5

Polymer-based resistive sensors for smart textiles

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Abstract: This chapter covers resistive sensors (electrical passive response), which are classified according to the external stimulus to which they respond: mechanical, chemical or temperature. Currently in the textile field, hard, heavy and rigid sensors are prohibited in favor of light and flexible ones, as most polymers are not electrically conductive. However, two families of compounds are suitable for use in sensor applications (i.e. having the mechanical behavior and electrical conductivity close to that of polymers): conductive polymer composites (CPC) and intrinsically conductive polymers (ICP). In this chapter, textile based resistive mechanical (elongation and compression), chemical (solvent and humidity) and temperature sensors are described.

Key words: resistive sensors, mechanical sensors, chemical sensors, temperature sensors, CPC, ICP.

5.1 Introduction

It is generally accepted that a sensor is a device that reversibly produces a measurable electrical response to a physical, non-electrical, stimuli. By analogy with electronic components, if A sensor consumes energy (but does not produce it) it will be named a 'passive sensor', otherwise it will be named an 'active sensor'. Active sensors produce an electrical charge or electrical potential, such as piezoelectric sensors, photocells or thermocouples. The field of passive sensors is wide and so split into specific families according to their electrical passive response, such as resistance, impedance, capacity, etc. (Fraden, 1996).

This chapter deals with resistive sensors only, those whose electrical resistance changes in response to external stimuli. Resistive sensors are classified according to the external stimulus to which they respond, mechanical, chemical and temperature being the most common stimuli. Apart from in the textile field, these sensors are not necessarily resistive: most temperature sensors are thermocouples (based on the Seebeck effect: Besançon, 1985) and some chemical/solvent sensors are based on an optical measurement (absorption spectrum of chemical species: Fraden, 1996). As far as possible in the textile field, hard, heavy and rigid materials are avoided in favor of light and flexible ones. Metals, ceramics and electronic components are therefore avoided in favor of polymer-based materials. Obviously, these stiff conductive materials (typically metal) can be formed into filament, or

thread, and used as sensor structures. The main problem is that in most cases polymers are not electrically conductive. However, two families of compounds have the mechanical behavior close to that of polymers, while also being electrically conductive: conductive polymer composites (CPC) and intrinsically conductive polymers (ICP).

5.1.1 Conductive polymer composites (CPC) sensors materials

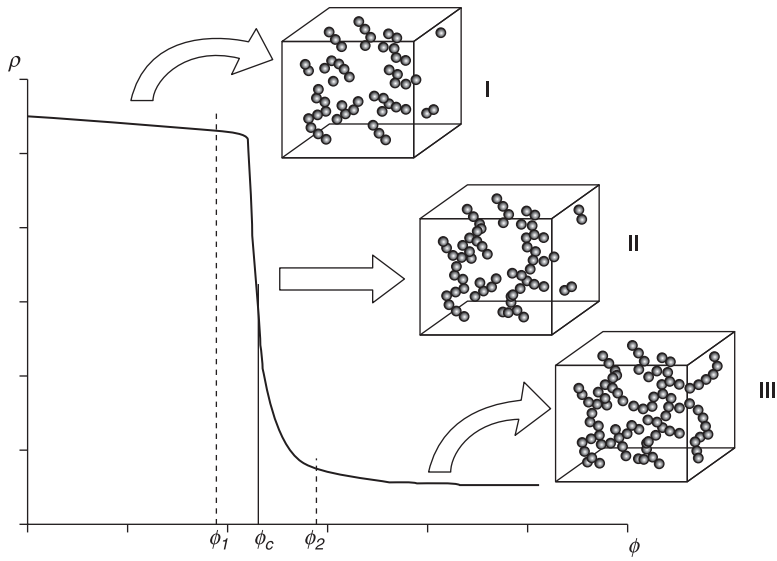
CPCs are based on a mix of polymer matrix and electrical conductive filler. The matrix can be a thermoplastic (polyester, polyamide, etc.) or thermoset (epoxy resin, polyurethane, etc.) polymer. The fillers mainly used are divided into three groups:

1. *carbon filler*: carbon fiber, graphite, carbon black (CB), carbon nanotube (CNT), fullerene, etc.;
2. *organic conductive filler*: powder of ICP, insulator particles coated with ICP, etc.;
3. *metal-based filler*: silver particles, glass particles coated by silver, copper sulphide, indium tin oxide (ITO), etc.

The borders of the final group are unclear, because it also contains electro-conductive ceramic compounds. However, the most commonly used fillers are carbon fillers, since they are stable (no oxidation under normal conditions), easy to use, lightweight and inexpensive (except CNT). The choice of the filler is often linked to the end use. The size and amount of filler required to achieve the desired properties (mechanical, rheological, conductivity) are often the limiting factors. For example, a filler content above 4% is rarely appropriate for melt spinning of nanocomposites. Indeed, the addition of a filler induces a dramatic increase in the viscosity, which hinders spinning to multifilaments (Devaux *et al.*, 2011).

