INTELLIGENT TEXTILES FOR MEDICAL APPLICATIONS: AN OVERVIEW

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INTRODUCTION

The discovery of shape memory materials in the 1960's and intelligent polymeric gels in the 1970's were however generally accepted as the birth of real smart materials. The concept 'Smart Material' as such was defined in Japan in 1989. It was not before the late 90's that intelligent materials were introduced in textiles. The first textile material that, in retroaction, was labelled as a 'smart textile' was silk thread having a shape memory (by analogy with the better known 'shape memory alloys' which will be discussed later in this chapter).
It is a new type of product that offers the same potential and interest as technical textiles.

What does 'smart textiles' mean exactly?

Smart textiles can be described as textiles that are able *to sense* stimuli from the environment, *to react* to them and *adapt* to them by integration of functionalities in the textile structure.

The stimulus as well as the response can have an electrical, thermal, chemical, magnetic or other origin.

Advanced materials, such as breathing, fire-resistant or ultrastrong fabrics, are according to this definition not considered as intelligent, no matter how high-technological they might be.

The extent of intelligence can be divided in three subgroups[1]:

- passive smart textiles can only sense the environment, they are *sensors*;
- active smart textiles can sense the stimuli from the environment and also react to them, besides the sensor function, they also have an *actuator* function;
- finally, very smart textiles take a step further, having the gift to adapt their behaviour to the circumstances.

Sometimes, the change in the material is clearly visible, but sometimes it takes place on a molecular level, completely invisible to the human eye.

The application possibilities offered by these materials are only limited by human imagination.

Initially, smart clothing will find applications in fields where the need for monitoring and actuation can be of vital importance, such as a medical environment, and with vulnerable population groups (new borns, elderly). These kind of textiles include for example wearable smart textiles (biomedical clothing), designed to fulfil certain functions, but apart from that without any fringes. However, as experience and familiarity will increase and hence breaking down barriers, the field of application will in the long term definitely widen to more daily applications such as sports and leisure, the work environment and so on. More casual applications are possible as well, which are expected to be functional as well as fashionable. It also can go as far as daily skin care, where the comfort factor is even more critical. But also smart wound dresses, bandages and hygiene applications are envisaged.

The main factors to be overcome in the initial phase of the development will be the communication between textile engineers and medical people, in order to be able to define and demonstrate the benefits of new applications.

Why textiles?

Textiles show several advantages. Clothes are unique in several aspects.

They are extremely versatile in products as well as processes. The building stones of the textile material are *fibres* or *filaments*. Innumerable combinations of these source materials result into a whole range of textile materials. Fibres are available in a very broad range of materials, single or combined: natural or synthetic, strong, elastic, biocompatible, biodegradable, solid or porous, optical or electro-conductive. They can have varying lengths, fineness, cross-sectional shape, surface roughness, etc. Fibres of various origins can be arranged at random or in a strictly organised way in yarns or fabric structures. From this, even 3-dimensional structures can be constructed. After treatments they allow the creation of very special properties such as hydrophilic/hydrophobic nature, antimicrobial, selective permeability etc. Textile materials are able to combine advanced multifunctionality with traditional textile properties.

Clothes are our own personal house. They can be made to measure, with a perfect fit and high level of comfort. Clothes make contact with a considerable part of the body. They are a common material to all of us, in nearly all of our activities. They look nice and attractive, the design and look being adapted to the actual consumer group. We all know how to use them. Maintaining textiles is a daily practice: house as well as industrial laundry are well developed.

And last but not least: textiles and clothes can be produced on fast and productive machinery at reasonable cost.

These characteristics open up a number of applications that were not possible before, especially in the area of monitoring and treatment, such as:

- Long term or permanent contact without skin irritation,
- Home applications,
- Applications for children: in a discrete and careless way,
- Applications for the elderly: discretion, comfort and aesthetics are important.

It is clear that the intelligent character of the textile material can be introduced at different levels. It can occur at fibre level, a coating can be applied, other threads can be added to the textile material, it is even possible to closely connect completely independent appliances with the textile.

Full success however will only be achieved when the sensors and all related components are entirely converted into 100% textile materials. This is a big challenge because, apart from technical considerations, concepts, materials, structures and treatments must be focus on the appropriateness for use in or as a textile material. This includes criteria like flexibility, water (laundry) resistance, durability against deformation, radiation etc.

As for real devices, ultimately most signals are transformed into electric ones. Electroconductive materials are consequently of utmost importance with respect to intelligent textiles.

THE EVOLUTION OF SMART TEXTILES

The first generation of intelligent clothing uses conventional materials and components and tries to adapt the *textile design* in order to fit in the external elements. They can be considered as e-apparel, where electronics are added to the textile. A first successful step towards wearability was the ICD+ line at the end of the 90's which was the result of co-operation between Levi and Philips. This line's coat architecture was adapted in such a way that existing apparatuses could be put away in the coat: a microphone, an earphone, a remote control, a mobile phone and an MP3 player. The coat construction at that time did require that all these components, including the wiring, were carefully removed from the coat before it went into the washing machine. The limitation as to maintenance caused a high need for further integration.

The Wearable Motherboard[2] is probably the first intelligent suit that can be used for medical purposes. The basic shirt includes an optical wiring structure that can detect penetration of the shirt and an electrical wiring system that can be equipped with conventional sensors to measure different body parameters. More details will be given later on.

Alternatively, conductive textile materials are utilised. Infineon[3] has developed a miniaturised MP3 player, which can easily be incorporated into a garment. The complete concept consists of a central microchip, an earphone, a battery, a download card for the music and an interconnection of all these components through woven conductive textiles. Robust and wash-proof packing protects the different components.

No matter how strongly integrated, the functional components remain non-textile elements, meaning that maintenance and durability are still important problems. In the next generations, the components themselves are transformed into full textile materials.

THE FUNCTIONS OF SMART TEXTILES

Basically, 5 functions can be distinguished in a smart suit, namely:
- Sensors
- Data processing
- Actuators
- Storage
- Communication

The above different components have a clear role, although not all smart suits will contain all functions. The functions may be quite apparent, or may be an intrinsic property of the material or structure. They all require appropriate materials and structures, and they must be compatible with the function of clothing: comfortable, durable, resistant to regular textile maintenance processes and so on.

Sensor function

Introduction

Ultimately the goal is to create clothing with integrated sensor function. To reach this goal two tracks can be followed:
- based on existing sensor technology, sensors can be miniaturised until they can be integrated into garments;
- the textile fabric itself can be given sensing properties.

Both developments are under research. The first option is driven by the electronics industry, the second by the textile industry.

The textile is in contact with the skin over a large body area. This means that monitoring can take place at several locations at the body.

Some examples of body parameters that are mentioned in literature are

- Temperature.
- Biopotentials: cardiogram, myography.
- Acoustic: heart, lungs, digestion, joints.
- Ultrasound: blood flow.
- Motion: respiration, movement.
- Chemicals (sweat).
- Electric proterties of the skin.
- Mechanical properties of the skin.
- Pressure: blood.

It will be clear to the reader that this list is not tentative. Odour for instance, colour of the skin at different wavelengths could mean something. Indeed, we all see when a person we're familiar with is not feeling well, while a mother can smell her child has fever.

These parameters are measured at the surface or in the upper body layers.

Extensive work will need to be done in the medical sector itself to identify alternative parameters and their meaning. Multiparameter analysis, correlations between parameters could reveal unexpected combinations. Also, variation of parameters at different positions at the body, variations in time may provide relevant information. It is a chicken-or-egg question: no one has been able to do the exercise because of lack of suitable systems, and consequently no one makes systems as the feasibility has been demonstrated.

Sensors in general and textile sensors in particular struggle with the following problems:

- The flexibility and deformability required for comfort interfere with sensor stability,
- Biosignals tend to have relatively low amplitude (e.g. μV),
- Long term stability is affected by wear and laundry.

The first generation of intelligent clothing consists of conventional components attached to the textile structure. Step bystep they are being replaced by true textile materials. Several studies are going on in the area of health monitoring, with various levels of transformation into full textile structures. An overview is given in the table below:

Name	Application	Parameters	Level of transformation
Mamagoose (B)[4]	Sudden infant death	Heart and respiration rate	Washable suit with detachable electrodes
ANBRE (B)[4]	Body movement	3D motion capture	Detachable components
Smart shirt[5]	Military, health care	Penetration-respiration-heartrate-temperature-blood	Detachable components, integrated wiring
Life shirt[6]	Health care	ECG, respiration, blood pressure	Detachable components
Smartex[7]	Health care	ECG, respiration, motion	Woven textile sensors
Intellitex[8]	Children's health care	ECG, respiration	Knitted textile structures, textile antenna
VTAM[9].	Health care	ECG, respiration, fall	Partly textile structures

Some examples will be discussed in more detail in the following paragraphs in order to demonstrate the principles, results and limitations.

Heart signals

Heart signals are one of the basic parameters in healthcare. The heart is basically a muscle that is controlled by the brain through electric impulses. The body being a vessel filled with aqueous electrolyt, these signals can be detected in all of its parts. Small metal plates are commonly used to capture these signals while instruments are analysing the results, extracting the required parameters such as frequency, phases etc.

Several research projects are being conducted that use electro-conductive textile structures instead of the metal plates.

The Intellitex suit[8] is the name of a prototype suit that was developed by a Flemish consortium of universities and companies. It is a biomedical suit meant for the long term monitoring of heart rate and respiration of children at the hospital. To measure the heart rate and even an ECG, the *Textrodes* were developed. The Textrodes have a knitted structure and are made of stainless steel fibres (by Bekintex, B). Electrogels are not being used in order to overcome skin irritation. This enables long term monitoring but has a negative impact on the contact with the skin. For children, a nice design makes them want to wear the suit, and they can be monitored without disturbing them.

The Textrodes make direct contact with the skin. Results have shown that the electrode's textile structure is an important parameter. When changing the structure, a different contact surface with the skin is obtained. Finer structures with more protruding fibres for instance will more easily adapt to the heterogeneous skin surface, which results in a more intense contact between the electrode and the skin. In turn, this results in a lower impedance of the skin electrode system. A compromise has to be found between the sense of comfort and the intensity of the contact with the skin. A knitted structure has the advantage of being stretchable. Elasticity is a required property for close fitting of the suit around the thorax.

To measure the ECG, a three-electrode configuration is used[10]. Two measurement electrodes are placed on a horizontal line on the thorax, a third one, acting as a reference ('right leg drive'), is placed on the lower part of the abdomen

In order to assess their performance, the signal originated from a conventional electrode (gel electrodes by 3M) and the textile electrodes were recorded at the same time. The results of these measurements are shown in Figure 1.
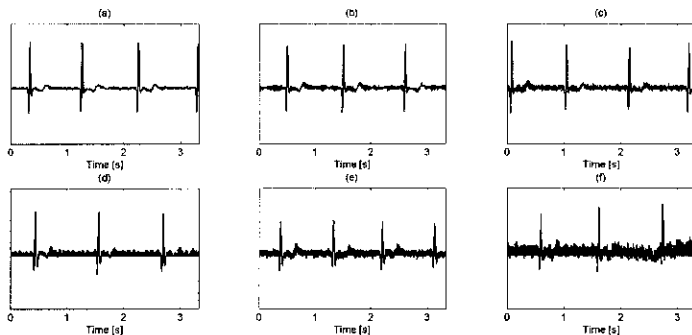

Figure 1 – Conventional electrodes (a, b, c) versus textile electrodes (d, e, f) in 3 different configurations

The figures demonstrate the accuracy of the signal of the textile electrodes. The quality and the reliability of the signal will be compared to standard electrodes in extensive clinical testing.

Strain sensors: respiration and motion

Textile materials composed of fibres form complex networks of conducting parts that make multiple contacts. During deformation a number of mechanisms take place:
- The number of contact points changes
- Fibres are extended
- Fibre cross-section is decreased

The number of contact points changes drastically at low extension values, whereas real fibre deformation takes place at higher levels of strain. An increase in number of contact points reduces the electrical resistance, whereas fibre extension and reduction of cross-section lead to an increase of the electrical resistance. As a result, the electrical resistance changes due to deformation in a way that depends mainly on the textile structure.

