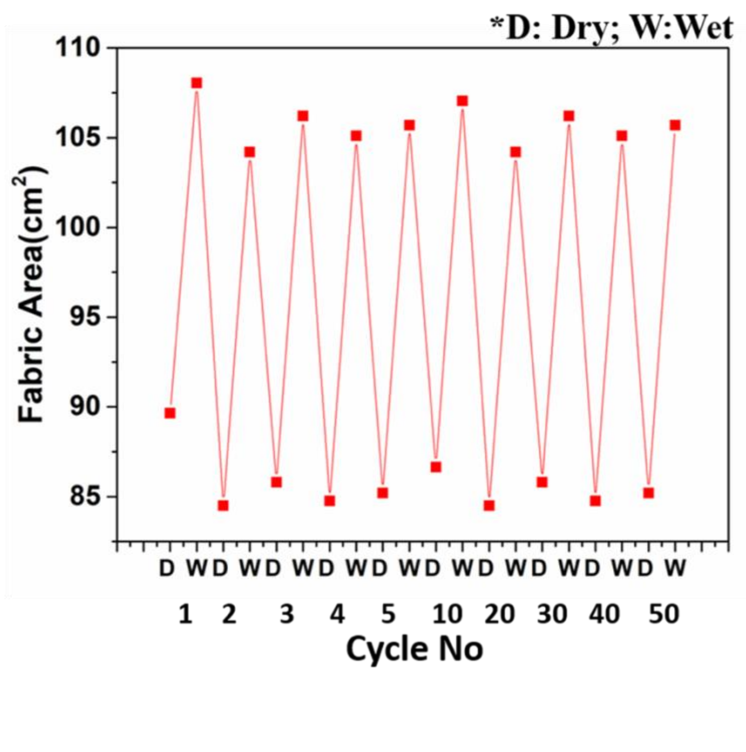


Figure 35 Reversible changes in area of knitted woolen fabric in dry and wet states over fifty cycles

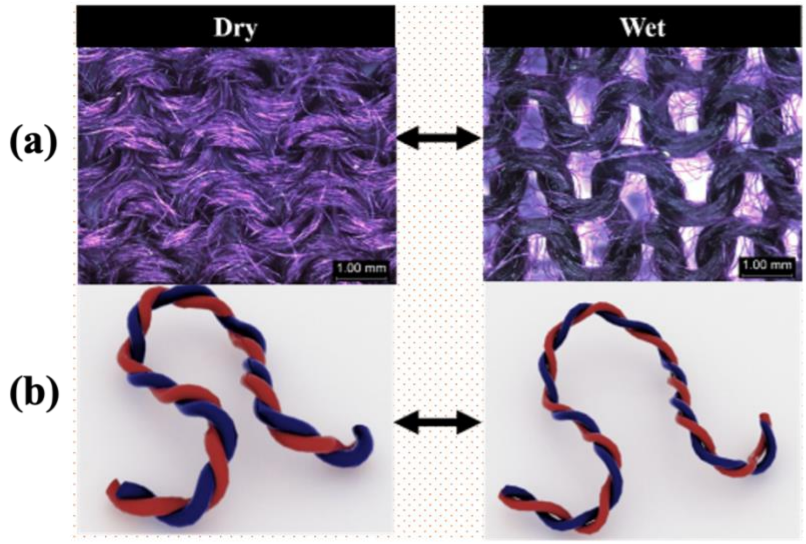


Figure 36 Changes in the shape of loops in the knitted woolen fabric: (a) Light microscopy images of dry and wet fabrics, and **(b)** Schematic of loop shape change in dry and wet states

Thus, water absorption by the knitted woolen fabric results in pore size change, thereby allowing thermoregulation for the wearer in a sweat-inducing environment. **Figure 37** shows the change in the pore area of the knitted woolen fabric with different amounts of absorbed water, which indicates the unique pore size change ability of the knitted woolen fabric. As can be seen from **Figure 37,** pore opening increased with increasing amount of absorbed water, which is further confirmed from the light microscopy images of the samples **(Figure 38).** A closer observation of the images reveals a sudden considerable increase in pore opening with an increase in water absorption from 0% to 25%, followed by a gradually increase in pore opening because of the limited deformability of the fabric. Similar shape memory responses were obtained from different knit architectures such as tuck- and miss-stitched fabrics **(Figure 39)**.

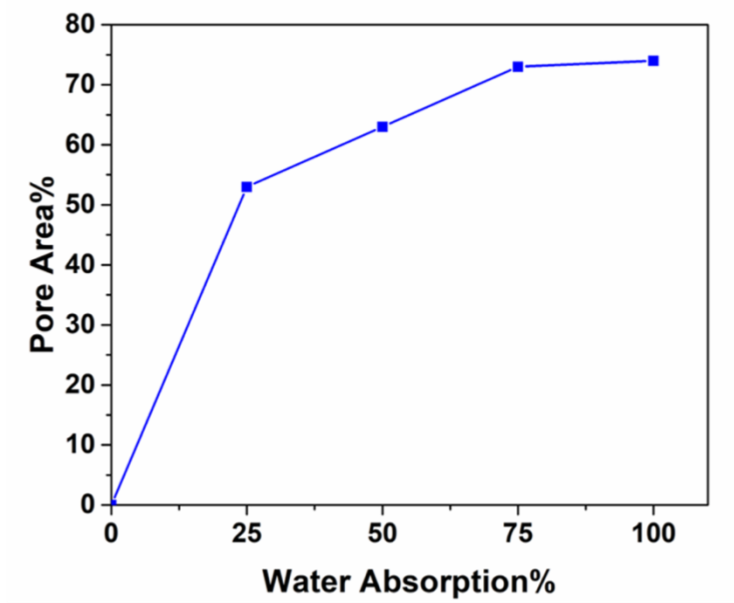


Figure 37 Water actuation mechanism of knitted woolen fabric: Change in pore area of the knitted woolen fabric with change in water absorption

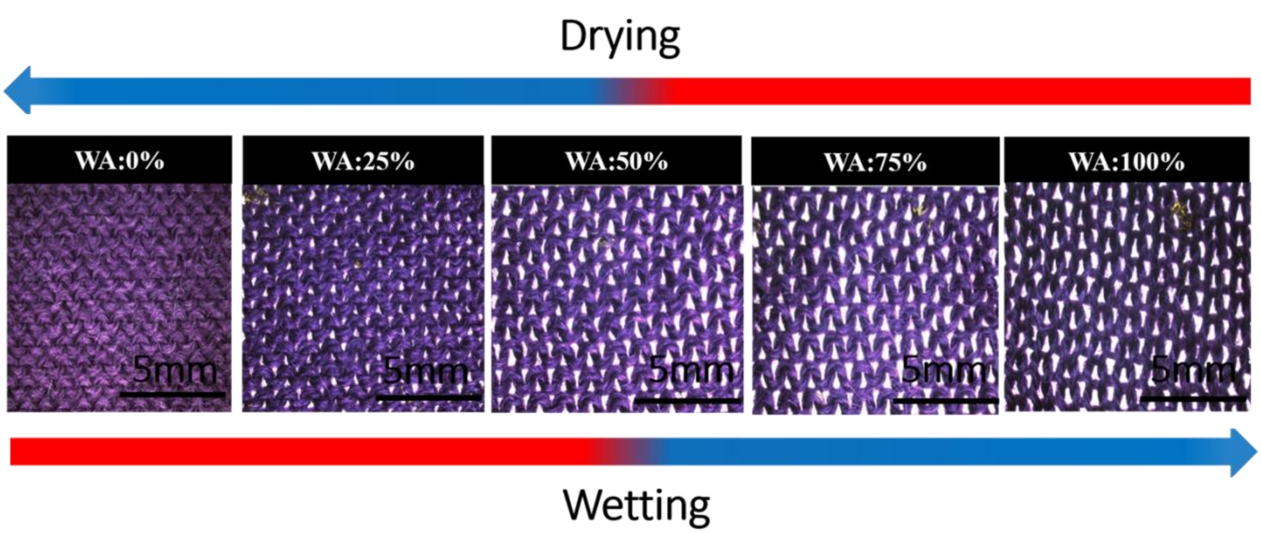


Figure 38 Water actuation mechanism of knitted woolen fabric: Light microscopy images of pore opening of knitted woolen fabric with increasing water absorption (back layer)

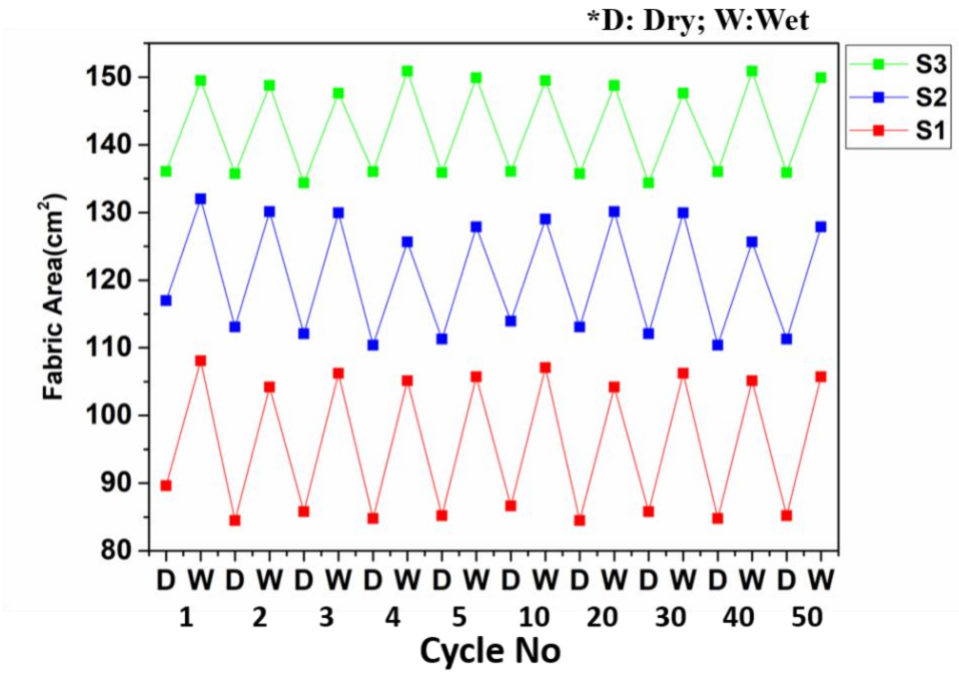


Figure 39 Reversible changes in the areas of different knitted woolen fabrics in dry and wet states over fifty cycles

4.3.3 Cooling Performance of Woolen Knitwear

The key factors affecting the cooling performance of textiles are heat insulation, mass transfer in the form of vapor and liquid through the clothing, and body heat exchange with the surroundings through conduction, convection, radiation, and evaporation[207]. The degrees of body heat exchange with the surroundings through conduction, convection, evaporation and radiation were 5, 15, 20, and 60% respectively[17]. Thus, to understand the effect of water-responsive pore size change of the knitwear on cooling performance, we have investigated these four aspects of heat transfer accordingly in terms of air permeability (convection), thermal conductivity, water vapor permeability and radiative cooling effect.

Figure 40a shows the air permeability of the fabric with different amounts of absorbed water. As can be seen, the air permeability increased with increasing water content of the fabric because of the structural changes in the yarns and fabric stimulated with water, i.e., the increase in yarn length and decrease in yarn diameter, which led to the opening of the knit pores, resulting in fabric expansion **(Figure 36).** Therefore, the woolen fabric is considered to exhibit adaptive heat convection due to the pore actuation effect. These results confirm that thermal convection management is related to pore actuation, as reported by Zhong et al.[82].

Figure 40b shows the variation in the thermal conductivity (k) of the material with the water content of the woolen fabric. The results indicate the ability of the material to transfer heat when in contact with skin**.** As can be seen, there is a significant positive correlation between the water content and thermal conductivity of the fabric. This further evidence the structure-shifting ability of the fabric, indicating that the water-responsive SME affects heat transfer through the fabric. A strong relationship between thermal conductivity and moisture/water has been reported in literature[208]. The thermal conductivity of water is higher than that of dry air by over 95%; therefore, the absorption of a small amount of water enhances the thermal conductivity of the material.

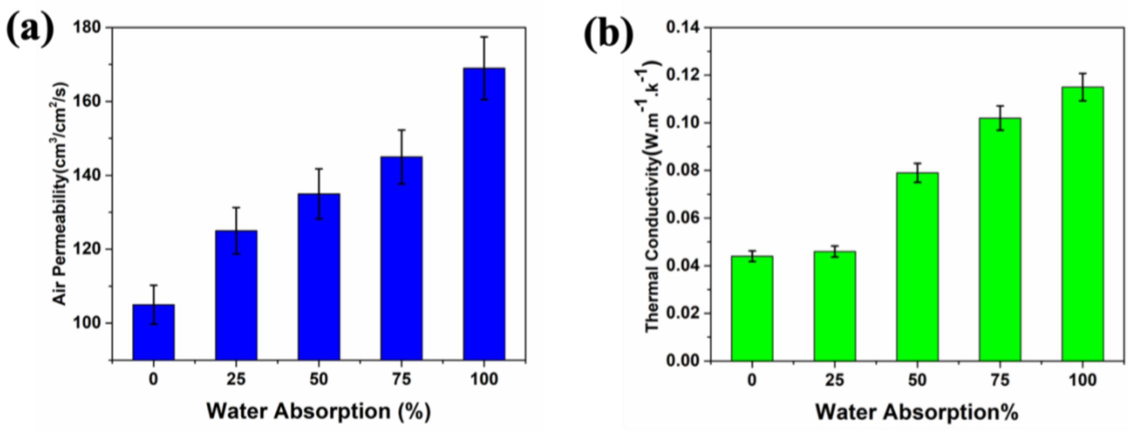


Figure 40 Cooling performance of water-actuating woolen knitwear: (a) Air permeability; and **(b)** Thermal conductivity

The transfer of heat and moisture from a wet skin due to heavy sweating through a textile material depends on the water vapor transmission rate (WVTR). The WVTRs of the fabric under different environmental temperatures and relative humidity (RH) values are shown in **Figure 41a** and **b,** respectively. The results suggest the possibility of obtaining smart vapor transmission adaptability. As can be seen in **Figure 41a,** the WVTR increased with increasing water absorption at all temperatures. In conjunction with the environmental temperature for different humidity, the WVTR values of the samples increased significantly with increase in water gradient **(Figure 41b).** This is because the water vapor diffusion rate of the sample increased due to the opening of the pores with increasing water absorption. The WVTR of the fabric significantly increased with an increase in temperature and a decrease in RH. It can therefore be assumed that water-responsive woolen knitwear can enable smart thermoregulation under different surrounding temperatures and humidity, which is consistent with the findings of Pakdel et al.[209].

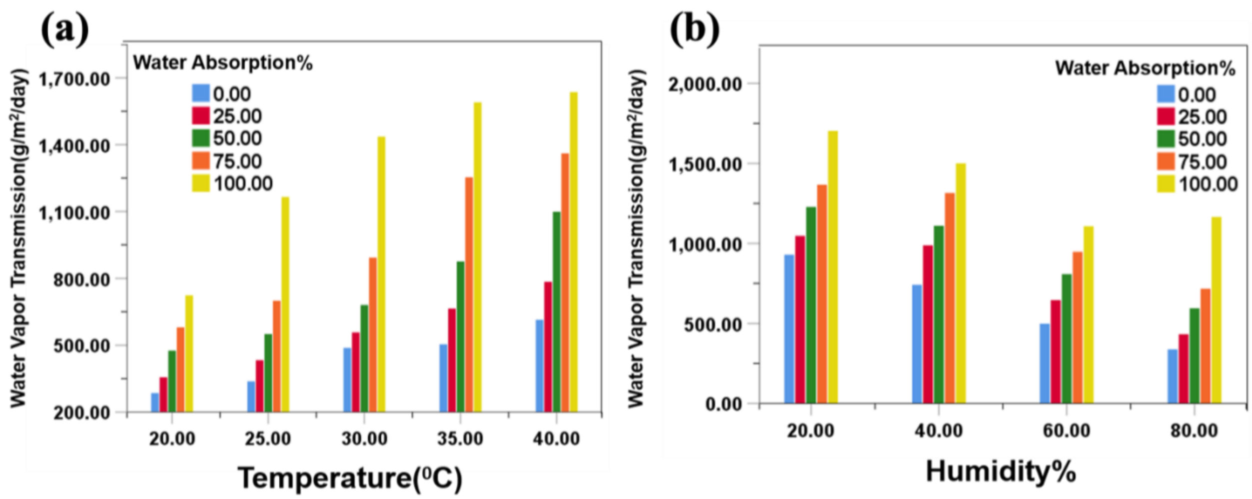


Figure 41 Variation in WVTR of the woolen fabric as a function of (a) Temperature (constant environmental humidity: 80% RH) and **(b)** RH (constant environmental temperature: 25 °C)

The radiative heat loss was determined from the thermal images of the dry and wet fabrics in equilibrium that are shown in **Figure 42a**. The temperatures of the dry and wet wool samples are 31.16 °C and 24.72 °C, respectively, which indicate that the wet samples have a cooler surface due to radiative cooling. The radiative heat loss was quantitatively determined by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopic measurements performed in the range of 9.5–10 µm, as the human body absorbs and loses heat largely (> 40%) through IR radiation centered around 10 µm; the results are shown in **Figure 42b**[23]. As can be seen, the IR transmission of the wet samples in the range of 9.65–9.95 µm is higher than that of the dry samples. Thus, the wet samples enabled the radiative cooling of the skin due to the change in the loop shape of the wet fabrics, as shown in **Figure 36.**

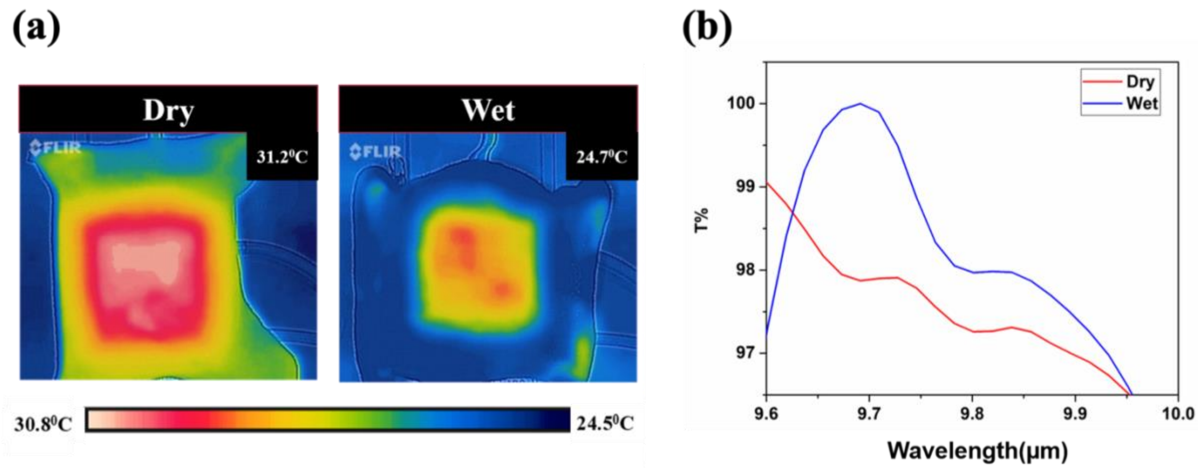


Figure 42 Cooling performance of water-actuating woolen knitwear (a) Thermal images of woolen fabric in dry and wet states, and **(b)** IR transmittance through the dry and wet knitted woolen fabric

4.3.4 Theoretical Analysis of Shape Changes for Thermoregulation

A knitted woolen fabric follows a complex constrained path over a multi-scale structure. When the wool fibers are spun into a single yarn, they form a helical structure because of the twisting process **(Figure 43).** By ignoring the migration of fibers in the yarn's radial direction, the helical locus of the fiber in the yarn can be expressed as:

$$\boldsymbol{S}(s) = \left\{ r_f \cos(\frac{2\pi}{l_f} s), r_f \sin(\frac{2\pi}{l_f} s), \frac{L_{sy}}{l_f} s \right\}, \ (1)$$

where r_f is the radius of the spin of the fiber in a single yarn, l_f is the length of the fiber, L_{sy} is the corresponding yarn length in a turn of the fiber, and s is the arc length from (r_f, 0, 0) to an arbitrary point S.

