Part III

Chromic and conductive materials

11

Introduction to chromic materials

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11.1 Introduction

Chromic materials are the general term referring to materials, which change, radiate or erase colour. Chromism as a suffix, means reversible change of colour and by extension, a reversible change of other physical properties. Due to colour changing properties, chromic materials also are called chameleon materials. This colour changing phenomenon is caused by the external stimulus and chromic materials can be classified depending on the external stimulus of induction:[1]

- photochromic: stimulus is light
- thermochromic: stimulus is heat
- electrochromic: stimulus is electricity
- piezochromic: stimulus is pressure
- solvatechromic: stimulus is liquid
- carsolchromic: stimulus is an electron beam.

Chromism has been studied since before the 1900s and the main applications are in the areas of photochromism, thermochromism and electrochromism such as paints, inks, tiles, eyeglasses, windows and many optical applications.[3] The most applied chromic solutions in textiles and fibre materials are the two first groups, photochromic and thermochromic.

Photochromic materials change their colour by light and these materials are both organic and inorganic, but the most studied are organic photochromic materials. There are also photochoromic materials called heliochromic compounds, which are activated by unfiltered sunlight and deactivated under diffuse daylight conditions. Therefore they are suitable for sun lens applications.[7]

Thermochromic materials change their colour as a result of reaction to heat, especially through the application of thermochromic dyes whose colours change at particular temperatures. Two types of thermochromic systems have been used successfully in textiles, the liquid crystal type and the molecular rearrangement type.[1]

Electrochromic materials are capable of changing their optical properties (transmittance and/or reflectance) under applied electric potentials; when that potential is stopped or it goes into reverse, these materials retain or return to their original optical state in a reversible way. The variation of the optical properties is caused by insertion/extraction of cations in the electrochromic film.[4]

Piezochromism is the phenomenon where crystals undergo a major change of colour due to mechanical grinding. The induced colour reverts to the original colour when the fractured crystals are kept in the dark or dissolved in an organic solvent.[7]

Solvatechromism is the phenomenon, where colour changes when it makes contact with a liquid, for example, water. Materials that respond to water by changing colour are also called hydrochromic and this kind of textile material can be used, e.g., for swimsuits.[1]

11.2 Photochromic materials

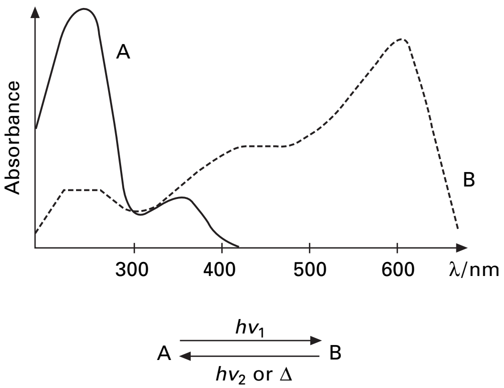
Photochromic materials change colour reversibly with changes in light intensity. Usually they are colourless in a dark place and when sunlight or UV-radiation is applied the molecular structure of the material changes and it exhibits colour. When the relevant light source is removed the colour disappears. Changes from one colour to another colour are possible by mixing photochromic colours with base colours.[2]

In photochromic pigments the structure changes when it is exposed to sunlight or ultraviolet radiation, causing a colour change. The reversible change can be colourless to colour or, by a combination of photochromic conventional dyes, one colour to another. The lifetime of these compositions is rather short for industrial applications or building applications.

Photochromic materials are used in lenses, paints, inks and mixed to mould or cast materials for different applications.[2] Photochromic compounds in textiles are used mainly for decorative effects in jacquard fabrics, embroideries and prints in different garments.

11.2.1 Definitions of photochromism

Photochromic compounds are chemical species having photochromic properties. There are two major classes of photochromic materials, inorganic and organic; most inorganic materials are based on silver particles. Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra (Fig. 11.1).[7] The



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thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).

The bistability of organic photochromic compounds is of special interest for optical data memory systems (photon-mode erasable optical recording media). Numerous other uses have also been explored with encouraging results; applications concerning single molecules, polymers and biological molecules. In the case of optical storage memory systems, the interest in photochromic compounds is based on the fact that photon-mode recording has certain advantages over the heat-mode, regarding resolution speed of writing and multiplex recording capability. Also fatigue due to material movement is eliminated. Despite these advantages, the photochromic molecules still await a wide range of practical applications. The reason is that they must fulfil many other requirements, e.g., can be cycled many times without loss of performance and thermal stability.[8]

The fact that some chemical species can undergo reversible photochemical reactions goes beyond the domain of variable optical transmission and includes a number of reversible physical phenomena such as optical memories and switches, variable electrical current, ion transport through membranes, variable wettability, etc. For this purpose, organic photochromic compounds are often incorporated in polymers, liquid crystalline materials, or other matrices.[7]

11.2.2 Photochromic applications

Photochromism is simply defined as a light-induced reversible change of colour; a most common example of that phenomenon is photochromic spectacles that darken in the sun and recover their transparency in diffused light. The first commercial spectacles used glass lenses impregnated with inorganic salts (mainly silver) but in recent years organic photochromic lenses are replacing the inorganic ones.[7]

Photochromic phenomena are presently also being used in many textile applications like T-shirts, handbags and caps. There is, e.g., nightwear, which indoors is white while in daylight the colour changes to blue, green, purple or whatever. The California-based company SolarActive International manufactures a wide variety of photochromic products including colour-changing textured yarns for textile knitting and weaving and embroidery threads stimulated by UV-light.[6] Embroidery threads are made by using mass pigmentation of polypropylene in the molten state with different photochromic compounds. Polypropylene fibre is then produced by melt spinning to serve as the basis of solar-active thread. The thread appears white on fabric when indoors and/or away from UV-light. Outside, rainy or sunny, the UV radiation penetrates the thread, activating the photochromic compounds which change the thread to specific colours. The threads return to white when removed from UV-light within about one and a half minutes. The colour-changing effect has been tested and proven to last for more than 2000 alternations, in and out of UV-light, which is equivalent to the life of a garment. Since the photochromic material is not just a coating but a part of the polypropylene, the material does not wash off and remains with the fibre for the life of the product.[5]

The Swedish Interactive Institute has developed a curtain made from a colour-changing material sensitive to UV-light. A computer-controlled UV lamp dynamically illuminates various parts of the curtain thereby creating a dynamic textile pattern depending on a computational interpretation of certain given information. The textile can thus be connected to a computer as a kind of display.[9]

One commercial application of photochromic textiles includes the fabrics of Taiwan company Super textile Corp. These high-tech photochromic fabrics utilise a special microcapsule dye technology that changes colour upon absorbing sunlight and UV radiation. The fabrics can be combined with other coating materials and dyestuffs to help produce a colourful effect. These products are non-hazardous and they can be used in general applications such as knapsacks, dolls and warning signs.[10]

11.3 Thermochromic materials

Thermochromic materials change colour reversibly with changes in temperature. The materials can be made as semi-conductor compounds, from liquid crystals or using metal compounds. The change in colour occurs at a predetermined temperature called the thermochromic transition. This can be altered by adding doping agents to the material.[3] Thermochromic materials using encapsulated dyes were developed in the 1970s. The technology was patented by Japanese companies and subsequently used mainly in the textile and novelty industries.[11] Thermochromic materials are used in a variety of commercial products including textiles and novelty items, toys and baby spoons.

Most thermochromic commercial products are derived from liquid crystals or complicated mixtures of organic dyes. Both of these methods require the materials to be microencapsulated. This results in a variety of limitations including poor thermal stability and difficulty in processing. In addition, some materials that are currently available are toxic and easily extracted from most plastics and therefore not approved for use in articles that come into contact with food products.[12] Thermochromic materials are used as well for fun purposes and for many useful applications like instrumentation, warning, information and indicating data, e.g., body thermometers.

11.3.1 Definitions of thermochromism

Thermochromism is the reversible change in the colour of a compound when it is heated or cooled. The thermochromic colour change is distinguished by being quite noticeable, often dramatic and occurring over a small or sharp temperature interval. The mechanics of thermochromism have been investigated since the beginning of 1970. There are different mechanisms according to which materials are used. The following four materials are used in thermochromism:[13]

1. organic compounds
2. inorganic compound
3. polymers
4. sol-gels.

Organic compound thermochromism

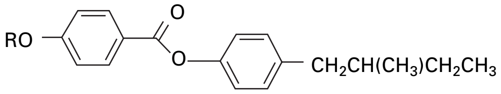
Organic compound thermochromism has various applications for fibres, optical sciences, photo-storage instruments and optical sensors. The mechanism responsible for thermochromism varies with moleculer structure. It may be due to an equilibrium between two molecular species, acid-base, keto-enol, lactim-lactam, or between stereoisomers or between crystal structures. We can divide this into three parts on the basis of materials:[13]

1. variation in crystal structure
2. stereoisomer
3. molecular rearrangement.

The advantages of thermochromism of these organic compounds are that colour change takes place sharply and that there are many factors to control temperature easily. Two types of these thermochromic systems have been used successfully in textiles, the liquid crystal type and the molecular rearrangement type.[1]

Liquid crystal type

Thermochromic liquid crystals show different colours at different temperatures because of selective reflection of specific wavelengths of light from their structure. In an appropriate temperature range intermediate between a low-temperature crystalline phase and a high-temperature isotropic liquid phase, these materials form a cholesteric liquid crystal. In a cholesteric liquid crystal, changes in temperature result in thermal expansion, which leads to a change in layer spacing and hence pitch and therefore the colour change observed will vary with temperature.[13] These materials are used in the manufacture of thermochromic printing ink. Thermochromic liquid crystals have the advantage that they express a finely coloured image, but they have the disadvantage of high cost and low colour density.



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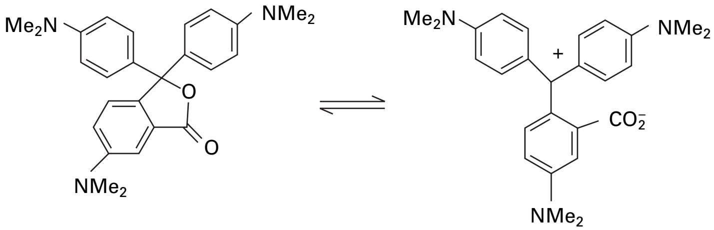
Molecular rearrangement type

The molecular rearrangement of an organic compound that arises from tautomerisation, such as that which occurs as a result of, for example, an acid-base, keto-enol or lactim-lactam equilibrium, can lead to an increase in the conjugation of the molecule and formation of a new chromophore. Such molecular rearrangement can be effected by a change in temperature or by alteration of the polarity of the solvent and/or the pH of the system. Because of the pH-dependent chromism, the temperature-dependence of the acid-base equilibrium means that pH sensitivity can result in thermochromic behaviour.[13]



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According to the definition of thermochromism given earlier, crystal violet lactone does not exhibit thermochromism, as the equilibrium is pH- rather than temperature-dependent; indeed, the ring-opening reaction does not occur, even on heating low pH values (below approximately pH4) the coloured form predominates, while an increase in pH results in the equilibrium moving to the left, with the effect that the system becomes colourless.

Inorganic thermochromism

Many metals and inorganic compounds are known to exhibit thermochromic behaviour either as solids or in solution. Inorganic thermochromic systems have not enjoyed widespread textile applications as the observed change in colour often occurs in solution at high temperature. The majority of textile end-uses demand a reversible, solid system that is suitable for application by printing and that exhibits distinct colour changes over a small temperature range.[13]

11.3.2 Thermochromic applications

Colorant manufacturers and academic research organisations have worked for many years to develop fast colouring matters by researching dyes and pigments that are chemically inert and physically unresponsive once they have been applied to a substrate.[14] Thermochromic organic colorants have been developed for use in producing novel coloration effects in textiles as well as other applications. In the textile sector most thermochromic applications are the same as photochromic ones, like T-shirts and caps, which use thermochromic inks for decoration purposes. An increase in temperature produces a reversible change in colour and the heat from direct sunlight is enough to produce the change.[15]

The diverse range of non-textile applications to which thermochromic materials have been put include thermometers and temperature indicators for special purposes like security printing and non-destructive testing. They can indicate the proper temperature, e.g., cold enough for storage or hot enough for serving.[12] Compared with other markets, the textile sector generally lags behind in the exploitation of thermochromic materials. One reason is that the colour changing temperature of the majority of these materials lies well above room temperature, typically over 100–200 °C and have not so much use for producing thermochromic effects on textiles.

There are, however, thermochromic materials based on a special class of liquid crystalline substances and by using these it is possible to achieve significant changes in colour appearance over narrow temperature ranges, 5–15 °C, and also to detect small variations in temperature, < 1 °C.[14] The Japanese company Pilot Ink Co. Ltd have worked for a long period with thermochromic materials and have also a significant amount of patents. Pilot Ink Co. is the leading company developing especially thermosensitive materials for different mouldings like toys and hoses. Thermosensitive material is coloured by mixing the three primary colours so it can display virtually any hue from white to black. The thermosensitivity is functional at temperatures ranging from –10 °C to 60 °C, within the range of ordinary manufacturing processes.[15]

11.4 Colour-changing inks

The two major groups of colour-changing inks are thermochromic, which change colour in response to temperature fluctuations, and photochromic, which respond to variations in exposure to UV light (primarily sunlight). Both materials are reversible and will change colour over and over again with the appropriate exposure.[17]

11.4.1 Temperature-sensitive inks

The two types of thermochromic inks are liquid crystals and leucodyes.[t] The most famous thermochromic application ever, the 'mood ring', was a liquid crystal. Today liquid crystals are used in many products, including aquarium thermometers, stress testers, and forehead thermometers. Unfortunately, liquid crystal thermochromics are very difficult to work with and require highly specialised printing and handling techniques.

The other type of thermochromic ink, the leucodye, is used in wide range of applications, e.g., for textiles, security printing, novelty stickers, product labels and advertising specialities. Some products printed with leucodye thermochromic inks change from one colour to another, rather than transitioning from coloured to clear. This is achieved with an ink that combines a leucodye with a permanent-colored ink formulation. For example, the ink manufacturer may formulate a green ink by adding a blue leucodye to a yellow ink. In its cool state the printed ink layer is green and once warmed reverts to yellow as the leucodye becomes clear or translucent. Leucodyes can be designed to change colour at various temperature ranges, from as low as –25 °C up to 66 °C. A wide range of colours is also available.

In order to function, a leucodye requires a combination of chemicals working together in a system. This special system of materials needs to be protected from the components of the ink to which it is being added, so it is microencapsulated. The microencapsulation process takes a small droplet of the leucodye and coats a protective wall around it. The leucodye microcapsules contain the complete colour-changing thermochromic system, which, when added to inks, give them their colour-changing properties.

Under normal conditions, the thermochromic leucodye inks have a shelf life of six months or more. After they are printed, they function or continue to change colour for years. The post-print functionality can, however, be adversely affected by UV light, temperatures in excess of 121 °C and aggressive solvents. Thermochromic textile inks will withstand about 20 washings before showing a significant deterioration and can last even longer when dried without heat. Chlorine bleach is not recommended, because this will degrade the performance of the printed ink on textiles.[17]

11.4.2 Light-sensitive inks

Photochromic inks change from clear when indoors to coloured when taken outdoors. UV-light changes the chemical structure of the photochromic material and makes it absorb colour like a dye. It then reverts to a clear state when the UV source is removed. The colour change can occur thousands of times, depending on the application. A photochromic dye can also change from one colour to another when it is combined with a permanent-pigment ink. These inks are also available in a full range of colours, including a four-colour process system. One of the most popular uses for photochromic inks is on screen-printed garments such as T-skirts.

In their pure state, photochromics are powdered crystals that must be dissolved in the inks to which they are added. Some manufacturers microencapsulate the photochromics in their own system, as with leucodye microcapsules. Microencapsulating photochromic systems enables them to be used in inks that cannot dissolve them, such as water-based systems.

Photochromic material is inherently unstable and actually changes its chemical structure when exposed to UV light. Because the dye is so vulnerable in its excited state, stabilisation is the prime challenge for photochromic ink manufacturers. Without stabilisation most photochromic inks would not last even a few days in sunshine and may even expire before being printed.

A properly stabilised photochromic ink will last for years in store before printing, but even the best of them will withstand only a few months of outdoor exposure after printing. The best photochromic textile inks will withstand about 20 washings after printing and are more susceptible to the negative effects of chlorine bleach than their thermochromic counterparts. Bleach must never be used on garments printed with photochromic inks.[17]

11.5 Electrochromic materials

Electrochromic materials are materials that change colour upon application of an electrical potential. Electrochromic systems have been used successfully in the past in mirrors and windows for anti-glare and anti-reflective applications. However, other potential applications, including large area privacy/security glazing and high-contrast angle-independent dynamic displays have not yet reached the market. This is due to the limitations of existing electrochromic materials.[18]

Collaborative research efforts in different companies, universities and research centres have concentrated on studying electrochromic applications in fibres and textiles. One example of this kind of research work is carried out by Clemson University, Georgia Institute of Technology and Furman University in the USA and the goal is to create colour tunable fibres and fibre composite structures. This is being accomplished by incorporating into or onto fibres, molecular or oligomeric organic chromophoric devices capable of colour change over the visible portion of the electromagnetic spectrum by the application of a static or dynamic electric field. Anticipated applications for this type of material will include wall and floor coverings, camouflage materials and fabric based electronic displays which can change colour or information display content based on the electric field applied. Such fields will be low-voltage fields (3–5 volts). One very interesting effect found with this work is the possibility of information storage and retrieval from organic fibres based on molecular recognition. This may lead to microdevices encapsulated in fibres for a variety of technical applications.[19]

Electrochromic materials, which change their optical properties in response to an electric field and can be returned to their original state by a field reversal, have major advantages:[20]

- a small switching voltage (1–5 V)
- they show specular reflection
- they possess a grey scale
- they require power only during switching
- they exhibit adjustable memory, up to 12–48 hours.

11.5.1 Definitions of electrochromism

Electrochromic material changes colour in a persistent but reversible manner by an electrochemical reaction and the phenomenon is called electrochromism. Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction. It results from the generation of different visible region electronic absorption bands on switching between redox states. The colour change is commonly between a transparent (‘bleached’) state and a coloured state, or between two coloured states. When more than two redox states are electrochemically available, the electrochromic material may exhibit several colours and may be termed as polyelectrochromic or can be said to possess multicolour-electrochromism. This optical change is effected by a small electric current at a low d.c. potential of the order of a fraction of a volt to a few volts.[21]

11.5.2 Electrochromic applications

Electrochromic devices are the most popular technology for large area switching devices. Much of this technology is being developed for building and automotive windows, mirrors and glazing applications. Electrochromic materials are finding applications as specialised displays, electronic books, paper-like, and banner displays. Many chromic materials can be fabricated on plastic substrates, which is an advantage for future display aplications.[20]

One example of an innovation is a paper-thin electrochromic display developed by the Siemens company. The display is controlled by a printed circuit and can be powered by a very thin printable battery or a photovoltaic cell. The goal is to be able to create the entire device – the display and its power source – using the same printing method, so that manufacturing costs would be as low as possible. Siemens expects to achieve this by 2007.[22]

Textile integrated display applications have been developed by France Telecom: a flexible, battery-powered optical fibre screen is woven into clothing. Each plastic fiber-optic thread is illuminated by tiny LEDs that are fixed along the edge of the display panel and controlled by a microchip. The threads are set up so that certain portions are light when the LEDS are switched on, while other sections remain dark. These light and dark patches essentially act as pixels for the display screen.[23]

IFM's patent Electric Plaid™ is a combination of textile display technology and design material. The novel fabric contains interwoven electronic circuits from stainless steel yarns and thermochromic colour-changing ink, which are connected to drive electronics. Flexible wall hangings can then be programmed to change colour in response to heat from the conducting wires.[23] Electrochromic inks have some applications in textiles, e.g., jacket, which could be black and every now and then it displays a pictures.[20]

11.6 Conclusion

The majority of applications for chromic materials in the textile sector today are in the fashion and design area, in leisure and sports garments. In workwear and the furnishing sector a variety of studies and investigations are in the process by industrial companies, universities and research centres. There is a large number of patents, especially in Japan and in the USA, in different ranges of chromic materials, but many innovations still await their commercial applications.

Most photochromic materials are based on organic materials or silver particles. The lifetime of these compositions is rather short for industrial applications. Most thermochromic materials are organic materials, having a short lifetime and a limited range of temperature. For various applications, especially for textile applications, there is a need to develop the wide range of temperature and lifetime properties of these chromic materials. Electrochromic materials in textiles have many promising applications. There is, however, a demand for a considerable volume of scientific study in different areas of expertise before these can be put into large-scale production.

Chromic materials are one of the challenging material groups when thinking about future textiles. Colour changing textiles are interesting, not only in fashion, where colour changing phenomena will exploit for fun all the rainbow colours, but also in useful and significant applications in workwear and in technical and medical textiles.

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12

Solar textiles: production and distribution of electricity coming from solar radiation applications

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12.1 Introduction

This chapter is devoted to the incorporation of solar cells into textile fabrics. It reflects the increasing commercial interest in solar cells and the versatility which their integration into textiles would afford. After the background to the theme of the chapter has been set, a brief outline of the design and mode of action of solar cells is given. We then discuss the specifications that textile fabrics have to meet to be practical substrates for solar cells, and we also discuss the challenges in meeting these specifications. Suitable textile constructions are considered, together with a few commercial examples. An important aspect of a textile-based solar cell is the conferment of electrical conductivity on the textile, and strategies that have been devised for achieving conductivity are given. The final section outlines the wide variety of potential applications for solar cells in textiles.

12.2 Background

There is increasing concern worldwide about the huge dependence on oil as a source of energy. Although coal resources are immense, their extraction and use tend to potentially damaging environmental problems. There are concerns too about nuclear fission as a source of energy, and controlled fusion has yet to be proven feasible. Consequently, there is growing interest in harnessing energy by other means that do not rely on the consumption of reserves, as with oil and coal, nor involve dangers (real and perceived) with utilising nuclear fission. Total renewable resources available are more than adequate for human needs, but are unevenly distributed across the globe and generally have large diurnal and seasonal variations. They are often more appropriate for distributed power supplies rather than for centralised power stations and electrical energy distribution.

These alternative energy sources are numerous, and include geothermal, wind and waves, renewable natural products (biomass) and ocean tides.

However, the source of direct energy which arguably arouses the greatest potential is the sun itself. There are numerous examples of attempts to utilise solar energy for storage of chemical energy (mimicking natural photosynthesis) and for the storage of electrical energy in batteries. In particular, devices in which sunlight is absorbed through a dye on titanium dioxide particles, Grätzel cells, may either give an electrical current through a liquid electrolyte, or in other configurations may produce hydrogen by electrolysis of the liquid thus storing the energy they provide from sunlight rather than directly powering an electrical load.[1] Nevertheless, greatest success has been achieved in the direct conversion of solar power into electrical energy, with the aid of photovoltaic devices, 'solar cells'. Apart from using an 'endless' source of energy, the application of photovoltaic devices offers a number of other advantages: the technology is clean and noiseless, maintenance costs are very small, and the technology is attractive for remote areas, which are difficult to supply by conventional means from a grid.

12.3 Solar cells

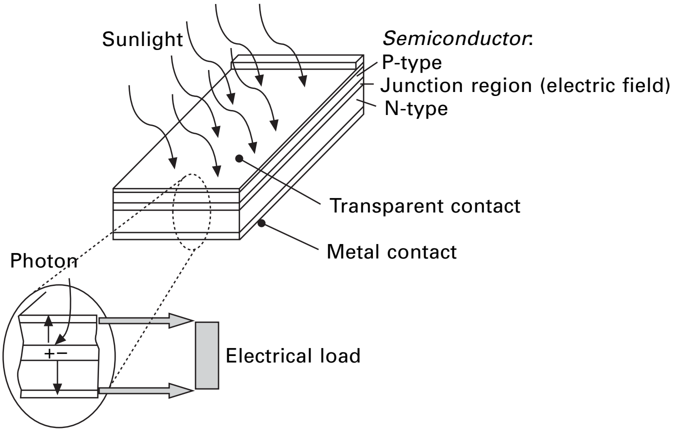
Sunlight may be converted into electricity by heating water until it vaporises, and then passing the steam through a conventional turbine/generator set. However, this triple conversion of energy (optical to thermal to mechanical to electrical) has losses at each step and it should be more efficient to convert optical energy directly to electrical energy. This is the function of photovoltaic cells, which are solid-state devices in which photons release valence electrons from the constituent atoms. Thermodynamics limits the efficiency for conversion of solar radiation by a simple photovoltaic cell to ~32%, and today's crystalline cells can approach this (Si cells have achieved ~24% conversion efficiency); multiple junction cells have a thermodynamic limiting efficiency of ~66% and triple junction cells have achieved ~32%.

To see how this works, and the implications for cells on flexible materials, we need a little semiconductor science. In a semiconductor, valence electrons are freed into the solid, to travel to the contacts, when light below a wavelength specific to that solid is absorbed (i.e. the electron binding energy). This threshold wavelength must be selected to provide an optimum match to the spectrum of the light source; too short a wavelength will allow much of the radiation to pass through unabsorbed, too long a wavelength will extract only part of the energy of the shorter-wavelength photons (the part equivalent to the threshold wavelength). The typical solar spectrum requires a threshold absorption wavelength of ~800 nm, in the near infra-red, to provide the maximum electrical conversion, but this still loses some 40% of the solar radiation. Further losses occur through incomplete absorption or reflection of even this higher energy radiation. The current that is delivered by a solar cell depends directly on the number of photons that are absorbed:

the closer the match to the solar spectrum and the larger the cell area the better.

As well as a current (i.e. number of electrons per second), electrical energy has a potential associated with it (i.e. the voltage) and this is determined by the internal construction of the cell, although it is ultimately limited by the threshold for electron release. In conventional silicon solar cells (as illustrated schematically in Fig. 12.1), there is an electrical field built into the cell by the addition of minute amounts of intentional impurities ('dopants') to the two cell halves; this produces what is known as a PN junction. The junction separates the photon-generated electrons from the effective positive charges (known as 'holes') that pull them back and in so doing, generates a potential of ~0.5 volts. This potential depends on the amounts of dopants, and on the actual semiconductor itself. Multiple junction cells have integrated layers stacked together during manufacture, producing greater voltages than single junctions.

The power developed by a solar cell depends on the product of current and voltage. To operate any load will require a certain voltage and current, and this is tailored by adding cells in series and/or parallel, just as with conventional dry-cell batteries. Some power is lost before it reaches the intended load, by too high a resistance in the cells, their contacts and leads. Note that at least one of the electrical contacts must be semitransparent to allow light through, without interfering with the electrical current. Thus optimising the design of a solar cell array involves optics, materials science, and electronics. A historical view of photovoltaic technology was given by Goetzberger *et al.* in 2003.[2]



12.1 Schematic of a photovoltaic cell.

12.4 Textiles as substrates

Despite the many attractions of solar cells as vehicles for providing energy, the way in which they are constructed provides problems in application. Typically, solar cells are either encased between glass plates, which are rigid and heavy, or the cells are covered by glass. Glass plates are fragile, and so care has to be taken with their storage and transport. The rigid nature of solar cells requires their attachment to flat surfaces and, since they are used outdoors, they have to be protected from any atmospheric pollution and adverse weather.

It is, therefore, not surprising that increasing attention has been turned to the construction of lighter, flexible cells, which can still withstand unfavourable environments, yet nevertheless maintain the durability required. Several examples have recently appeared of solar cells in plastic films. Examples are the 'power plastic' developed by Konarka Technologies Inc.[3] in which the cell is apparently coated or printed onto the plastic surface, and an integrated flexible solar cell developed at Sky Station International Inc. for high-altitude and stratospheric applications.[4] Iowa Thin Technologies Inc. have claimed the development of a roll-to-roll manufacturing method for integrating solar modules on plastic.[5]

However, whilst the successful incorporation of solar cells into plastics represents an important step in the expansion of solar cell technology, still greater expansion of the technology would be achieved through their incorporation into textile fabrics, especially if the cells are fully integrated into the fabrics. Textiles are materials with a huge range of applications and markets (some established for thousands of years!), and they can be produced by a number of fabrication processes, all of which offer enormous versatility for tailoring fabric shape and properties. The different types of woven, knitted and nonwoven constructions that can nowadays be achieved seem almost infinite, and indeed technical uses are beginning to be found for crocheted and embroidered constructions.[6,7,8]

Some examples of the application of solar cells in textiles have now been reported. Architect, Nicholas Goldsmith, has designed a solar tensile pavilion which, while providing shade and shelter, can also capture sunlight, and transform it into electrical power.[9] The skin of the tent consists of amorphous silicon cells, encapsulated and laminated to contoured panels of the woven fabric. Zabetakis *et al.* have recently described the design of an awning, which provides protection from the sun and at the same time converts the incident sunlight into electricity.[10] A type of sail has been designed in which attached to the sailcloth are strips of flexible solar cells.[11] The incorporation of the solar cells has been designed to allow for expansion of the sailcloth when wind blows on it.

Textiles offer further advantages too. Fabrics can be wound and rewound. Thus, Warema Renkhoff GmbH in Germany has developed a retractable woven canopy,[12] in which energy is collected from the solar cells integrated into the canopy, and then stored. The stored energy is applied to the operation of the winding drive motor. In addition, textile fabrics can be readily installed into structures with complex geometries, a feature which opens up a number of potential applications (discussed later).

12.5 Technological specifications

Conventional single crystal silicon cells may produce 0.5 V when not connected to a load, but this falls according to the current that is drawn, until it reaches zero for a short-circuited load. The current in bright sunlight may be a few amps from a square metre of cells but this will fall towards zero if the resistance of a connected load is steadily increased. Optimum performance (and hence highest conversion efficiency) of a solar cell or array therefore requires the electrical load and the current vs. voltage characteristic of the solar cells to be matched. This load matching may be a severe limitation on provision of power to a desired load, if the available area is insufficient. On the other hand, when the cell area is very large there is ample provision for selecting an appropriate combination of current and voltage. One potential advantage of a low-cost flexible array is the ability to tailor the interconnections between individual cells at the manufacturing stage, and perhaps with some contact designs to enable this to be done by the user.

As was noted above, the current delivered by a solar cell depends not only on the illumination but also directly on the illuminated cell area. This is a fundamental barrier to the applications that can be addressed by a restricted area of cells, such as would be available on clothing, for instance. The voltage from a solar cell does not depend on cell area, but on cell construction, and there are ways to increase this voltage above that given by the simple ‘single junction’ devices, by stacking cells on top of each other, usually no more than three in total.

This added complexity generally reduces the production yield, and requires careful optimisation of each cell. Since the same current must flow through each cell in the stack, each cell must generate exactly the same current. Therefore an increasing thickness is required for each cell into the stack if it is to produce current from a successively weaker flux of light. This is more readily achieved by making the topmost cells absorb the shortest wavelength light, and successive cells the longer wavelengths, by adjusting their compositions to match the desired spectral bands. In amorphous silicon cells, this adjustment is achieved by alloying other elements into the semiconductor. The addition of carbon makes the cells more transparent to long wavelengths and the addition of germanium increases the long wavelength absorption.

It is therefore apparent that providing a series of standard solar cell arrays, usually labelled by their 'peak-watt' output (that given in a stated sunlight intensity), allows the user to make up an electrical supply to meet particular needs, as long as the space available is not too restricted. Large-scale users can readily couple any cell array to either an active load-matching circuit or to a buffer energy store (e.g. electrochemical battery), but small-scale users would probably need more choice of array size and shape. Flexible textile cells would address this shortcoming of traditional cells and arrays.

12.6 Challenges to be met

The active cell components, the semiconducting layers, therefore have a great part to play in determining the cell performance, not only from an efficiency point of view (i.e. matching the illumination spectrum) but also from the load matching perspective. The separate improvement of both output current and voltage demands effective optical absorption and efficient photo-generated charge separation. There may be unavoidable trade-offs in meeting both of these simultaneously. Textile substrates offer new ways of improving the optical absorption in thin layers by scattering light that passes through the layer back into the layer for a second chance of absorption. Rough surfaces in conventional silicon cells are sometimes a source of electrical problems but substrate texturing has always been seen as a possible tool for advanced thin-film cell design.

Transferring some of the best features of amorphous silicon cell technology to a flexible textile substrate device[13] would provide more rapid evolution of the new cells than a separate development based on single crystal cell technology, given the processing temperature restraints of the preferred textiles. There are still plenty of challenges in ensuring efficient charge collection from a stack of thin layers on a non-planar base.

Finally the word 'textile' still often suggests applications in clothing, but users would expect to have the same performance from a solar cloth as from a passive cloth, with respect to folding, wear, washing, abrasion, etc. Few of these properties have yet been tested with coatings of the type used in solar cells, nor have solar cells been assessed in such conditions, even if hermetically sealed with a thin polymer layer.

12.7 Suitable textile constructions

The successful integration of solar cells into textiles has to take into account the type of fibre used and the method of textile fabrication. The selection of a type of fibre is strongly influenced by its ability to withstand prolonged irradiation by ultraviolet (UV) light. Fibre selection is also governed by the temperatures required to lay down the thin films comprising the solar cell, although it has been shown that nanocrystalline silicon thin films, an improved form of amorphous silicon, can be successfully deposited at temperatures as low as 200 °C, and under the appropriate conditions even single crystal silicon may be grown, albeit epitaxially on silicon wafers.[14] These two factors of UV resistance and maximum temperature restrict the choice of commodity fibres. Commercial polyolefin fibres melt below 200 °C. Cotton, wool, silk and acrylic fibres start to decompose below this temperature. Polyamide fibres are likely to be too susceptible to UV radiation.

Polyethylene terephthalate (PET) fibres, however, are viable substrates. They melt at 260–270 °C and exhibit good stability to UV light.[15] They are commercially attractive too because of their existing widespread use. Thus, fabrics composed of a large variety of PET grades are currently available. PET fibres possess good mechanical properties and are resistant to most forms of chemical attack.[15] They are less resistant to alkalis, but a solar cell would not normally find use in an alkaline environment. Fabrics constructed from PET fibres should, therefore, be suitable as substrates for solar cells, whilst also possessing flexibility and conformability to any desired shape.

Fabrics composed of glass fibres produced from E-glass formulations[16] could also be used. One advantage could lie in their transparency, as with plate glass in conventional solar cells. Moreover, the price of E-glass is similar to that of PET.[17] E-glass fibres, however, suffer from poor resistance to acids and alkalis and are prone to flexural rupture. Other glasses are more stable to environments of extreme pH. S-glass is used for specialist sports equipment and aerospace components, but its price is approximately five times that of E-glass.[16]

Many high-performance fibres, which readily withstand temperatures up to 300–400 °C, could also be considered, although aramids would not be sufficiently stable to UV radiation. Examples of suitable high-performance fibres could be polybenzimidazole (PBI) fibres, polyimide (PI) fibres and polyetheretherketone (PEEK) fibres. However, these fibres are expensive. There are clear commercial attractions, therefore, in adopting PET fibres.

The type of textile fabric construction is also important to the performance of the solar cell. The type of construction affects the physical and mechanical properties of a fabric, and also its effectiveness as an electrical conductor. Where conduction in textile fabrics is required, woven fabrics are generally considered to be best,[18,19] in that they possess good dimensional stability and can be constructed to give desired flexibilities and conformations. Moreover, the yarn paths in woven structures are well ordered, which allows the design of complex woven fabric-based electrical circuits.[18]

Knitted structures, on the other hand, do not retain their shapes so well, and the rupture of a yarn may cause laddering. These problems are heightened if the shape of the fabric is continually changing, as in apparel usage. Nonwoven fabrics do not, as yet, generally possess the strength and dimensional stability of woven fabrics. More significantly, the construction of electrical circuits in them is limited, because their yarn paths are highly unoriented. Embroidery, however, may offer an opportunity for circuit design.

12.8 Conductive layers for PVs

Solar cells require two contacts in a sandwich configuration, with the active semiconductor between them. At least one of the contacts must be transparent to solar radiation, over the waveband which the semiconductor absorbs. Conventional crystalline silicon cells have a thick metal contact on the back surface, and a gridded metal contact on the front surface. They do not require complete coverage of the front surface because the top layer of silicon is sufficiently conducting (‘heavily doped’) to deliver the photo-current without significant resistance losses. Amorphous silicon cells, like most thin-film cells, have a more insulating top semiconductor layer and so require the whole surface to be contacted. This is achieved without blocking the incoming light, by a layer of transparent conducting oxide (TCO) such as ZnO or Indium tin oxide (ITO), often with other elements added to enhance the conductivity without reducing the transparency. In addition, a fine gridded contact is often superimposed to further improve the current collection efficiency.

It is also possible to build the cell with the light entering through the substrate: this is known as the superstrate configuration. Typically a glass sheet, coated with TCO is then covered with thin-film semiconductor, which in turn is covered by an opaque metal layer. Textile substrates are unlikely to be sufficiently transparent that this construction may be used, although it is not necessary for the material to be transparent enough to show an image through it, only to be translucent. Hence the textile material is likely to be coated with a conducting layer that may be opaque. Alternatively, the textile may itself form part of the active cell structure, either enabling the conduction of photo-current generated within an imposed semiconductor, or in future materials, enabling photo-currents to be generated within the fabric (probably by semiconducting polymers). Organic solar cells, or polymer solar cells still have a long process of development before they can be considered for this application, perhaps being a more intractable problem than the inverse application of light-emitting polymers.

Unless the textile can be made from conducting fibres, an additional material is needed, that should not degrade the other desirable textile properties. It is possible, of course, to incorporate metal fibres within a fabric, but it is questionable whether these can make sufficiently good contact to the whole thin-film cell area. They may be helpful in addition to a thinner, continuous conductor. Although polycrystalline silicon can be sufficiently conducting to enable only partial coverage by the contacting layer, it generally requires much higher processing temperatures, before or after its deposition, than most textiles can withstand.

We therefore require a continuous conducting layer to be placed over the whole textile surface before adding the semiconductor. The choice of materials (probably metals) is determined by electrical conductance (lower conductance requires thicker layers), compatibility with the substrate (chemically, physically, and during processing), and compatibility with the semiconductor (chemically and work function value). In addition, the mechanical behaviour of the conductor in a cell that can flex or twist will depend on its composition, thickness and adhesion.

There are several options to be considered, using both physical and chemical coating techniques, to obtain the correct composition and conformality with a non-planar surface. These will deposit metals or TCOs at the limited temperatures allowed by the preferred textiles. Physical coating methods include sputtering from a solid target in an argon atmosphere and simple evaporation from a solid source (either thermally or with an electron beam), and both are widely used in the optics, electronics, and engineering industries. Chemical methods are based either on the decomposition of a volatile compound of the conductor by heat or electrical plasma, or on the deposition of a coating from a solution, usually driven by an electrical current. These methods are also in widespread use within industries. There are a few additional methods that are applicable for certain materials, such as dip- and spray- and spin-coating, that would be appropriate for the conducting polymers that are being developed now. These do not conduct well enough for photovoltaic cells, because they generate low voltage electrons that cannot overcome the resistance of a long path through a poor conductor.

The compromise solution to retaining substrate flexibility with high electrical conductivity may be to use a conducting polymer layer on the textile, or incorporated within its structure, superimposed by a thin, more-conducting metallic layer. If this layer breaks during flexure then the minute gaps will be bridged by the underlying organic conductor, whose limited conductivity will not be a problem over such short paths. This also allows the semiconductor to be in contact with its preferred metal (say aluminium for silicon), avoiding the inclusion of resistive barriers that can exist at other semiconductor/conductor interfaces.

12.9 Future trends

The successful integration, on a commercial basis, of solar cells into textiles opens up a whole range of fresh applications. Many of these applications are likely to exploit the flexibility and light weight of textile fabrics. They can, for example, be placed over the curved surfaces of buildings. They can also be installed in spaces which may otherwise be inaccessible, as in automotive, marine and aerospace equipment. In addition, textile fabrics can be rolled up, transported to a desired location and then unrolled at that location. Thus, the technology would then be beneficial to those living in remote areas, where there is no supply of electricity from the grid, fuel may be scarce and expensive, and maintenance of equipment is uncertain. Moreover, it could be used to get power quickly to disaster areas, hit by earthquakes, hurricanes, floods or fire.

However, as is already becoming apparent, many applications will also exploit existing applications of textiles. As already noted, there is interest in incorporating solar cells into awnings and canopies, and even into sails. It may also be that the presence of solar cells in apparel will be particularly beneficial, for example, to maintain the temperatures of young children, the elderly and hospital patients, or to power sensing elements for temperature and movement.

As polymer, and other organic, semiconductors become better developed, following a similar but slower path to that of organic light-emitting diodes, they will become increasingly attractive alternatives to inorganic semiconductors in solar cells. Their use would enable lower cost deposition technology to be used, replacing chemical vapour deposition, even in its low-temperature, plasma-driven form, by coating methods based on liquids rather than vapours. Dye-sensitisation for solar spectrum matching may eventually become a practical reality, thus leading to ‘high tech’ solar cells being produced by means similar to conventional printing and dyeing of cloth, but this is now a fantasy.

12.10 Sources of further information

Basic Research for Solar Energy Utilisation provides a survey of the current status of solar technology and discusses future developments, from a US Department of Energy workshop in Bethesda, Maryland, USA, in April 2005 (published by Argonne National Laboratory).