The main parameter that influences the electrical properties of the CPC is the filler concentration. The transition from the insulating (polymer alone and polymer with low filler content) to the conductive state is obtained at a critical filler concentration (ϕ_C). This value, known as the percolation threshold, can be determined from the conductivity evolution as a function of the conductive filler (Fig. 5.1) and corresponds to the inflexion point (Kirkpatrick, 1973). This change in the electrical conductivity is explained by the creation of continuous conductive paths through the material (State III in Fig. 5.1, i.e. filler content above ϕ_C).

It is well-established that at the percolation concentration threshold the sensitivity of the sensor is optimal (Feller *et al.*, 2002(a,b), 2003). Indeed, external stimuli (e.g. mechanical, thermal or chemical) act mainly on the dimensions, therefore on the volume of the CPC sensor. Thus, by exposing a CPC sensor to a stimulus, it is the equivalent of increasing or decreasing its volume and thus diluting or concentrating the conductive fillers. When the volume of the fraction of filler artificially varies, the electrical conductivity changes following the percolation curve of the system being considered. CPC sensors based on this



5.1 Evolution of conductivity (ρ) as a function of conductive filler content (ϕ). I-Insulator composite, II-composite in percolation range, III-conductive composite (Cochrane, 2011).

behavior are known as electrical percolation type *X* sensor (EPT*X*S), with X corresponding to the external stimulus (mechanical, temperature, chemical, solvent, moisture, etc.).

Often the material resistance in the percolation range (State II in Fig. 5.1) is too high to be measured by conventional electrical apparatus. Thus it is necessary to find a good compromise between the sensitivity (dependence of conductivity on filler content and maximum near electrical percolation concentration) and the global conductivity leading to a sufficiently low resistance for it to be easily measurable.

5.1.2 Intrinsically conductive polymers (ICP) sensors materials

Intrinsically conducting polymers (ICP), also called 'synthetic metals', are inherently conducting or semi-conducting in nature, due to the presence of a conjugated π electron in their molecular structure. A high level of conductivity can be achieved though oxidation–reduction reactions or acid-base treatments with a suitable dopant (doping). Polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI) propose some of the best compromises between electrical conductivity, stability and processability. ICPs can be classified as (Stenger-Smith, 1998):

- *Oxidized* (*conducting*): the polymer form, which has electrons removed from the backbone, resulting in (radical) cations.

- *Neutral* (*insulating polymer*): the polymer form in its uncharged state. This can be referred to as a 'reduced' form of the oxidized polymer.
- *Reduced* (*conducting*): the polymer form, which has electrons added to the backbone, resulting in (radical) anions.

Conducting polymers are either made directly by electro- or oxidative-polymerization or polymerized and then oxidized chemically or electrochemically. Conductive polymers are provided both as solid compounds, liquid dispersions or solutions. The liquid versions can be easily applied onto a textile substrate by coating methods (Skrifvars, 2008).

5.1.3 Resistive sensors: general sensing principle

It is well-established that ordinary resistive sensors are governed by the law:

$$R = \rho \times \frac{L}{S} \qquad [5.1]$$

where R is the electrical resistance of sample (Ω); ρ is the electrical resistivity of material (Ω.m); L is the distance between measurement electrode (m); and S is the section surface area of sample (m^2).

From Eq. 5.1, to obtain variation on the electrical resistance, it is necessary for the external stimulus to act either on the geometry of the sample (L and/or S) or/and on the electrical resistivity (ρ) of the material. Sensor geometry can be affected by mechanical stress or thermal expansion of the material. For most materials, electrical resistivity (ρ) is an intrinsic variable and depends only on temperature (Fraden, 1996), but for CPC and ICP, it is otherwise. For CPC materials, the matrix (polymer) plays a key role. The electrical resistivity of filler remains constant (temperature dependence only), while global electrical resistivity of CPC can change according to several external parameters such as stress, moisture, temperature, etc. External stimuli can act on the polymer matrix (swelling, crystallinity degree, etc.), on the filler (aspect ratio, electrical conductivity, etc.), on the interface matrix/filler or filler/filler (decohesion, contact resistance, etc.) and on the arrangement between matrix and filler (dispersion, agglomeration, segregation, etc.). For ICP materials, the oxidation state of polymer, the doping rate, and the quality of lateral contact between polymer chains strongly influence the global electrical conductivity.

5.2 Mechanical resistive sensors

Mechanical sensors are based on resistive materials or structures whose electrical resistance changes reversibly according to an applied stress (elongation or pressure). The term 'piezoresistive sensor' is commonly used. For mechanical resistive sensors, the sensing mechanism is based on at least one of the following three:

1. change in electrical resistance of textile structure (e.g. stretching or deformation of textile structure);
2. change in electrical resistance of material not affected by fillers disconnection;
3. change in electrical resistance of material affected by fillers disconnection.

In real-case examples, the three changes often occur simultaneously and so it can be difficult to identify the dominant mechanism.