Using equation 1, the curvature (κ) and torsion (τ) of the fiber in a single yarn (as seen from sections a and b in **Figure 43)** can be expressed as equations 2 and 3, respectively.

$$\kappa = \lim_{\Delta s \to 0} \left| \frac{\Delta \varphi}{\Delta \boldsymbol{s}} \right| = \frac{\left| \boldsymbol{S}'(\boldsymbol{s}) \times \boldsymbol{S}''(\boldsymbol{s}) \right|}{\left| \boldsymbol{S}'(\boldsymbol{s}) \right|^3} \quad (2)$$

$$\tau = \lim_{\Delta s \to 0} \left| \frac{\Delta \psi}{\Delta \boldsymbol{s}} \right| = \frac{\left(\boldsymbol{S}'(\boldsymbol{s}), \boldsymbol{S}''(\boldsymbol{s}), \boldsymbol{S}'''(\boldsymbol{s}) \right)}{\left| \boldsymbol{S}'(\boldsymbol{s}) \times \boldsymbol{S}''(\boldsymbol{s}) \right|^2} \quad (3)$$

By substituting equation (1) into equations (2) and (3), we obtain equations (4) and (5), respectively.

$$\kappa = \frac{4\pi^2 r_f}{l_f} \quad (4)$$

$$\tau = \frac{2\pi L_{sy}}{l_f^2} \quad (5)$$

By rearranging equations (4) and (5), we obtain equations (6) and (7), respectively.

$r_f = A\kappa$, $A = \frac{l_f}{4\pi^2}$ (6)

$L_{sy} = B\tau$ $B = \frac{l_f^2}{2\pi}$ (7)

Based on the ideal packing form of yarns, the diameter (d_{sy}) of a single yarn can be expressed as follows:

$d_{sy} = 2 \cdot \max\{r_f\} = 2 \cdot \max\{A\kappa\}$ (8)

Based on the analysis, the L_{sy} and d_{sy} of a single yarn can be determined from the curvature and torsion of the fibers (equations (7) and (8), respectively). The diameter of a single yarn decreases when the fibers straighten upon wetting, whereas the length of a single yarn increases when the fibers extend along the axial direction of the yarn upon wetting.

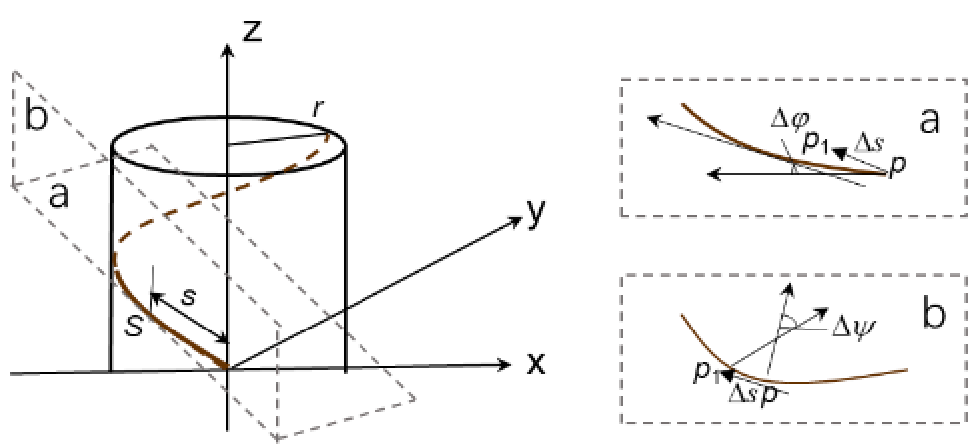


Figure 43 Schematic of helical structure of the twisted fiber in the yarn: (a) curvature definition and **(b)** description of torsion

Similarly, the changes in a single yarn have a domino effect on the plied yarn. By expanding the helix along the cylinder generatrix of a single yarn, we can obtain a hypotenuse by the topological mapping of the helical locus of the single yarn, as shown in **Figure 44.**

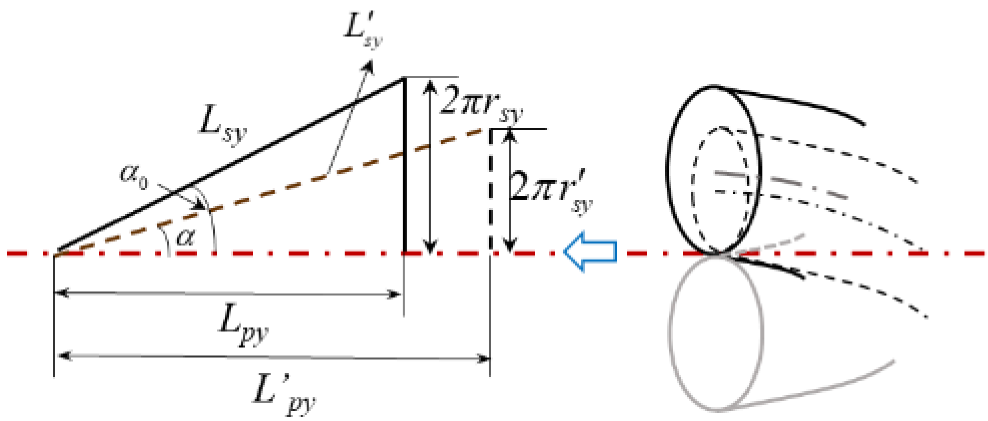


Figure 44 The expanded view of a single yarn and the change in diameter

When the plied yarn becomes wet, the diameter of the single yarn decreases because of the unbending deformation of the internal fibers of the plied yarn, as discussed above. The changes in the diameter and length of a single yarn are illustrated in **Figure 29**. The geometric relationship yields equation (9).

$$L_{sy}^2 = L_{py}^2 + (2\pi r_{sy})^2 \quad (9)$$

By differentiating equation (9) with respect to L_{sy}, we obtain equation (10).

$$\frac{dL_{sy}}{L_{sy}} = \frac{L_{py}^2}{L_{sy}^2}\frac{dL_{py}}{L_{py}} + \frac{(2\pi r_{sy})^2}{L_{sy}^2}\frac{d(2\pi r_{sy})}{2\pi r_{sy}} \quad (10)$$

By setting the strain of the length and diameter of a single yarn as ε_{lsy} and ε_{rsy}, respectively, and the strain of the length of the plied yarn as ε_{lpy}, we obtain equation (11).

$$\varepsilon_{lsy} = \frac{L_{py}^2}{L_{sy}^2}\varepsilon_{lpy} + \frac{(2\pi r_{sy})^2}{L_{sy}^2}\varepsilon_{rsy} \quad (11)$$

Then,

$$\varepsilon_{lpy} = \frac{\varepsilon_{lsy} - \sin^2\alpha_0 \varepsilon_{rsy}}{\cos^2\alpha_0} \quad (12)$$

Hence, the changes in the length of the plied yarn are mainly associated with the changes in the diameter and length of the single yarns. This demonstrates the experimental results **(Figure 29 and Figure 30b)** that the length of the plied yarn possesses the coincident change trend with the length of each single yarn, while the length of plied yarn increases when the diameter of single yarn decreases based on equation 12. The relationship between the changes in the length of the plied yarn and the changes in the length and diameter of the single yarns considering the initial helical angle as $\alpha_0 = \pi/6$ are shown in **Figure 45.**

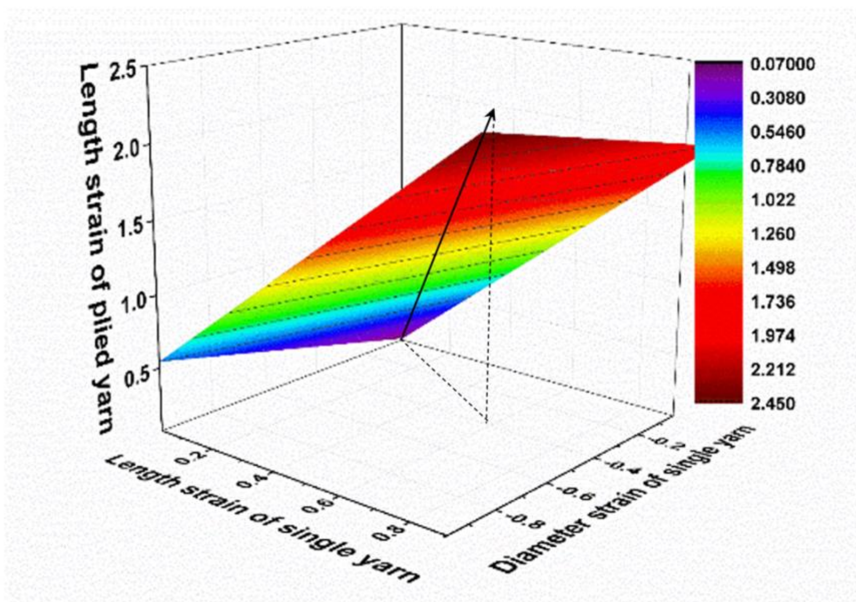


Figure 45 Relationship between strain of diameter and length of single yarns and that of length of plied yarns (initial helical angle, $\alpha_0 = \pi/6$)

Considering the knitted fabric to be a two-dimensional topological network, the knitted loop structure and a unit of the knitted fabric are shown in **Figure 46**

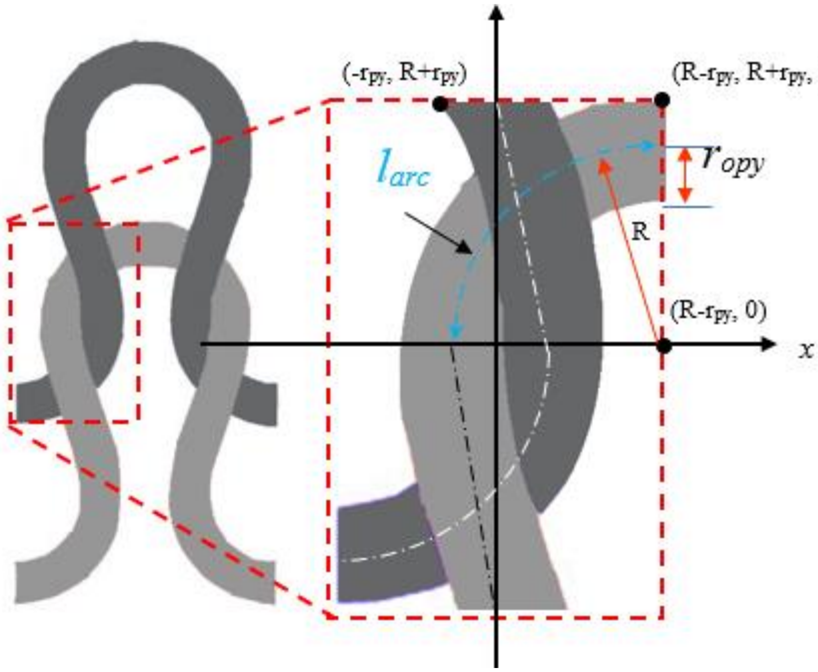


Figure 46 Schematic of a knitted structure and a unit of the knitted fabric

The loop distance between adjacent knitted loops along the wale and course directions can be expressed as equations (13) and (14), respectively.

$$D_A = 4\left(R - r_{py}\right) = \frac{2}{\pi} l_{arc} - 4r_{py} \quad (13)$$

$$D_B = 2\left(R + r_{py}\right) = \frac{1}{\pi} l_{arc} + 2r_{py} \quad (14)$$

Here, l_{arc} is the length of the arc in the loop **(Figure 46).** Equation (13) indicates that the loop distance in the wale direction of the knitted fabric increases with an increase in loop length and a decrease in the diameter of the plied yarns. It can also be deduced that the dimensional changes in the wale direction are larger than those in the course direction with an increase in l_{arc} and a decrease in r_{py}, as observed from equations (13) and (14), which is consistent with the experimental results **(Figure 36).** Moreover, the porosity of the knitted fabric can be expressed as

$$\zeta = 1 - \frac{V_{p\text{-}yarn}}{V_{Fabric}} = 1 - \frac{\pi l_{loop} r^2}{D_A D_B t}, \quad (15)$$

where l_{loop} is the length of the entire knitted loop in a unit. Assuming the fabric thickness to be $t \approx 2.5d = 5r_{py}$ and $l_{loop} \approx 8R + 4r_{py}$ for similarity, we obtain

$$\zeta = 1 - \frac{8\pi}{5\delta - 60/\delta - 20}, \text{ where } \delta = \frac{l_{loop}}{d_{py}}. \quad (16)$$

Here, δ denotes the linear modulus of the stitch of the knitted fabric, which expresses the density of the knitted fabric. As can be seen from equation (16), the porosity of the knitted fabric increases with increasing loop length and decreasing diameter of the plied yarn. This in turn increased the linear stitch modulus of the knitted fabric, which indicates a loose structure. The results of theoretical calculation are consistent with the experimental results, that is, air permeability and thermal conductivity increased with an increase in the porosity of the knitted fabric **(Figure 40a and b)**

4.4. Applications

Textiles with dynamic pore opening and adaptive air-trapping ability enable thermoregulation[210]. The water-responsive pore actuation ability of our woolen knitwear arising from the SME opens up a new horizon for the use of woolen apparel as potential personal thermoregulating textiles. **Figure 47a** and **b** show a schematic illustration of the adaptive warming and cooling effects of the 100% woolen knitwear due to the synergistic effect of pore size and shape-changing ability in dry and wet states, respectively. As shown in **Figure 47**, when the fabric becomes wet due to high humidity or sweating, the sleeve opening increases, and upon drying, it returns to its original shape. The sleeve of the apparel is produced by the process shown in **Figure 48**. Hence, the woolen fabric can be used for the production of sustainable thermoregulatory garment, including socks. **Figure 49** shows a digital image of the application of our woolen knitwear in adaptive ventilation management.