The International Solar Energy Society is a major professional institution that encourages the research, development, and use of solar energy through a variety of channels including conferences, publications, and its website.

Electrotextiles and Giant-Area Flexible Circuits, editors Shur M.S., Wilson P.M. and Urban D., MRS Symposium Proceedings Volume 736, Materials Processing Society, Warrendale, Pennsylvania, USA, 2003. The volume contains papers presented at a symposium in Boston, Massachusetts, USA in 2002. It includes a wide range of papers on electrotextiles, i.e., textiles containing electronic components and circuits.

The website, http://www.solarbuzz.com/ provides up-to-date news and information about photovoltaic technology, prices and markets.

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13

Introduction to conductive materials

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13.1 Electric conductivity

When a voltage, U (in volts V), is applied between two points on a material an *electric field*, E, is set up. Depending upon the electrode geometry and other factors the electric field may or may not be uniform. Electrically charged particles in the material will experience an electrostatic force in the direction of the electric field equal to the product of their charge and the electric field. If the charges are free to move, the force causes them to *drift* through the material. The rate at which the charge is transported is known as electric *current*, I. This is a system property whose material equivalent is the *current density*, J (amps per square metre A/m^2).

Ohm's law, the result of empirical observations, states that current through a conductor *due to drift* is proportional to the voltage across it:

$$I = (1/R)\ U, \tag{13.1}$$

where R (in ohms Ω) is the resistance of the conductor to current flow. Ohm's law can also be expressed in terms of the material properties, field E and current density J as:

$$J = (1/\rho)E = \sigma E, \tag{13.2}$$

where ρ is the *resistivity* of the material ($[\Omega\ \mathrm{m}]$) and $\sigma = (1/\rho)$ is the *conductivity* ($[\Omega\ \mathrm{m}]^{-1}$). This implies that the mean velocity of the charged particles in the direction of the field, the so-called *drift velocity*, is proportional to the applied field.

Materials display an extremely wide range of resistivity, possibly wider than any other physical parameter. Superconductors have resistivity $<10^{-25}$ Ω m, typical metal conductors $\sim 10^{-8}$ Ω m, semiconductors $10^{-4} \ldots 10^{10}$ Ω m, and insulators 10^{10} Ω…10^{20} Ω m. Conductors exhibit a linear Ohmic current-density dependence upon electric field up to high current densities, even up to the point where they fuse. In semiconductors Ohmic behaviour is also observed at low fields. However, above a critical field the drift velocity, and hence the current, reaches a limiting value in semiconductors, resulting in an apparent increase of resistivity with the field. The basic unit of resistance measurement is the Ohm, and the basic unit of conductivity measurement is the siemens. Conductivity is the conductance as measured between opposite faces of a 1 cm cube of a given material. This measurement is in units of siemens/cm. The corresponding terms for specific resistivity are ohm-cm.

The conductivity of a material due to charge carriers is dependent on the electric charge on each carrier, its mobility, and the concentration of charges. Charge carrier species are many, e.g., electrons, holes, protons, and ions, but normally one charge carrier is likely to dominate. Mobility is dependent on the charge carrier's size and material structure, as in polymers, insulators, covalent bonding and crystal structures. The concentration of charge carriers may vary from near zero to more than one per atom ($<10^{29}$ m^{-3}).

13.1.1 Conductivity in metals

Early attempts to explain the electronic configurations of the metals with ionized atoms in which the free electrons form a homogeneous free moving sea of negative charge failed. The principal objection to this theory was that the metals should then have higher specific heats than they do. The *Pauli exclusion principle* states that no two electrons occupying the same space can have exactly the same energy, although two electrons can occupy the same energy level if they have opposite spin.

According to the band theory, any given metal atom has only a limited number of valence electrons with which to bond to all of its nearest neighbours. Extensive sharing of electrons among individual atoms is therefore required. This sharing of electrons is accomplished through overlap of equivalent-energy atomic orbitals on the metal atoms that are immediately adjacent to one another. This overlap is delocalised throughout the entire metal sample to form extensive orbitals that span the entire solid rather than being part of individual atoms. Each of these orbitals lies at different energies. The orbitals, equal in number to the number of individual atomic orbitals that have been combined, hold two electrons, and are filled in order from the lowest to the highest energy until the number of available electrons has been used up. Groups of electrons are then said to reside in *bands,* which are collections of orbitals. Each band has a range of energy values that the electrons must possess to be part of that band.

The highest energy band in a metal is not filled with electrons because metals characteristically possess too few electrons to fill it. The high thermal electrical conductivities of metals is then explained by the notion that electrons may be promoted by absorption of thermal energy into these unfilled energy levels of the band.[1]

13.1.2 Conductivity in plastics

Typical polymers are a type of molecular crystals, albeit with extremely large molecules, and therefore have very strong intra-molecular bonding but only very weak, van der Waals, inter-molecular binding forces. The relatively simple band theory model must therefore be modified for polymers. The energy bands in perfect crystalline structures, like metals, have infinite periodicity in all directions and the nuclei interact with the three-dimensional electron wave in the same way in any unit cell. On the other hand, the long polymer chains are essentially one-dimensional.

Intrinsically conductive polymers contain long conjugated chains formed by double bonds and heteroatoms. The polymers can be rendered conductive by modifying the π- and π-p-electron systems in their double bonds and heteroatoms. Charge carriers are electrons or holes originated by adding to the polymer certain blending or doping agents, which will serve as electron receptors or electron donors in the polymer. Thereby electron holes or extra electrons are formed in the polymer chain, enabling electric current to travel along the conjugated chain.[1] The conductive polymers were based on conjugated electron structures, so-called resonant structures. Typically the conductive polymer materials are semiconductors, say four decades less conductive than metal substances. Their light, moisture, and pH reactions were considered major disadvantages for the materials but, e.g., in sensors the features are more than welcome.[2]

Electrically conductive plastics are usually manufactured by mixing together electrically insulating polymers and electrically conductive fillers such as carbon black and metal particles or, for example, electrically conductive polymers. Charge carrier is electron or hole. The electrical conductivity of filled conductive polymers is dependent on mutual contacts between the conductive filler particles. The distance between the particles should be less than 100 Å when tunnelling of electrons is possible. Close to this value the conductivity may become nonlinearly temperature dependent.

Usually a well-dispersed conductive filler like carbon is needed in amounts of approximately 15–35 vol-% to reach percolation and produce composites having good conductance. Filler structure, especially aspect ratio, has a marked influence on the properties. In comparison acetylene black, structured carbon, and single walled carbon nano-tubes are needed 25, 15, and 2.5 wt-% respectively to reach percolation and good electrical conductivity. However, such conductive composites involve problems. Their mechanical and certain of their chemical properties are crucially impaired as the filler content increases and the polymer content decreases; their conductivity in dispersing of the filler into the matrix plastic is difficult.

13.2 Metal conductors

Metals are useful in practical applications when high conductivity is required, e.g., microelectromechanical systems (MEMS), electromagnetic shielding EMI, resistive heating, or signal transmission. Benefits are low cost and high electric performance. Carbon fibres are in many ways comparable with the metal fibre and discussed under the same title. Although relatively high conductivities (10^5 $[\Omega\ \mathrm{cm}]^{-1}$) can be obtained by the drawn blending of metal slivers and slivers composed of textile fibres, inherent problems persist.[3] Not only are metal fibres expensive, they can also be as much as five times heavier than some textile fibres – making a homogeneous blend difficult to produce. In addition, metal fibres are brittle and can abrade the spinning equipment. A final concern is that metal-containing fibres can produce a fabric with undesired touch – a 'metallised hand'.

Regardless of these limitations, successful attempts at blending metals and stabile slivers have been reported. Yarns, fabric, and non-woven materials of metal fibres are available. Combined materials are processable with normal textile machinery, but comfort properties, wear resistance, and maintenance robustness may be limited especially when metal content is increased. Especially steel fibres have found many applications such as antistatic textiles.

13.2.1 Ferric materials as conductors

Conductivity of steel is moderate, and the material is mainly suitable for conductive backing of carpeting and antistatic protective clothing. Another example of use is resistor applications, like electrically heating cloths. In practical applications stainless steel fibres should be used, and made from low-temperature ductile stainless steel AISI 316L (Ni 10-14% and Cr 16-18%) that has proved to have excellent use properties. Stainless fibres are markedly resistive. For continuous fibre, and 20% mixed to PES the electrical conductivities are $\sim 10^2$ $[\Omega\ \mathrm{cm}]^{-1}$ and $\sim 10^0$ $[\Omega\ \mathrm{cm}]^{-1}$respectively for Tex 200 g/1000 m yarns. Conductivity is also related to the yarn size.

Bending hardening of the fibre is evident, and limits the wrinkling of the steel fabrics. Also the nickel in the stainless steel may be a risk for allergy, especially with stainless steel like NY 601 or NY 845 containing 60 and 40 wt% of nickel. Combination of all these features limits the typical use of steel in technical textiles and certain sensors, e.g., bordered indicators.

13.2.2 Noble and colour metals

Copper, silver, and with certain limitations also gold, are markedly more conductive than any steel. Vacuum spraying is a relatively inexpensive method that produces metallic coated fibres with conductive properties as high as

10^4 [Ω cm]$^{-1}$. Unfortunately, this process has several limitations. There is adhesion between the metal and fibre creating an unstable construction, the process is difficult, and the fibres produced have low resistance to corrosion and wear.[3] Galvanic coating is comparable with vacuum spraying, but possible only for conductive fibre. Lately plasma sputtering has improved the quality, especially the coating thickness control, but adhesion between the metal and fabric is a problem.

The cost of colour metals is high, but due to their high electrical performance and ability to be drawn down to a very fine fibre they may introduce themselves as an attractive choice in various applications. Different mimic cable structures are developed for signal transportations and power. They are textile compatible, solid or stranded wires of copper, and silver with especially high conductivities (10^6 [Ω cm]$^{-1}$) coated with Silicon rubber, PTFE, PFA, FEP, or PE layer.

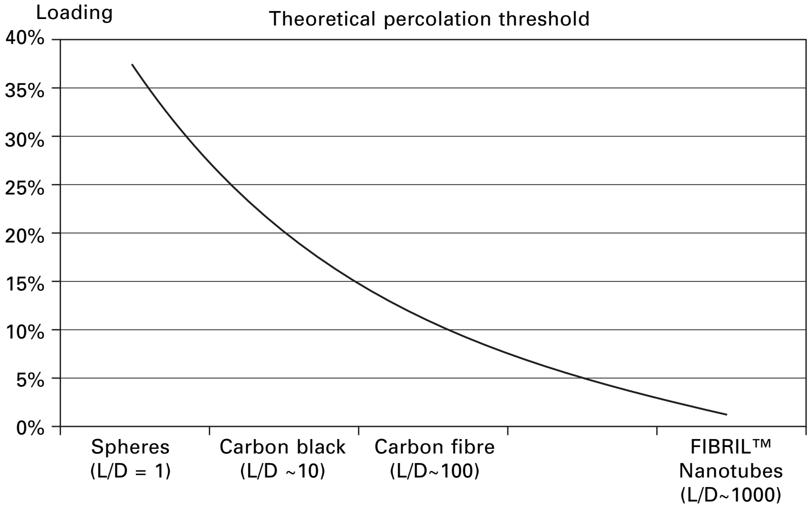
Recently silver has become more readily available due to new digital photography technology. Even if silver is reasonably reactive, its electric performance is attractive. Also the antibacterial performance of silver is emphasised.

13.2.3 Carbon as a conductor

Electrostatic discharge (ESD) protective clothing benefits from carbon fibre added textiles structures. Carbon fibre intraconductivity is close to that of metal. The conductivities of carbon fibre is ($10^5 \ldots 10^0$ [Ω cm]$^{-1}$) and especially if pure carbon is used conductivities as high as (10^2 [Ω cm]$^{-1}$) can be reached. Unfortunately carbon can be difficult to process. Combined structures in fibres, like Nylon, Carbon and Polyester-Carbon sandwich fibre result in markedly less conductivity ($10^{-10} \ldots 10^{-6}$ [Ω cm]$^{-1}$). Any amount of carbon in fibres will impart a black colour to the end product. Carbon is chemically but not very wear resistant. The thermal insulation properties are markedly better than those of metal. Even if the carbon fibre is black, high conductive material enables coloured cloth structures. The combination of features has made carbon fibre a desired conductive fibre for ESD application.

13.2.4 Carbon nano-tubes and their conductivity

Carbon nano-tubes and especially single walled CNTs are developing materials with extreme properties like super fibre mechanical strength, high thermal insulation, combined with metal conductivity. The conductivity properties are highly dependent on the molecular structural orientation in the CNT and number of the walls. Typical commercially available materials are multi-walled 10–12 nm fibre of 10–15 μm length, and 20–30 layered structure with intermediate properties. Grades are developing rapidly. High aspect ratios up to L/D ~1000 of the CNT and good electric performance makes it possible



13.1 Theoretical percolation threshold for different carbon fillers [4].

to produce conductive polymer-based fibre markedly with textile properties in the fibre. EMI fibre requires acetylene black 25%, which is hardly processable as a fibre, while single walled carbon nano-tubes require some 2.5 wt-% for respective properties, see Fig. 13.1.

Loading of 3 wt-% of CNT in plastic leads to conductivities ~10^{-6} $[\Omega \text{ cm}]^{-1}$. Lately polymer composite CNT yarns and even nano-fibre having a CNT core structure has been manufactured.[5] This development suggests that in future mechanically and electrically high-performing fibres can be manufactured from nano-tubes having properties similar to metal or better.

13.3 Ionic conductors

13.3.1 Metal salts

Certain metal salts like copper sulphide and copper iodide are predominantly utilised for electrically conductive coatings on fibres, as they are easily processable using ordinary textile technology. However, only low conductivities can be obtained. A variety of fibres have been used including nylon, polyester, wool and acrylic for antistatic applications such as carpets. Depending on the chemical and the process used, conductivities range from ($10^{-6}\ldots10^{-1}$ $[\Omega \text{ cm}]^{-1}$).

White metal compounds are low reactive and thus useful for bi-component fibre manufacturing. A typical structure is cell-core or side-by-side bi-component structure. A typical benefit of the solution is markedly textile-fibre-like properties with reasonable conductivity. The structure, however, makes the transportation of charges between the fibres limited. Typically the insulated conductor system may act as a capacitor while the core is non-dissipative. Conductivities range from (10^{-10}…10^{-8} $[\Omega\ \text{cm}]^{-1}$) with nylon and polyester.

13.3.2 Ionic polymer conductors

Ionomers and ionic polyelectrolytes are organic polymers which are conductive modified by forming ionic salts through their functional groups, for example, the neutralisation of carboxylic acid functional groups on the polymer with metal hydroxide. The carboxylic acid could be, e.g., from acrylic acids. Metal is preferably M^{1+} with oxidation number one like lithium Li or even more preferably potassium K providing a decade better conductivities.

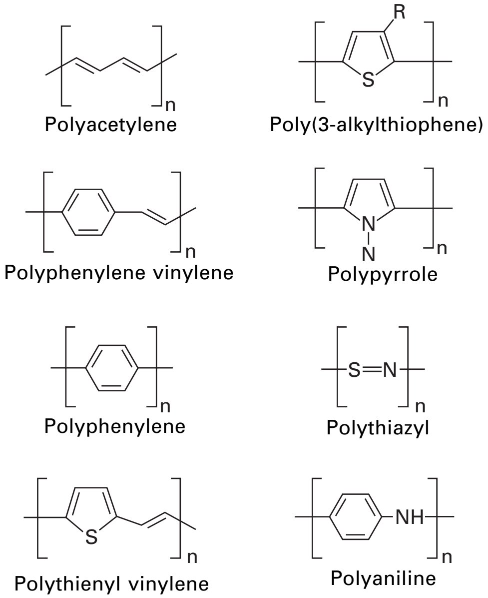
Contrary to the inherently conducting polymers, the charge carrier is ionic, including proton. Ions are more bulky in size and thus their mobility is low. The differentiation makes the conductive ionomers less conductive than most inherently conducting polymers. However, the ion systems are chemically markedly more sustainable and less coloured than conjugated polymer systems, which make the ionomers more robust against pH and oxygen, as well as easy to colour.

Polyelectrolyte containing polyester fibre materials have been developed for antistatic products. However, bi-component structured dissipative antistatic fibres are desired in a wide range for various fibre materials with different constructions and polymers with conductivity ranging from (10^{-10}…10^{-6} $[\Omega\ \text{cm}]^{-1}$).

13.4 Inherently conducting polymers

In 1977 Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger published their discovery that led to the 2000 Nobel Prize in chemistry. Since the early 1980s development has been great and today the inherently conductive polymers, such as polyaniline (PANI), polypyrrole (PPy), polytiophene (PT), and poly (perinaphtalene) (Pna) have achieved a level where many industrial applications have become reality. The materials have become more practical because of improved resistance to oxygen and better processability. The advantage of the intrinsically conductive plastics is the ease of varying their conductivity as a function of the amount of the doping agent, i.e., the degree of doping, especially within low conductivity ranges. Achieving the low conductivities with, e.g., filled conductive plastics is difficult.

The level of conductivity achieved in inherently conductive polymers (ICP) depends on the molecular structure of the polymer backbone, the degree of doping, and the nature of the counter ion species incorporated. Controlled doping of polymers enables engineering their conductivity values


Polyacetylene

Poly(3-alkylthiophene)

Polyphenylene vinylene

Polypyrrole

Polyphenylene

Polythiazyl

Polythienyl vinylene

Polyaniline

13.2 Chemical structure of various electrically conducting polymers.

in a large range. Orientation is one of the most important factors to enhance the conductivity of π-conjugated polyenes.[6] Today a wide variety of conducting polymers is available (see Fig. 13.2).

A common feature of all ICPs is poor processability. This derives from the fact that ICPs form a rigid, tightly packed chain structure that is essential for interchain charge hopping, but prevents the polymer intermixing with solvent molecules. To overcome this problem the chemical structure of ICPs has been modified by substituted derivatives, copolymers, polyblends, colloidal dispersions, coated latexes and composites.

The electric properties of polymers are essential for their successful application in the electronics industry. There is an ever-increasing demand for polymers which show antistatic behaviour. These polymers are employed as packing materials for microelectronic devices that are sensitive to electric discharges. The use of modern organic conductors (as opposed to the more traditional carbon black or salts) as fillers for the production of antistatic polymers is advantageous, especially for the formation of films.

13.4.1 Highly conductive materials

Polyacetylene (PA) was the first polymer exhibiting high conductivity comparable with metals if exposed to oxidising agents like iodine vapour. Oxidation forms charge carriers on the conjugated polyene structure, especially

13.3 Isomeric forms of polyacetylene.

of p-type conductivity. PA exists in two isomeric forms: *trans* and *cis*, see Fig. 13.3. The *trans* form is the thermodynamically stable form at room temperature.

In 1977 A. J. Heeger *et al.* reported on AsF_5-doped PA films showing electrical conductivity that could be systematically and continuously varied over a range of 11 orders of magnitude. The highest conductivity achieved was 2.2 $[\Omega \text{ m}]^{-1}$ in the case of *trans*-rich PA with AsF_5-doping. Halogen-doped (iodine) *trans*-PA led to conductivity of about 1.6 $[\Omega \text{ m}]^{-1}$. The highest room temperature results were obtained in the case of *cis*-PA doped with AsF_5 showing an electrical conductivity value of 5.6 $[\Omega \text{ m}]^{-1}$.[7] Those films were described as flexible, crystalline and silvery.[8]

Gaseous acetylene was interface polymerised on a uniform solution of polymerisation catalyst, or on a metal or glass surface coated with the catalyst solution. Linear high molecular weight PA was formed into films and fibres. PA fibres were obtained by polymerising PA on the surface of a glass fibre or steel wire that had been dipped in the catalyst solution.[9]

Polyacetylene is one of the most promising materials for applications in optoelectronics. The conductivity of the polymer after doping is equal to that of copper, and some forms of polyacetylene have record values of non-linear third-order optical susceptibility.

Low stability by polyene chain to defects of polyacetylene has been the major obstacle in the way of practical applications of this polymer. Conformational defects in acetylene polymerisation relate to the conditions of solid state formation, especially in *cis-trans* isomerisation. Acetylene polymerisation with rhenium catalysts provides a route to highly ordered polyacetylene blends to oxidation and doping.

When acetylene is polymerised in solutions of certain saturated polymers, nanoparticles of polyacetylene are formed. These nanopolyacetylene blends appear to be stable, have low defect content, and exhibit a set of unique optical properties, which are not characteristics of standard polyacetylene modifications. The electronic structure with low Raman scattering, thermochromism and the transparency band in the optical spectrum in the near infra-red field of the highly ordered nanopolyacetylene outlines new potential applications.[10]

Polyacetylene films exhibit conductivity dependence on film orientation. Films are oriented by stretching. Stretched films show about twenty times increased conductivity compared with as-grown films.[11] Films of I_2-doped polyacetylene and polyisoprene diblock copolymer have been made. The microstructure of those films turned out to be a thermoplastic pseudo interpenetrating polymer network. At nano-scale the rod-like structure of I_2-doped polyacetylene was formed.[12]

In order to overcome problems of practically non-processibility of PA, different kind of copolymers incorporating PA has successfully been synthesised. It has been demonstrated that PA can be made soluble by making copolymers with polyisoprene, polystyrene or polybutadiene.[13] The stability of electrical conductivity and antioxidation ability of PA films have been improved by air or argon (Ar) plasma treatment. The *cis*-configuration content decreased while the *trans*-configuration content of PA increased with increasing Ar plasma power.[14]

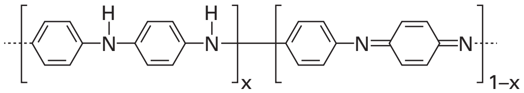
13.4.2 Polyaniline and its derivates

Polyaniline (PANI), see Fig. 13.4, is one of the most widely studied ICPs. There are several reasons for that including simple preparation, relatively good environmental stability and good electrical conductivity. As a common feature to all ICPs PANI has a poor solubility in most common organic solvents that leads straight to the difficulty of processability. But it can be overcome by substituting nitrogen atom or benzene ring with a suitable atom or group.[15] Aniline monomer has toxicological limitations.

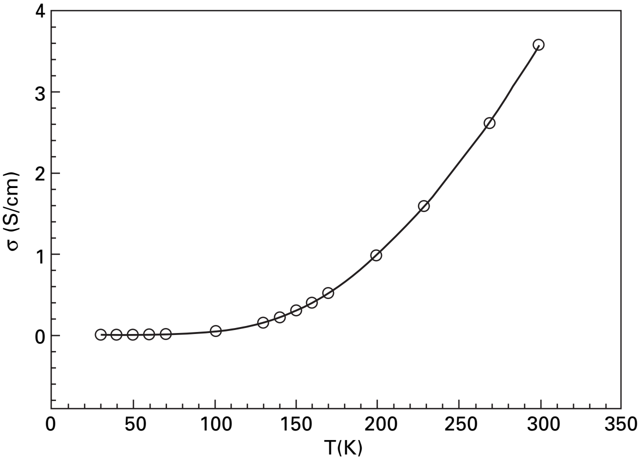
The general structure of PANI is depicted in Fig. 13.4. This is called emeraldine base (EB) PANI. It is partly oxidised. The other possible configurations are luecoemeraldine base (fully reduced) and pernigraniline (fully oxidised) base PANI that are unstable in air and not electrically conductive. The emeraldine salt form of PANI can be synthesised by the chemical or electrochemical oxidation of aniline in an aqueous acid solution. It can also be synthesised by doping EB with aqueous protonic acids, which yields a nine to ten orders of magnitude increase in conductivity. This is accompanied by colour changes of the polymer varying from blue to green.[16]

Conductivity of PANI pellet reduces while temperature decreases, which is contrary to metals typically (see Fig. 13.5). Neither is the voltage-current dependency of PANI at various temperatures does resemble that of metals as can be seen in Fig. 13.6. However, at temperatures above 300 K polymer PANI starts to act according to Ohm's law.[17]

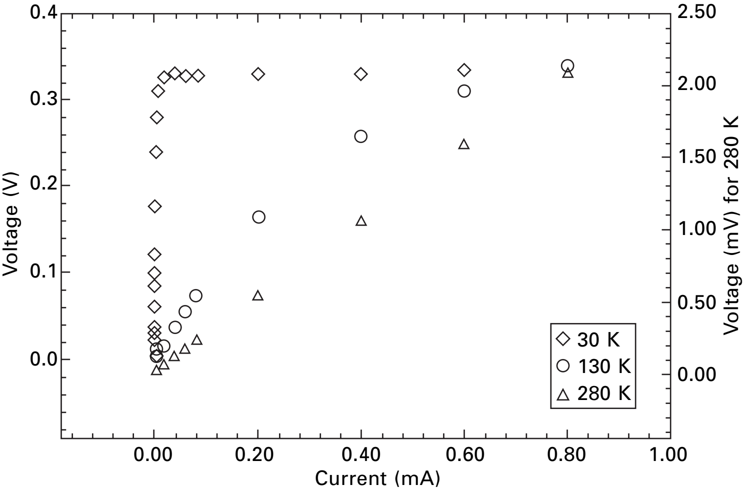
In Fig. 13.7 is expressed current density against the electric field strength for bulk PANI-EB plaque, with a thickness of 2.2 mm. In the electric field above 4 kV/mm current becomes unstable, and at approximately 4.5 kV/mm



13.4 Molecular structure of polyaniline.



13.5 Conductivity of polyaniline as a function of absolute temperature [17].

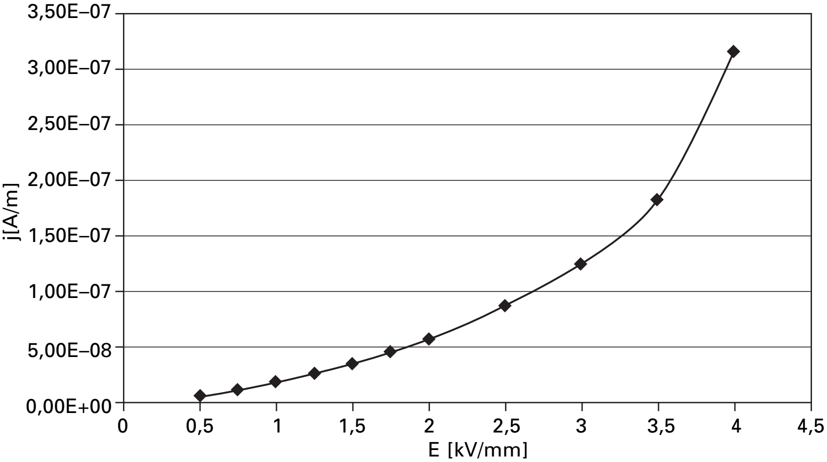


13.6 Polyaniline voltage-current behaviour at various temperatures [17].

electric breakthrough takes place. Breakthrough tests indicate that the PANI-EB has less probability of failure at impulse voltages of 300 kV/mm than carbon black mixed compounds.[18]

13.4.3 Semiconductive polymers

Polypyrrole (PPy) is a widely researched π-electron conjugated conducting polymer, because of its good electrical conductivity, good environmental

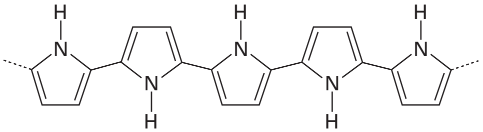


13.7 Current density (A/mm^2) against the electric field strength (kV/mm) for 2.2 mm thick PANI-EB Plaque [18].

stability in ambient conditions, and fewer toxicological problems. However, as a conjugated conducting polymer, the brittleness of PPy limits its practical uses. The processability and mechanical properties of this material can be improved either by blending PPy with some polymers or by forming copolymers of PPy. Thus PPy-based composites may provide the fibres or fabrics with electrical properties similar to metals or semiconductors.[19]

PPy (see Fig. 13.8) is prepared by an oxidative polymerisation process. It can be made either chemically through solution processing or electrochemically through polymer deposition at an electrode. Both processes involve electron transfer. The polymerisation proceeds via the radical cation of the monomer that reacts with a second radical cation to give a dimer by elimination of two protons. Dimers and higher oligomers are also oxidised and react further with the radical cations to build up the PPy chain.

PPy is readily polymerised in aqueous solution by a wide variety of oxidising agents like $FeCl_3$[20, 21], $(NH_4)_2S_2O_8$[22], $CuCl_2$[21]. The reaction speed is higher in the case of $(NH_4)_2S_2O_8$ (a few minutes) and is slower for $FeCl_3$ (e.g. 6 h[21]). Also different kinds of dopants are used. Dopant concentration has the same effect on the reaction speed as oxidants; increase in dopant concentration slows down the polymerisation reaction.



13.8 Molecular structure of polypyrrole.

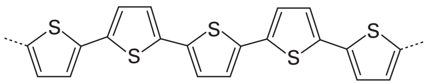
It has been demonstrated that additives like anion surfactants can increase the conductivity of chemically synthesised PPy. The addition of sodium bis(2-ethyl) sulfosuccinate (AOT) into the polymerisation solution including $Fe_2(SO_4)_3$ as an oxidant, improved the conductivity of PPy several orders of magnitude depending on the PPy/AOT ratio[23] (see Table 13.1). The chemical oxidative polymerisation method for PPy synthesis is recommended if a large amount of polymer is needed. By applying this method PPy can be deposited both onto conducting and non-conducting substrates like metals, glass, plastic, textile, etc. In the case of an electrochemical preparation typically PPy films are galvanostatically deposited on a platinum electrode surface using a one-compartment cell containing an aqueous solution of pyrrole and oxidising agent.

Another method of preparing pyrrole and also thiophene polymers is plasma polymerisation. The usual procedure in this case is that the monomer is first plasma polymerised in the form of a thin film on top of the substrate. Then the specimens are exposed to the vapours of the doping agent (e.g. iodine) in order to introduce charge carriers into the plasma-polymerised structures. Resulting polymer structures have proven to have a higher degree of cross-linking and branching. The morphology of those films is smoother and more uniform than chemically polymerised analogues, but electrical conductivity (in the order of $10^7 \ldots 10^9$ Ω/sq mm) and environmental stability are poor.[25] Although PPy is prepared in its oxidised conducting state, the resulting polymer can be subsequently reduced to give the insulating form. Reversible electrochemical switching between the conducting and insulated state causes a colour change from blue-black to yellow-green.

Polythiophene (PT, see Fig. 13.9) is a material researched especially for field effect transistors (FET). An important requirement for the successful

Table 13.1 Electrical conductivity of chemically polymerised polypyrrole using different oxidisers/dopants

Oxidiser/dopant	Conductivity, $[\Omega\ m]^{-1}$
$FeCl_3$	0.02 [21]
$CuCl_2$	$6 \cdot 10^{-7}$ [21]
DBSA (dodecylbenzenesulfonic acid)	0.01 [24]
$Fe_2(SO_4)_3$	$3.9 \cdot 10^{-4}$ [23]
$Fe_2(SO_4)_3$: AOT (20:1)	0.045 [23]



13.9 Molecular structure of polythiophene.

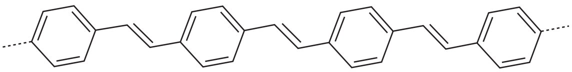
implementation of organic semiconductors in microelectronic switching and memory devices is the availability of both p- and n-type organic semiconductor materials. Organic n-type conducting polymers remain less developed than p-dopable materials partly due to the lack of electron-poor polymers. One promising attempt to create n-type conducting polymer is poly(3-perfluorooctylthiophene)[26] that was prepared by organometallic coupling. This material has shown reversible reduction, large Stokes shift and is soluble in supercritical CO_2. Another claim of synthesis of the n-type semiconductor has been made using fluoroarene thiophene.[27]

It has been found that unstretched PT films have a highly planar structure that is converted to a uniaxial structure by means of one-way stretching. The same study on PANI showed random orientation for unstretched PANI film. One-way stretching led to the uniaxial orientation that was incorporated with an increase in electrical conductivity.[28]

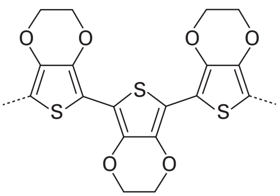
13.4.4 Optically active inherently conducting polymers

Poly(p-phenylene vinylene) (PPV, see Fig. 13.10) is an electrically conductive polymer that has good physical, electrical and optical properties essential for applications. The properties of PPV can be conveniently engineered over a wide range by the inclusion of functional side groups. The optical band gap of ~ 2,6 eV and bright yellow fluorescence make PPV suitable in applications like light-emitting diodes and photovoltaic devices. This is the polymer that can be both n- or p-doped by chemical or electrochemical means.[29]

Poly-3,4-Ethylenedioxythiophene, (PEDOT, see Fig. 13.11) is a conducting polymer based on a heterocyclic thiophene ring bridged by a diether. This means it has the same conjugated backbone as polythiophene. Its properties make it very easily processable. It can be spin-coated onto a huge variety of conductive and non-conductive substrates including glass, silicon, chromium, gold, etc.



13.10 Molecular structure of poly(p-phenylene vinylene).



13.11 Molecular structure of poly-3,4-ethylenedioxythiophene.

The combination of properties obtained by coating polymer films with polypyrrole or 3,4-polyalkylendioxythiophenes was heretofore unavailable in other systems. The coated films are permanently antistatic (independent of relative humidity), have a surface resistance of 10^2–10^5 Ω, are transparent, heat sealable and vacuum mouldable. Films coated with 3,4-polyalkylenedioxythiophene show a higher conductivity and possess greater environmental stability than polypyrrole.[30]

Nano-scale films of PEDOT and PPy have been prepared in a continuous roll-to-roll process using the vapour-phase polymerisation method. Thin films of ferric chloride doped conductive PPy and PEDOT on plastic substrates, in which neither matrix polymers nor binders are used for the film forming process, are obtained at nano-level thickness. The thickness of the resulting films varied depending on reaction time and temperature. The surface resistance changed with the time of exposure to monomer vapours, and the value was in the range of 10^3 … 10^5 Ω/sq mm for 20 … 60 nm thick films and 600 Ω/sq mm for >600 nm thick films. These films had a very highly ordered surface morphology. PEDOT films especially demonstrated a highly ordered crystal microstructure, with high anisotropy, parallel to the substrate film.[31]

A novel method for the preparation of transparent conducting polymer patterns on flexible substrates has been presented. This method, line patterning, employs mostly standard office equipment, such as drawing software, a laser printer, and commercial overhead transparencies, together with a solution or dispersion of a conducting polymer. A seven-segment polymer-dispersed liquid-crystal display using electrodes of the conducting polymer poly(3,4-ethylenedioxythiphene) doped with poly(4-styrene sulfonate) (PEDOT/PSS) was prepared. Also a method to fabricate an eleven-key push-button array for keypad application was presented. Electrode films were characterised using microscopy images, AFM, conductivity measurements, and tests of film stability.[32] A p-type thin film transistor (TFT) was prepared using PEDOT and PPy for gate electrode and active layer, which were made by photolithographic micro patterning. Polyvinyle cinnamate and epoxy were used for the insulating layer through spin coating.[33]

13.5 Application technologies for conducting fibre materials

Generally unmodified ICPs have very poor mechanical properties, they are insoluble, non-melting, and thus not processable. Some progress in mechanical processing has been achieved by mixing ICPs with conventional processable polymers. It has been recognised for some time that the electrical properties of ICPs can best be exploited by their incorporation into host structures that provide the required mechanical and physical properties for a given application.

Textiles produced both from naturally occurring and synthetic fibres are suited to this purpose.

ICPs immobilised by a textile substrate could be used for a number of applications. These electroconductive textiles can be used in the production of clothing which functions as wearable strain gauges for use in biomechanical monitoring, or direct biofeedback devices for sports training and rehabilitation. In this clothing physical changes in the textile causes changes to electrical resistance or electrical conductivity that can be monitored. Other applications include the production of clothing articles that change their thermal insulation or moisture transport characteristics in response to changing climate conditions. Electrically conductive textiles can also be used in applications where antistatic or EMI shielding properties are required. A further application is for use in heating devices such as car seats, car seat covers and gloves.

Requirements for ideal electrically conductive textiles are the possibility to integrate electronic components seamlessly into the conventional textile structure, stable electrical properties and withstanding normal wear and be washable. From the technological point of view it would also be desirable for conventional textile dyeing or printing techniques to be used in the production of the electrically conductive textiles. Limitations in this case are poor solubility of the ICPs and some monomer precursors in water.

In the case of using *in-situ* polymerisation of the ICPs onto a substantially non-conductive textile substrate there is no apparent bonding between substrate and ICP layer. That normally leads to the abrasion or displacement of the polymer layer from the substrate. During laundering the textile may suffer from rapid loss of conductivity. Also ICPs can suffer from oxidation or dedoping that causes changes (usually for the worse) in electrical conductivity. In the following sub-sections the most common techniques for applying ICPs on textiles and other surfaces are discussed.

13.5.1 Extrusion and compounds

Doped PANI sustains high temperature for a short time like dozen of seconds up to 350…380 °C without irreversible loss of conductivity. However, the doped PANI salt is not melt processable but is more like organic filler. For processing the doped PANI salt it has to be plasticised. This is possible through coordinating to the PANI a doping able surfactant like sulfonic acid, and then complex the system with certain metal soaps like zinc stearate. The plasticised system is then processable in an extruder and can form under controlled conditions an interpenetrating network (IPN) with a selected matrix plastic.

The IPN structure is necessary for conductivity, but it is sensitive to heat >230 °C and shear rates >300 s^{-1} for several minutes. The feature limits the processability of the PANI blends. Typical polyamide and polyester fibre materials blended with PANI are most difficult to melt spin, even if that is possible with polypropylene. The three-component complex system also has limited long-term stability.[34]

13.5.2 Solution coating

Solution coating of various materials with a layer of ICP includes spreading the solution on the surface of the substrate material, followed by the evaporation of the solvent. Besides the difficulties concerned with the desired uniform coating the main problem is the insolubility or even poor solubility of most ICPs in nearly all solvents of practical interest. During recent years some progress has been made in the chemical modification of the parent ICP structures in order to get more soluble polymer derivatives. Some examples are the introduction of an alkyl chain into the 3-position of pyrrole monomer, or an alkoxy group into the ortho-position of the aniline monomer. But such a distortion of the molecular structure leads to a drastic decrease in electrical conductivity of the resulting polymers.[35]

Doped PANI can form solution with toluene and in certain conditions with water. The solution can be blended in polymer fixative solution. The combined solution is useful for coating cloth structures with controlled amounts of PANI reaching the ESD properties and reasonable sustainability on the textile fibres.

13.5.3 *In-situ* polymerisation

Chemical oxidative deposition of ICPs onto different kinds of fibres and textile materials makes new composite materials useful for several applications. *In-situ* chemical polymerisation can be made by two distinct methods. The first one is principally bulk polymerisation taking place in solution, where part of the resulting polymer deposits onto the surface of the substrate material immersed into the polymerisation solution, but part of it precipitates as a bulk polymer. In this case it is clearly recommended to maximise the amount of polymer deposited on the surface of the substrate and this can be achieved by choosing a suitable concentration of reaction components, oxidant to monomer ratio, pre-treatment of substrate surfaces.[35]

The other approach is a chemical polymerisation provided directly onto the surface. In this case, the surface to be coated is enriched either with monomer or an oxidising agent, and after that is treated with a solution or vapour of either oxidiser or monomer respectively. This ensures that polymerisation takes place almost exclusively on the surface. The disadvantage of this method is that in order to get a uniform layer of ICP onto the surface, the preliminary layer of either monomer or oxidiser should also be uniform, but achieving this is usually not easy. The reason for that can be the poor or non-porosity of the substrate that prevents the proper absorption of the initial solution. In the case of non-porous substrates the surface needs pre-treatment (corona treatment, etc.) in order to reduce the surface energy of the substrate.

One of the first attempts to cover textile fabric with an electrically conductive coating was made by Gregory *et al.* Polyamide 6 and 6,6 as well as polyethylene terephthalate and quartz fabrics were covered by *in-situ* chemical polymerisation with PANI or PPy coatings. The resulting films had smooth and coherent structures. Each single fibre of the composite structure was uniformly coated by ICP. Resistivity varied from 120 to 12,000 Ω/sq mm depending on the polymer.[20]

In-situ PANI-coated cotton fabrics have been demonstrated. Besides improved electrical conductivity such a fabric showed improved flame retardancy compared to pure cotton. The reduced electrical conductivity resulting from washing was compensated by redoping the material in 1 M HCl for two hours. That led to even lower resistivity (~10^3 Ω) values than initially after polymerisation (~10^4 Ω). The possible applications proposed are in industry, stealth technology and special anti-flammable clothing.[36]

A PPy-carbon fibre composite with a carbon fibre content of 15–20% was prepared by the chemical polymerisation of pyrrole. The resulting composite has high tensile strength and good thermal stability. Such a material could be used as a cathode material for a rechargeable battery, where carbon fibres act as an electrically conductive skeletal electrode for current collection with a specific capacity of 91 mA h/g.[37]

Wet spinning of PANI fibres has been demonstrated from a solution of Polyaniline doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) in dichloroacetic acid (DCA) into various coagulation solvents, including acetone and butyl acetate. The resulting fibres are inherently electrically conductive and may be cold drawn. The conductivity of an 'as-spun' fibre is typically between 0.7 and 1.3 $[\Omega\ m]^{-1}$, rising to 12 … 19 $[\Omega\ m]^{-1}$ after drawing at room temperature to a draw ratio of ~500%. The Young's modulus of the fibre spun into butyl acetate is 40 ± 10 MPa, and the tensile strength at break is 50 ± 10 MPa. The diameter of 'as-spun' fibres is about 200 μm.[38]

13.5.4 Polymerisation in supercritical fluid

Non-conductive fibre materials can successfully be covered by thin films of ICPs. The use of such coated fibres in textile products that require washing is still problematic because the coating is worn out quite soon. Improved washing resistivity has been achieved using *in-situ* polymerisation of PANI and PPy in supercritical CO_2 onto polyester and polyamide fibres.

