

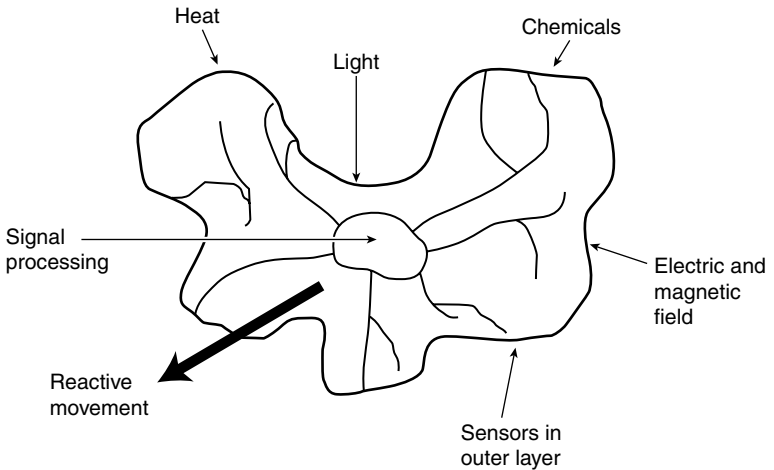
Smart technology for textiles and clothing – introduction and overview

XIAOMING TAO

1.1 Introduction

Since the nineteenth century, revolutionary changes have been occurring at an unprecedented rate in many fields of science and technology, which have profound impacts on every human being. Inventions of electronic chips, computers, the Internet, the discovery and complete mapping of the human genome, and many more, have transformed the entire world. The last century also brought tremendous advances in the textile and clothing industry, which has a history of many thousands of years. Solid foundations of scientific understanding have been laid to guide the improved usage and processing technology of natural fibres and the manufacturing of synthetic fibres. We have learnt a lot from nature. Viscose rayon, nylon, polyester and other synthetic fibres were invented initially for the sake of mimicking their natural counterparts. The technology has progressed so that synthetic fibres and their products surpass them in many aspects. Biological routes for synthesizing polymers or textile processing represent an environmentally friendly, sustainable way of utilizing natural resources. Design and processing with the aid of computers, automation with remote centralized or distributed control, and Internet-based integrated supply-chain management systems bring customers closer to the very beginning of the chain than ever before.

Looking ahead, the future promises even more. What new capacities should we expect as results of future developments? They should at least include terascale, nanoscale, complexity, cognition and holism. The new capability of terascale takes us three orders of magnitude beyond the present general-purpose and generally accessible computing capabilities. In a very short time, we will be connecting millions of systems and billions of information appliances to the Internet. Technologies allowing over one trillion operations per second are on the agenda for research. The technology in nanoscales will take us three orders of magnitude below the size of most of today's human-made devices. It will allow us to arrange atoms and molecules inexpensively in most of the ways



1.1 A single cell living creature is an example of smart structures.

permitted by physical laws. It will let us make supercomputers that fit on the head of a fibre, and fleets of medical nanorobots smaller than a human cell to eliminate cancers, infections, clogged arteries and even old age. Molecular manufacturing will make exactly what it is supposed to make, and no pollutants will be produced.

We are living in this exciting era and feeling the great impacts of technology on the traditional textiles and clothing industry, which has such a long history. Traditionally, many fields of science and engineering have been separate and distinct. Recently, there has been considerable movement and convergence between these fields of endeavour and the results have been astonishing. Smart technology for materials and structures is one of these results.

What are smart materials and structures? Nature provides many examples of smart structures. The simple single-celled living creature may highlight the fundamentals. As shown in Fig. 1.1, various environmental conditions or stimuli act on the outer layer. These conditions or stimuli may be in the form of force, temperature, radiation, chemical reactions, electric and magnetic fields. Sensors in the outer layer detect these effects, and the resulting information is conveyed for signal processing and interpretation, at which point the cell reacts to these environmental conditions or stimuli in a number of ways, such as movement, changing chemical composition and reproductive actions. Nature has had billions of years and a vast laboratory to develop life, whereas humankind has just begun to create smart materials and structures.

Smart materials and structures can be defined as the materials and structures that sense and react to environmental conditions or stimuli, such as

those from mechanical, thermal, chemical, electrical, magnetic or other sources. According to the manner of reaction, they can be divided into passive smart, active smart and very smart materials. Passive smart materials can only sense the environmental conditions or stimuli; active smart materials will sense and react to the conditions or stimuli; very smart materials can sense, react and adapt themselves accordingly. An even higher level of intelligence can be achieved from those intelligent materials and structures capable of responding or activated to perform a function in a manual or pre-programmed manner.

Three components may be present in such materials: sensors, actuators and controlling units. The sensors provide a nerve system to detect signals, thus in a passive smart material, the existence of sensors is essential. The actuators act upon the detected signal either directly or from a central control unit; together with the sensors, they are the essential element for active smart materials. At even higher levels, like very smart or intelligent materials, another kind of unit is essential, which works like the brain, with cognition, reasoning and activating capacities. Such textile materials and structures are becoming possible as the result of a successful marriage of traditional textiles/clothing technology with material science, structural mechanics, sensor and actuator technology, advanced processing technology, communication, artificial intelligence, biology, etc.

1.2 Development of smart technology for textiles and clothing

We have always been inspired to mimic nature in order to create our clothing materials with higher levels of functions and smartness. The development of microfibres is a very good example, starting from studying and mimicking silk first, then creating finer and, in many ways, better fibres. However, up to now, most textiles and clothing have been lifeless. It would be wonderful to have clothing like our skin, which is a layer of smart material. The skin has sensors which can detect pressure, pain, temperature, etc. Together with our brain, it can function intelligently with environmental stimuli. It generates large quantities of sweat to cool our body when it is hot, and to stimulate blood circulation when it gets cold. It changes its colour when exposed to a higher level of sunlight, to protect our bodies. It is permeable, allowing moisture to penetrate yet stopping unwanted species from getting in. The skin can shed, repair and regenerate itself. To study then develop a smart material like our skin is itself a very challenging task.

In the last decade, research and development in smart/intelligent materials and structures have led to the birth of a wide range of novel smart products in

aerospace, transportation, telecommunications, homes, buildings and infrastructures. Although the technology as a whole is relatively new, some areas have reached the stage where industrial application is both feasible and viable for textiles and clothing.

Many exciting applications have been demonstrated worldwide. Extended from the space programme, heat generating/storing fibres/fabrics have now been used in skiwear, shoes, sports helmets and insulation devices. Textile fabrics and composites integrated with optical fibre sensors have been used to monitor the health of major bridges and buildings. The first generation of wearable motherboards has been developed, which has sensors integrated inside garments and is capable of detecting injury and health information of the wearer and transmitting such information remotely to a hospital. Shape memory polymers have been applied to textiles in fibre, film and foam forms, resulting in a range of high performance fabrics and garments, especially sea-going garments. Fibre sensors, which are capable of measuring temperature, strain/stress, gas, biological species and smell, are typical smart fibres that can be directly applied to textiles. Conductive polymer-based actuators have achieved very high levels of energy density. Clothing with its own senses and brain, like shoes and snow coats which are integrated with Global Positioning System (GPS) and mobile phone technology, can tell the position of the wearer and give him/her directions. Biological tissues and organs, like ears and noses, can be grown from textile scaffolds made from biodegradable fibres. Integrated with nanomaterials, textiles can be imparted with very high energy absorption capacity and other functions like stain proofing, abrasion resistance, light emission, etc.

The challenges lie before us, as the research and development of smart technology and its adoption by industries depend upon successful multidisciplinary teamwork, where the boundary of traditional disciplines becomes blurred and cross-fertilization occurs at a rate much higher than that seen previously. Some of the research areas can be grouped as follows:

For sensors/actuators:

- photo-sensitive materials
- fibre-optics
- conductive polymers
- thermal sensitive materials
- shape memory materials
- intelligent coating/membrane
- chemical responsive polymers
- mechanical responsive materials
- microcapsules
- micro and nanomaterials.

For signal transmission, processing and controls:

- neural network and control systems
- cognition theory and systems.

For integrated processes and products:

- wearable electronics and photonics
- adaptive and responsive structures
- biomimetics
- bioprocessing
- tissue engineering
- chemical/drug releasing.

Research and development activities have been carried out worldwide, both in academic/research institutions and companies. Research teams in North American, European and Asian countries have been actively involved, with noticeable outcomes either in the form of commercial products or research publications.

1.3 Outline of the book

This edited book, being the first on this topic, is intended to provide an overview and review of the latest developments of smart technology for textiles and clothing. Its targeted readers include academics, researchers, designers, engineers in the area of textile and clothing product development, and senior undergraduate and postgraduate students in colleges and universities. Also, it may provide managers of textile and clothing companies with the latest insights into technological developments in the field.

The book has been contributed by a panel of international experts in the field, and covers many aspects of the cutting-edge research and development. It comprises 17 chapters, which can be divided into four parts. The first part (Chapter 1) provides the background information on smart technology for textiles and clothing and a brief overview of the developments and the book structure. The second part involves material or fibre-related topics from Chapters 2 to 9. Chapter 2 is concerned with electrically active polymer materials and the applications of non-ionic polymer gel and elastomers for artificial muscles. Chapters 3 and 4 deal with thermal sensitive fibres and fabrics. Chapter 5 presents cross-linked polyol fibrous substrates as multifunctional and multi-use intelligent materials. Chapter 6 discusses stimuli-responsive interpenetrating polymer network hydrogel. Chapter 7 is concerned with permeation control through stimuli-responsive polymer membranes prepared by plasma and radiation grafting techniques. Chapters 8 and 9 discuss the

Table 1.1 Outline of the book

Chapter no.	Sensors/actuators	Signal transmission, processing and control	Integrated processes and products	Bio-processes and products
1	✓	✓	✓	✓
2	✓			
3	✓		✓	
4	✓		✓	
5	✓		✓	
6	✓			
7			✓	
8	✓			
9	✓			
10	✓	✓	✓	
11	✓		✓	
12			✓	
13		✓	✓	
14		✓	✓	
15				✓
16	✓			✓
17			✓	✓

principles, manufacturing and properties of optical fibre sensors, with emphasis on fibre Bragg grating sensors.

The third part contains five chapters, with a focus on integrating processes and integrated structures. Chapter 10 provides an overview of the developments and key issues in fibre-optic smart textile composites. Chapter 11 presents hollow fibre membranes for gas separation. Chapter 12 describes embroidery as one way of integrating fibre-formed components into textile structures. Chapters 13 and 14 are on wearable electronic and photonic technologies. Chapter 13 provides insights on adaptive and responsive textile structures (ARTS). Chapter 14 describes the development of an intelligent snowmobile suit.

The fourth part, embracing the last three chapters, is focused on bioapplications. Chapter 15 outlines various bioprocesses for smart textiles and clothing, and Chapter 16 concentrates on tailor-made intelligent polymers for biomedical applications. Chapter 17 describes the applications of scaffolds in tissue engineering, where various textile structures are used for cells to grow.

We have only seen a small portion of the emerging technology through the window of this book. The possibilities offered by this smart technology are tremendous and widespread. Even as the book was being prepared, many new advances were being achieved around the world. It is the hope of the editor and contributors of this book that it will help researchers and designers of future smart fibres, textiles and clothing to make their dreams a reality.

Electrically active polymer materials – application of non-ionic polymer gel and elastomers for artificial muscles

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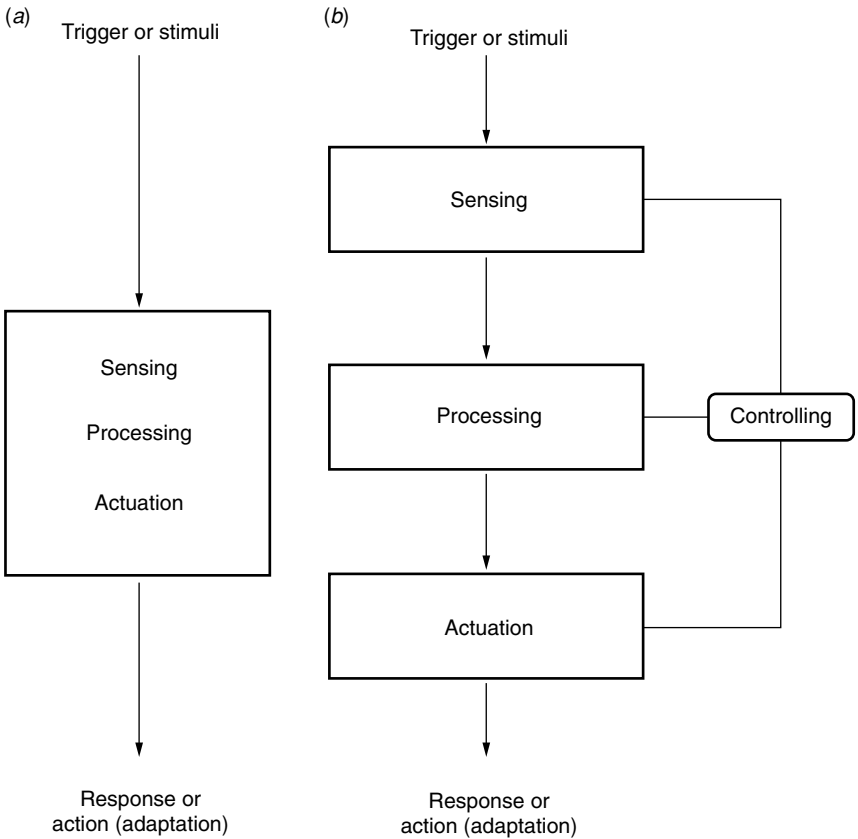
2.1 Introduction

Many attempts have been made to functionalize polymer materials as so-called ‘smart’ or ‘intelligent’ materials (see Fig. 2.1).^{1–5} Artificial muscle or intelligent actuators is one of the targets of such attempts. Historically, actuator materials have been investigated mainly in inorganic compounds.⁶ Particularly, triggers used for actuation are usually investigated in an electric field application because of the ease of control. Polymer materials investigated from this point of view are very limited and have been known to generate much smaller strain than inorganic materials.^{6–8}

On the other hand, polymer materials such as polymer gels have been known to generate huge strain by various triggers such as solvent exchange, pH jump, temperature jump, etc., although the response and durability are rather poor and they have not been used in practical actuators.¹

In the field of mechanical engineering, the development of micromachining procedure is facing the requirements of the technologies of microfabrication and micro-device assembly, and there are high expectations of the emerging smart materials that can greatly simplify the microfabrication process.^{9–12} Under these circumstances, the polymer gel actuator is mentioned as one of the most likely candidates as a soft biological muscle-like material with large deformation in spite of its poor durability.^{1,2} Much research has been done on solid hard materials as actuators like poly(vinylidene fluoride) (PVDF), which is a well-known piezoelectrical polymer, and in which crystal structures play critical role for the actuation and the induced strain is very small compared to the gel artificial muscles that will be described in this chapter. Although PVDF needs electrically oriented crystal structure in it, the materials that will be discussed in this chapter do not require such a limitation.