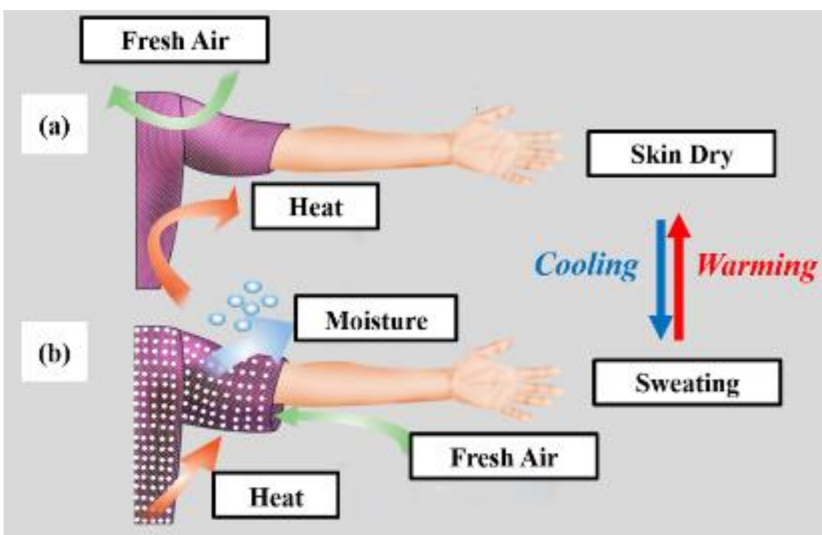


Figure 47 Proposed application of water-actuating woolen knitwear: (a) Warming effect on dry skin and **(b)** cooling effect upon sweating

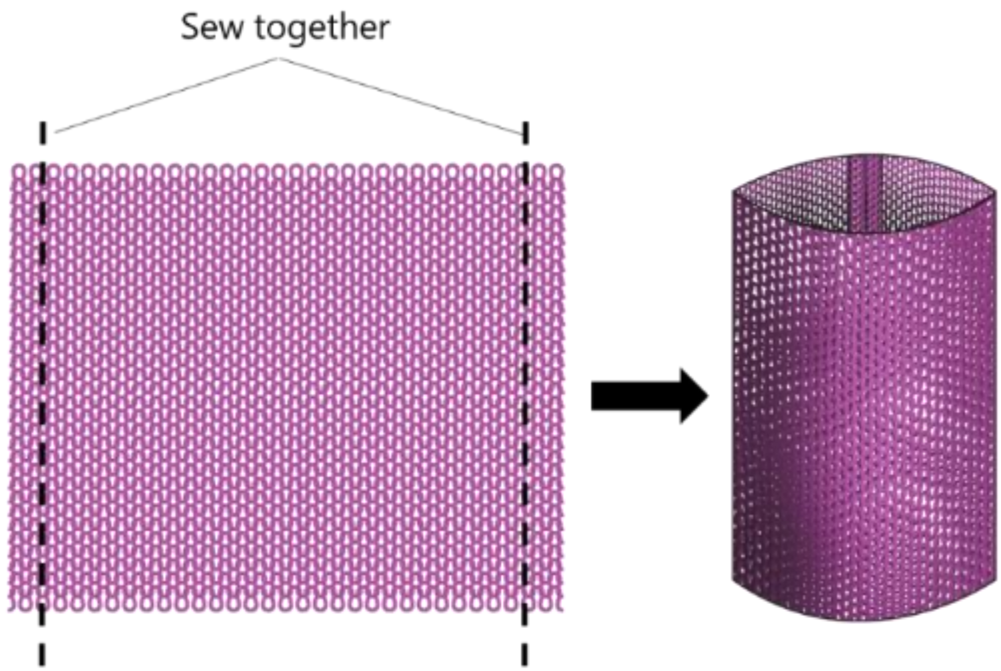


Figure 48 Schematic of the fabrication process of woolen knitwear for application as thermoregulating garment

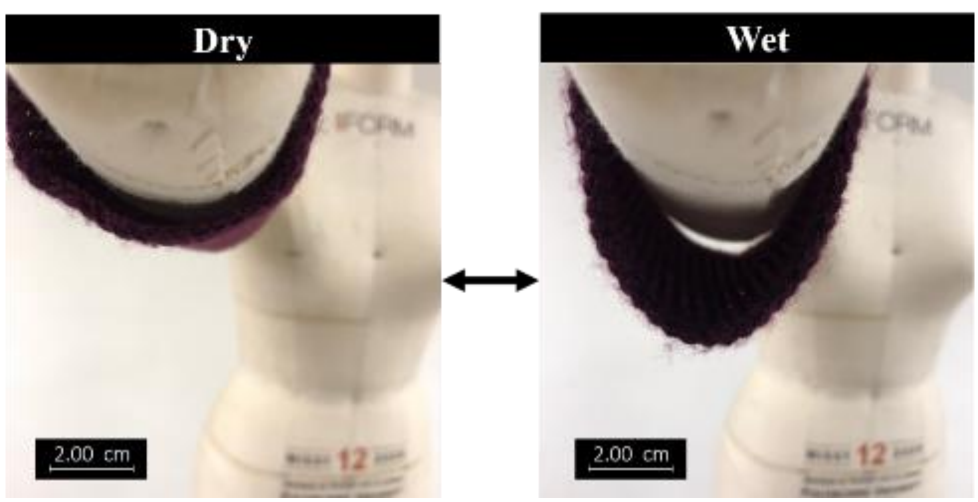


Figure 49 Digital images of application of water-gradient-responsive woolen knitwear: adaptive ventilation management in dry and wet states.

4.5. Summary

As a second skin of the human body, clothing offers protection, aesthetic quality, and courtesy. Because of the inability of materials to adapt to different weather conditions, different clothing is required for different seasons, namely, thin and open garments for summer, thick and closed ones for winter. Moreover, our body maintains its internal core temperature (37 °C) through sweating and shivering. Herein, we report a discovery that is contrary to available public and professional knowledge, that is, woolen knitwear can provide not only warmth, but also a cooling sensation when a body sweat. The fascinating water-responsive pore size change of the knit pores keeps the skin dry, thus helping to maintain a constant body temperature, providing comfort and safety.

Chapter 5 Knit Architecture for Water-Actuating Woolen Knitwear and Its Personalized Thermal Management

5.1Research Highlights

- Manufacturing of smart woolen structures with excellent cooling properties links to certain parameters such as a change in a loop formation, loop shape, and yarn arrangement upon stimulation of body fluid.
- Herein, textile knit structures with different physical and mechanical properties have been prepared using water-responsive descaled wool fibers and their smart heat and moisture regulation behaviour have been investigated and compared to detect the fabric architectural effect on water-actuation and cooling performance of the woolen garment.
- Unbalanced structure controls fast heat and mass transfer from the human body which may offer a promising year-round clothing material to the wearer.

Related Publication

1. **Mohammad Irfan Iqbal,** Fengxin Sun, Bin Fei, Qingyou Xia, Xin Wang, and Hu, Jinlian*. "Knit Architecture for Water-Actuating Woolen Knitwear and Its Personalized Thermal Management." ACS Applied Materials & Interfaces 13.5 (2021): 6298-6308.

5.2 Introduction

Personalized thermal management (PTM) clothing has made a significant contribution to health care textiles by maintaining thermal stress of human being round the year. It can provide a year-round thermoregulation fabric with a cost-effective manner by maintaining the core body heat of human beings[209]. The human body is a system that works best at a certain range of core temperature for instance, $(37\pm0.5)^{o}$ C which is influenced by the clothing micro and macro environments[80]. To maintain this core temperature, the balance between heat generation and heat loss to the environment is vital for survival. Changes in core body temperature may have a serious effect on daily human life and can lead to sickness[211]. It has been observed that the variation in ±7°C core temperature could be a cause of death[17]. Therefore, PTM clothing has made a profound contribution to health care textiles as well as smart textiles industry. Numerous materials and approaches such as phase-change materials[74-77, 212], shape-memory polymers[82, 182, 213], smart membranes [214-216], smart coating [217], smart spider silk[218], IR responsive materials[23, 188], nanoporous polyethylene[97, 98, 187], living organisms[196], conductive polymers[100, 101], bifacial fabric[219] and wearable devices[102, 103, 193] have been developed to fabricate textiles with personal thermal management ability. However, the limitations of most of the materials are the slower response time, harmful to nature, complex processability, and high cost, which confine their applications in industrial scale.

A reasonable approach to tackle this issue could be to apply mechanically engineered responsive textile fibrous materials. By far, only a few attempts have been successfully carried out and proposed to develop comfort textiles using responsive engineered textile fibers and structures. In brief, by imposing more versatile bicomponent structure techniques, a triacetate-cellulose side-by-side structure along with CNT coating fibers has been developed that can successfully modulate

IR heat transmission through the fabricated textiles[23]. However, the use of CNT on textiles could lead to a serious health hazard via organic human cells damage[220]. Furthermore, a bilayer knitted structure consisting of hydrophobic porous polyester fibers and hydrophilic cellulose fibers has been fabricated that can allow higher water vapour and IR transmission with a change in environmental condition[221]. Besides these, it has been noted that the cooling performance of this kind of fabric exceeds 105% higher than the conventional cotton textiles, which makes it ideal for manufacturing thermoregulatory apparel. Personalized Cooling textiles using moisture driven silk fibers and mechanically engineered silk yarns has recently been reported that can show excellent actuation performance upon body sweat because of their change in chemical nature along with physical structural change[113]. Natural fibre based moisture responsive artificial muscles using cotton, wool and flax have also been investigated and proposed to apply in smart textiles for developing personal cooling textiles[4, 202, 222, 223]. It has been concluded that the anisotropic property of natural fibers due to their intrinsic chemical and physical nature provides contractile motion stimulated by moisture that may help to develop textile structures with active cooling performance. These studies demonstrate the potential use of mechanically engineered textile structure on smart comfort behaviour for personalized thermal management garment.

Wool is a keratinous hierarchical biopolymer animal hair [107]. The moisture absorption ability of animal hairs is usually greater than the traditional natural fibers such as β-folded protein and cellulose because of the existence of a large number of water-absorbing groups within the chemical structure.[111] It has also been noted that wool generates a certain amount of heat when it is wet. Hence, it is mainly considered for natural warmth and thermal insulator. Because of this, wool is suitable for clothing particularly used for keeping the body warm and hence losing its demand in the global fibre market every year[108]. Nevertheless, the heats of wool wetting decrease to zero at saturation regain of wool (16%)[224]. Interestingly, the influence of hierarchical structure, for instance, cuticle, ortho and paracortex of animal hairs on water absorption property of hair fibers have been noted[225]. The presence of fatty acid layer along with scales in the outer surface of wool cuticle layers creates a hydrophobic and rough surface which may prevent maximum sweat/water absorption. Moreover, overlying scales with sharp edges point to the tip of fiber which is responsible for the high shrinkage of the wool garment during the wetting process. As a result, a lock-like structure has been noted causing irreversible felting shrinkage with zero shape memory behavior[226]. Therefore, it is a great need to obtain descaled wool fibers for applications in shape memory garment.

In a physical investigation of water interaction with wool, the wool fibre displayed neglected longitudinal swelling (1.2%) and significant diametral swelling (16%) over a similar change of moisture content from dry to wet[227]. Hence, considering the chemical interaction between water molecules and animal hairs consequently showing the shape memory effect and this leads to many researcher's attention towards rediscovering the wool biopolymer as a smart material. The presence of α-keratin biopolymers plays a significant role in water stimulated shape memory effect of animal hairs. It is a hygro-responsive polymer and because of that, the fibre can back to its initial shape from a deformed shape without any external force[110]. The hierarchical biopolymer hair material consists of crystals, hydrogen (HB) and disulfide (DB) bonds among its intra- and inter-macromolecules. Due to these chemical structural features, animal hairs from sheep, goat and camel can show smart functions[107]. Moreover, the shape memory ability of these responsive materials has been discussed and analyzed extensively. It has been demonstrated that the camel hair has shape memory effect upon heat, water, redox agent and UV-light stimulation [111]. The dimensional changes of the hydrogel-coated wool yarns at wet and dry state have also been studied.

It has been reported that the length of hydrogel-coated wool yarns varied in the presence of water and, once dried, elongated again[112]. Moreover, in a recent study, it has been proposed that animal hair wool could be a smart natural fibre that can provide a single cloth which works for both hot and cold weather[211]. However, most of the research up to now focus on to reveal the smart function of textile material using animal hairs like wool. The effects of material architecture on the smart function of wool hair have not been investigated yet. Therefore, in-depth investigation on fabric stage using various fabric architecture such as a change in a loop formation, loop shape and yarn arrangement on switching point of fabric shape transformation is required.

Herein, we fabricate four different knitted structure such as single jersey, tuck knit, miss knit, and double knit having balanced and unbalanced loop arrangement using smart wool fibre that has water responsive pore actuation ability. The cooling performance of these knitted structures has also been reported and their heat and mass transfer properties are compared. The plain knitted structure provides higher pore actuation and cooling performance than double knit structure consequently exhibiting excellent shape transformation ability with the advantages of higher cooling performance **(see Figure 50)**

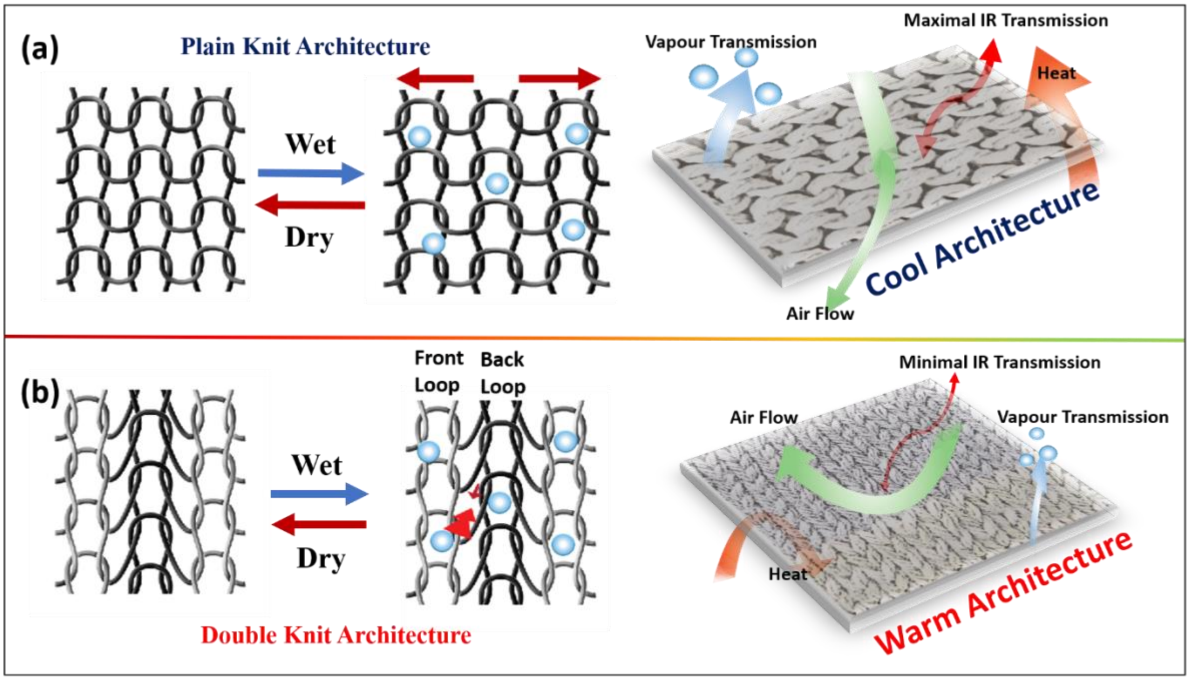


Figure 50 Influence of knit architecture on water-actuation of woolen knitwear: (a) Plain architecture provides maximal cooling (b) Double knit architecture provides minimal cooling

5.3. Results and Discussion

5.3.1 Shape Memory Performance

The presence of fatty acid layer along with scales in the outer surface of wool cuticle layers creates a hydrophobic and rough surface which may prevent maximum sweat/water absorption. Moreover, overlying scales with sharp edges point to the tip of fiber which is responsible for the high shrinkage of the wool garment during the wetting process. As a result, a lock-like structure has been noted causing irreversible felting shrinkage with zero shape memory behaviour. Therefore, it is of great need to obtain descaled wool fibers for the fabrication of garment with shape memory effect. Therefore, 100% raw wool fibers **(see Figure 51a)** were descaled **(see Figure 51b)** using chlorine to enhance their water responsiveness. Chlorination, one of the most traditional and widely used approaches for wool descaling. An optimum process parameter was followed to control the degree of removal of scales with minimal damage of structure[180]. In brief, the scaled fibers were treated in an ultrasonic bath (35 kHz, 40 W) containing sodium hypochlorite (5 g/l), hydrochloric acid (1 g/l), and nano-calcium carbonate (10 g/l) at 37 °C for 45 min. To characterize the effect of the descaling process on the mechanical property of fibers the tensile stress-strain curve for both pristine and descaled wool has been obtained **(see Figure 19).** There is a decrease in stress for descaled wool has been identified which may be caused due to the reduction of the excess fatty layer from the fibre surface. Nevertheless, the decreasing trend is not significant which makes the descaled fibers ideal for subsequent processing.

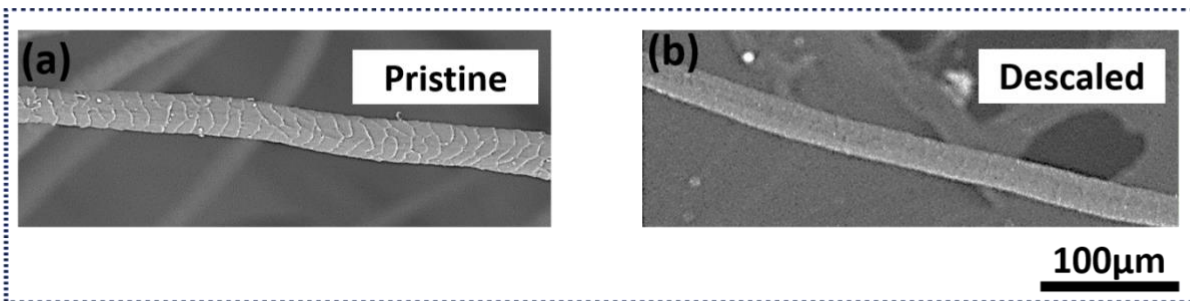


Figure 51 SEM images of (a) Pristine (b) Descaled wool fibre

The water responsive shape memory performance of descaled wool fibre used for fabrication of knitwear in this study has been demonstrated in **Figure 52a.** It has been observed that the descaled wool fibers exhibit significant shape memory properties with 70% shape fixity, and 80% shape recovery **(see Figure 52b).** Because of the fibre water-sensitive shape memory effect, the yarn can provide smart behaviour such as shape change and water actuation effect through deformation of length and diameter **(see Figure 52c).** It has been noted that the dimensions of as-prepared yarns such as length and diameter using these fibers show notable shape memory effect in response to water for 50 consecutive cycles **(see Figure 52d).** Therefore, this study confirms that the shape memory behaviour of wool yarn is associated with fibers shape change during hydration and dehydration process which predominantly depends on intermolecular vibration and fibre mechanical property[211].