Mechanical sensors are characterized by gauge factor (or sensitivity) (k, Eq. 5.2). k is the ratio of relative change in electrical resistance $\left(\frac{\Delta R}{R_0}\right)$ to the mechanical strain $\left(\varepsilon = \frac{\Delta L}{L_0}\right)$:

$$k = \frac{\Delta R}{R_0} \times \left(\frac{\Delta L}{L_0}\right)^{-1} \qquad [5.2]$$

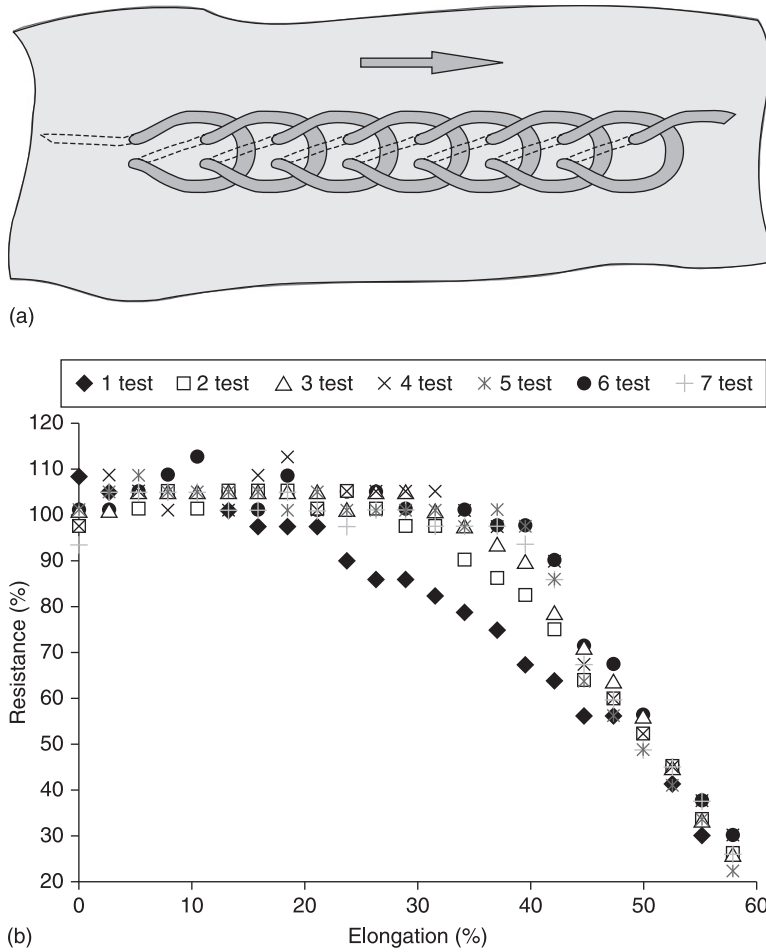
where k is the gauge factor; ΔR is the change in strain gauge resistance (Ω); R_0 is the unstrained resistance of strain gauge (Ω); ΔL is the change in length (m); and L_0 is the length of unstrained strain gauge (m).

5.2.1 Elongation resistive sensors

Conventional strain gauges are resistive sensors, but they are used only for low elastic materials such as concrete or steel. However, one study shows that by a clever assembly in a 'curved beam', these gauges can be used to evaluate the rigid extension of plain weave (Heinrich and Saari, 1975). This solution is bulky and induces a very important local stiffening of textile. The need to develop resistive elongation sensors specific to textile applications (lightweight, flexible, elastic and washable, if possible) is important.

Sensors based on change in electrical resistance of textile structures

The first family of elongation resistive sensors consists of 'potentiometer per contact', where neither the material resistivity nor its geometry varies. There are changes in the overall macroscopic textile structure that influence electrical resistance. This kind of sensor is similar to conventional potentiometer sensors. One of the best examples to illustrate this family of elongation measurement systems is made of a stainless steel (non-elastic materials) yarn crocheted chain on elastic fabric. This type of sensor can be obtained by embroidering or sewing a conductive thread onto an elastic textile support (Fig. 5.2(a), Strazdiene *et al.*, 2007). When the stitches are stretched, the efficiency of the electrical contact between the conductive thread increases and then the electrical resistance of the device decreases (Fig. 5.2(b), Strazdiene *et al.*, 2007). Based on this system,



5.2 (a) Embroidering stretch sensor and (b) example of measurement (Strazdiene *et al.,* 2007).

dynamic anthropometric data can be measured in the range of 4 to 16% of elongation (Strazdiene *et al.*, 2007).

It is also possible to build these sensors out of knitted structures. Highly resistive yarns (or thread) can be knitted and placed into flat textiles (woven or another knit) to construct stretch sensors (Yoshikai *et al.*, 2009; Glazzard and Kettley, 2010). The main problem of these sensor types is their lifetime. After each elongation, the stitch sensor does not return to its initial configuration (electrical resistance). The repeatability is poor. The system has a hysteresis and becomes less sensitive with the number of uses.