This gives textile structures piezo-resistive properties enabling their use as strain or deformation sensor. From such signals, motion and even position can be extracted. Indirectly, such structures can be used to estimate the level of pressure exerted by a bandage on the skin which is an important parameter for instance for prevention of scar formation[11].

The intellitex suit

The Intellitex suit mentioned earlier combines heart and respiration rate measurements in one garment. The respiration sensor is a knitted belt called *'Respibelt'*. It is also made of a stainless steel yarn. The accuracy and stability of this sensor are illustrated in Figure 2. The basic concept of this sensor could also be used as a strain sensor, for instance to control tension applied in pressure bandages.
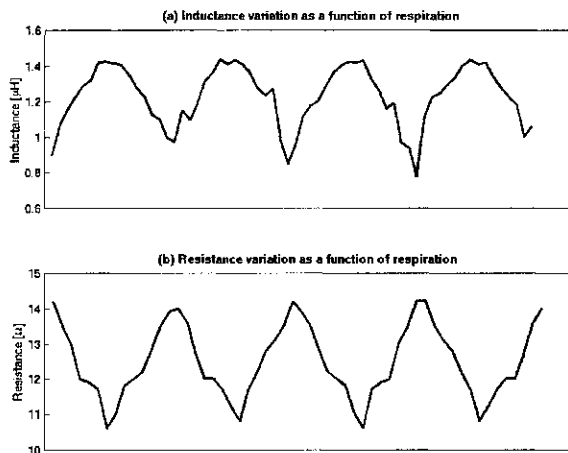

Fig. 2 – respibelt signals

The signals show the inductance resp. resistivity of the belt during breathing. Inductance analysis considers the belt as a circular circuit and reacts on changes in cross-section within the belt. Resistivity reacts on changes in circumference of the chest due to the breathing motion.

Although long term stability turns out to be acceptable (fig. 3), one can expect that long term use will require regular calibration procedures. Indeed a textile is subject to repetitive deformation during wearing, and chemicals may be deposited during laundry. Inevitably this will affect its conductivity.
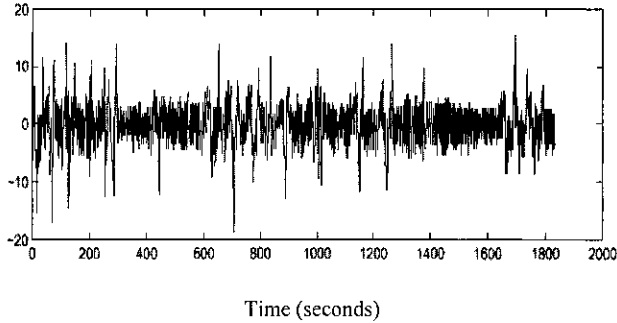

Time (seconds)

Figure 3 – long term monitoring with Respibelt

The Lifeshirt™ by Vivometrics

The LifeShirt™ that has also been addressed in Table 1 is a sleeveless undergarment, made of a comfortable and washable stretch-material. The fabric of which the shirt is made, contains one or more elongated bands of elastic material. Each of these bands is stretchable in the longitudinal direction and contains at least one conductive wire[12]. This wire is shaped in a sinusoïdal arrangement. For monitoring certain physiological functions where a higher degree of sensitivity and accuracy is required, more wires are used. They form a single continuous conductive circuit that encircles the monitored area as many times as there are wires. The bands of elastic material may be formed in any conventional way, which includes warp knitting, weft knitting, weaving, braiding or a nonwoven construction. Warp knitting however is preferable, because it is easy to create bands having narrow widths. The conductive wire is either incorporated into the elastic fabric structure or is sewn to the surface afterwards. A copper wire is used as conductive wire. The wires are attached to a monitoring unit.
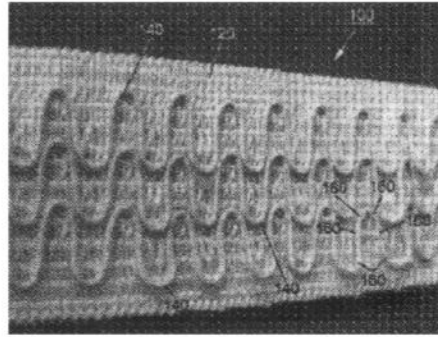
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Figure 4 – Conductive wires in a sinusoïdal arrangement
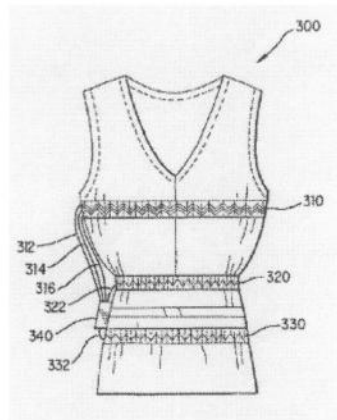
(Source : US Patent 6,341,504)

Figure 5 – Concept of the LifeShirt™

(Source : US Patent 6,341,504)

The technology on which the Lifeshirt™ is based is inductive plethysmography (IP). Plethysmography is derived from the Greek words "plethysmo", which means "to increase" and "graphos", which means "to write". It is the recording of changes in the volume of a limb or an other part of the body, as blood moves in and out of it.

IP sensors are arrays of sinusoidally arranged electrical wires, surrounding certain body areas and are called plethysmography bands. Movements of the body sections covered by the LifeShirt™ sensors, generate magnetic fields that are converted into voltage changes over time, i.e. waveforms. These waveforms are proportional to changes in cross sectional area.

Analysis of body movements

Information on body kinetics is important with respect to for instance detection of falls, identification of activity, rehabilitation, sports and dance, ergonomics.

CEA-LETI has developed a 3D orientation tracker based on conventional accelerometers and magnetometers[13]. The system is based on a simplified skeleton model, which describes main bones and joints with rotational constraints.

Hands in particular are able to perform very complex movements in a very accurate way. Reduced abilities to control the hand have a significant impact on a person's life. A smart glove could help to make a detailed analysis of a person's hand movements allowing identification of right and wrong movements. Lorussi et al[14] have developed a sensorised glove and algorithms that enable to measure position and posture of the hand. The basic sensor is a piezoresistive sensor that is developed at the University of Pisa and Smartex[15]. Threads or fabrics are given their sensing capacities by coating them with rubber loaded with a micro-disperse carbon phase. The conductive elements are immobilised in the structure through a treatment at a temperature of 130°C. The sensor that is obtained is a strain sensor: there is a relation between the imposed strain and the variation of the resistance that is measured.

Pressure sensors

Pressure sensors are quite important in medical application, as pressure plays a significant role in several processes such as occurrence of bed sores, prevention of scar formation etc. Basically two principles are being used in textile pressure sensors.

A first example is a pressure sensitive textile material that is already on the market is Softswitch™. The **Softswitch™** technology[16] uses a so-called 'Quantum Tunnelling Composite (QTC)[17]. This composite has the remarkable characteristic to be an isolator in its normal condition and to change in a metal-like conductor when pressure is being exercised on it. Depending on the application, the pressure sensitivity can be adapted. Through the existing production methods, the active polymer layer can be applied on every textile structure, a knitted fabric, a woven fabric or a nonwoven. The pressure sensitive textile material can be connected to existing electronics.
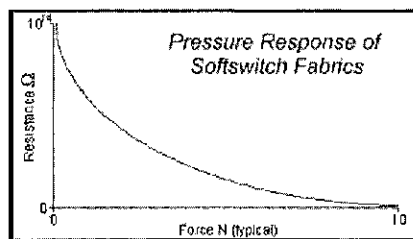

Figure 6 – Quantum Tunnelling effect

(Source: Softswitch™)

A similar textile material that has the property to be pressure sensitive, was developed by a team of the Design for Life Centre from Brunel University in Surrey. The English firm Eleksen[18] commercialises the Sensory Fabric under the name **Elektex™**.

The Sensory Fabric[19,20] consists of two layers of electrically conductive textile, separated by a layer of non-conductive mesh. Each conductive, or partially conductive fabric sheet constitutes an electrical switch contact. The layer of non-conductive mesh in between serves to keep the two conductors apart. When the textile is pressurized, the top conductive sheet is pushed through the holes in the mesh to make electrical contact

with the lower conductive sheet. If the pressure is light the conductive fibres in the central layer will only just make contact to open up a continuous channel and the resistance of the channel will be high. However when a high force is applied more conductive fibres will get in contact and the resistance in the channel will be relatively low. The variable resistance in the channel is therefore dependant on the pressure applied. The pressure necessary to make contact between the two outer conductive layers also depends upon the size of the meshes and the thickness of the insulating layer. In this way, the fabric can be adapted to its application. The fabric can be designed for a light touch as well as for a more positive interaction, as required. The fabric can be used as pressure sensor, switch or other sensor.

The basic material of the Sensory Fabric consists of a combination of conductive fibres and nylon. This combination results into a durable, reasonably priced, washable and even wearable 3D structure.

Optical fibres: a multifunctional tool

Fibre Bragg Grating (FBG) sensors are a type of optical sensors receiving a lot of attention during the last few years. They are used for the monitoring of the structural condition of fibre-reinforced composites, concrete constructions or other construction materials. At the Hong Kong Polytechnic University, several important applications of optical fibres have been developed for the measurement of tension and temperature in composite materials and other textile structures[21]. FBG sensors look like normal optical fibres, but inside they contain at a certain place a diffraction grid that reflects the incident light at a certain wavelength (principle of Bragg diffraction) in the direction where the light is coming from. The value of this wavelength linearly relates to a possible elongation or contraction of the fibre. In this way, the Bragg sensor can function as a sensor for deformation.

One could also think of using them as a spectroscope. Spectroscopy is a technique commonly used in textile finishing to analyse colour, chemical composition, temperature etc. Optical fibres could take light to the skin and collect reflected and transmitted light. The light enters the skin over a depth of some millimetres up to about 5 centimeters, depending on the wavelength (UV up to infrared). So why not use it to analyse such parameters at the skin and in the upper body layers?

Colour change mechanisms: sensors we can see

The concept of producing textiles that readily vary in colour has long been an anathema to the textile colourist, for whom achieving permanency of colour has been a primary goal. During this search, particular colorants have shown a sensitiveness towards light, pH, temperature and many other sources. Indicator colorants that change colour in various conditions have been used for a long time alredy in chemistry.

Thermochrome dyes have increasingly been the subject of investigation over the past decades for use in producing novel coloration effects in textiles as well as other applications[22]. When thermochrome dyes are used for the printing of textile materials, an intelligent fabric is obtained which can change colour under the influence of a stimulus, in this case the temperature. Two types of thermochrome dyes were successfully applied in the textile sector: liquid crystals and molecular rearrangement. In both cases the dyes are captured in microcapsules and applied on the textile as a pigment.

Thermochrome pigments were launched on the market under the brand name Licritherm by the firm Merck. Such dyes can give a fast and accurate indication of temperatures and temperature distribution.

An analogous phenomenon is *photochromism*, where the colour will change under the influence of light. Photochromism is defined as the reversible change in colour of a chemical substance under the influence of electromagnetic radiation. The chemical bond passes from a form A to a form B, each of them with their own absorption spectrum and hence colour. If the product is exposed to UV radiation (activation), this causes a colour change, if the light source is removed, the colour will disappear.

Recently, the firm Procter & Gamble announced their intention to launch an intelligent slip on the market. The aim is to notify the female wearer when ovulation is coming or when she will start to menstruate. To determine the *ovulation*, a layer of silicones is used covered with a thin plastic film. The silicones react to hormonal changes that are characteristic for the ovulation period and expand a little. The small thickening modifies the refraction of the light, resulting in a violet dot on a golden background. To determine *the menstruation period*, two indicators are necessary. In the first place, a resin is used which turns blue at the presence of the smallest trace of blood. The second product is an acid which turns red at a pH between 4 and 7. These two indicators together give a purple colour, approximately four hours before the start of the menstruation.

Data processing

Data processing is one of the components that are required only when active processing is necessary to realise a smart and adequate response. The main bottleneck at present is the interpretation of the data. Textile sensors could provide a huge number of data, but what do they mean? Problems are:

- Large variations of signals between patients,
- Complex analysis of stationary and time dependent signals,
- Lack of objective standard values,
- Lack of understanding of complex interrelationships between parameters,

A second problem is the feedback and control algorithms. It is quite clear that the best response on a given situation will be highly dependant on the person. Some persons will require stronger reactions than others. Moreover bio-responses are very complex even for a given person time dependant. This will require smart algorithms that are capable of learning continuously on the immediate response of the body on a reaction of the textile.