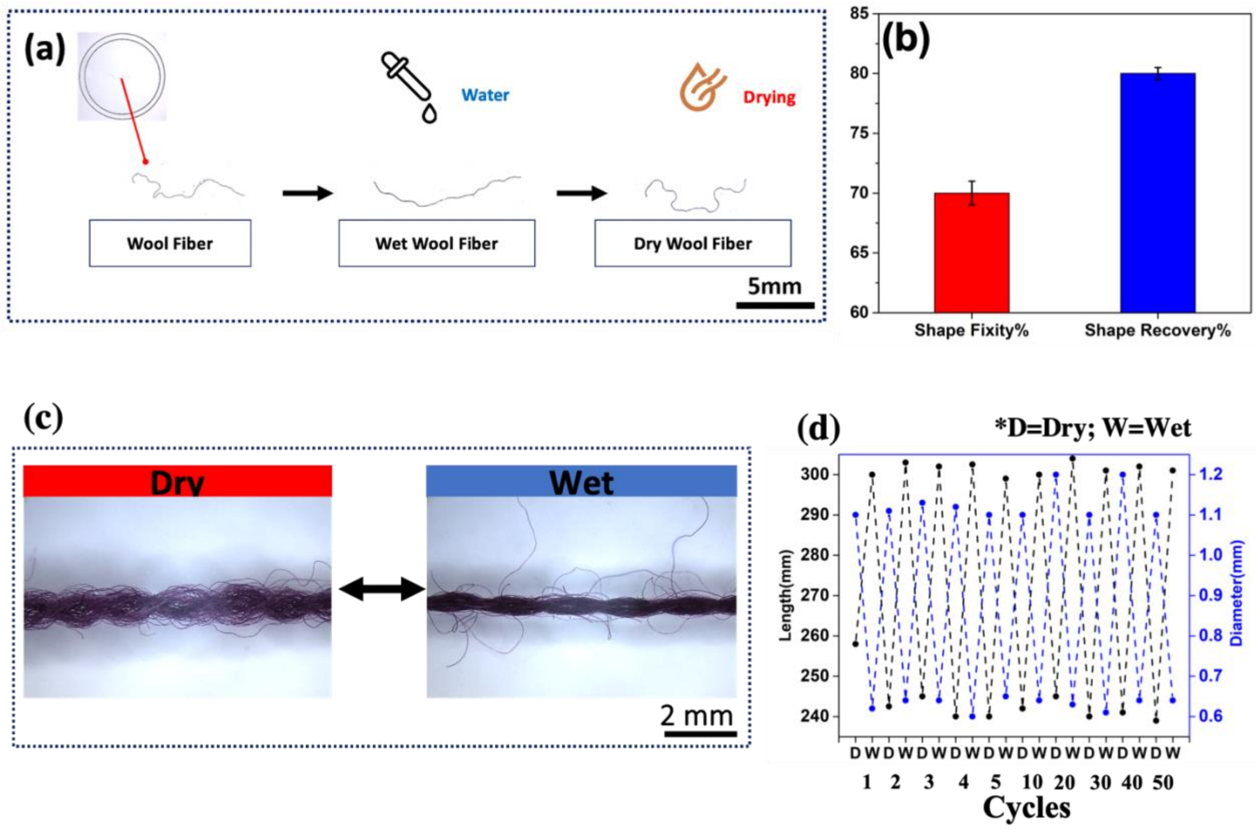


Figure 52 Shape memory performance (a) Light microscope images of descaled wool fibre at dry and wet state (b) Shape fixity and shape recovery ratio of wool fibre (c) Light microscope images of woolen yarn at dry and wet state and (d) Longitudinal & diameter shape change of woolen yarn over 50 cycles

On account of the structural transformation of yarns, the structure of the relevant fabrics would be influenced significantly, which could be appraised by the characterization of fabric area changes. The shape-shifting effect of fabric area due to fibre and yarn shape memory effect for 50 consecutive cycles has been noticed in **Figure 53.** As depicted in **Figure 53,** area changes of as-prepared four different kinds of fabrics revealed that fabric architectural properties are a considerable factor in the practical application of smart yarn and fibre. It has been noted that the woolen knitwear of S1, S2 and S3 showed an almost similar trend of shape-shifting behaviours whereas S4 exhibits poor shape memory response in comparison with those samples. Based on this, to understand the theory of the influence of knit architecture on water actuation and thermal management properties the following study would be carried out in the structure with maximum shape memory effect (S1) with the structure of minimum shape memory response (S4).

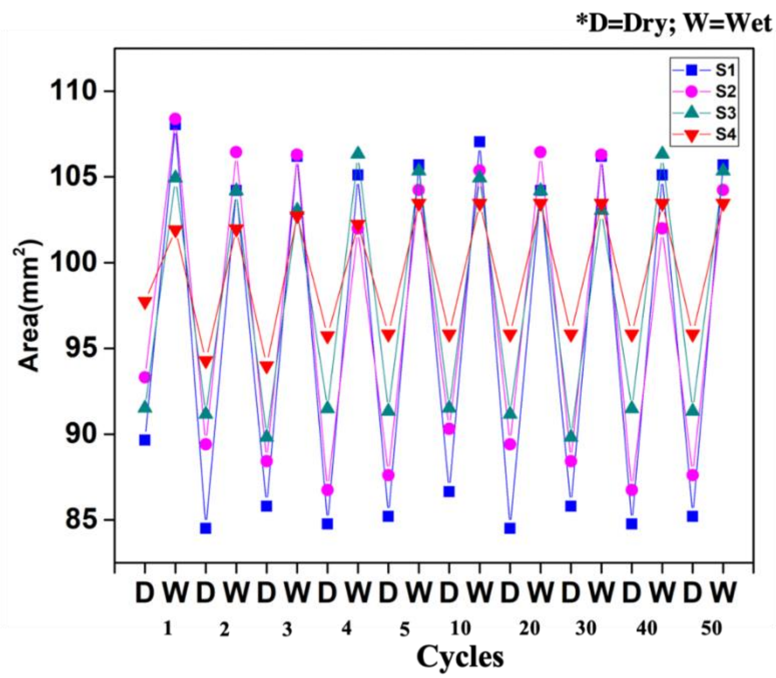


Figure 53 Shape memory performance: Area changes of four as-prepared woolen knitwear over 50 cycles

5.3.2 Water Actuation Performance

In this study, we have observed after completion of full wool-water interaction the maximum pore opening effect is achieved for both the fabrics over a time scale 120 seconds. However, it has been noted from **Figure 54** that S1 has excellent water actuation effect with an increase in water absorption percentage. It may be attributed to a varying degree of structure shifting behaviour exhibited by both as-prepared fabrics after various degree of water stimulation.

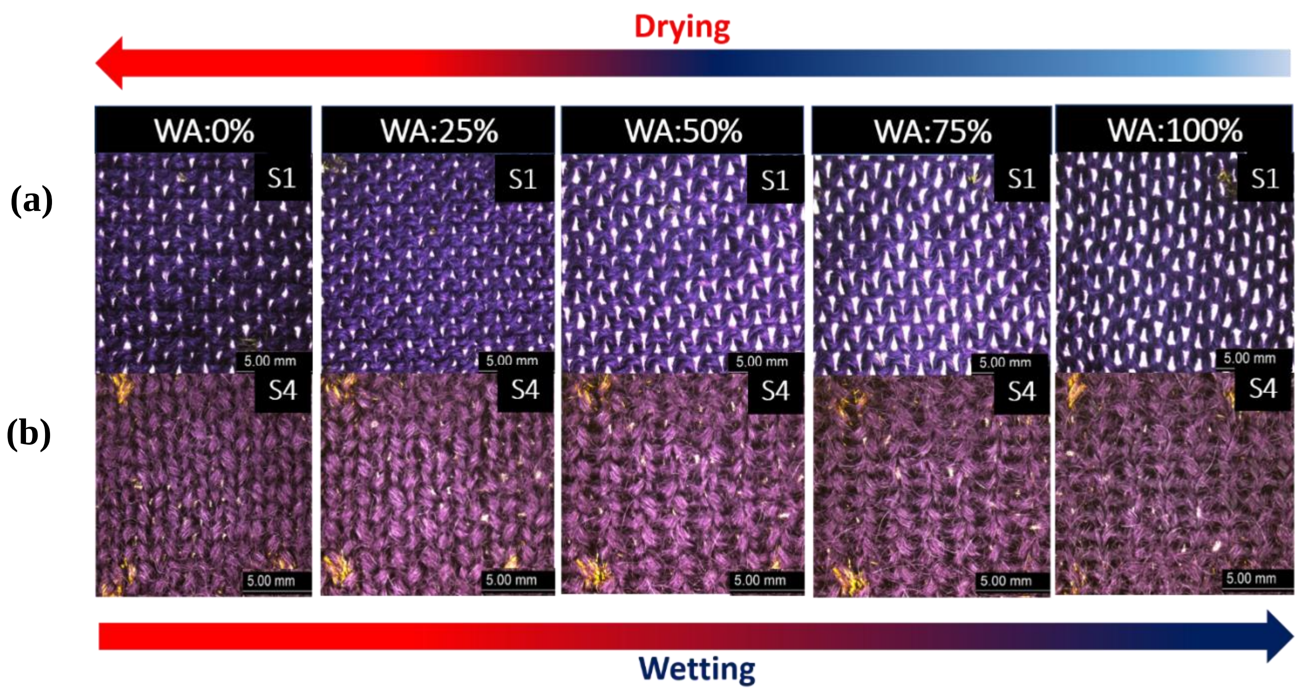
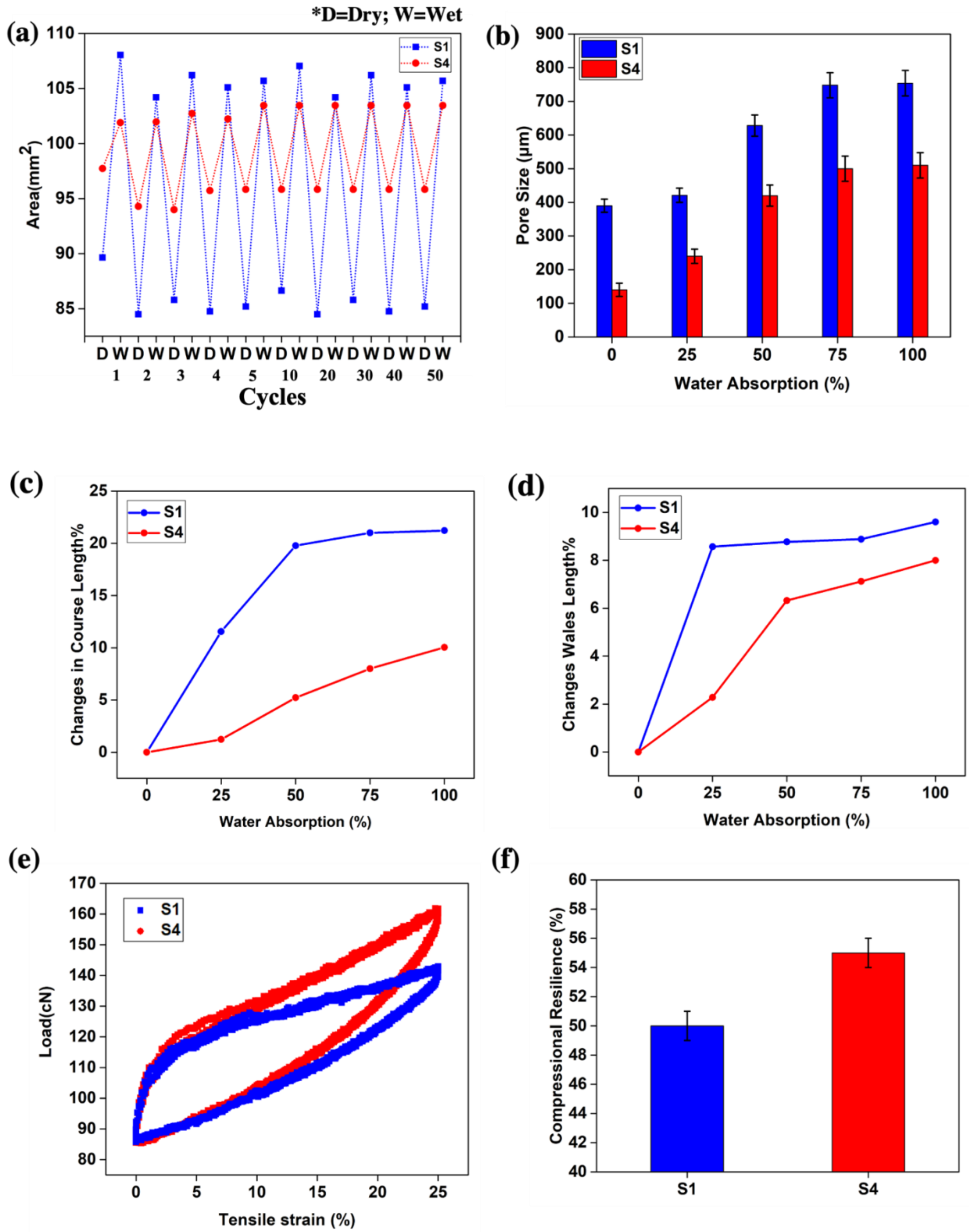


Figure 54 Light microscopic images of the studied fabric (a) Single Jersey(S1) and (b) Double Knit(S2) at different water absorption%.

It can be observed from **Figure 55a** that for both the knit structure arrangements, the tested samples have shape changes and recovery phenomenon. However, S1 has shown significantly higher area changes with recovery behaviour. In contrast, S4 shows lower area changes and recovery responses. The changes in the area with stimulation of different degree of water is a significant factor, which would be dramatically influenced the changes in pore size over time **(see Figure**

55b). These results are likely to be related to the fabric technical structure. It has been further observed that for sample S4 there is a negligible change in length in both direction course-wise and wales wise **(see Figure 55c and d).** The sample S4 requires higher mechanical force for a certain strain% (25) than S1 in terms of tensile load **(Figure 55e).** For low-stress mechanical properties, the S4 showed higher compressional resilience **(Figure 55f)** with high bending **(Figure 55g)** and shear rigidity **(Figure 55h)** subsequently providing lower shape change and shape-shifting performance. This situation can be further explained by the number of fibers in the fabric structure. The number of fibers in the unit area increases, the loop shape changes and recovery decreases as the cohesive force increases between each fibre consequently improving fabric stability and reduces elasticity in a width direction. It can thus be suggested that fabrics with a higher density such as S4 **(Figure 56i)** have a lower and irregular pattern of shape change and recovery behaviour along with lower pore opening effect.


*D=Dry; W=Wet
(a)
Area(mm^2)
S1
S4
D W D W D W D W D W D W D W D W D W D W
1 2 3 4 5 10 20 30 40 50
Cycles
(b)
Pore Size (µm)
Water Absorption (%)
(c)
Changes in Course Length%
Water Absorption (%)
(d)
Changes Wales Length%
Water Absorption (%)
(e)
Load(cN)
Tensile strain (%)
(f)
Compressional Resilience (%)

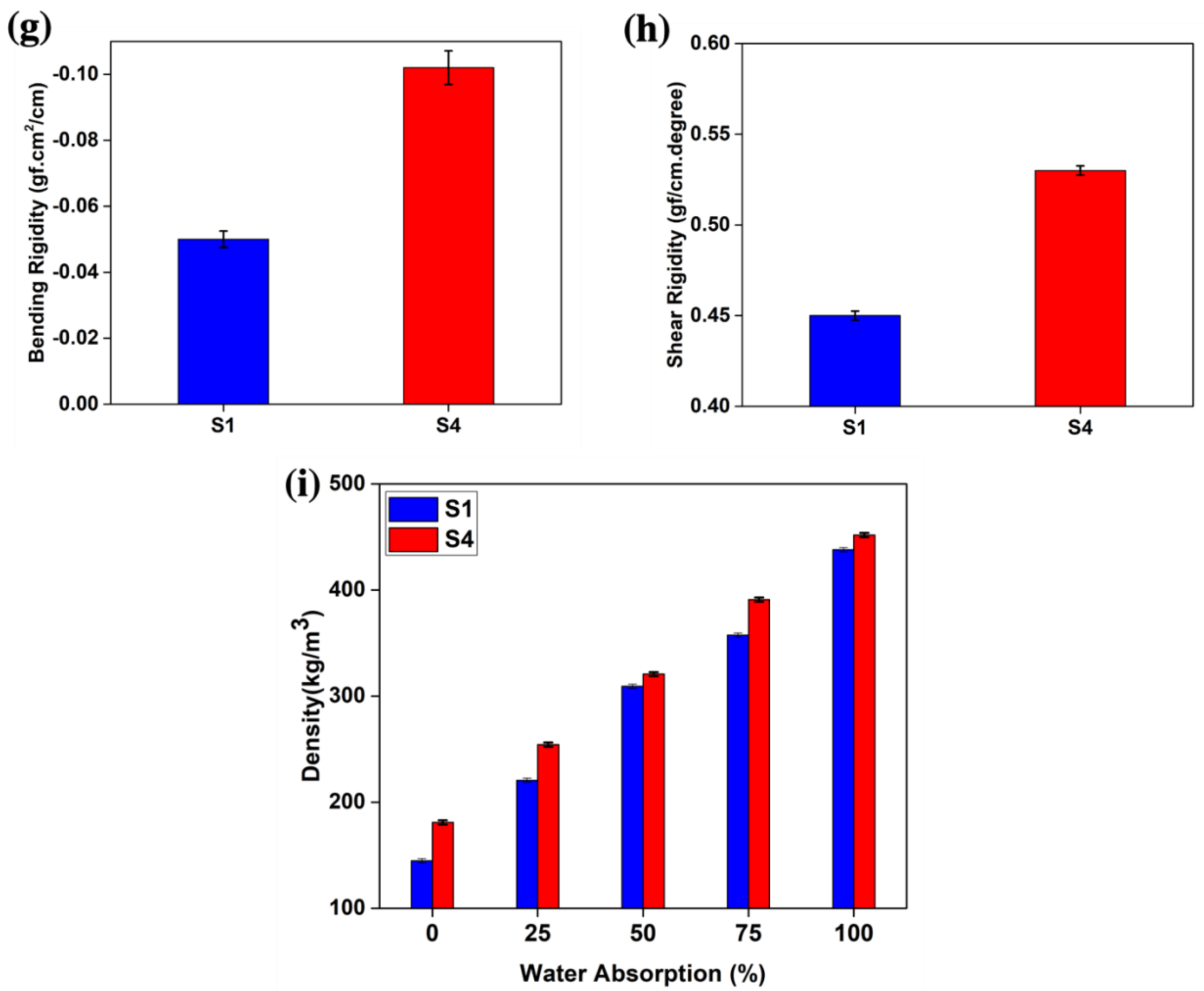
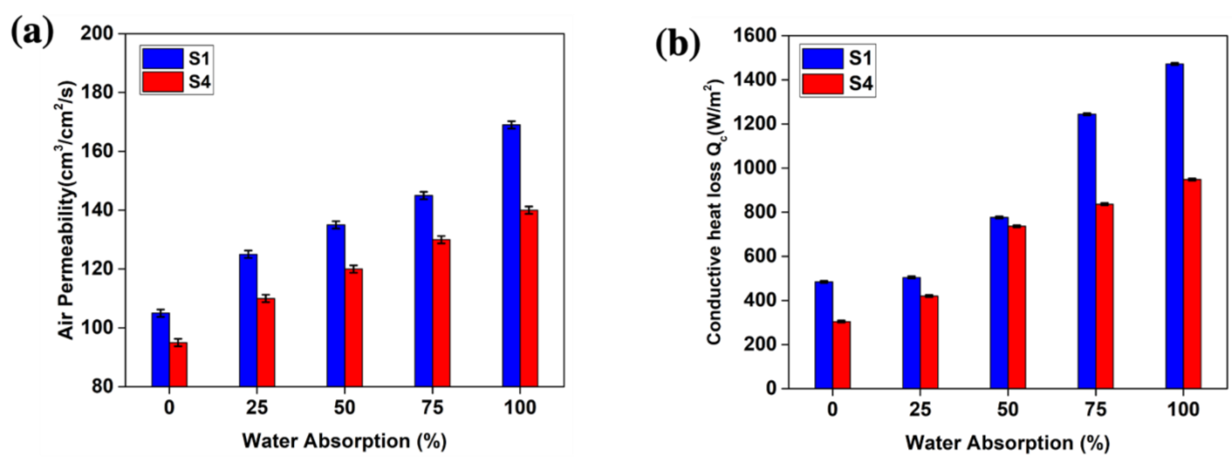