Conventional electrically induced actuation has been carried out mostly on ionic polymer gels. The reason is simply because ionic species are highly



2.1 Concepts of autonomic systems and materials. Three processes (sensing, processing and actuation) are incorporated in materials (in one system): (a) in autonomic materials, while they are separated and must be unified by a controlling system; (b) in conventional autonomic systems.

responsive to the electric field. Ionic gels have proved to be excellent electroactive actuator materials.^{1,2}

However, we tried electrical actuation of non-ionic polymer gel or elastomers. Why must non-ionic polymer gel be used for electrical actuation? Because non-ionic polymer gel is superior to ionic polymer gel in several ways, if it can be actuated by an electric field. In ionic gel materials, electrolysis is usually inevitable on the electrodes, and this is accompanied by a large electric current and heat generation. In other words, electrochemical consumption is inevitable, although this fact has not been mentioned in most papers. In non-ionic polymer gels, no such process is encountered, and this leads to the good durability of the materials. In addition to these advantages, the responding speed and magnitude of the deformation were found to be much

faster (10 ms order) and larger (over 100%) than those induced in polyelectrolyte gels. The motion reminds us of real biological muscle.

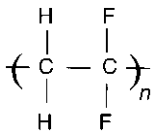
The concept of the mechanism is simple and can be applied to conventional polymer materials, including materials commonly used in the fibre and textile industries. The concept is also applicable to non-ionic elastomers that do not contain any solvent. The method we present will provide a promising way for developing future artificial muscle. Several concepts developed by other researchers and successfully used for actuating gels are also introduced in comparison with our method.

2.2 Polymer materials as actuators or artificial muscle

Polymer gel is an electroactive polymer material.¹³ There are various types of electroactive polymeric materials. As mentioned in the above section, polyelectrolyte is one of them and is most commonly investigated as an electroactive gel. We will come back to discuss this material in more detail in the next section.

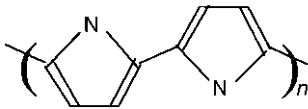
Ferroelectric polymer materials like PVDF or its derivatives are mentioned, since they behave as ferroelectric materials (see Fig. 2.2).^{14,15} They have crystallinity and the crystals show polymorphism by controlling the preparation method. Much detailed work has been carried out on piezoelectric and/or pyroelectric properties, together with their characteristics as electroactive actuators. These materials have long been mentioned as typical electroactive polymers. Through these materials, it is considered that the strain induced in the polymer materials is not large. The electrostrictive coefficient is known to be small for polymers. These are non-ionic polymers and the induced strain originates from the reorientation or the deformation of polarized crystallites in the solid materials.

There is another type of electrically active polymer that is known as the electroconductive polymer, in which polymer chains contain long conjugated double bonds, and this chemical structure adds electroconductive properties to the polymers. In these cases, the electrically induced deformation is considered to have originated from the electrochemical reactions such as the oxidation and reduction of the polymer chain. For the deformation, some additives such as dopants have been known to be necessary for effective actuation. Therefore, the electrical actuation of these materials has been

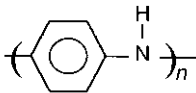


2.2 Chemical structure of poly(vinylidene fluoride) (PDVF).

(a)



(b)



2.3 Chemical structures of (a) polypyrrole and (b) polyaniline.

investigated in the presence of water, similar to the case of polyelectrolyte gels. Polypyrrole and polyaniline are typical examples (see Fig. 2.3).^{16–19}

2.3 Peculiarity of polymer gel actuator

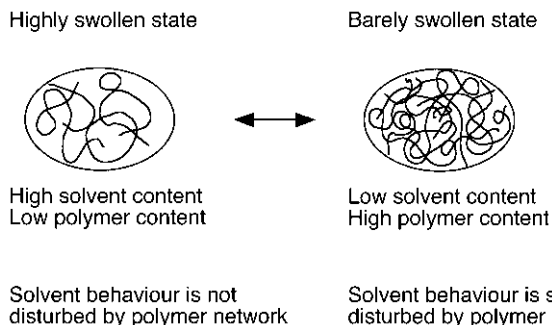
Polymer gels differ in various ways from hard solid polymer materials.^{1,2} The polymer chains in the gel are usually considered to be chemically or physically cross-linked and to form a three-dimensional network structure. For instance, polymer gel is usually a matter swollen with its good solvent, and the characteristics are diversified from a nearly solid polymer almost to a solution with very low polymer content but still maintaining its shape by itself. This extreme diversity in physical properties widens the function of the gel (see Fig. 2.4).

From the standpoint of the actuator, the gel behaves like a conventional solid actuator or biological muscle, or like a shapeless amoeba. The gels also have various actuating modes, symmetric volume change with swelling and de-swelling, asymmetric swelling behaviour, symmetric deformation and asymmetric deformation (see Fig. 2.5). The strain induced in the gel can also be extremely large, depending on the cross-link structure in the gel.^{20,21}

2.4 Triggers for actuating polymer gels

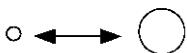
As can be expected from the diversified physical characteristics of the gel and the wide variety of the actuating modes, there are various triggers for the actuating polymer gels.

The triggers can be classified into two categories, chemical triggers and physical triggers (see Fig. 2.6). As chemical triggers, solvent exchange includes jumps in solvent polarity (e.g. from good solvent into poor solvent),²² in pH (e.g. in weak polyelectrolyte gel from a dissociated condition into an associated condition)²³ and in ionic strength (utilizing salting-out or coagulation).²⁴ These

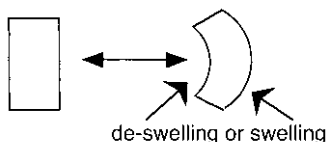


2.4 Extreme diversity in physical property widens the function of the gel.

(a) Swelling and de-swelling



(b) Asymmetric swelling or de-swelling



2.5 Various actuating modes of polymer gels: (a) swelling and de-swelling, (b) asymmetric swelling or de-swelling.

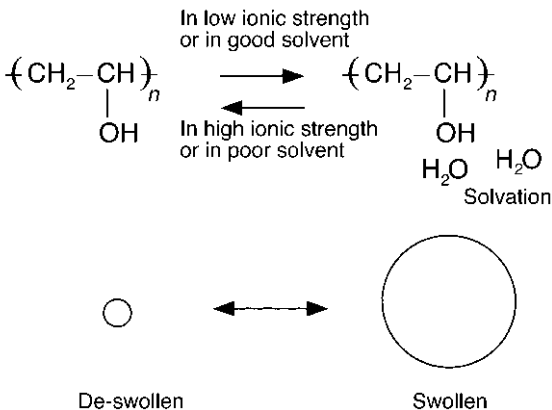
(a) Chemical triggers

- pH change
- oxidation and reduction
- solvent exchange
- ionic strength change

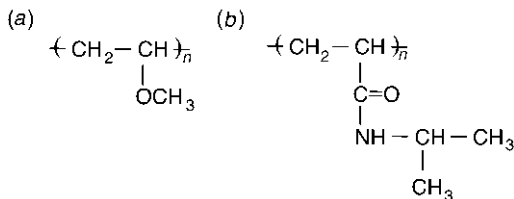
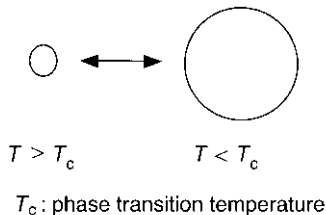
(b) Physical triggers

- light irradiation
- temperature change
- physical deformation
- magnetic field application
- electric field application
- microwave irradiation

2.6 Triggers for polymer and/or gel actuation can be classified into two categories: chemical and physical.

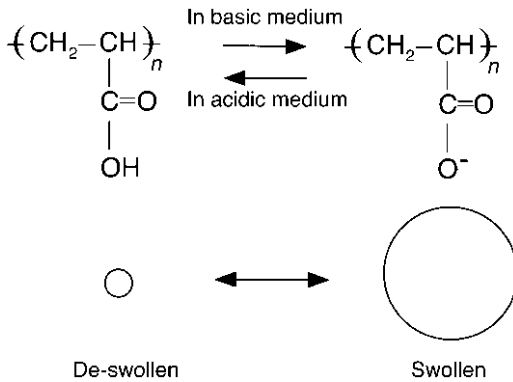


2.7 Chemical triggers including solvent exchange. These types accompany swelling and de-swelling of the solvent, and the deformation is usually symmetric as long as the gel has a homogeneous structure.

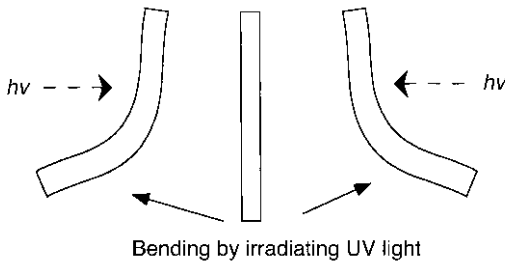


2.8 Temperature jump as a physical trigger: (a) poly(vinyl methyl ether) and (b) poly(*N*-isopropyl acrylonide).

two types accompany swelling and de-swelling of the solvent, and the deformation is usually symmetric as far as the gel has a homogeneous structure (see Fig. 2.7). Temperature jump, which is a physical trigger, can also induce symmetric deformation in particular polymer gels where the solubility has a critical transition temperature. Typical examples are the gels of poly(vinyl methyl ether) and poly(*N*-isopropyl acrylamide).^{25,26} These gels have high water absorption at low temperatures and de-swell at the characteristic critical temperature around 30–40 °C (see Fig. 2.8). The transition temperature can be controlled by changing chemical structure.^{27,28} In the case of urease immobilized gel, the addition of urea, a substrate of



2.9 Chemical trigger can induce swelling and de-swelling of gel, e.g. substrate of urease, urea, is changed into ammonia and the ammonia induces swelling and de-swelling by varying pH.



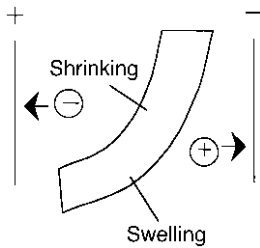
2.10 Light-induced deformation of polymer film. Example shown is the case of PVC film containing spirobenzopyrane.

urease, induces swelling and deswelling by utilizing the pH change induced by the enzyme reaction (see Fig. 2.9).^{29,30}

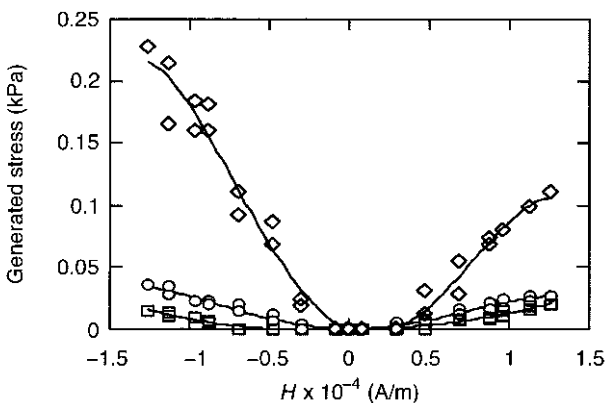
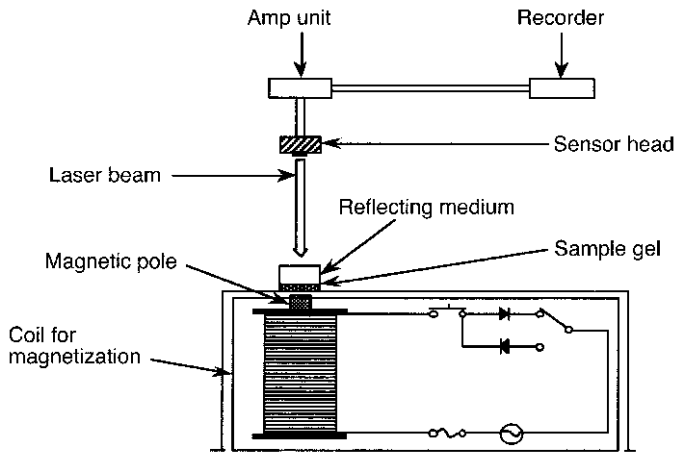
A physical trigger such as light irradiation is useful for actuating a gel in which the light-induced reversible isomerization occurs and the isomerization accompanies physical strain.^{31,32} In this case, the change is usually asymmetric and the gel bends toward or against the direction of the irradiation, depending on the photoinduced reaction (see Fig. 2.10).