The main advance of using this technology during coating by *in-situ* polymerisation is that the environment of super critical fluid, the structure of matrix polymr expands so that the monomer is able to penetrate into the matrix. That way the interpenetrating network (IPN) of covering ICP and matrix polymer is created. The IPN is conductive and well protected, and thus is formed into a markedly more sustainable conductive polymer coating layer.[34]

13.5.5 Electrochemical polymerisation

Another possible method for *in-situ* polymerisation is an electrochemical polymerisation of monomers at electrodes, performed either in aqueous or in organic solutions. Although much knowledge on the polymerisation mechanism and redox transformations taking place during reversible oxidation and reduction of ICPs was obtained using electrochemical polymerisation, its use is strongly restricted by the use of conducting substrates.[35] Another aspect is the limited size of substrates; no large area surfaces can be covered by ICPs by electrochemical methods. Several studies have shown that films of ICPs obtained by this method are also very porous and of poor quality.

13.5.6 Electrostatic spinning

Electrostatic spinning has been used as a coating method. This is the only industrially viable method to produce nanofibres in scales of sub-micron (especially 20–500 nm) from solutions of different polymers and polymer blends. Polymer melt can be used in the electro-spinning process, but fibres thinner than 1 μm are more easily made from polymer solutions in an acceptable solvent.

In the electrospinning process, a high-voltage electric field is generated between an oppositely charged polymer fluid contained in a glass syringe with a capillary tip and a metallic collection screen. As the voltage is increased, the charged polymer solution is attracted to the screen. Once the voltage reaches a critical value, the charge overcomes the surface tension of the suspended polymer cone formed on the capillary tip of the syringe of the glass pipette and a jet of ultra-fine fibres is produced. However, the field 1…5 kV/cm is markedly lower than that required for partial discharge in the material. As the charged fibres are spread out, the solvent quickly evaporates and the fibres are accumulated randomly on the surface of the collection screen. Typically the operation voltages are 20 … 40 kV from device to earth that makes the operation of the process still possible in a converting line without special arrangements.[39]

If the process and material parameters are correctly set, electro spinning of polymer materials from ultra light non-woven-like layers with density of 0.001 … 0.05 g/m^2 and fibre diameter 0.1 … 0.8 μm. This means that the consumption of the inherently conductive material is very low. In the case of blended polymers it is even lower. The nanofibres appear light or light green while normally PANI fibres are dark green or black.

It has been demonstrated that conducting polymer blends can be electro-spun using low hazard solvents like water-alcohol and organic acids (formic acid). Various polymers like polyvinyl alcohol, polyethylene oxide and polyamide blends with about 20% conducting PANI doped with 2-acrylamido-2-methyl-1-propanesulfonic acid have been electro-spun utilising fields in magnitude of 2.5 kV/cm providing fibre size of 100 … 400 nm. Fibre thickness can be controlled by means of molecular weight of the base polymer, and the electric field strength. Very thin coating (< 0.15 g/m^2) can reduce surface resistance down to ESD requirements.[39]

It has been found that no fibres of pure PANI can be electrospun. The fabrication of nanofibres of PANI doped with camphorsulfonic acid (HCSA) blended with polyethylene oxide (PEO) is discussed by Ko.[40] It was found that at least 2 wt% PEO is essential in the blend as no fibre formation occurs in PANI/HCSA dissolved in chloroform alone since the viscosity and surface tension of the solution is not high enough to maintain a stable drop at the end of the capillary tip. Further, addition of more doped PANI does not increase the viscosity of the polymer solution as PANI/HCSA has a very low solubility in chloroform.

13.6 Future trends in conductive materials

Electrically conductive fibres usually lack typical textile fibres' properties such as comfort, wear resistance, and dyeability. These problems can be solved by modifying the fibre structure, finishing technologies and using new materials. Wear resistance problems are increasingly solved by means of coating of traditional textile fibres with conductive materials. Alternatively, the bi-component and other advanced fibre structures are utilised.

Heat and especially washing sensitivity requires limitation in cloth handling such as special washing processes. New, promising and more attractive solutions are the more tolerant materials, especially the ionomer and carbon nano-tube blends. The same development trend also enables improved colour and appearance for the cloths. Further progress is towards the creation of entirely new, superconductive and performing fibre materials based on the new nanofibres and carbon nano-tubes.

Printable electronics is based on conductive polymers. Printing is made on smooth substrates that are typically plastic films. Application to textiles is then most suitable through lamination technology. MEMS based on, e.g., low-temperature co-fired ceramics can be integrated as well.

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14

Formation of electrical circuits in textile structures

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14.1 Introduction

In its simplest definition, an electrical circuit is meant to interconnect electrical elements to form a functional system. The 'electrical elements' could be sensors, actuators, transistors, power sources, etc. Electrotextiles represent enormous potential in creating a new generation of flexible/conformable and multifunctional textile structures for many electrical and electronic systems. In their current state, in many cases, sensors and other electronic devices have been built on or incorporated into textile-based structures using the available technologies; whereas in other cases new technologies, materials, and systems are being developed to form fabric-based electrical devices and systems. A fabric-based electrical circuit is an essential infrastructure necessity for these ongoing efforts.

This chapter provides an overview of recent developments in the area of textile-based electrical circuits, describing processes used to fabricate these circuits and highlighting issues and problems associated with these. Some of the issues that are involved in the development of fabric-based electrical circuits include formation of interconnects and disconnects between orthogonally and otherwise intersecting conductive threads at certain points in the electrical circuit. Evaluation of mechanical and electrical properties of fabric-based electrical circuits and important issues related to these properties are also discussed. This chapter also covers methodologies for attaching electrical devices to the conductive elements incorporated into or on the surface of the fabrics (similar to surface mount technology in printed circuit boards). The research carried out in this area has already been applied to develop commercial products for civilian and military use. The discussion includes applications of the electrical circuits including flexible multi-chip modules, fabric-based antennas, and fabric-based sensors and sensor systems.

Achieving electrical switching is an important part of developing integrated circuits. The chapter also covers ongoing efforts by researchers to develop transistors on fibers or thin films that could eventually be integrated into fabrics to form integrated circuits.

The chapter concludes with a discussion on the opportunities and challenges in the development of fabric-based electrical circuits, a critical component for the evolution of fully integrated electronic textiles with transistors and integrated circuits, sensors and other electronic devices built into the textile structures.

14.2 Development of textile-based circuits

Conventional printed circuit boards are multi-layered structures that have a conductive wiring pattern inscribed on insulating substrates.[1–4] Printed circuit boards are usually made from copper-clad organic laminated materials like epoxy or phenolic resins embedded with reinforcements like glass. The interconnect patterns are inscribed on each copper clad laminate using photolithography or electron beam lithography. These conventional printed circuit boards are not flexible beyond a certain point. In many applications like hand-held electronic devices and laptops, it is desirable to have circuit boards that can be bent or flexed easily. In order to form flexible circuit boards, printing of circuit patterns is carried out on polymeric substrates such as films. Fabric based circuits potentially offer additional benefits of higher flexibility in bending and shear, higher tear resistance, as well as better fatigue resistance in case of repeated deformation.

Needless to mention that textiles used in everyday life already offer platforms to functionalize many useful applications. Extensive work is being carried out in the area of electronic textiles to develop electrical circuits on fabric-based substrates so as to achieve a higher level of circuit flexibility. In section 14.4 we discuss the different materials and processes employed for the development of fabric circuits. We also discuss certain steps that are required to form fabric-based circuits like the formation of cross-over point interconnects and disconnects the next part of section 14.4 discusses the different methodologies that have been used by researchers to attach integrated circuits (chips) and rigid multi-chip modules to flexible electrical circuits. This is followed by a discussion on the properties of thin film and fiber-based transistors.

14.3 Fabrication processes

Different processes that have been described in literature for the fabrication of fabric based circuits include embroidery of conductive threads on fabric substrates, weaving and knitting of conductive threads along with non-conductive threads, printing or deposition and chemical patterning of conductive elements on textile substrates.

14.3.1 Embroidery

Embroidery is a traditional variety of usually decorative needlework in which designs are created by stitching strands of some material onto an appropriate substrate. Circuits can be formed by employing manual or numerically controlled embroidery of conductive threads on fabrics made of insulating materials. The insulating fabric could be woven, non-woven, or knitted. One of the advantages of this process of fabric circuit formation is that the conductive threads can be embroidered in any shape on the fabric irrespective of the constituent yarn path in a fabric. Moreover, one does not need to perform a lot of machine preparation before fabric circuits can be formed. In contrast, in woven circuit formation, conductive threads in the warp direction have to be placed in the appropriate positions before weaving. Orth[5] has described machine sewing and embroidery as one of the most stressful textile manufacturing processes. In sewing conductive threads on fabric substrates, the threads encounter various levels of stresses and friction. This requires an embroidery thread to have relatively high strength and flexibility because of the stresses due to bending and shear and the tortuous path it has to traverse to form a secure stitch.

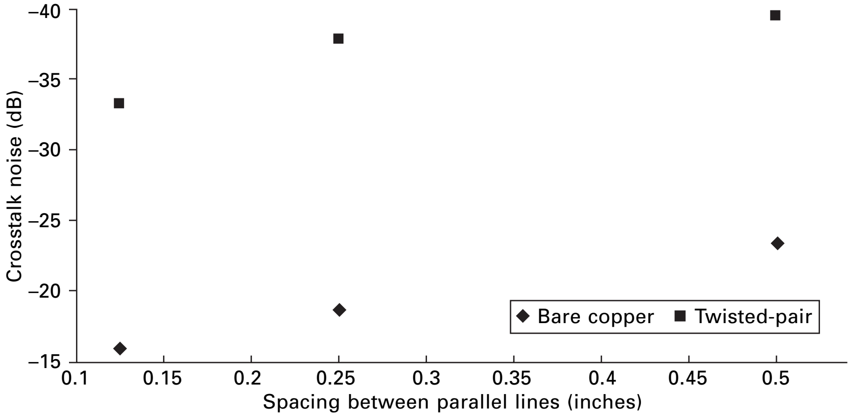
Formation of electrical circuits on textiles, by numerically controlled sewing processes has been described, by Orth *et al.*[6] and Post *et al.*[7, 8] Their primary method of circuit patterning was numerically controlled embroidery using conductive threads. Different circuit elements that were embroidered on woven fabric substrates included pads for attachment of devices to the embroidered circuit, conductive bus lines interconnecting different devices on fabric-based multi-chip modules, and elements of a tactile sensor. Orth *et al.*[6] developed embroidered circuitry to form a conformable fabric keyboard, pressure sensors, a transmitter system, and a musical jacket having embroidered keypad and bus lines. Orth *et al.*[6] also developed a polymeric thin film-based module which could be incorporated into textile products to form a sensor readout network.

One of the primary disadvantages of embroidery as a means of circuit formation is that it does not allow formation of multi-layered circuits involving conductive threads traversing through different layers as is possible in the case of woven circuits. Moreover, the stresses mentioned earlier can lead to yarn breaks. Although discontinuities in normal sewn fabrics may not be a problem, discontinuities are not desirable in fabric circuits. Joins or splices to fix the discontinuities in sewn conductor lines may lead to undesirable additional impedance. This problem of breakage of conductive threads may also be encountered in other processes of circuit development like weaving and knitting but is slightly less pronounced as compared to sewing.

14.3.2 Weaving and knitting

Conductive threads can be woven into a fabric structure along with non-conductive threads to form an electrical circuit. In the weaving process, two sets of orthogonal threads, called warp and filling, are interlaced with each other. In the process of weaving, the warp yarns lying in the long direction of the fabric are separated in two layers to form an orthogonal interlacing path for the other set of yarns called weft.[9–10] Weaving of electrical circuits can be carried out on conventional weaving machines by making appropriate modifications required to weave conductive threads. One can have a high degree of control in the placement of conductive elements in these circuits by using a jacquard shedding system that allows each warp thread to be addressed individually in order to control the order of interlacement of the threads most precisely. One can form a weave design based on the electrical circuit design and feed it into the jacquard weaving machine controller. This enables one to form complicated circuit patterns on fabrics in an automated manner. One of the limitations of using weaving for making electrical circuits is that the conductive threads have to be placed at predetermined locations in the warp direction while forming the warp beam or from a creel during set up of the machine. Different kinds of conductive threads can be supplied in the weft or filling direction and inserted using the weft selectors provided on a weaving machine. Some modifications to the yarn supply system of the machine may be needed in order to process the conductive threads that are more rigid.

Formation of woven circuits, according to a given fabric design, has been reported by Dhawan *et al.*[11–16] In their work they used a rapier weaving machine and placed the conducting threads on a separate creel. They reported using different kinds of conductive yarns like steel, copper, and silver-coated polyester yarns. Signal integrity issues, like crosstalk noise in certain conductive lines due to switching of signals in neighboring lines, were reported. They also investigated multi-layered fabric circuits and woven fabric-based transmission lines. To improve signal quality, Dhawan *et al.*[11–16] developed coaxial transmission-line-like thread structures by wrapping an insulated conductive thread with a conductive thread and twisted-pair thread structures by twisting two insulated copper threads. They reported significant reduction in crosstalk noise with twisted-pair (see Fig. 14.1) and coaxial yarns. A woven transmission cable, in which a number of conductive warp elements are interwoven with weft elements, has been described by Piper.[17] In this transmission cable, the relative arrangement of ground and signal lines determines the characteristic impedance of the cable. This transmission cable showed a low value of impedance even at very high signal frequencies. Placement of ground lines in between the signal carrying lines leads to a lower level of crosstalk noise in neighboring signal lines of the cable.



14.1 Crosstalk noise between woven interconnect lines for a 1 Volt signal (1 MHz frequency) sent into an aggressor line: crosstalk noise vs. spacing between the twisted pair and bare copper lines.[12]

Investigation of woven fabric-based signal transmission lines has been described by Kirstein *et al.*,[18] Cottet *et al.*,[19] and Locher *et al.*[20] Polyester yarns twisted with an insulated copper filament were woven to develop structures similar to coplanar waveguides.[18, 19] The conductive threads were separated from each other by any number of non-conductive threads. In coplanar waveguides, the signal lines are surrounded by ground lines in order to prevent coupling between neighboring signal lines at high frequencies.[18,19] In the case of fabric-based coplanar waveguides, one, two, and three signal (S) lines were woven with one or two ground (G) lines on each side of the signal lines to form GS, GSG, GSSG, and GSSSG configurations of signal and ground transmission lines. Electrical parameters like line impedance, insertion loss, and crosstalk noise were determined using time and frequency domain analysis.[18,19, 20]

Jayaraman *et al.*[21] have described the development of a woven garment (called the sensate liner) with intelligence capabilities. The garment consists of woven optical fibers running in a helical path along the length of a tubular woven fabric. The optical fibers lie between a signal transmitter and a receiver. An optical signal sent by a transmitter travels along the optical fiber, is reflected back from the receiver, and goes back to the transmitter. The time taken for the full signal traverse is known based on the length of the optical fiber. In case of penetration of the fabric by a ballistic object, the incident signal is reflected back from the point of the penetration. Hence, the signal reaches the transmitter before the normal time, implying that it was disrupted by a penetration and rebounded back. In this garment, electrically conducting fibers were also woven into the fabric in the longitudinal direction. These fibers formed an interconnect between a computer and sensors attached to the fibers.

Lebby *et al.*[22] described the development of a conductive fabric-based communicative wristwatch. The wristband of this watch was developed by weaving conductive and non-conducting yarns. An electronic unit and a power source were integrated into the wristband. The conductive yarns provided interconnection between the different electronic elements attached to the conductive threads of the wristband fabric. Development of a conductive fabric, with electrical anisotropy, has also been reported by Yoshida *et al.*[23] In this fabric, conducting and non-conducting yarns were arranged in orthogonal directions. This allowed current to flow only in the direction of the conductive threads, thereby leading to the anisotropic electrical properties.

Formation of knitted conductive fabrics was carried out by Farringdon *et al.*[24] to develop fabric-based stretch sensors. These sensors measure strain from changes in resistance of the knitted conductive strips. Although circuit boards or multi-chip modules have not been developed on knitted fabrics, development of a conductive knitted fabric to form stretch sensors[24] can provide some insight into the feasibility of using knitting[25] as a process for developing electrical circuits. In most conventional weft knitting machines, like a flatbed machine, the conductive threads can be knitted in the fabric only in one direction, i.e., the course (or cross) direction. Hence one can form transmission line cables made up of knitted conductive threads interspaced by non-conductive threads. As knitted fabrics are generally stretchable, the conductive transmission lines developed from knitted fabrics would be expected to exhibit variability in impedance characteristics due to opening and closing of the conductive loops. In order to keep the conductive element in a knit structure straight, one can also insert a conductive thread in the course direction such that the conductive thread is embedded into the fabric between two courses formed from non-conductive threads.

14.3.3 Patterning conductive elements on fabrics

Patterning conductive materials on fabric substrates to form electrical circuits and to achieve conductivity gradients have been reported in the literature.[26–27] Processes that have been employed to form a patterned conductive path on fabric surfaces include deposition of polymeric or non-polymeric conducting materials and subsequent etching, reducing, or physical removal of the conductive materials from certain regions. Thus, the conductive material that is not removed forms a patterned electrical circuit or a region of higher conductivity. Other processes include *in-situ* formation of conductive polymeric films on fabric substrates and subsequent patterning of the films using one of the techniques described above.[26–28] While some have investigated printing of conductive lines on fabric substrates, others[18–28] have looked at chemical plating and subsequent patterning of fabrics. The biggest problem associated with patterning of circuits from thin conductive films (polymeric or metallic) deposited on fabric substrates is that use of an etching agent for forming a circuit pattern leads to non-uniform etching, as some of the etching liquid is absorbed by the threads of the underlying substrate fabric.[20,26–27] Another problem with deposition of conductive films on fabric substrates is that bending the fabric may lead to discontinuities in conductivity at certain points. This problem also exists in printed electrical circuits as conductive materials such as inks or pastes with metallic particles as fillers[29] printed on fabric substrates are stiff and are prone to cracking on bending. Electrical properties, mainly resistivity, of conductive inks and conductive silver loaded epoxies, were evaluated by Cadogan *et al.*[29] They employed the conductive inks and epoxies to form interconnects with conductive threads of a sensate liner.[21]

DeAngelis *et al.*[26] described the development of conductive fabrics by selectively patterning a conductive polymeric film deposited on fabrics. Firstly, a conductive polymer film was coated all over a woven or knitted fabric substrate. After coating the whole fabric, a mask was applied in certain areas of the fabric. In the unmasked areas, the conductive polymer degrades on application of the etching material. Thus one gets a design or pattern of conductive polymer on a flexible textile substrate. The area of the fabric having the conductive polymer has high conductivity and the uncovered area has low conductivity. Instead of depositing a layer of conducting polymer on top of the substrate, conductive polymers can be synthesized on the surface of the fabric itself.[26] Kuhn *et al.*[27] described the formation of a conductive polymer film on the surface of textile materials. A yarn or a fabric was placed in an aqueous solution of a polymerizable material and a conductive polymer layer was formed on the surface of the fabric in the presence of an oxidizing agent. This process can be used to form electrical circuit patterns on a fabric.

Adams *et al.*[30] described the development of an electrically conductive fabric having non-uniform conductivity. Development of this fabric involved coating a substrate fabric with a thin layer of conductive polymer and subsequent removal of the polymeric coating from certain regions of the fabric using high-velocity water jets. These regions have a lower value of electrical conductivity as compared to the regions where the conductive coating has not been removed. Gregory *et al.*[31] also described the development of a conductive textile fabric having a conductivity gradient. A conductive polymeric film (doped polypyrrole) was coated on a fabric substrate and a chemical reducing agent was applied to certain regions of the fabric. Application of a reducing agent to the doped conductive polymer on top of the fabric substrate caused conductivity of that region to be changed. The reducing agent was applied to certain parts of the conductive fabric for varying conditions of time, concentration and temperature thereby changing the conductivity of the conductive polymeric film in varying degrees. The process described by

Gregory *et al.*[31] could also be potentially employed for forming patterned electrical circuits on fabric substrates.

14.4 Materials used

In order to form electrical circuits in textile structures different kinds of non-conductive, and conductive materials are assembled into fabrics. These materials include conductive fibers and yarns, conductive materials deposited on thin films, or organic and inorganic conducting materials deposited on top of fabric substrates.

14.4.1 Conductive fibers and films

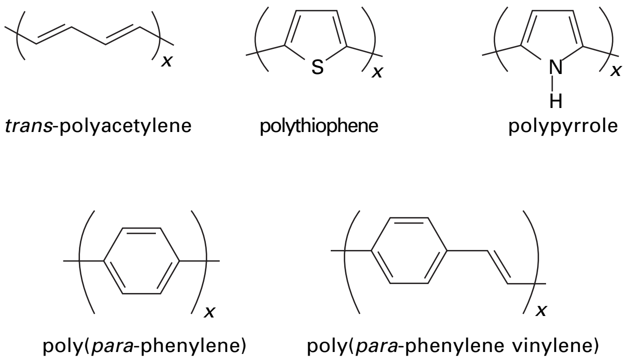
In general, the materials employed for the formation of fabric-based electrical circuits include metallic yarns, yarns made from conductive polymers, polymeric threads containing high levels of conducting particles (carbon, silver, etc.), and conducting thin inorganic films. Resistivity values of some of the commercially available conductive fabrics are given in Table 14.1.

Intrinsically conductive polymers like polyaniline, polypyrrole, polyacetylene, polythiophene, poly(p-phenylene), poly(p-phenylene vinylene) and poly(para-phenylene) are some of the materials that have been investigated for forming conductive fibers employing solution spinning processes.[32] The structure of some of these polymers is shown in Fig. 14.2. Conductivity in most of these polymers is based on a π-conjugated system which is formed by the overlap of carbon p_z orbitals and the presence of alternating single and double bonds in the polymer chains.[33–34] Intrinsically conductive polymers are doped to achieve a higher value of conductivity. A comparison of conductivities of conducting polymers as compared to those of metals, inorganic semi-conductors, and insulators is shown in Fig. 14.3.[35] Electrical conductivities of the intrinsically conducting polymers range from that typical of insulators $<10^{-10}$ S/cm to that typical of semiconductors such as silicon ($\sim10^{-5}$ S/cm). Conductivity levels for doped conductive polymers are much higher. Iodine doped acetylene has a conductivity of $\sim10^{5}$ S/cm, a value very close to that of metals. Conductivities of electronic polymers are transformed through the process of doping such that increasing the doping level increases the conductivity of these polymers. Both n-type (electron donating) and p-type (electron accepting) dopants are employed to introduce conducting properties in electronic polymers. The doping process involves exposing intrinsically conductive polymer fibers or films to dopant vapors or solutions.

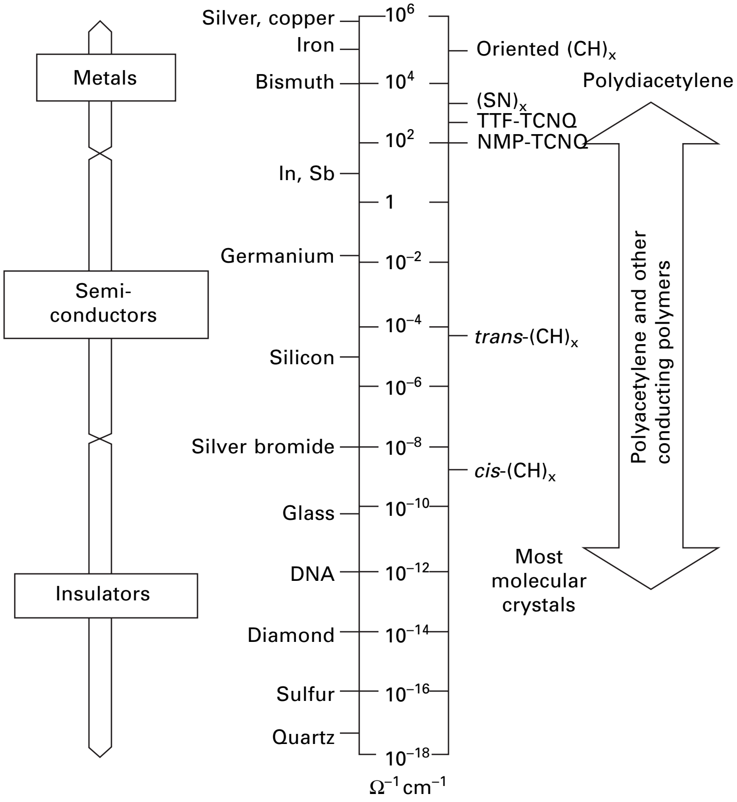
Conductive polymeric fibers were developed by Mattes *et al.*[36–37] and these fibers could be integrated into fabrics to form electrical circuits. A 20.1 wt%. solution for spinning emeraldine base (polyaniline) fibers was prepared by Mattes *et al.*[37] in the solvent N-methyl-2-pyrrolidinone (NMP). The polymer

Table 14.1 Resistivity values of commercially available conductive fabrics[28]

Name	Composition	Production process	Resistivity	Manufacturer
FlecTron	Copper coated polyester taffeta	Electroless copper plating process	<0.1 ohms/sq	Less EMF
Phantom Fabric	Copper coated polyester mesh (90 threads/inch)	Copper plating process	~10 ohms/sq	Less EMF
Zell Conductive Fabric	Tin/copper coated plain weave nylon taffeta ripstop	Copper and tin plating process	<0.09 ohms/sq	Less EMF
FlecTron N-Conductive	Nickel/copper coated polyester taffeta	Electroless copper and nickel plating process	<0.1 ohms/sq	Less EMF
Softmail Fabric	Microfine stainless steel fibers and nylon plain weave	Plain weave process	300 ohms/sq	Less EMF
Shieldex Supra	Tin/copper coated plain weave nylon overcoated with conductive acrylic and polyethylene	Copper and tin plating process	~0.1 ohms/sq	Less EMF
Conductive Felt	Silver coated nylon non-woven	Silver plating process	~0.3 ohms/sq	Saquoir Industries
SeeThru Conductive	Silver coated nylon knit	Silver plating process	5.0 ohms/sq	Less EMF
Snowtex 001.43	Textured 56 AWG copper wire and polyester plain weave	Texturing (kinking) process for yarn making to strain relieve Cu wire	<0.1 ohms/sq	Snowtex
Snowtex 001.44	Textured 56 AWG copper wire with thin insulating coating and polyester plain weave	Texturing (kinking) process for yarn making to strain relieve CU wire	Insulated	Snowtex
Snowtex 001.45	Textured 56 AWG copper wire with thin insulating coating and polyester plain weave	Texturing (kinking) process for yarn making to strain relieve Cu wire	Insulated	Snowtex



14.2 Repeat units of some intrinsically conductive polymers.[32–33]



14.3 Comparison chart of conductivities in S-cm^{-1} for conducting polymers when compared with metals, semi-conductors, and insulators.[35]

solution was extruded through a one-inch air gap directly into a water coagulation bath at 5 °C where the solvent was removed from the nascent polyaniline. The take-up speed was varied between three to ten feet per minute. Conductive fibers can also be developed by slitting a Kapton® polymeric film and depositing gold on top of the slit film pieces as described by Bonderover *et al.*[38] They took a 50-micron thick sheet of ®Kapton E and deposited silicon nitride on it at 150 °C. The silicon nitride layer was patterned using conventional photolithography and wet etching. Using this patterned silicon nitride layer as an etch mask, the Kapton sheet was etched right through by employing a high-power-density oxygen plasma. A gold film of 100 nm thickness was then deposited on top of the Kapton slit films using e-beam evaporation.

Conducting polymeric films have also been deposited on woven, knitted, and nonwoven fabric surfaces and patterned using photolithography and subsequent chemical etching. Some of the polymeric materials employed are polyaniline, polypyrrole, polyacetylene, and polythiophene.[32–34,39] Instead of depositing polymer on top of a fabric substrate as described earlier[26,31] some researchers have described the development of polymers on the fabrics by first impregnating the fabrics with monomers and subsequently carrying out polymerization at the appropriate conditions.[27]

14.4.2 Non-conductive elements

Some of the materials that have been employed for the formation of fabric-based electrical circuits are nylon, polyester, or acrylic fibers, yarns, or fabrics.[11–16] These non-conductive threads serve to separate the conductive threads from shorting each other. Employing a high-temperature-resistant material like Nomex for forming the insulating material is useful as signal-carrying conductive threads can heat up while carrying a high current. Gorlick *et al.*[40] employed Nomex threads to form conductive fabric webbing by weaving the Nomex yarns along with steel threads. The other non-conductive materials that could be used to form a substrate, on which conducting (polymeric or metallic particles) material could be deposited, include polyester spun-bonded non-woven fabrics, polyurethane electrospun non-woven fabrics, and polyester electrospun fabric.[41] The main considerations in choosing the non-conducting fibers are ease of processing, temperature requirements and, maybe most importantly, requirements for the primary function of the substrate. Depending on the application, the primary function may be comfort, protection, etc.

®Kapton is a polyimide film by DuPont.

14.4.3 Formation of crossover point interconnects

As described in earlier sections, electrical circuits can be developed by weaving or knitting of conductive threads into a fabric structure in order to interconnect electronic devices placed at different points on the fabric. In order to route the signals in these circuits, interconnections need to be developed between orthogonal conductive threads and these interconnections can be termed as crossover point interconnections. Different techniques can be employed to form crossover point interconnections like resistance welding, adhesive bonding, air splicing, and soldering.

Dhawan *et al.*[11–16] described resistance welding as one of the best methods for forming crossover point interconnects[11,13,16] for its simplicity and resulting minimal damage to neighboring non-conductive fibers. The process led to the formation of less rigid fabric-based circuits as it relied on controlled heating and melting of the orthogonal conductive threads at the crossover point. Two kinds of resistance welding processes, i.e., top-bottom probe welding and parallel gap welding were used to form crossover point interconnects in fabrics containing steel and copper threads. DC resistance values of the fabric samples having welds at the crossover points were found to be less than those for woven copper samples without any weld.

Another method to form interconnections between orthogonal threads is soldering. Generally, this leads to a rigid fabric as the solder blobs are larger than the weld points formed using resistance welding. Moreover, one may need to use a controlled amount of solder for this process to be reliable for multiple crossover point interconnects.

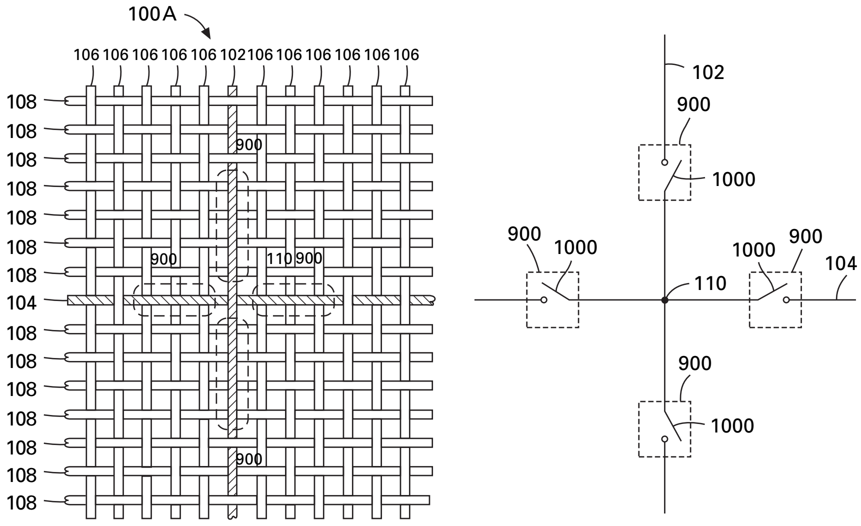
Locher *et al.*[42] employed a conductive adhesive to form interconnection between two orthogonally woven conductive wires. Firstly, insulation was removed (at the crossover point of these conductive wires) from the two orthogonally woven conducting wires using a laser ablation process. Subsequently, the crossover point interconnect was formed using a conductive adhesive.[42]

In order to develop integrated circuits using transistors developed on fibers, one may need to form interconnections between drain, gate or source metal pads on the fibers containing the transistors and orthogonal conductive threads. Lee *et al.*[44] have reported the formation of transistors directly on fibers.[44] They employed conductive aluminum and stainless steel wires as the gate of the transistor. For the operation of this back-gated field effect transistor, interconnections were made to the metallic wires forming the transistor gate. These interconnections could be made anywhere along the fiber, where the coatings are not present or are removed. Contacts to the source and drain regions of the transistor could be made by conductive lines woven into the fabric, orthogonal to the direction of the fiber containing the transistor. They proposed physical contact as being the only means of interconnection between the conductive threads and the source and drain contact pads and did not employ thermal, electrical or light energies to form crossover point interconnections as suggested in the patent by Dhawan *et al.*[43]

14.4.4 Formation of disconnects of conductors

Woven electrical circuits require formation of disconnects at certain locations along a conducting yarn so as to control the signal path in the circuitry. These disconnects may be cuts or switches that could be switched on and off. In woven fabrics, the disconnects can be formed by creating a fabric with 'floats' at certain points. These floats could be selectively cut by appropriate cutters to form the disconnects. Interestingly, Dhawan *et al.*[14] reported formation of disconnects using a properly set up parallel gap resistance welding technique. They formed disconnects by using a very high value of weld current such that a break in the conductive fibers could be created.

A patent by Dhawan *et al.*[43] describes the formation of disconnects employing one of thermal, electrical or light energies. This patent also describes a process by which a programmable grid array could be developed in textile-based electrical circuits by developing switching elements like transistors on woven threads such that there is a transistor on every thread around the crossover point of the orthogonal threads, as shown in Fig. 14.4. Thus current



14.4 Figures demonstrating means of developing programmable circuitry in woven fabrics by developing switching elements like transistors on woven threads such that there is a transistor on every thread around the crossover point of the orthogonal threads.[43]

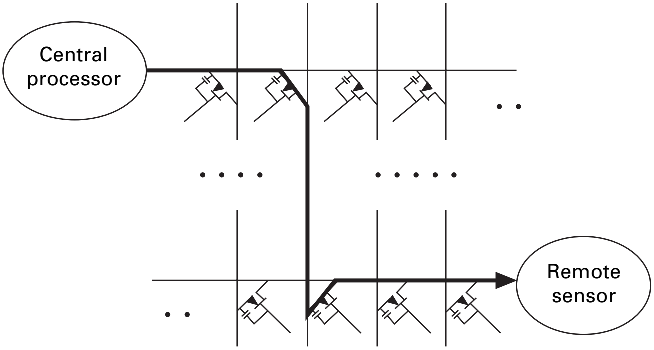
flowing into and from the crossover point can be switched according to the switching of the transistors in a programmable manner.

Lee *et al.*[44] have proposed fabrication of transistors at the crossover points of orthogonally woven fibers. This would allow formation of gate array switching grids such as the one shown in Fig. 14.5. Lee *et al.*[44] developed one of the most important elements in the formation of such a gate array switching grid, which is the formation of transistors directly on fibers.[44]

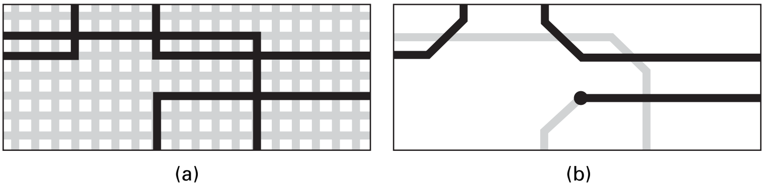
A conventional printed wiring board layout has 45° bendings when the trace direction changes from horizontal to vertical.[42] On the other hand, in a woven fabric structure, only perpendicular interconnection layouts can be implemented. This is illustrated in Fig. 14.6,[42] where the black lines indicate the path used for routing electrical signals in a textile fabric. Recently, Locher *et al.*[42] have also described the process of making disconnects in order to avoid short-circuits with the rest of the routing. They formed these disconnects or cuts by using laser light with a fluence greater than 4 J/cm^2.

14.4.5 Attachment of devices

Attachment of electronic devices to conducting elements integrated in the fabric poses numerous challenges in the field of electronic textiles. Devices



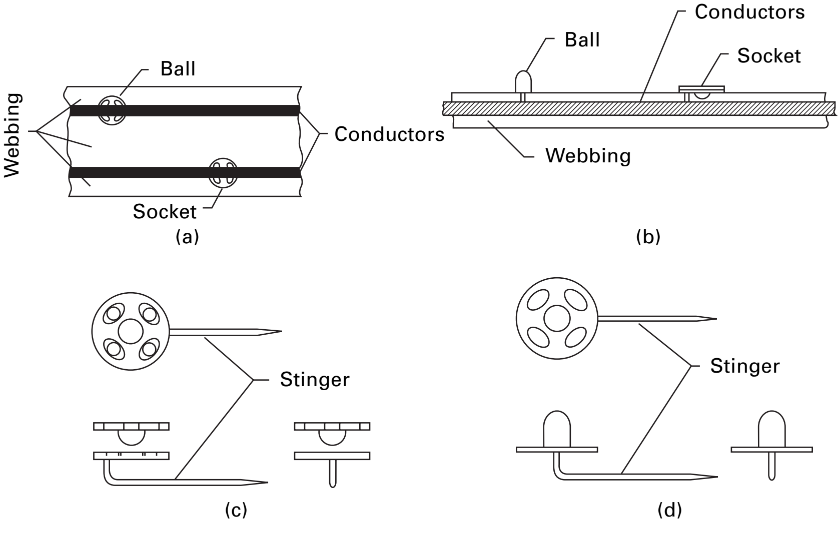
14.5 A schematic demonstrating the concept of a gate array switching network[44] © 2005 IEEE.



14.6 (a) Perpendicular routing layout in a woven fabric and (b) 45° bend in the trace when going from horizontal to vertical direction.[42]

that may be attached to the conductive elements of a textile fabric include rigid and flexible circuit boards, multi-chip modules and individual integrated circuit packages. It is desirable that individual chip packages be directly connected or bonded to conductive threads or conductive elements of a fabric, so as to form a more flexible and conformable electronic textile. The attachment of these devices could be carried out either by using physical contact between snap-connectors, conducting yarns, and electronic devices or by employing soldering or thermal bonding techniques.

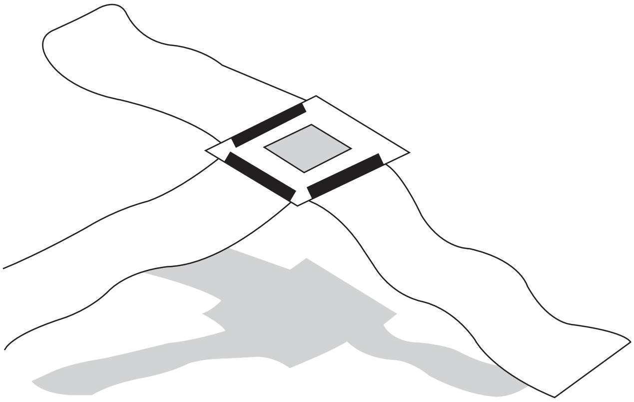
Gorlick[40] described the development of a fabric-based power bus and data network for wearable electronic devices. To form a conductive fabric-based power bus and data network, a webbing was woven from Nomex and steel yarns with two pairs of multi-stranded stainless steel conductors woven directly into the webbing as shown in Fig. 14.7. A means of connecting conventional electronics with this fabric webbing was also proposed. The electronic devices can be attached to these suspenders (the conductors of the fabric webbing) by using electrical surface connectors like sew-on ball and socket snap connectors as shown in Figs. 7(c) and (d). As shown in Fig. 14.7(d), the ball of the snap connector is connected to a stinger (an L-shaped wire soldered to the ball of the connector), which is inserted into the conductive fiber bundle of the fabric webbing, thereby making an electrical contact with the conductive fiber of the webbing. A socket connector, shown in Fig. 14.7(c), could also be employed to interconnect electronic devices with the connectors. Electric



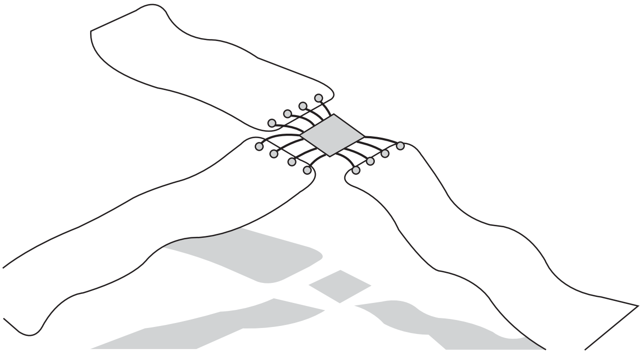
14.7 (a) and (b) Woven fabric webbing used to interconnect electronic devices to conductive fabrics using snap connectors, (c) a socket connector, and (d) a ball connector.[40]

suspenders made from the fabric webbing were transformed into a shared low-voltage, DC power bus for digital wearable devices.