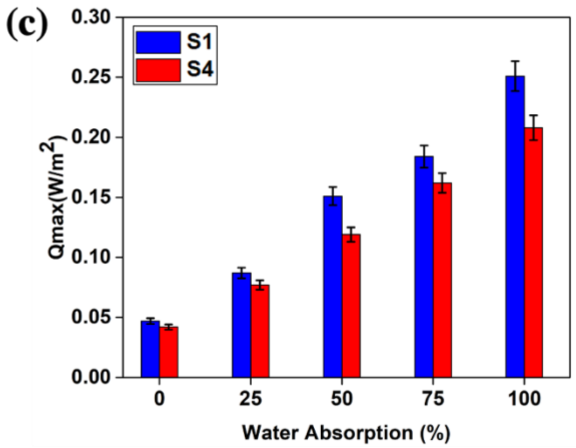
Figure 55 Physical properties of woolen knitwear (a) Area changes at dry and wet condition over 50 cycles (b) Pore size changes at various degree of water absorption; Changes in length (c) Course direction and (d) Wales direction; Mechanical properties (e) Tensile load (f) Compressional resilience (g) Bending rigidity and (h) Shear rigidity of S1 and S4 as prepared fabrics; (i) The density of as prepared S1 and S4 fabric at various water absorption%

5.3.3 Thermal Management

To show the realization of water actuated knit architecture effect on thermal comfort property, the comfort management properties of as-prepared S1 and S4 fabric have been conducted. **Figure 56a** provides the experimental data on air permeability for both the woolen knitwear at various degree of water absorption such as 0,25,50,75 and 100%. In this figure, there is a clear trend that the air permeability of fabric increases with an increase in water absorption level. However, for sample S4 the increase in air permeability detected experimentally is lower than the S1 sample when water absorption percentage increased from 0% to 100%. This situation is explained by the percentage of sample area and pore size change over a different degree of water absorption as shown in **Figure 55a and b.** It can be seen from this figure that the change in area for the sample S4 is lower than the S1. Hence, the increase in air permeability value of S4 is limited upon water stimulation and is most probably a consequence of the lower pore size properties within the fabrics.

The terms conductive heat loss (Q_c) and Q-max have been used to measure heat transferability and a surface instant warm/ cool feeling during skin interaction with the material due to heat conduction. The measured conductive heat loss and Q-max of S1 and S4 knitted structures in terms of percentage increase of water are shown in **Figure 56b and c** respectively. It is apparent from the figure that there is a significant positive correlation between water content, conductive heat loss (Q_c) and Q-max of the fabrics. Another important finding is that the fabric structures do influence in terms of heat transfer through the fabric. According to **Figure 56b,** the percentage increase of heat loss at different degree of water absorption level is significantly higher for both of the fabrics. These results can be explained by the amount of water in the fabric structures. The thermal conductivity of water is higher, leading to higher heat loss in fabrics with a high degree of hydration level[211]. Moreover, the heat loss by conduction at different degree of water absorption level for single jersey structures is significantly higher than the double knit. The key factor which contributes to heat loss with a constant temperature difference is heat flux. Based on previous researches, denser fabric provides lower heat flux[228]. So double knit fabrics **(See Figure 55i)** which have higher density have a lower heat flux. Hence, the heat loss for conduction is lower for S4 at various degree of water absorption. Furthermore, in line with the heat loss by conduction, the overall Q-max value recorded for Sample S1 was higher than the sample S2 in different degree of hydration state **(Figure 56c).** The observed increase in Q-max for sample S1 could be attributed to the surface roughness of the tested samples. It has been observed from **Figure 56d**, the geometrical surface roughness of the sample S1 is lower. As a result, it provides a smoother hand feel and a higher cool touch sensation than the sample S4. These results are in good agreement with recent studies indicating that there is a strong relationship between Q-max and fabric surface roughness [229].





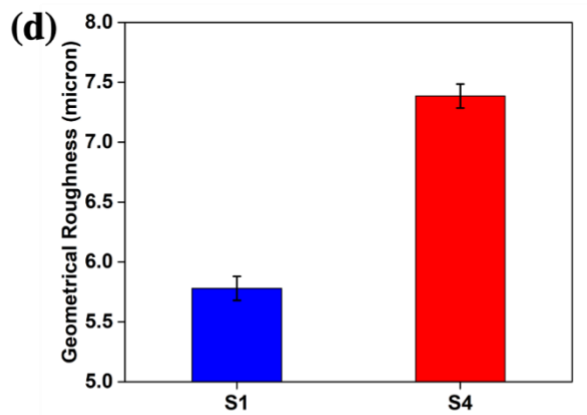


Figure 56 Thermal management investigation of water actuated different woolen knit architecture (a) Air permeability (b) Conductive heat loss (c) Q-max Value and (d) Geometrical roughness

To further provide insights into the radiative heat dissipation ability of the samples, thermal images of dry and wet wool knitted fabrics under a steady-state using a closed heat source are shown and compared in **Figure 57a**for both the architecture. Furthermore, the surface temperatures of the samples in both dry and wet conditions are recorded and illustrated in **Figure 57b**. As displayed in the figure the surface temperature in the wet state increased for both the structure, suggesting higher radiative heat dissipation capacity compared to a dry state. However, it can be seen radiative heat loss capacity of lighter fabric S1 **(Table 3)** is higher than the S2 in both dry and wet condition. Because of this excellent IR heat transfer ability of S1 samples, it can provide maximum cooling performance than S2 samples. These findings are consistent with the current understanding of the effect of thickness on fabric IR heat transmittance property, as it is generally acknowledged that thicker fabrics are most resistant to IR heat transmission[230].

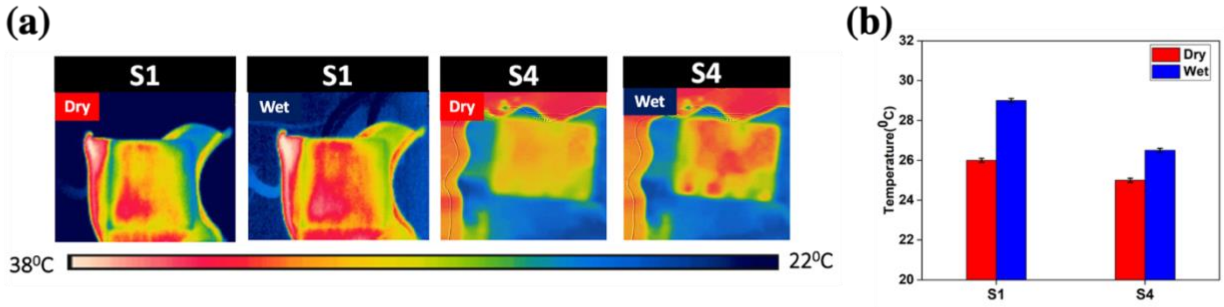


Figure 57 Thermal management investigation of water actuated different woolen knit architecture (a) Q-max Value and (b) Variation in surface temperature

For the sake of in-depth investigation into the mass transferability of both the architecture, the water vapour transport; evaporation and wicking performance were measured. The results of WVTR gave an idea about the possibility of obtaining smart vapour transmission changing according to both temperature and moisture/water. It has been noted from **Figure 58a and b** that both the fabrics have temperature and moisture responsiveness. However, S1 had higher water vapour transmission at different water absorption under different environmental temperature than that of double knit structure S4. In compared to environmental temperature, the WVTR values of sample S1 found to be significantly higher than S4 at different humidity level. Previous research has established that water vapour transmission was lowest in bulky and hairy fabrics and highest for fabrics with open structures[231]. Hence, the water vapour diffusion rate of sample S1 was the highest because of their maximum pore actuation ability with water gradient compared to double knit structure (S4). However, the WVTR values of both the fabric improved significantly when the ambience had a higher temperature and lower humidity.

Furthermore, wicking and drying rate of fabrics were examined and that is a significant parameter to show how efficiently the body sweat can spread and evaporate quickly. As demonstrated in **Figure 58c and d,** the evaporation rate and wicking distance of sample S1 were much higher, which indicates that S1 exhibits better drying and faster liquid transport property over sample S4. These results are likely to be related to fabric technical architecture. The fibers and yarns in sample S1 and S4 are in differential mechanical stress which could lead to the formation of differential porous structures within the yarn structures of these samples. Hence, they showed different surface wettability and intrinsic liquid transport resistance, which play key roles in the wicking and drying performance of the samples.

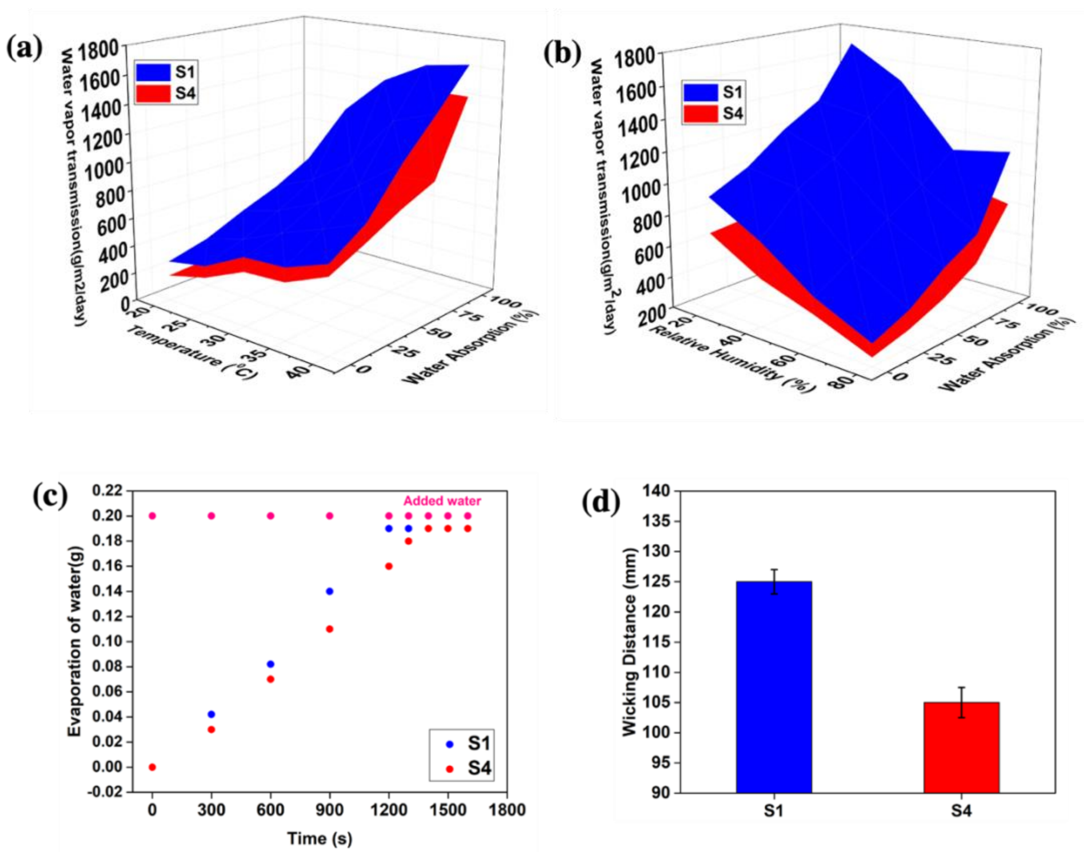


Figure 58 Thermal management investigation of water actuated different woolen knit architecture (a) WVTR values at different temperatures (Environmental humidity: 80%RH);(b) WVTR values at different RH% (Environmental Temp: 25^{0}C); (c) Evaporation of water ;and (d) Wicking distance

5.4 Theoretical Analysis for Tunable Structure Shifting Mechanism

Single wool yarn is generally spun by twisting fascicular sliver of wool fibers to helical structures. Therefore, when the yarn is assumed as an ideal packing structure by ignoring the fibre migration along yarn's radial direction, the diameter $d_{s\text{-}yarn}$ and length $l_{s\text{-}yarn}$ of single yarns can be expressed by equations 1 and 2, respectively based on the spatial geometry relations,

$$d_{s-yarn} = 2 \cdot \max\{r_{fibre}\} = 2 \cdot \max\{\frac{l_{fibre}}{4\pi^2}\kappa\} \quad (1)$$

$$l_{s-yarn} = \frac{l_{fibre}^2}{2\pi}\tau \quad (2)$$

Where r_{fibre} is the radius of the spin of a fibre in a single yarn, κ is the curvature of the fibre with a maximum radius of spin, l_{fibre} denotes the length of the fibre and τ represents the torsion of the fibre. As can be seen, the diameter $d_{s\text{-}yarn}$ and length $l_{s\text{-}yarn}$ of single yarns are mainly determined by the curvature and torsion of fibres. The fibers in the single yarns straighten after wetting, causing the reduction of fibre's curvature, which further reduces the diameter of the single yarn; while the length of single yarns increases with the extending of fibers along the axial direction of the yarn when they are in the wet state.

Two single yarns can be twisted into a plied yarn, and thus the changes of the fibers also contribute to the variation of plied yarns. By expanding the helix along the cylinder generatrix of the single yarn, we can get a hypotenuse by the topological mapping of the helical locus of the central axis of the single yarn **(see Figure 59)**

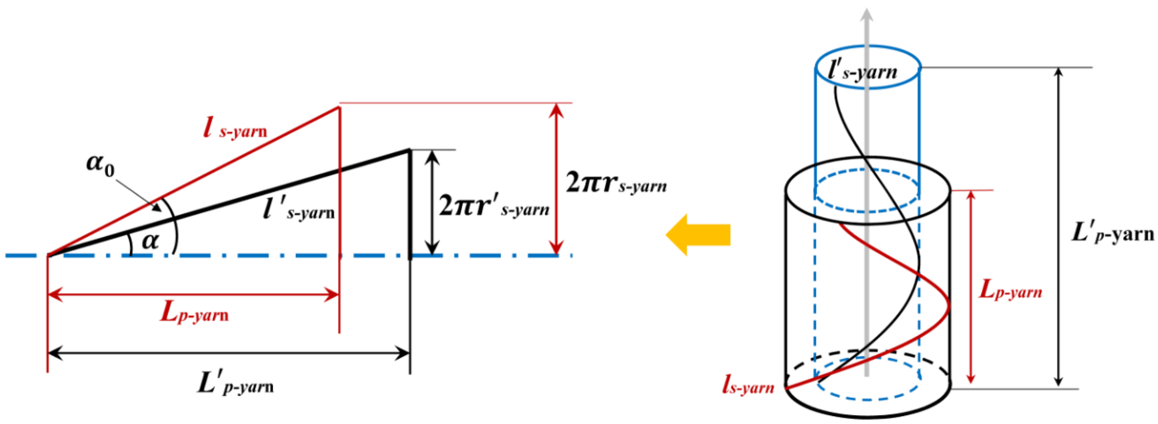


Figure 59 The expanded view of a single yarn before (solid line) and after (dashed line) changes of yarn diameter and length

From the geometry relation in **Figure 60**, the following equation is obtained,

$$l_{s-yarn}^2 = L_{p-yarn}^2 + (2\pi r_{s-yarn})^2 \quad (3)$$

By differentiating equation 3 by $l_{s\text{-}yarn}$, we get,

$$\varepsilon_{ls\text{-}yarn} = \frac{L_{p-yarn}^2}{l_{s-yarn}^2}\varepsilon_{lp-yarn} + \frac{(2\pi r_{s-yarn})^2}{l_{s-yarn}^2}\varepsilon_{rs-yarn} \quad (4)$$

Where $\varepsilon_{ls\text{-}yarn}$ represents the strain of length of single yarn; $\varepsilon_{rs-yarn}$ is the strain of diameter of single yarn and $\varepsilon_{lp\text{-}yarn}$ is the strain of length of plied yarn. Rearranging the equation 4, it yields,

$$\varepsilon_{lp\text{-}yarn} = \frac{\varepsilon_{ls-yarn} - \sin^2\alpha_0 \varepsilon_{rs-yarn}}{\cos^2\alpha_0} \quad (5)$$

From equation 5, it shows that the length changes of the plied yarn are mainly associated with the changes in the diameter and length of single yarns. Physically, it proves that the length increases with the increase of the length and the decrease of the diameter of single yarns **(see Figure 5.4c)**