In the case of electric field application, the gels usually bend, because the field application induces asymmetric charge distribution and hence the asymmetric strain in the gel.^{1,2} Asymmetric charge distribution can easily be induced in polyelectrolyte gels, and this is why polyelectrolyte gel has mainly been investigated as an electroactive polymer material (see Fig. 2.11).

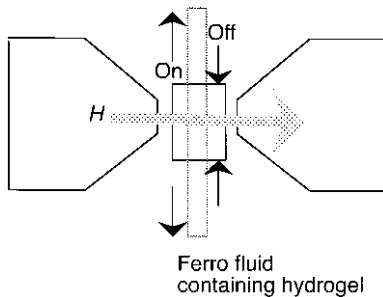
Magnetic field application can also induce a strain in a gel when a structure or species sensitive to the magnetic field is contained in it. We first proposed the idea of applying a super paramagnetic fluid to a gel.³³⁻³⁵ The gel was found



2.11 Electrically induced deformation. In the case of electric field application, the gels usually bend, since field application induces asymmetric charge distribution and hence the asymmetric strain in the gel.



2.12 Magnetic field active gel utilizing super paramagnetic property of a ferro-fluid-immobilized gel. \diamond , ferrofluid 75 wt%; \circ , ferrofluid 50 wt%; \square , ferrofluid 25 wt%.



2.13 Magnetic field induced large deformation. By turning the magnetic field (H) on and off, the gel deforms instantly.

to be sensitive to the magnetic field gradient and to induce strain very sensitively, and the structure change in the gel was investigated (see Fig. 2.12). Zryhni and his coworkers investigated the same materials and found discontinuous deformation of the gel by controlling the magnetic field (see Fig. 2.13).^{36–38}

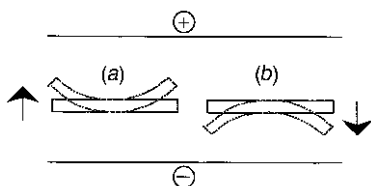
2.5 Electro-active polymer gels as artificial muscles

Amongst the polymeric actuator materials mentioned above, polymer gel has an important property as a huge strain generating material. As mentioned in the previous section, the electric field is one of the most attractive triggers for practical actuation. Electroactivity has been mentioned in connection with polyelectrolyte gels, since they contain ionic species. However, ionic species are not only sensitive to an electric field, but also usually electrochemically active, and accompany electrolysis on the electrodes. Electrochemical reactions often result in increased current and heat generation. These processes only dissipate energy, and do not contribute to strain generation. Thus, electrochemical reactions are an undesirable process in most cases. In spite of their many difficulties for practical actuators, polyelectrolyte gels and related materials still remain at the forefront of electroactive polymer materials.

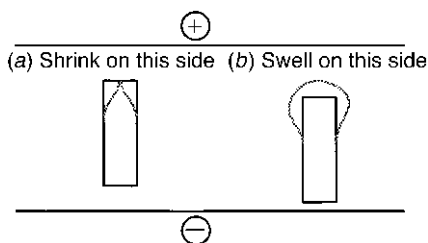
To overcome difficulties in polyelectrolytes, such as electrochemical consumption on the electrodes, we investigated the electroactive properties of the non-ionic polymer gel.

2.5.1 Electroactive polyelectrolyte gels

As pointed out in the previous section, polyelectrolyte gels have been investigated as electroactive actuator materials. The concept originates from the presence of electroactive ionic species in the gels. The ionic species can



2.14 Bending deformation of a poly(acrylonide-co-sodium acrylate) gel in aqueous solution. Bending direction is changed with sodium acrylate content in the gel. Acrylic acid content was controlled by hydrolysing poly(acrylonide) gel. The mechanism was explained with the results shown in Fig. 2.15.



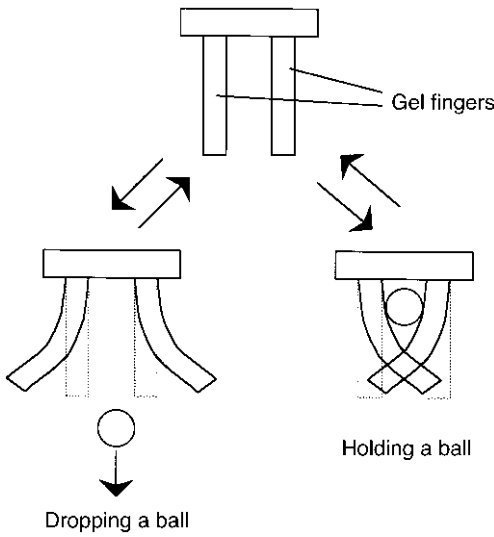
2.15 Electrically induced asymmetric deformation of a poly(acrylonide-co-sodium acrylate) gel. Sodium acrylate content is (a) low, and (b) high. In (a) the gel shrinks on anode side, but swells in (b).

migrate and form localized distribution and/or electrochemical reactions in the gel, which cause its deformation.

2.5.1.1 Poly(acrylic acid) gel

Among polyelectrolyte gels, poly(acrylic acid) (PAA) gel was the first polyelectrolyte investigated as an electroactive polymer gel. Shiga et al. found that PAA gel can be deformed by DC electric field application in the presence of salt.³⁹⁻⁴¹ A PAA gel rod was immersed in the saline aqueous solution (see Fig. 2.14). The platinum electrodes were apart from the gel surface, and the DC field was applied from both sides of the gel. Shiga et al. found a slow bending motion of the gel, the magnitude of bending depending on the salt and its concentration. They also found an asymmetric deformation of the gel, when the field was applied apart from both ends of the gel rod (see Fig. 2.15). In this case, the gel shrinks at one end and swells at the other end. The motion is explained by asymmetric swelling behaviour under the field. The deformation is explained by the following equation derived by Flory:

$$\pi = \pi_1 + \pi_2 + \pi_3 \quad [2.1]$$



2.16 Gel finger in aqueous solution. Polymer gel contains poly(acrylic acid and poly(vinyl alcohol). One electrode is occluded in the gel, and the other electrode is exposed in the solution.

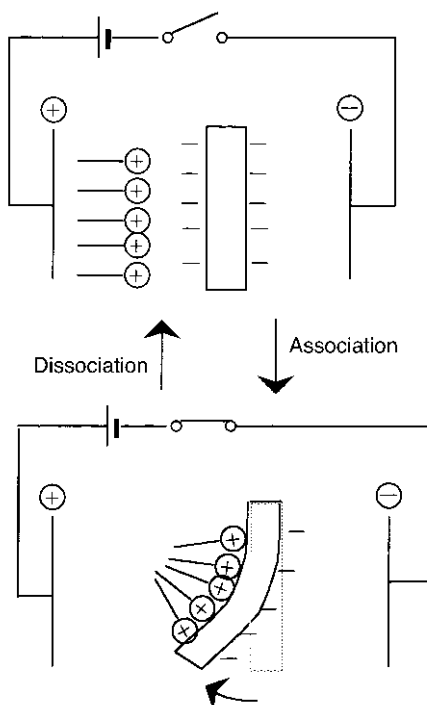
$$\pi_1 = - [\ln(1 - v) + v + xv^{1/2}]RT/V_1 \quad [2.2]$$

$$\pi_2 = (v^{1/3} - v/2)RTv_e/V_0 \quad [2.3]$$

$$\pi_3 = (\Sigma c_i - \Sigma c_j)RT \quad [2.4]$$

where π is the overall osmotic pressure which is the summation of the three types of osmotic pressure, π_1 , π_2 and π_3 , which originate from the interaction between the polymer chain and solvent, from the rubber elasticity of the gel, and from the concentration differences of the ionic species inside and outside the gel, respectively. The parameters v , x , V_0 , v_e , V_1 , c_i , c_j , R and T are the polymer volume fraction, the interaction parameter between polymer and solvent, the volume of dried polymer, the effective chain number in the network, the molar volume of the solvent, the concentration of species i in the gel, the concentration of species j in outer solution, the gas constant and the absolute temperature, respectively.

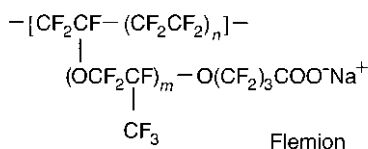
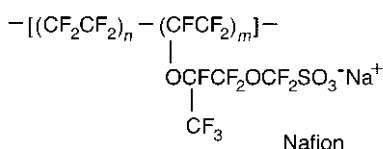
The process was considered to originate from an osmotic pressure gap induced by the localization of ionic species of different solvation power. In this movement, electrolysis usually occurred on the electrodes. Shiga et al. optimized the preparation method in order to overcome the difficulty. They put the electrodes on the gel surface, and successfully demonstrated the gel finger in aqueous solution (see Fig. 2.16).



2.17 Association and dissociation of polyelectrolyte gel of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) with cationic surfactant was found to undergo worm-like motility in aqueous solution.

2.5.1.2 Poly(2-acrylamido-2-methylpropanesulfonic acid) gel

Poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel was found to undergo worm-like motility (see Fig. 2.17).⁴²⁻⁴⁴ The principle of this deformation is based on an electrokinetic molecular assembly reaction of surfactant molecules on the hydrogel, caused by both electrostatic and hydrophobic interactions and resulting in anisotropic contraction to give bending towards the anode. When the field is reversed, the surfactant admolecules on the surface of the gel lift off and travel away electrically towards the anode. Instead, new surfactant molecules approach from the opposite side of the gel and form the complex preferentially on that side of the gel, thus stretching the gel. Surfactants such as *N*-dodecylpyridinium chloride (Cl_2PyCl) were used, which adsorbed within a second and is easily calculated to give a complex formation ratio less than 1×10^{-3} , explaining that the quick and large bending under an electric field is dominated only by the surface complexation and shrinkage of the gel.



2.18 Ion-exchange polymer-metal composite film of Nafion, of Dupont or Flemion of Asahi Glass Co. Ltd. can bend remarkably by applying low voltage.

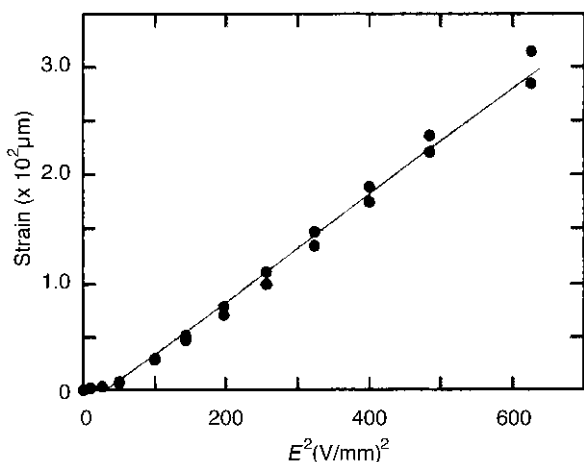
2.5.1.3 Perfluorosulfonate ionomer gel

A hydrogel of perfluorosulfonate ionomer (Nafion of Dupont) film, thickness of *ca.* 0.2 mm, was found to be an effective electroactive material (see Fig. 2.18).⁴⁵⁻⁴⁸ This material can be actuated by a DC field application of low voltage such as 3 volts. Success was attained by the development of the chemical deposition of the electrode on the membrane surface. The principle of the deforming mechanism is somewhat similar to the case of other polyelectrolyte gels. That is, the membrane requires the presence of water and salts, and an encounter of electrochemical consumption is principally inevitable. However, the response time and durability are much higher than with the other gel materials. Moreover, the actuating process is not seriously affected by electrochemical reactions, provided the operating conditions are adequately controlled. Improvement of the efficiency can be considered to originate from the chemical structure of the membrane, and the coexistence of the strong hydrophobicity and strong hydrophilicity in a polymer chain.

2.5.2 Electroactive non-ionic polymer gels

Reviewing the above-mentioned materials, one of the serious defects of polyelectrolyte gels is the electrochemical consumption on the electrode under an electric field application. The electrochemical consumption causes poor durability of the polyelectrolyte gels and limits their application fields.

Therefore, the authors tried to utilize non-ionic polymer gels as actuating materials with large deformation. The results show that the idea works in a far

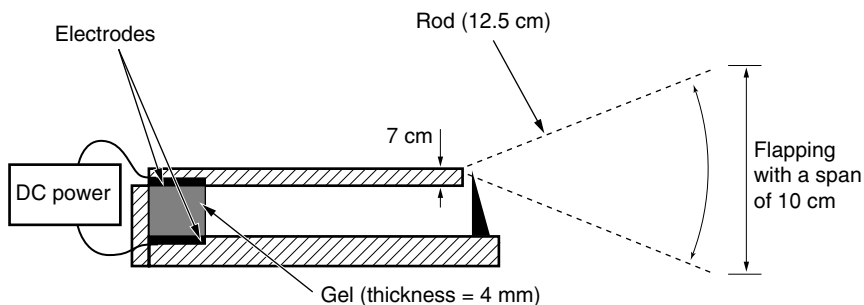


2.19 Dependence of strain in the direction of the field on the electric field.

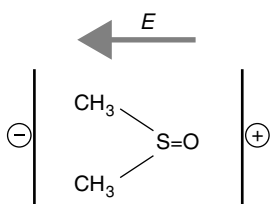
more efficient manner than expected, but the mechanism turned out to be not the same as they expected initially. The feature will be described below in a little detail.