Apart from this, the textile material in itself does not have any computing power at all. Pieces of electronics are still necessary to fulfil this task. However, they are available in miniaturised and even in a flexible form. They are embedded in water proof materials, but durability is still limited. The interconnections with the data transmitting component is at present still a weak point.

Research is going on to fix the active components on the fibres (Ficom project[23]).

Many practical problems need to be overcome before real computing fibres will be on the market: fastness to washing, deformation, interconnections, etc.

Actuators

Actuators respond to an impulse resulting from the sensor function, possibly after data processing. Actuators make things move, they release substances, make noise, heat up or cool down, and many other.

Mechanical actuators

Mechanical actuators make fibres move in the textile structure, changing properties like thermal insulation, permeability etc. A more ambitious objective is to create fibres with muscle like properties. When such fibres would be integrated in clothes that fit as a second skin, the textile could provide considerable support or even take over body motion. Such fibres can be incorporated in the textile in any predetermined form so that any movement can be obtained. The fibres would need to be electro-active materials capable of reaching a contraction of up to 50% or more, high contraction forces, with a short reaction time and low voltage actuation. Real challenges in this area are the development of very strong **mechanical actuators** that can act as artificial muscles. Performant muscle-like materials, however, are not yet within reach[24]. Recently some promising results have been presented that could open up this window[25].

Current available mechanical actuators provide a mechanical reaction in response to thermal, chemical or physical impulses. Some examples will be given hereafter.

Shape memory materials

Shape memory materials return to a predetermined form above a given transition temperature. Shape memory materials exist in the form of metal alloys and polymers. They exist in the form of threads. Although shape memory polymers are cheaper, they are less frequently applied. This is due to the fact that they cannot be loaded very heavily during the recovery cycle.

To comprehend the functioning of a memory alloy, its *crystalline structure* should be examined. All shape memory alloys present two distinct crystalline structures or phases :

- *martensite*, occurring at lower temperatures and
- *austenite*, occurring at higher temperatures.

The phase in which the alloy is situated depends upon the temperature and the pressure exercised on the object. We consider the best known shape memory alloy: a NiTi-alloy (Fig. 7).
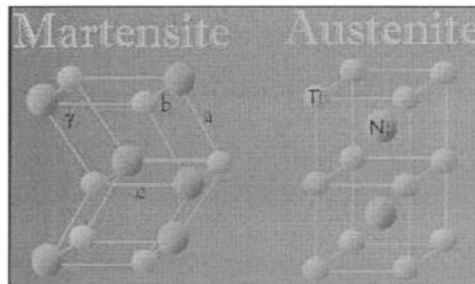

Figure 7 – Martensite and austenite structure.

The martensite and the austenite structure are clearly distinct. The a, b and c sides in the martensite grid all have different lengths. When pressure is exercised on the grid, these lengths will adapt themselves to compensate the pressure. The angle γ can also change as a function of the pressure exercised. Thanks to these properties, a shape

memory alloy in the martensite structure can easily be transformed. In the austenite phase however, the structure is very strictly defined, so that a predetermined shape is regained in this phase.

Shape memory alloys (Nitinol, a Nickel-Titanium alloy) are currently used as stents. Until now, few textile applications are known. The Italian firm, Corpo Nove, in co-operation with d'Appolonia, developed the Oricalco Smart Shirt[26]. The shape memory alloy is woven with traditional textile material resulting into a fabric with a pure textile aspect. The trained memory shape is a straight thread. When heating, all the creases in the fabric disappear. This means that the shirt can be ironed with a hair dryer. An additional feature is that due to the structure of the fibres that have been embedded in the sleeves, the sleeves will automatically roll up at higher temperatures, providing a better cooling effect for the wearer.
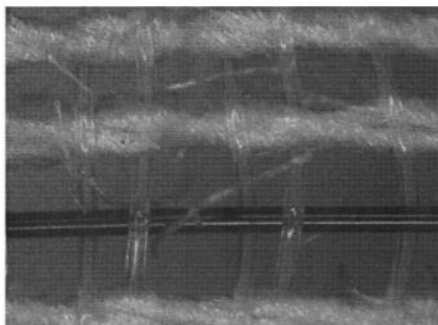

Figure 8 – Close-up of the Oricalco-fabric

Programming a metal alloy is not only a time-consuming procedure, it also involves heat treatment at temperatures of several hundred degrees Celsius. Polymers are programmed into shape in seconds at about 70 °C. And they can withstand deformations of several hundred percent. whereas shape-memory alloys can undergo a maximum deformation of only about 8%. Furthermore, they are much more expensive than polymers.

Transition temperature of polymers can be changed quite easily: with one set of monomers, you can have a whole set of shape-memory materials.

An example: one component, oligo(e-caprolactone) dimethacrylate, furnishes the crystallizable "switching" segment that determines both the temporary and permanent shape of the polymer. By varying the amount of the comonomer, n-butyl acrylate, in the polymer network, the cross-link density can be adjusted. In this way, the mechanical strength and transition temperature of the polymers can be tailored over a wide range. Homopolymers of both monomers are known to be biocompatible, opening the door for biomedical applications. In addition, poly(∈-caprolactone) is biodegradable. For biomedical applications, biodegradability represents an additional advantage over Nitinol.

Recently developed shape memory polymers belong to the group of **polyurethanes**. They are thermoplastic polymers having their glass transition temperature at a range of – 30°C till 100°C. Mitsubishi Heavy Industries commercialises these polymers in the form of hydrophilic vapour-transmitting membranes.

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Gel based actuators

Polymer gels differ in many ways from solid materials. Polymer chains in the gels are 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. From the standpoint of an actuator, the gel behaves like a conventional solid actuator or like a shapeless amoeba. The gels also have various actuating modes, symmetric or asymmetric deformation behaviour, depending on the structure in which it is used.

There are a wide range of triggers that cause the actuating deformation:

Chemical triggers:

- pH
- Oxidation and reduction
- Solvent texchange
- Ionic strength change

Physical triggers:

- Light irradiation
- Temperature change
- Physical deformation
- Magnetic field
- Electric field
- Microwave irradiation

Gels incorporated in fibres at the level of the fibres or in the actual textile structure allows designing systems that open up or close down in response to one of the triggers mentioned above.

An example of yarn consisting of a gel core wrapped with Z- and S- twisted filaments is derived from nature: worms contract their body by local expansion of body diameter. The result is an elementary version of an artificial muscle[27].
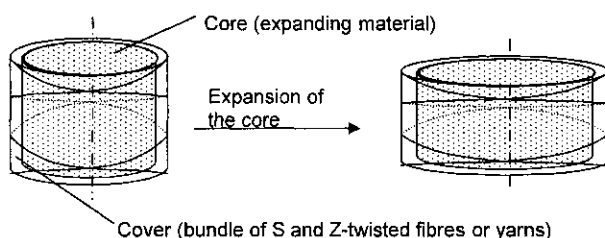

Core (expanding material)

Expansion of the core →

Cover (bundle of S and Z-twisted fibres or yarns)

Fig. 9 – structure of a gel based mechanical actuator

PH triggered polymers

In 1950, two researchers (W. Kuhn and A. Katchalsky) developed fibres being able to contract under the influence of a pH change. However, a disadvantage was the slow

reaction time of the polymer: the change lasted for some minutes. Through the years, other fibres have been developed having much shorter reactions: from a few seconds (DeRossi 1987) to a few tenths of seconds (Suzuki 1989). These fibres also have a high tensile strength.

The degree of contraction and the developed forces equal those of a human muscle. At the University of New Mexico, Albuquerque, USA, research is going on into the development of artificial muscles. To this end, a polyacrylonitrile fibre, ORLON[1] is used. A few years ago, researchers discovered that PAN fibres are able to contract when the degree of acidity in the surroundings changes. In two tenths of a second, they can shrink 20%, this is almost as fast as a human muscle. Depending on the degree of acidity, PAN fibres can contract to half or a tenth of their original length. Moreover, the fibres are strong: they can bear up to four kilograms per square centimetre. This is more than a human muscle.

A big disadvantage of these PAN muscles is the need of a chemical activator. The possibilities would become more extensive if one would succeed in having the artificial muscles functioning with electricity for example.

Chemical actuation

Chemical actuators release specific substances in predefined conditions. The substances can be stored in 'containers' or chemically bound to the fibre polymer. The coat of the container or the chemical bonds steer the release rate.

Containers consist of the full fibres coated with smart coatings, micro and nano-capsules with well designed shells or molecules like cyclodextrins. The latter have constant release rates.

Materials that release substances already have several commercial applications. They release fragrance, skin care products, antimicrobial products etc.. However, actively controlled release is not obvious, although some basic research projects have started. Release could be triggered by temperature, pH, humidity, chemicals, and many other.

Obviously, controlled release opens up a huge number of applications as drug supply systems in intelligent suits that are also capable of making an adequate diagnosis.

Microcapsules

Micro-encapsulation was developed in the paper industry in the 1940's. The pharmaceutical industry discovered the potential of micro encapsulation (ME) in the 1970's, as a technique to formulate unstable compounds, and to regulate their release.

In the last decade, several industries have developed applications of ME, where the prime goal is mostly storage and controlled release of products (fig. 10).

A microcapsule is usually 1 up to 7 µm in size and consists of a shell, that forms a permanent or temporary container that wraps the contents. Relatively speaking, the contents is a huge core consisting of particles with specific properties or chemically reactive components. Fluids, gases or solid materials can be stored. The shell can range from permeable to fully impermeable. It protects the core and acts as release controller. It is made from natural or synthetic polymers. Release can be controlled by diffusion (which in itself can be controlled by physico-chemical agents), triggered by mechanical

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[1] ORLON is an acryl fibre produced by the company Du Pont

action (rupture of the shell), (bio)chemical agents (dissolution of the shell, slow or fast), or by thermal action (melting of the shell).
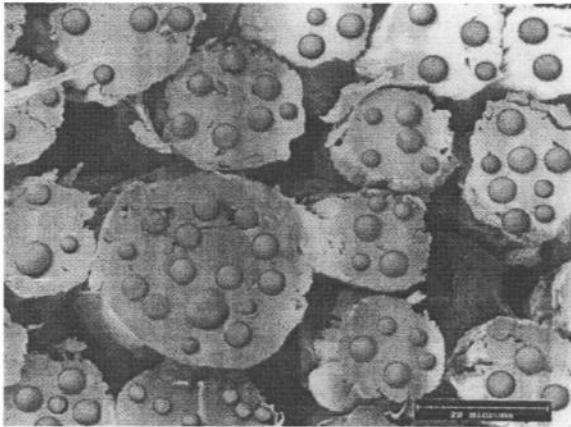

Figure 10 – Micro-capsules in fibres
(Source OUTLAST)

In micro-encapsulation in general the number of commercial applications in the textile industry continues to grow particularly in the textile industries of Western Europe, Japan and North America. The move by the more developed countries into textiles with new properties and added value, into medical textiles and technical textiles for example has encouraged the industry to use micro-encapsulation processes as a means of imparting finishes and properties in textiles which were not possible or cost-effective using other technologies. Textile manufacturers are demonstrating increasing interest in the application of durable fragrances to textiles as well as skin softeners. Other potential applications include, insect repellents, dyes, vitamins, antimicrobials, phase change materials and in specific medical applications, antibiotics, hormones and other drugs. Smaller capsules equals:

o   Harder to break
o   Better control of release
o   Durable effect
o   Increases complexity of production process
o   Increases price

Thermal actuation

Thermal actuators can have several levels of activity. Actual heating or cooling systems have the highest impact on thermal comfort. Adaptive insulation adjusts its level of thermal conductivity according to temperature. Materials with super high thermal absorption capacity will support the wearer to maintain his temperature.

Active heating/cooling systems

Conductive materials can act as an electric resistance and can consequently be used as a *heating* element. Polartec has recently presented a heating fleece[28].

On the other hand, *cooling* is a more complex process. D'Appolonia has presented a cooling shirt for F1 racers. Tiny cooling tubes are integrated in the jacket, a liquid that is cooled by a central Peltier cooling element is circulated through these tubes.