Elastic narrow fabric, composed of Lycra fibres and polyamide coated carbon particles, can be used as elongation sensors. The materials and structures used are able to reduce hysteresis (Shyr *et al.*, 2011). For this kind of sensor, the conductive fibers are elastic but the detection of elongation is mainly a function of geometrical structure, not the elongation of the conductive fibre. Similarly, if a very thin-coated or printed conductive layer (CPC or ICP) only coats some fibers of the textile structure, global electromechanical behavior appears as a 'potentiometer per contact' rather than a sensor where electrical resistance varies with dimension (see below: 'Sensors based on change in electrical resistance of material non-affected by fillers disconnection'). These supported ICP sensors can be obtained by coating or inkjet printing (Wu *et al.*, 2005; Zhang *et al.*, 2006; Calvert *et al.*, 2008).

In all these cases, the number and efficiency of electrical contacts between the conductive yarn (pure conductive material fibre, fibre coated by conductive material or textile coated by conductive material) dominate the performance of the sensor. This results in a decrease of electrical resistance when efficiency of contact, therefore sensor length, increases. These sensors exhibit a negative gauge factor (k, Eq. 5.2), even if the bulk materials have classical piezoresistive behavior.

Sensors based on change in electrical resistance of materials non-affected by fillers disconnection

This second family of elongation resistive sensors is similar to conventional elongation sensors governed by Eq. 5.1, where only gauge dimension affects the electrical resistance (Fraden, 1996). Elongation induces almost entirely the geometrical change of the gauge. Elongation sensors generally have a high aspect ratio (>25), low thickness (e) and width (l), and high length (L) (i.e. rectangular cross section). Electrical resistance modification, resulting from elongation in the length direction, is mainly caused by length and not section variation ($S = e \times l$). For this kind of gauge, the gauge factor (k) does not exceed 6 and is directly linked to the Poisson ratio of conductive material (Window, 1992).

This family includes the textile (or at least flexible) elongation sensors made of ICP, where macromolecular chains are randomly oriented (isotropic ICP), and CPC sensors that are filled with a large amount of conductive filler (i.e. filler content much higher than percolation concentration, ϕ_C). The electromechanical behavior of CPCs containing a large content of filler is governed mainly by Eq. 5.1: ρ is quasi non-dependent on elongation (during stretching, the ratio between disconnected conductive paths and connected conductive paths is low) and only dimensions of the sensor (L and S) varies.

ICP is already used in standard strain gauges when large deformation is required. ICP-based conductive fibers can be easily obtained by coating. In the case of PANI-coated PET (Kim *et al.*, 2004), the process produces electroconductive fibers with good mechanical properties (i.e. mechanical properties of core fiber) and flexibility, allowing knitting or weaving (Neelakandan and Madhusoothanan,

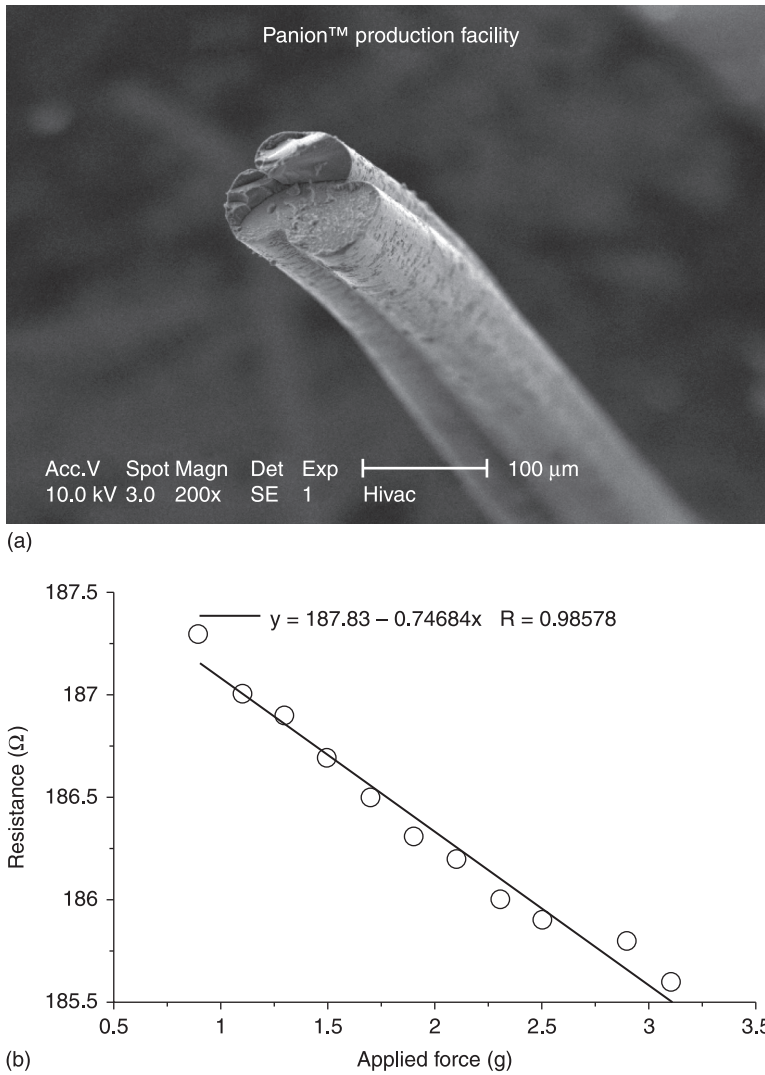
2010). Studies of the electromechanical properties of these products show that coated fibers can be used as a fibrous sensor (Kim *et al.*, 2006).