2.5.2.1 Strain in the direction of the field

Poly(vinyl alcohol)–DMSO gel was prepared by combining physical cross-linking and chemical cross-linking with glutaraldehyde (GA). After the chemical cross-linking, the physical cross-links were eliminated by exchanging solvent into pure DMSO.⁴⁹ The chemically cross-linked gel thus obtained has an electronically homogeneous structure. Therefore, the PVA–DMSO gel has no intrinsic polarization in its structure, and electrostrictive strain generation is expected by applying a DC electric field. The results agree with this expectation, and the strain is proportional to the square of the field (see Fig. 2.19).⁵⁰ The strain observed reached over 7% in the direction of the field. The response time is very fast, the large strain is attained within 0.1 s, and the shape of the gel is instantly restored by turning off the field. The current observed is around 1 mA at 250 V/mm, which is much smaller than those of polyelectrolyte gels. The current can be depressed by further purification of the polymer and solvent. This performance is much faster than conventional polyelectrolyte gels. We can demonstrate the electro-activated quick strain in the flapping motion by amplifying the strain by 300 times. It is suggested that the flapping motion be accelerated up to 10 Hz, though the demonstration was carried out at 2 Hz (see Fig. 2.20).



2.20 Flapping motion induced by an electrostrictive deformation of a non-ionic polymer gel swollen with a dielectric solvent.



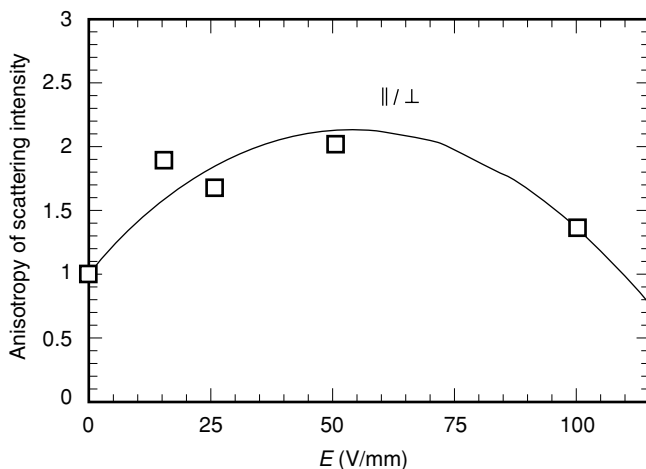
2.21 Structure of dimethylsulfoxide and its orientation by an electric field. Polarized Raman spectroscopy can be employed for investigating the molecular orientation under the field.

2.5.2.2 Electrical orientation of solvent

The strain induced in the direction of the field cannot be explained by the electrostatic attractive force between the electrodes. The effect of the electrostatic field was expected to be less than 25% of the observed strain under our experimental conditions. We therefore have to find another explanation for the strain generation in the gel.

Initially, we expected the orientation of solvent molecule under an electric field to lead the strain generation in the gel, through the changes of interactions between solvent and solute polymer, which forms the gel network.⁵¹

In order to observe the effect of the electric field on the orientation of the solvent, DMSO, Raman spectroscopy was employed. The molecule has a strong dipole moment, and can be expected to orient along the field direction (see Fig. 2.21).⁵² It is oriented very efficiently even in relatively low electric fields, but the orientation decreases over the maximum field intensity (see Fig. 2.22).⁵³ The deformation of the gel becomes greater in the region of the higher field than that of the maximum orientation, suggesting that the solvent orientation is not directly related to the deformation of the gel.



2.22 Electrically induced orientation of DMSO. DMSO orients very efficiently even in relatively low electric field, but the orientation decreases over the maximum field intensity.

2.5.2.3 Bending and crawling motion accompanying huge strain

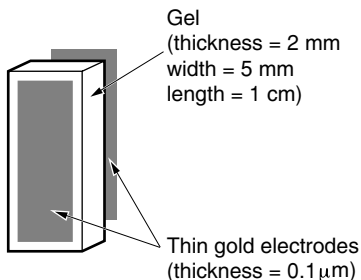
In observing the contraction along the direction of an electric field, brass plates were used as electrodes. The strain in the perpendicular direction of the field was also observable. In these measurements, the bending deformation of the gels was prevented or completely depressed.

When we carefully observed the gel deformation, solvent flow and some asymmetric deformation was suggested in the gel. But conventional electrodes or a thin metal sheet of 10 μm thickness did not lead to any effective deformation. We used very thin gold electrodes whose thickness was 0.1 μm , and covered both surfaces of the gel with the thin metal sheet. The metal sheet is soft enough and does not disturb even a slight deformation of the gel.

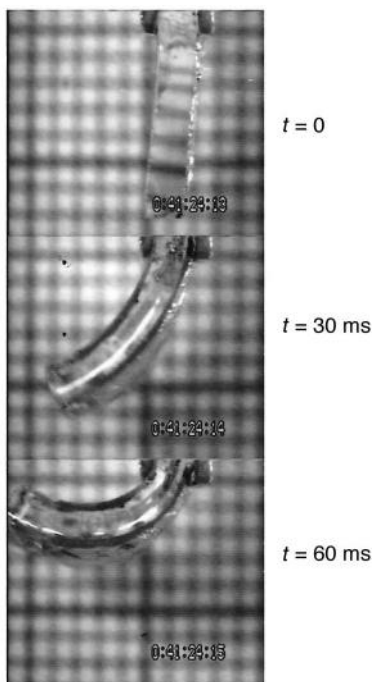
By applying a DC electric field to the gel, the gel bent swiftly and held the deformation as far as the field was on (see Fig. 2.23).^{54–56} The bending was completed within 60 ms, and the bending angle reached over 90 degrees. By turning off the field, the strain was released instantly, and the gel resumed its original shape (see Fig. 2.24). The curvature turned out to be proportional to the square of the field (see Fig. 2.25).

Taking the gel size (length 1 cm, width 5 mm and thickness 2 mm) into account, and assuming the gel volume does not change in the deformation, the strain in the gel can be estimated to be over 140% in length.⁵⁷ The electric current observed in this motion was less than 30 μA under the field of 500 V/mm.

This response and the huge strain attained in the PVA–DMSO gel is the

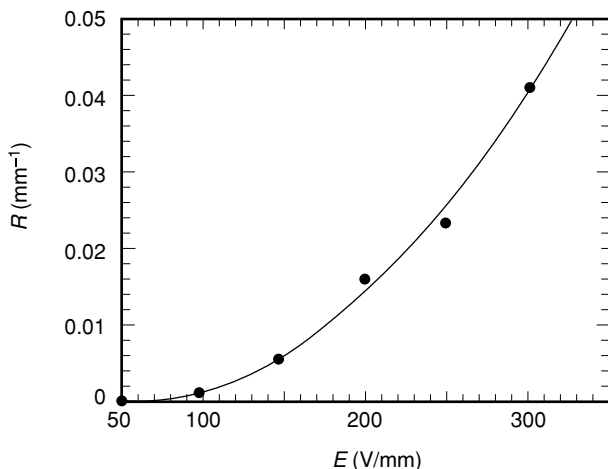


2.23 Assembling an electroactive non-ionic gel. The metal sheet was soft enough and does not disturb even a slight deformation of the gel.

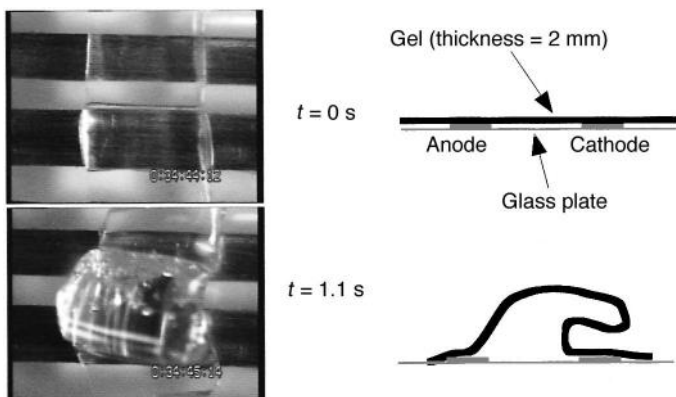


2.24 Swift bending of a non-ionic polymer gel. By applying a DC electric field to the gel, the gel bent swiftly and sustained the deformation while the field was on.

largest value among the electroactive polymer gel materials reported so far. The low current suggests that there is much less energy loss in this motion compared with the conventional polyelectrolyte gels. The energy loss as heat was much less than that of Nafion or Flemion membrane overall, therefore it is far less when the size (thickness and surface area) of the gel is taken into account.



2.25 Dependence of bending curvature on an electric field.

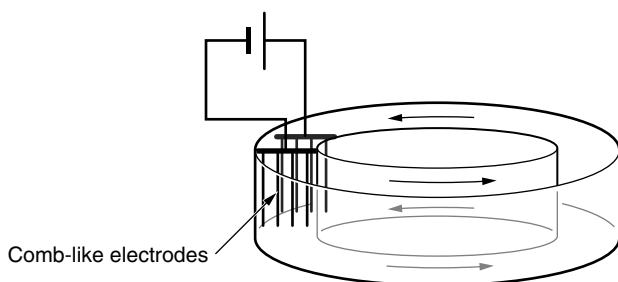


2.26 Crawling motion of a non-ionic polymer gel.

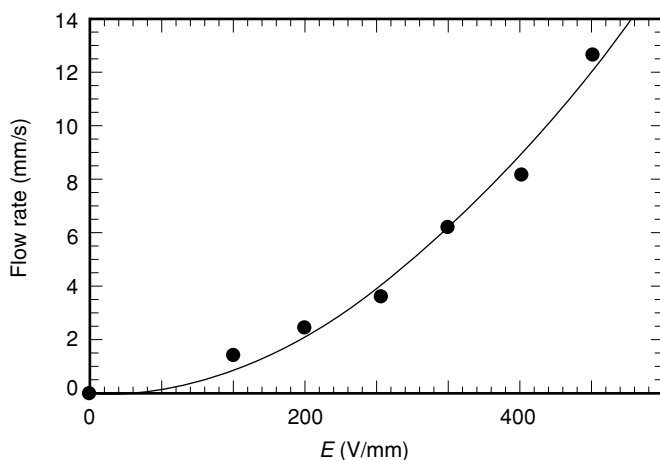
The gel could also show a crawling-type deformation.⁵⁴ This is a novel type of motion. The crawling motion was observed when a naked gel was placed on an electrode stripe array. The motion was completed in *ca.* 1 second (see Fig. 2.26).

2.5.2.4 Origin of the asymmetric pressure distribution in the gel

Such a remarkable swift bending or crawling of a non-ionic polymer gel cannot be explained by osmotic pressure gradient, which is usually considered to be the reason for electrically induced bending in polyelectrolyte gel. As pointed out in the previous section, the solvent flow was suggested in the gel. We investigated the effect of an electric field on its flowing property.⁵⁴



2.27 Electric field-induced flow of a dielectric solvent. A pair of cone-like electrodes were dipped in a circular tray filled with DMSO.

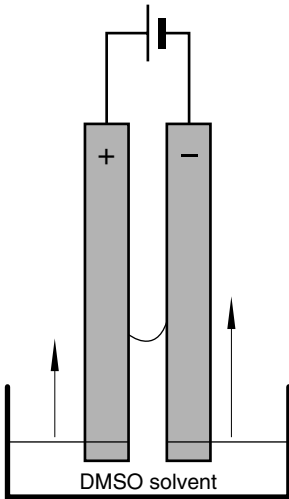


2.28 Dependence of a flow rate on an electric field. The flow rate was proportionally increased with the square of the field.

A pair of comb-like electrodes were dipped in a circular tray filled with DMSO (see Fig. 2.27). When a DC field was applied, the solvent started flowing from anode to cathode. The flowing rate was measured by using polystyrene powder floating on the solvent as a probe. The flow rate increased proportionally with the square of the field (Fig. 2.28). This result suggests that the pressure gradient is generated between the electrodes.

In order to establish a quantitative estimation of the pressure gradient, a theoretical treatment was carried out under some hypotheses shown below:⁵⁸

- 1 Only one value of ion mobility exhibits for a kind of ion.
- 2 The turbulence in the gel can be neglected for the calculations of the pressure buildup.
- 3 The ionizing and accelerating electrodes do not interfere with pressure buildup.



2.29 Solvent DMSO is drawn up between the electrodes.

- 4 Although only a very small resultant current exists, it is enough to determine the field distribution.
- 5 Different types of ions do not interfere with each other in the pressure buildup.
- 6 Surface charges on solvent boundaries have a negligible effect on ion current and field distribution.

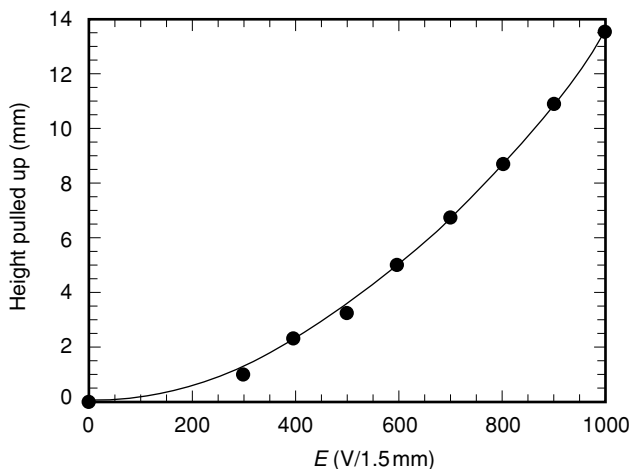
The following equation was deduced for the pressure distribution in a gel:

$$p(x) - p(0) = \frac{9}{8} \varepsilon \left(\frac{V - V_0}{d} \right) \frac{x}{d} \quad [2.5]$$

where $p(x) - p(0)$, ε , V , V_0 and d are pressure gaps between the two positions 0 (on the gel surface) and x (at x in the gel from the gel surface) in the direction of the field, dielectric constant, voltages on the gel surface and at x in the gel, and the thickness of the gel, respectively.