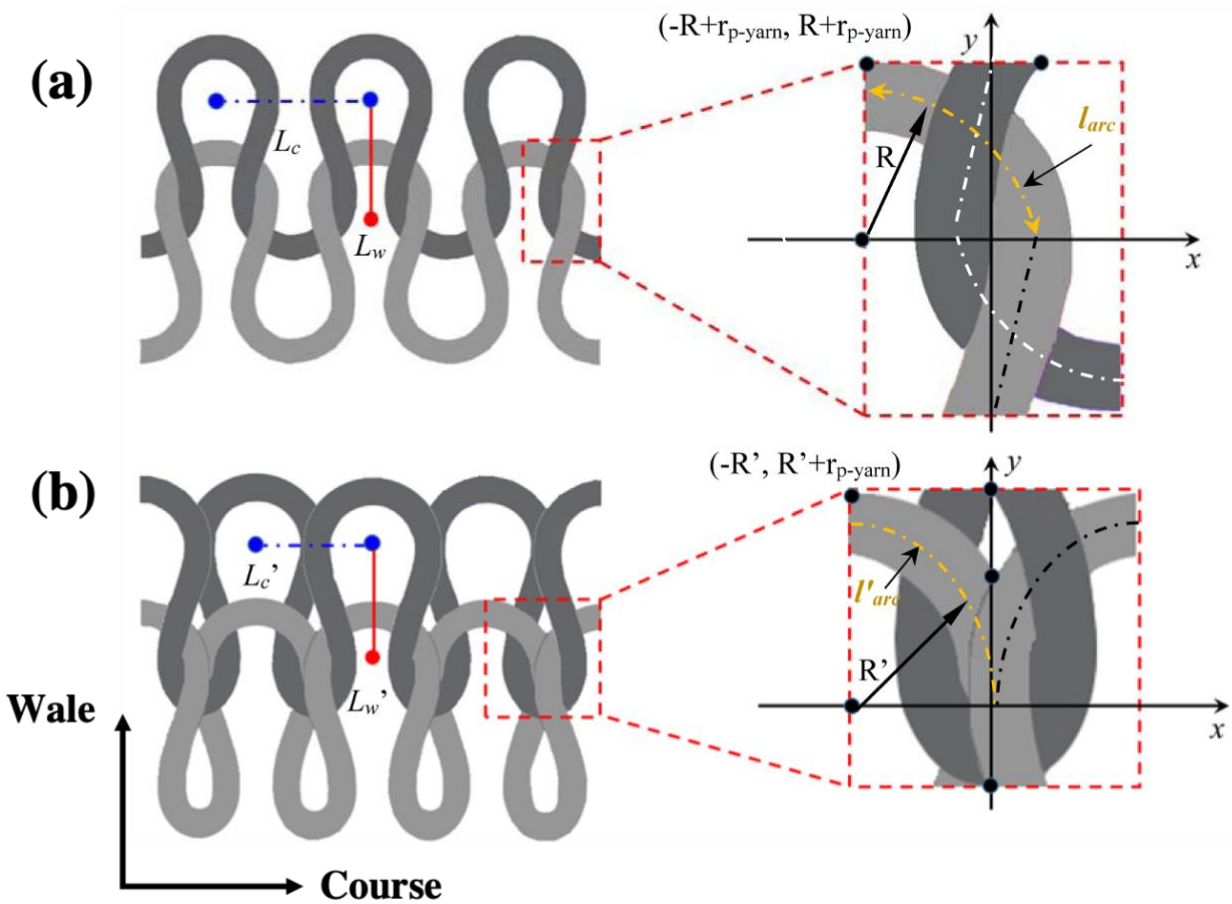


Figure 60 The knitted structures and the enlarged view of a unit for (a) single jersey and (b) double knit

The changes of the plied yarns spontaneously result in a domino effect to induce the changes in the porosity of the wool knitted fabrics. By assuming the single jersey and double knit as the quasi-two-dimensional symmetrical structure, we can get their ideal geometry models as shown in **Figure 60** Quantifying the fabric count through the knitted stitch distance along knitting course direction, leads to equations 6 and 7 for the course loop distances L_c for single jersey and L'_c for double knit as,

$$L_c = \frac{8l_{arc}}{\pi} - 4r_{p-yarn} \quad (6)$$

$$L'_c \leq \frac{4l'_{arc}}{\pi} \quad (7)$$

Where R and R' are the arc radius, and l_{arc} and l'_{arc} are the length of the arc in the loop for the single jersey and double knit, respectively **(see Figure 60)** The L'_c of double knit varies based on the knitting parameters, and here the appearance of double knit in **Figure 60b** shows a typical structure with the adjacent loop intersecting with each other, which occurs as long as the L'_c meet,

$$L'_c = \frac{4l'_{arc}}{\pi} - 2r_{p-yarn} \quad (8)$$

Similarly, the wale loop distance L_w for single jersey and L'_w for double knit can be given as,

$$L_w = \frac{4l_{arc}}{\pi} + 2r_{p-yarn} = \frac{2l_{arc}}{\pi} + 3r_{p-yarn} + (R - r_{p-yarn}) \quad (9)$$

$$L'_w = \frac{2l'_{arc}}{\pi} + 3r_{p-yarn} \quad (10)$$

Since the radius of the loop must be larger than the radius of the yarn, that is $R > r_{p\text{-}yarn}$, it follows from equations 6 to 8, and equations 9 and 10 that $L_c > L'_c$ and $L_w > L'_w$. Therefore, the structure of the double-knit fabrics is more compact than that of single jersey due to the overlap of the adjacent front and back loops. By differentiating equations 6 and 8 and equations 9 and 10 by $r_{p\text{-}yarn}$ and assuming a reasonable small difference in the length of the arc of the two structures, we get,

$$\frac{\partial L_c}{\partial r_{p-yarn}} = 2\frac{\partial L'_c}{\partial r_{p-yarn}} \quad (11)$$

$$\frac{\partial L_w}{\partial r_{p-yarn}} = \frac{\partial L'_w}{\partial r_{p-yarn}} + \frac{\partial (R - r_{p-yarn})}{\partial r_{p-yarn}} \quad (12)$$

Here $R - r_{p-yarn}$ is the radius of the pore in a knitting unit. Physically, the pore must become larger when the coverage (the volume of knitting yarn in this structure) gets smaller in a given area, so the term $\partial(R - r_{p-yarn})/\partial r_{p-yarn} > 0$. Therefore, it can be induced from the equations 11 and 12 that the dimensional area changes in the single jersey are larger than those of the double knit when the fabrics get wet, which is consistent with the experimental results, that is, the single jersey has better thermoregulation effect compared to double knit. Moreover, the pore size of the fabric can be expressed by the uncovering ratio of yarns in knitting fabrics as,

$$\delta = \frac{l_{loop}}{2r_{p-yarn}} \quad (10)$$

Here $l_{loop}^2 \propto L_c L_w$ from the previous study[232]. Thus, the uncovering ratio of the single jersey is higher than that of double knit. In other words, there is small pore size in the double knit structure, which can be explained that there is the existence of higher overlaps of loops in the double knitted fabrics, and thus the structure is considered thicker than single jersey. Therefore, the single jersey with regular and light structures would be more suitable for manufacturing the knitted fabrics with proposed shape memory function for personalized thermal management.

5.5. Summary

Personalized thermal management using water-actuated woolen knitwear has great potential for smart textile production. However, woolen knitwear exists in a wide range of forms with different derivatives. Manufacturing of smart woolen structures with excellent cooling properties links to certain parameters such as a change in a loop formation, loop shape, and yarn arrangement upon stimulation of body fluid. To address this issue, textile knit structures with different physical and mechanical properties have been prepared using water-responsive descaled wool fibers and their smart heat and moisture regulation behaviour have been investigated and compared to detect the fabric architectural effect on water-actuation and cooling performance of the woolen garment. The evidence suggests that the technical structure of the fabrics plays a crucial role in pore actuation and fabric cooling performance. The water-actuation and thermal management ability of single jersey were greatly enhanced because of unbalanced structures with lower mechanical stress among the loops and yarns. The experimental data is also in line with the theoretical analysis. Hence, unbalanced structure controls fast heat and mass transfer from the human body which may offer a promising year-round clothing material to the wearer. This material can give a similar response upon contact with body sweat and the humid environment and hence can act as a skin-like fabric. Their possible application can lie in different fields, such as thermoregulation, functional clothing, sportswear and medical care.

Chapter 6 Woolen Respirators for Thermal Management

6.1 Research Highlights

- Robust respirators using biobased wool fibers for both personal protection and thermal management is achieved
- The effect of moisture responsive wool fibers on the cooling management of respirators is explored
- The contribution of the electret effect on filtration performance is investigated

Related Publication

1. **Mohammad Irfan Iqbal,** Shi Shuo, Jiang Yuenzhang, Bin Fei, Qingyou Xia, Xin Wang, Wenbo Hu and Hu, Jinlian*."Woolen Respirators for Thermal Management" Advanced Materials Technologies 6.6 (2021): 2100201.

6.2 Introduction

The high demand for the personal protective equipment (PPE) to combat with recent COVID-19 pandemic[233], many health care industries rushes to produce PPE, especially respiratory mask as many as possible. It has been suggested that COVID-19 pandemic can under control in a matter of weeks if only everyone would start wearing masks[234]. Respiratory protective masks are usually used to safeguard the public from uncontrollable airborne contaminants from gases, dust, vapours, particulates and aerosols[235]. Therefore, over the time of this COVID-19 outbreak respiratory masks play a vital role in the well-being of medical workers and public[236, 237]. It plays a major role to prevent and lessen the chance of disease transmission from person to person in the form of aerosols or droplets[238-240]

Respiratory masks help to protect the users based on physical, mechanical and sometimes by chemical filtration mechanisms[241, 242]. However, severe life-threatening conditions may happen by the nature of barrier properties to human thermo-physiological performances. The current pandemic situation has stimulated the demand for respiratory masks to new heights. As a result, a variety of fake and claimed functional mask with lower protective efficiency appeared in the market to meet the sudden demand[243, 244]. Most respiratory masks are simple in their appearance and designed to fit a different type of users. However, being simple they can interfere with breathing, thermal balance, tactile sensations, eyesight, communication, psychological feelings, eating, sneezing and other equipment attached to the body[245-247]. This situation is further worsened during, high-intensity work, weather conditions are extremely hot or cold, humid or dry environment, improper fitting, poor ventilation and uncomfortable clothing. However, these problems have been currently identified in masks made only for occupational users. The average time of wearing a mask by the public has increased significantly due to the current pandemic season[248].

The increase in the duration of using a mask every day has led to different kind of problems to its regular users causing discomfort, sickness, allergy, vision issues, accidents, low performance, difficulty in breathing and sometimes even death especially for non-occupational users as suggested by extensive news reports [249-251]. Amid the alarming situation, the effectiveness of commercially available consumer masks in protecting the end-users against various infections along with thermal comfort is yet to be improved.

A human being has two vital respiratory organs: the mouth and the nose. Optimal microclimate outside the mouth in a face mask can avoid allergy, inflammation, suffocation, even mouth diseases due to heat stress, moisture accumulation, bacterial build-up, air resistance and pollution. Effective control of all possible factors must maintain an intact biological metabolism; the thermal equilibrium and mass exchange between macro-and microclimates is essential to ensure physiological comfort and balance. Research indicates that the relationship between filtration efficiency and comfort is complicated[252, 253]. For instance, the tight-fitting N95 respirators have lower breathability and can cause discomfort for extended periods of wear. This study depicted that factors like pressure drop, vapour transmission, the goodness of fit, and lightweight directly affect user comfort.

Many researchers have studied air filtration performance and proposed various promising materials with a high level of particulate matter (PM) capturing efficiency for various applications[254-263]. However, due to the complex relationship between filtration performance and comfort, there is a lack of investigation considering both properties in respirators for personal protection. So far there have been few studies which provide respirators with high filtration efficiency along with considerable thermal comfort performance for individual personal protection. For example, Yang et. al.[26] proposed a dual-mode mask with high filtration performance using fibre/nanoPE for cooling and fibre/Ag/nanoPE for warming; Habchi et. al. [264] suggested to use phase change material (PCM) in face mask to prevent microenvironment heat and mass transfer in the cold season; Nazir et. al.[265] incorporated Polyamide-6 nanoweb to enhance filtration and comfort performance of nonwoven face mask; Ullah et. al.[266] recommended PVDF based reusable and robust with enhanced breathing comfort nanofibrous filtering piece as respirators; Rubino et. al.[267] developed salt-functionalized membrane with high filtration and breathability characteristics; Zhao et. al.[268] fabricated cleanable air filters that can capture $PM_{2.5}$ level particulate matter with a high level of moisture transferability; Liu et. al.[269] reported ultrathin nano network may provide air filters for personal protection with high efficiency and super breathable property; Li et. al. [270] verified electret polyvinylidene fluoride (PVDF) based ultrafine and curly wool-like nanofibers had excellent $PM_{0.3}$ filtration efficiency with low air resistance performance for personal protective respirators. Although all these approaches can provide high filtration with thermo-physiological comfort, however, these approaches have certain limitations such as high cost, non-biodegradable, complex processibility, toxicity, poor heat and mass transfer and poor hand feel.

A solution to this could be to develop biobased respirators with smart cooling function. . It is now well established from various studies that biomaterials are being engineered into smart textiles for functional comfort management. A recently developed moisture induced wearable silk textile is able to demonstrate exceptional actuation efficiency due to a change in its chemistry and structural change during wetting[113]. Biomaterial based moisture sensitive artificial muscles using cotton, wool, and flax were also investigated and proposed to be used in smart textiles to create personal textiles for cooling[4, 202, 222, 223, 271].

Wool is keratinous biopolymer hair[107]. Animal hair's ability to absorb moisture is typically greater than the typical other natural fibers such as β-folded protein and cellulose due to the presence of large numbers of water-absorbing groups within the chemical structure[204]. The hierarchical biopolymer hair substances consist of crystals, hydrogen (HB) and disulphide (DB) bonds among its intra- and inter-macromolecules. Due to these chemical structural features, animal hairs from sheep, goat and camel are able to show smart functions[107].It was also noted that wool produces a certain amount of heat when wet. It is therefore primarily considered for natural warmth. However, the heat of wetting gradually decreases at maximum regain of wool (16%)[224]. Interestingly, in a recent study it has been proposed that wearable woolen knitwear can be cool because of their shape memory performance and may provide thermal balance in both hot and cold environment[272, 273].

Therefore, to overcome the drawbacks of the currently used face mask for thermal management and meet the demands for the sustainable healthcare industry, we designed respirators with smart biobased wool fibers for cooling management **(Figure 61).** This work can foster new ideas of using smart natural fibers in a face mask for personal protection along with thermophysiological comfort.

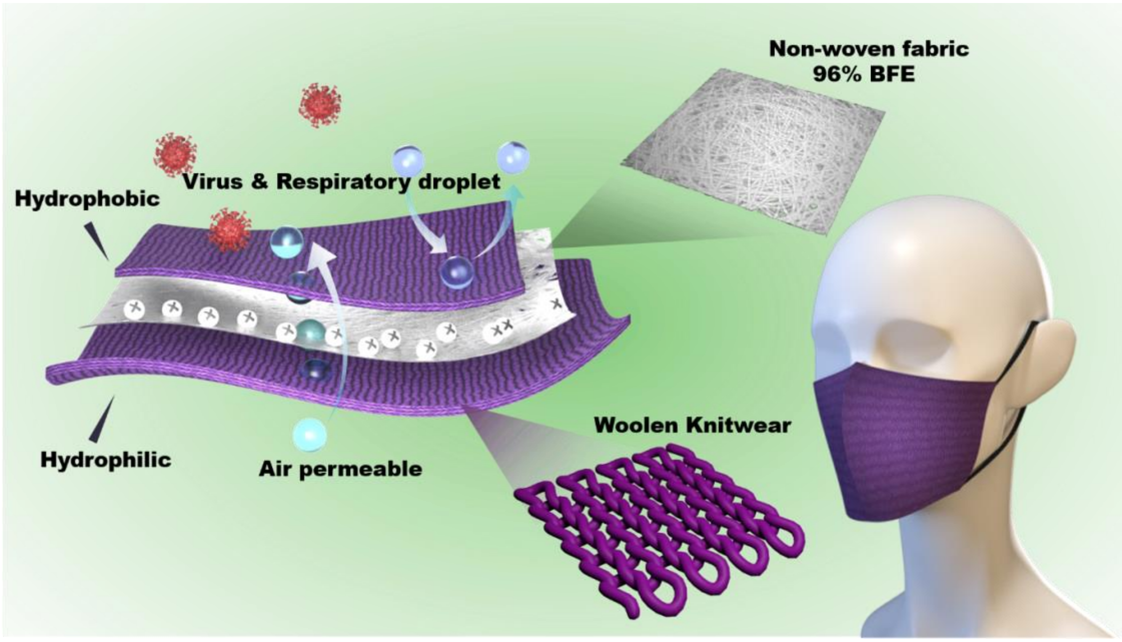


Figure 61 Woolen respirators for thermal management

6.3. Results and Discussion

6.3.1 Morphological and Structural Properties of Polypropylene Fabric

Electrostatic-assisted melt blown nonwovens with an areal density of 30 GSM were produced using a pilot-scale machine. The diameter of the hole was 0.2 mm, and the air plate angle was 60°. **Figure 62a** shows the illustrative SEM images of the as-prepared E-PP fabric. It has been depicted that the collector distance does influence the morphology of the web, which would serve as an important parameter for fibre diameter and pore size distribution. As presented in Figure 63b and c, bar charts of fibre diameter and pore size versus collector distance revealed that with an increase in collector distance up to a certain level the diameter of fibers and pore size decreased. It is fascinating to observe that the collector distance up to 15 cm, there is a formation of large beads with an uneven surface structure **(Figure 62a).** However, the surface morphology without beads and fine fibre diameter and pore size observed at 20 cm. The formation of beads below 20 cm may be due to agglomeration of PP particles. Besides, shorter collecting time worsened the high-speed cool air stretching which may lead to poor filtration properties with high pore size and diameter of the fabric. To enhance the protective performance of the filters through electrostatic attraction a high voltage field was introduced in the web. Figure 63d displays the surface charge of the filters at various collector distance, indicating that electret strength decreased with the increase of distance. This may be attributed to the change in electric field strength(kV/cm). However, no significant change is found due to the variation in distance. Hence, the change in the distance has a lower influence on electret properties of the web.