In general, the coating process (and sometimes inkjet printing) on textiles can easily produce ICP-based sensors, which will act as standard piezoresistive gauges. However, if the coating thickness is low, the structure (textile + coating) will tend to behave as a 'potentiometer per contact' and not as a classical gauge. Also thin coating of ICP produces anisotropic materials, whose piezoresistivity will depend on macromolecular organization. Similarly, behavior of pure ICP fibers (i.e. PANI) is due to the small diameter and stretching applied to the fiber during its production (Mattes, 2004; Bowman and Mattes, 2005). Due to this anisotropy, the resistance of pure PANI fiber decreases with applied load (negative gauge factor, k) (Fig. 5.3, Mattes, 2004). This can be explained by macromolecular organization of the PANI backbone. Stress increases the drawing of the backbone and quality of lateral contact between chains. The major problem of ICP mechanical sensors are their great sensibility compared to other environmental parameters (temperature, solvent, water, etc.) and their poor stability due to oxidation in comparison to CPC materials (i.e. stainless steel fiber or silver platted fiber).

Sensors based on change in electrical resistance of materials affected by fillers disconnection

This third family consists of Electrical Percolation Type Mechanical Sensors (EPTMS) and contains only CPC sensors. Elongation induces a geometrical change due to the aspect ratio (variation of L and/or S) and also the modification of electrical resistivity (ρ) of the materials. Indeed, if the conductive filler content is near, but above, the percolation concentration (ϕ_C), the electrical conductivity is very sensitive to volume change of the material due to stretching. A small volume change breaks a lot of conductive networks (disconnections), causing a large variation in the overall resistivity of the CPC. EPTMS exhibit a gauge factor (k, Eq. 5.2) far above that of conventional piezoresistive sensors (k below 6: Fraden, 1996) and sometimes comparable to semiconductor gauges (k between 40 and 200: Fraden, 1996). In addition, with CPC materials, conductive particles come close and conductive paths disconnect leading to conduction arising from hopping and tunnelling (Donnet *et al.*, 1993). Indeed, if the conductive particles are near, but are not in contact with each other, activation energy is required to produce a pair of charges (negative and positive) in which their migration is from site to site, resulting in conductivity.

The term 'hopping' refers to the sudden displacement of a charge carrier from one site to another neighbor. This hop usually includes the passage of a potential barrier and tunneling conduction (Dyre and Schroder, 2002). The main difference between a metallic conduction and hopping conduction (or tunneling) corresponds to the decrease of the metallic electrical conductivity with temperature, while the



5.3 (a) PANI fiber and (b) resistance dependence against applied force (Mattes, 2004).

hopping conductivity increases. Thus, to determine the conduction type of a CPC (metallic or hopping), one solution is to observe the electrical behavior according to the temperature (Mott, 1973).

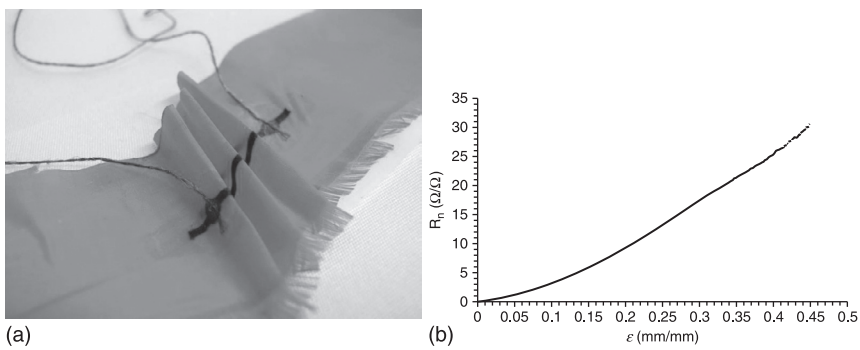
EPTMS in the textile field can be present as a coating or pure fiber of CPC. Coating textile materials (fiber, yarn, fabric, knit, etc.) with CPC is relatively easy, because the process is often appropriate to the filler's content allowing electrical conduction. Inkjet printing can be used only when the viscosity, which depends on

fillers content and solvent quantity, is compatible with the process. CB is the most commonly used filler, due to its suitable price and electrical conductivity. Thus, some authors using a thermoset elastomer and CB have developed a series of items of clothing that can detect movements of particular body parts (Lorussi *et al.*, 2004; Bartalesi *et al.*, 2006). Other similar studies (My Heart, 2011) have also shown the same possibility.