This equation suggests that the pressure gradient generated in the gel is proportional to the dielectric constant of the gel and to the square of an electric field. As the solvent content of the gel is *ca.* 98% in our experimental system, the dielectric constant of the gel can be assumed to be the same as that of the solvent. By taking the bending elasticity of the gel and the estimated pressure, we could attain excellent agreement between our experimental data and theoretical estimation (see Fig. 2.29).

In order to see the effect of the polymer on the electrically induced deformation, another type of experiment was carried out. A pair of plate electrodes were



2.30 Dependence of drawn-up height of DMSO on the electric field.

dipped in the solvent, and the DC field was applied between the electrodes. The solvent was pulled up between the electrodes (Fig. 2.30). The height was theoretically estimated by the following equation:

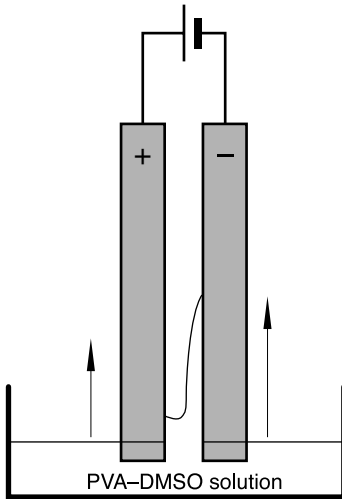
$$h = \frac{1}{2}(\varepsilon - \varepsilon_0)(V/d)^2/\rho g \quad [2.6]$$

where h , ε , ε_0 , V , d , ρ and g are liquid surface height, dielectric constant of the gel, dielectric constant of vacuum, voltage applied, distance between the electrodes, density of the gel and gravitational constant.

The curve in Fig. 2.30 was calculated to be one, and is in good agreement with the experimental data. However, when we used a DMSO solution of PVA, the height was much less than that observed in the solvent and, furthermore, was extremely asymmetric on both electrodes (see Fig. 2.31). The solution tends to climb up onto the cathode surface, but not onto the anode, suggesting that the above equation is no longer applicable for the polymer solution.

These phenomena imply that the polymer solution has the tendency to retard the discharging process. The discharge retardation causes the accumulation of the charge on the cathode side in the gel and enhances the pressure gap between the cathode side and the anode side in the gel. Thus, the presence of the polymer network also plays an important role in efficient bending deformation.

For more detailed analysis, further quantitative investigation must be carried out.



2.31 Climbing of PVA-DMSO solution onto an electrode under the field.

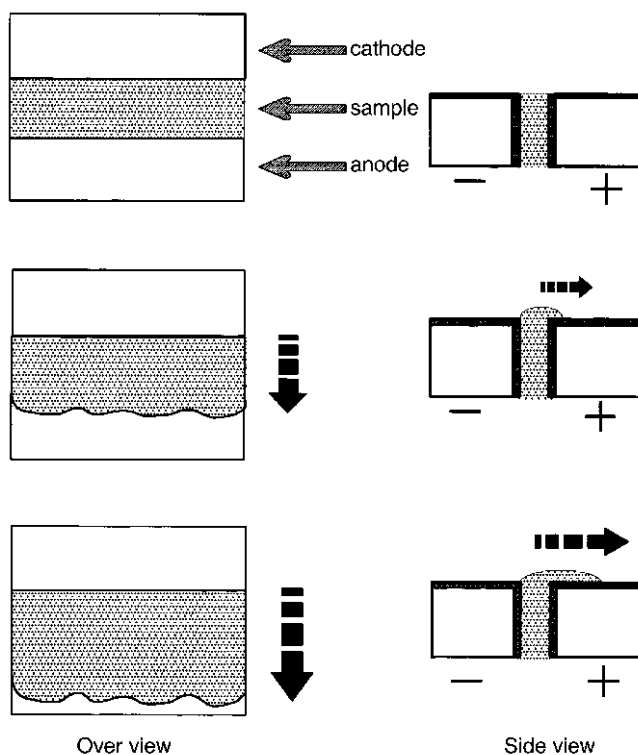
2.5.2.5 Applicability of the 'charge-injected solvent drag' method for conventional polymers

The concept proposed in the previous section can be described as the 'charge-injected solvent drag' method. The advantage of the method is its wide applicability to conventional non-ionic polymeric gel-like materials. We have been working on several non-ionic materials for soft artificial muscles that can be actuated in air.

Here, the case of poly(vinyl chloride) (PVC) will be shown briefly. In the case of PVC, we used plasticizers as solvent. Although tetrahydrofuran is a good solvent for PVC, its boiling point is too low for the preparation of the stable gel at ambient temperature in air. In the example shown, the PVC gel plasticized with dioctylphthalate (DOP) was found to creep reversibly like an amoeba by turning on and off the electric field (see Fig. 2.32).⁵⁹ The electrically induced deformation was suggested to be the asymmetric distribution of the injected charge. The mechanism is somewhat similar, but not the same, to that for the non-ionic polymer gel, since the solvent flow has not been confirmed in plasticized PVC.

2.6 From electro-active polymer gel to electro-active elastomer with large deformation

Non-ionic polymer gel swollen with dielectric solvent is shown to be extremely deformed, as is the non-ionic polymer plasticized with non-ionic plasticizer.

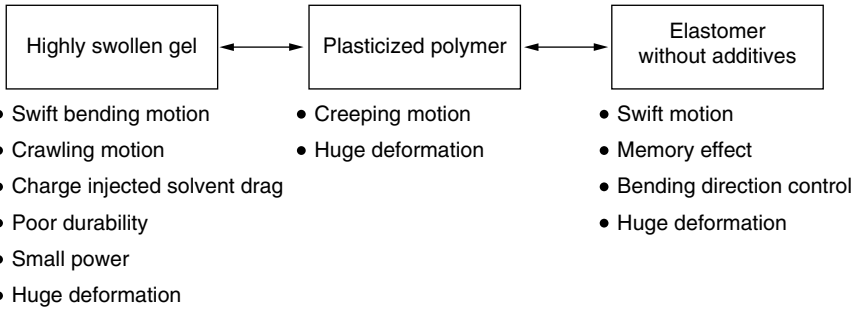


2.32 Creeping motion of poly(vinyl chloride) plasticized with dioctylphthalate. PVC gel plasticized with dioctylphthalate (DOP) was found to creep reversibly like an amoeba by turning the electric field on and off.

The mechanism suggested for the gel actuation was 'charge-injected solvent drag', and that for the plasticized polymer was 'asymmetric charge distribution of injected charge'.

The latter mechanism can be applied to the non-ionic elastomers in which the motion of the polymer chain is relatively free and so is the migration of the injected charges. The migration of the injected charge and the balance of the charging and discharging rates must be a critical factor to the deformation provided the electrostatic interaction is a major factor in the actuation.

The experimental results on polyurethane elastomers support the concept described above.⁶⁰⁻⁶³ In addition to our expectations, some novel features of the motion are being clarified in detail, such as memory effect, bending direction control, and so on (Fig. 2.33).



2.33 Wide span of large deforming non-ionic electro-active actuator materials from polymer gel, through plasticized polymer, to elastomer with no additives. A prosperous future for the conventional non-ionic polymer materials as autonomic materials can be expected.

2.7 Conclusions

In this chapter, various types of electroactive polymers were introduced. Some of them have a long history as electroactive materials. Recently, however, polymer gels and/or elastomers, which have no intrinsic polarization in their structure and do not contain any ionic species either, have been found to show huge strain by applying electric fields with a low electric current. Energy dissipation occurring as heat is much less than the conventional polyelectrolyte materials. The concepts of 'charge-injected solvent drag' and 'asymmetric charge distribution of injected charge' are proposed as a possible mechanism of the huge deformation. These concepts can be applied to various non-ionic conventional polymers. The author strongly expects that the concepts expand the field of actuator to that of practical artificial muscle, and contribute to the development of the micro-machine or nano-machine in the future.

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3.1 Development introduction

3.1.1 Introduction

The human body is itself is an automatic thermo-regulated organism. The body constantly generates heat, CO_2 and H_2O by the metabolism of food and muscle activity. The human body controls the release speed of heat by blood vessel dilatation or constriction, muscle and sweat gland activity, etc., and then regulates the body temperature.

It has been shown that the most comfortable skin temperature is 33.4°C . When the temperature of any part of the skin differs by within $1.5\text{--}3.0^\circ\text{C}$ of this ideal temperature, the human body is unaware of the warmth or coolness. If the difference is more than $\pm 4.5^\circ\text{C}$, the human body feels discomfort. In addition, a core body temperature of 36.5°C is required, and a rise or fall of 1.5°C can be fatal. A balance between the rates of heat loss and heat generated must be maintained. When the thermal resistance of their clothing is insufficient, and a person stays in a relatively low temperature condition for a long time, the body temperature drops. The human body must produce more heat by eating more food or increasing exercise. Also, the body will adjust to the heat loss by constricting the blood capillaries within the skin. Hypothermia may result, if the core temperature is lower than 35°C . Conversely, in a hot environment, the body must cool itself. The body generates heat and the heat absorbed by the skin from the environment must be dissipated. Under these conditions the body will dilate the blood capillaries, which enables the evaporation of water diffused from the body interior to increase, thereby increasing the cooling effect. This action is known as insensible perspiration. If the environment temperature increases further, the body will activate sweat glands and evaporate liquid water for increased cooling, known as sensible perspiration. In some special environments, due to the high temperature or high thermal resistance of the clothing, hyperthermia can result if the body fails to dissipate sufficient heat.

The traditional heat insulation materials, for example, fabrics such as cotton, hemp, silk, wool and polyester, polyamide and polyacrylic fibre, etc. provide a degree of resistance to body heat loss, which is determined by the number of air pockets present in the fabric. The solar ray selective absorbing textile that has been manufactured since the late 1980s can absorb the near infra-red ray in the sun rays, and convert it to heat, thus enhancing the inner temperature of the clothing. The far infra-red textile that has been produced since the late 1980s can absorb the body's irradiated far infra-red ray and turn it to heat, enhancing thermal resistance. The ultra-violet absorbing and cool-feeling fabric that has been industrialized since the beginning of the 1990s can absorb the ultra-violet and reflect the near infra-red rays from the sun, lowering the inner temperature of the clothing. All of these new functional textiles are one-way thermo-regulated heat insulating materials.

To keep the skin temperature within the 30.4 to 36.4 °C interval, we must put on or take off our clothing according to the external temperature. If clothing could automatically change its thermal resistance according to the temperature, it could control the speed of heat release, and then regulate the inner temperature. We would not need to put it on or take it off very often, and the proper inner temperature would not only increase body comfort, but also reduce fatalities.

3.1.2 Development history

The heat-storage and thermo-regulated textiles and clothing are newer concepts: they are two-way thermo-regulated new products, and have been studied for more than 30 years. The development history of heat-storage and thermo-regulated textiles and clothing is outlined in Table 3.1.

Scientists have increasingly been studying the manufacture process and properties of heat-storage and thermo-regulated textiles and clothing for several decades. There will be more reports about basic, dynamic thermal resistance and its applications in the near future.

3.2 Basics of heat-storage materials

There are three types of heat storage: sensible, latent and chemical reaction heat storage. Latent heat storage is the most important way of storing heat, and is also called 'phase change heat storage'. Latent heat-storage materials have been widely used for about 40 years.

The US National Aeronautics and Space Administration (NASA) accelerated the application research of latent heat-storage materials for the space laboratory in the 1960s. They were used to improve the protection of instruments and astronauts against extreme fluctuations in temperature in

Table 3.1 Development history of heat-storage and thermo-regulated textile and clothing

Time	Researcher	Research introduction	Ref. no.
1965	Mavelous and Desy	Designed a heat-insulating garment containing molten lithium salts pouches. The salts exchanged heat with water in the pouches and the hot water was circulated to tubing throughout the garment.	1
1971	Hansen	Incorporated CO ₂ into liquid inside the hollow fibre. When the liquid solidified and the solubility of the CO ₂ decreased, the diameter of fibre increased and the heat-insulating ability rose.	2
1981	Vigo and Frost	Incorporation of hydrated inorganic salts into hollow fibres.	3
1983	Vigo and Frost	Incorporation of polyethylene glycol (PEG) and plastic crystal materials into hollow rayon or polypropylene fibre.	4
1985	Vigo and Frost	Coated PEG on the surface of fabrics. The thermal storage and release properties of the fabrics were reproducible after 150 heating and cooling cycles. <i>Chemical Week</i> and <i>Wall Street Journal</i> reviewed Vigo's research work.	5 6, 7
1987	Bruno and Vigo	The thermal storage and release, anti-static, water absorbance, reliancy, soil release and conditional wrinkle recovery of PEG-coated fabrics were studied.	8
1988	Bryant and Colvin	A fibre with integral microcapsules filled with phase change materials (PCM) or plastic crystals had enhanced thermal properties at predetermined temperatures.	9
	Vigo and Bruno	PEG was cross-linked on the surface of knit fabrics.	10
1989	Vigo et al.	Coated PEG modified the resiliency and resistance to the oily soiling, static charge, pilling, wear life and hydrophilicity of fabric and fibres.	11
1990	Watanabe et al.	Melt spun heat-releasing and heat-absorbing composite fibre using aliphatic polyester as core or island component, fibre-forming polymer as sheath or sea component.	12
1991	Zhang	Designed the heat insulation clothing containing CaCl ₂ ·6H ₂ O pouches.	13
	Mitsui Corp.	Licensed Vigo's invention and commercialized skiwear and sportswear that contain fabrics with cross-linked polyols.	14
	Neutratherm Corp.	Licensed Vigo's invention and commercialized fabrics incorporating PEG. The fabrics were used for thermal underwear.	14
1992	Mitamura	A composite fibre was melt spun by using polytetramethylene glycol (av. MW 3000) as a core, and poly(ethylene terephthalate) (PET) as a sheath.	15

Table 3.1 (cont.)