Jung *et al.*[45] carried out attachment of electronic devices to conductive elements of a woven fabric. In one of the device attachment methods proposed by them, a flexible circuit board acts as an interface between the woven conductive threads and the integrated circuit. The integrated circuit is attached to the flexible circuit board as shown in Fig. 14.8. Conducting threads are connected to the electrodes and pads on the flexible circuit board by soldering. In another interconnect method, bonding wires are used to connect integrated circuits and conductive (having an insulating coating) threads woven into fabric strips. Insulation of the woven conductive threads is first removed by laser treatment and then tiny metal contact plates are soldered to these threads. Then, insulated bonding wires are used to connect the metal plates to the integrated circuit bond pads (Fig. 14.9).



14.8 Flexible circuit board used to form interconnects between an integrated circuit and the conducting threads woven into narrow fabric strips.[45]



14.9 Wire bonding of narrow fabric strips containing conducting threads to an integrated circuit.[45]

Post *et al.*[7] have described several methods for producing device-fabric interconnects. They found that soldering devices to the conducting threads in the fabric, bonding the electronic components using conductive adhesives, or stapling components into conductive stitched circuits were not very effective processes in producing these interconnects. Packages called plastic threaded chip carrier (PTCC) packages, having long conducting threads, were designed by them.[7] The leads of the plastic thread chip carrier packages were woven or stitched into the fabric circuitry. In order to manufacture threaded packages, a bare die or integrated circuit was taken and fine gold wires were bonded onto gold plated bond pads of the integrated circuit chip using thermo-compression. The other end of the fine gold wire was connected to a copper lead frame. Flexible and conformable conductive threads were micro-spotwelded to the lead frame stubs and the structure was sealed in a plastic carrier.

Lehn *et al.*[46] have suggested some designs for attaching electronic modules and devices to textile fabrics such that these devices are easily attachable and interchangeable.[46] A comparison between the different device attachment methods like raised wire connectors, solders, snap connectors, and ribbon cable connectors, is provided in Table 14.2. According to them, soldering produces reliable electrical connections to conductive threads of an electronic textile fabric but has the disadvantage of not being compatible with several conductive threads or materials like stainless steel. Moreover, soldering of electronic devices to threads that are insulated is a more complex process

Table 14.2 Advantages and disadvantages of different device attachment methods[46]

Type	Pros	Cons
Solder	solid electrical connection, strong physical connection, small, light, comfortable, not, noticeable	slow connection process, wire compatibility issues, wire breaks, alignment issues, mid-wire stripping, exposed wire protection expensive
Snaps	connection/reconnection ease, common use	slow connection process, soldering or welding issues, connection size, weak physical connection exposed leads
Ribbon Cable Connector	insulation displacement, common part, insulated connection, alighment tolerance, reliable connection	size, installation difficulty wire breaks
Raised Wire Connector	single textile side, no threads, low profile	weak fabric connection

involving an initial step of removal of insulation from the conductive threads in the regions where the device attachments are desired and insulation of the soldered region after completion of the soldering process. Another device connection method described by Lehn *et al.*[46] is to attach snap connectors to conductive fibers or wires integrated into a textile fabric and subsequently attaching electronic devices or circuit board elements to these snap connectors. According to Lehn *et al.*[46] different ways of attaching snap connectors to conductive threads integrated into fabrics include soldering or welding of these connectors to the conductive threads or sewing of the snap connectors to the base fabric employing conductive or non-conductive sewing threads. The main advantage of employing snap connectors is the ease of attachment or removal of electronic devices from these connectors, whereas the main disadvantages are the large size of the device and the weak physical connection formed between the snap connectors and the devices. Ribbon cable connectors employ insulation displacement in order to form an interconnection with insulated conductor elements integrated into the textiles. A v-shaped contact cuts through the insulation to form a connection to the conductor. Firstly, the ribbon cable connector is attached to the conductive threads in an e-textile fabric and subsequent electronic devices and printed circuit boards are attached to the ribbon cable connector. One of the advantages of employing ribbon cable connectors for device attachment is the ease of attachment and removal of the electronic devices to form the electronic textiles.

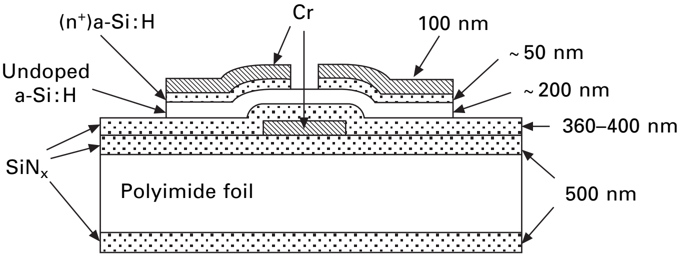
14.4.6 Development of film or fiberbased transistors and integrated circuits

As mentioned before, electrical switching is an important part of developing integrated circuits. The ability to form transistors on fibers, yarns, or thin films would enable fabrication of integrated circuits on flexbile textile-based substrates. Initial studies of thin film transistors and transistors developed on fibers are starting to be carried out.[47–53]

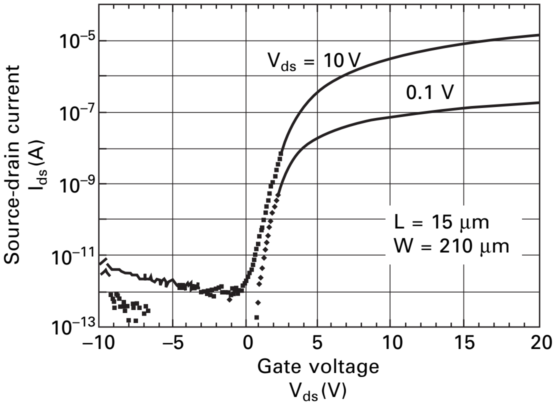
The main problems associated with transistors developed on flexible polymeric substrates is that the channel layer is based on either amorphous hydrogenated silicon or on nano-crystalline silicon layers deposited on the flexible substrates. The fact that these depositions are carried out on non-crystalline substrates and at a lower temperature (due to a lower glass transition temperature of the polymeric substrates), leads to the non-crystalline nature of the deposited films. Thus, the carrier mobilities are generally lower in these thin film transistors as compared to transistors developed on rigid planar silicon wafers. Another problem encountered in thin film transistors is a large gate leakage current due to porosity of the films, leading to a non-ideal turn-on in the transfer characteristics. Silicon dioxide gate dielectrics deposited at lower temperature may also have high levels of hydrogen in them and can be porous. Moreover, the interface between the gate dielectric and the amorphous or nano-crystalline channel of the thin film transistors has a higher defect density as compared to transistors developed on silicon wafers or other rigid substrates. A brief overview of the different kinds of thin film transistors is provided below, which is followed by a section that describes the development of these transistors on thread-like structures. However, using such transistors on flexible planar substrates has been useful for flexible display applications where the switching rate of pixels is low, and the size of the transistor can be large. For computing applications thin film transistors are typically avoided since the speed and performance of conventional transistors is significantly superior. In terms of consumer applications of thin film transistors for flexible displays the main problem remains packaging to handle the mechanical stresses, and in the case where organic materials are used protection from moisture penetration and protection from ultraviolet light.

Amorphous and nanocrystalline thin film transistors

As one typical example, Gleskova *et al.*[50–51] described the development of hydrogenated amorphous silicon thin film transistors on flexible substrates. They employed RF-excited plasma-enhanced chemical vapor deposition to deposit a hydrogenated amorphous silicon at a low temperature (150 °C) on a polyimide foil substrate. A silicon nitride (SiN_x) layer was used as a gate dielectric in this transistor, which had a bottom gate structure as shown in Fig. 14.10. The dielectric constant of the silicon nitride deposited at 150°C, and measured at 1 MHz, was found to be 7.46. Chromium was used as the gate electrode material and un-doped hydrogenated amorphous silicon was used as the transistor channel. The transfer characteristics of this transistor are shown in Fig. 14.11. In these transistors, there is substantial gate leakage as shown by the existence of a substantial source-drain current for gate voltage less than zero volts. The value of linear mobility for these transistors was found to be 0.5 $cm^2V^{-1}s^{-1}$. Gleskova *et al.*[54–55] also studied the effect of



14.10 Schematic cross-sectional view of a thin film transistor fabricated on a flexible polyimide substrate[51] © 1999 IEEE.



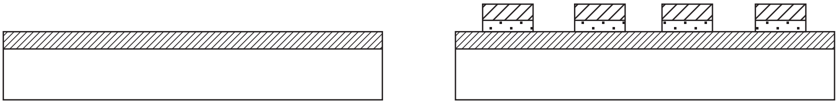
14.11 Source-drain current as a function of gate voltage for V_{ds} = 0.1 and 10 V. The substrate thickness is 2 mils[51] © 1999 IEEE.

mechanical strain on the properties of thin film transistors and reported that application of a compressive strain leads to an instantaneous increase in the mobility of carriers in the transistor.

As another example, Cheng *et al.*[49] developed thin film transistors based on nanocrystalline hydrogenated silicon deposited on Kapton substrates employing a staggered top gate, bottom source-drain geometry. The thin film transistors were developed on a nanocrystalline silicon seed layer on top of the Kapton substrate. Development of the crystalline structure of the channel layer takes place on top of this seed layer as shown in Fig. 14.12. The depositions and processing were carried out at 150 °C. This process for fabrication of thin film transistors ensures that the nanocrystalline channel layer is formed towards the end of the fabrication process sequence ensuring no plasma etch damage to it. Hole mobility of approximately 0.17 $cm^2V^{-1}s^{-1}$ was observed for p-channel thin film transistors and an electron mobility of approximately 23 $cm^2V^{-1}s^{-1}$ was observed for the n-channel thin film transistors developed on Kapton substrates. Despite showing a much better hole mobility as compared to hydrogenated amorphous silicon thin film transistors,[50–51] these transistors were not found to be suitable for the development of CMOS transistors as they had high gate leakage characteristics, as shown in Fig. 14.13. The silicon dioxide gate layer deposited at 150 °C contains excessive hydrogen, is electrically unstable and porous. The large leakage current is due to the porosity of the films and leads to a non-ideal turn-on in the transfer characteristics.

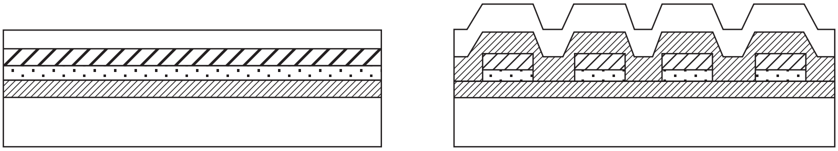
Organic thin film transistors

Organic thin film transistors have a channel layer composed of conjugated polymers, oligomers, or small organic molecules. These transistors generally



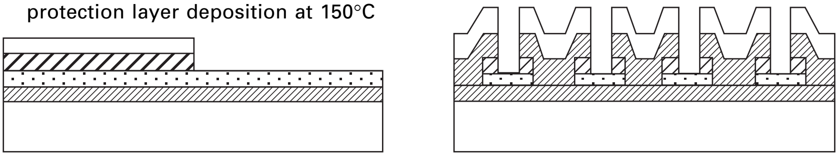
1. 50 nm i nc-Si seed layer deposition on substrate at 150°C

6. p^+/n^+ nc-Si and Cr S/D patterning



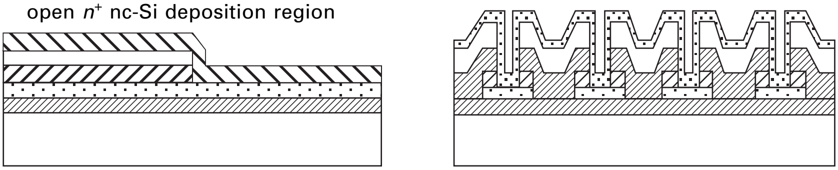
2. 50 nm Cr evaporation followed by 60 nm p^+ nc-Si and 100 nm SiO_2 protection layer deposition at 150°C

7. 50 nm i nc-Si channel layer deposition followed by gate dielectric deposition



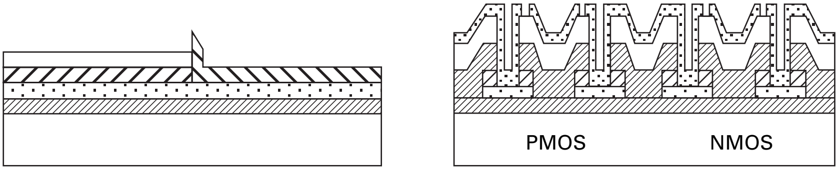
3. SiO_2 and p^+ nc-Si patterning to open n^+ nc-Si deposition region

8. Contact hole opening



4. 60 nm n^+ nc-Si deposition at 150°C

9. 200 nm Al evaporation

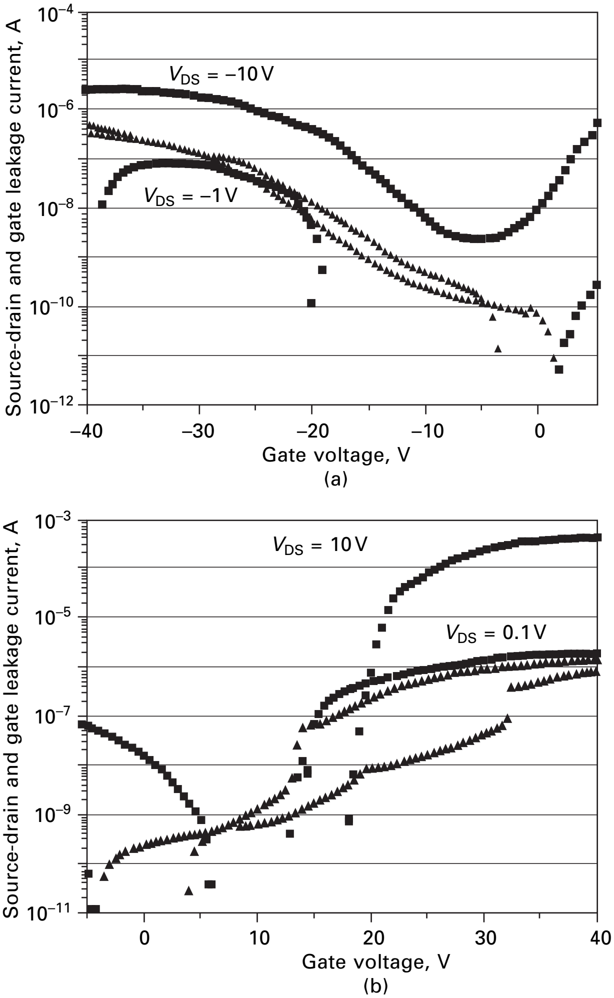


5. n^+ nc-Si region patterning

10. Al gate source/drain contact opening

14.12 Process sequence for fabricating a CMOS device on a flexible Kapton substrate. A nanocrystalline (nc) silicon seed layer is first deposited at 150 °C followed by the steps described above[49] © 2003 IEEE.

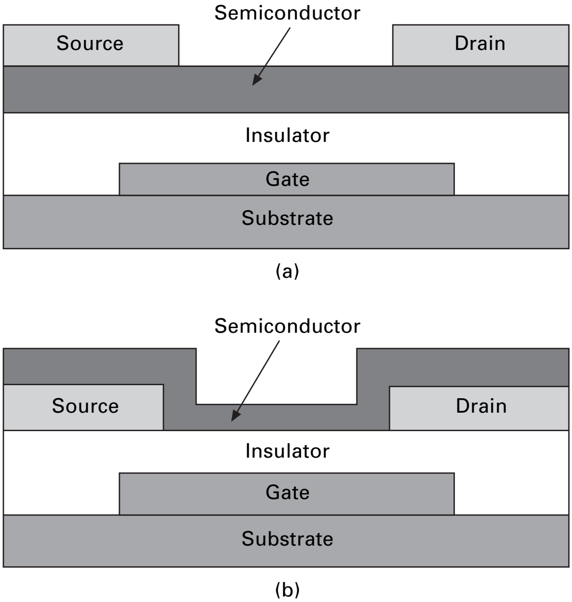
have lower mobilities as compared to those developed from inorganic single crystalline semiconductors and therefore cannot be employed for high-speed switching applications. Although these transistors are inferior to transistors developed on rigid single crystalline substrates, they offer a few advantages over hydrogenated amorphous and polycrystalline silicon-based thin film transistors. Potentially, organic thin film transistors could be developed at lower costs as compared to amorphous and polycrystalline silicon-based thin film transistors.[56] Moreover, the ability to develop organic transistors at room temperature can enable their fabrication on thin polymeric films, which



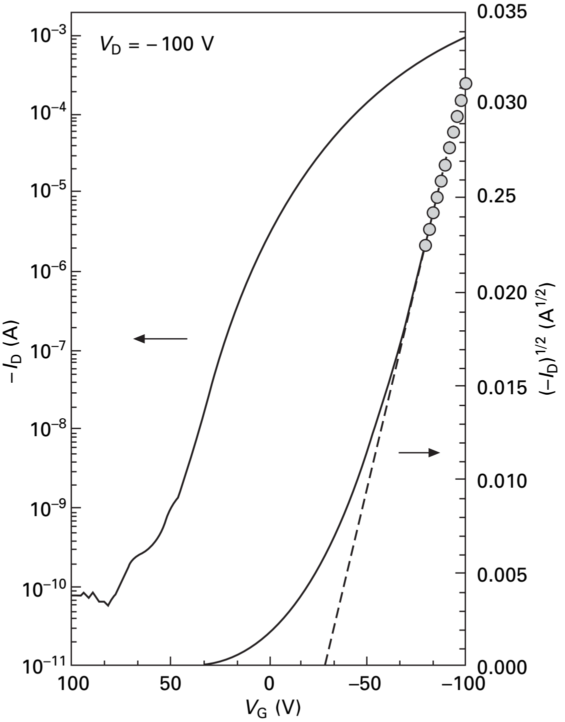
14.13 Transfer characteristics of (a) n-channel and (b) p-channel thin film transistors fabricated using a nanocrystalline hydrogenated silicon channel layer. The width (W) and length (L) of the channel were 200 and 30 microns respectively[49] © 2003 IEEE.

have a much lower glass transition temperature as compared to silicon or glass. This is in contrast to amorphous and polycrystalline thin film transistors which require processing at elevated temperatures of above 350 °C.

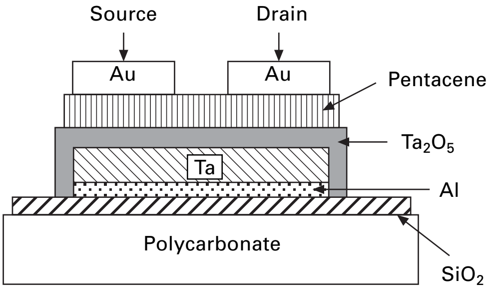
Some of the materials from which organic thin film transistors have been developed are polymers like Polyacetylene, Polythiophene, Poly(3-hexylthiophene), and Polythienylenevinylene or organic molecules like Pentacene and α-ω-dihexyl-quaterthiophene. Pentacene-based thin film transistors with a mobility as high as 1.5 $cm^2V^{-1}s^{-1}$ have been reported, whereas mobilities of polymeric thin film transistors are in the range of 0.045–0.22.[56] Pentacene based organic thin film transistors also demonstrate higher levels of on to off current ratios (I_{on}/I_{off}) as compared to polymeric thin film transistors. Two organic thin film device configurations are shown in Fig. 14.14. Transfer characteristics of a Pentacene-based organic transistor developed by Dimitrakopoulos *et al.*[57] are shown in Fig. 14.15. The mobility of this transistor was calculated from this plot as 0.16 $cm^2V^{-1}s^{-1}$. Inoue *et al.*[58] developed organic thin film transistors on flexible polycarbonate substrates by using Tantalum oxide as the gate insulator. Pentacene was used as the organic semiconductor channel layer material and the thickness of its layer was 50 nm. A layered structure of aluminum (50 nm) and tantalum (200 nm) was used for forming the gate electrode and the gate oxide was developed by anodizing the tantalum metal deposited as the gate electrode, as shown in Fig. 14.16. These organic thin film transistors demonstrated good transistor characteristics like low threshold voltage (approximately 1.1 V) and a low leakage current. Development of organic transistors on flexible substrates was also carried out by Yoshida *et al.*[59] and Bonfiglio *et al.*[60] Park *et al.*[61] also report developing organic thin film transistors using poly-3-hexylthiophene as the channel layer. However, much work remains to be done to ensure the environmental stability of organic transistors outside of laboratory conditions.



14.14 (a) Top-contact device, with an organic semi-conducting layer onto which source and drain electrodes are evaporated, and (b) bottom-contact device, with the organic semiconductor deposited on source and drain electrodes.[56]



14.15 Drain current I_D versus gate voltage V_G and $|I_D|^{1/2}$ versus V_G for a pentacene OTFT having a heavily doped n-type Si gate electrode, with L.4.4 m and W.1.5 mm.[56–57]

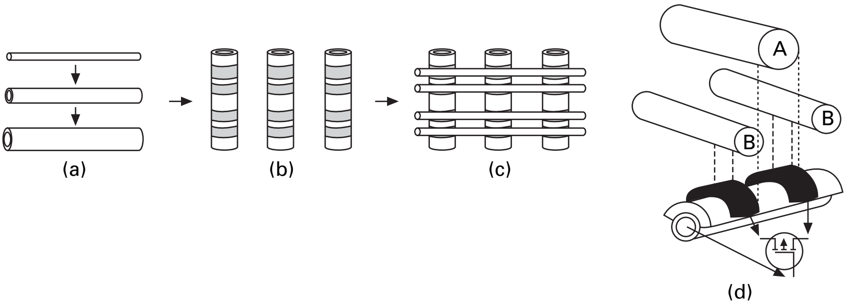


14.16 Structure of an organic thin film transistor developed on a flexible plastic substrate.[58]

Thin film transistors on threads or polymeric slit films

The development of transistors on threads is potentially exciting since it implies the possibility of the formation of integrated circuit structures in fabrics by appropriately forming interconnects using textile processes. However, this excitement should be tempered by the realization that forming the correct interconnections is a formidable task. One also would need to design the circuitry such that it is fault tolerant and able to withstand a much higher number of defects than circuits on a silicon chip. At this stage of technology development, transistor fabrication on fibers is a major step in electronic textile development and may provide a methodology for signal routing, signal amplification, sensing, or low-level computation within a textile.

Lee *et al.*[44,52] fabricated organic pentacene-based back-gated thin film transistors directly on fibers employing a weave-masking process as shown in Fig. 14.17. Conductive aluminum and stainless steel wires (125–500 μm) formed the gate of the transistor and these wires were coated with a thin layer of gate dielectric. Silicon-dioxide, deposited using low temperature chemical vapor deposition, and cross-linked poly-4-vinylphenol were used as the gate dielectric materials. A 150–250 nm silicon-dioxide layer was deposited at 450 °C employing the low-temperature chemical vapor deposition process and using a high ratio of oxygen to SiH_4 in the gas mixture. The fiber was coated with a poly-4-vinylphenol dielectric layer by preparing a poly-4-vinylphenol casting solution, adding poly(melamine-co-formaldehyde) cross-linking agent into the solution, and finally annealing and cross-linking the polymer at 100 °C and 200 °C respectively. The fiber was subsequently coated, via the evaporation process, with a 90 nm layer of pentacene as the channel material. Interconnections to the metallic core of the fiber, which forms the gate of the transistors, could be made anywhere along this coated fiber. The active areas of the transistor are defined by the over-woven masking fibers having a diameter of 50 μm. Channel length of these transistors is thus equal to diameter of the masking fiber (50 μm). Subsequently, 100 nm of gold is evaporated in the gaps between the masking fibers to form the source and drain pad regions. Contacts to the source and drain regions of the transistor

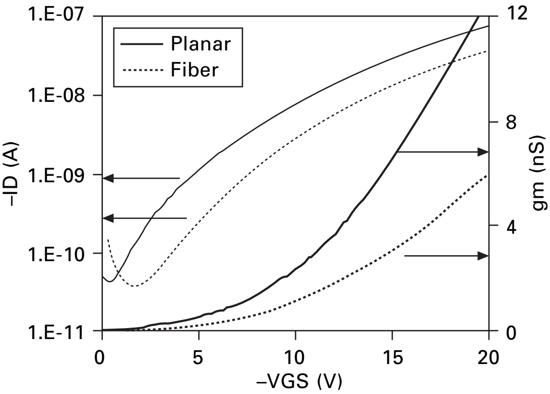


14.17 The process flow for developing transistors on fibers via the weave masking technique: (a) deposition of gate oxide and channel layers, (b) pattering of the source and drain pads employing overwoven fibers, (c) interconnections with orthogonal yarns, and (d) a schematic demonstrating the masking fibers A and the interconnect fibers B[44] © 2005 IEEE.

could be made by conductive lines woven into the fabric, orthogonal to the direction of the fiber containing the transistor. Transfer characteristic of these transistors are shown in Figs. 14.18(a) and (b). The fiber transistors, having silicon dioxide as the gate dielectric, had a significant gate leakage and a high defect density. High defect density of the silicon dioxide layer was primarily due to the high surface roughness of the substrate aluminum wires. This resulted in low dielectric strength and high low-field leakage current through the gate oxide layer. These fiber-based organic transistors exhibited mobility of approximately 0.5 $cm^2V^{-1}s^{-1}$.

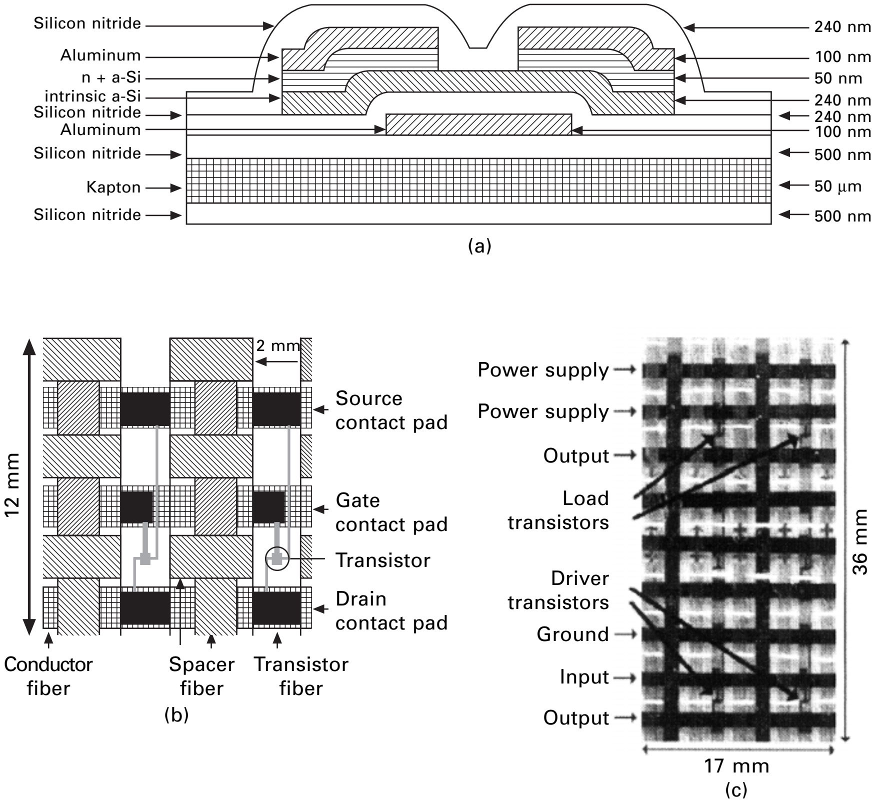
Gnade *et al.*[62] fabricated thin film transistors by depositing layers of n-doped and intrinsic amorphous silicon on silicon nitride films on flexible Kapton films employing plasma enhanced chemical vapor deposition. Gate, source and the drain gold contact pads were deposited by using the thermal deposition process and all the patterning was carried out using photolithography. These transistors exhibited a high threshold voltage of 4 V and a relatively high gate leakage current of 4 pA. Gnade *et al.*[62] and Bonderover *et al.*[63] described the development of yarn-like transistors by slitting films, with multiple transistors formed on it, into thin strips using the plasma etching process. These films were integrated into woven fabric structures as yarns. Gnade *et al.*[62] demonstrated formation of digital logic functionality on these woven structures by making appropriate interconnections, using conductive strips, between the different yarn-like thin-film transistors.

Bonderover *et al.*[38] have developed an integrated circuit prototype using amorphous silicon-based transistors developed on silicon nitride-coated Kapton films. A schematic of a thin film transistor, comprising of an intrinsic amorphous



14.18 Transfer characteristics for fiber-based and planar field effect transistors using the silicon-di-oxide gate dielectric. For the planar transistor, W/L = 250 μm/25 μm and gate oxide thickness = 220 nm. For the fiber transistor, W/L = 250 μm/25 μm and gate oxide thickness = 250 nm[44] © 2005 IEEE.

silicon-based channel layer, is shown in Fig. 14.19. Fabrication of these transistors is carried out at approximately 150 °C employing conventional processing methods. Multiple transistors are arranged in the form of columns on the wide film and individual transistor fibers are detached from this wide film by employing the slit-film technique. These thin film transistors have a threshold voltage of 7.5 V and carrier mobility of 0.13 $cm^2V^{-1}s^{-1}$. These slit transistor fibers are interwoven along with spacer fibers and conductive fibers to form an active load N-MOS inverter circuit having appropriate interconnections to the input, output, ground, and power lines. The inverter is reported to operate at frequencies of up to 1 kHz, the operation frequency being dependent on the time taken to turn the transistor on, which is in turn dependent on the overlap and gate capacitances of the circuit.[38]



14.19 (a) Schematic of a thin film transistor developed on a Kapton thin film, (b) schematic of arrangement of the conductor fibers, the spacer fibers, and the transistor fibers to form the transistors, and (c) circuit woven from active component fibers, a logic inverter[38] © 2004 IEEE.

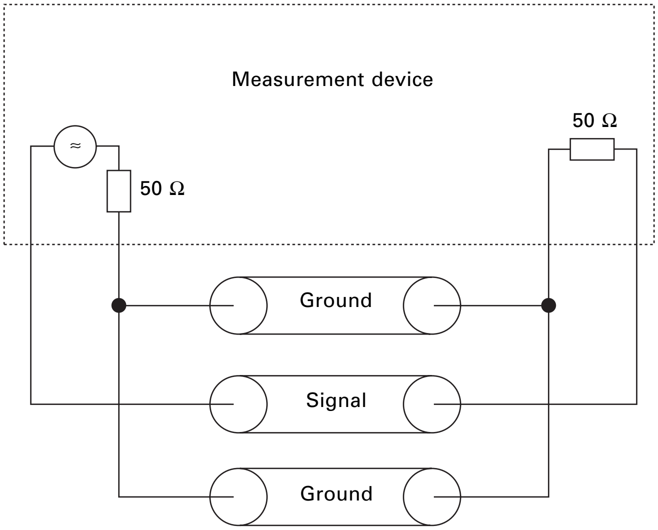
14.5 Characterization

Characterization of electronic textile circuits obviously involves evaluation of their electrical behavior. However, these being primarily textile structures, properties that are of value in a textile product may be of significant importance. These properties are flexibility, breathability, comfort, etc. These and other such properties may be more or less important depending on the application.

14.5.1 Evaluation of electrical properties

Resistance and impedance evaluations

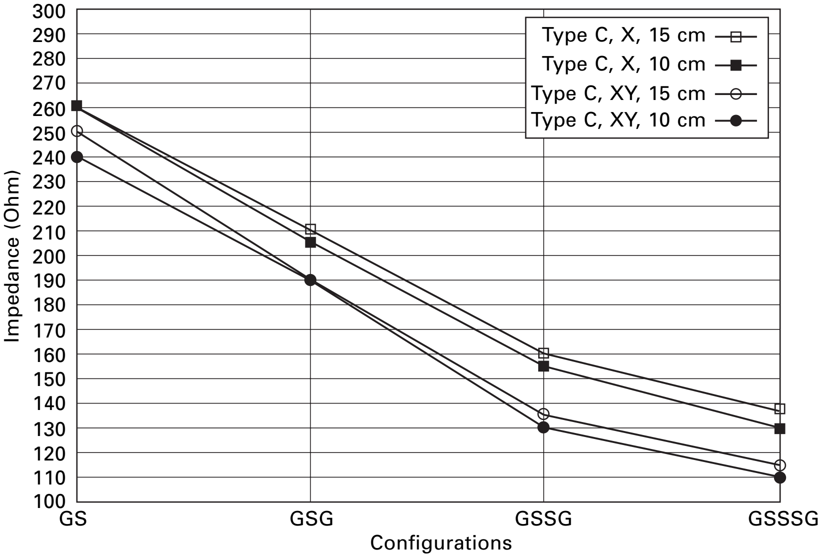
Kirstein *et al.*[18–20] applied methods of microwave technology to evaluate the frequency response of woven transmission lines and to develop a theoretical model to describe signal transmission in textiles.[19] Configurations similar to coplanar waveguides were developed in the woven circuits by weaving the copper-polyester yarns in the warp direction. In the coplanar waveguide structures, the signal line is surrounded on either side by ground lines to minimize parasitic coupling between neighboring signal-carrying lines. Electrical parameters like line impedance, insertion loss, far end crosstalk, etc., were determined for the different configurations of woven coplanar waveguides using time and frequency domain analysis. The impedance measurements were made by measuring the signal reflections along the transmission line with time domain reflectometry (TDR). The block diagram of the measurement setup is depicted in Fig. 14.20.



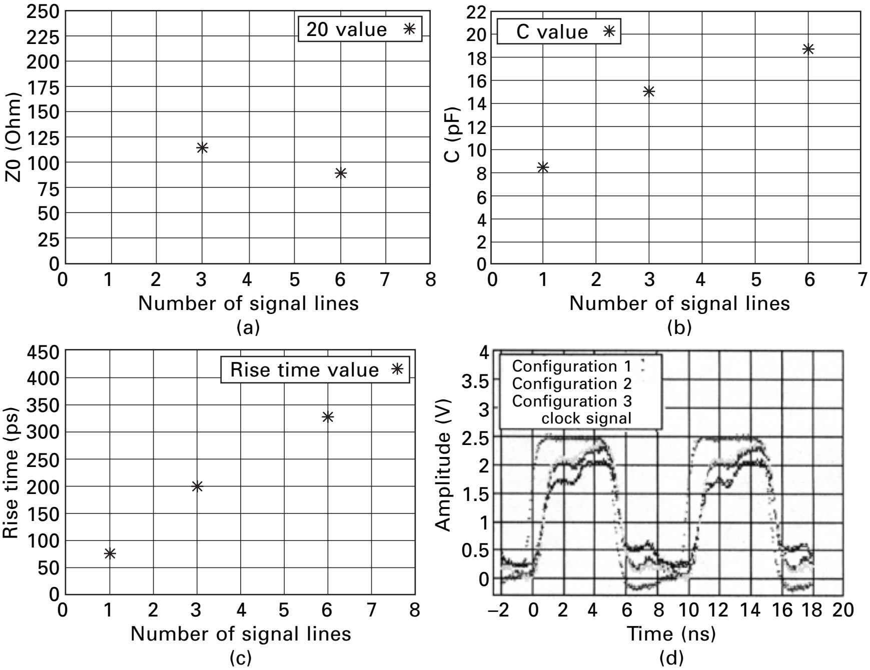
14.20 Setup to evaluate woven fabric-based transmission lines using time domain reflectometry (TDR)[19] © 2003 IEEE.

Reliable connection of the textile samples with the measurement equipment was made by connecting the fabric transmission lines with patterned solder pads on one side of a FR4 laminate on SMA connector on the other side. It was reported that when the GSSSG configuration was used, the value of coplanar waveguide impedance was lower as compared to the GSSG or GSG configurations as shown in Fig. 14.21. Moreover, it was observed that the impedance of the woven transmission lines showed variation with time and this was attributed to irregularities in the fabrics. Based on the measured values of impedance, inductance, capacitance, and resistance for the different transmission lines, a theoretical transmission line model was also developed through simulation using the SPICE software.[19] Kirstein *et al.*[18] evaluated the impedances, capacitances, signal rise times, and output signal profiles of three configurations of textile-based co-planar waveguides – the first configuration consisting of two ground (G) lines enclosing one signal (S) line, the second consisting of two ground (G) lines enclosing three signal (S) lines, and the third consisting of two ground (G) lines enclosing six signal (S) lines. Variation of these parameters as a function of number of signal lines in the textile-based coplanar waveguides is shown in Fig. 14.22 and is attributed to dependence of transmission line properties of coplanar waveguides on the width or number of signal lines and spacing between signal and ground lines.[18]

Circuits were developed by Dhawan *et al.*[11–16] on a rapier weaving machine by weaving conductive threads into a fabric in order to interconnect electronic



14.21 Impedance measurements for different woven transmission lines.[20]



14.22 Variation of the following properties of a textile-based coplanar waveguide transmission line as a function of number of conductive signal threads in the coplanar waveguide – (a) characteristic impedance, (b) line capacitance, (c) signal rise time, and (d) output signal for a 100 MHz clock input signal.[18]

devices placed at different points on the fabric. In order to route the signals in these circuits interconnections were developed between orthogonal conductive threads (crossover point interconnections) employing different techniques like resistance welding, adhesive bonding, air splicing, and soldering. In order to evaluate the resistance of the crossover point interconnects, Dhawan *et al.*[11–16] employed two-point probe resistance measurements using a multimeter. Four-point probe measurements of these fabric circuits were also investigated. DC resistance values of the fabric samples having welds at the crossover points, were found to be less than those for woven copper samples without any weld. Impedance values of the different crossover point interconnects were also determined by measuring AC signal (square wave) reflections from the crossover point interconnects. Slade *et al.*[28] also reported DC resistance evaluations of conductive fabrics using the four-point probe measurement system. They measured the resistance of one inch by one inch conductive fabric samples employing four-point probe measurements on an HP LCR meter. The conductive fabrics evaluated by them included metal-coated fabrics and fabrics woven from metal-plated and metal-foil wrapped yarns. The four-point probe technique is conventionally employed for characterization of semiconductor devices and materials and has been described by Runyan *et al.*[64] and Schroeder.[65]

Signal integrity issues

Researchers working in the area of electronic textiles realize that there are numerous challenging issues to be addressed like achieving reliable and robust interconnect formation, improving signal integrity (crosstalk noise), maintaining textile characteristics (lightweight, flexibility, strength, conformability, etc.), providing efficient means of power generation/harvesting, and addressing washability and weatherability for wearable electrotextiles.[66–68] In order to study and evaluate AC signal crosstalk noise in woven circuits, Dhawan *et al.* used AC signals varying between 10 KHz–15 MHz on woven transmission lines (called aggressor lines) and evaluated the effect of these signals on the neighboring quiet lines (carrying no signal).[12,66–67] They observed that the magnitude of crosstalk noise increased as the spacing between the conducting lines is decreased, see Fig. 14.1. Moreover, as the frequency of the signals transmitted through the aggressor line is increased, the magnitude of the crosstalk noise also increased. Coaxial transmission-line-like thread structures were developed by wrapping an insulated conductive thread with a conductive thread and twisted-pair thread structures were developed by twisting two insulated copper threads. Dhawan *et al.* also observed that there was a significant reduction in crosstalk noise when twisted-pair (see Fig. 14.1) and coaxial yarns were used to form these circuits.

Crosstalk noise, i.e., noise induced on a quiet line or a signal line due to change in signal on neighboring signal-carrying lines, between two neighboring signal lines was evaluated by Kirstein *et al.*[18] and it was reported that the value of crosstalk reduced substantially if the neighboring signal lines were separated by a ground line.[18]

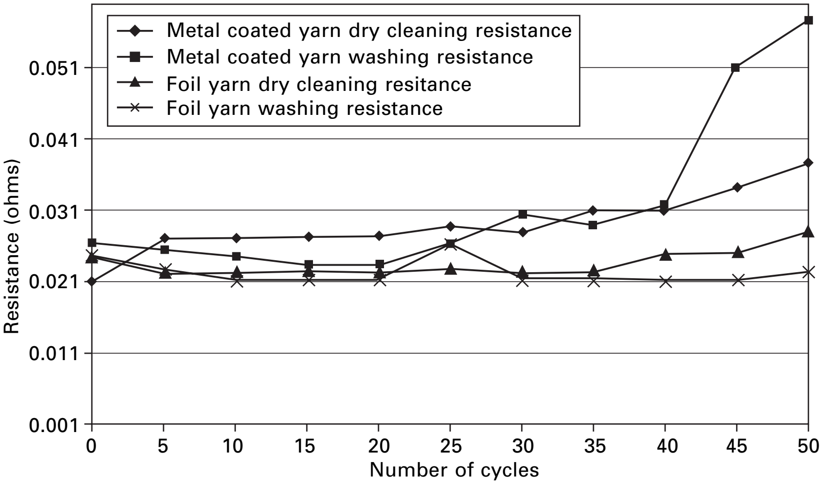
14.5.2 Mechanical properties

Several researchers have investigated the physical properties of fabric-based circuits for their mechanical and endurance characteristics.[5,28,69–70] Some researchers have evaluated the mechanical properties to determine the lifetime of these fabric circuits, when used in everyday life. The effect of flexing, bending, or abrasion on electrical properties of these circuits have also been evaluated.