Apart from clothing, this type of sensor, based on CB and a highly elastic matrix (thermoset elastomer or thermoplastic elastomer), can be used in aeronautics or for the monitoring of composite structures. In the former, the CPC sensor consists of selective coating (track) localized on a fabric (parachute canopy in Fig. 5.4(a,b)) (Cochrane *et al.*, 2007, 2010; Cochrane, 2011) and in the latter, the CPC sensor consists of coated yarns introduced during the weaving process in the preparation of the composite (Nauman *et al.*, 2011(a,b)).

The melt spinnability of low aspect ratio conductive fillers (the majority of conductive fillers) is limited. Indeed, for this type of filler, percolation concentrations (ϕ_C) are often incompatible with spinning processes in terms of the melt flow index. However, CPC based on CNT have a high aspect ratio (above 10^5) and are spinnable to produce yarns used as mechanical sensors. The electrical response of CNT-based CPC to a mechanical stress is classically explained by the increase of distance between individuals or aggregated CNT (this distance exceeds the hopping and tunneling distance) (Wood *et al.*, 2000; Bilotti *et al.*, 2010; Ciselli *et al.*, 2010).

Even if a single fiber of CPC has electromechanical behavior that can make an EPTMS, when this fiber is included in textile structures (i.e. by weaving, knitting, non-woven or braiding), the total (material + structure) electromechanical behavior becomes complex. Thus an elongation textile structure sensor composed of fiber, based on CNT, belongs to the 'potentiometer per contact' sensor family.



5.4 (a) Elongation sensors made of CPC track (Cochrane *et al.*, 2010) and (b) its resistive response against elongation ($k = 31$) (Cochrane *et al.*, 2011).

Textile applications of elongation resistive sensors

The relatively low cost sensors (i.e. potentiometer per contact based on commercial conductive yarn, stainless steel) have been employed in robotic, design, musical instrument, keyboard and health monitoring applications (Eng, 2009; Fashioning Technology, 2011).

Applications of elongation sensors within the human-centered field are mainly in:

- medical or paramedical, to detect and record human motions for rehabilitation or to monitor patient health (Calvert *et al.*, 2008; My Heart, 2011);
- sport, to learn good posture (Lorussi *et al.*, 2004; Bartalesi *et al.*, 2006);
- glove to recognize sign language, to monitor movement or give tactile sensibility to robots (Bartalesi *et al.*, 2006; Yoshikai *et al.*, 2009).

Other fields of application are the monitoring of textile structures such as parachutes (Cochrane *et al.*, 2007, 2010; Cochrane, 2011) or structural composites (Nauman *et al.*, 2011a,b).

5.2.2 Resistive pressure sensors

Resistive pressure sensors are less developed because, in general, capacitive sensors are preferred. Nevertheless 'all or none' textile (switch) sensors exist and are used, for example, to create deported keyboards for mp3 players. The use of conductive foam can provide 'textile' pressure sensors. In this case, as stress flattens the structure, the foam porosity decreases artificially (i.e. the density of conductive material increases) until local disappearance and the material as a whole becomes more conductive. Foam 'densification' increases the number of conduction paths and thus makes the material more conductive. The use of resilient foam (i.e. with a highly elastic behavior) provides a very good reversibility (reduced wear of the sensor) (Dunne *et al.*, 2006). Standard polyurethane (PU) foam can be impregnated by conductive material (CPC, ICP) to obtain pressure sensing composites (Brady *et al.*, 2005). Foam can easily be introduced and connected between two textiles layers.

Pressure sensors can also be based on the use of conductive yarns combined with hook and loop (Velcro™) (Perner-Wilson and Buechley, 2011) or spacer fabrics (Buechley *et al.*, 2008). In these systems, pressure sensors operate as potentiometers per contact, whereby only the efficiency of contact between the conductive material changes (changes in the overall macroscopic structure). Some tutorials (Lovell and Buechley, 2010) and craft books, such as *Fashioning Technology* (Fashioning Technology, 2011) and *Fashion Geek* (Eng, 2009), propose interesting varieties of textile-based switches.

5.3 Chemical resistive sensors

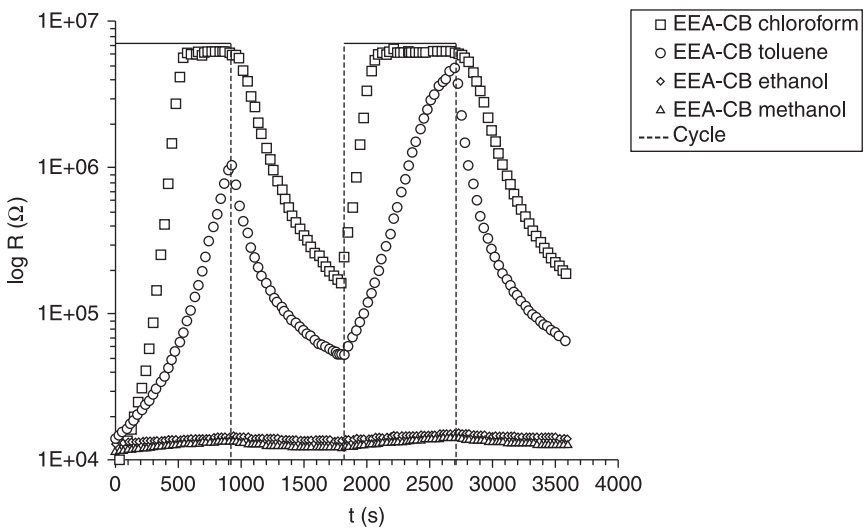
In addition to mechanical impact, environmental factors such as liquids or volatile solvents can considerably modify the electrical resistivity of the CPC or ICP. This