Time	Researcher	Research introduction	Ref. no.
1992	Bryant and Colvin	Fabrics coated with a binder containing microcapsules filled with PCM or plastic crystals.	16
1993	Vigo	The antibacterial properties of PEG-coated fabrics were studied.	17
	Umbile	Fabrics were coated with a binder containing microcapsules filled with PEG (av. MW 300–4000).	18
	Momose et al.	A blend of linear chain hydrocarbon, particles of ZrC, thermoplastic elastomer and polyethylene is used as a coating materials for nylon fabrics	19
	Colvin and Bryant	A cooling garment contained pouches containing macroencapsulated PCM.	20
1994	Renita et al.	The wicking effect, antibacterial and liquid barrier properties of non-woven coated with PEG were studied.	21
	Bruno and Vigo	Formaldehyde-free cross-linking PEG-coated fabrics were studied.	22
	Bruno and Vigo	The dyeability of PEG-coated polyester/cotton fabric was investigated.	23
	Tsujito et al.	Carpet coated with a binder containing microcapsules filled with paraffin.	24
	Imanari and Yanatori	Heat insulation clothing with pouches containing paraffin and salts was designed.	25
1995	Pause	The basic and dynamic thermal insulation of fabrics coated with or without microencapsulated PCM was studied.	26
1996	Zhang et al.	The heat storage and crystallizability of PET-PEG block copolymers were studied.	27
	Zhang et al.	Melt spun composite fibre using aliphatic polyester, PET-PEG, paraffin or PEG as core component, fibre-forming polymer as sheath component.	28
	Sayler	PCM with melting point 15–65 °C incorporated throughout the structure of polymer fibres.	29
1997	Zhang et al.	Melt spun heat-storage and thermo-regulated composite fibre using PEG (av. MW 1000–20 000) as core component, polypropylene as sheath component.	30
	Outlast Inc.	Properties of the fibres were studied.	31
	Frisby Inc.	Coated fabrics and wet spinning polyacrylic fibre containing microencapsulated PCM came onto the market.	32
	Vigo	Intelligent fibrous substrates with thermal and dimensional memories were studied.	33
1999	Pause	The basic and dynamic thermal insulation of coated fabrics and non-woven containing microencapsulated linear chain hydrocarbons were studied, and the skin temperature of a simulated skin apparatus in 20 °C and –20 °C conditions were measured.	34

space. Latent heat-storage materials were used in the lunar vehicle and the Sky lab project for the Apollo 15 mission in the 1980s.³¹

3.2.1 Sensible heat-storage materials

There is an obvious temperature change during the heat-absorbing and release process of sensible heat-storage materials. Water, steel and stone are widely used sensible heat-storage materials. Water is the cheapest, most useful sensible heat-storage materials in the temperature interval from 1 °C to 99 °C at 1 standard atmosphere. The absorbing heat content of water for a 1 °C rise in temperature is 4.18 J/g.

3.2.2 Latent heat-storage materials

Latent heat-storage materials are also called phase change materials (PCM). PCM can absorb or release heat with a slight temperature change. PCM may be repeatedly converted between solid and liquid phases to utilize their latent heat of fusion to absorb, store and release heat or cold during such phase conversions. The latent heats of fusion are greater than the sensible heat capacities of the materials.

Material usually has three states. When a material converts from one state to another, this process is called phase change. There are four kinds of phase change, 1 solid to liquid, 2 liquid to gas, 3 solid to gas, 4 solid to solid.

Heat is absorbed or released during the phase change process. The absorbed or released heat content is called latent heat. The PCM, which can convert from solid to liquid or from liquid to solid state, is the most frequently used latent heat-storage material in the manufacture of heat-storage and thermo-regulated textiles and clothing. The melting heat-absorbing temperature interval is from 20 to 40 °C, and the crystallization heat-releasing temperature interval is from 30 to 10 °C. The phase change temperature of hydrated inorganic salts, polyhydric alcohol–water solution, polyethylene glycol (PEG), polytetramethylene glycol (PTMG), aliphatic polyester, linear chain hydrocarbon, hydrocarbon alcohol, hydrocarbon acid, etc., is in this interval.

3.2.2.1 Hydrated inorganic salts

Hydrated inorganic salt is an inorganic salt crystal with n water molecules. The hydrated inorganic salt that can be used in the manufacture of heat-storage and thermo-regulated textiles and clothing usually has a heat-absorbing and -releasing temperature interval of about 20 to 40 °C. Some of the hydrated inorganic salts are listed in Table 3.2. It was observed that incongruent melting and super cooling of most inorganic salt hydrates incorporated into,

Table 3.2 The hydrated inorganic salts³⁵

Hydrated inorganic salts	Melting point (°C)	Melting heat (kJ/kg)	Density kg/m ³		Specific heat capacity (J/(kg K))		Heat-storage density (MJ/m ³)
			Solid	Liquid	Solid	Liquid	
CaCl ₂ ·6H ₂ O	29	190	1800	1560	1460	2130	283
LiNO ₃ ·3H ₂ O	30	296					
Na ₂ SO ₄ ·10H ₂ O	32	225	1460	1330	1760	3300	300
CaBr ₂ ·6H ₂ O	34	138					
Na ₂ HPO ₄ ·12H ₂ O	35	205					
Zn ₂ SO ₄ ·6H ₂ O	36	147			1340	2260	
Na ₂ SO ₄ ·5H ₂ O	43	209	1650		1460	2300	345

or topically applied to, fibres occurred after several heating/cooling cycles. Lithium nitrite trihydrate lasted 25 cycles, calcium chloride hexahydrate lasted only a few cycles, and sodium sulfate decahydrate only one cycle.

3.2.2.2 Polyhydric alcohol

2,2-Dimethyl-1,3-propanediol (DMP), 2-hydroxymethyl-2-methyl-1,3-propanediol (HMP) and 2-bis-(hydroxyl methyl)-1,3-propanediol are often used as PCM. They produce endothermic and exothermic effects without a change in state at temperatures far below the melting point of the substance; the heat absorption and release of such substances is called the heat of transition. However, they are not suitable for the manufacture of heat-storage and thermo-regulated textiles and clothing due to their phase change temperature being higher than 40 °C. However, if two of the polyhydric alcohols are mixed, the phase change temperature can be in the range 24 to 40 °C.^{35,36}

3.2.2.3 PEG and PTMG

Polyethylene glycol is one of the most important PCMs. The melting temperature of PEG is proportional to the molecular weight when its molecular weight is lower than 20 000. The melting point of PEG that has an average molecular weight higher than 20 000 is almost the same. The PEGs with molecular weight lower than 20 000 are listed in Table 3.3. The PEGs with molecular weight from 800 to 1500 have melting points of about 33 °C.

The maximum theory melting point of PTMG is 43 °C. The PTMG is used as PCM in some patents. The melting point of PTMG with molecular weight 3000 is 33 °C, and the heat of melting is 150 J/g.¹⁵ However, the crystallization

Table 3.3 The phase change behaviour of different molecular weight PEG measured with DSC³⁷

PEG sample	Average molecular weight	Melting point	Melting heat (kJ/kg)	Crystallization point	Crystallization heat (kJ/kg)
1	400	3.24	91.37	-24.00	85.40
2	600	17.92	121.14	-6.88	116.16
3	1000	35.10	137.31	12.74	134.64
4	2000	53.19	178.82	25.19	161.34
5	4000	59.67	189.69	21.97	166.45
6	6000	64.75	188.98	32.89	160.93
7	10 000	66.28	191.90	34.89	167.87
8	20 000	68.70	187.81	37.65	160.97

point is supercooling due to the weak interaction between the molecular chain of PTMG. This limits its application.

3.2.2.4 PET-PEG block copolymer

When the average molecular weight of PEG used in the synthesis of PET-PEG block copolymer is higher than 1540, and the PEG weight content in block copolymer is more than 50%, the PEG segment can crystallize alone. The melting point measured by DSC of the PEG segment is 6.86 °C.²⁷ When the average molecular weight of PEG is 4000, and PEG weight content is 50%, the melting point of the PEG segment is 33.05 °C, and the melting endotherm is 30.56 J/g. The PET-PEG block copolymer can be melt spun into fibre.

3.2.2.5 Linear chain hydrocarbon

Linear chain hydrocarbon is a byproduct of oil refining. The formula is C_nH_{2n+2} . The melting and crystallization points of hydrocarbons with $n = 16 \sim 21$ are in the temperature range 10 to 40 °C, Table 3.4. The commodity linear chain hydrocarbon is usually a mixture of $n \pm 1$ or $n \pm 2$.

Linear chain hydrocarbons are a non-toxic, inexpensive, extensive source of raw materials, suitable for varied usage. They are the most important PCMs in the manufacture of heat-storage and thermo-regulated textiles and clothing.

3.2.2.6 Others

Organic acid, alcohol and ether, for example decanoic acid, 1-tetradecanol, and phenyl ether, at proper phase change temperature, can also be used as PCMs.

Table 3.4 The phase change properties of linear chain hydrocarbons^{9,25}

Phase change materials	Number of carbon atoms	Melting point (°C)	Heat of melting (kJ/kg)	Crystallization point (°C)
<i>n</i> -hexadecane	16	16.7	236.58	16.2
<i>n</i> -heptadecane	17	21.7	171.38	21.5
<i>n</i> -octadecane	18	28.2	242.44	25.4
<i>n</i> -eicosane	20	36.6	246.62	30.6
<i>n</i> -heneicosane	21	40.2	200.64	

3.3 Manufacture of heat-storage and thermo-regulated textiles and clothing

3.3.1 Phase change materials or plastic crystal-filled or -impregnated fibres

3.3.1.1 Hydrated inorganic salt-filled or -impregnated fibres

Vigo and Frost filled hollow rayon fibres with $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}/\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.³ When the content of lithium nitrate trihydrate within the rayon is 9.5 g per gram of fibre, the heat endotherm is 302.63, 312.24 and 156.32 J/g, respectively, and the heat exotherm is 221.95, 176.39 and 40.96 J/g, respectively, in the temperature interval -40 – 60 °C, after one, ten and 50 heat–cool cycles. It is quite obvious that the decrease of heat capacity of the fibre is greater after more heat–cool cycles.

3.3.1.2 PEG-filled or -impregnated fibres

Although many inorganic salt hydrates within hollow fibres were initially effective in imparting heat-absorbing and -releasing characteristics to hollow fibres, they exhibited unreliable and poor thermal behaviour on repeated thermal–cool cycles. In 1983, Vigo and Frost filled fibres with 57% (wt./wt.) aqueous solution of PEG, with average molecular weight (average MW) of 400, 600, 1000 and 3350.⁴ Hollow fibres were filled with PEG by aspirating aqueous solutions of the various different average molecular weights at, or above, room temperature through fibre bundles tightly aligned inside an O-ring until visual observation indicated that the fibres were completely filled. The filled fibres were then placed horizontally and cooled at -15 °C or lower. Excess moisture was removed from the modified fibres by drying them to constant weight in the presence of anhydrous $\text{CaSO}_4(\text{a})$ in a desiccator for 24 h. The measured results of DSC show that the heat-absorbing and -releasing

capacity of filled hollow polypropylene fibre is 1.2–2.5 times that of untreated fibre, and that of filled hollow rayon is 2.2–4.4 times that of untreated rayon.

3.3.1.3 Polyhydric alcohol filled or -impregnated fibre

Vigo and Frost filled hollow rayon and hollow polypropylene fibre with 2,2-dimethyl-1,3-propanediol (DMP)³⁶ and impregnated non-hollow rayon with DMP. The heat-absorbing capacity of treated hollow polypropylene fibre was 136.68 J/g in the temperature range 72–102 °C, and the heat-releasing capacity of treated hollow polypropylene fibre was 120.38 J/g in the temperature range 77–47 °C. It is less obvious that there is a decrease of the heat capacity of the fibre after 50 heat-cool cycles. The fibre is not suitable for clothing textiles, due to its high phase change temperature.

3.3.2 Coated fabric

3.3.2.1 Fabrics coated with PEG

Although the PEG and polyhydric alcohols were effective as heat-storage and -release agents in modified fibres/fabrics, they were only suitable for applications that did not require laundering of the fabrics, since they were still water soluble. Vigo and Frost studied fabrics coated with cross-linked PEG in 1985.⁵ The average MW of PEG was from 600 to 8000. Fabrics were treated with aqueous solutions containing the following cross-linking agents: 40% solids dimethyloldihydroxy-ethyleneurea (DMDHEU), 40% solids dimethylolethyleneurea (DMEU), 50% solids dimethylolisopropyl carbamate and 80% solids trimethylolmelamine. Acid catalysts used were $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid in a mole ratio of 20 to 1, NaHSO_4 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. PEG was also present in the pad bath. The cotton, PET and wool fabrics having thermal activity were produced using 50% aqueous solutions of the PEG-600 or PEG-1000 containing 8–12% DMDHEU and 2.4–3.6% mixed catalysts ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid). All fabrics were padded to wet pickup of about 100%, dried and cured, then machine washed and dried. The PET treated with 50% aqueous solution of PEG-600, was dried at 60 °C for 7 minutes, and cured at 160 °C for 3 minutes. The weight gains were 42.9%, and the heat-absorbing capacity was 53.92 J/g measured by differential scanning calorimetry (DSC). The heat capacity was 53.08 J/g after ten heat-cool cycles. There was no obvious decrease of the heat capacity of the fibre.⁵ The heat-absorbing capacity of untreated polyester fabric was 42.21 J/g and 40.12 J/g.