The effects of washing and dry-cleaning on the electrical properties of conductive fabrics were evaluated by Slade *et al.*[28] The fabrics evaluated by them included narrow fabrics woven from Ni-Ag-Cu coated fibers and Ag-Cu metal foil wrapped yarns and metal-coated fabrics shown in Table 14.1.

One of the metal-coated fabrics evaluated by them was FlecTron, a polyester fabric on which copper and nickel were deposited by electroless plating. The narrow-woven conductive fabrics and the metal-coated fabrics were washed in a commercial washing machine ten times and then dried in a dryer for 40 minutes. The washing cycle included a hot wash and a cold rinse cycle using bleach powder and detergent. After the wash and drying cycles, fabric samples were evaluated for electrical resistance using a four-point probe measurement system on an LCR meter. This procedure was carried out 50 times. Similarly, the conductive fabric samples were dry-cleaned ten times and the electrical resistance was measured. This procedure was also carried out 50 times. The conductive material was removed from the fabric surface when the metal-coated fabrics were washed or dry-cleaned. SEM images of the fabric samples also confirm that metal-coated fabrics are more abraded as compared to the fabrics made from foil-based yarns. The resistance values, as seen in Fig. 14.23, for conductive fabrics made from metal-coated yarns increased as more washing and dry-cleaning cycles were performed while those made from foil-based yarns had very little increase in resistance. The main reason for increase in resistance of conductive fabrics made from metal-coated yarns is that some of the coating material was abraded and removed on washing and dry cleaning.

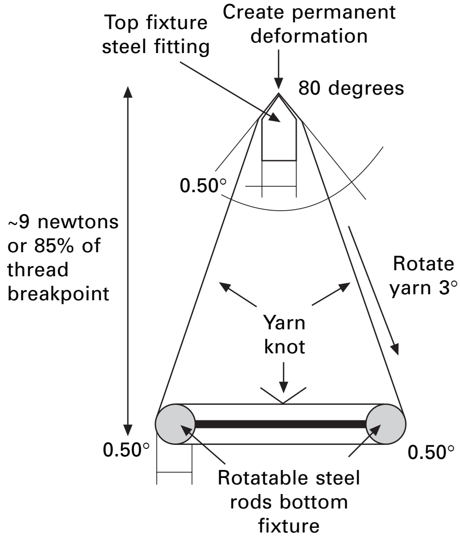
Conductive threads used for making fabric-based circuits need to have certain characteristics depending on the process employed for making the fabric circuits. As mentioned earlier, for sewing and embroidery of conductive threads high levels of flexibility and tenacity are desired. The conductive threads have to withstand high levels of stresses that are involved in the



14.23 Increase in resistance as a function of wash cycles for woven conductive fabrics made from different conductive yarns.[28]

process of sewing or embroidery.[5] They also need to be flexible as they have to change shape a number of times to unwind from the bobbin and to form loops. Orth[5] evaluated mechanical properties of conductive threads that are used for producing embroidered circuit fabrics. The objective of her research was to observe if the conductive threads are permanently deformed if they are bent and loaded in a manner shown in Fig. 14.24. This testing procedure was labeled as the 'Curl test' by Orth[5] and involved running a yarn loop over a top metal point fixture and under two rotatable steel rods to provide tension, looping, and rotation of the thread by a certain distance. The yarn loops were loaded to around 85% of the breaking load of the yarn, reloaded to 50–90% of the original loading, and then removed and monitored for machine sewability. The yarns were considered machine sewable only if the loop diameter was less than 1/16 inch and the ratio of the loop diameter to the loop length (loop aspect ratio) was less than 1/3. It was determined that a 100% continuous stainless steel yarn was not suitable for sewing due to the large diameter of its loops and a loop aspect ratio close to 1. Similarly, a steel-polyester composite yarn containing 70% non-continuous steel fibers and 30% Kevlar was found to be unsuitable for sewing. A steel-polyester composite yarn, containing 20% non-continuous stainless steel fibers and 80% polyester fibers, and a rayon embroidery thread were considered machine sewable according to the criteria described above.

Slade *et al.*[69] carried out tests for tensile fatigue and tensile strength of fabric-based USB cables. The USB cables were developed by them by integrating 28 AWG twisted pair copper wires into narrow woven fabrics and



14.24 The 'Curl test' used for measuring the permanent deformation of conductive threads upon bending and loading.

passed group 6 signal integrity test requirements. The tensile fatigue and tensile strength of these USB cables were carried out on a strength tester using a load profile that varied from 0 to 250 pounds for 5,000 to 40,000 cycles. The test results showed that these USB cables passed signal integrity tests even after 40,000 cycles of loading and unloading and that the first version of the USB cable developed by Slade *et al.*[69] had an ultimate strength of nearly 2,000 lb. These USB cables were also tested for bending fatigue resistance under a load of 250 pounds and passed signal integrity testing after 35,000 cycles. Moreover, Slade *et al.*[69] carried out abrasion testing by draping a length of cable over a hexagonal steel bar such that one end of the cable was attached to an oscillating drum while the other was attached to a two-pound weight. The abrasion test indicated that the power conductor wires protruded from the USB cable fabric after 1,000 abrasion cycles and the shielded twisted pair wires after 4,000 cycles.

The mechanical properties of fabric-based electrical circuits are determined not only by the structure of the fabric but also by types of fibers, films or yarns forming these circuits. As the mechanical properties of the conducting and non-conducting elements of fabric-based circuits are very different, one has to ensure that the best electrical characteristics of fabric circuits are achieved without sacrificing the often desirable physical characteristics like conformability and flexibility. Slade *et al.*[70] developed a number of different kinds of textile-based USB cables and evaluated them for their bending stiffness. They developed a flexible USB cable with shieldings of braided conductive threads. In the USB cable called USB v3.0, the inner conductors were made up of insulated metal-clad textile-based yarns shielded by a flexible braided shield made from metal-clad textile-based yarns. The different USB cables were tested for their bending stiffness using a heart loop test (FED STD 191A-5200). This standard textile test procedure was slightly modified to measure bending stiffness of electronic circuit fabrics. The procedure involved making deflection measurements as weights were applied. In order to ensure accuracy, an optical comparator was employed to make the deflection measurements instead of a ruler. Load-deflection curves were obtained from these measurements. Their results indicated that the USB cable called USB v3.0 was less stiff as compared to the cable called USB v2.0, which had copper inner conductors with a foil shielding. The USB v3.0 cable was not only flexible but also exhibited a shielding effectiveness that complied with USB specifications for signal frequencies lying in the 30 MHz–1 GHz range.

14.6 Applications

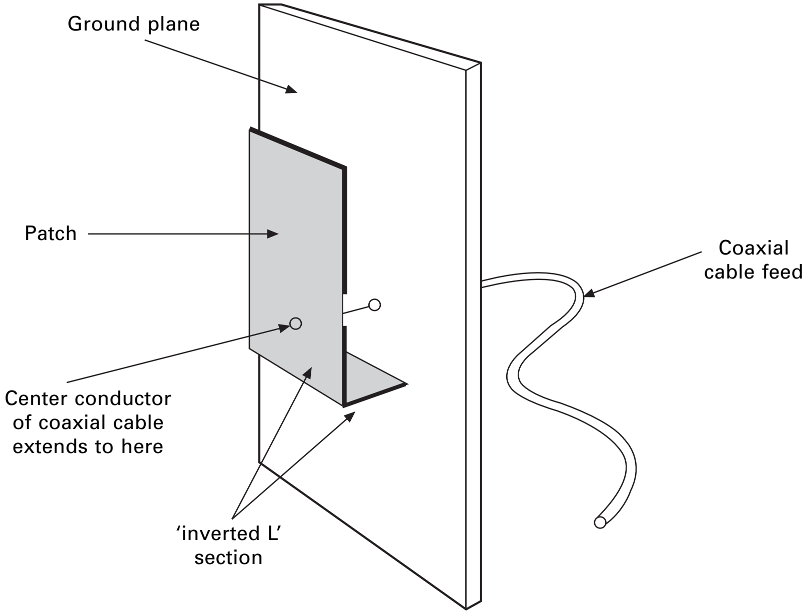
14.6.1 Fabric-based antennas

Loop antennas, helical antennas, whip antennas, patch antennas, thin wire dipole antennas, cylindrical dipole antennas, and biconical antennas are some of the different kinds of antennas developed on rigid substrates.[71–78] Antennas are characterized on the basis of properties like radiation pattern, beam width, radiation intensity, directivity, gain, efficiency, impedance, range, quality factor, and loop inductance.[76] Currently, research is being carried out to develop antennas on flexible and conformable fabric substrates so that easily deployable large-sized antennas or arrays of antennas could be fabricated.[74–78]

Slade *et al.*[74] and Massey *et al.*[75] have described the development of fabric-based dual loop antennas. Antennas described by Slade *et al.*[74] were based on the Merenda antenna design developed by BAE systems. The design consists of two loops that are orthogonal to each other. These antennas produce a nearly spherical radiation pattern and are operational in the 30–88 MHz frequency range. The biggest advantage of employing these antennas is the decrease in consumed power as compared to conventional antenna technology. This dual loop antenna was formed on a fabric attachment of conductive fabric strips incorporated in a vest so that two orthogonally intersecting loops are formed.

Slade *et al.*[74] have also developed loop antennas that could be integrated into pockets or flaps of battledress uniforms. These antennas were employed for signal transmission or reception in the 225–400 MHz frequency range. Conventional loop antennas that are developed on chips and rigid circuit boards are small and have a very high electrical loss resistance. In order to have a lower value of loss resistance as compared to radiation resistance, large sized loops of the antenna are desired. Fabricating antennas on fabric substrates provides the ability to develop very large sized antennas as fabric circuits (with the antenna pattern) several meters long and can be easily developed on woven or non-woven substrates.

Massey[71] reported the development of patch and planar inverted F antennas on textiles.[71–73] These patch antennas could be integrated into several parts of a textile garment such as the shoulders or the back.[72] Planar inverted F antennas consist of a conducting patch, which is connected to the center conductor of a coaxial feed cable as shown in Fig. 14.25. The conducting patch has an inverted L section that is connected to the ground plane. The conducting patch and the ground planes were developed by electroless plating of a rip-stop nylon fabric with copper. It was reported that the patch could also be developed by coating of knitted fabrics. These planes were separated from each other by a thin foam layer. The ground plane in the patch antenna isolates the electromagnetic fields of the human body (wearing the textile-based antenna fabric) from those of the antenna. A coaxial cable feeds transmitter or receiver signals to the patch antenna by connecting its center conductor to the conducting fabric patch and its outer conductor to ground. Massey[71] has reported that efficiency of the fabric-based patch antennas can be improved by having better impedance matching between the feed coaxial



14.25 Planar inverted F antenna consisting of an inverted L section of a conducting patch, a ground plane, and a coaxial cable feed[71] © 2001 IEEE.

cable and the patch antenna. The distance between the point, where there is a short between the patch and the ground plane and where the coaxial cable joins the patch, was optimized to obtain the best value of impedance matching in these antennas.

14.6.2 Sensors

Patent number 6341504[79] describes the development of an inductive sensor that is based on integrating conductive threads into a stretch fabric in the form of loops. These loops change dimension when the fabric is stretched, thereby leading to a change in inductance of the loops. This inductive sensor fabric is used as a device to monitor the physiological characteristics of patients. A commercial product called life-shirt, based on an inductive sensor, has been developed by Vivometrics[80] and this shirt simultaneously monitors several parameters without affecting the patient.

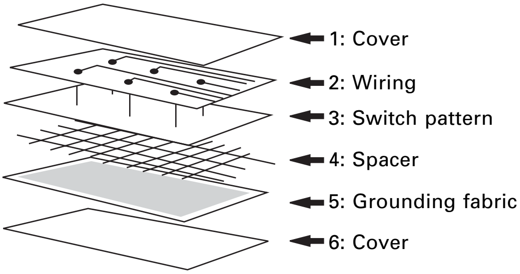
De Rossi and his coworkers[81–85] at the University of Pisa have done some of the pioneering work in the area of strain sensing using textile substrates. Their work is relevant for many applications including motion sensing and physiological monitoring. De Rossi *et al.*[81] demonstrated remarkable strain and temperature sensing capability of conventional elastomeric fabrics coated with a thin layer of conducting polymer polypyrrole. They demonstrated the piezoresistive properties of these fabrics by fabricating a sensing glove. The change in resistance caused by fabric strain due to finger movement was measured. Lorussi *et al.*[83] applied the same concept to instrument a sensing sleeve that is capable of sensing body posture. They used printed carbon-filled rubber layers on fabric and created an interconnected array of sensors to determine the surface strain fields induced by movement. The composite material used in the sensor fabrication has an appropriate level of conductive particles embedded in an elastomeric binder. Resistivity of the composite is altered due to application of pressure.

Various sensing devices and systems compatible with textiles (or sometimes textile based) for continuous monitoring of physiological and behavioral parameters for health care have been proposed.[84–87] In all cases use of functionalized materials enabled design and fabrication of sensors and electrodes. Scilingo[84] reported using knitted fabrics made of stainless-steel-wrapped viscose yarn as electrodes to monitor electrocardiogram and electromyogram signals. Additionally they also reported using elastic fabrics coated with carbon-loaded rubber to monitor respiratory changes. Similar efforts to design electrodes and strain sensors for health monitoring have also been reported by Paradiso *et al.*[86]

Jones[88] has also developed flexible tactile sensor fabrics that show substantial resistance change when compressed. A composite material, made up of metal particles embedded in an elastomeric binder, is employed to form this sensor. On application of force to the composite material, metal particles move closer to each other, leading to greater quantum tunneling between the conducting particles. This leads to a substantial reduction in the measured resistance of the sensor fabrics.

Inaba *et al.*[89] have developed fabric-based tactile sensors that are distributed on the body of the robot. This sensor suit has 192 sensing regions and each of these works as a switch, i.e., it allows current to flow wherever pressure is applied on the garment in that region. The tactile sensor fabric consists of six layers of fabric as shown in Fig. 14.26. On applying pressure to the sensor fabric, an electrical contact is made between the switch pattern of one of the layers of the sensor and the ground layer, thereby completing the circuit. The electrical signal produced upon application of pressure to the sensor fabric is multiplexed on a video signal to produce sensor images.

Capacitive and resistive fabric-based weight sensors for automotive seats have been described by Gilbert *et al.*[90] Such weight sensors could be employed for controlled deployment of automotive airbags in accordance with weight of the occupant sitting on an automotive seat. The capacitive weight sensor comprises a foam layer between two conductive fabric layers. When pressure or weight is applied to the top fabric of this sensor assembly, the foam layer is compressed and the capacitance between the conductive fabrics is changed.



14.26 Structure of a tactile sensor made of an electrically conductive fabric[89] © 1996 IEEE.

Hence, change in the value of the capacitance between the two conductive fabrics is employed to detect the change in thickness of the foam layer between the conductive fabrics. Gilbert *et al.*[90] also describe the development of a resistive weight sensor. In this application, a compressible foam layer having a series of holes is placed between two conductive fabric layers. On application of force on the fabric, contact between the top and bottom conductive fabrics is made. This leads to a decrease in the measured resistance between the two conductive fabric layers, which can be measured.

Textile-based acoustic sensor arrays have been developed by Luthy *et al.*[91] and Grant *et al.*[92] for accurate tracking and location of targets via beam-forming and triangulation. These acoustic arrays act as a passive listening system where the sensitivity can be directed in a particular direction similar to the passive sonar system present on submarines. The acoustic arrays can be employed for detection of vehicles, aeroplanes, or troop movements. When using the time delay triangulation method the location of the origin of gunshots can be detected. Fabric-based acoustic arrays can be easily and quickly deployed, be camouflaged to suit the surroundings, and have the ability to flex and conform to the surroundings. They can also be integrated into tents and fabric vehicle covers. They fabric-based acoustic arrays (5 × 4 arrays) were developed by weaving (using a jacquard weaving machine) conductive elements, like twisted-pair yarns and copper wires, into large area textile substrates and subsequent attachment of microphones at certain locations.

14.7 Potential for the future

The field of electronic textiles has advanced to the point where increasingly more sophisticated products are being marketed. At the last Techtextil Exhibition (2005) in Frankfurt there were at least eight different companies showing their electronic textile products. However, the products are limited to a few areas of flexible input devices (keyboards, etc.), limited vital sign monitoring devices, and others. The vast potential of electrotextiles in areas of military, biomedical, homeland security/public safety, transportation, consumer products, and other applications are not yet explored.

One of the key elements in the integration of electronics in textiles is textile-based circuits and relevant interconnect technologies. Some of the challenges obviously are materials related. Development of better polymer-based conductive fibers is essential to this effort. Additionally, development of robust and reliable interconnect technologies compatible with polymer/textile materials are key in the realization of the full potential of electrotextiles. There are obviously other challenges, conductive fibers and yarns in fabric-based circuits do not maintain fixed positions compared to rigid circuit boards or an integrated circuit. There are problems encountered in forming continuous ground planes between different layers of the multi-layered fabric circuits. Signal integrity problems such as variability of signal noise due to crosstalk or simultaneous switching associated with these must be addressed. Better fabric circuit design including computer-aided design tools to lay out the fabric circuits, as well as development of appropriate fault-tolerant yarn and fabric structures are needed.

Potential application of electrotextiles is numerous. It spans through all the segments where textile materials or products are used today and beyond. Most of the applications proposed in the literature seek to multi-functionalize existing textile products, e.g., heated undergarments. Other proposed applications, such as a flexible keyboard is entirely new. Textile-based circuits are particularly attractive for very large area applications, e.g., deployment of sensors, for its light weight and ease of deployment and removal.

Much of the ongoing research in the area of textile-based electrical circuits is likely to pave the way toward development of flexible and conformable integrated circuits entirely from textile-based materials. Development of fiber/yarn based transistors would potentially allow switching in textile circuits. These transistors then may be configured to form inverters, gates and eventually, large-scale integrated circuits on fabrics. The eventual goal is to turn existing trends in hanging mostly silicon-based hard devices on textiles into truly conformable, rollable, washable, and sometimes wearable form.

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15

Stability enhancement of polypyrrole coated textiles

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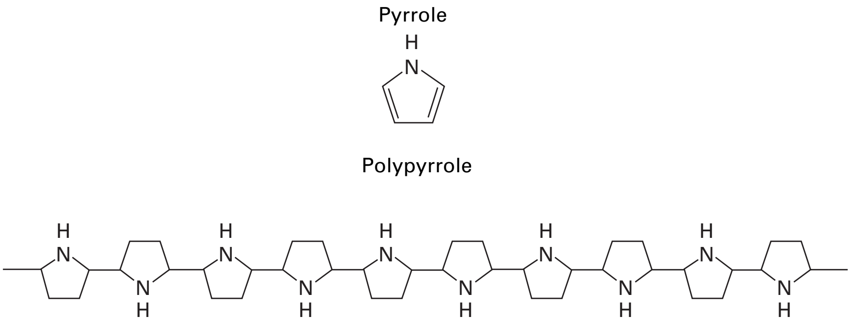
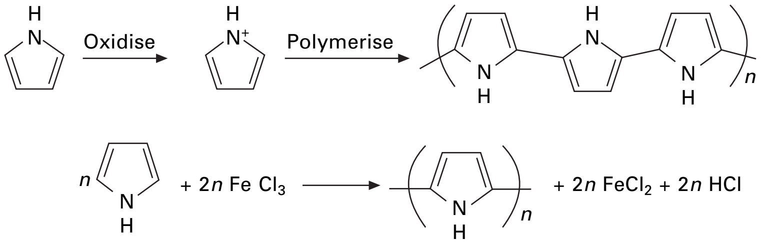
15.1 Introduction

Polypyrrole (Ppy) has been widely developed for actuators, chemical sensors, biomaterials, batteries, gas separation films, etc., owing to its easy preparation, good conductivity and non-toxicity.[1–7] When it forms composites with a number of fabrics, the obtained electrical conductivity can also be used in the field of electromagnetic insulation and microwave absorbance, etc. This is mainly due to the combination of the mechanical properties of the flexible fabrics, electrical and microwave properties, and bio-compatibility of the Ppy coatings.[8–12] In recent years, it has been found that the conductivity of the Ppy-coated fabrics is sensitive to strain deformation leading to the development of different sensing devices to measure and control the various movements of the human body for training, shape analysis or rehabilitation.[10,13–16] However, Ppy-coated textiles exhibit the problem of relatively low sensitivity and stability. The Ppy-coated Nylon-spandex shows a strain sensitivity $\left[\frac{\Delta R}{\varepsilon R_o}\right]$ of only about 2 for a deformation of 50%[13] and 3 for the Ppy-coated PET/Spandex.[10] They are also sensitive to external stimuli during applications. The stabilisation enhancement, without a great sacrifice of initial conductivity and, more importantly, the strain sensitivity, becomes a critical analysis.

Polypyrroles are formed by the oxidation of pyrrole or substituted pyrrole monomers as shown in Fig. 15.1. Electrical conductivity of Ppys coating or film involves the movement of positively charged carriers or electrons along their polymer chains or hopping of carriers between chains. The conductivity of Ppy can range up to 10^2 Scm^{-1}. With the inherently versatile molecular structures, Ppys are capable of undergoing many interactions. Oxidation of polypyrrole can be carried out either by (i) electro-polymerisation at a conductive substrate, i.e., electrode with an external potential applied, (ii) chemical polymerisation in solution or (iii) vapour deposition by means of a chemical oxidant.[17] In order to obtain a wide variety of chemical and electrical properties of polypyrrole, the control of fabrication condition and selection



15.1 Polymerisation of polypyrrole.



15.2 Polymerisation process of pyrrole and $FeCl_3$.[18]

after treatments is critical. The mechanical properties of Ppy vary widely from strong, tenacious materials to extremely brittle ones, depending on the chemical structure, fabrication condition and the application environment. The polymerisation process of polypyrrole based on the oxidative transition of metal ions, ferric chloride ($FeCl_3$), is summarised in Fig. 15.2.

15.1.1 Electrical properties – conductivity

The electrical properties of conducting polymer coated textiles are important as they can help determine the ability of polymers to transfer electrical signals along the conductive structure, store information, trigger responses, convert and store energy. Electrical conductivity in Ppy films involves movement of positively charged carriers or electrons along polymer chains and hopping of carriers between chains. The experimental parameters encountered during synthesis have an influence on the polymer conductivity. In electrochemical polymerisation, the solvent, counterion and monomers used during synthesis influence the electrical properties of the resulting polymer. By employing different metallic salts, such as $FeCl_3$, $Fe(NO_3)_3$, $Fe(ClO_4)_3$, $Fe_2(SO_4)_3$, etc., in polypyrrole polymerisation, the conductivity of polymers ranging from 10^{-5} to 200 Scm^{-1} can be obtained.[18] However, the quality of the Ppy conductive coating may be reduced by the presence of nucleophiles during polymerisation. Water itself is a nucleophile, attacking the pyrrole ring to form carboxyl groups that break down the polymer chain and lead to a decrease in conductivity and mechanical properties.[23] The presence of a small amount of water affects the rate of polymer growth and its resultant conductivity.

15.1.2 Chemical properties

The chemical properties of polymer structures determine the response of the conductive textiles to the external stimuli. Ppys are inherently versatile molecular structures, capable of undergoing many interactions such as Ppy/Cl, Ppy/dodecyl sulphate and Ppy/polyacrylic acid.[19] They are particularly strong anion exchangers that are capable of undergoing hydrophobic interactions. Other ion exchange groups such as carboxyl groups or self-doping sulfonate groups can be added to the pyrrole monomers prior to polymerisation. As polymerisation of polypyrrole can be carried out in aqueous solutions, it enables a wide range of counterions to be incorporated into the structure. Since the crystallinity of polypyrrole chains in all forms of fabrication are low,[20] polymerisation of polypyrrole mainly occurs at the α-carbons. This is the ideal Ppy chain formation with the spatial orientation of pyrrole moieties along the main chain, while the pyrrole units alternate in a planar arrangement to form, ideally α-α couple polypyrrole. However, magic angle spinning NMR and IR techniques indicate the involvement of β-carbons in the bonding of most polymers, which denotes the presence of branching.[18] Diffraction patterns of Ppy chains are not oriented parallel to each other as those of poly (β,β'-dimethylpyrrole) but aligned at random.[21] These variations in mechanical, chemical and electrical properties of the Ppy-coated fabrics as well as their strain sensitivity are governed by structural chain orientation but can be controlled by fabrication conditions. As reported by Oh *et al.*[13] the Ppy-coated Nylon-spandex showed a strain sensitivity $\left[\frac{\Delta R}{\varepsilon R_o}\right]$ of only 2 for strain deformation of 50% and Kim *et al.*[10] developed the Ppy-coated PET/Spandex strain sensors with strain sensitivity up to 3 for a large strain deformation of 50%. However, by modifying the fabrication conditions and a combination of sequences of after-treatments, we can develop the e-textile strain sensors with strain sensitivity up to ~120 or higher.[22]

15.1.3 Mechanical properties

The mechanical properties of Ppy coating on textiles vary widely from strong, tenacious materials to extremely brittle ones.[23] Mechanical properties including tensile strength, and elongation to break are affected by the polymerisation conditions. It was reported that there was a decrease in tensile strength and breaking elongation as the polymerisation temperature was decreased.[17] Apart from the solvent used during polymerisation and before chemical vapour deposition, different types of counterion used as well as the wet pick up of the solutions containing oxidising have an influence on the molecular weight of the Ppy films, degree of cross-linking, molecular order, conductivity and resistance to environmental effects.[64]

The aim of this chapter is to review the degradation of the Polypyrrole coating due to both intrinsic and extrinsic changes as mentioned in Section 15.2. The stabilisation methods developed by others through pre-ageing treatments for extrinsic instabilities and the control of fabrication for intrinsic instabilities are discussed in Section 15.3. Extrinsic pre-ageing treatment includes acid and alkaline treatment, as well as annealing processes[24,25] while intrinsic modifications of the polypyrrole films includes the applications of dopants or metal ions during the fabrication process or voltage applications.[26,46] In Section 15.4, a method of producing Ppy-coated textiles with high strain sensitivity and good stability is discussed. The newly developed method includes the combination of new fabrication processes such as the method of printing and chemical deposition, large anions dopants application and low-temperature after-treatments including purification and annealing processes.

15.2 Conductivity changes of polypyrrole films on textiles

The electrical conductivity of Ppy is ascribed to electrons hopping along and across polymer chains with conjugated double bonds.[26] The higher electrical conductivity of Ppy is due to the presence of a larger number of positive charge carriers. This is related to the doping or oxidation level of the polymer. In general, the presence of higher positively charged ions in the Ppy chains will result in more polarons being available, together with longer and parallel polymer chains which contribute to a higher level of conductivity.

As the mobility charges or number of the charges varies, the conductivity of polypyrrole also changes. The theoretical mechanism of the mobility of charges in Ppy is governed by the conjugation length of Ppy polymer chains and the distances between inter-chains.[27] Basically, the conductivity of the e-textile sensors and their stability are influenced by both or either intrinsic or extrinsic factors in nature.[28]

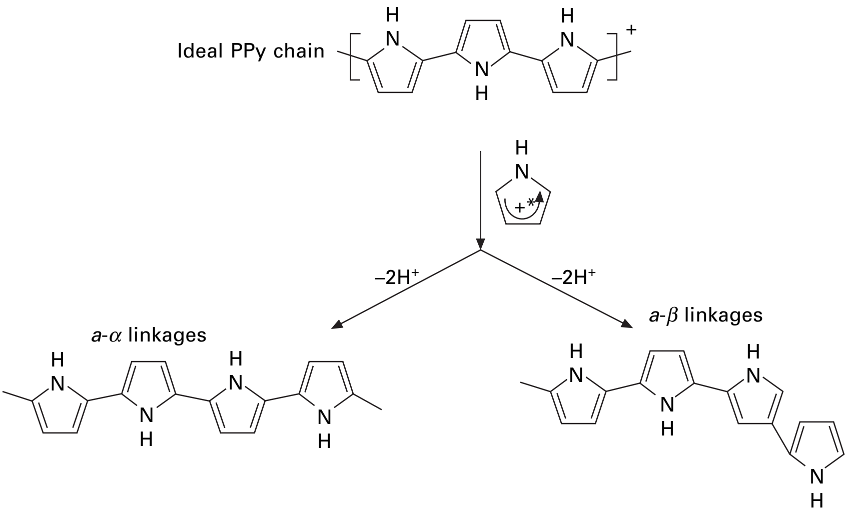
15.2.1 Intrinsic instability

Intrinsic instability is mainly dealt with by conformation changes in the polymer backbone activated during the thermal annealing process. The charged sites may be de-stabilised by oxidation which completely reverses the doping or undoping process. The oxidation of Ppy is more vigorous at high temperature, typically at temperatures higher than 230 °C.[29] This kind of effect is thermodynamic in origin and causes irreversible chemical reaction between the charged sites of the polymer chain and the dopant counterion or the π-system of an adjacent chain. Instability caused by thermal ageing may be due to the loss of structural order of the polymer backbone caused by oxygen attack on the counterion to the Ppy backbone. This irreversible chemical reaction introduces sp^3 defects along the polymer chain causing the irreversible breakage of the conjugation. As a result, the resultant polymer consists of a variety of conjugation lengths which will greatly reduce its conductivity.[30–33] Furthermore, other mechanical structures of the Ppy films including both thickness and surface morphology are also critical. In general, the Ppy films with higher conjugation lengths and doping level in the polymer backbone are characterised by higher molar mass and higher thickness. This type of film benefits by reducing the permeability of the Ppy films to external stimuli like oxygen and water. Experimental investigations have identified the proper fabrication methods including dopant applications, types of solvent, applied voltage, concentration of chemicals, and reaction temperature that can control the mechanical structures of the Ppy.[18] Longer deposition time, lower applied potential and reaction temperature, and higher concentrations of monomer and electrolyte are favourable for the conductivity and stability.[18]

15.2.2 Extrinsic instability

The instability of Ppy in ambient conditions is due to the reaction of the polymer backbone with oxygen, water or damaging radiation that lead to an irreversible loss of conjugation and conductivity.[24,26,29,34–38] This attack comes from the external environment, and is called 'extrinsic instability'.[30,32,33,39] Since oxygen and hydrogen will react with nitrogen and carbon in the Ppy polymer chain the aromatic ring will be opened and shortened. As a result, degradation of conductivity will occur.[26,40–41] The ideal process for polypyrrole polymer is the oxidation of pyrrole units, the α-α coupling during polymerisation. However, the reactions of Ppy with oxygen and water may attack the α and β positions of the pyrrole unit. There are two possibilities for attack. Firstly, the hydroxide ion (OH^-) attacking the β-position on the pyrrole unit may be considered as one of the most important solution degradation reactions. The oxidised polymer chains may undergo nucleophilic attack by the oxygen of the surrounding polymerisation media giving C-O bonds. Oxidation and phototropic processes may transform C-O bonds into C=O bonds.[42]

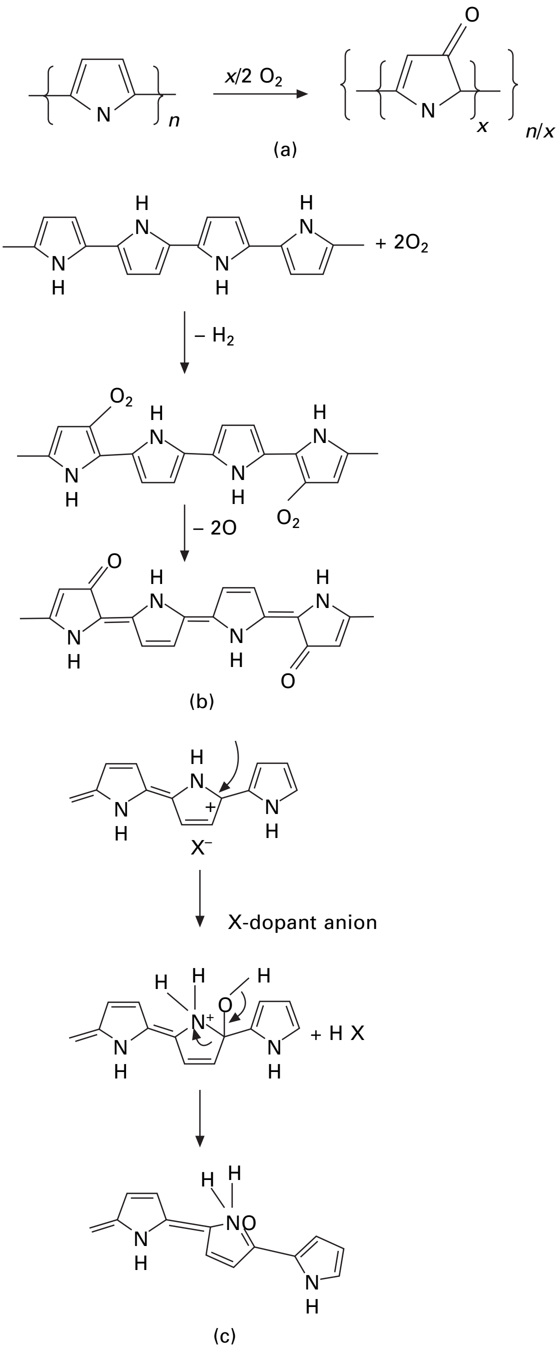
Figure 15.3 shows a possible degradation mechanism[36] indicating the formation of a carbonyl group and the shortening of the polymer chain. This chemical reaction between polymer chain and oxygen, water or damaging



15.3 Possible reaction ways for pyrrole-pyrrole linkages in Ppy generation.[18]

radiation causes the formation of carbonyl, ester and hydroxyl groups, leading to the reduction of positive charge carriers on the polymer chain.[39] Secondly, the hydroxide ion may attack the α-position of the pyrrole unit that disrupts conjugation.[43] This nucleophilic attack and pyrrole ring opening mechanism have been proposed by Otero *et al.*[44] to explain the degradation of Ppy at anodic potentials in aqueous solutions. The changes of chemical structure of Ppy in air[36] and the interaction in water[26] are shown in Fig. 15.4(b) and 15.4(c) respectively. The degradation due to the diffusion of oxygen into the conductive film and the reaction of oxygen with Ppy backbone leading to the loss of conductivity were verified by the XPS examination.[12] The amount of carbonyl functional groups, i.e., oxygen content of the Ppy-coated fabrics after ageing, indicated a significant increase. The rate of degradation is related to the oxygen concentration within the Ppy film and relative humidity. The difference between the initial conductivity ($\Delta\sigma$) versus time ($t^{1/2}$) was initially linear, and the rate of oxygen diffusion into the film would limit the rate of decay.[26,34,36,45]

Other than water or oxygen, polymer can be attacked by alkaline solutions during finishing treatments or laundering can promote polymer ring oxidation and ion exchange between Ppy and OH^- at the initial stage.[24,45] Prolonged base treatment can give rise to the formation of covalent bonds such as C-O and C=O that may create bonding between the hydroxyl ion and the pyrrole structure, and thus shorten the conjugation length of the polymer. This reaction causes the instability of the Ppy films at the initial stage. Although the Ppy films can be stabilised after reaching equilibrium the conductivity will be lost.



15.4 Mechanism for the attack of Ppy with (a) presence of oxygen, (b) air and (c) water.[26]

15.3 Stabilisation of the Ppy

In this section, the review of the stabilisation methods is based on the principles of intrinsic and extrinsic instabilities of polypyrrole films.

15.3.1 Dopant applications

There are two main ways to explain the stabilisation of Ppy films by dopant applications. Firstly, the carbonium chains doped with counter-anions balance the charge on the Ppy films and thus reduce the opportunities for oxygen to attack the C or N in the Ppy chain. Secondly, the surface structure of Ppy films is modified by dopants to produce a denser and smoother surface morphology so as to inhibit oxygen attacking the Ppy chains. Ppy conductive films with more porous morphology can be obtained through the use of smaller size dopants which contributes to the relative instability of the films. In contrast, the relative stability of the Ppy film can result from the formation of a smooth surface using large-sized dopants such as anthraquinone-2-sulfonic acid (AQSA)[47] or benzenesulfonate and perchlorate[31] and p-toluene sulphonate, p-chlorobenzene sulphonate.[61] These dopants with aromatic anions exhibit better stability with less easy detachment from the origin polymer structure as well as fewer attacks from external stimuli.[61] The stability enhancement induced by doping with large organic anions such as dodecylbenzenesulfonate (DBS)[48] is mainly due to the localisation of the large anions in the Ppy polymer chains as their mobility is greatly reduced once the Ppy films are doped. The large anions will not easily be affected by the external stimuli during the redox process and can prevent the doping and un-doping of Ppy films.

15.3.2 Acid and base treatments

Base treatment of the Ppy films renovates the (OH^-) blocking of the reactive sites and restrains the reactions of the Ppy film with oxygen and water. However, base treatment of the Ppy films may result in the de-protonation of the polypyrrole chains leading to the loss of initial conductivity (>40%).[24,37] A longer base treatment process enhances the stability of the polymer but at the expense of conductivity.[24] It is, however, important to note that the initial base treatment has already resulted in the significant loss of conductivity. On the other hand, doping Ppy films with various protonic acids such as HCl and sulfonic acid can provide stability without greatly reducing the initial conductivity.[25] The XPS characterisation for the surface chemical composition of Ppy film indicated that both acid and base treatments resulted in the elimination of reactive sites.[37] An increase in the C-Ox species was observed from the Ppy films after the acid and base treatments which result in the elimination of reactive sites in the Ppy structure. Munstedt[31] reported an increase in long-term stability for Ppy films by treating with sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) at the elevated temperature (80 °C and 140 °C). The enhanced stability was attributed to the decrease in permeability of the Ppy films to oxygen and water which could retain up to 70% of its initial conductivity after 100 days at 140 °C.

15.3.3 Thermal annealing

The annealing process causes the restructuring of the Ppy polymers which may be partly due to the evaporation of residual solvent. Solvent plays an important role in the specific salvation process by stabilising the π segments along the polymer chain. Reordering within the Ppy film based on thermal annealing improves the local ordering within the Ppy films and decreases the defect concentration.[49] Large numbers of voids and pores were observed in the micrographs with increasing annealing time, which hindered the path of conducting channels and thus decreased the conductivity.[38] Scanning Electron Microscopy (SEM) micrographs performed by Singh *et al.*[50] confined the cauliflower structure of the poly (N-methylpyrrole-pyrrole) film which had totally disappeared after annealing for 29 hours. After that no change in the conductivity was observed. Hence, reordering of the polymeric chain is a crucial factor in the determination of conductivity and stability.

15.3.4 Voltage applied

The degree of conductivity and the stability enhancement may be related to the nature of the counter-anions doped in the Ppy films. Onyang and Li investigated the effect of voltage on the conductivity of Ppy[46] and found that there was an increase of 65% and 47% for conductivity of the film doped with TsO^- and NO_3^- respectively after applying a higher voltage. The Ppy(TsO^-) film remained stable while the Ppy(NO_3^-) dropped back to its original value quickly after the treatments. The doped counter-anions are used for balancing the charges on the chains in the Ppy films. When a voltage is applied to the films, an electric field will be set up between the two electrodes. The counter-anions doped in the film will tend to move under the electric field. When reaching a certain voltage level, the counter-anions move to a quasi-stable, higher-energy position. At this time, the chain structure of the film changes and its conductivity increases. After the voltage treatment, the quasi-stable structure may relax. The relaxation of the TsO^- counter-anion is less easy when compared with NO_3^- and BF_4^-. After the voltage treatment for a longer period, the Ppy(TsO^-) film remains a higher conductivity, as the ion size for TsO^- is larger than NO_3^- and BF_4^-. In addition, the cyclic redox reaction of Ppy polymer structure by alternative potential applications may lead to the conformational changes of polymer structure from *trans* to gauche orientation and shorten the conjugation length.[51] However equilibrium can be reached at 1200 cycles of the redox reaction.[51]

15.3.5 Structural modification of the Ppy film

The Ppy film thickness and layer structure may contribute to the stability of conductivity.[31] As the outer layers of the Ppy films are oxidised, they create a barrier to oxygen diffusion from outer boundaries to the inside structure. The oxygen permeability of the material is decreased and the rate of conductivity decay is much reduced. Ultimately, the stage is reached where the oxidised outer skin protects the pristine core from further oxidation and this is called 'self-stabilisation'. It was found that when the Ppy films had greater thickness, up to 100 μm, the conductive film could withstand thermal stability up to 200 °C.[52] Thicker conductive films can be produced through longer deposition time, lower applied potential for electrochemical polymerisation, higher reaction temperature, and higher concentrations of monomer and electrolyte.