Semi-active temperature regulation can be achieved by using micro capsules filled with waxes that have a melting point near the targeted temperature.

Adaptive insulation

At the end of the nineties, the DCTA R&TG (Defence Clothing & Textiles Agency), Colchester, UK[29] started research into the use of shape memory alloys for developing heat-protecting clothing.

In the experiment, springs made of a shape memory alloy (nitinol) are used. At room temperature the springs are in a flat state. At increasing temperatures the springs will open up. The system consists of two separate layers, in which cotton bands are introduced in order to incorporate the springs. The springs are only fixed at the outside layer, so that they are minimally obstructed when expanding. The springs used are conic and have a 25 mm diameter. Air is a good insulator. Under the influence of the transformed springs, both textile layers will move away from each other as a result of which an insulating air layer is formed between them. The springs only have a one-way function: when cooling down, they will not regain their original shape unless a mechanical action is applied.

Depending on the shape transitions, garments can be obtained with increasing level of insulation at high or at low temperatures.

An example of the design is given in fig. 11.
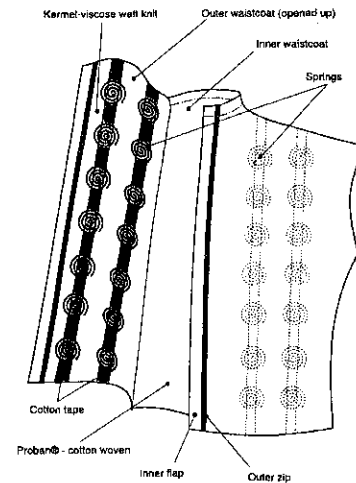
Figure II – Protective waistcoat with incorporated springs made of a shape memory Alloy.

Also during the Gulf War the DCTA R&TG (Defence Clothing & Textiles Agency)[30] was searching for materials with adaptive ventilation characteristics. The purpose was to cope with the huge temperature differences that occur in the desert without additional weight for the soldiers. They came up with materials based on the

structure of pine cones that remain closed in wet conditions (e.g. because of sweating during the day) while opening up when dry (e.g. at night when feeling cold).

The fabric (fig. 12) consists of a knitted structure coated with a polymer having a high hygral expansion coefficient. U-shaped holes are punched in the fabric. The "valves" obtained in this way are pushed open when the coating expands when getting humid and close down again when the coating regains it original shape when dry.
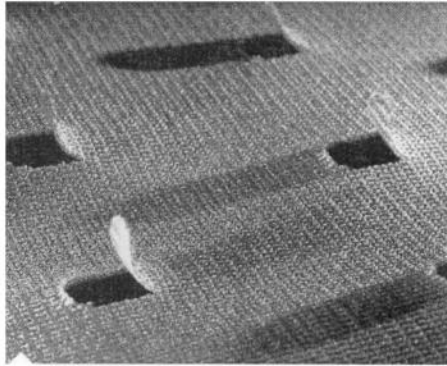

Figure 12 - Pine cone mimic for adaptive ventilation effect

Phase change materials PCMs

The concept of micro-encapsulation of PCMs was developed by the NASA at the end of the 70s and the beginning of the 80s. NASA was looking for materials to protect its delicate instruments against the extreme temperature fluctuations prevalent in space. NASA already publicised a 'Phase Change Materials Handbook' in 1971 describing more than 500 of these substances, which distinguished themselves by phase change temperatures and their ability to capture heat.

Phase change materials are materials whose phase changes within a predetermined and restricted temperature interval. The energy involved in changing phase between liquid and solid can be up to 200 times higher than the energy involved in heating up or cooling down an equal mass of material. The heat capacity of water and a wax used in PCM is given hereafter (fig. 13);
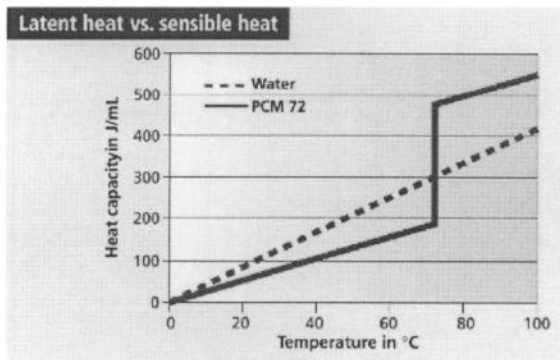

Figure 13 – Melting process of a PCM

The most famous example of such a material is water/ice, which at the freezing point changes from the fluid into the solid state. However water is not an appropriate material for body temperature control: phase transition temperature is 0°C, far away from targeted body temperature, and water molecules are too small, they would slowly migrate through the shell of the capsule.

The phase change materials used in the textile sector are usually paraffin waxes in the solid or liquid state. These are hydrocarbons with a different chain length, such as heneicosane ($C_{21}H_{44}$), eicosane ($C_{20}H_{42}$), nonadecane ($C_{19}H_{40}$) and octadecane ($C_{18}H_{38}$). With these materials, the phase change occurs within a temperature area that lies in the vicinity of the body temperature. The substances used in the textile sector are characterized by their capacity to capture or release large quantities of warmth without changing in temperature.

The microcapsules are integrated in a textile material in the actual fibre mass, in a coating or in a foam.

Electric actuation

Electrostimulation is the stimulation of muscles by electrical impulses. It is a complex process with many physiological effects. Electroconductive textile structures can be used to take the electric impulses to any part of the body[31,32].
Research is going on on the effect of electrostimulation on

- activation: e.g. when a "power circuit" is interrupted somewhere as a result of which the impulse from the brains does not reach the muscles[33,34,35,36].
- strengthening: by repeated stimulation; for example when there is temporary immobility to prevent the muscle mass from degrading to such a degree that certain functions disappear for good (e.g. mobility)[37]
- blood circulation: electrostimulation can have a positive effect on the blood circulation, which is for example the case when there is insufficient mobility, heart deficiency/insufficiency, diabetes,…[38]
- stimulation of the skin for a better sensorial performance

Several other physiological effects exist and are the subject matter of many studies, some of which are undoubtedly relevant for this textile applications[39,40,41,42].

Energy

Although usually not a goal as such, smart suits often need some storage capacity, as the suit must be able to function as a stand alone unit. Sensing, data processing, actuation, communication, all these usually need energy, mostly electrical power. Efficient power management will consist of an appropriate combination of energy supply and energy storage capacity in combination with an efficient distribution strategy of components and computing power.

Sources of energy that are available to a garment are for instance body heat, mechanical motion (elastic from deformation of the fabrics, kinetic from body motion), radiation, etc.

Infineon[43] had the idea to transform the temperature difference between the human body and the environment into electrical energy by means of thermogenerators. This principle is known as the Seebeck effect. The prototype is a rigid, thin micromodule that is discretely incorporated into the clothing (fig. 14).

Figure 14 – Thermogenerator by Infineon

The module itself is not manufactured out of textile material. However, the line of thought is set. The use of solar energy for energy supply is also thought of. At the University of California, Berkley, a flexible solar cell is developed which can be applied to any surface[44].

At the moment, all energy transformation mechanisms are far too little efficient to foresee in full power supply. Some microwatts can be gained, just enough to drive single low power components like sensors.

As mentioned before, energy supply must be combined with energy storage. When hearing this, one thinks of batteries. Batteries are becoming increasingly smaller and lighter. Even flexible versions are available, although less performant. Currently, the lithium-ion batteries are found in many applications. Fibre batteries made of super capacitor fibres are under development.

Communication

For intelligent textiles, communication has many faces: communication may be required
- within one element of a suit,
- between the individual elements within the suit,
- from the wearer to the suit to pass instructions,
- from the suit to the wearer or his environment to pass information or instructions.

Within the suit, communication is currently realised by either optical fibres[45], either conductive yarns[46] or conventional electrical wires. They all clearly have a textile nature and can be built in the textile seamlessly. Communication with the wearer is important as the wearer may want to be informed on some of the information an intelligent suit has gained. This could be achieved for instance by the following technologies:

For the development of a flexible textile screen, the use of optical fibres is obvious as well. France Telecom[47] has managed to realise some prototypes (a sweater and a backpack). At certain points, the light from the fibre can come out and a pixel is formed on the textile surface. The textile screen can emit static and dynamic colour images. In order to increase the resolution, the concept will need to be reviewed, as currently one pixel requires several optical fibres. Nevertheless, in this way, these clothes are uplifted to a first generation of graphical communication means.

Pressure sensitive textile materials[16,48], as mentioned earlier, allow putting in information, provided a processing unit can interpret the meaning of pressing specific areas of a textile, i.e. it must understand the commands.

This technology is already applied to make "soft" telephones and a folding keyboard. The ElekTex™ fabric is also used in the development of car seats, with the aim of having an optimal weight distribution in order to increase the seating comfort (fig. 15).
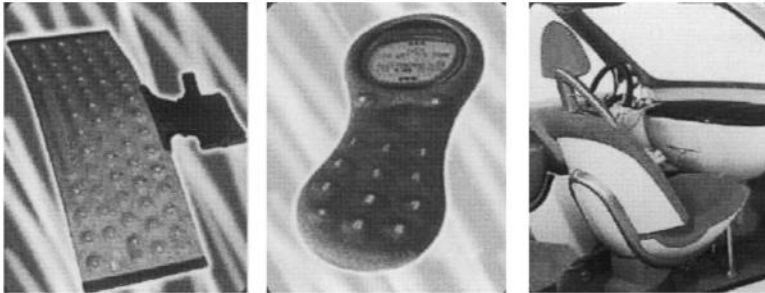

Figure 15 – Products manufactured from Elektex™.
(Source : Eleksen)

Communication with the wider environment is very important in medical applications. As the wearer often is in risky conditions, help must be provided instantly in case of threatening events. The concept of a stand alone suit does not allow direct contact, so wireless communication is required. This can be achieved by integrating an antenna. The step was also taken to manufacture this antenna in textile material. The advantage of integrating antennas in clothing is that a large surface can be used without the user being aware of it. In the summer of 2002, a prototype was presented by Philips Research Laboratories, UK and Foster Miller, USA on the International Interactive Textiles for the Warrior Conference (Boston, USA).

An example of a communication network linked to a smart suit is given in fig. 16:
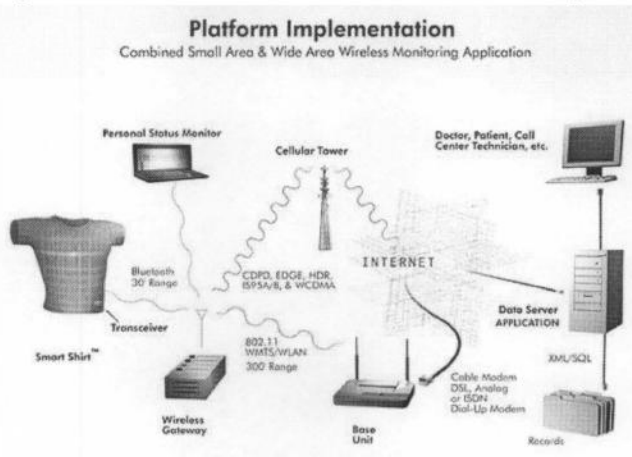

Figure 16 – Communication with the Smart Shirt from Sensatex [1].
(Source : Sensatex)

WHAT WILL A SMART SUIT LOOK LIKE IN THE FUTURE?

Let us dream of a suit that combines a number of approaches to prevent us from and to protect against falling injuries.

The suit will at all times adjust the environment in order to minimise the risk on falling, for instance by controlling the illumination around the wearer.

The suit measures body parameters that indicate reduction of stability or increased risk on falling, for instance due to variations in blood pressure. The suit will provide the necessary medication to stop this. Or the suit will warn the wearer or a responsible person.

The suit detects instant loss of stability, and the built in muscle like fibres contract, trying to keep the wearer in an upright position, thus preventing falling.

The suit detects that the wearer is falling, in spite of all its efforts. The necessary parts of the suit transform into protective zones, for instance by built in air bags or by local thickening and hardening.

The suit detects that the wearer has fallen, analyses the impact and provides an adequate reaction, such as fixing ruptures, providing medication, calling for help should this be necessary.

It will be quite clear to the reader that the potential of smart textiles reaches far beyond our imagination.