allows for the detection of external stimulus and creates chemical sensors in textile forms. Detection mechanisms are based on the modification of a material's electrical conductivity. However, the electrical modification is different for the two families of CPC and ICP.

5.3.1 CPC chemical resistive sensors

The CPC polymer matrix has the ability to swell. If a 'good' solvent (liquid or volatile) is in contact with a CPC, it diffuses into the polymer and expansion results. Hence, the inter-fillers distance increases and the conductive network of electrical fillers is modified. An increase of electrical resistance is observed due to the disconnection of individuals or clusters fillers (Electrical Percolation Type Solvent Sensor, EPTSS). Concerning the liquid solvents, a review (Villmow *et al.*, 2011a) defined what signifies a 'good' solvent, as referred to above. In fact, the dissolution of a polymer starts with the first step where the polymer swells. The solvent is described as 'bad' if it does not lead to any swelling of the polymer. To obtain efficient sensors, a high rate of detection, reversible and reproducible responses, must be achieved. That is why the choice of the solvent/polymer system governs the selectivity and detection range. The example in Fig. 5.5 shows that the matrix choice is crucial in chemical sensing.

The tested CPC is based on a poly(ethylene-co-ethyl acrylate) filled with 37 wt.% of carbon black (EEA-CB composite). Several successive cycles of



5.5 Evolution of electrical resistivity of a poly(ethylene-co-ethyl acrylate)-carbon black (EEA-CB) in the presence of solvents (Feller and Grohens, 2004).

solvent exposition (first solvent vapor, then air) was applied. The responses are entirely different in function to the nature of the used solvent. A good solvent, such as chloroform or toluene, diffuses inside the polymer and causes swelling and the disconnection of fillers. In the case of chloroform, a plateau in resistivity is reached faster than that of toluene. In fact, the latter has a lower diffusion within the polymer. However, the EEA-CB shows no sensitivity to ethanol and methanol, because both are non-solvents within the polymer matrix. Two detection mechanisms can be considered according to the affinity of the polymer with the vapor or liquid, that is, if the detected substance is a solvent or a non-solvent of the polymer.

Change of polymer matrix by solvents

As explained earlier, with the solvent detection by CPC, the polymer solubility in the considered solvent plays a major role. Indeed, the polymer swelling leads to the filler's separation by disconnection of macromolecular chains. The solubility of the polymer and diffusion of solvent through the chains determine the EPTSS sensitivity. As with temperature sensing (Section 5.3), a positive vapor coefficient (PVC), corresponding to the increase in resistance in the presence of solvent, and a negative vapor coefficient (NVC), are identifiable. Authors have presented these effects on different systems. Zhang et *al*. (2005) presents the detection of tetrahydrofuran (THF) by nanocomposite polystyrene (PS)/CNT. The sudden swelling of the polymer first causes a marked increase in electrical resistance (the PVC effect) and after a long exposure to THF, the polymer solubility causes a decrease in the viscosity, which allows exchange of the fillers and the reformation of the electrical network (the NVC effect).

Change of polymer matrix by non-solvents

In the detection of vapors by CPC involving a non-solvent, water vapor has been widely studied. Thus, hydrophobic polymers were tested. In the presence of water vapor, a drop in the electrical resistance of the composites was observed, corresponding to an increase in electrical conductivity. Two mechanisms may explain the increase of electrical conductivity (Yang *et al.*, 1996; Rubinger *et al.*, 2007; Su and Wang, 2007). The first is the absorption of water molecules by the polar groups of the polymer, whereby electrolysis of adsorbed water allows the transport of protons (H^+) between the anode and the cathode. The adsorbed water leads to a decrease in the ionic interactions between polar polymer groups and thus enhances ion mobility. The second is the adsorption of water molecules by fillers, such as CNT. The second mechanism becomes more dominant as the filler content in the composite increases. The sensitivity of these composites can be improved by the addition of salts. In the case of the composite Poly(Methyl MethAcrylate)(PMMA)/CNT (Su and Wang, 2007), the incorporation of

potassium hydroxide (KOH) increases the amplitude of sensitivity due to ion mobility within the composite.

One CPC can be sensitive to several solvents. Therefore, the use of a combination of chosen CPC can improve the selectivity of the global sensor or can have some interesting applications. For example, an e-*nose* has been created by combining specific CPC. Composed of an array of CNT-based CPC transducers, vapors of nine single organic solvents can be discriminated using a classical recognition technique and principal component analysis (Castro *et al.*, 2011).