Tensile stress-strain performance is a significant parameter in daily uses of filter materials. It has been intensively influenced by sample physical structure. **Figure 62e** presents the mechanical character of the as-prepared filters at a different distance. The tensile stress of E-PP filters at 20cm showed maximum performance. This may be because of the existence of finer and even diameter within the structure with better reinforcement effect. Therefore, 20 cm sample is considered for further discussion.

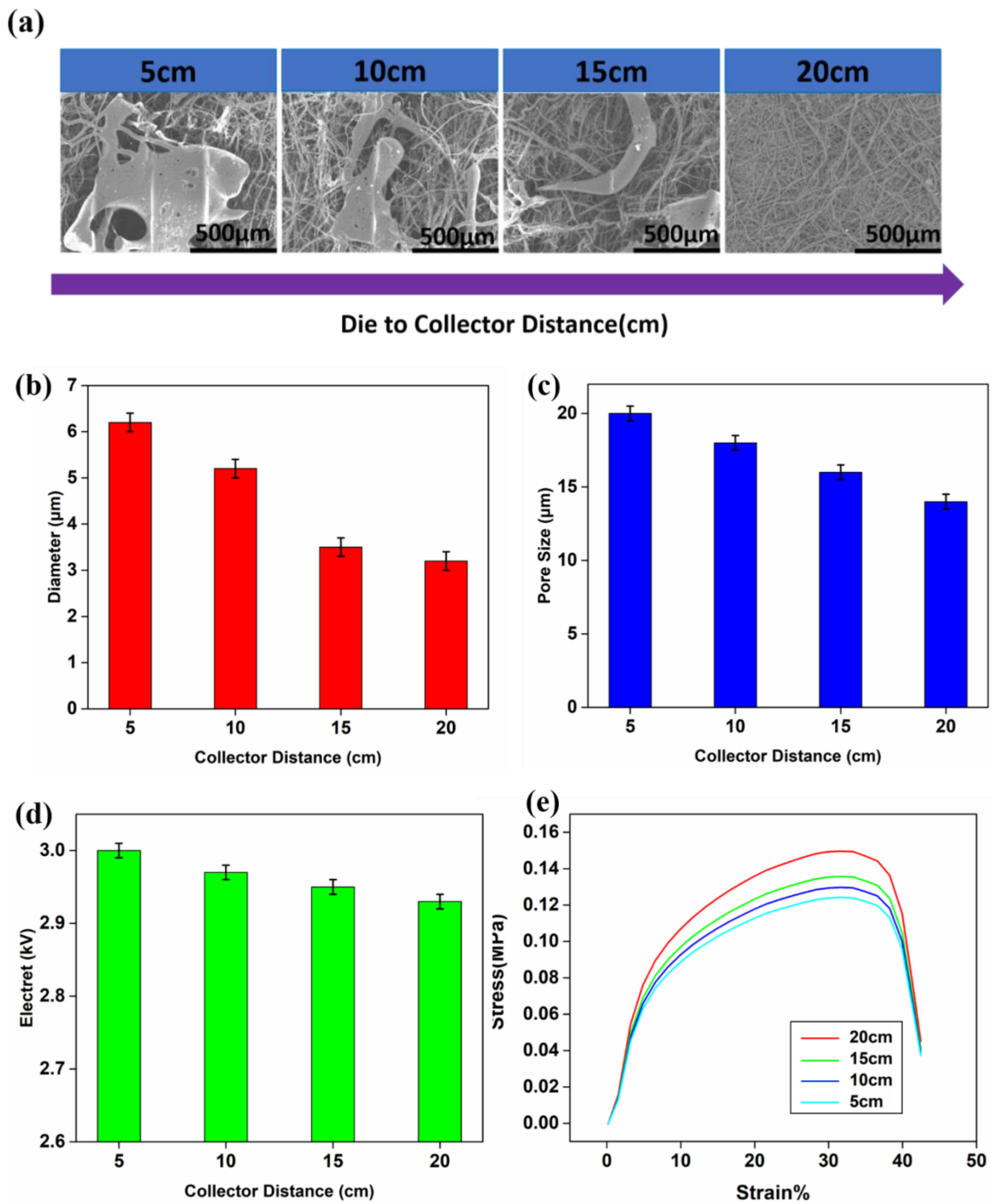


Figure 62 Morphological and structural properties (a) SEM images (b) Diameter (c) Pore size (d) Electret and (e) Mechanical Property of E-PP at various collector distance.

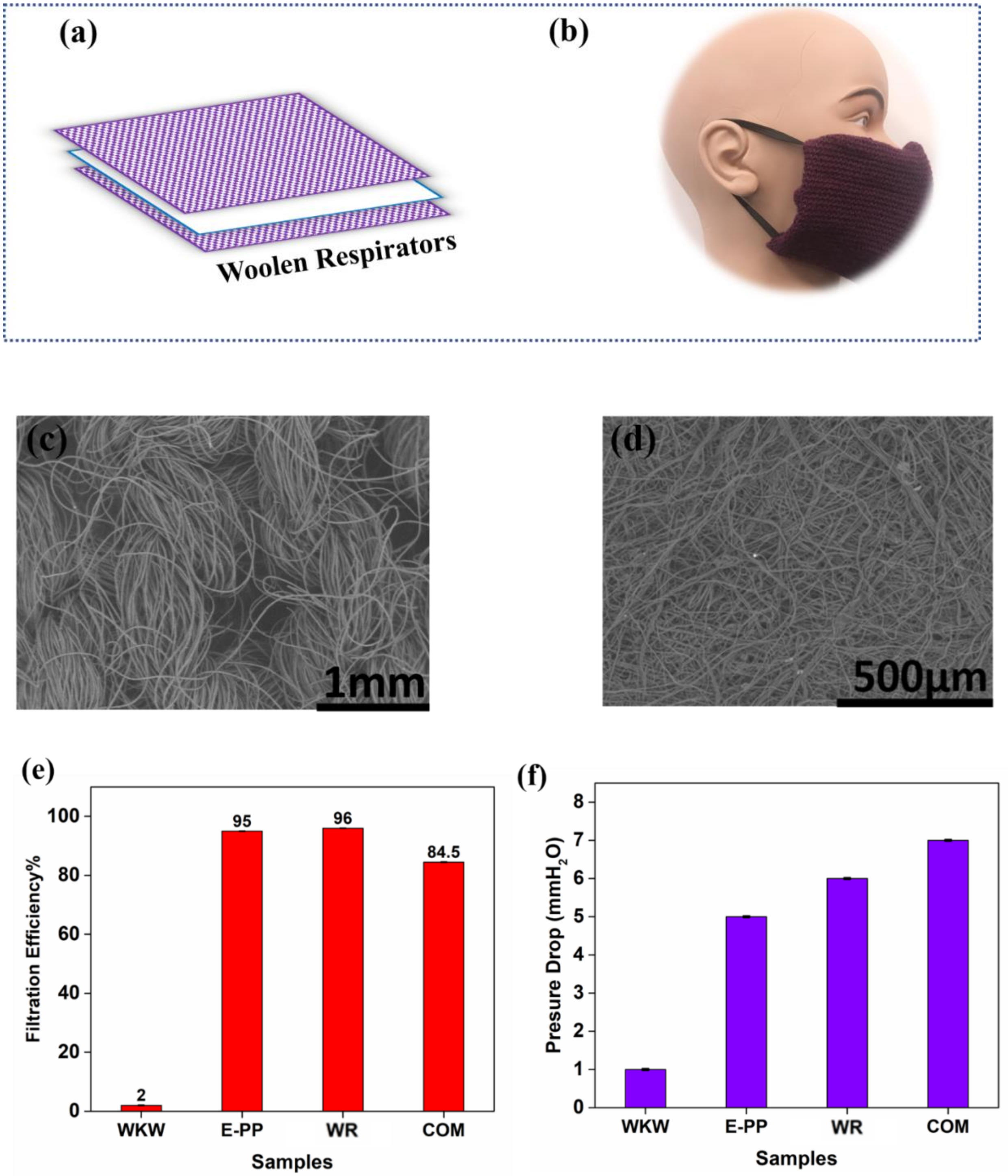
6.3.2 Physical and Protective Performance of Woolen Respirators

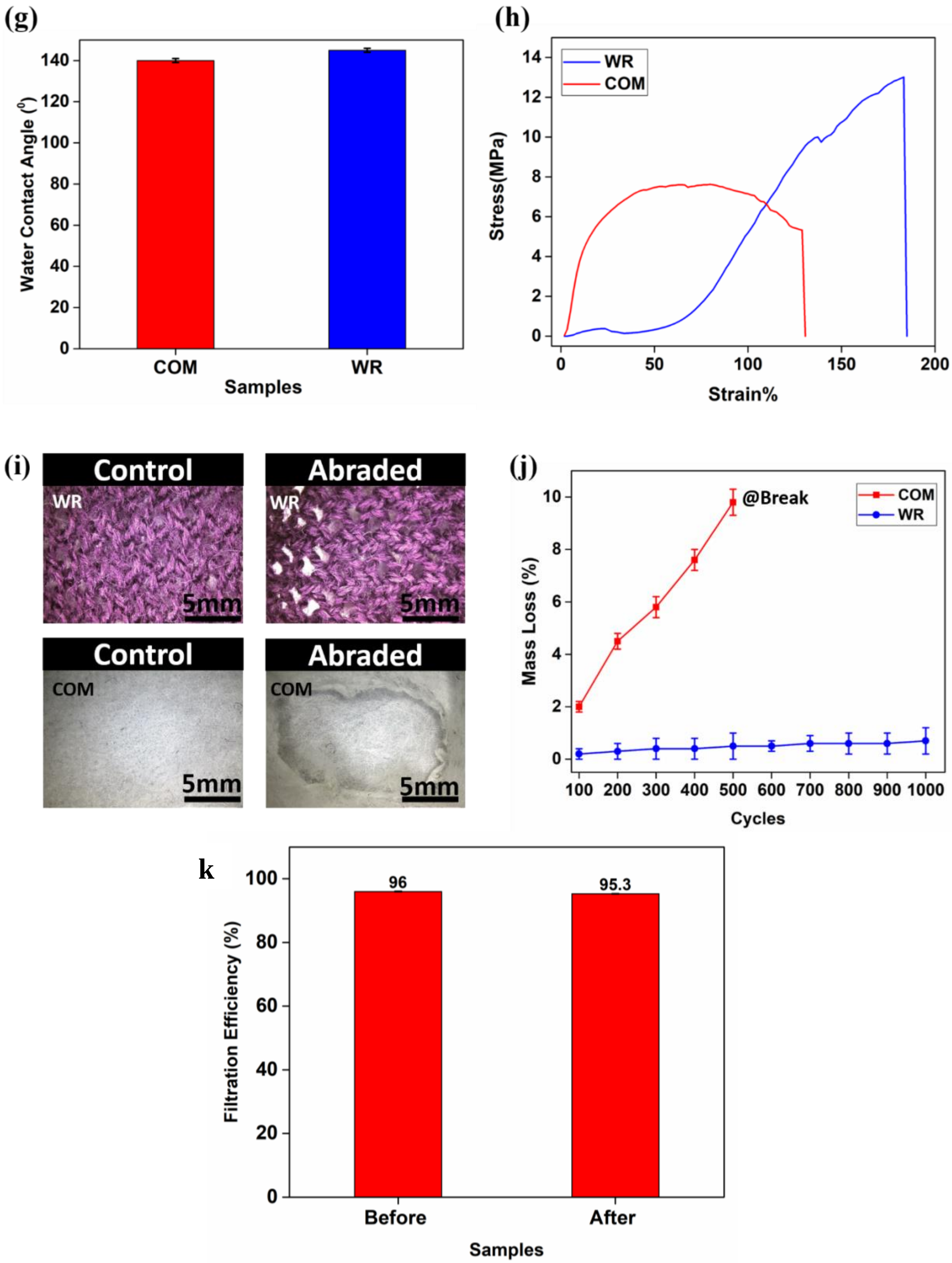
The fabrication process of our proposed respiratory filters having woolen knitwear (WK) as top and bottom layers with barrier electret-polypropylene (E-PP) layers in the middle are presented in **Figure 63a.** The photographs of as-prepared woolen respirators (WR) displayed in **Figure 63b**. The as-prepared woolen knitwear has been prepared using woolen yarn with shape memory effect. Recently, water-actuating woolen knitwear has been introduced as cooling textiles [211]. Hence this water/sweat driven woolen knitwear may enhance thermal comfort performance of the respirators both in hot and cold. Besides, wool fibre has good biodegradability. Generally, it takes about half a year for animal fibre to degrade in soil. Compared with other man-made fibres, it has a lower environmental impact and is a sustainable fibre. It has been mentioned that when the landfill time reaches 6 months, wool is integrated with the soil[274]. The melt-blown polypropylene filter layer with an electrostatic charge was designed using electret-melt blown techniques**.** The use of this highly efficient E-PP filter layer with biodegradable, sustainable and cool-wool knitwear may provide excellent personal protection and cooling performance. The surface morphology of both the filter materials was observed by the SEM images **(Figure 63c and d)**. The wool knitwear showed extremely high pore size and diameter compared to melt-blown. Hence, the filtering efficiency (**Figure 63e)** by the knitwear was extremely low (2%) due to the existence of a bigger pore size. In contrast, the E-PP showed higher filtration efficiency (95%) because of its high surface electret charge along with higher mechanical filtration effect. Nevertheless, the combination of woolen knitwear and melt-blown layer can achieve filtration efficiency around 96%, which is much higher than the commercially available filter materials for the mask. Besides of filtration efficiency, pressure drop has been characterized to measure the air transmission ability by the filter materials (**Figure 63f)**. Remarkably, our proposed design can achieve high filtration efficiency along with a low-pressure drop at the same time, compared with a commercial mask.

The splash resistance is used to measure the penetration of body fluid (blood, saliva) by the filter layers. Various kinds of contagious microorganisms like viruses, bacteria and fungal, the spurted body fluids may carry. The splash resistance of our designed materials was visualized by the water contact angle of the barrier layer. The high-water contact angle of as-prepared WR confirmed that our sample is extremely splash resistant **(Figure 63g).** Hence providing wearer safety from micro liquid droplets, containing the various bacterial and viral load. Thus, the proposed woolen respirators have better splash resistance that can enhance protective performance and can be rated as ASTM level 1 mask.

Mechanical test of the WR samples was performed and compared with a commercial mask to assess the mechanical robustness of our proposed samples (**Figure 63h)**. It has been noted that our proposed design has higher tensile robustness along with better elongation ability than the typical commercial mask, which makes it ideal for stretcher face mask application.

The durability of the samples was determined by measuring abrasion resistance and mass loss% of the fabric over 1000 cycles. **Figure 63i** exhibits light microscope images of control and abraded samples with 1000 cycles for both WR and commercial mask. It has been noted that the surface of the commercial mask seriously damaged at 500 times abrasion. However, WR can withstand similar abrasion cycles without any surface damage. Besides, we found that mass loss% for the commercial mask was significantly higher at maximum abrasion cycle, compared with WR (**Figure 63j)**. Therefore, the commercial mask is found to be poor abrasion resistive cloth with the production of higher microplastic during prolonged use, which is directly connected with poor product quality and wearer health. Moreover, to ensure filtration efficiency after the abrasion test, filtration testing has been carried out and added in the supporting information **(Figure 63k).** We have noticed in this study a slight or negligible change of filtration efficiency occurred after the abrasion test. This may be because there is a negligible mass loss% of the upper layer of WR without damaging the E-PP barrier layer during abrasion test over 1000 cycle **(see Figure 63i).** Also, the electrostatic contribution of wool during abrasion may influence the filtration efficiency[275].