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DELIVERING CELL THERAPY FOR CHRONIC WOUNDS

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ABSTRACT

"Living bandages" containing patients' own skin cells can help treat previously non-healing chronic wounds such as diabetic foot ulcers, venous leg ulcers and burns. These chronic wounds affect some 6 million people in Europe and the US, and are a huge drain on the resources of healthcare providers. There is a strong clinical need for an effective delivery system that enables cells to be introduced into a wound bed to kick start the healing process. Early patient trials using a plasma polymer material have been highly encouraging, with healing demonstrated in diabetic foot ulcers and other non-healing wounds.

INTRODUCTION

The development of the culture techniques for producing integrated sheets of epidermal cells (cultured epithelial autografts - CEAs) was a breakthrough in introducing laboratory expanded cells to benefit patients with severe burns. However, the majority of researchers who have experience of the technique also find that it is difficult to get reliably good results. Despite this, the technique is also being used for treatment of patients with chronic non-healing wounds.

This underscored the need for an alternative strategy for delivering cells from the laboratory to the patient. Against this background we have developed a chemically defined surface (TranCell) which will support keratinocyte attachment, proliferation and subsequent transfer of these cells in a sub-confluent state to the wound bed. The work describing the preparation of this chemically defined surface and the culture of cells on the surface has been described previously. [1-4]

A method of delivery of autologous keratinocytes to promote healing of resistant diabetic neuropathic foot ulcers is reported.

METHODS

The process of developing a suitable material for clinical delivery of patients' cells is described, along with cell culture details and selection criteria for suitable patients with non-healing wounds.

Development of TranCell Surface

The carrier surface for keratinocyte attachment and transfer to wound beds was developed using a technique of plasma polymerisation. Plasma polymerisation allows the deposition of a functionalised, pinhole free film onto a flexible backing surface. Because the film can be deposited directly onto most surfaces, regardless of geometry, the technique is ideal for treating gauzes, fibres, stents and patches, where their effective use for clinical applications is clear. Full details have been published previously. [1-3] In brief, plasma polymerisation is a controlled surface engineering technique which can produce "cell-friendly" surfaces. In the plasma polymerisation process, a plasma is

created by evacuating a vessel and then refilling it with a volatile gas. The gas is then energised using radio-frequency power, to produce a range of energetic species.

Thin polymeric films can be deposited from the plasmas of small organic compounds. In plasma polymer (PP) deposition, there is fragmentation of the starting compound and a wide range of new functional groups can be incorporated in the deposit. A fine degree of control over surface functional group concentration can be readily achieved, and the polymers can be deposited directly onto most surfaces, regardless of geometry. The coating obtained is chemically stable and its composition is determined by analysis using X-ray photon electron spectroscopy (XPS)[5-6].

In our early studies, we compared surfaces functionalised with acid, amine or alcohol groups and established that keratinocytes much preferred attachment to acid functionalised surfaces.[1-2] We then extended this work to confirm that keratinocytes would proliferate on an acid functionalised surface as well as they would on a collagen I coated surface.[3]

To obtain a material that could be used clinically, we then used a medical grade polymer (not treated for cell attachment) onto which we deposited the acid functionalised plasma polymer surface by plasma polymerisation. We then went on to verify that keratinocytes would attach to this surface but readily leave it for an *in vitro* human wound bed model (sterilised human dermis containing basement membrane proteins).[4] This surface (referred to as TranCell) is being developed through a University spinout company, CellTran Ltd.

Culture of Keratinocytes for Clinical Use

Local Ethical Committee approval was obtained for a proof of concept study using TranCell to deliver autologous keratinocytes for the treatment of diabetic foot ulcers.

Keratinocytes derived from split thickness skin biopsies were initially expanded by growing them in 75cm^2 tissue culture flasks containing lethally irradiated Swiss 3T3.J2 feeder layers and keratinocyte medium[7]. When the desired confluency was achieved the cells were rinsed in PBS and the exhausted i3T3 cells were removed by incubating in 5mls of 0.02% EDTA solution at 37^{0}C. Once the i3T3 cells became detached they were rinsed off using PBS. The still attached keratinocytes were then detached from the tissue culture plastic in a similar manner using trypsin-EDTA (0.05%trypsin (Difco Laboratories, Detroit, USA)/0.02% EDTA w/v). The cells were aspirated into a quantity of FCS to neutralize the trypsin prior to pelleting by centrifugation (200g x 5 minutes) and resuspended in a defined volume of fresh KM.

These cells were then expanded further, detached before reaching confluence, pelleted and then resuspended in a cryopreservative mixture of 10% DMSO and 90% FCS. The cell suspension was then transferred to cryovials and frozen down at a controlled rate of 1°C per minute. After a minimum of 4 hours the cryovials were transferred to liquid nitrogen for storage to allow repeated applications to the patient's wound on a weekly basis.

Forty-eight hours before the keratinocyte coated TranCell dressing was required for application, the cells were brought up from frozen, pelleted to remove the cryopreservative as soon as they were adequately thawed. The pelleted cells were then re-suspended in keratinocyte media. A cell count was performed and the keratinocytes seeded at a density of at least 1x10^6 per 6cm diameter TransCell surface (3.5 x 10^4/cm^2). The number of dressings prepared depended on the needs of the patient. After 24 hours of culture at in a humidified incubator at 37°C with a 5% CO^2- in- air atmosphere, the keratinocyte media was changed to cholera toxin free keratinocyte media. At this point a sample of media was withdrawn and placed on a blood agar plate and cultured to test for

sterility. If the sterility test was clear after 24 hours a small piece of the keratinocyte coated TranCell was removed and stained with MTT-ESTA to ensure viability of the cells before application to the wound.

Diabetic Foot Ulcers

This paper reports on the treatment of two patients with diabetic neuropathic foot ulcers resistant to conventional and experimental treatment (including standard care, special off-loading shoes, topical application of platelet-derived growth factor) with weekly applications of TranCell dressing.

Inclusion criteria

The patients included in this paper were aged between 40 - 60 years, had a history of diabetes mellitus (type 1) for 20 - 30 years and a history of chronic neuropathic foot ulcers between 3 months and 4 years duration. All patients had a diagnosis of neuropathy affecting the lower limbs with intact circulation (palpable dosalis pedis and posterior tibialis pulses).

Exclusion criteria

Patients were excluded if they had actively infected foot ulcers, ischaemic toes or impalpable foot pulses (dorsalis pedis, posterior tibialis) on the affected foot, acute Charcot neuropathic osteoarthropathy, if they refused to attend the foot clinic for the weekly assessment of their ulcers and application of TranCell dressings or were judged not to be sufficiently compliant with the recommendations concerning off-loading and the regularity of the TranCell dressing changes.

Patient treatment

Each patient received off-loading methods tailored to their needs for a period of at least 3 weeks prior to commencing treatment with autologous cells and their ulcers were assessed weekly during the patient's visit to a multidisciplinary diabetic centre. Standard assessment involved podiatry, wound bed debridement if necessary, off-loading methods including the use of semi-compressed felt, hexagonal shoes, half-shoes.

Cells on TranCell were applied once a week to the ulcers and replaced after 4 days with an absorbing dressing (Allevyn/Lyofoam) with semi-compressed felt and adhesive tape). The response to treatment was documented using photographs during these weekly visits and wound healing was defined as complete closure of the ulcer with full re-epithelialisation. Healed ulcers were subsequently followed-up for a period of 6 months.

RESULTS

Diabetic Foot Ulcers

The 'as–presented' diabetic ulcers (Figs. 1 and 3) responded to the treatment with complete healing after 6 - 8 applications of TranCell (Figs. 2 and 4) The ulcers responded to autologous cell delivery by a gradual decrease in depth and size with the

development of granulation tissue on the ulcer base followed by complete closure with epithelialisation.

The healed ulcers were assessed once weekly in the multidisciplinary clinic during the first month and twice monthly during the following 5 months.
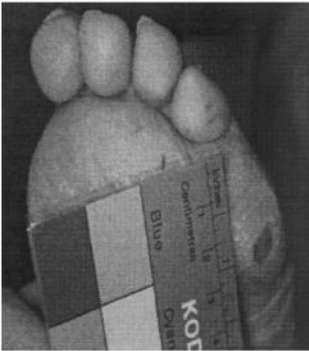
There were no recurrences in the healed ulcers after 6 months of follow-up and no side-effects were noticed during or after the treatment with TranCell.
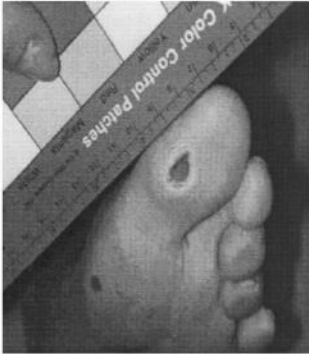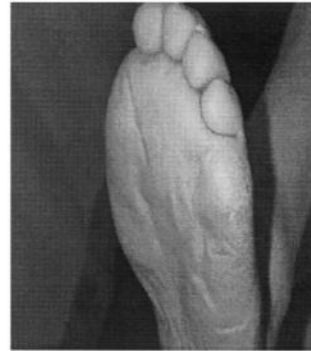

1. Ulcer 1 before treatment

2. Ulcer 1 after 8 treatments

3. Ulcer 2 before treatment

4. Ulcer 2 after 6 treatments

DISCUSSION

In this proof of concept study, we used a new cell delivery dressing seeded with autologous keratinocytes and applied weekly to diabetic neuropathic foot ulcers previously resistant to standard and experimental treatment. We observed the gradual formation of granulation tissue followed by re-epithelialisation leading to full closure of the ulcer. Ulcers that healed did not recur during 6 months of follow-up. There were no adverse reactions to the dressings during treatment or in the 6 months of follow-up. The treatment schedule was also compatible with the running of a busy diabetic foot clinic.

How the application of autologous cells leads to wound healing cannot be determined from this observational study. Previous work on cultured epithelial autografts have demonstrated that these can act as biological dressings providing a temporary covering to wound beds while releasing growth factors that promote permanent re-epithelialisation by stimulating the proliferation of quiescent keratinocytes in the wound bed[8]. Photographic and clinical observations of these wounds would be compatible with the autologous keratinocytes acting as biological bandages and stimulating re-epithelialisation from the margins. We also cannot rule out that cells may have transferred *in vivo* (as we have previously documented in an *in vitro* dermal wound bed model)[4]. We were able to obtain sufficient keratinocytes to deliver a course of treatment from a small split thickness biopsy within a relative short time (2 weeks) and the approach was acceptable to patients. We believe that this novel method of delivering autologous keratinocytes offers promise in the treatment of diabetic foot ulcers.

We need to go on to assess the efficacy of this approach in the healing of resistant foot ulcers by treating greater numbers and using appropriate controls. We also need to do more work to determine its mechanism of action. However, we feel able to conclude the method of delivering autologous keratinocytes is promising, well tolerated by patients and can easily be combined with standard care of diabetic foot ulceration.

CONCLUSIONS

Plasma polymerisation is a suitable technology for delivering cells to wound beds, with positive preliminary results in diabetic foot ulcers. Although it is too early to interpret the mode of action, the methodology should be suitable for a wide variety of chronic non-healing wounds as well as acute wounds.

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TEXTILE FINISHING FOR THE PRODUCTION OF NEW GENERATION MEDICAL TEXTILES

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ABSTRACT

Development of theoretical principles of technology and manufacture of prolonged action textile based materials for medical purpose is a new scientific - practical tendency in textile chemistry. The "know-how" of prolonged action medical bandages "Koletex"®, based on use of technology of printing or dressing, is proposed.

Efficiency of medical bandages is defined by a choice of a textile material type, type of a polymer – the medicine carrier (thickener), and medical properties depend on the chosen medical product introduced into a textile material together with the thickening. The printing technology allows one to obtain on a basis of biporous textile material a "double depot", from which the medical product is controllably released and transported into a human organism (into a wound, through skin and into a malignant tumour as well) and performs a medical effect.

Medical bandages "Koletex"® are widely used in Russia in medical practice: 20 types of production in various areas of medicine for different purpose (surgery, neuralgia, stomatology, oncology, dermatology, gynecology etc.).