15.3.6 Addition of metal salts

In the early 20th century, Liu and Hwang[26] investigated the modification of Ppy in the electronic configuration by metal ions. Cu(I) was used to enhance the conductivity and stability of Ppy. The reason arises from the deposition of Cu(I) onto Ppy which is mainly used to stabilise the N^+ ions. Consequently, the original N^+ is stabilised into the Cu-Ppy complex. The Cu-Ppy complex is more stable to external stimuli and less porous morphology films will be produced. A more porous structure and larger specific surface area facilitate the attacking gas diffusing into the films. Therefore Cu-modified Ppy may contribute to the relative stability based on the viewpoint of the decrease in permeability of the Ppy film to water by adding large-sized metal ions into the film.

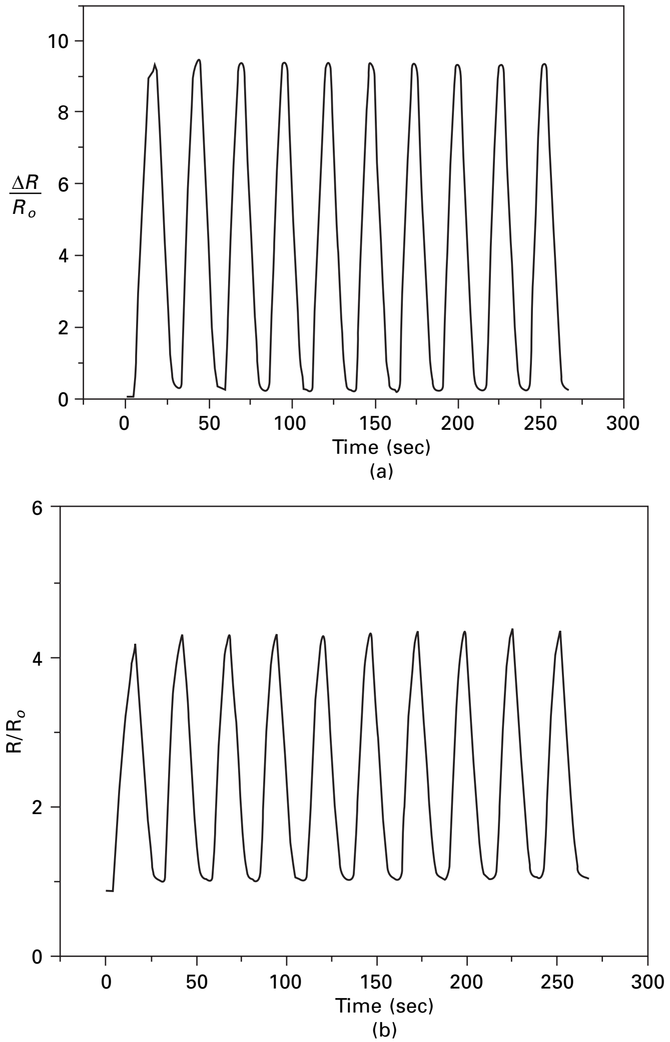
15.4 Experimental results of stability enhancement

The conductive fabrics prepared by the solution polymerisation of pyrrole on the surface of fabrics show a low strain sensitivity of not more than 3, although the deformation is as large as 50%.[6,11] This phenomenon is related to the thickness of the conductive coating on the textile. The conductive coating is composed of multi-layers of Ppy deposited on the fabric surface during the solution polymerisation. When the coated fabric is elongated, the multi-layers of Ppy may not change in the same way as the substrate. Unless it is under very large deformation the relative position and contact of the conductive Ppy coating may not change much with the elongation of the fabrics. This leads to a small change in conductivity resulting in low strain sensitivity. For this reason, the method of using printing and chemical vapour deposition (CVD) to obtain a relatively much thinner coating of Ppy on the surface of a Tactal (83%)/Lycra (17%) fabric was employed. It was probably due to the existence of elastic Lycra that the prepared composites showed good reversibility under large-strain deformation of up to 100%.

15.4.1 Printing and chemical vapour deposition

Polypyrrole-coated fabrics were prepared by combining the printing and chemical vapour deposition. Fabric composed of 83% Tactel and 17% lycra was first printed with the solution containing sodium dodecyl benzene sulfonate (DBS) and $FeCl_3$ in ethanol solvent, and the wet take-up after each immersion was controlled. The fabrics and pyrrole monomer were transferred to a desiccator for the chemical vapour deposition. The vapour phase polymerisation of polypyrrole proceeded on the surface of the fabrics under vacuum for 24 hours. The black fabrics so obtained were washed with de-ionized water and ethanol, respectively, and then purified at 40 °C in a vacuum. The strain-stress properties of the Ppy-coated fabrics were obtained using an Instron testing Instrument (Model 4466) under the standard testing conditions of 25 °C and 65% RH. The fabrics were repeatedly stretched and relaxed for ten cycles with the maximum extension up to 12.5 mm (50% deformation) in each cycle. The conductivity change of the sensing fabrics in both the stretched and relaxed states was recorded using a digital multi-meter (Keithley Model 2010) to investigate its strain sensitivity. SEM images of the Ppy-coated fabrics were obtained using a scanning electron microscope (Leica stereoscan 440). ATR-FTIR spectra were determined by means of a Bio-Rad FTS-6000 spectrometer.

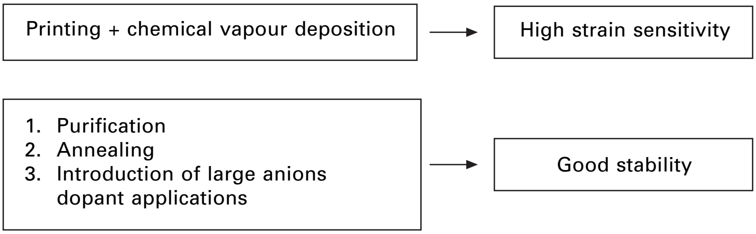
The typical curves of conductivity change versus the strain of Ppy-coated fabrics prepared by printing and CVD as well as solution polymerisation during the ten cycles of elongation and relaxation measurements are illustrated in Figs 15.5(a) and 15.5(b), respectively. The resistance of the sensor prepared by the combination of printing and CVD increases sharply with extension up to a large deformation of 50%. The sensing curves are almost the same during the ten cycles of the test, indicating that the sensor has very good repeatability. The strain sensitivity is $\left[\frac{\Delta R}{\varepsilon R_o}\right]$, where ΔR is the resistance change of the fabric under extension and R_0 is the original resistance, i.e., the resistance of the fabric in the relaxed state. It can be calculated from Fig. 15.5 that the strain sensitivity of the sensor is as high as about 20. Based on the developed printing and chemical vapour deposition process as shown in Fig 15.6, the fabric sensors can be further enhanced through annealing treatment and dopant application. Higher strain sensitivity up to 120 can also be obtained



15.5 The conductivity change versus the elongation of Ppy-coated fabrics prepared by (a) printing and CVD and (b) solution polymerisation (deformation = 50%).

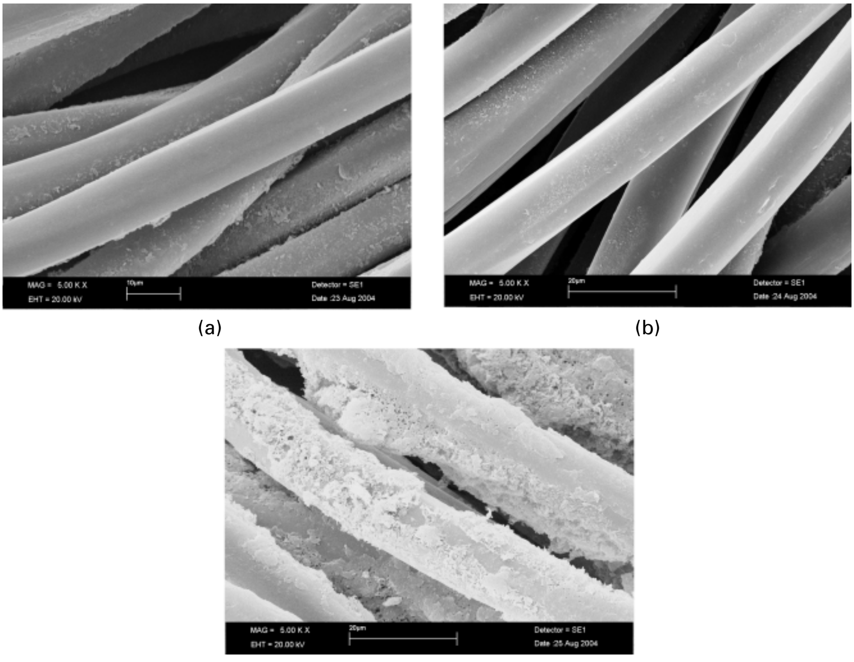
after further stabilisation processes including purification and low temperature annealing. In contrast, the sensor prepared by solution polymerisation also shows repeatable sensing curves during the cyclic tests, but its strain sensitivity is as low as about 6.

In addition to high sensitivity, good environmental stability is especially important for its possible application in smart garment, rehabilitation and biomedical fields. It was reported that a smooth and dense layer of Ppy film



15.6 Strategy for preparing a flexible strain sensor from the Ppy-coated fabrics with both high sensitivity and good stability.

was more resistant to the attack of oxygen and water molecules, thus enhancing its stability.[7,15–16] Figures 15.7(a) and (b) show the scanning electronic micrograph of the film of Ppy-coated fabrics prepared by printing plus CVD and by solution polymerisation, respectively. It is revealed that the fabrics coated with Ppy formed by CVD exhibits a much smoother surface, while the coated fabric prepared by the solution polymerisation is featured with a rough surface. The smooth morphology further explains the advantages in


(a) (b) (c)

15.7 SEM images of Ppy-coated fabrics prepared by (a) printing and CVD without DBS doping, (b) by printing + CVD with DBS and (c) by solution polymerisation.

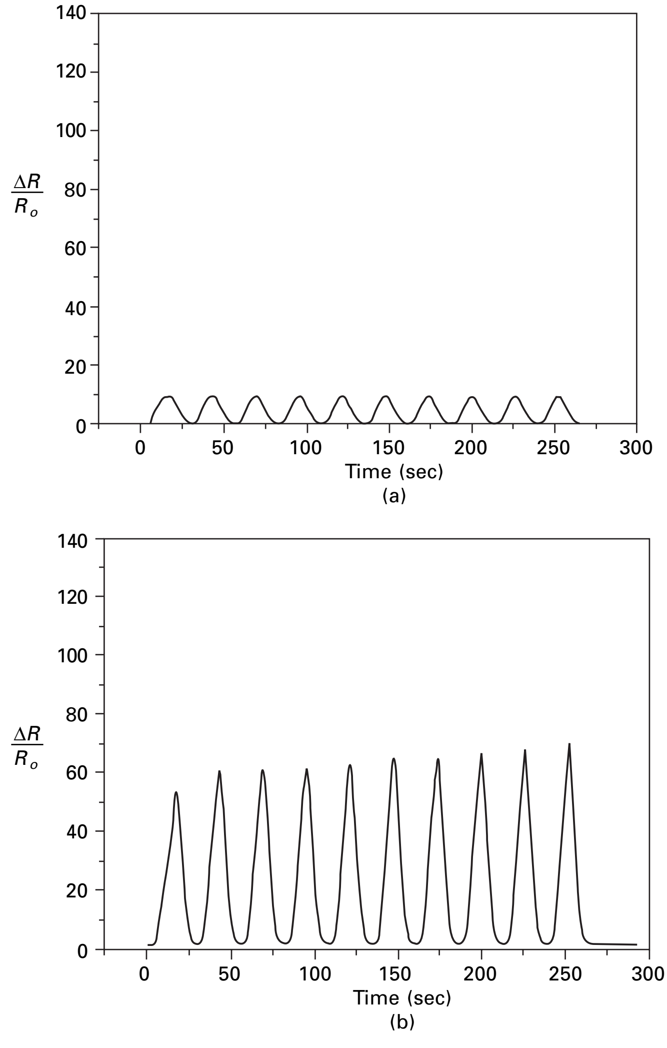
strain sensitivity. Strain sensitivity of the deposited conductive film can further be enhanced by the combination of purification and annealing processes. Annealing is a method used for improving the stability of the conductive fabrics. R. Singh *et al.* investigated the effect of heat annealing on the conductivity and surface structure of Ppy, and found that annealing would lead to the removal of residual solvent as well as the restructuring and reordering of the Ppy chain, thus stabilising the conductivity.[53] However, the most recommended annealing processes[50] involve a very high temperature, usually over 100 °C. This is not beneficial to textile substrates containing Lycra because it may degrade the quality of Ppy-coated textile materials. Therefore, low-temperature annealing processes for Ppy coated fabric containing Spandex materials are used.

15.4.2 Purification

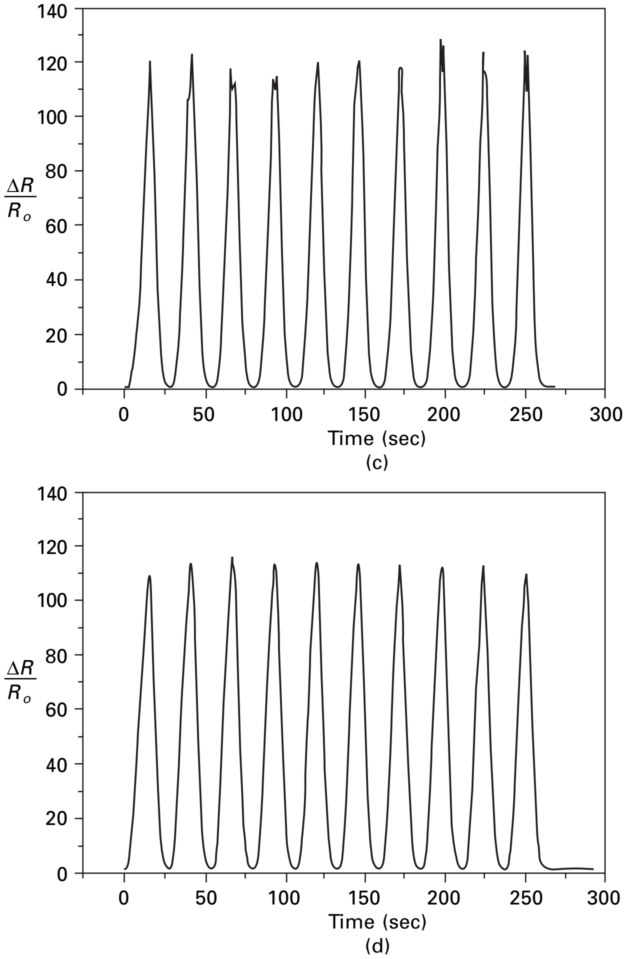
Purification of samples under vacuum drying at around 40 °C shows a significant improvement in strain sensitivity. The vacuum drying process promotes the efficiency of removal of impurities or residual solvents, allowing the conductive coating to respond to strain deformation. The strain sensitivity $\left(\frac{\Delta R}{\varepsilon R_o}\right)$ approximately doubled the values from the samples without vacuum drying (~20) to those with vacuum drying about (~60). Figure 15.8(a) shows the diagram of the resistance change of the fabric sensors without any treatment in response to large strain deformations up to 50% extension. Under ten consecutive cyclic extensions, the change of resistance in the extension of Ppy-coated textiles indicates an excellent linearity and repeatability. Except for the first cycles of extension, the responses of all other cycles are nearly identical with the strain sensitivity $\left(\frac{\Delta R}{\varepsilon R_o}\right)$ approaching 20. Under the same dimension of resistance magnitude, it is very clear that vacuum purification treatment significantly improves the strain sensitivity of the Ppy-coated fabric As shown in Fig. 15.8(b). However, in all cases the linearity of the sensing curves remains excellent except for a slight variation in the sensitivity at peak strain (near 50%).

15.4.3 Annealing

In order to avoid destroying the structure and stability of the fabrics, annealing was carried out by heating at a maximum of 60 °C under vacuum for ~40 hours. Figure 15.8 shows the curves of conductivity change of a strain sensor under cyclic extension before and after annealing. It is obvious that the annealing process increases the strain sensitivity and improves the repeatability of sensing curves during the repeated cyclic extension, which indicates an improved stability. Although annealing at 60 °C will increase the initial conductivity, the relative effect is much lower when compared with high-temperature annealing processes.[22] More importantly, the strain sensitivity is also enhanced. The performance of the e-textile sensor can further enhance the strain sensitivity $\left(\frac{\Delta R}{\varepsilon R_o}\right)$ of the Ppy-coated e-sensor up to (~120) by the combination of low-temperature purification and vacuum heat treatment under



15.8 Strain sensitivity of PPy-coated sample (a) without vacuum drying and heat treatment, (b) with vacuum drying, (c) with vacuum drying and heat treatment under nitrogen atmosphere, (d) with vacuum drying and heat treatment under vacuum.



15.8 Continued

nitrogen medium at 60 °C for 40 hours. Figure 15.8(c) shows the great improvement of strain sensitivity of the Ppy-coated fabric sensor under heat treatment in nitrogen medium. The heat treatment process at a temperature of 60 °C significantly increases the strain sensitivity but without affecting the linearity of the textile sensor. Similarly, only light variations of resistance change at peak strain level are observed.

15.4.4 Introduction of large anions

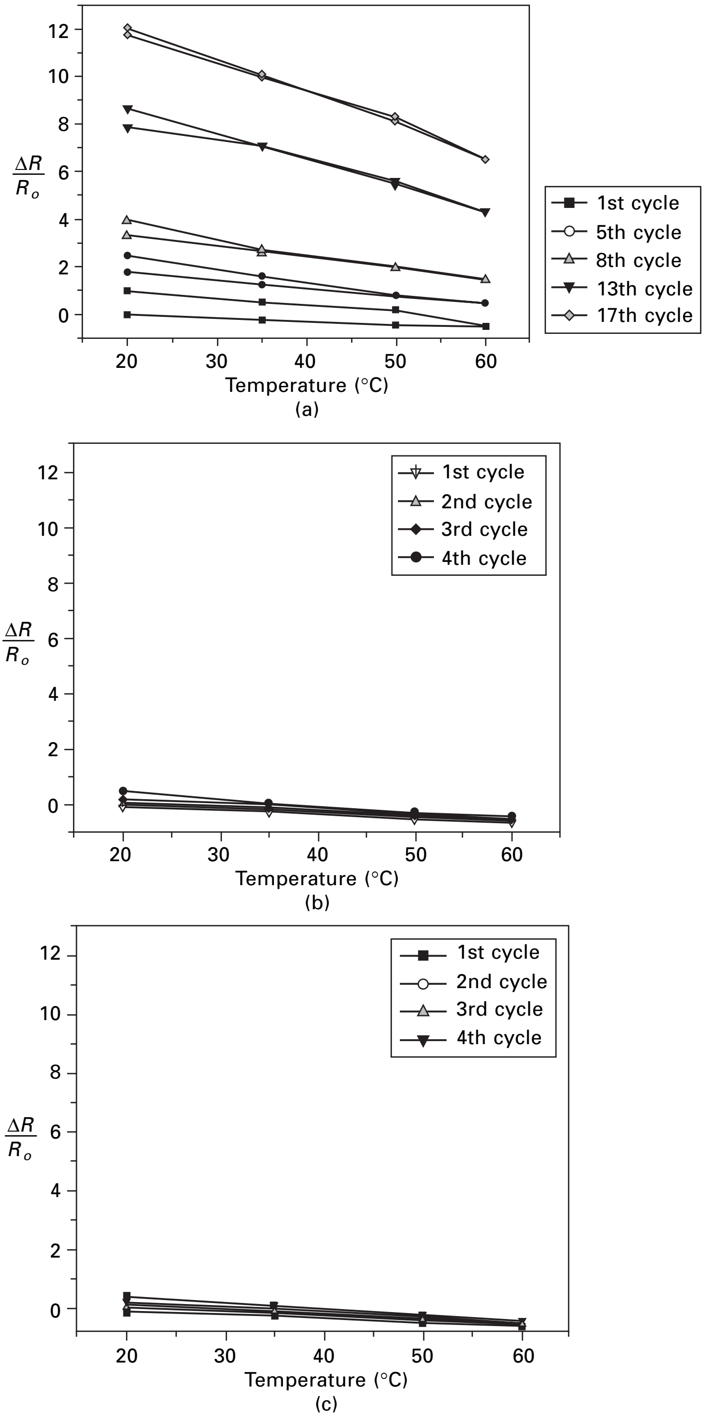
As mentioned in Section 15.3, dopant can effectively affect the stability and conductivity of Ppy.[53–56] Ppy film doped with larger anionic species such as dodecylsulfate and dodecylbenzenesulfate displayed smoother morphology than the cauliflower-like appearance of Ppy/Cl^- or Ppy/ClO_4^- film.[50] Ppy doped with dodecyl benzene sulfonate anion shows more compact morphology and higher conductivity than Ppy/Cl^-. The introduction of large-sized anions in the Ppy film will result in enhancing the thermal and humidity stability. The large size dopants are difficult to be de-doped even at high temperature and humidity. Furthermore, the Ppy/Cl^- system was reported to have worse stability than those doped with organic acid. It was also found that the Ppy-coated film prepared by both the solution polymerisation or printing and chemical vapour deposition with only Cl^- as the counterion would increase the resistance by more than tenfold after storage for several months. The results agreed with those obtained from Scilingo *et al.* that the conductive fabrics prepared by solution polymerisation with inorganic ClO_4^- as the counterion faced the problem of rapid decrease in conductivity.[57]

Considering the fact that the doping agent should be of low toxicity for practical application, as a result, sodium dodecyl benzene sulfonate, a bulky aromatic sulfonate, was consequently used as the additional doping agent for the preparation of conductive fabrics so as to provide good stability. This bulky anion has a long aliphatic chain and its large dopant ion is more stable than the small Cl^- ion, which has been extensively investigated for the preparation of Ppy film with potential applications in movable pixels or micro-actuators.[58–60,62,64] In addition, its inclusion in the Ppy film is expected to give a smoother morphology and more compact coatings. It may protect the Ppy from the penetration and attack of air and moisture, and improve the stability of the sensor of the Ppy-coated fabrics.

15.4.5 Temperature and humidity ageing

The conductivity degradation of Ppy is closely related to its reaction with oxygen, especially under elevated temperature and moisture environments. Therefore, the stability of the developed strain sensors based on the combination of printing and chemical vapour deposition with or without DBS anions was thoroughly investigated by the thermal ageing and humidity ageing tests. The thermal ageing test is composed of a few cycles of heating and cooling tests. Both thermal and humidity ageing tests were carried out by recording the conductivity change of the Ppy-coated fabrics placed in a climatic chamber (Hotpack Series 922) where both the temperature and humidity could be controlled. For thermal ageing, the humidity is always kept at 65% RH. The temperatures investigated include 20, 35, 50 and 60° C, and the temperature changed every two hours. The humidity ageing was carried out at 30 °C. The humidity investigated included 40, 55, 70 and 90% RH and the humidity changed every two hours.

Figure 15.9a shows that the difference in resistance between the heating and cooling cycle is significantly irregular during the ageing process. The

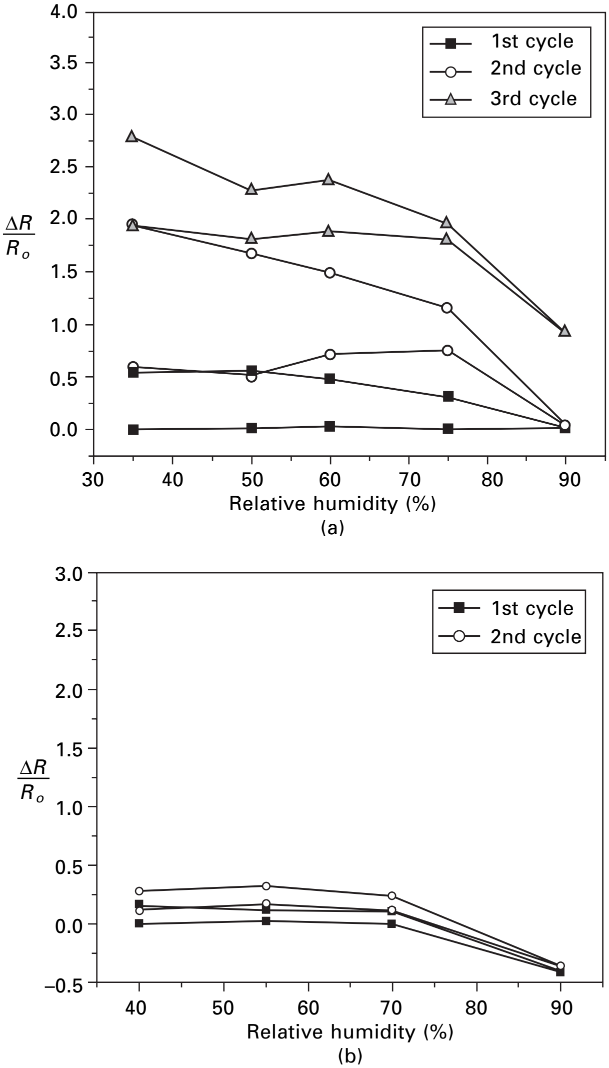


15.9 Cyclic temperature sensitivity of the samples fabricated (a) without any DBS doping and heat treatment, (b) without DBS doping but with vacuum heat treatment at 60 °C for 40 hours and (c) with both DBS doping and vacuum heat treatment.

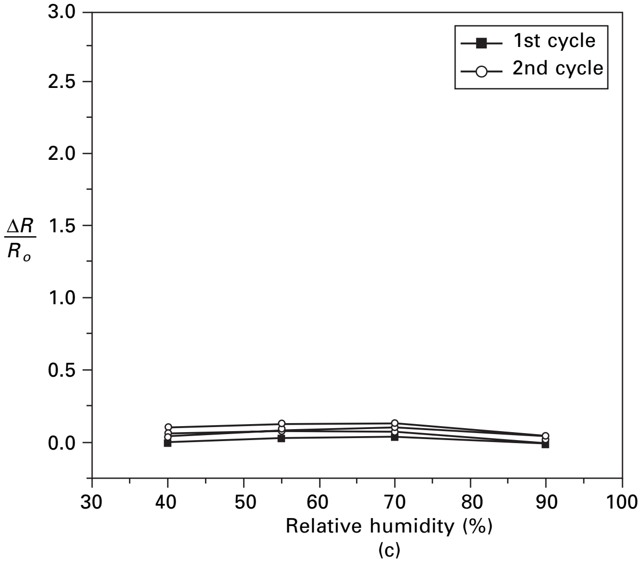
cyclic temperature sensitivity of the sample showed a significant hysteresis at the starting point but was reduced to around 8% after eight cyclic ageings. They were further reduced to around 2% for a continuous heat ageing of 17 cycles. However, the thermal ageing process introduces the problem of drastically increasing the sensor resistance up to over 4500 K ohm after thermal ageing, which is too high for a practical strain sensor. The problem can be compensated by the vacuum heat treatment and DBS doping. It can be seen in Figs 15.9(b) and (c) that vacuum heat treatment reduces the hysteresis of the thermal changing curve effectively. The hysteresis of samples with vacuum heating at 60 °C successfully reduces the hysteresis from around 40% at the 4th cycle to around 10%. Application of DBS doping can further enhance the stability of the sensor by significantly reducing the hysteresis of heating and cooling curves to about 7.8%. In addition, the repeatability and linearity of the sensing curves towards temperature also enhanced the sensing functions, as shown in Fig. 15.9. A slight increase in resistance is observed only after each heating-cooling cycle, which may be related to the stability of the dopant ion and the rearrangement of the Ppy chain during annealing processes.

Humidity can also exert an influence on the conductivity of Ppy. The adsorbed moisture can promote the free motion of doping ions in the Ppy film, thereby increasing its conductivity.[20] Moisture can react with Ppy to decrease the conductivity.[26,61] It also shows a strong synergetic effect with oxygen on the degradation of Ppy.[61] Therefore, the stability of the sensor was further investigated by humidity ageing. Figure 15.10(a) shows the results of cyclic humidity sensing. Ppy-coated samples fabricated without DBS doping or thermal annealing shows a tremendous increase in hysteresis, at the 3rd cycle up to 30%. It can be seen in Figs 15.10(b) and (c), both DBS applications effectively eliminate the influence of humidity on the textile sensors. After heat treatment, the sensing curves to humidity reduce tremendously, particularly at the 2nd humidity cycle the hysteresis goes down from without heat treatment at around 85.5% to only 14.5% after heat treatment. Since it shows better linearity the sample is less sensitive to humidity. The results are further improved by application of DBS doping as reflected by the dropping of hysteresis between the wetting and drying cycles down to 3.8% for the sample with DBS and vacuum heat treatment. From the above results of cyclic humidity sensing, the findings show that the sample containing DBS doping has very little effect on the conductivity of the samples and is even insensitive to humidity change.

The thermal and humidity ageing tests show that the conductivity of the strain sensor fabricated from the Ppy-coated fabrics is only slightly dependent on the humidity and temperature, but it exhibits very high strain sensitivity. Therefore, it can be concluded that within the investigated ageing range of humidity and heating, the effect of the temperature and humidity on the conductivity of the strain sensor can be minimised, which is very important for its potential application. However, strain sensitivity will also be reduced after the storage of e-textile sensors in ambient condition for a long period of nearly one year as shown in Fig. 15.11.



15.10 Cyclic humidity sensitivity of the samples (a) without any DBS doping and vacuum heat treatments, (b) without DBS doping but with vacuum heat treatment, and (c) with DBS doping and vacuum heat treatment.



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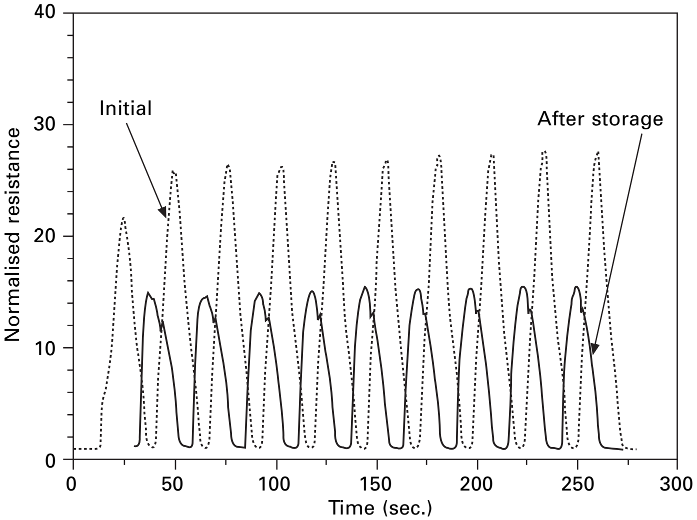

15.11 The conductivity change versus the strain of sensors prepared at room temperature before and after storage.

15.5 Conclusion

In summary, a flexible strain sensor produced from the polypyrrole-coated stretched fabrics and featured with both high strain sensitivity and good stability has been developed. It is proposed that the combination of printing and chemical vapour deposition of thin coatings of polypyrrole on the fabric surfaces will result in high strain sensitivity. The relatively lower temperature (60 °C) annealing treatment of the Ppy-coated fabrics and the introduction of bulky dodecyl benzene sulfonate anions into the polypyrrole backbone help improve the stability of the Ppy-coated sensors. The developed e-textile sensors based on the Ppy-coated fabrics are suitable for applying to sensing garments, wearable hardware and rehabilitation, etc.

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16

Electrical, morphological and electromechanical properties of conductive polymer fibres (yarns)

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16.1 Introduction

The textile industry has made considerable advances in the fields of intelligent and multifunctional textiles materials, mainly in the sectors of high-performance textiles, yarns and fibres. In addition, the demand of the electrically conductive fibres (or yarns) and textiles is rapidly growing up concerning industrial materials such as sensors, electrostatic discharge, electromagnetic interference shielding, dust and germ-free clothing, corrosion protecting, monitoring, data transfer in clothing and for military applications such as camouflage and stealth technology.[1–8] For all applications previously mentioned, the basic element is the textile fibre. The novel electrical properties can be obtained by modifying or integrating electronic devices into the traditional textile materials. An overview of methods related to the realisation of conductive textiles is given below.

Commercialised conductive spun or filament fibres are prepared by dispersion of the conductive particles such as silver, nickel, stainless steel, aluminium, graphite and carbon black into a common polymer matrix. In order to obtain the highly conducting blends, both high concentration of charges and homogeneous blending morphology are necessary. However, high concentration of charges in matrix polymer implies brittleness of blends and high producing cost. The modification of fibre (yarn) using inherently conductive polymers seems to be an interesting approach. Conductive polymers show the electrical properties due to their conjugated double bond chain structures, which derive both their conducting or neutral (non-conducting) forms. However, they are inherently insoluble or infusible due to their strong intermolecular interactions. The production of high quality conducting blends with conventional polymers by melt mixing or by solution casting is still at the development stage.[9–17]

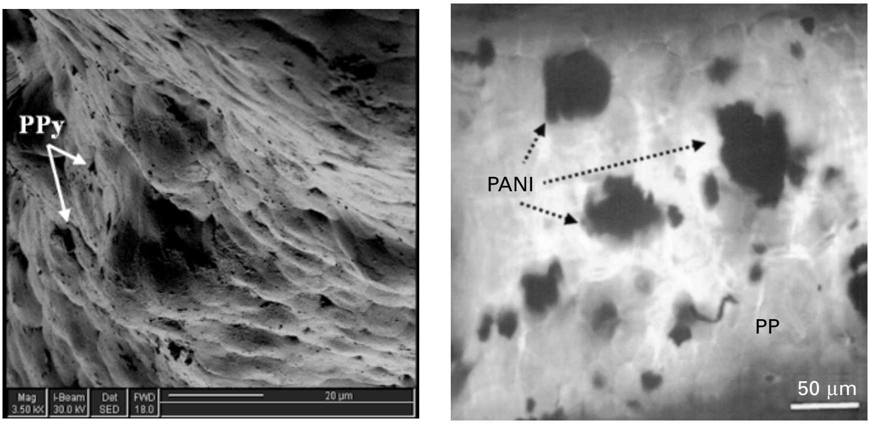
Among the conjugated conducting polymers, polyaniline (PANI) and polypyrrole (PPy) have attracted much interest worldwide due to their tremendous environmental, thermal and chemical stabilities. Polyaniline exists in a variety of oxidation states from leucoemeraldine (completely reduced) to emeraldine (partially oxidised) to pernignaniline (completely oxidised). Most broadly studied forms of polyaniline are the emeraldine base form and the emeraldine salt form. With a simple doping process by charge transfer chemistry or by acid-base (protonation) chemistry, polyaniline converts the semiconducting emeraldine base form (10^{-5} S/cm) to the metallic emeraldine salt form (10^{2} S/cm).[18–20]

16.2 Preparation of conductive fibres – overview

In this study, a doped polyaniline in salt form has been used in order to prepare the conductive fibres. The originality of our research approach is to prepare the conductive yarns which are able to transport information or to be used as textile sensors, preserving at the same time 'textile' mechanical properties such as light weight, elongation, bending, shearing and twisting. These textile properties are very important because the conductive fibres are transformed in textile structures by weaving, knitting or other manufacturing processes. Therefore, two different methods have been developed to synthesise conductive yarns with textile mechanical properties. The first method is based on conductive polymer composites (CPCs) using the 'melt mixing process' and the second method is performed using the 'coating process'.

16.2.1 Method 1: melt mixing process

One of the effective methods is dispersing conductive fillers in a thermoplastic polymer matrix and blending by mechanical mixing process. Shacklette *et al.* reported that a conductive form of polyaniline (Versicon,™ Allied-Signal, Inc.) is dispersible in polar thermoplastic matrix polymers such as polycaprolactone and poly (ethyleneterephthalate glycole).[21] Ikkala *et al.* reported on conducting polymer composites prepared by blending thermoplastic polymers such as polyolefin, polystyrene with Neste complex (polaniline salt complex developed by Neste Oy and UNIAX). In their report, 1–20 S/cm of conductivity has been obtained in the range of 1–30 wt% of Neste complex.[10] In addition, the morphological properties and percolation threshold of conductive filler on conductive polymer blends have been studied. At this point, the melt spinning process was our first approach for preparing conductive composites fibres. Polyaniline emeraldine salts form (PANI), PPy and graphite were melt mixed with polypropylene (PP) or low-density polyethylene (LDPE) using a co-rotating twin-screw extruder. However, the conductivity of these monofilaments was not satisfactory, even when 40% of charges are added in matrix polymer. This can be explained by the non-homogeneous morphological structures of conductive fillers in PP, as we can see in Fig. 16.1(a).[22] The particles of conductive polymers were not completely dispersed and formed



(a) (b)

16.1 SEM photographs of (a) PP/PPy (20% in weight) blends and (b) aggregation of PANI charges in PP polymer observed by optical microscopy.

aggregates due to their strong intermolecular interactions (see Fig. 16.1(b)). The melt mixing process could be improved by changing the melting temperature, mixing time, or mixing speed. The other method, using solvent (solution blending) to prepare conducting polymer composites, is proposed in order to obtain highly conductive CPCs with better dispersion morphology.

16.2.2 Method 2: coating process

Even though conductive polymers can be electrochemically produced in fibre or film forms, they show weak mechanical properties precluding their application in traditional textile processes. Considering this difficulty, thin coating or polymerising using conducting solutions on the surface of textiles (fibres) should be a reasonable method to create conductive textile fibres. Since polypyrrole coated polyester textiles have been developed by Milliken Research Corporation, many research groups are actively involved in this field.[23] In addition, polyaniline coating or *in-situ* polymerisation on non-woven fabric, nylon 6, cotton, polyester fabric and Nomex fabric have been recently reported.[24–26]

The soluble conductive form of PANI may be obtained by protonation with functionalised protonic acid, denoted as H^+ (M^--R).[27] H^+M^- is a protonic acid group and may be sulfonic acid, carboxylic acid, phosphonic acid, etc. The proton of the protonic acid reacts with imine groups of polyaniline and the M^--R group serves as the counterion. R is an organic group that can be compatible with nonpolar or weakly polar organic solvents such as N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), xylene and m-cresol.

Efficient doping methods of PANI with dodecylbenzene sulfonic acid (DBSA) or camphor sulfonic acid (CSA) were reported.[14–16,28] The PANI chains tend to form extended chain conformation in the presence of DBSA, and therefore electrons transported between polymer chains should be enhanced. In the polyaniline/solvent system, the film-like agglomerates of polyaniline take place on the solution-solid (substrate) interface when the solvent is removed. In our research work, this spontaneous molecular assembly has been used to coat conductive polymers on a fibre surface, and has been successfully applied to yarns and even fabrics. PANI coating was carried out during the impregnation of textile yarns in the PANI solutions. Electrical, morphological, electromechanical and electrical properties of the conductive yarns were investigated.

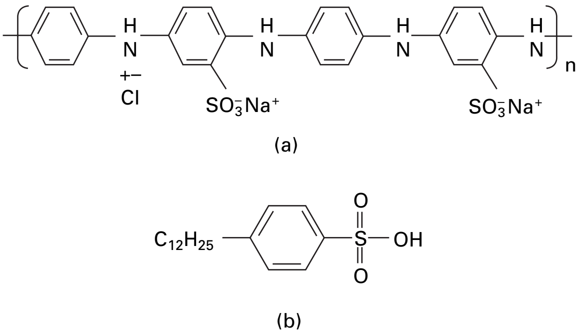
16.3 Experimental

16.3.1 Materials

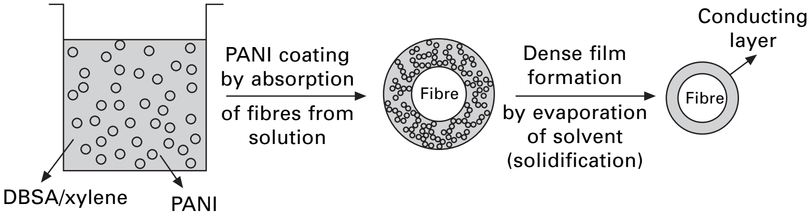
Emeraldine salt form of polyaniline (PANI) was supplied by Sigma-Aldrich Chemical Company. Dodecylbenzene sulfonic acid (DBSA, Fluka) was used to obtain an homogeneous conducting PANI solution in xylene solvent. The chemical structures of used materials are shown in Fig. 16.2. The commercial polyethylene terephthalate (PET) spun yarn (111 dtex) and PET filament yarn (292 dtex) were supplied by Hyosung (Korea). Ultrahigh molecular weight polyethylene (UHMW-PE, Dyneema®, 220 dtex) yarn was supplied by the DSM Company (Netherlands).

16.3.2 Solution preparation and coating process

PANI and DBSA (1:0.5 w/w in ratio) mixtures were dissolved in xylene in order to prepare different PANI solutions ranging from 3–10 wt%. These



16.2 Chemical structures of used materials in this study. (a) polyaniline salt form and (b) dodecyl benzene sulfonic acid.



16.3 Overview of the coating process used in this study.

solutions were stirred vigorously for three hours at 90 °C and treated in an ultrasonic bath for two hours. The continuous coating process was performed using an experimental device which may be equipped with several baths filled with PANI solution. Textile yarns were dipped into the solution in the presence of a dry airflow around the coated yarns surfaces to enhance solvent evaporation and the solidification of a PANI layer on the fibre surface. The take-up speed of PANI-coated yarn in a bobbin was controlled taking into consideration the drying dynamics during the experimental procedure. The scheme of the coating process on the fibre surface using PANI solution is represented in Fig. 16.3. All the coated yarns were indicated using an abbreviation. For example, PANI/PET spun 3% means PET spun yarn coated with 3% of PANI solution.