(g)
Water Contact Angle (⁰)
140
120
100
80
60
40
20
0
COM
WR
Samples
(h)
WR
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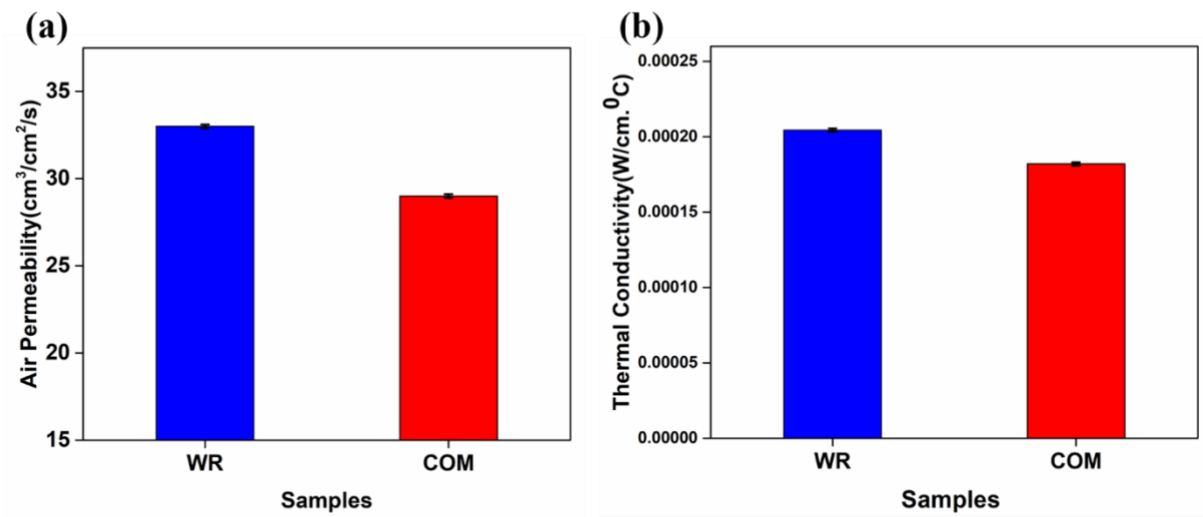
Stress(MPa)
14
12
10
8
6
4
2
0
0
50
100
150
200
Strain%
(i)
Control
Abraded
WR
WR
5mm
5mm
Control
Abraded
COM
COM
5mm
5mm
(j)
@Break
COM
WR
Mass Loss (%)
10
8
6
4
2
0
100 200 300 400 500 600 700 800 900 1000
Cycles
k
Filtration Efficiency (%)
100
80
60
40
20
0
96
95.3
Before
After
Samples

Figure 63 Physical and protective performance of woolen respirators (a) Schematics of 3-ply of woolen respirators (b) Photographs of woolen mask (c) SEM images of woolen knitwear (d) SEM images of E-PP (e) Filtration efficiency% (f) Pressure drop (g) Water contact angle (h) Mechanical property (i) Light microscope images of control and abraded surface and (j) Mass loss% during abrasion (k) Filtration efficiency% before and after abrasion test

6.3.3 Thermal Management of Woolen Respirators

To understand the effect of woolen knitwear on the thermal comfortability of the proposed as-prepared respirators, the dry and wet heat management properties of WR fabric has been conducted and compared with polypropylene (PP) based commercial mask. We first investigate the dry heat transfer by quantifying the air permeability, thermal conductivity and skin temperature with the materials (**Figure 64 a-d)**. In **Figure 64a,** it has been noted that the fabricated samples have higher air permeability than the 3-ply mask, uncovering the fact that there is a notable impact of highly porous knit structure on as-prepared WR thermophysiological comfort. Previous researches[211] further confirm fabric can significantly enhance air permeability with high pore size. Besides air permeability, the dry heat loss in terms of heat conduction has also been performed. It can be seen from **Figure 64b**, the conductivity of WR fabric is slightly higher than that of the commercial mask. Based on the literature[276] the thermal conductivity value (K) for wool fibers is 33% higher than thermoplastic PP. As a result, the K values obtained from experimental measurement were higher than the PP based commercial mask. To further verify the cooling effect of WR filters we used a simulated skin with a temperature of 34^0C (**Figure 64c)**. It can be seen from **Figure 64d**, skin temperature rises by 1.3^0C for WR than for commercial mask with 3^0C. Such variation in skin temperature is maybe because the overall pore size of WR is higher than the commercial mask which makes it ideal for cooling management application.

To evaluate the wet heat transfer in vapor form, we further experimentally measure the water vapor transmission profile for WR and commercial mask at different humidity and temperature level. **Figure 64e** demonstrates water vapor transmission performance of WR and commercial mask with the different humidity level at 25^{0}C. Because of the moisture responsive pore actuation effect, WR has shown a significant increase in vapor transmission is compared with a commercial mask with an increase in humidity level. A similar response has been noted for WR at a different temperature level with constant humidity **(Figure 64f)**. This is maybe because with higher temperature level, the sample gets moistened and pore size of woolen knitwear increased. Therefore, we believe dynamic pore size changes of WR upon higher moisture and temperature level enhance the evaporative cooling effect and enhance thermal management. This study supports evidence from previous observations.



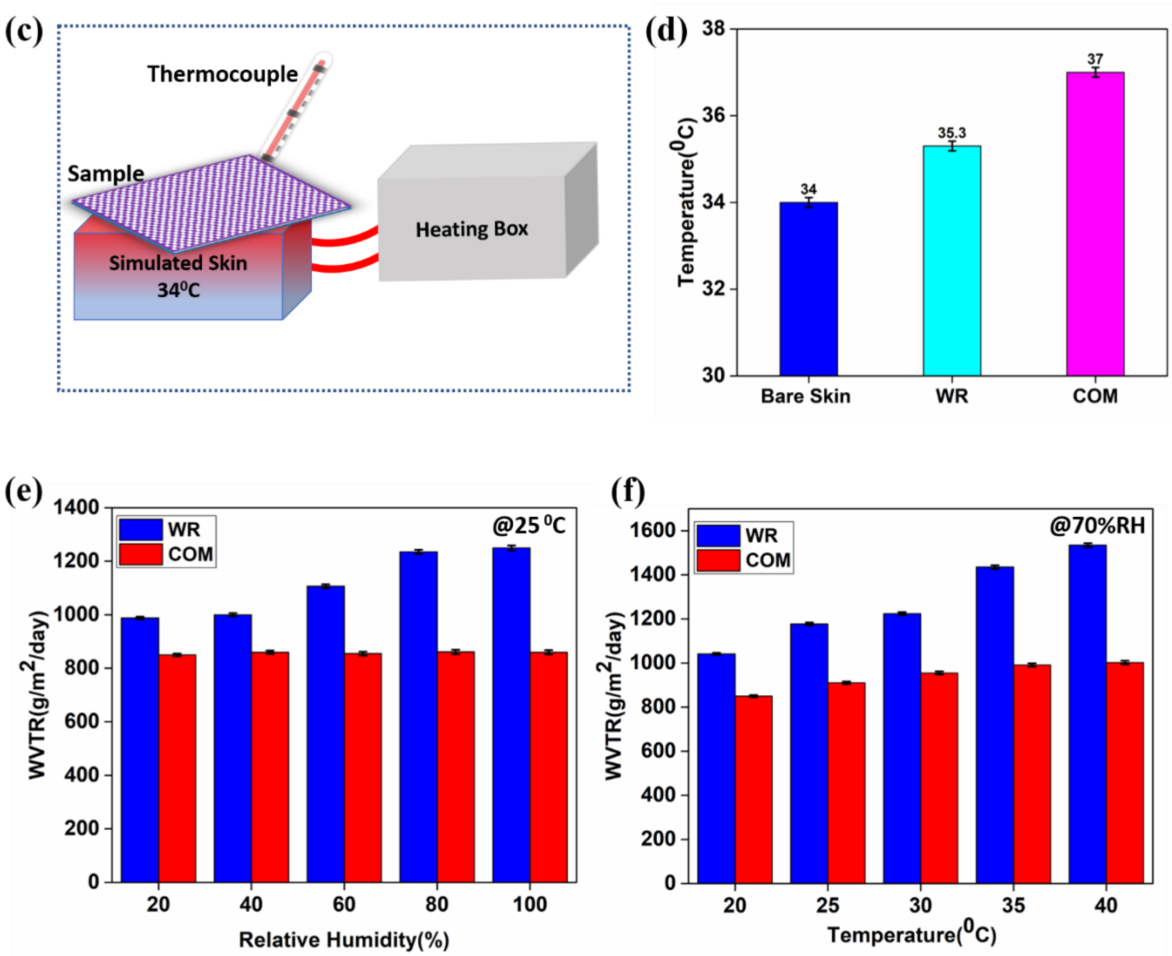


Figure 64 Thermal management of woolen respirators (a) Air Permeability (b) Thermal Conductivity (c) Schematic of skin temperature measurement (d) Skin Temperature of bare skin, woolen respirators and commercial mask (e)Water vapour transmission at different humidity and (f) Water vapor transmission at different temperature

6.3.4 Wear Trial

Wear trials are the well-acknowledged approach to examine the performance, comfort, useability and applicability of any kind of personal protective equipment. Therefore, the performance of our as-prepared woolen respirators is tested and compared with the commercial mask through subjective evaluation (**Figure 65a-f). Figure 65a and b** exhibited the picture of wearing both of the masks by the participant during the test. This study evaluated the perceived comfort performances in a supplied sample considering three major dimensions such as sensory, phycological and thermal comfort. **Figure 65c** shows the sensory comfort of the samples. The participants rated woolen respirators with the highest mean scores 4.1±0.2 than the commercial mask (2.5±0.2). This may be attributed due to the material quality and properties as most of the participants commented that woolen respirators have better softness, stretchiness and lower tension on face during wearing. In **Figure 65d** the participants favoured woolen respirators due to material which contain moisture responsive wool with a cool-feel touch on the face. In contrary, the commercial mask has a rough surface and was considered hot and humid over testing time by the participants. Hence, woolen respirators rated with mean score 4.3±0.6 than the commercial mask (3.3±0.6) in terms of thermal comfort. Phycological comfort strongly depends on aesthetic pleasure by the users. Woolen respirators rated high in terms of design and colour. As a result, in **Figure 65e** phycological comfort showed the highest rating (4.6±0.2) over commercial mask (3.4±0.2). The overall rating for both masks is presented in **Figure 65f.** Overall, the users appreciate woolen respirators for its better outlook, hand feel, thermal comfort and sustainability.

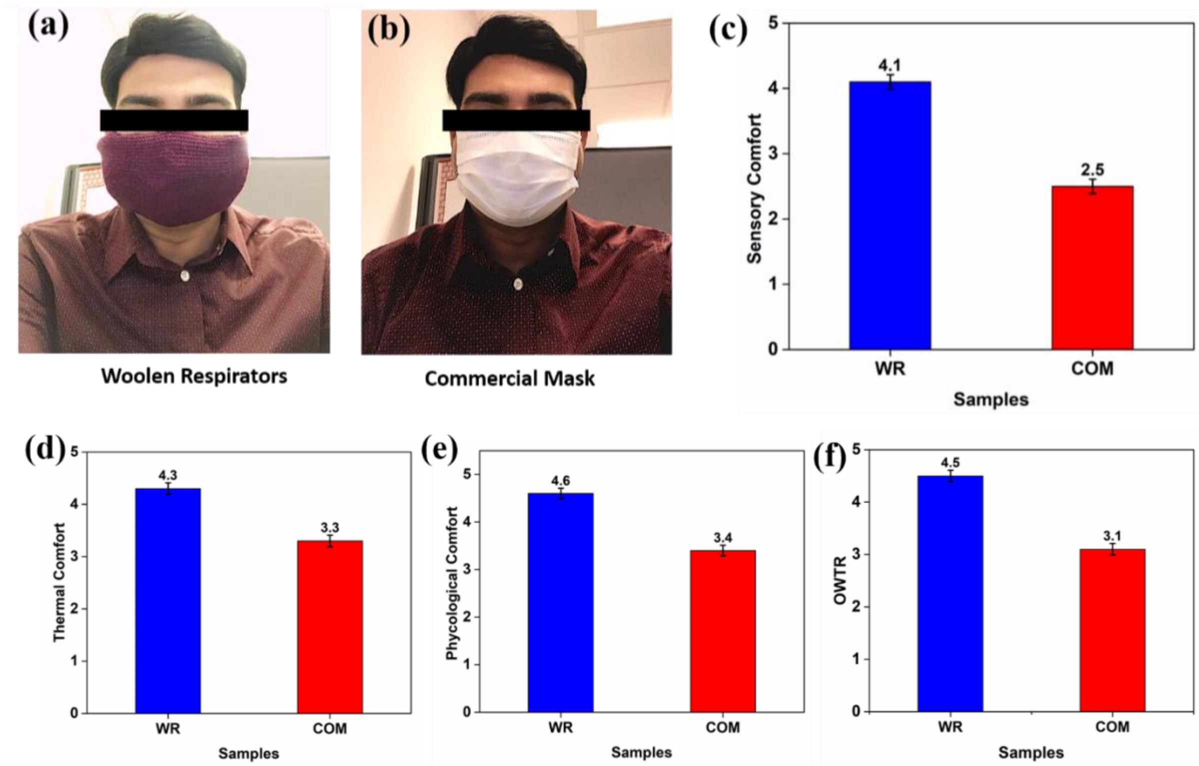


Figure 65 Wear trial evaluation (a) Photographs of woolen respirators during wearing (b) Photographs of the commercial mask during wearing (c) Sensory comfort (d) Thermal comfort (e) Phycological comfort and (f) Overall wear trial rating (OWTR)

6.4 Summary

COVID-19 pandemic recently has a great impact on personalized protection and healthcare, especially in the area of the respiratory mask. However, due to the complex relationship between filtration performance and thermal management, there is a lack of investigation considering both characters in respirators. Keratin based biomaterials such as wool are recently well acknowledged as skin-like materials because of their superior moisture-actuation performance. To incorporate protective function against bacteria, virus, microdroplet and particulate matter, melt-blown polypropylene can be introduced as a barrier layer. Herein, a robust and sustainable bio-based woolen respirator with the superior ability of cooling management are prepared using simple knitting and melt-blown technology. The as-prepared respirators provide excellent protection from airborne particulate along with the high level of cooling, compared with a commercial mask. Moreover, it exhibits a high rating during wear trial. This provides a new insight to develop high quality sustainable respiratory mask with an excellent cooling performance from functional biomaterials.

Chapter 7 Conclusions and Suggestions for Future Research

As a second skin of the human body, clothing offers protection, aesthetic quality, and courtesy. Because of the inability of materials to adapt to different weather conditions, different clothing is required for different seasons, namely, thin and open garments for summer, thick and closed ones for winter. Moreover, our body maintains its internal core temperature (37°C) through sweating and shivering. Herein, we report a discovery that is contrary to available public and professional knowledge, that is, woolen knitwear can provide not only warmth, but also a cooling sensation when a body sweat. The fascinating water-responsive pore size change of the knit pores keeps the skin dry, thus helping to maintain a constant body temperature, providing comfort and safety. Our multidimensional approach has shown promising results and potential for natural fibre based mass production of smart textiles for comfort management at lower costs. Additionally, our work will increase the understanding of mechanism about the smart properties of wool fibres. Conclusion of the interesting results that we have obtained through our research is summarized in this chapter.

7.1 Water-Actuating Woolen Knit Pores for Thermoregulation

Woolen knitwear is generally considered winter clothing that provides warmth. In this study, we designed a knitted fabric using 100% descaled wool yarn and investigated its adaptive thermoregulation in terms of change in pore size, water vapor permeability, thermal conductivity, air permeability, and IR transmission under various sweat levels. Contrary to intuition and worldwide public and professional knowledge, it is fascinating to see that wool can provide a cooling sensation during sweating. The water-responsive pore size change of the knit pores makes the wearer feel warm when there is no/less sweat and cool during sweating such as during exercising and in summer. Particularly, the results demonstrate the water-responsive pore actuation ability of the knitted woolen fabric that is sensitive to the amount of water absorbed by the fabric because of the synergistic shape-shifting effect of the wool fiber, yarn, and fabric. The pore area increased by more than 70% at 100% water absorption, and the air permeability of the knitted woolen fabric increased significantly to 60% with increasing water absorption in hot environments such as the conditions caused by heavy exercise. The thermal conductivity of the knitted woolen fabric increased with increasing water absorption, and the IR transmission of the wet fabric in the IR region of 9.6–10 μm (human body thermal radiation) was higher than that of the dry fabric. In addition, the surface temperature of the moistened samples was lower (24.7 °C) than that of the dry samples (31.2 °C), as determined by thermal imaging. Moreover, the results of theoretical analysis are in good agreement with the experimental results. Thus, the knitted woolen fabric with water-responsive pore actuation ability due to shape shifting can be considered an all-weather apparel material with body sweat acting as a stimulator for thermoregulation.

7.2 Knit Architecture for Water-Actuating Woolen Knitwear for Thermoregulation

In this study, effect of fabric structure on pore on/off ability of water responsive woolen knitwear was investigated. We have fabricated four different knit structure using water responsive wool yarn that can exhibit smart shape changing behaviour along with pore on/off character upon water stimulation. In our study the wool in fibre and yarn stage provides excellent longitudinal and diametral shape change, and because of the unbalanced loop arrangement in single jersey, loop shape within the fabrics can be altered better compared to double knit fabrics. Therefore, single jersey fabric displayed maximum cooling performance with increase in water absorption. The air permeability and conductive heat loss of single jersey woolen knitwear at maximum water absorption level were 30% and 55% higher than those of double knit structure. This suggests that water responsive woolen knitwear with unbalanced structure is more breathable and cooler compared to balance structured double-knit fabric. Besides, the cool touch feeling of the single jersey was 50% greater than that of the double-knit fabric when the absorption level was 100%. Moreover, in harmony with the air permeability values, the water vapor transmission for single jersey fabrics was found to be increased significantly compared to double knit structure from the dry samples to wet samples for each set of climatic condition. In addition, single jersey showed the higher radiative heat loss both in dry and wet conditions than the double knit in thermal images, which indicated that the single jersey sample can provide better radiative cooling effect compared to double knit samples. The research has also shown that the evaporation rate and wicking distance of single jersey are much higher. Through the theoretical analysis above, we thus believe that the key parameters for exhibiting smart knit pore switch on/off ability are greatly influenced by the fabric architecture and their ratio of change in course and wales direction upon water stimulation. Overall, this study strengthens the idea that the ability of woolen knitwear with single knit architecture has maximum water responsiveness that can improve thermoregulation in hot and humid climate. Thus, the woolen knitwear along with single jersey structure can be considered as apparel material for all over the year.

7.3 Woolen Respirators for Thermal Management

A biobased cooling respirator is realized by fabricating moisture responsive woolen knitwear with PP barrier layer. The as prepared woolen respirators exhibit excellent thermal comfort and personal protection and can be durable for a long time than the commercially available mask in the community market. It also exhibits superior wear trial rating during the subjective trial. The evidence from this study suggests that biomaterials with smart function and design can be utilized as personal protection equipment with the desired comfort. Overall, this study not only achieves robust woolen respirators for cooling management but also expand the application of keratin-based biomaterials in establishing sustainable wearable healthcare industry.

7.4 Suggestions for Future Research

Based on the outcomes of this study, the research on adaptive comfort clothing using wool fibers can be further extended as follows:

1. Yarn with different spinning parameters can be utilized to explore the effect of process parameters on smart behaviour of wool fibres.
2. Woven Geometry can be used to realize the relationship between smart behaviour of the fibres, yarns and woven fabric structures.
3. Wool fibre-based actuator and sensor can be fabricated to search the potentiality of using smart natural fibre on electronic textiles.
4. Blended wool fibers can be used to investigate the influence on the shape change of the materials upon stimulation with heat and water.
5. Other protein fibres with stimuli responsive ability can be used and the influence of such materials on the adaptive behaviour of clothing as well as on thermal comfort properties can be examined and compared with wool.

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