THE STRUCTURE OF MEDICAL TEXTILES

Manufacture of textiles and medicines has been known from the beginning of civilization. Nowadays the independent scientific - practical tendency under general and very capacious name "Medical Textile" was generated. The new curing properties are added to the main properties of textiles. This branch of technology includes many directions the main ones of which are:

- antimicrobial textile materials having prophylactic properties and used in medical institutions by patients and the medical personnel, and in private life;

- materials for medical treatment on the textile basis containing medicinal substances of various medical action: bandages, napkins, applications, plasters etc.

The report presented is dedicated to the second direction – application of bandages on a textile basis, carriers of medical products. This direction has received an important development in the last 15 – 20 years [1-4] and has caused to life the vast assortment of medical bandages and applications for which the protective function remains and includes medical action supplemented by means of medicinal substances disposed on the surface or within textile material.

Medical bandages with medical products [4] being biporous (macro- and micro-) sorbent have essential advantage over other kinds of sorbents. Introduction of medicinal substances into textile material is realized by physical immobilization of medical product upon the textile material[5]. We choose this way [1–4] for creation of medical textile materials. It assumes physical immobilization of a medical product in the polymer that fills pores of biporous textile material and forms on its surface a layer (film) of polymer, filled with a
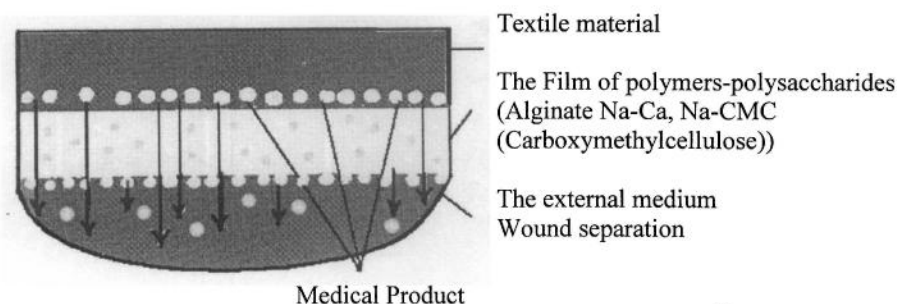
Textile material

The Film of polymers-polysaccharides
(Alginate Na-Ca, Na-CMC
(Carboxymethylcellulose))

The external medium
Wound separation

Medical Product

Fig 1. Structure of a medical bandage "Koletex"®

medical product. The original sandwich – a composite medical textile material "Koletex"® is formed and its structure is schematically shown on fig.1.

Developed by us [1-4] the conception, manufacture and application of textile based medical bandages of the "Koletex"® family (composite medical textiles) includes the following principles:

· use of textile materials as the carrier matrix for medical products;

· use of the polymeric compositions containing medicinal substances, for filling porous structure of textile materials;

· use of various (soluble and insoluble natural, synthetic) medical products depending on destination in medical bandages – applications;

· use of the technology of finishing manufacture (printing, finishing) for applying medical polymeric composition on textile material;

· use of various textile materials (a fabric, jersey, nonwoven) as a matrix depending on destination of medical material;

· use as polymer carriers of medicines traditionally used in textiles thickening substances licensed for medical application (alginates, carboxymethylcellulose (CMC) etc.).

This complex approach has allowed us to create and launch on the Russian market a family (more then 20 kinds in assortment) of medical bandages "Koletex"®. This so called "Russian Matreshka" is capable for prolonged (about 7 days) controllable releasing into an organism of the medicines necessary for various treatment purposes.

MODEL OF MEDICINE'S MASS-TRANSPORT INTO A HUMAN ORGANISM FROM A MEDICAL BANDAGE

Development of a model is necessary for creation of material with properties preset by doctors (concentration of a medicine in a wound, time of imposing of a bandage, localization of imposing etc.). In the course of development, the model of a medical product mass-transport from a treatment bandage into a human organism as an external medium was accepted. The structure of a production multilayered (composite) material – depot is shown (Fig. 1). The structure of the internal medium changes depending on destination of a bandage are as follows in the two sections, A and B.

A. The mass-transport of medicine occurs in a wound filled with exudation. The wound can be considered, as internal liquid medium of a small module (M = 1-3) of complex structure (exudation the plasma of blood containing electrolytes etc.). The part of a medical product depending on its solubility is carried away from a wound through lymphatic and circulatory systems. Thus we have mass-transport from multilayered swollen (due to contents of a wound) biporous textile material, filled with gel thickener, into a wound with small volume of a liquid and with constant ablation of a part of diffusant from a wound. Such a system is described by the kinetic equation (1) [1, 6]:

$$\frac{\partial Q(t)}{\partial t} = Sq(t) - WQ(t) \tag{1}$$

and its kinetic solution according to Crank [7] may be described by equation (2):

$$C_t = \frac{2C_0 D_1 l}{h} \sum_{n=1}^{\infty} \frac{1}{wl^2 - \beta_n^2 D} \left[\exp(-\frac{D\beta_n^2 t}{l^2}) - \exp(-wt) \right] \tag{2}$$

$WQ (t)$ – rate of a medicine ablation from a wound;
$Q (t)$ – current amount of medicine in medium's volume;
$q (t)$ – flow of medicine to a wound from a bandage;

β - roots of the equation $\beta tg - \gamma = 0$, where $\gamma = \varepsilon w \frac{l}{D}$;

C_0 – concentration of a medicine in a bandage;
D – diffusion factor of a medicine;
h – depth of the external liquid medium (wound);
l – thickness of a swollen polymeric layer of a bandage.

Experimental data on liberation kinetics of medical products from a medical bandage into the modelling liquid (equation 2), simulating a wound, are represented at Fig. 2. The peak of the medical product liberation from a medical bandage kinetic curve corresponds to
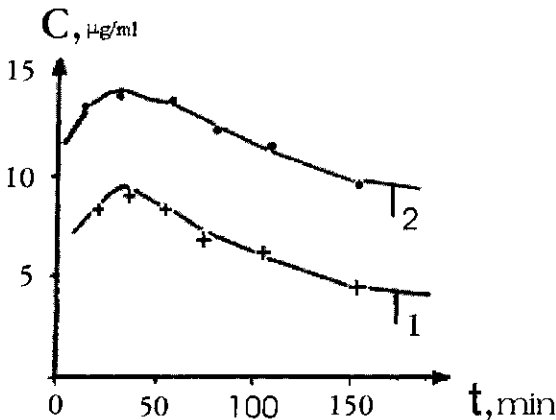

Fig 2. Change of a Furacillin medicine concentration in an external medium during desorption into water with the rate of ablation w. A thickener – Na-CMC, M=10: 1. $w_1 - 3,3 \times 10^{-3}$ c-^{1} 2. $w_2 - 1.5 \times 10^{-3}$ c-^{1} (Knitted cloth from polyamide fibres)

an initial "knock-out dose" of medicine, frequently necessary for effective treatment action and is caused by presence on a surface a multilayered material, an easily swelling polymer

film with inbuilt medicine. This medicine quickly migrates during drying to a surface of a polymer film and into the wound. Then, more slowly, the residuary part of a medicine leaves the swollen superficial layer of polymer and the polymer from the fibre pores. The higher the polymer swelling rate, the higher the medicine desorption rate.

After the "knock-out dose" the medicine could be liberated gradually into a wound within 5-7 days, i.e. a very valuable property of medical material prolongation is provided. Prolongation of medical action of "Koletex"[®] bandages is caused by structure of composite material and, first of all, by distribution of a medicine in structure of the polymer inhibiting diffusion of a medicine from a bandage. The polymeric material carries out a double role:

a) The role of thickener from which the necessary amount of a medicine is transferred onto a textile material and is distributed in the porous structure of textiles,

b) Inhibiting diffusion of a medicine in a wound of the viscous medium due to swelling of polymer in wound liquid and formation of gel,

c) Obligatory medical treatment function (hemostatic, wound-healing etc.), i.e. a medicine role.

B. Mass-transport of medicine occurs through a skin (trans-dermal).

In this case it is necessary to take into account a complex multilayered histological structure of skin. On the basis of literary data [8] human skin consists of three layers of various thickness and density:
- external horn (0.02 mm);
- cellular layer – epidermis (0.05 mm);
- derma (1.3 mm).

In each layer medicine mass-transport is considered as diffusion:

$$\frac{\partial C_i(z,t)}{\partial t} = D_i \frac{\partial^2 C_i(z,t)}{\partial z^2} \tag{3}$$

In this differential equation in partial derivatives (physical sense of conformity to the second Fik's law) $C_i(z, t)$ – concentration of a medicine in the i-ths layer, z – thickness of the layer, t – time, D_i – coefficient of diffusion in the i- ths layer.

The equation (3) is solved analytically or by numerical methods under certain boundary conditions [7] and under the condition of a continuity of concentrations and flows in all layers.

The choice of boundary conditions are:

a. $C_i(z = o,t) = 0$. Concentration of a medicine on border of a horn layer is constant. Two cases of boundary conditions on derma's internal border are considered:

b. $\frac{\partial C_3(z = l_3,t)}{\partial z} = 0$. The medicine does not leave the limits of derma.

c. $C_3(z = l_3,t) = 0$. The medicine is quickly carried away with a flow of blood from derma.

The numerical solution of the equation (3) with the help of the special program, based on the finite-difference scheme, enabled calculation of the time evolution of concentration profiles for penetration of a medicine into a skin. Typical concentration profiles are presented at Fig. 3.
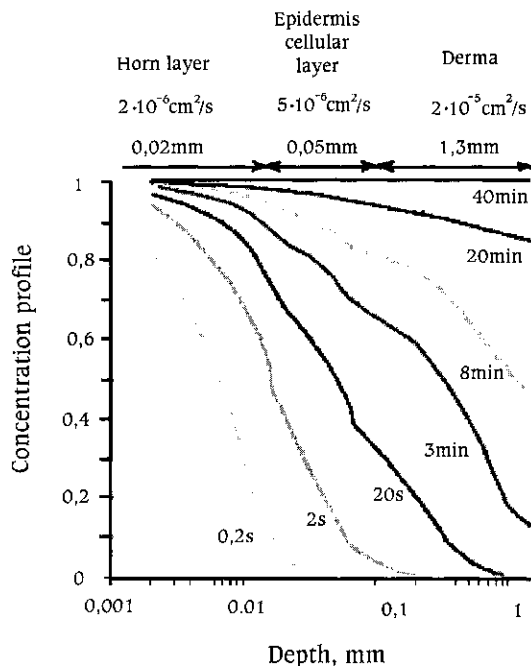
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Fig 3. Distribution of concentration of glycerin inside dermal integument at different moments of time.

The concentration of glycerin at an external surface of a horn layer was considered as a constant, and the derma external surface (the right side at the figure) was assumed impenetrable. Thickness of a horn, cellular layer and derma were accepted equal to 0.002 cm, 0.005 cm and 0.13 cm accordingly, and factors of diffusion of glycerin were considered equal to $D_1 = 2 \cdot 10^{-6} cm^2/s$, $D_2 = 5 \cdot 10^{-6} cm^2/s$ and $D_3 = 2 \cdot 10^{-5} cm^2/s$.

Equations (1-3) of two models of medicine mass-transport into a wound and through skin have good prognostic power and allow controlling the liberation of a medicine from a medical bandage into a wound or into a human skin. For regulation of medicine mass-transport rate it is possible not only to use kinetic models, but also to change technological parameters during manufacturing medical textile [9].

CHOICE OF TEXTILE MATERIAL, TECHNOLOGY, POLYMER - THICKENER AND MEDICAL PRODUCT

The choice of a type of textile material – the carrier of a medicine, first of all is caused by the very ideology of creation of medical napkins "Koletex"® as double depot. On the assumption that textile material, being a biporous sorbent, will have greater or smaller sorption capacity in relation to a medicine, depending on its total porosity, and its accessibility for penetration by polymeric composition with a medicine and the very medicine (Fig. 1). This total porosity depends on a textile type, on interlacing pattern, on chemical nature of fibres etc.

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In addition to this basic requirement (sorption capacity of textile), the complex of the following medical requirements is made:

- Hygroscopicity,
- Air- and vapor-permiability, the wound should "breathe",
- Absence of friability (separated fibres may infect a wound),
- Feel, drapability, making for adjacency to a surface of a body,
- Absence of shrinkage in a wound,
- Atraumaticity,
- Ability to maintain sterilization by various ways,
- The unilateral applying to a surface of a textile material of a polymeric composition,
- Textile material should be well combined with a surface of a body,
- Textile material should have the license of the Ministry of Health for its use.