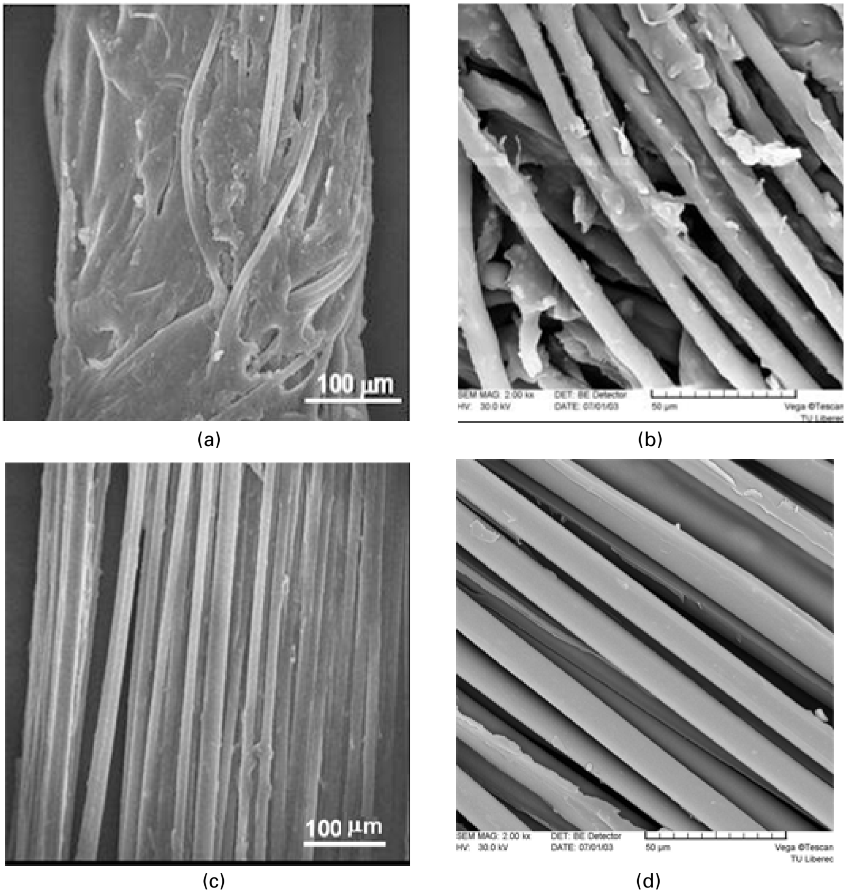
16.3.3 Morphological and electrical characterisation

The electrical resistance of PANI-coated conductive yarns was measured with an Agilent 34401A multimeter at 25 °C, 55.56 HR%. Detailed coated fibre surface images and cross-sections were obtained using a scanning electron microscope (SEM, JEOL 100 CX model ASID4-D) and a focus ion beam system (FIB, Strata™ DB 235, FEI company). The SEM samples were gold-sputtered before observation.

16.4 Results and discussion

16.4.1 Morphological properties of PANI-coated yarn

Figure 16.3 shows the surface characteristics of PANI-coated PET spun and filament conductive fibres. The geometrical structures of spun and filament yarns are quite different. Spun yarns contain inherently many discontinuous fibres showing the bulky structures with many interstices (see Fig. 16.4(a) and (b)).[22] Most of these interstices are filled with PANI particles during the coating process. However, the structure of filament yarns is more uniform (fibres are often parallel). During the coating process, the bulky surface of spun yarns should influence the filling efficiency of PANI compared with



(a) (b)

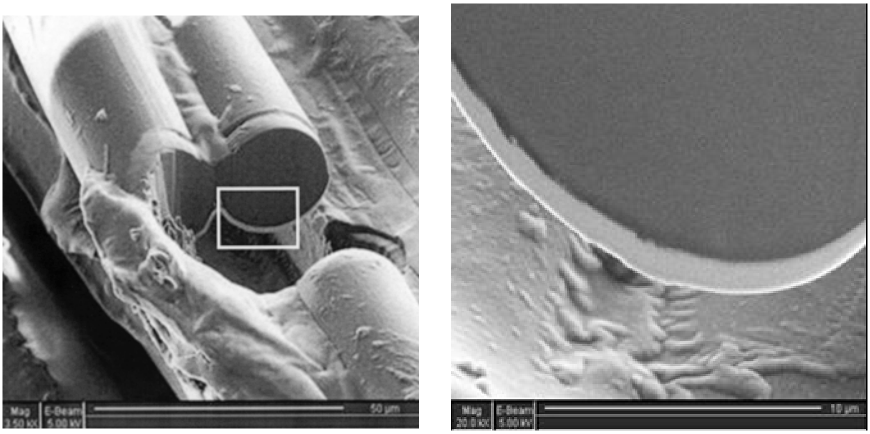
(c) (d)

16.4 SEM photographs of PANI-coated polyester spun (a), (b) and filament (c), (d) conductive fibres

the filament one. This phenomenon is supposed to improve contacts among PANI chains therefore the conductivity increases. Figure 16.5 shows a cross-sectional SEM photograph of the PANI-coated PET filament fibres. A thin and compact PANI conducting layer (< 1 micron) was observed on the fibre surface.

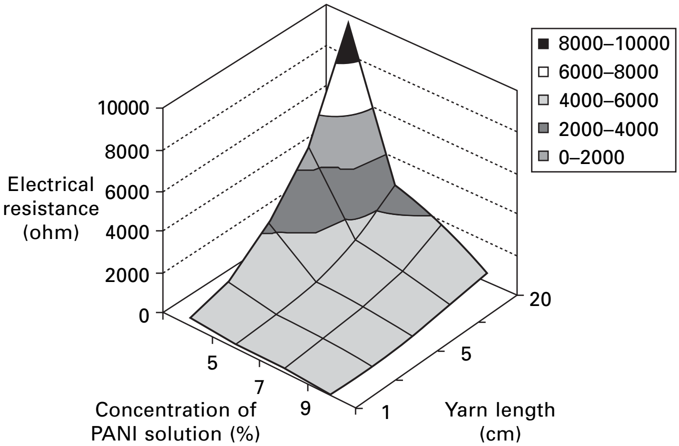
16.4.2 Electrical resistance of conductive yarns

The electrical resistance (Ω) of PANI-coated conductive yarns decreases as the concentration of PANI solution increases and the yarn length decreases. It is obvious that the concentration of PANI solution is important to obtain good electrical properties. The electrical resistance (Ω) below 5% of PANI solution coated PE yarns is significantly higher than that of PE conductive



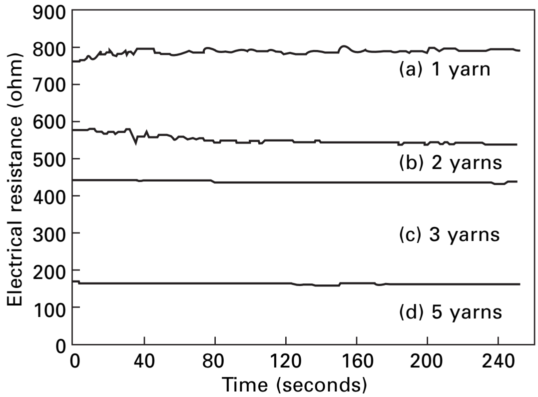
(a) (b)

16.5 Cross-sectional SEM photographs of PANI-coated polyester filament conductive fibres.



16.6 Electrical resistance of PANI-coated PE conductive yarns.

yarns coated with highly (7–10%) concentrated PANI solutions as can be seen in Fig. 16.6.[29] It was also observed in Fig. 16.7 that the electrical resistance decreases for PANI-coated PE conductive multiple yarns. However, the gelation of highly concentrated PANI solution occurs in short periods of time. The faster gelation occurs for over 8% of PANI solution compared to the 3~7% of PANI solution during the experimental procedure. The gelation of PANI solution is an irreversible reaction and is related to strong intra- and inter-chain bonding of hydrogen between secondary amine and tertiary imine groups of PANI. This gelation of PANI solution should be considered as an obstacle to the homogeneous coating of the fibre surface.[30] The temperature



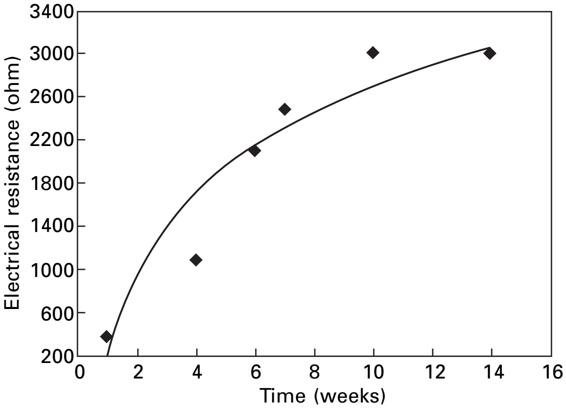
16.7 Comparison of electrical resistance for 5 cm of PANI-coated PE conductive multiple yarns.

of the PANI solution also influences the solidification of solution as well as the evaporation of solvent. In order to obtain a homogeneously coated conductive fibre using PANI solution, the temperature and the concentration of solution and the take-up speed of yarn from the solution have to be carefully controlled.

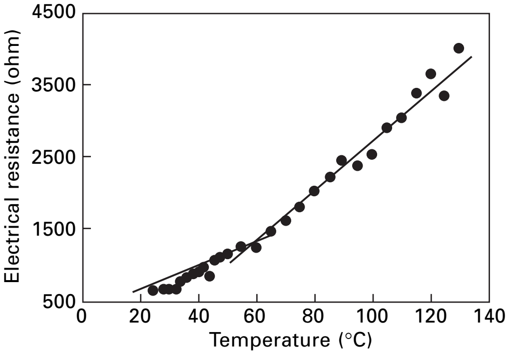
16.4.3 Environmental effects on the electrical properties

The environmental effects including times, thermal and ultraviolet (UV) radiation on the electrical properties of PANI-coated conductive yarns were studied. The ageing effect with time on the electrical properties of PANI-coated conductive yarns was studied under standard conditions (at 25 °C, 55.56 HR%). The electrical resistance for 5 cm of PANI/PE 7% conductive yarn increases for 12 weeks as we can see in Fig. 16.8.[31] The external protective layer on the conductive yarns could improve their electrical stability.

The influence of the temperature on the electrical resistance of PANI-coated PE conductive yarns is shown in Fig. 16.9. The electrical resistance increases slowly up to 55 °C. After passing this critical temperature, the electrical resistance increases more quickly. It is possible to notice that our conductive yarns may be used below 55 °C (critical temperature point) preserving their electrical properties.[31] This phenomenon may be explained by the combined actions of the fibre substrate and dopant used. Figure 16.10 shows the results from thermogravimetric analysis of the PE fibre, PANI powder, PANI-coated PE fibre and PANI/DBSA film. PANI powder is thermally stable up to almost 270 °C under nitrogen, and the decomposition of PE fibre is accelerated from 300 °C. PANI-coated PE conductive fibre is also thermally stable to up to 220 °C. However, thermal degradation of the PANI/DBSA



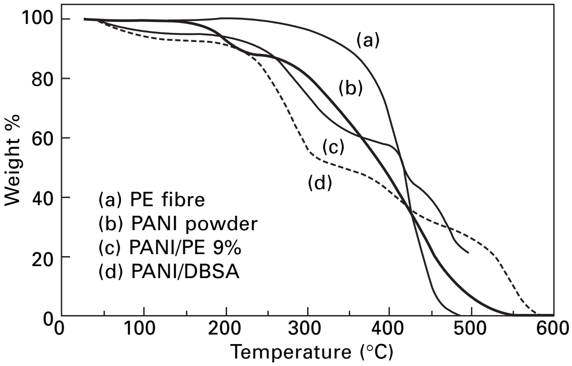
16.8 Electrical resistance of PANI-coated PE conductive fibres at time.



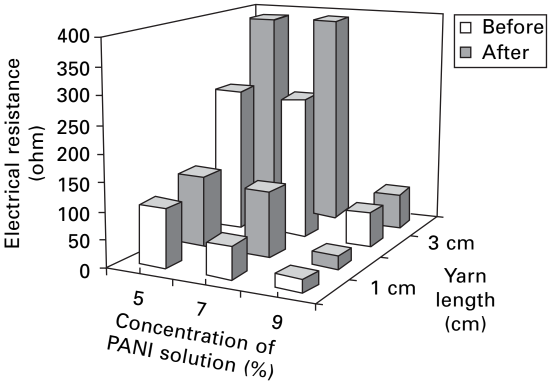
16.9 Influence of the temperature on the electrical resistance of PANI-coated PE yarns.

(dopant) film occurred faster. This result suggests that the dopant used strongly influences the thermal stability of conductive yarn coated with doped PANI solution (see Fig. 16.10, line d).

Generally, incident UV light has sufficient energy to provoke a catalysed decomposition of the polymer. The active chain ends produced by photodegradation may react with the polymer structure, producing cross-links that generate the brittleness of the polymer.[32] The UV sensitivity study is important to determine the photo-degradation behaviour of PANI-PET conductive yarns for textile applications. PANI-PET 6% and 10% conductive yarns that have been exposed to UV radiation for 80 hours show an important decrease of conductivity as we can see in Fig. 16.11.



16.10 TGA scans of (a) PE fibre, (b) PANI powder, (c) PANI-coated PE fibre and (d) PANI/DBSA film.

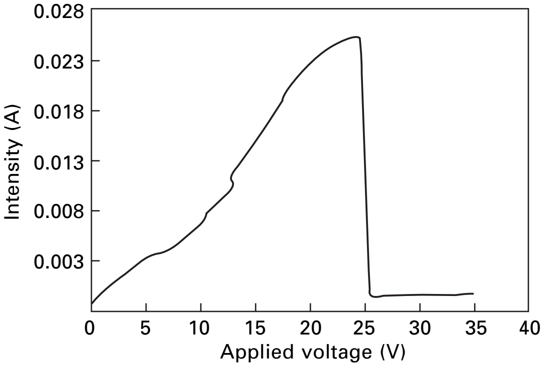


16.11 Electrical properties of PANI-coated PE conductive yarns before and after UV treatment.

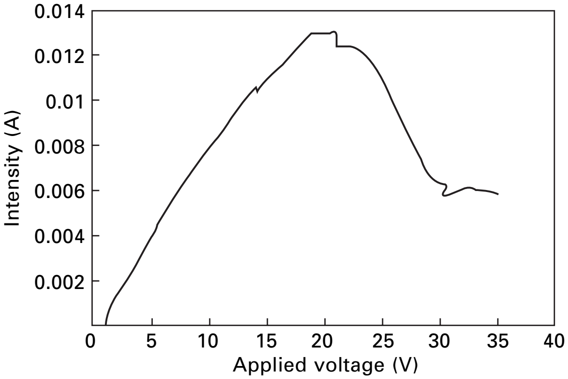
16.4.4 Damage of power handling

It is important to study the specific electrical properties of conductive yarns such as damage of power handling and tension threshold of conduction. Power handling of PANI-coated PET spun, PET filaments and PE conductive yarns are studied in this section.[33] Figure 16.12 shows the intensity (I) according to the applied voltage (V) for 5 cm of PET spun conductive yarns coated with 10% of PANI solution. The threshold tension of conduction ranging between 1.5 and 2 V and the supported maximum voltage (V_{max}) is 24.5 V for an intensity of 0.0025 A. The maximum power handling is thus 0.6 W for 5 cm of PANI coated PET spun yarn.

On the other hand, PANI coated PET filament and PE conductive yarns show different behaviours of IV curves. The maximum voltage for 5 cm of PANI/PET 9% is approximately 20 V and the curve of intensity decreases



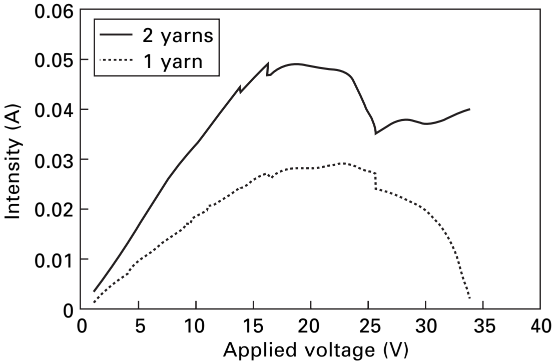
16.12 Intensity (I) as function of the applied voltage (V) for 5 cm of PANI/PET spun 10%.



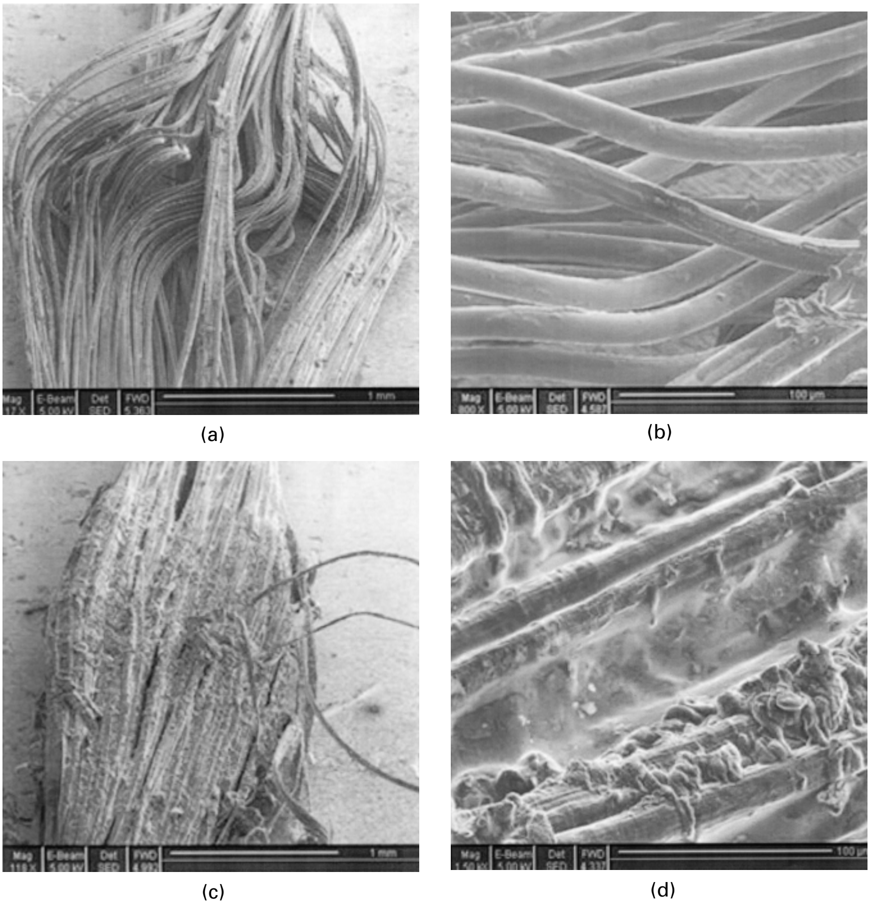
16.13 Intensity (I) as function of the applied voltage (V) for 5 cm of PANI/PET filament 9%.

irregularly from this point. The maximum power handling is approximately 0.25 W for 5 cm of PANI coated PET filament yarn, as shown in Fig. 16.13. In addition, the intensity of one yarn and two of PANI/PE 9% yarns increases linearly up to 15 V of applied voltage as we can observe in Fig. 16.14. At the rupture point of 15 V, the intensity for one fibre and two fibres is 0.027 A and 0.05 A, respectively. This result implies that the maximum power handing for one and two yarns should be 0.42 W and 0.75 W.

The electrical behaviour at maximum power handling of conductive yarns is not yet explained, but the local deformations of conducting layer at rupture are thought to play an important role. The morphological modification of the PANI conducting layers on the PET and PE fibre surface can be observed in Fig. 16.15. We suppose that the local temperature increases at maximum voltage and causes local deformation of the PANI layers which are responsible



16.14 Intensity (I) as function of the applied voltage (V) for 5 cm of PANI/PE 9%.



(a)

(b)

(c)

(d)

16.15 Morphological modification of PANI layers on the surface of PET (a), b) and PE (c), (d) conductive yarns at maximum power.

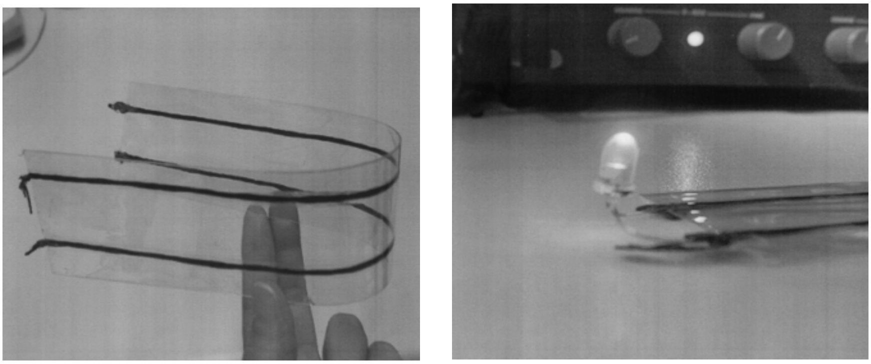
for conduction. The PANI chains on the conducting layers are locally disconnected and the conductivity decreases.

16.5 Applications: prototype

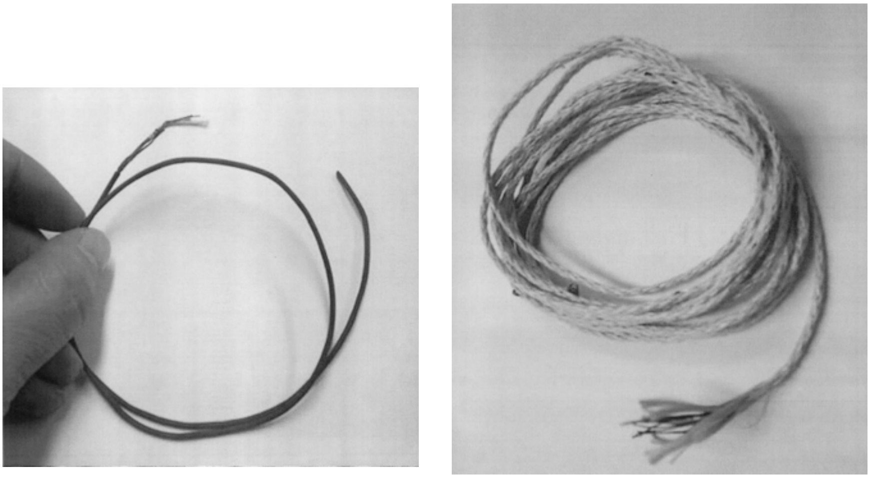
Since the prepared conductive fibres are based on the textile, the surfaces of conductive fibres have to be protected with an external layer in order to increase their stability and insulate them electrically. We have developed three different types of protecting layers for PANI-coated conductive fibres.[33] The first is covering the conductive fibres with a plastic film to protect fibres from abrasion. This prototype is flexible and lightweight as we can see in Fig. 16.16(a). These yarns can be used to transfer the electricity of approximately 3–6 V to light up the LED of 20 mA (see Fig. 16.16(b)). This prototype may also be used for transfer information. The second prototype is prepared by covering the conductive yarns with thermo retractable polyolefin tube (see Fig. 16.17(a)). The third prototype uses a weaving machine. PANI-coated conductive multiple yarns are protected by weaving a layer of Kevlar® fibres (see Fig. 16.17(b)). These prototypes show various possibilities for applications preserving the electrical and mechanical properties of textiles.

16.6 Conclusion

We have introduced the concept of conductive textile yarn preparation using two different methods, melt mixing and coating process. In this study, polyaniline (PANI) coated polyester and polyethylene conductive fibres have been prepared and analysed. From SEM photographs, we observe that approximately 1 micron of the PANI layer was deposited on the fibre surface. The electrical resistance of PANI-coated fibres decreases as the concentration


(a) (b)

16.16 (a) Prototype of conductive yarns covered with plastic films and (b) LED lighting test.


(a) (b)

16.17 (a) Prototype prepared using thermoretractable tube and (b) conductive yarns protected by Kevlar® fibers

of PANI solution increases. The concentration of PANI solution is important to obtain the homogeneous coating on the fibre surface. The threshold value of solution is between 6–9% of PANI concentration for our study. PANI-coated conductive fibres show sufficient electrical properties for various applications preserving their original strength and flexibility. Though PANI powder shows good thermal stability, the electrical properties of PANI-coated conductive fibres decrease at high temperature. Power handling and destruction of PANI-coated conductive yarns were also studied. It could be improved by using multiple yarns. Local deformation of PANI layers occurred at maximum current caused by increasing the temperature and the electrical properties have been modified. Three different prototypes of conductive multiple yarns have been developed in our laboratory using external protecting layers. These prototypes are expected to be used as conducting yarns, fibrous sensors, and connection devices in smart clothing or for electromagnetic shielding applications.

16.7 Acknowledgements

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17

Multipurpose textile-based sensors

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17.1 Introduction

In this chapter the classification of textile-based sensors has been carried out as a function of the measurement method which may be optically or electrically oriented. In the first case, frequently the Fiber Bragg Grating (FBG)[1] principle is used in order to determine the sensor dynamic stress[2–5] or temperature variations.[6–7] In the second case, the impedance following the same kind of physical modifications of the sensors' structure is measured. Usually, it is possible to measure only the electrical resistance but sometimes it is also necessary to measure the capacity and/or the inductance of the sensors. This depends mostly on the sensors' geometry.

This chapter is focused only on textile-based sensors using electrically oriented measurements, more precisely the electrical resistance. The most appropriate method to achieve this is to use electrically conductive polymers that are compatible with textile materials and structures. Therefore, two approaches are possible:

- coating the textile surfaces using conductive polymers also called 'organic synthetic metals'
- production of composites containing non-organic particles whose behaviour may be explained by metallic conduction theory.[8–11]

The common point of these two approaches is that polymers and metallic particles were used because of their good electrical properties (conductivity), facility of employment with temporal stability, oxidation resistance, and low cost.

Intrinsically conductive polymers (ICPs) have been considered as promising materials with their highly conducting properties in which polymer chains contain long conjugated double bonds.[12–13] These materials can be simply prepared using electrochemical or chemical oxidative methods but most ICPs are infusible or insoluble in common organic solvents. However, significant advanced solution processing of ICPs has been developed over the last decade to improve their low solubility. For example, chemical modification of monomers with dopants has been enhancing the solubility in the case of polythiophene (PT) and polyaniline (PANI).[14–18] Among the conductive polymers, polyaniline (PANI) was used in our first approach to obtain conductive polymer textile sensors. The mechanical and thermal influences on the electrical properties of PANI coated textile sensors are studied and discussed in Section 17.2.

On the other hand, among non-organic particles, carbon black[19] seems to offer the optimal compromise between electrical conductivity and price compared to other metal particles such as gold, silver and copper, etc. Electrically conductive polymer composites (CPCs) are obtained by blending (generally by melt mixing) an insulating matrix polymer (thermoplastic or thermosetting plastic) with conductive fillers like carbon black (CB), carbon fibres or metallic particles. However, adding the fillers to the matrix to impart conductivity generally modifies the mechanical properties of composites.[20–21] In addition, using alternative thermoplastic elastomeric (TPE) matrices seem to be more interesting because these composites do not always exhibit the best balance of properties for sensor applications. For pressure or deformation of CPCs sensors, the analogy with ferroelectrics suggests that the maximum sensitivity of electrical response to mechanical compression and elongation may be expected at conductive particles concentrations corresponding to a percolation threshold of electric conductivity.[22]

It is important to analyse the electrical conductivity of composite materials as a function of the filler concentration in order to identify the percolation threshold. It is well established that sensor sensitivity at this threshold point should be optimal.[23] In this case the global sensor conductivity is often not sufficient for measuring applications. In fact, this conductivity usually does not fit the measurement systems. For that reason it is necessary to find a good compromise between sensitivity and global conductivity which leads to optimal resistance of the sensor system. This resistance depends also on sensor geometry and dimensions. Finally, it means that the threshold point (equivalent to filler concentration) should not be selected if the global resistance of the sensor system does not fit the measurement system and the sensor will be made according to the compromise sensitivity ↔ global resistance. Moreover, other external parameters such as temperature, presence of solvent vapour and relative humidity (for example) may significantly affect a CPC electrical properties.[24–25] If there is a simple relationship between electrical conductivity and these external parameters and if the influence of each parameter can be identified, the composite has potential application as a sensor. For example, if the temperature influences strongly the electrical resistance and other parameters have non-significant influence, the composite material should be used as a temperature sensor.

17.2 Conductive polymer textile sensors

17.2.1 Sensors based on electrically conductive polymers – overview

Intrinsically conductive polymers (ICPs) such as polyaniline, polypyrrole, polythiophens and their derivatives show electrochemical reactions like the oxidation and the reduction of the polymer chains. They may also be sensitive to redox environment, temperature, humidity, and inorganic/organic vapours. One of the potential applications of ICPs has been extended from sensor devices to their use as transducer-active polymers in various sensing configurations (pressure, temperature, chemical and biological stimulus). Table 17.1 shows the various application areas and current commercial applications of ICPs as sensors.[26]

In this chapter, we have focused on the preparation of conductive polymer textile yarns for applications in the field of electro-mechanical fibrous sensors. PANI-based conductive yarns were prepared using a coating process that involves the transition system from a solution of PANI into a solid 'gel' phase on the fibre surface. We then investigate the mechanical and thermal effects on their electrical resistance.[27–28]

Table 17.1 Several potential applications of conductive polymers

General applications	Sensor configurations
• Electrostatic dissipation • Absorption of radar frequencies • EMI (electromagnetic interference) shielding • Polymer electrolytes • Photovoltaics • Catalytic layer • Redox mediation • Chemically and biologically sensitive on/off redox switch • Chemically and biologically modulated resistor • Molecular recognition and perconcentration • Polyelectrolite gels as actuators or artificial • Electrochromic devices and smart windows	• Potentionmetric chemical sensor • Amperometric sensor • Conductimetric sensor • Voltammetric sensor • Electromembranc sensor • Combined conductive electroactive polymer membranes of polypyrrole and transistor (FET) device (CHMFETs) • Artificial muscles as electrochemopositioning devices

17.2.2 Experimental

Materials

The following two important factors were carefully considered for the coating process. Firstly, the organic solvent has to be compatible with textile substrates without modifying their mechanical properties. Secondly, one of the challenges to improve the mechanical property of the PANI-coated textile yarns is to use high-modulus fibres like wholly aromatic polyamide fibre, carbon fibre, polyacrylate fibre or ultra high molecular weight polyethylene fibre.[29] Considering these two factors, the commercial polyethylene terephthalate (PET) spun (111 dtex, Hyosung) and ultra high molecular weight polyethylene (UHMW-PE, Dyneema®, 220 dtex, DSM Company) yarns have been used as fibre substrates because of their good solvent resistance and mechanical properties.

Sample preparation

The emeraldine salt form of polyaniline (PANI-ES, Sigma-Aldrich) and dodecylbenzene sulfonic acid (DBSA, Fluka) mixtures of 1:0.5 in weight ratio were dissolved in xylene to prepare PANI solutions ranging from 7 to 10 wt%. These solutions were stirred vigorously for three hours at 90 °C and treated in the ultrasonic bath for two hours. The continuous coating process was performed using an experimental device which may be equipped with several baths filled with PANI solutions. PANI-coated yarns were taken up in the presence of a dry airflow around coated yarn surfaces to enhance solvent evaporation. The thickness of the PANI layers on the fibre surface was approximately one micromet.

Electro-mechanical properties measurement

A tensile test was performed using a tensile tester (MTS®, Mechanical Testing and Simulation) with its software 'testworks' at 20–25 °C, 65 RH%. The sample length was fixed at 50 mm between two electrodes and the speed of traction was 12 mm/min. At the same time, the electrical resistance of the conductive yarns was measured with an Agilent 34401A multimeter. Figure 17.1 shows the electro-mechanical test set-up (middle) with two electrodes (20 mm × 20 mm) connecting the fibres to a multimeter and the tensile test machine.

17.2.3 Results and discussion

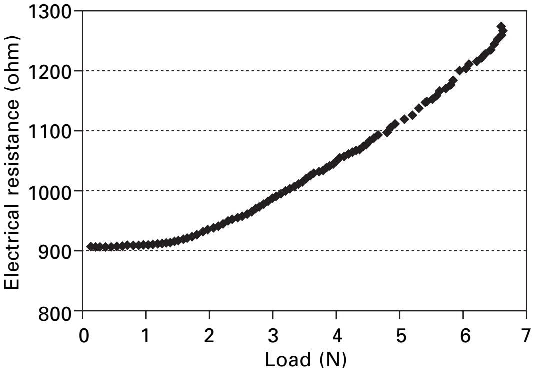
Mechanical sensor applications

In this section, we discuss several experimental results of conductive yarn sensors coated with 7%, 9% and 10% of PANI solutions. More detailed

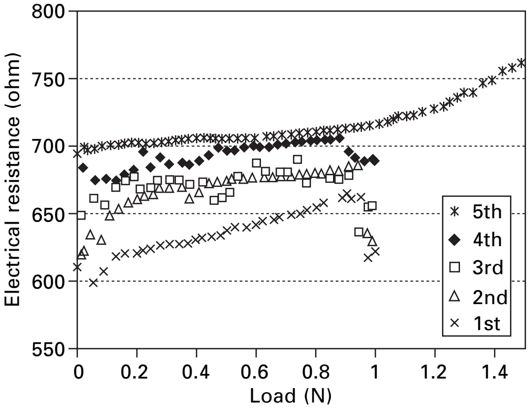
17.1 (a) Electrodes in copper (b) head of electro-mechanical test.

study of the influence of the PANI concentration on the electrical resistance of coated yarns is given in Chapter 16. The dependence of the electrical resistance of conductive yarn on different elongations is shown in Fig. 17.2. The electrical resistance of the conductive PANI coated PET spun yarn increases slightly with an increase of the load. The increase of the electrical resistance is accelerated from the stretching yield point (approximately at 1.5 N) of used PET spun yarn. From the yield point of fibre substrate, the deformation of conductive PANI layers on the fibre surface is accelerated. The morphological structures and interactions among PANI chains have an important influence on conductivity. We suppose that with the increase of PANI molecular chain distances by micro-cracks in conductive layers, the number of connections between polymer chains decreases. In fact, the conductivity mechanism could not be explained only with a single chain theory.

Conductivity of polymers is rather a superamolecular phenomenon. The interactions of chains, defects at the molecular level, the direction and the



17.2 Electro-mechanical property for 5 cm of PET conductive yarn coated with 9% of PANI solution at different loads (N).



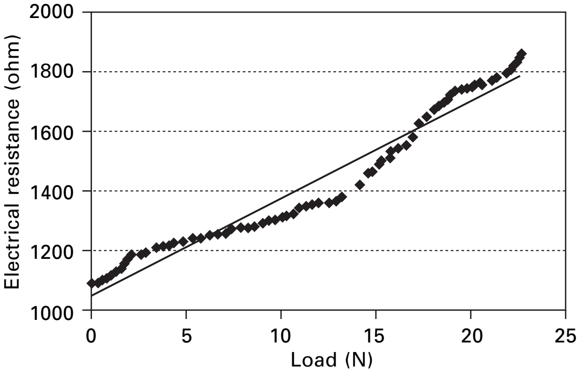
17.3 Repeated cycles of stretch recovery tests for PET conductive yarn coated with 9% of PANI solution.

arrangement of the chains and the chain distances are regarded as the important parameters for conductivity.[30–31] Therefore, models of solitons and polarons have been very popular to explain this mechanism in conductive polymers. The ability of conductive yarns to recover from deformation was also studied by means of the strain recovery test. The stretching and recovery cycles for PANI coated PET spun yarn were repeated four times up to 20% of the breaking load, and the fifth stretching was continued until breaking point. Electrical resistance decreases as a function of applied load for each cycle as we can see in Fig. 17.3. The loss of electrical resistance was approximately 12–15% of the initial value. The mechanical abrasion inducing this loss could be reduced using external protection of the sensor.

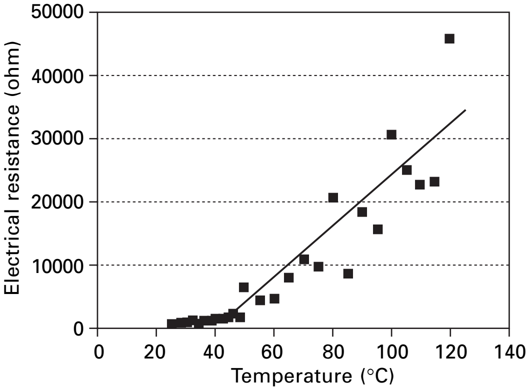
The electro-mechanical properties of PANI coated Dyneema® conductive yarns were also studied. The tensile test of conductive yarn was continued up to 90% of its breaking load and the electrical resistance was measured at the same time. The electrical resistance of PANI/Dyneema® conductive yarn increases about two times at 20 N of the load as we can see in Fig. 17.4. It can be explained that the PANI conducting layers on the fibre surface change their compact and continuous forms under strain. However, PANI coated Dyneema® yarns were not totally broken due to their important mechanical properties (resistance to break). The electro-mechanical properties are very important to confirm the possibility of applications of our conductive yarns as electromechanical fibrous sensors.

Temperature influence on electrical resistance

The thermal stability of conducting yarns is an important parameter. The study of thermal dependence of conductive yarns beyond a certain temperature should be interesting for their applications as temperature sensors. The influence



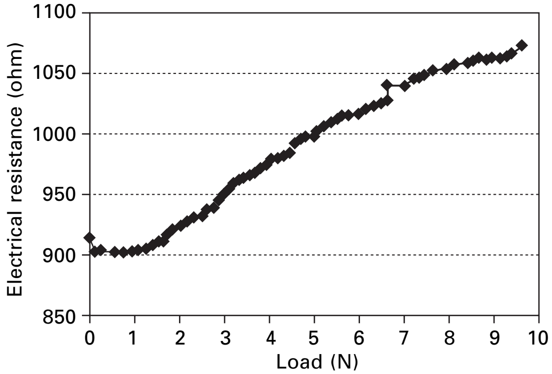
17.4 Electro-mechanical property at different loads for 5 cm of Dyneema® conductive yarns coated with 7% of PANI solution.



17.5 Temperature influence on the electrical resistance for 5 cm of PET conductive yarns coated with 10% of PANI solution.

of temperature on the electrical resistance of PET conductive yarns coated with 10% of PANI solution is shown in Fig. 17.5. The electrical resistance of conductive yarns increases slightly until 55 °C, then increases quickly at higher temperatures. It is possible to notice that our PANI coated PET conductive yarns may be used below 55 °C without important modification of the electrical properties and as a temperature sensor beyond 55 °C.

The temperature influence on the electro-mechanical properties of PANI coated Dyneema® yarns was also studied after treating the yarns in an oven at 70 °C for 24 hours in order to determine the thermal recovery properties of sensors. We can observe in Fig. 17.6, that the electrical resistance increases under strain, but sample sensitivity remains sufficiently for strain measuring applications after the thermal treatment. However, brief exposure at a higher temperature did not cause any serious deterioration of the electro-mechanical properties.



17.6 Temperature influence on the electro-mechanical properties for 5 cm of Dyneema® conductive yarns coated with 9% of PANI solution.

17.2.4 Discussion and conclusion

Polyaniline (PANI) based polyester (PET) and polyethylene (Dyneema®) conductive textile yarns were prepared by a coating process and their electro-mechanical properties and temperature influence on the electrical properties were studied. Our conductive yarns showed interesting properties for electrical applications preserving the original strength and flexibility of used textile substrates. The thickness and morphology of the coating conducting layer are considered as important parameters on the electrical response to stimuli. The coating layer properties can be modified by the concentration of conducting materials in solution, the applied tension and take-up speed of the yarns (fabric) and drying conditions of the coating process. The electrical stability to environmental damage (thermal, abrasion and humidity, etc.) of coated yarns should be controlled using an external protecting layer. Further improvement of processing is expected to enable the utilisation of conductive yarns in a wide range of potential applications such as fibrous sensors, flexible textile connections or for electromagnetic shielding (EMI).

17.3 Conductive polymer composites (CPCs) textile sensors

17.3.1 Materials and methods

Materials

For the realisation of the CPCs, ethyl-vinyl acetate (EVA) with density 0.94 g/cc (EVA 1080 VN5, ElfAtochem) and EVOPRENE with density 1.16 g/cc (EVOPRENE 007, AlphaGary) were used as matrix polymers. These

Table 17.2 Characteristics of Printex L6 (Degussa Corp.)

	Particle diameter (nm)	Structure (DBPA number)	Surface area (m^2/g)	Volatiles (%)
Printex L6	18	122	250	<1

thermoplastic elastomers (TPE) were selected because of their outstanding mechanical properties for various applications (weak Young's modulus and high elasticity). The filler (conductive particles) was a high structure carbon black (HSCB), Printex L6 supplied from Degussa Corp. The characteristics of this HSCB are given in Table 17.2.