If the weight gains of the fabric were less than 20%, only the antistatic performance of the fabric was improved, and the thermal activity was not obvious. Fabrics treated with PEG-600/DMDHEU and an appropriate acid

catalyst had weight gains of 27–47% and were thermally active compared to the untreated and cross-linked controls. When concentrations of less than 8% DMDHEU were used in the treatments with PEG-600, the weight gains were not sufficient to impart thermal activity to the fabric. Conversely, when higher concentrations of DMDHEU were used ($> 12\%$) or when zinc nitrate catalysts were used at any DMDHEU concentration, extensive cross-linking occurred and the fabric was thermally inactive. When DMDHEU and the mixed acid catalyst were used with PEG of higher molecular weights (> 3350), there was little reaction, resulting in low add-on. Preliminary cross-link density and thermal analysis data indicate that the PEG are insolubilized on the fibres and exhibit thermal activity only when the PEG are of low crystallinity and can react with the polyfunctional cross-linking agent. Further experiments demonstrated that a wide range of one-step curing conditions (with temperatures as low as $80\text{ }^{\circ}\text{C}$) could be utilized to insolubilize the polymer on fibrous substrates and provide superior thermal storage and release properties than those obtained by the two-step (dry/cure) process that employed high curing temperatures.¹⁴

However, the DMEHEU or DMEU can be gradually decomposed to release toxic formaldehyde. A formaldehyde-free cross-linking system was discovered using a stoichiometric amount of sulfonic acids and glyoxal to form polyacetals with the same polyols.²² These polyacetals exhibit the same multifunctional properties and are durable to laundering.

3.3.2.2 *Fabrics coated with polyhydric alcohols*

Polyhydric alcohols undergo solid-to-solid thermal transitions (SSTs). The often-used plastic crystals are DMP (DSC onset mp $126\text{ }^{\circ}\text{C}$) and 2-hydroxymethyl-2-methyl-1,3-propanediol (HMP, DSC onset mp $181\text{ }^{\circ}\text{C}$). The 50% (wt./wt.) aqueous solutions of the plastic crystals were made for subsequent application to fabrics.⁵

Regardless of fibre type, all fabrics immersed in 50% aqueous solutions of the DMP and padded to about 100% wet pickup, then dried at $100\text{ }^{\circ}\text{C}$, had only slight weight gains after conditioning. Presumably, the high vapour pressure of the DMP precludes the conventional or elevated temperature drying of treated fabrics.⁵

In contrast to the other plastic crystal substance DMP, the HMP did not volatilize from the fabric when it was dried at conventional or elevated temperature to remove excess water. The modified fabrics had heat contents of $87.78\text{--}104.5\text{ J/g}$ on heating and $79.42\text{--}96.14\text{ J/g}$ on cooling after one to ten thermal cycles. The heat contents of HMP-treated fabrics were 1.7–2.5 times those of untreated fabrics. The fabrics are not suitable for clothing textiles, due to their high phase change temperature.

3.3.2.3 *Fabrics coated with a binder containing microcapsules*

Bryant adapted a coating to apply to a substrate such as a fabric in order to enhance the thermal characteristics thereof.¹⁶ The coating includes a polymer binder in which are dispersed integral and leak-resistant microcapsules filled with PCM or plastic crystals that have specific thermal properties at predetermined temperatures.

Zuckerman invented a coating composition for fabrics including wetted microcapsules containing PCM dispersed throughout a polymer binder, a surfactant, a dispersant, an antifoam agent and a thickener.⁴⁰ The most preferred ratios of components of the coating composition of the invention were: 70 to 300 parts by dry weight of microcapsules for each 100 parts by dry weight of acrylic polymer latex, 0.1% to 1% dry weight each of surfactant and dispersant to dry weight of microcapsules, water totalling 40% to 60% of the final wet coating composition and antifoam agent of from 0.1% to 0.5% dry weight to total weight of the final wet coating composition.

The microcapsules containing $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as PCM were also used for the fabric coating.

Umible had coated a woven polyester with a mixture of microcapsules and polymer binder.¹⁸ The coating layer is composed of 1: 1–3 (wt. ratio) mixtures of microcapsules containing PEG with average MW 300–4000 and a polyacrylic binder. The coated fabric evolves heat at 7–11 °C, and absorbs heat at 28–31 °C. Umible thought the fabrics were useful for garments for workers in freezer units and mountaineering.

3.3.2.4 *Other coated fabrics*

Momose invented a coating agent containing *n*-octadecane 80, *n*-hexadecane 20, thermoplastic elastomer kraton G1650 12, linear polyethylene 20, ZrC 10 and an antioxidant 0.2 part.¹⁹ The mixture was melted and mixed to give a non-bleeding solid with heat content 129.48 J/g and good shape-retaining properties. The mixture was molten at 140 °C and applied to a nylon cloth to give a textile with good heat storage properties, useful for skiwear.

3.3.3 Fibre-spinning

Heat-storage and thermo-regulated textiles can be manufactured by filling hollow fibres or impregnating non-hollow fibres with PCM and plastic crystals or coating fabric surfaces with PEG, plastic crystals or microcapsules. There are still some defects in the wash-resistance, durability and handle of the heat-storage and thermo-regulated textiles produced by these processes. The fibre-spinning process has developed quickly since the 1990s.

3.3.3.1 *Composite fibre-spinning*

The copolymers of diacid, for example, glutaric acid, hexanedioic acid and decanedioic acid, with diols, for example, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol have heat-absorbing and -releasing properties.¹² The melting points of some of the aliphatic polyesters are in the temperature range 20–40 °C, but their crystallization points are usually beyond the temperature range 30–10 °C.⁴¹ Watanabe used the mixture of two aliphatic polyesters as the core component, PET as the sheath component, and melt spun to produce heat-absorbing and heat-releasing synthetic conjugate fibres for heat-insulating garments.¹²

PTMG was used as the core component in the composite fibre-spinning process.¹⁵ A composite fibre that uses PTMG as the core and PET as the sheath was designed.

3.3.3.2 *Fibre spun with a mixture*

When aliphatic polyester or polyether is used alone as the core or island component in the composite fibre-spinning process, the spinning process is very hard to control, due to its very low melting viscosity. If the aliphatic polyester or polyether is blended with ethylene copolymer, the melting viscosity of the mixture can be high enough for the fibre-spinning process.

Zhang et al. had studied the melt spinnability of PEG alone, and PEG mixed with ethylene–vinyl acetate as the core component, and polypropylene as the sheath.³⁰ The results showed that the PEG could be spun alone only when the average MW was higher than 20000. When the average MW was higher than 1000, it could be melt spun well for the PEG and ethylene–vinyl acetate 1:1 (wt./wt.) mixture. Sayler's invention showed that the preferred weight percentages are about 55% PCM, about 15–21% polyolefin, about 7–11% ethylene copolymer, about 7–15% silica particles and about 7.5% microwave-absorbing additives.²⁹

The mixture of paraffin and polyethylene was melt spun into the fibre directly. The surface of the fibre was coated with epoxy resin in order to prevent leakage of the paraffin.

3.3.3.3 *Fibre with integral microcapsules*

Embedding the microcapsules directly within the fibre adds durability as the PCM is protected by a dual wall, the first being the wall of the microcapsule and the second being the surrounding fibre itself. Thus, the PCM is less likely to leak from the fibre during its liquid phase, thus enhancing its life and the repeatability of the thermal response.

Bryant and Colvin produced a fibre with integral microcapsules with PCMs or plastic crystals.⁹ The fibre has enhanced thermal properties at predetermined temperatures. The microcapsules can range in size from about 1 to about 10 microns. In fabricating the fibre, the desired microencapsulated PCMs are added to the liquid polymer, polymer solution or base material and the fibre is then expended according to conventional methods such as dry or wet spinning of the polymer solutions and extrusion of the polymer melts. According to the report, the maximum content of PCM in the polyacrylic fibre is about 10%. The minimum filament denier is 2.2dtex.³¹

3.3.4 Heat-storage and thermo-regulated clothing

3.3.4.1 *Water circulation clothing*

This kind of clothing is usually used as protective clothing for extremely warm or cool environments. It uses ordinary water as a sensible heat-storage material, circulating warm water in winter and circulating cool water in summer through tubing that is incorporated into the body garment or vest. A battery-powered pump circulates the water through the tubing in the suit load. It has been commercialized for several decades.

3.3.4.2 *PCM pouches attached to clothing*

These garments were designed by Mavleous and Desy,¹ Zhang,² Colvin³ and Imanari and Yanatori.²⁵ They use PCMs instead of water as heat-storage materials. They are used in extreme high or low temperature environments for body cooling or warming.

3.3.4.3 *Heat-storage and thermo-regulated textile clothing*

As the manufacturing technology of heat-storage and thermo-regulated fibres and textiles became more advanced, new types of clothing came onto the market. The PEG-coated fabrics produced by the Mitsui Corporation were used as ski- and sportswear.¹⁴

Outlast Inc. and Frisby Inc. licensed the thermal regulation technology from Bryant of Triangle Research and Development Corporation in about 1991. Since then, the scientists at Outlast and Frisby have worked diligently to create thermal regulating materials for use in many different products. The microcapsules were either coated onto the surface of a fabric or manufactured directly into polyacrylic fibres. Other heat-storage and thermo-regulated textile products, such as blankets, sleeping bags, underwear, jackets, sports garments, socks, ski boots, helmets, etc., have come onto the market since 1997.^{31,32} Output has gradually increased in the last 3 years.

3.4 Properties of heat-storage and thermo-regulated textiles and clothing

3.4.1 Thermal resistance

3.4.1.1 Traditional thermal resistance

The traditional thermal resistance is measured by the standard stationary methods (for example, those involving the use of a guarded hot plate apparatus). But in Pause's opinion, none of these methods is suitable for the determination of materials with PCM, because a long continual thermal stress could activate the phase change which would lead to measurements that deviate significantly from those that should be obtained.²⁶ Some experiments are still necessary in order to enable us to decide whether this is true.

The thermal resistance of coated fabrics with or without microcapsules was measured by Zuckerman et al.⁴⁰ The thermal resistance of coated fabrics with microcapsules is higher than that of untreated fabrics; the results are listed in Tables 3.5 and 3.6. That is mainly due to the action of binder that seals the cloth pore of the fabric.

3.4.1.2 Dynamic thermal resistance

There are phase change materials on the surface of the fibre or in the fibre, so the fabric or fibre is going to absorb heat in the temperature range 20–40 °C, and release it in the range 30–10 °C. Vigo and Frost studied the endotherm and exotherm behaviour of the fabrics and fibres by DSC.^{3–5} The plots of DSC measurement are shown in Fig. 3.1 and 3.2.¹⁴ But the DSC measuring results were not translated to the thermal resistance of the textile.

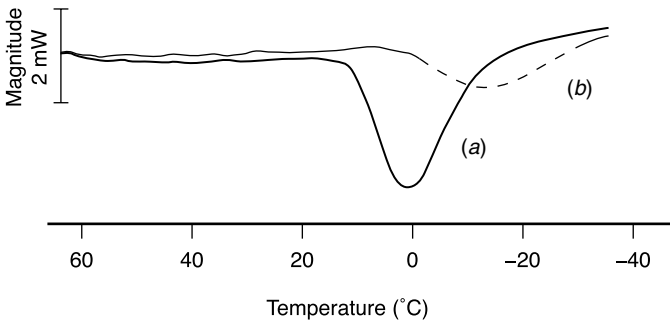
When Neutratherm Corporation studied a wear trial with 50 human subjects

Table 3.5 Thermal resistance of coated fabrics⁴⁰

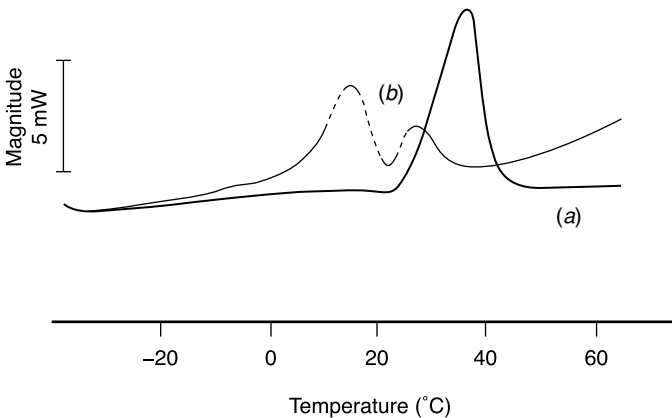
Materials tested	Acrylic with PCM	Acrylic without PCM	Substrate with PCM	Substrate without PCM
Wt/unit area (g/m ²)	270	250	227	207
Stand thickness (mm)	5.40	5.63	0.63	0.61
Compressibility (lb)	12	16	13	20
Raw density (kg/m ³)	49	44	360	339
Thermal conductivity (w/m K)	0.0398	0.0342	0.1012	0.1782
Thermal resistance (m ² K/w)	0.1281	0.1491	0.0057	0.0029
Specific thermal capacity (kJ/kg K)	3.022	2.391	2.468	1.840

Table 3.6 The basic and dynamic thermal resistance of coated fabrics²⁶

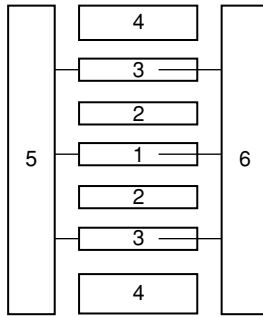
Test material	Basic thermal resistance (m ² K/W)	Dynamic thermal resistance (m ² K/W)
Membrane material	0.0044	
Membrane material/foam coating	0.0187	
Membrane m./foam/40 g/m ² PCM	0.0181	0.0863
Membrane m./foam/90 g/m ² PCM	0.0176	0.1481



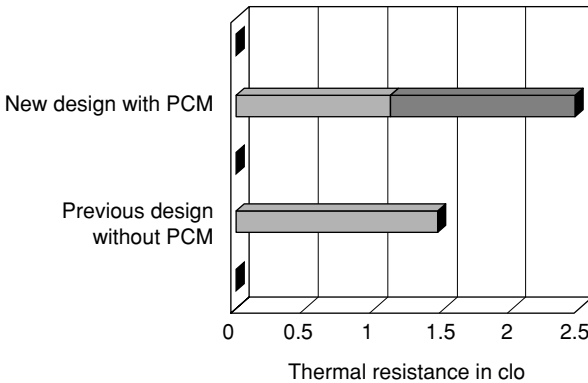
3.1 DSC cooling scans (10 °C/min) of melt-blown polypropylene treated with PEG 1000/DMDHEU and dried/cured: (a) 1.5 min/90 °C and (b) 5 min/100 °C.