The final choice of a textile material - the carrier of a medicine - is done in view of a range of applications of a medical bandage (weeping wound, stoppage of bleeding, trans-dermal supply of a medicine etc.). Knitted cloths have the highest porosity, therefore we have chosen them for the majority of types of medical bandages where high concentration (capacity) of a medicine and the maximal prolongation of medical action is required.

In each case (now 20 types of medical bandages "Koletex"®) the special kind of textile material was proved. In all cases the textile material should be allowed for use in medicine, as well as all other components of medical bandages.

If we want to create on the basis of a textile material double depot of a medical product with prolonged medical action it is necessary to use various traditional technologies of finishing manufacture, however not all of them will provide the necessary effect [9].

- The method of an exhaustion of a liquid bath with a medicine (periodic dyeing) does not fit, since the majority of medicines have no affinities to fibres.

- Pad-dry methods do not allow introduction of the high amounts of a medicine into a material because of specifically low solubility of medicines.

- Technology of printing with penetration of a thickened printed composition with a medicine into porous structures of textile.

- Technology of finishing which provides penetration of thickened composition with a medicine into porous structures of textiles.

Two last technologies have ensured necessary prolonged medical effects. In both cases, formed after applying and drying in structure of textile, the polymeric film of a thickener inhibits liberation of a medicine from a medical bandage, being a diffusion barrier to a medicine on a way to a wound or to the intact skin.

The choice of a polymer - thickener is defined by availability of its license for use in medicine, by an opportunity to influence positively the medical effect and by good printing-technical (rheological) properties of printed compositions. From these points of view the best complex of properties, in comparison to all traditional thickeners for printing, are salts of an alginic acid - alginates (the medical form is used).

To all positive qualities of alginates as thickeners is added, as well as for many other sea products, these "friendliness" to human beings: large amount of microelements, with extremely high hemostatic properties (many of carboxylic-group containing substances are hemostatics), have a positive influence on a wound regeneration.

The choice of a medical product is a prerogative of physicians and is determined by assignment of a medical bandage. One or several medicines may be introduced into a

bandage, interactions between which should be avoided. In case of imposing a bandage on a wound with the purpose of stopping bleeding it should have hemostatic, antimicrobial and anesthetizing properties. If the medical bandage is used in oncology it contains specific anticarcinogenic preparations: cytostatics, which detain growth of cancer cells or radiosensitizers and the photosensitizers, which accelerate destruction of cancer cells.There are also some general and specific requirements for the medicines in case of other medical problems (stomatology, gynecology, dermatology, surgery etc.

Table 1 Ranges of application and assignments of medical bandages "Koletex"®

Range of application of "Koletex"®	Styptic napkins with Furagin*	Napkins with Furagin*	Napkins with hexedinechloride	Napkins with propolis	Napkins with propolis and with Furagin*	Napkins with urea*	Napkins with dimethylsulfoxide	Napkins with jexydol*	Napkins with 5-fluorouracil*	Napkins with metronidozol*
For an emergency stop of a bleeding	♦									
For a stop of nasal bleedings	♦									
For healing cuts, excoriations, abrasions, fissures, wounds unhealing for a long time		♦	♦	♦	♦		♦			
For removal of hypostases and hematomas after injuries						♦	♦			
For healing trophic ulcers				♦	♦		♦	♦		
For elimination of consequences of a diabetes (trophic ulcers, diabetic feet)							♦	♦		
Burns of a various origin, including after radiation				♦	♦		♦			
Bedsores (prophylaxis and treatment)		♦	♦	♦	♦					
Postoperative stitches, fistulas		♦	♦				♦			
Cervical erosion				♦	♦					♦
Eczema, a skin itch, stings of insects				♦	♦		♦			
Parrodontosis, a stomatitis		♦		♦	♦					♦
Treatment neck skin cancer and mucous membranes									♦	♦
Rheumatic arthritis							♦			
Scleroderma							♦			

* Napkins are issued in variant with sticky edges (territories) for fixing on a body

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We, as technologists, should know those properties of medical products which may affect the "know-how" of medical bandages. It is necessary to design technological processes in such a way that the pharmacological efficiency of a preparation would not be reduced.

The solubility of the medicine especially strongly influences the rate of its liberation (mass-transport) from a bandage. This mass-transport rate of medicine may be increased, if necessary, by certain additives. In a case of trans-dermal supply of a medicine into an organism from a medical bandage it is necessary to enter into its structure the substances facilitating diffusion of a medicine through a skin.

RANGES OF APPLICATION OF MEDICAL BANDAGES "KOLETEX"®

Now NPO "Textilprogress" produces medical bandages of the following assignment and ranges of application shown in Tab.1. Ranges of application and medical assignment of napkins "Koletex"® are constantly extending.

And furthermore there is another application of suggested technology – manufacture of cosmetic face masks "Texal"®. Cosmetic stuff liberates from a mask based on textile material and transfers into a face skin. In the case of cosmetic masks "Texal"® the basic scientific problem is to provide fast enough trans-dermal (through a face skin) penetration of cosmetic stuff.

CONCLUSION

The scientific - practical direction presented in the report is a fine illustration of the fact that principles and technologies, methods and ways of textile chemistry may be used with success in new areas and in a new ways, for example for the creation of materials of medical assignment, namely medical bandages of the "Koletex"® family and cosmetic masks "Texal"®.

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THE EFFECT OF AMMONIA AND SULPHUR DIOXIDE GAS PLASMA TREATMENTS ON POLYMER SURFACES

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ABSTRACT

Gas discharge plasma treatment can be used to modify the surface properties of biomaterials for a variety of biomedical applications. An established application is the use of oxygen and nitrogen plasmas to improve the hydrophilicity of surfaces, encouraging cell attachment and subsequent growth. The physical properties and surface chemistry of the biomaterial influences cell attachment and subsequent culture. In-situ cells are surrounded by a complex extracellular matrix (ECM) containing fibronectin, laminin, collagen types I-V, and proteoglycans. In this study, ammonia and sulphur dioxide gases have been chosen with the objective of incorporating carboxylic acid, sulphur and nitrogen containing groups on the surface.

Aim: To investigate the effect of gas plasma treatments on untreated polystyrene Petri dishes and apply the technology to tissue engineering scaffolds.

Methods: Untreated tissue culture Petri dishes (TCPD) (35 mm $\varnothing$) were gas plasma treated with either ammonia, sulphur dioxide or ammonia followed by sulphur dioxide gases in a low temperature radio-frequency gas plasma chamber. An orthogonal design was used to optimise the treatments, which looked at the effect of varying the power, distance between the (upper and lower) plates and treatment time. To determine changes in hydrophilicity, the static contact angle was measured using image analysis equipment. Samples were kept in the laboratory and the contact angle of the surface measured one, three and six months after gas plasma treatment. To investigate the surface changes some samples were analysed using the X-ray Photoelectron Spectrometer (XPS) at the RUSTI, CLRC Daresbury Laboratory, UK.

Results: The untreated TCPD (controls) had a static contact angle of $53.5 \pm 0.8°$. Gas plasma treatment with ammonia lowered the contact angle to approximately 25 - 30° after 1 month, which remained relatively constant at 3 and 6 months depending on the treatment parameters. Treatment with sulphur dioxide produced more variable results. Overall treatment with ammonia followed by sulphur dioxide produced the greatest change in hydrophilicity lowering the contact angle to between $18.3 \pm 4.2°$ and $29.7 \pm 2.0°$ for all four sets of parameters. The XPS spectra show changes in the O1s and C1s groups and the introduction of N1s, S2p and S2s groups in the treated samples

Conclusions: Ammonia and sulphur dioxide plasma treatments do alter the surface functional groups in the biomaterial, increasing the hydrophilicity of the surface. In this study the greatest increase in hydrophilicity was observed after treatment with ammonia followed by sulphur dioxide. However, to successfully apply the results to tissue engineering scaffolds, the effect on cell attachment, coverage and morphology must be evaluated on the optimised surfaces.

INTRODUCTION

Gas discharge plasma treatment can be used to modify the surface properties of biomaterials for a variety of biomedical applications, without affecting the bulk properties of the material. An established application is the use of oxygen and ammonia plasmas to improve the hydrophilicity of surfaces, such as tissue culture dishes[1], encouraging cell attachment and subsequent growth. Gas discharge plasma treatment is also used to modify surfaces for cell attachment, which are then further treated with biological components, such as ECM and bioactive peptides[2, 3]. To ensure a material is biocompatible the surface and bulk properties must be adapted to the tissue in contact with the material and if the device is internal, extracellular fluid or blood.

BACKGROUND

Under physiological conditions cells are surrounded by a complex extracellular matrix (ECM) containing fibronectin, laminin, collagen types I-V, and proteoglycans (glycoproteins)[4]. They are basically composed of long chain polypeptides, which contain containing C,H,N,O and S atoms bonded together forming various charged functional groups at the surface. Cell attachment and subsequent culture on materials depends on the surface characteristics. Over the years much effort has been directed towards maintaining 3-D differentiated cells in culture. One successful widely used technique involves coating the surface with an ECM. However the ECM is commonly derived from animal sources and consequently carries a potential virus risk e.g. bovine spongiform encephalopathy (BSE), porcine endogenous retrovirus (PERV) and possibly other, as yet unknown viruses. Depending on the device, it can also be difficult to coat the cell attachment surface.

An objective of this study is to minimise the number of process steps required before cell attachment and growth is encouraged by using gas discharge plasma treatment only. Numerous gases have been used in gas discharge plasma research but only in a few cases has the effect of the treatment on the material surface been quantified, with little or no data about the actual operating conditions. In most cases the authors do not offer any explanation as to why they have chosen their particular gas. Ammonia and sulphur dioxide gases have been chosen in this study with the aim of incorporating carboxylic acid, sulphur and nitrogen containing groups on the surface. Carboxylic acid groups have been shown to promote osteoblast, fibroblast and endothelial cell attachment, whereas methyl groups do not[5]. In this study an orthogonal design[6] has been employed, which will allow process optimisation.

AIMS AND OBJECTIVES

The objective of this study is to investigate the effect of ammonia and sulphur dioxide gas plasma treatments on untreated tissue culture polystyrene dishes (TCPD). The main aim is to encourage cell attachment and growth by looking at the effect different gas discharge plasma treatments have on contact angle, cell adhesion and surface properties.

METHODS

Untreated TCPD (35 mm ∅) were gas plasma treated with either ammonia, sulphur dioxide or ammonia followed by sulphur dioxide gases in a low temperature rf gas plasma chamber (system shown in Fig. 1).
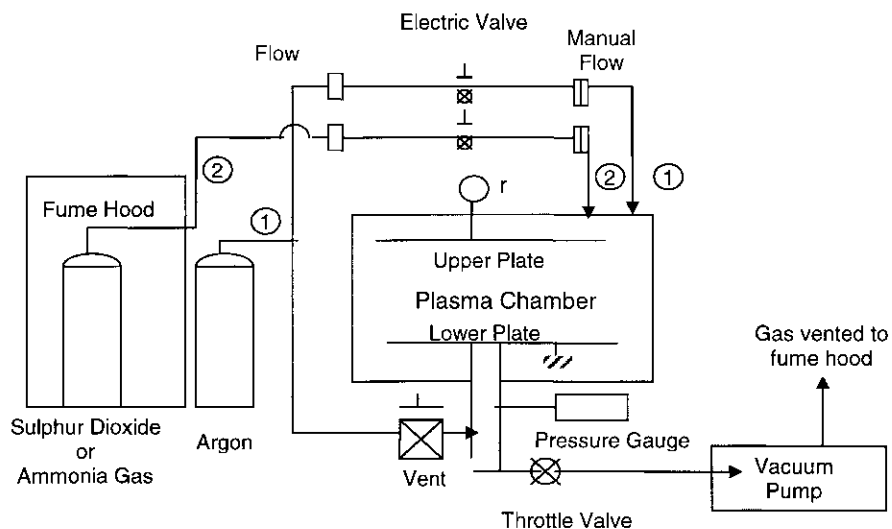

Figure 1. Schematic drawing of the low temperature rf gas plasma system.

An orthogonal design was used to optimise the treatments, which looked at the effect of varying the power, distance between the (upper and lower) plates and treatment time. The pressure was kept constant at 100 mtorr. The orthogonal design $L_4 2^3$ is shown in table 1 with the parameters.