A novel method via solvent at low temperature was developed in our laboratory as an alternative to the usual filling process (melt mixing) used to make the CPCs. The polymer (EVA or EVOPRENE) and the CB (Printex L6) were introduced, in adapted quantities, into a closed beaker with chloroform. The solution was heated between 35 °C and 60 °C then stirred for approximately 100 minutes. Then the mixtures were dried until all the chloroform evaporates (approximately 24 hours). The final result was a homogeneous bloc of CPCs. The filled polymer was cut into pellets. At least six samples of TPE with different values of filler contents of HSCB were prepared.

To undertake the characterisation (mechanical and electrical) of the CPCs, compression moulded plates were prepared. The CPC pellets were sandwiched between teflon frames heated at 170 °C (EVOPRENE) or at 200 °C (EVA) for two minutes without pressure followed by repeated pressure cycling at 50×10^5 Pa (50 bar) in order to remove air bubbles. Plates were then cooled to ambient temperature.

In addition to preparation of plate samples, the previous solution was used to prepare textile oriented samples by coating on a Nylon fabric. These samples were used to verify the compatibility of a new filling process with textile structures (fabrics, yarns). Moreover, these samples were used to measure the electrical resistivity-strain behaviour and the effect of external parameters on electric resistivity.

Methods

Stress-strain behaviour for uniaxial tension was measured at room temperature with sample gauges cut from the compression moulded plates. The distance between the grips was 35.0 mm and the thickness of a sample gauge was 1.0 mm. Gauges were deformed at the rate of 50 mm/min with a classical uniaxial tensile testing machine (MTS®). Electrical resistance was measured with a multimeter (Agilent 34401A). Each CPCs sample (width 20 mm, thickness 1.0 mm) cut from the compressed moulded plates was placed

Table 17.3 Characteristics of Nylon fabric used in this study

	Warp	Weft
Linear mass (dtex)	33	
Surface mass (g.cm^{-2})	42	
Young's modulus (Mpa)	930	200
Elongation at break (%)	24	46

between two copper electrodes. The measurement device was interfaced to a computer to record and process data.

For the textile-based sensor obtained by coating of 6.6 Nylon fabrics (Table 17.3), samples with dimensions 300 mm × 50 mm were used. The same multimeter and uniaxial tensile tester were used, but strain rate was fixed to 16 mm/min in order to have a sufficient number of points because of the low frequency of acquisition imposed by the measuring system. Both instruments were controlled by a computer. These samples were used to measure changes in conductivity during stretching.

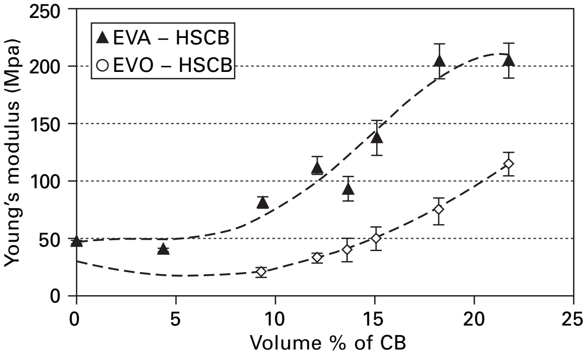
The effect of external parameters (temperature and relative humidity) on electrical conductivity has been quantified by carrying out measurements on fabric samples (Nylon fabrics coated by CPCs) placed in a climatic chamber (FLONIC®). The electrical resistance for a given temperature and relative humidity was measured for at least two hours, which is the time necessary for the chamber's regulation. Finally, the mean value obtained during the last 30 minutes was recorded and used in the further processing.

17.3.2 Results

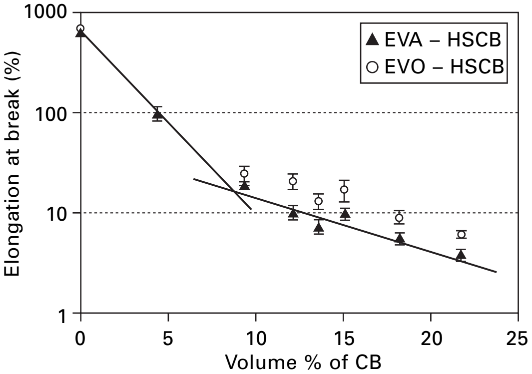
Mechanical properties

As a first step, the reinforcement effect of the CB nanoparticles for two thermoplastic elastomers (TPE) was investigated. The evolution of Young's modulus as a function of the CB content expressed in vol% was plotted in Fig. 17.7. It is obvious that Young's modulus of the composites increases with an increase of CB content. Since the Young's modulus of the inorganic fillers is usually much higher than those of polymers, this is typical behaviour for polymer/inorganic composites.

The influence of CB content on elongation corresponding to the break point of a compressed sample is shown in Fig. 17.8. The shape of these influences confirms the generally known fact that an elongation corresponding to the break point of polymeric composites decreases with an increase of the filler content. This behaviour is common for polymers filled with rigid inorganic particles. For EVA-CB composites, the curve suggests two different elongation phenomena. This result confirms the theory that the clusters formed by the



17.7 Young's modulus of the EVA-HSBC and EVO-HSBC composites.

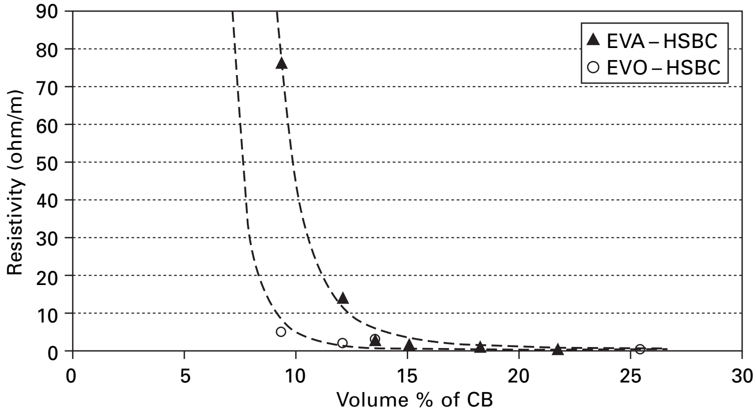


17.8 Elongation corresponding to the break point of compressed samples of the EVA-HSBC and EVO-HSBC composites.

conductive particles build a path not only for electrons but also for the formed microcracks that can grow easily into a crack of catastrophic size when the filler concentration is above a certain level.[32] For our composite EVA-CB, this 'catastrophic' filler concentration can be estimated to 8.4 vol% of CB.

Electrical properties without strain

The dependence of electrical conductivity of the EVA-CB and EVO-CB composites on the filler content is shown in Fig. 17.9. The resistivity as a function of filler content showed the typical S-shaped behaviour with three regions (dielectric, transition and conductive). Samples with low filler content were nonconductive. The step decrease in electrical resistivity was observed for different concentrations of fillers in spite of the fact that the CB used and



17.9 Electrical resistivity as function of filler contents.

the filling process are the same. Generally, electrical resistance depends on two parameters: the first is related to the concentration, the size of conductive CB particles and their 3D geometry configuration (dispersion, homogeneity…). The second is related to the physico-chemical compatibility between CB particles and matrix polymer. It is important to notice in Fig. 17.9 that for the same CB particles and the same concentration (for instance 9 vol%), the electrical resistance varies from 6 Ω.m for EVO-CB to 75 Ω.m for EVA-CB. Therefore, it is possible to conclude that EVO is more compatible with the CB particles that EVA. For higher concentrations, this difference is smaller. The concentration corresponding to a step decrease (threshold) is called the percolation concentration (Cp). It characterises the concentration of the filler where an internal network of particles is formed within the matrix and the material becomes electro-conductive. The percolation concentration was arbitrarily defined (identified) as an inflection point in the empirical fitting curve. For EVA-CB composite, the percolation threshold can be estimated to be lower than 9 vol% and for EVO-CB composite; it was roughly 7.5 vol%. The value obtained for the EVA-CB composite fits that obtained from Fig. 17.8. For this composite, mechanical and electrical percolations occur for around 9 vol%.

For applications as textile sensors, it is important to have a relatively high conductivity (< 1 Ω.m), high elasticity and high elongation at break at the same time. As recently shown, the mechanical properties decrease when the vol% of CB increases. It was thus necessary to fill the polymer with a minimum vol% of CB. However, for an identical resistivity (for instance 0.5 Ω.m) the necessary rate of CB in the EVA composite (21.7 vol%) was higher than the rate of CB in the EVO composite (15.1 vol%).

Electrical properties under strain of textile oriented sensor

These measurements were carried out on Nylon samples (300 mm × 50 mm) partially coated with EVA-CB composite, 21.7 vol%. The coating zone, positioned in the centre of Nylon samples, parallel to weft threads, has a dimension of 67 mm × 1 mm. The dependence of relative electrical resistivity of the EVA-CB composite on the elongation of the Nylon sample partially coated is shown in Fig. 17.10. The resistance of coating without elongation was arbitrary normalised to 1. The curve shows a very important increase of resistivity when the elongation increases slightly.

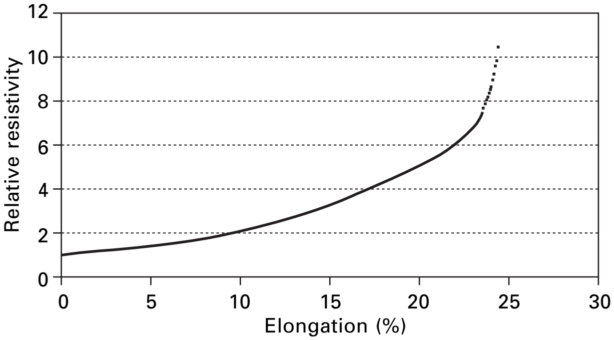
The variation of the resistivity was quasi-linear until 10% of elongation with the coefficient of correlation of 0.97. Unfortunately, the phenomenon was non-reversible because the yield stress of the Nylon fabric was approximately 3%. The sensitivity, K (see eqn 17.1)[28] of the pseudo-sensor was very good (~ 10).

$$K = \left(\frac{\frac{\Delta R}{R}}{\frac{\Delta l}{l}} \right) \qquad 17.1$$

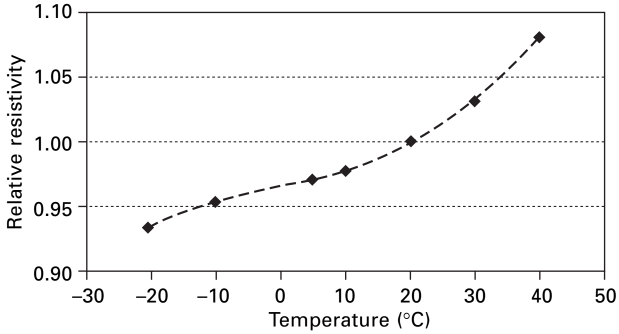
For comparison the coefficient *K* of a classical metal gauge (copper-nickel) is 2.1. Moreover, a classical metal gauge has a range between 0.1 and 0.5% of elongation.[33]

Effect of external parameters on electrical properties

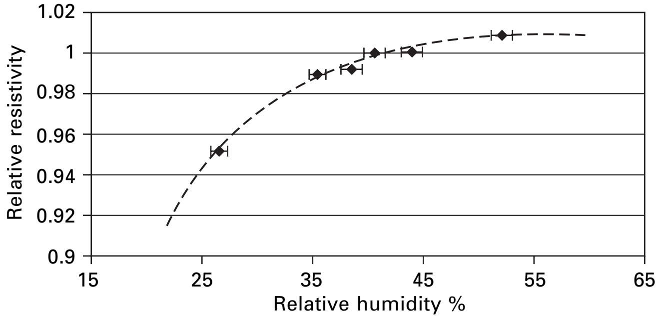
The dependence of relative electrical resistivity of EVO-CB (18.25%) composite on the temperature is shown in Fig. 17.11. Measurements were taken on Nylon fabrics partially coated by EVO-CB composite. The relative humidity



17.10 Relative electrical resistivity versus elongation of Nylon fabric coated with EVA-CB (21.25 vol%).



17.11 Temperature influence on the relative resistivity.



17.12 Influence of relative humidity on the relative resistivity.

was maintained at 40% ± 2.5% during measurements. The resistivity obtained at 20 °C was normalised to 1. The curve shows a non-linear behaviour. However, the relative resistivity variation was weak (0.2%/°C in the range between –20 °C and 40 °C) compared to the variation caused by lengthening (see p. 339). Therefore, it should be possible to make corrections according to the temperature; an approximate measurement of this one, would be sufficient.

The influence of the relative humidity on the relative electrical resistivity of EVO-CB (18.25%) composite is shown in Fig. 17.12. Measurements were taken on Nylon fabrics partially coated by EVO-CB composite. During measurements, the temperature was maintained at 20 °C ± 1 °C. The resistivity obtained at 40% of relative humidity was again normalised to 1. As for the effect of temperature on relative resistivity, the curve shows non-linear behaviour. However, the relative resistivity variation was weak (0.2%/1 RH%, in the range 25–55 RH%) compared to the variations caused by lengthening.

Taking into account the current results, two solutions may be envisaged: (i) bring corrections to data coming from the sensor using a calibration curve or (ii) realise a protection against moisture around the sensor. The first solution implies the realisation of cyclic measurements to detect the possible presence of a hysteresis. Therefore, the second solution seems to be simpler. However, we must be sure that this protection does not disturb the mechanical behaviour of the sensor.

17.3.3 Discussion

The electrical conduction of insulating polymers charged with conductive particles inducing a metallic behaviour is due only to physical phenomena. As shown earlier the resistivity as a function of filler content showed the typical S-shaped behaviour with three regions; dielectric, semi-conductive and conductive. In the dielectric region, the number of particles is not significant enough to form an electric driver network from one end to the other of the sample. On the other hand, if the number of conductive particles is significant and the network is continuous, electric conduction is assured. The transition between these two phenomena takes place at a critical rate of conductive particles called the 'percolation threshold'.

To create a sufficiently sensitive sensor, it is necessary that the rate of conductive particles of the composite should be slightly higher than the rate of percolation. Indeed, when the composite is lengthened, the number of electrical contacts between particles will decrease. If, in spite of this fall, the number of contacts remains high, electrical conductivity will not be affected. Lengthening a composite of concentration slightly higher than the percolation threshold will cause a significant loss in the number of contacts. The electrical sensitivity of the composite with respect to lengthening will thus be significant.

The polymer of the composite is useful to bind the carbon particles among them. The polymer should have the two following properties to avoid sensor deterioration during successive deformations:

1. The elastic range of the polymer should be larger than the sensor's potential extent of measurement.
2. It must be compatible (from the aspect of physicochemical adhesion) with the carbon particles. Thus, during deformations, the particles will not be exposed and electrical conduction will always be assured.

17.3.4 Conclusion

Realisation of a CPC solution at a low temperature was adequate to produce either composite pellets (useful for, for example, creating plates) or textile matter (fibres, yarns or fabrics) by coating. The results obtained with composite plates confirm that it is possible to detect the percolation threshold, either by electrical or mechanical measurements.

First results, concerning the behaviour as a sensor of the composite coated on a fabric, are encouraging. Below 10% of lengthening, the behaviour is quasi-linear and the sensitivity is four times more significant than for a traditional metal gauge. The composite is also rather sensitive to the moisture and the temperature. Calibration curves can be plotted to bring correction to the data according to these parameters. To improve the determination of the characteristics of the sensor, cyclic measurements (for lengthening, temperature and moisture) have to be carried out. The applications of a sensor as a textile-compatible lengthening gauge are numerous: intelligent boat's sails or aeronautic structures (parachutes), monitoring of deformable structures, etc. Moreover, if the composite is not deformed mechanically, a good sensitivity to moisture enables its use as a fast response moisture sensor.

17.4 Perspective

The use of intelligent materials reacting to external stimuli is growing in the field of technical textiles. Many products involving electrically conductive textiles exist on the market. In the majority of cases metal particles or carbon black were used to create conductive textile structures. In this chapter, the preparation of conductive materials based on textiles using two different methods, coating and solvent mixing process have been explained. The goal of our researches was to prove the feasibility of new textile materials (fibres and fabrics) for electronic sensing applications, electro-mechanical or thermal data acquisition or even for data transfer elements. Future research and development should be focused on the creation of new textile materials with semi-conductive properties enabling the 'weaving' or 'knitting' of electronic circuits and devices.

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18

Textile micro system technology

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18.1 Textile micro system technology

During the last ten years micro system technology has not only focused on the size of the components but also on their flexibility. Importantly, the integrated electronic components are more and more based on flexible foils to avoid mechanical stress between the components and to be able to focus on new applications with new demands. In other words, the smaller the electronic devices the more mobile the final systems can be and the more flexible the electronic substrates the more wearable they become. That is why the focus is on:

- conductive structures on transparencies as new flexible electronic substrate
- printable conductive, semiconductive and insulating material to wire up the flexible electronic boards and to prepare printable electronic devices
- new technology to connect electronic devices on the flexible substrates.

But the electronic is only one component of a micro system. It needs to integrate power sources, sensors, actors, and input and output devices to communicate, to display and to transfer data.

Data transfer may occur first on a body area network, to collect the data from small sensor units via flexible data lines or wireless to a larger unit in the personal area network. This unit might be linked to a gateway to a wide area network or even with the internet. The Fraunhofer Institut für Photonische Mikrosysteme has already presented the first example of a flexible system based on electrodes placed on transparencies connected to a measuring unit which is located on the same transparency to measure the electrocardiogram (ECG) in a running project.[1] Importantly, for the development of such telemedical systems as well as for control units in hard- or even non-accessible units of machines and other technical devices, flexibility becomes more and more critical.

Nowadays we are able to integrate into our clothing such micro systems and electronic components due to their decreasing size and greater flexibility.

But clothing or, generally speaking, textile structures, are not simply flexible. Textiles are pliable. They have a non-rigid shape. They are pliable and depending on the structure more or less elastic. Furthermore, textile structures are permeable to air and moisture because of their inherent microstructure and that is much more than we can expect from a foil-based structure. So, why do we not use textiles to create micro systems?

Their advantage of being non-rigid is at the same time their disadvantage. Until now, no technology to create, handle and connect electronic or mecatronic micro components on such pliable microstructures existed, apart from textile technologies. The dilemma is that micro system technology as well as the electronic focus on lithographic structures and all technologies to generate, handle and to link such structures to prepare electronic devices or micro systems are focused on this basic technology and substrates.

Before we can start to use fabrics and textile structures as new substrates for electronic devices and as basic substrates to create micro systems it is necessary to have a closer look at the textile structures, their dimensions, the lateral resolution of such structures and the possibilities of textile technologies to design the structures needed to create textile-based electronics and micro systems.

18.2 Textiles are inherent microstructures

Let us examine more closely the classic textile technologies and their possibilities to create microstructures. A view of fabrics under the microscope show us the enormous variety of textile structures mainly designed to create new patterns, ornaments and decorations but also to have new functionalities or to improve textile properties. When we are going to use such structures for the applications mentioned above, we should know which kind of structures are available by weaving, knitting, warp knitting, braid and embroidery.

18.2.1 Weaving

The structuring possibilities of weaving can be illustrated with the example of the CMY Colour Weaving developed in the TITV Greiz.[2,3] The CMY Colour Weaving permits the creation of photographic images on inferior floating Jacquard weavings on a uniform white or black warp beam together with defined coloured weft threads. The technology is based on a systematic analysis of weaves to obtain virtual colours on three basic colours (either RGB or their inverse colours CMY) together with a white and black thread. The procedure is based on a 4i × 4i matrix or 3i × 3i if the key thread (white in the case of RGB or black for CMY) is not used. The best result was obtained on a 8 × 8 matrix which permits over 28,000 colours with a woven virtual pixel size of about 1 mm^2. Furthermore, the systematic analysis of all binding possibilities yields several opportunities, to design identical colours on the same matrix size. Therefore the virtual colour binding sets can be subdivided into several classes. A systematic selection of binding of different classes enables us to give shape to the surface of the coloured weaving without loss of quality and colour impression. Finally, it permits the concealment of a code in each virtual pixel using bindings with the same virtual colour but from different classes. This is then readable with a commercial scanner.

Such a woven structure can be compared to a monitor and the hidden code shows that it is even possible to store permanent data. The minimum matrix size of 3 × 3 yields the best resolution of the resulting woven image of 10,323 pixels per square inch (ppsi) by use of a weaving machine with Satin quality (120 threads cm^{-1} = 305 threads per inch) or 2,567 ppsi by use of Taft quality (60 threads cm^{-1} = 152 threads per inch). These resolutions of more than 10,000 ppsi (Satin quality) and more than 2,500 ppsi (Taft quality) are much greater than the resolution of our TVs and comparable with a 17 inch monitor resolution in the different graphic modes. A 17-inch monitor driven with the lowest resolution 640 × 480 pixels corresponds to 2,581 ppsi with 800 × 600 pixels to 4,032 ppsi and with 1024 × 768 to 6,606 ppsi. Therefore the Taft quality would correspond to a 640 × 480 pixel monitor resolution and the Satin quality would be even superior to the 1024 × 768 pixel monitor resolution and additionally do not forget the possibility to store hidden information. An amount of 2*(1280/8)*1*2*..*8 bits = 1,032,192,000 bits = 129,024,000 Byte = 129 MByte » 89,600 pages » 896 books can be theoretically stored on one woven image using 1280 warp threads per image, the same number of weft threads as an 8 × 8 elementary binding set. This is a vast amount of information on a piece of fabric of 4 inch × 4 inch when woven in satin quality or 8 inch × 8 inch on a Taft machine. Nobody would recognise the woven image as a carrier of such a huge amount of information.

This means that as soon as we are able to weave conducting and semiconducting threads together with non-conducting threads to create interactive weave crossings, then textile displays and electronic boards will be available. Furthermore, it can be shown that multi-layer weaving allows us to create electrical contacts or to avoid such a contact of conducting threads in the warp and weft directions. This is the basis to create the well-known structures used in micro system technology, e.g., electrode comb structures, double electrode comb structures also known as interdigital structures, meander and coil structures, as has been shown in refs 8–9. The interdigital structure is the most important structure to prepare gas sensors and in combination with piezoelectric materials to build actuators. Furthermore these structures with their double comb electrode structures can be used to design batteries, super capacitors and even light sources. Until now interdigital structures may only be prepared with comb electrode distances below 300 μm by lithographic techniques.

18.2.2 Knitting

Knitting structures are special mesh structures. If we look at Nylon stockings the size of a single mesh is in the micrometre range using monofilament yarns of 22 dtex (2.2 tex) or even less. (For those) who are not familiar with the units used for yarn size, it is given as the ratio of the weight and the length of a thread either in tex or numometric (Nm): 1 tex = 1 gkm^{-1} and 1 Nm = 1 mg^{-1}. A thread material density of 0.8 gcm^{-3} and a size of 2.2 gkm^{-1} yields a yarn diameter of the monofilament of 59.2 µm.

Recently, knitted structures were not used as electronic substrates apart from a few examples where textile heating was based on a knitted structure. The main interesting point of knitted structures is the possibility to get the thread back from such structures. This is called back-knitting and permits the modification of textile material in the shape of a fabric with a high surface. Hence, all textile finishing procedures known to handle knitting may be used to modify the surface of the thread and after back-knitting the modified threads are available. In this way each filament of the threads of the textile surface can be covered by conducting material. It can be done by use of carbon or conducting polymer dispersions or by chemical deposition of very thin metal layers. It will be shown later that it is possible to prepare highly conducting thread materials based on this well-known but partially forgotten technology. Furthermore, and this is the message of this chapter: remember the classic old textile technologies when trying to build flexible electronic and microstructures. One cannot be performed without the other.

18.2.3 Braiding

Braid is manufactured by interlacing three or more threads forming a flat or tubular narrow fabric. The difference from other textile technologies is that braiding allows the creation of microstructures without the need to make use of miniaturised tools. The yarn is directly fed from the bobbins to the braiding point. The dimension of a braid depends only on the count of the yarn, the number of threads, and the type of binding therefore it will be possible to produce braids that are much smaller in dimension. This makes braiding an ideal technology for textile micro-engineering.

18.2.4 Embroidery

In the traditional definition, embroidery is a technique of decorative needlework in which designs are created by stitching strands of some material onto a layer of another material. Embroidery has traditionally been used to decorate clothing and household textiles.

Up until now most embroidery used textile threads stitched onto a woven fabric, but recently embroidering has become ever more important in technical applications ranging from fibre reinforcement to electronic circuits. Stitches may be executed in wires and embroidery can be worked onto non-traditional materials such as plastic foils. One unique feature of embroidering is the possibility to place stitches in any desired direction forward, backward, and sideways. Very complex multi-layer patterns can be produced in this way.

Furthermore, we can construct a thread from two highly conducting Elitex® threads insulated against each other and coated with a paste containing copper doped zinc sulphide particles and insulated by a polyacrylnitril coating. Such a thread construction driven by an AC voltage of 110 V generated by an EL-converter from a low DC battery voltage can be illuminated and integrated in embroidery.

18.3 Goal of the application of compliant textile structures

All of these examples illustrate that textile structures provide a means to create compliant structures in the millimetre and micrometre range with many advantages over lithographic structures. These structures have the potential to combine micro- and nanostructuring. Especially noteworthy is the conducting textile microstructure base on conducting metallised threads (cf. Statex®, Shieldex® and Elitex®), which can be surface modified by use of electrochemical methods and allow the formation of thin structured layers in the 100 nm scale. The available methods to modify conducting thread surfaces and to create functional bonds to covalently link other molecules are already being used to modify electrodes to build chemical sensors (listed in Table 18.1).

Table 18.1 Overview of electrochemical surface modification technology applicable to metallised threads and textile structures

Electrochemical technique	Aim
Galvanic metal deposition	Tailor made conductivity of the thread material, protection against corrosion of the underlying metal layers and formation of alloys
Electro-deposition of paint	Deposition of insulation and protection layers in the micrometre scale
Electro-polymerisation	Deposition of conducting polymers in the micro- and nanometre scale on non-conducting nanolayers containing functional groups for further surface modification with enzymes, etc.
Anodisation	of the surface to protect against corrosion, create sensoric properties and textile electrode material for energy storing and electrochromic devices
Electro grafting (J. Pinson *et al.* 1995)	Covalent bonding of funtionalised molecules on electrode surfaces

Table 18.2 Interactions of the applications of smart textile structures in smart textiles and in new technical applications

Smart textiles	
Textiles with novel functions	Novel textile materials for technical applications
occupational wear leisure wear welfare home care/home monitoring medical care medical textiles business wear	textile microsystems textile-based electronic textile microstructuring textile nanotechnology – micro-nano-coupling
Interactions on both directions	

Such new conducting and sensory textile structures can be applied in two areas. On one hand they are technical textiles and may be used in fields where textiles are till now not in use like in the area of flexible electronic and to build new compliant microsystems but on the other hand the new compliant electronics and microsystems permit to integrate such devices into our clothing and other textile structures used in our cars, public transport in occupational clothing in the medicine or in the area of home care and home monitoring offering new possibilities for telemedical applications. These interactions are summarized in Table 18.2.

18.4 First attempt: textile electronic circuit technology based on copper wires in a lattice structure with interconnections and interruptions

An attempt to use a fabric as a substrate for electronic circuit technology has been described in ref. 10. The fabric consists of copper wires woven between conventional textile threads. The spatial arrangement of the copper wires is chosen to achieve appropriate features for chip mounting which was carried out using an electrically conductive glue. Some plain electronic circuits and a textile keypad[11] were built using this technology.

The most important advantages of these woven substrates in comparison with flexible foils and printed circuits or electronic boards are their mechanical non-rigidity, air permeability and low mass. The use of metal wires, however, is a limiting factor for the textile manufacturing process because of large differences in the tensile modulus of metal wires and conventional yarns.

18.5 Galvanic modification of yarns

In the preceding sections we have shown that textiles are inherent microstructures with fantastic properties. They are flexible and much more mechanically stable than foils and they are compliant structures. However, until now we did not have the right materials or we applied the wrong materials to use textile structures as electrodes, sensors and even as parts of a microelectronic structure. Metal wires, when they are integrated in textile structures or even when the threads are prepared from combinations of metal wires and conventional threads, have, on one hand, a negative influence on the properties of the resulting fabric and on the other hand, permit the highest conductivity. Applications of metal-containing pastes or other conducting materials do not permit the conductivity needed and cause many problems trying to reach the fastness expected from fabrics. The aim of this section is to give an overview of promising materials and composite structures as well as electrochemical finishing techniques to prepare them for textile substrates.

Chemical metallised threads are an interesting alternative and they are already available on the market.[12] They are used to produce textiles with antistatic properties or to shield electromagnetic waves. The metal layers are thin enough to be undamaged in the textile processing to form the final product, but they are too thin to achieve the conductivity necessary for the applications mentioned above. Furthermore, conducting inks are available to form a precursor structure on textile substrates. Based on both materials electrochemical techniques may be applied to increase the conductivity of such pre-structured slightly conducting textile structures or to improve the surface properties to avoid corrosion of the metal layers to reach the fastness expected. Electrochemical or galvanic deposition processes are the least expensive way to coat or modify a precursor structure.

The conductivity of such precursor structures is insufficient for electrodes, sensor structures or to build electronic devices, but sufficient for a further galvanic metal deposition by using special coating procedures and galvanic baths. The precursor structure can be electrochemically modified by metals and even noble metals,[7] as well as by electropolymerisation[15] and electrodeposition of paint. The metals can be electrochemically oxidised to form oxide structures with semiconducting properties. The textile precursor structure allows the coating of various zones with various metals, metal oxides and even new materials. Firstly, applications of textile substrates structured in this way will be presented.

A new and very interesting material which may be used to develop electrochemical finishing technologies and which allows textile microstructures to be created, are polyamide threads and yarns chemically coated with a silver layer of about 1 micrometre.[12] The thin metal layer remains stable on the polyamide filaments and does not significantly change the thread properties.

Such yarns can be processed by most textile technologies without serious problems and permit the preparation of textile microstructures by the use of the available monofilament Ag-PA-threads with a size of 22 dtex.

We tested the galvanic deposition of several metals including gold, platinum, copper, nickel, zinc as well as additional silver on different textile substrates. The microscopic images show reasonably smooth metal deposition on each filament of a pre-metallised thread by use of optimised galvanic baths. Furthermore, the threads galvanised by gold and platinum have been used as electrodes to record cyclic voltammograms in organic electrolytes using a well-known test redox system (ferrocene/ferrocenium). The cyclic voltammograms show a comparable potential window to that recorded on a disc electrode prepared from the same metal. The peak current dependence on the scan rate behaved as expected for an array of microcylindrical electrodes. This means that the galvanic noble metal layers on top of the thin silver metallisation on the polyamide filaments are tight and behave ideally even under such harsh conditions as in organic solvents. This offers the possibility to do further electrochemical modifications and to prepare modified thread electrodes for sensor and even actuator applications. On the basis of zinc depositions it is possible to get light-sensitive zinc oxide layers and by the use of the deposition procedures described by Schlettwein *et al.*[16] dye-modified solar electrodes may be prepared.

It is difficult, however, to control such electrochemical depositions on a textile substrate done on a laboratory scale. As soon as we think about a production technology plenty of problems have to be solved. That is why we should focus on easy applications to optimise the galvanic deposition on a textile precursor structure. Such easy applications are to prepare structures like antennas, textile electronic bus systems or as flexible electronic boards. We investigated the influence of the amount of galvanic-deposited metals on the basic structure with respect to conductivity and the loss of flexibility of the textile substrate. The conductivity available on thus prepared Elitex®-Materials may be even larger than 10^4 $\mathrm{Scm^{-1}}$. That means the conductivity is increased by more than one order of magnitude compared to the pre-metallised thread material and is following the treatment at the same level as lead and mercury.

On the basis of these results, woven and embroidery structures have been prepared to create textile antenna coils for transponder applications. Antennas made from woven three-layer Jacquard weavings show the best properties. In the bottom layer the metallised warp threads are located. These threads are insulated by an intermediate non-conducting textile layer against the metallised weft threads in the top layer. By use of special weave bindings the metallised threads are connected to create a coil where two neighbouring weft threads are the start and end of the coil.[7] The transponder chip may be fixed on the coil structure ends. The coil resistance may be reduced to about

10–20 Ωm^{-1} and permits a reading distance with the Philips i-code System of about 50 cm. In a similar way a textile bus to pick up the signals from a textile keyboard (shown on the TechTex in 2000) was created.[6]

It is possible, furthermore, to weave interdigital structures (electrode structures with a shape of two merged combs) similar to the lithographic structures used in sensor applications. Interdigital structures may also be applied instead of optically transparent electrodes to build electroluminescence devices. Reference 7 shows the possibility to use woven interdigital structures to prepare textile electroluminescence devices. The distance of the thread electrodes in such woven structures is less than 300 µm. It has been shown that this is inferior to the critical distance to create electroluminescence.

All these structures look very promising but there is a considerable drawback when electrolytes containing cyanides are used. The removal of cyanide from the galvanic or electrochemical fabrics can only be done with an extremely high expenditure by a cascade of several washings and vacuum draining depending on the composition of the fabrics. As soon as the fabric contains natural fibres it became impossible. Therefore it was necessary to develop a new technology to produce highly conducting thread material. From the galvanic deposition on single threads it was known that threads with a silver layer of a thickness in the range of one up to two micrometres still behave like a textile thread and may be woven or used by other textile technologies. That is why we developed a galvanic bath connected with vacuum draining and washing to galvanise pre-metallised knitting. This knitting yields threads with a conductivity up to $5 \cdot 10^{-4}$ Scm^{-1} by back-knitting. That means it is possible to produce threads with a resistance of a few Ω per metre length depending on the thread size. When the size of the thread is larger than 23 tex the resistance is below 20 Ωm^{-1}.

18.6 Light effects based on textiles with electrically conductive microstructures

With the galvanically treated Ag/PA-Elitex® threads it is possible to weave double comb structures similar to the lithographic structures used in sensor applications. Interdigital structures may also be applied instead of optically transparent electrodes to build electroluminescence devices. Reference 6 shows the possibility to use woven double comb structures to prepare textile electroluminescence devices based on a woven structure (EL-weave) using 22 dtex Ag/PA-Elitex® threads as comb electrode material. The distance of the thread electrodes in such woven structures is less than 300 µm. It has been shown that this is below the critical distance to create electroluminescence. However, textile interdigital EL-weaves with an electrode distance larger than 200 µm show a different dependence on the stimulation frequency of the AC voltage. While EL foils show the highest light density of 60 Cdm^{-2}

in a frequency range of 400 Hz to 800 Hz, woven interdigital EL structures with an electrode distance larger than 200 μm have their highest light density at a characteristic frequency in the range of 1 kHz to 10 kHz depending on the size of the woven EL structure.

Optimal stimulation frequency decreases with the square root of the area of the woven interdigital structure depending on the inductivity of the secondary coil of the transformer of the EL converter. That means that in the case of woven EL structures with large thread electrode distances the resonance frequency of the oscillating circuit built from the capacity of the EL structure and the inductivity of the secondary coil of the transformer has to be found. The behaviour changes when the thread electrode distance becomes smaller than 200 μm. These new woven EL structures based on monofilament threads in the warp and weft direction with a weft density of 96 threads per centimetre (240 threads per inch) do not show such a sharp frequency dependence and may be stimulated as the EL foils in the frequency range of 400 Hz to 800 Hz yielding a light density of 40 Cdm^{-2} to 60 Cdm^{-2} and in the case of a stimulation with 150 V and 1 kHz, it reaches 80 Cdm^{-2}. Such woven EL structures can be easily screen printed with EL pastes illuminating in different colours to prepare luminescent/luminous images for advertisements, safety signs in buildings, cars, ships and aero plants.

18.7 Textile-based compliant mechanisms in microengineering and biomechatronics

Compliant mechanisms work by flexing all or some of their parts to transfer motion, force, or energy and, therefore, they are considered to be sophisticated flexible materials. Unlike their traditional rigid-body counterparts, compliant mechanisms do not contain moving parts that work together in order to carry out a function. Compliant mechanisms are made from one piece. This makes them ideal candidates for use as miniaturised components in microengineering. The application of textile materials and techniques in compliant mechanisms is the objective of ongoing research. Biomechatronics focuses on the development and improvement of mechatronic devices by transferring principles of medicine and biology into technical systems. Basically, it is the concept of taking ideas from nature and implementing them in another environment such as engineering and design. But first of all biomechatronics is an interdisciplinary system approach which involves biology, medicine, mechanical and electrical engineering, electronics, computer sciences, and system analysis. It leads to new designs which could not be realised in one of the disciplines alone. So biomechatronics becomes more than just a copy of nature.

18.7.1 Biological inspiration and technical implementation

The wings of insects and legs of spiders are two examples of compliant mechanisms where nature served as a pattern in textile microengineering of material-locked joints with fluidic drives. This development has been inspired by studies of the leg design and jumping in spiders. The spider leg represents a hollow structure with fluid drive which enables some species of spiders to jump over large distances. The whole spider leg, which is part of a rigid exoskeleton, is built from the same material, chitin polymer. The joints of the spider legs, however, consist of a flexible sealing membrane whose flexibility is due to a reduced degree of polymerisation within the chitin material. In this way a gradient of stiffness is produced along the spider leg. When applying pressure within the hollow tube the flexible membrane expands generating a torque and the spider leg is bent. A second example is the unfolding apparatus of the dragonfly's wing which can be understood as an arrangement of material-locked joints.

A bio-inspired technical system is a tube made from silicone rubber. Within a small region comprising the material-locked joint, the wall of this tube has an asymmetrical gradient of stiffness with respect to the tube's longitudinal axis. The artificial spider leg starts to bend in the same manner as its biological pattern does when pressure is exerted. The bending angle depends on the magnitude of the applied pressure. When testing some prototypes it became obvious that they were very imperfect replications of a real spider leg since the material-locked joint was blown up like a balloon. In contrast to the technical arrangement made from silicon rubber, the sealing up membrane of a spider expands only in one direction according to its internal structure. The study of this directionally dependent phenomenon was the starting point of efforts to use textile materials.[18]

18.7.2 Miniaturised material-locked joints based on textile materials

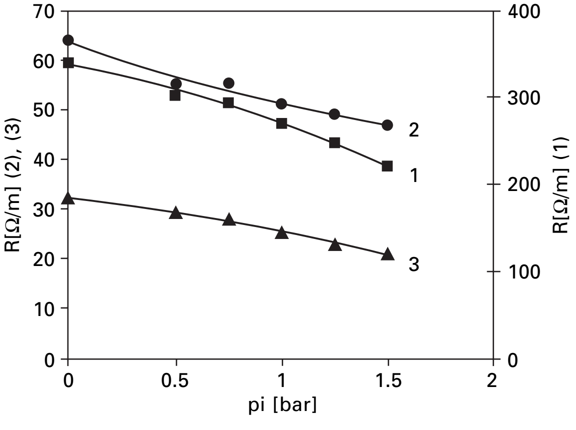
The construction principle of a material-locked joint based on textile materials may be illustrated by an elastic hollow cylinder with circular knit (or braid) and local stiffening. For its manufacturing, a flexible tube made from silicone rubber was enveloped with a circular knit. The local stiffening of the joint was effected by applying a small blot of glue resulting in an asymmetrical stiffening of the textile mesh structure. When applying pressure within the tube the joint undergoes a bending motion.

The most important advantage of this example is its simple construction and the possibility to produce it in an automated textile process as a running tape. The production process includes the following successive steps:

1. textile pattern design
2. manufacturing as an endless narrow fabric
3. local stiffening of the joints (adhesive, hot melt, welding)
4. making-up, i.e., tailoring to a given length and sealing of one end
5. attachment of hydraulic or pneumatic drive.

Taking into account that the material-locked joints are manufactured as endless textile cords it becomes obvious that they can be easily fitted to cascade systems of joints that can be tailored to any desired degree of flexibility and kinematics.

Most of the prospective applications of material-locked joints require a well-defined adjustment of their bending angle during operation. An appropriate means to equip flexible actuators with sensing capabilities is the integration of textile sensors. For this reason the knit which surrounds the flexible tube is made from electrical conductive threads. The knitted structure comprises a network of elementary electrical resistors whose magnitude changes systematically when the joint is deflected under application of pressure. So the resultant electrical resistance of the whole network, which can be easily measured, relates to the bending angle which depends on the pressure on its part. A flexible coating ensures a more stable operation and increased life expectancy of the sensor device. Some characteristic curves of electrical resistance plotted against pressure are also shown in Fig. 18.1. Using this effect, a simple pressure sensor with fast response was easily fabricated and could be used to study and to control motion sequences of material-locked joints. Combinations of flexible actuators with integrated textile sensors are straightforward to produce. The integration of sensors ensures mechatronic



18.1 Characteristic curves (electrical resistance versus pressure) of a pressure sensor comprising a flexible tube enveloped with an electrical conductive knit.

feedback for automatically controlled motion systems. Future R&D efforts are focused on braiding technology because it allows the creation of microstructures without the need to make use of miniaturised tools.

18.7.3 Benefits of textile-based material-locked joints

- continuous manufacturing process as endless tapes
- made from inexpensive textile materials
- can readily integrate sensors
- chemically inert
- slip-stick-free operation
- completely non-metallic construction
- compliance helps correct for misalignment in robotics
- ability to be miniaturised
- operation without electricity, fluidic drive only.

18.7.4 Applications

- walking machines, robots, actuators, manipulators
- grasping apparatus for minimally invasive and microsurgery
- joint prosthesis with human-like response
- shape-change applications
- inflatable unfolding mechanisms.

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