3.2 DSC heating scans (10 °C/min) of woven cotton pritchloth treated with PEG-1450/DMDHEU and dried/cured: (a) 2 min/100 °C and (b) 4 min/80 °C.



3.3 Testing arrangement. 1: Radiant (panel) heater with temperature sensor, 2: Testing sample, 3: Panel heater/cooler with temperature sensor, 4: Heat insulation, 5: Power supply for panel heater, 6: Computer for recording and processing of measured values.



3.4 Comparison of the total thermal insulation of the coated fabrics. ■, Basic thermal resistance; ■, Dynamic thermal resistance.

with cotton thermal underwear containing bound PEG, enhanced wind resistance was the property giving the highest percentage of satisfaction (82%) to the wearers.¹⁴

In order to measure the basic and dynamic thermal resistance, Pause designed a measurement method;²⁶ the basic arrangement of the measuring apparatus is presented in Fig. 3.3. The thermal resistance of the coated fabrics with microcapsules is shown in Table 3.6. The total thermal insulation values obtained for the coated fabrics with microcapsules containing linear chain hydrocarbon compared to the thermal insulation of the materials without microcapsules are shown in Fig. 3.4.

Pause compared the thermal insulation effects of a batting (thickness 24 mm) of polyester fibre, outer fabric (0.2 mm) and liner fabric (0.1 mm) with

a batting (thickness 12 mm) of acrylic fibre with incorporated PCM, outer fabric (0.2 mm) and liner fabric with PCM-coating.³⁴ The test results show that the basic thermal insulation of the textile substrate is reduced by approximately 30% when replacing the thick batting made of polyester fibres with a batting of acrylic fibres with incorporated PCM only 12 mm thick. However, the dynamic thermal insulation effect resulting from the heat emitted by the PCM inside the coated layer of the liner materials as well as inside the batting fibres more than doubled the thermal insulation effect of the new garment configuration. The total thermal insulation effect of the new garment exceeds the total thermal insulation effect of the previous garment by approximately 60%.

The dynamic thermal resistance of any one heat-storage and thermo-regulated fabric is not a constant. The dynamic thermal resistance of the fabric changes with time during the measurement process: it should be like a Gaussian distribution, just like the DSC plot. However, it is like a rectangle in Fig. 3.4. Pause's is the only report on dynamic thermal resistance. The main difficulty is in the design of new testing apparatus.

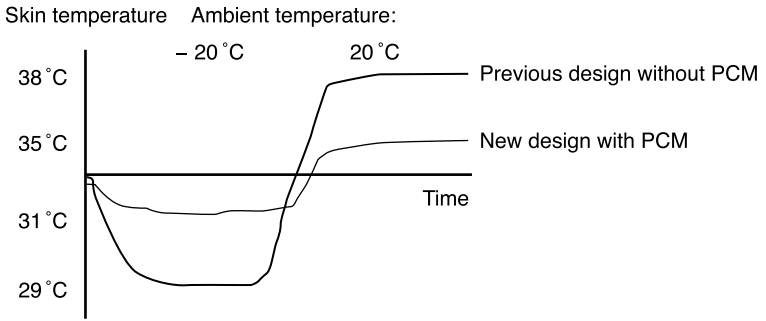
3.4.2 Thermo-regulating properties

There is no standard method for measuring the thermal regulating properties of heat-storage and thermo-regulated textiles and clothing. Much still needs to be done.

Watanabe et al. attached the plain fabric containing aliphatic polyester and the plain fabric containing PET on a metal plate.¹² The temperature of the plate was increased from room temperature to 40 °C, kept constant for a few minutes, and then reduced from 40 °C to 5 °C. The surface temperatures of the fabrics were recorded with an infra-red camera. The difference in the surface temperatures of these two plain fabrics can be calculated from the infra-red picture. The surface temperature of the fabric which is woven by fibre produced by poly(glutaric 1,6-hexanediol) as the core and PET as the sheath is 4.5 °C lower than that of the PET fabric at 40 °C, and 3.2 °C higher than that of the PET fabric at 5 °C.

Vigo and Bruno's preliminary experiments using infra-red thermograph indicated that fabrics containing the cross-linked polyols had a surface temperature difference as much as 15 °C lower than that of a corresponding untreated fabric exposed to a heat source.¹⁴

Neutratherm TM-treated cotton thermal underwear (based on Vigo's process) was evaluated during skiing and skiing-like conditions, and was found by wearers to be superior to untreated cotton thermal underwear by 75% or more with regard to preventing overheating and chilling due to wind and/or cold weather.¹⁴



3.5 Comparison of the thermo-regulated effect of the previous and the PCM garment design.

A thermal active fibre was manufactured using PEG (average MW 1000) as the core and PP as the sheath.³⁰ Zhang et al. manufactured a non-woven using this fibre. The temperature of a drying chamber with fan was kept steady at 50 °C. The temperature of a refrigerator was kept steady at 0 °C. The thermal active non-woven and normal PP non-woven with the same area density were attached on a thin metal plate. The inner temperature of these two non-woven was measured by thermocouple thermometer during the temperature interval up from 0 °C to 50 °C and down from 50 °C to 0 °C. The maximum inner temperature difference of thermal active non-woven and normal PP non-woven is 3.3 °C in a period when the temperature is rising, and 6.1 °C in a period when the temperature is falling.

The garment containing PCM was tested in a climatic chamber at various temperatures to determine the thermo-regulating effect from heat absorption and heat release of the PCM.³⁴ In this test, the garment samples were attached to a simulated skin apparatus, the temperature of which was measured over time at various ambient temperatures and metabolic heat rates. Based on these tests, time intervals were estimated within which the skin temperature could be stabilized within a desired temperature range. The test results for the two garments under ambient temperature exposures of - 20 °C and + 20 °C are summarized in Fig. 3.5.

The results show that, at both ambient temperatures, the temperature of the simulated skin on the back side of the new garment is stabilized in the comfort temperature range between 31 °C and 35 °C.³⁴ In Pause's opinion, that means the heat absorption and release of the PCM has created a thermo-regulating effect resulting in a comfortable microclimate temperature during the entire test. On the other hand, in the test of the previous garment, the skin temperature is in the discomfort temperature zones as low as 29 °C and as high as 38 °C.

In other reports, cold weather trials showed a usual drop of 3 °C in the skin temperature for control and only 0.8 °C for the heat-storage and thermo-regulated garment.

3.4.3 Antibacterial properties

The PEG-coated fabrics gain not only absorbed and released heat, but also antibacterial properties.^{17,22} The PEG-treated fabric can inhibit the growth of gram-positive *S. aureus* and gram-negative *E. coli* and *P. aeruginosa*.

The mechanism by which PEG-treated fabrics inhibit bacterial growth is being investigated by Vigo.¹⁷ It results from three factors. A slow release of formaldehyde from the DMDHEU cross-linking resin may have an antibacterial effect, as formaldehyde can be used as a disinfecting agent. The PEG may exhibit a form of surfactant behaviour, which also is known to reduce bacterial growth. A third explanation relates to the finish imparting thermal absorption and release properties. The temperature may reach beyond some micro-organisms' growth range, killing those species.

A thermal active non-woven were produced by PEG-treated 100% polypropylene spun bonded-melt blown-spun bonded. The PEG-treated non-woven inhibited bacterial growth.²¹ The most probable effects that inhibit microbial growth may be attributable to the surfactant-like properties of the bond PEG, which disrupts cell membranes due to the dual hydrophilic-hydrophobic characteristics of the PEG. This was reported in Vigo and Leonas's recent work.⁴²

3.4.4 Other properties

The cross-linked PEG treatment changes a fabric's properties relative to untreated fabrics. Properties imparted include heat-absorbing and -releasing, antibacterial activity, resiliency/antiwrinkling, wear, toughness, absorbency and exsorbency of liquids, improved abrasion and linting resistance, decreased static propensity and increased oily soil release.^{8,14,17}

3.5 Application

The possible applications of heat-storage and thermo-regulated textiles and clothing are under development. There are many possible end uses of these textiles.

3.5.1 Casual clothing

Heat-storage and thermo-regulated textiles can be used as casual textiles, for example, face fabric, liner fabric, batting, etc. Thermal underwear, jackets, sports garments and skiwear have now come onto the market.

3.5.2 Professional clothing

Examples are firefighter uniforms, bullet-proof vests, diver's coveralls, space suits, airman suits, field uniforms, sailor suits, etc. Special gloves for extremely high or low temperatures are being studied. Personnel supporting the operations of Air Force One now wear thermo-regulated flight gloves.

3.5.3 Textiles for interior decoration, bedclothes and sleeping bags

Heat-storage and thermo-regulated textiles can be used as curtains, quilts, quilt covers or batting. They are already used as sleeping bags.

3.5.4 Shoe lining

Heat-storage and thermo-regulated textiles can absorb, store, redistribute and release heat to prevent drastic changes in the wearer's head, body, hands and feet. In the case of ski boots, the PCM absorbs the heat when the feet generate excess heat, and send the stored heat back to the cold spots if the feet get chilly. This keeps the feet comfortable. Ski boots, footwear and golf shoes are coming onto the market.

3.5.5 Medical usage

PEG-treated fabric may be useful in medical and hygiene applications where both liquid transport and antibacterial properties are desirable, such as surgical gauze, nappies and incontinence products. Heat-storage and thermo-regulated textiles can keep the skin temperature within the comfort range, so they can be used as a bandage and for burn and heat/cool therapy.

3.5.6 Building materials

Such textiles can be used in architectural structures embedded in concrete, in roofs and in other building materials.

3.5.7 Other uses

They can be used as automotive interiors, and battery warmers. They can also be used in agriculture and geotextiles.

3.6 Development trends

The manufacture, properties and applications of heat-storage and thermo-regulated textiles have been extensively studied since the 1980s but their future development is still not very clear. It is expected that similar importance will be attached to improving comfort to the wearer as was seen in the development of breathable membranes (Gore-Tex, Sympatex).³¹ These textiles were selected as one of the '21 inventions that will shape the 21st century' by the editorial staff of *Newsday*.

The traditional heat insulation textile, which works by trapping heat in the dead-air spaces of a material, is meant to retain heat as long and efficiently as possible. The heat-storage and thermo-regulated textile is not a traditional textile or an evolutionary textile with higher heat insulation ability. The heat-storage and thermo-regulated textile keeps you warm when it is cool and cool when it is warm. It is a product that will make you more comfortable during extreme temperature changes. Thus, it is an intelligent textile.⁴³ When the temperature changes dramatically, the inner temperature of the heat-storage and thermo-regulated garment is stabilized in the comfort temperature range between 31 °C and 35 °C.^{32,34}

The thermo-regulated properties of the garment offered against extremes of cold and/or heat are available only for a limited period however, depending on the garment construction and the temperature of the environment. Thus it is more useful in an environment in which the temperature is quickly changing than in a steady temperature environment. However, if the released heat is not absorbed quickly, or the absorbed heat is not released, the textile loses its thermo-regulating function. To improve its durability, there is still much to be done.

3.6.1 Enhancing heat content

The maximum PCM load in the heat-storage and thermo-regulated polyacrylic fibre is 10%.³¹ In other words, the maximum heat content of the fibre is 25 J/g. The thermo-regulating function offered against extremes of cold and/or heat is available only for a limited period. The maximum heat content of the fabric is over 40 J/g in patent application and heat content over 50 J/g is possible in technology. The more PCMs there are in the textile, the longer the duration of temperature equalization.

3.6.2 Combining heat-storage and thermo-regulated textiles with trapped-air materials

The experiment results show that a thermo-regulated textile that can regulate inner temperature effectively must have enough high thermal resistance. How to combine the heat-storage and release technology with the trapped-air technology is an area for future research.

3.6.3 Combining with other energy conversion technology

The group VI transition metal carbon compound can convert near infra-red rays into heat.⁴⁴ If the particles of ZrC are added to the heat-storage and thermo-regulated textile, they can absorb the near infra-red rays of the sun in daylight and convert them into heat that makes the PCMs in the textile change phase from solid to liquid. The textile releases its heat to keep its temperature relatively steady when the inner temperature is lower than the crystallizing point of the PCMs.¹⁹

Some of the polyacrylic acid or polyacryl–nitrile copolymers can absorb moisture from the air and release heat. They can be made into fabrics that can regulate inner moisture and temperature but such fabrics are not durable for limited moisture absorbency ability. If the moisture-absorbing fabrics are laminated with heat-storage and thermo-regulated fabrics, the composite fabrics can absorb moisture or heat and prevent drastic changes in the inner temperature. This kind of fabric is useful for ski- and sportswear.

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