Table 1. Orthogonal Table $L_4 2^3$ and the parameters applied.

	Input Parameter		
Run	1	2	3
	Power (W)	Distance (mm)	Time (min.)
1	1. 100	1. 50	1. 1
2	1. 100	2. 30	2. 5
3	2. 40	1. 50	2. 5
4	2. 40	2. 30	1. 1

To determine changes in hydrophilicity, the static contact angle was measured using image analysis equipment and the contact angle computer program[7]. The image analysis set up consists of a camera placed in a light box to maintain consistency, which is

connected to a screen and computer. A computer program written in Semper 6 first calculates a threshold value, then this value is used to calculate the area of the drop in pixels. A syringe containing Indigo Solution (1g dissolved in 500 ml de-ionised water) was placed 3 cm above the treated TCPD and 18-20 µl of solution dropped from this height onto the surface. The image is then captured by the computer and appears as a dark circle on the screen, from which the area is calculated in number of pixels. The contact angle is calculated by inputting the number of pixels per cm, volume of the drop in ml and area of the drop in pixels into the contact angle computer program[7]. Samples were kept in the laboratory and the contact angle of the surface measured one, three and six months after gas plasma treatment. Where possible, the contact angle was measured twice on each dish and the data shown are the average of four dishes.

To investigate the surface changes some samples were analysed using the X-ray Photon Spectrophotometer at the RUSTI, CLRC Daresbury Laboratory, UK.

RESULTS

The untreated TCPD (control) had a static contact angle of 53.5 ±0.8°. Figure 2 shows the effect of time on contact angle after gas plasma treatment. Gas plasma treatment with ammonia lowers the contact angle to 24.9±1.5°-30.9±0.6° after 1 month, which remains around 26.8±0.2°-32.5±0.9° and 27.4±0.8°-36.0±5.6° at 3 and 6 months depending on the treatment parameters. Treatment with sulphur dioxide produced more variable results. Treatment 1 lowered the contact angle to 0.0° (where the solution spread immediately over the plate) while 1 month after Treatment 2, 3 and 4 the contact angle was 41.8±3.1°, 51.3±0.5° and 40.2±1.8°. Over time the contact angle rises and ranges from 38.4±1.3° to 51.3±0.5°. Overall treatment with ammonia followed by sulphur dioxide produced the greatest change lowering the contact angle to between 18.3±4.2° and 29.7±2.0° for all four treatments, except Treatment 1 where the contact angle was between 0.0° and 27.0±4.6°. For all three gases, Treatment 1 generally produced the lowest contact angles and compared to the other treatments the values remained lower over time.

Figure 3 shows the XPS results of the untreated TCPD (control), ammonia, sulphur dioxide and ammonia followed by sulphur dioxide treated TCPD at 100 mtorr, 100 W, 30 mm and 5 min (Treatment 2). The spectra show the introduction of N1s, O1s, C1s, S2p and S2s groups in the treated samples.

DISCUSSIONS

This study examined the changes in TCPD after plasma treatment by measuring the change in contact angle. The static contact angle of TCPD (53.5 ±0.8°) measured using the image analysis equipment and contact angle computer program[7] compares favourably with the value found by Gümüşderelioğlu and Türkğlu [8] 47.9°. The surfaces of TCPD have been described by France et al. [9] as variable with only limited value as a control. However, in this study the contact angle of untreated TCPD was calculated each time the static contact angle of the treated samples was determined and found to be stable in the range 52.3±0.8° to 54.4±1.1°.
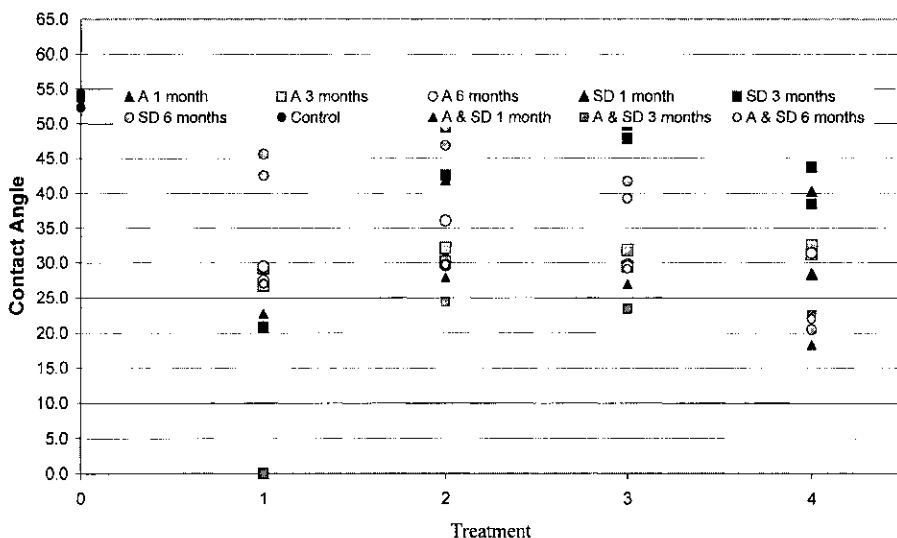
Figure 2. Effect of Time on Contact Angle After Gas Plasma Treatment

Where treatment 1 = Power 100 W, Distance 30 mm & Time 5 min; 2 = Power 40 W, Distance 30 mm & Time
1min; 3 = Power 40 W, Distance 50 mm & Time 5 min and 4 = Power 100 W, Distance 50 mm & Time 1 min.

Although all the gas plasma treatments lowered the contact angle, increasing the hydrophilicity of the surface, treatment with sulphur dioxide gas produced the most variable results. When the dishes are examined after treatment frequently a rainbow effect can be seen on the treated surface. Over time it was noted that some of the dishes contain very small beads of condensation and what appears to be a film. It may be that at the treatment conditions chosen a sulphur dioxide film is forming on the dish. XPS analysis of the treated samples confirms the presence of sulphur groups. However, these groups may be present in a surface film and not as functional groups attached to the surface. The presence of a film may also explain the variability after treatment with sulphur dioxide gas.

The ammonia followed by sulphur dioxide treated TCPD showed the greatest increase in hydrophilicity with the drop often spreading to cover the whole surface. While the ammonia treatment produced the most stable results. Generally over time the increase in hydrophilicity of the surface diminishes, which is most notable with the ammonia treated samples. After Treatment 3 with sulphur dioxide gas the hydrophilicity appears to decrease over time. If the very small beads of condensation (noted on some samples) are being incorporated into the contact angle drop this would alter the surface tension and may be the cause of this decrease. In future, samples will be stored under moisture-free conditions.
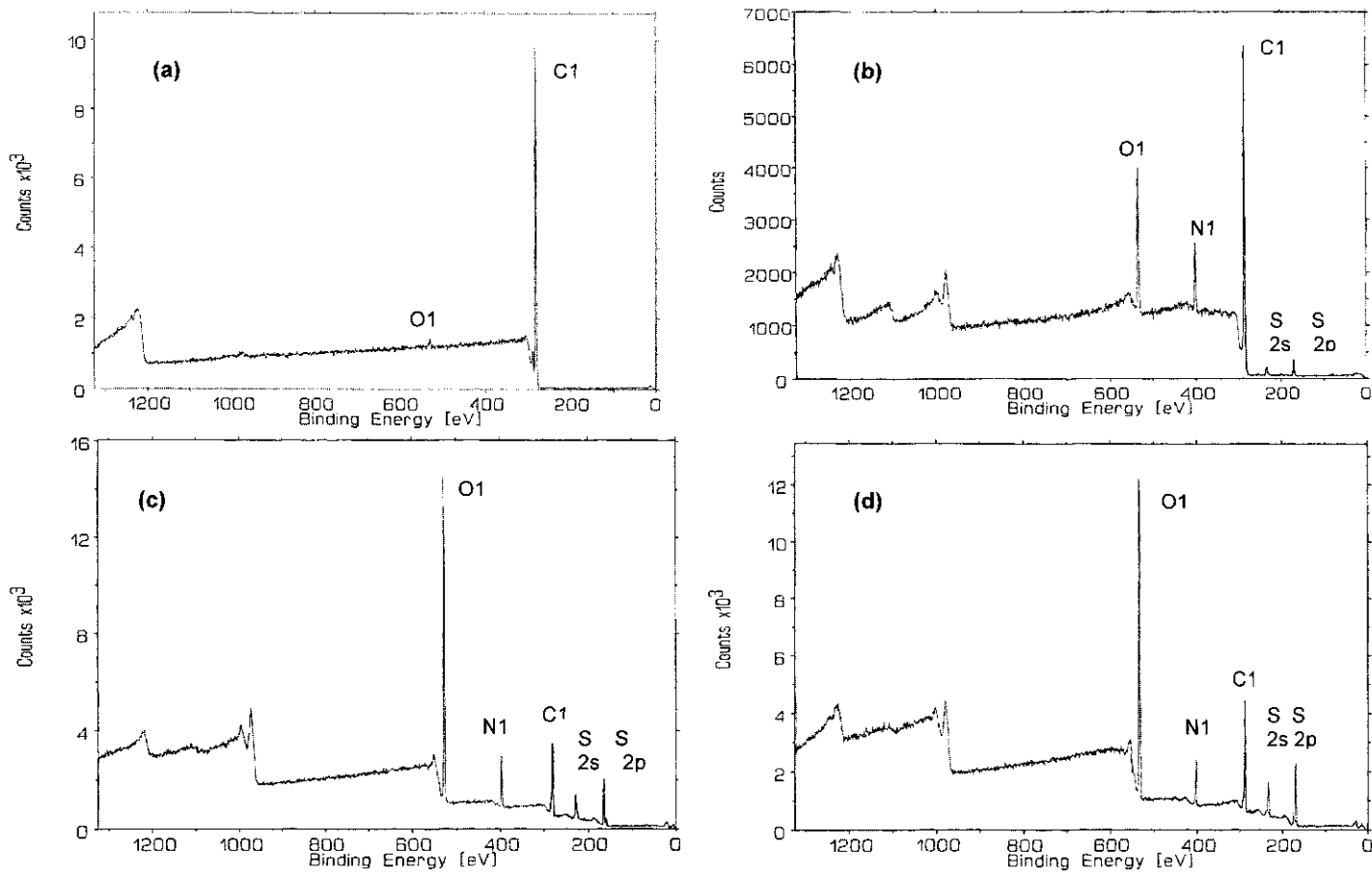
Figure 3. The XPS spectra of (a) untreated TCPD (control), (b) ammonia treated TCPD, (c) sulphur dioxide treated TCPD and (d) ammonia followed by sulphur dioxide treated TCPD.

Treatment 1 appears to produce the most stable results but further investigation into the correlations between the individual parameters (power, distance and time) is required. In this study the minimum treatment time is one minute, which may be too long for the sulphur dioxide treatments and treatment times below one minute should be investigated. Although, when the samples are examined under the electron microscope no changes in the surface, such as etching, are observed. The XPS results confirm that the surface has indeed changed, with gas plasma discharge treatment introducing new functional groups on the surface. The next step is to quantify these changes.

CONCLUSIONS

For internal devices, the physical surface properties of the material and chemical reactions at the interface, between the surface and extracellular fluid / blood, influence the absorption of molecules and subsequent attachment of cells. Gas plasma discharge treatment can be used to change the surface functional groups and increase the hydrophilicity of the surface. In this study treatment with ammonia followed by sulphur dioxide produces the greatest increase in hydrophilicity. It is hoped that the functional groups introduced by gas plasma treatment will bind molecules and peptides, such as growth factors, and act as cell anchorage sites.

FUTURE WORK

From the contact angle values it should be possible to calculate surface tension. Therefore, after investigating the interactions between the parameters, power, distance and time, it may be possible to select values for a defined surface hydrophilicity where the critical surface tension is in the range 60-120 mJm^{-2}; which is hinted at in literature as good for tissue adhesion[10]. However, the effect on cell attachment, coverage and morphology must be evaluated on the optimised surfaces.

Future uses include 3D tissue engineering scaffolds. Scaffolds can be constructed from fibres / yarns selected for their bulk properties, such as elasticity, strength and biocompatability, then plasma treated to encourage cell attachment and growth.

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