Change of conductive fillers

Different kinds of electrical conductive fillers can be used in this CPC (see Introduction). However, for chemical detection, the use of carbon fillers – carbon black (Dong *et al.*, 2004), carbon nanoparticles (Bouvree *et al.*, 2009) and CNT (Pötschke *et al.*, 2010) – is recommended due to their temperature and oxidation stability. But some studies have been realized with combinations, more or less surprising, of fillers. As an example, an EPTSS has been developed by fabricating a composite consisting of a conducting phase and an insulating phase, whose volume increases by the incorporation of a desired substance. This composite of montmorillonite with carbon shows a remarkable increase of resistivity in a humid atmosphere, due to the volume expansion of the montmorillonite phase by the incorporation of water. The resistivity increases in response to stepwise water vapor increase like a humidity sensor (Tsuyumoto and Iida, 2011). Another factor can be considered, because the fillers themselves are sensitive to the presence of a solvent. For example, by their large specific surface area, hollow geometry, nanometer size and high electronic mobility, CNTs have shown remarkable properties as chemical sensors. The porosity can absorb a significant amount of gases and liquids and some authors (Kong *et al.*, 2000; Valentini *et al.*, 2004) have observed a change of electrical properties after gas adsorption, and proposed the use of CNTs as sensors. The sensitivity of electrical fillers to vapors is smaller compared to the sensitivity of the polymer matrix.

Application on textiles

Conductive composites have been reported in several forms. Compression moulded plates (Villmow *et al.*, 2011b), or spray deposition by layer-by-layer techniques have been used to form the transducer film on a substrate (Castro *et al.*, 2009). Concerning textiles, melt-spun monofilament (Narkis *et al.*, 2000; Pötschke *et al.*, 2010) or multifilament (Devaux *et al.*, 2011; Fan *et al.*, 2011) fibers or directly in the structure of a woven fabric (Rentenberger *et al.*, 2011) have been studied. The liquid sensing properties were tested on the biphasic blend polypropylene (PP)/polycaprolactone (PCL) and a comparison between compression-moulded discs and melt-drawn filaments was achieved, indicating

higher responses from the discs (Pötschke *et al.*, 2011). Also traditional textiles can be modified for use as chemical detectors by coating, inkjet printing or surface treatment. In previous studies, authors have studied the gas sensing ability of PPy coated on different polyester textile fabrics (Kincal *et al.*, 1998), or of zinc oxide (ZnO) nanorod growth on the surface of cotton fabrics (Lim *et al.*, 2010).

5.3.2 ICP chemical resistive sensors

For ICP, the variations of electrical conductivity are caused not only by polymer swelling. The perturbation of the electronic network by chemical substances changes the electrical properties of the polymer. The extent of these changes can reveal the presence of chemical groups. The presence of a substance can disrupt the backbone network, inducing an electrical conductivity decrease in a doped polymer and conversely an electrical conductivity increase in an undoped polymer. The change of conductivity is the measurement principle in conducting polymers. The nature of the polymer and its degree of doping determines the generated perturbations (Lange *et al.*, 2008). For example, if PANI is oxidized in the presence of nitrogen dioxide (NO_2) gas (electron acceptor), the result is a decrease in its electrical resistance (Xie *et al.*, 2002). However, in PANI initially doped by protonation (addition of H^+), the presence of NO_2 leads to an increase of its electrical resistance (Yan *et al.*, 2007). In general, the electron donating gases (H_2S, NH_3, N_2H_4) reduce the electrical conductivity of the conducting polymer, while the electron accepting gases (NO_2, SO_2, O_3) dope the polymer and increase its electrical conductivity. Conducting polymers can be disrupted by chemical reactions, as discussed above, but also by physical adsorption of vapor. The adsorption of benzene, toluene and hexane leads to swelling of conductive polymers with a good affinity for these solvents and increases the distance between the lateral contact macromolecular chains. The distance of electronic groups decreases the electrical conductivity by a tunneling effect within the polymer.

The phenomena that can disrupt the electrical network of conductive polymers can be described as (Li *et al.*, 2007):

- the oxidation–reduction chemical reactions between the polymer and the solvent;
- the acid-base reactions between the polymer and the solvent;
- the solubility of the polymer in the solvent;
- the polarity of the polymer can create links, dipole–dipole.

The particular case of water vapor was also studied. Mostly, the electrolyte nature of water promotes the electrical conductivity of polymers by dipole–dipole interactions. Also, proton-conducting polymers improve the mobility of protons, leading to better charge transfer (Casalbore-Miceli *et al.*, 1997).

5.3.3 Textile applications of chemical resistive sensors

Main textile applications are health and personal protective equipment (i.e. military). Numerous products have already been developed or commercialized in several sectors to detect liquid or volatile solvents. In most cases, different physical principles, not only based on resistive measurement, are employed and integrated into the textile structure. For instance, the medical field has focused on the detection of substances that can be found in human sweat. The European project *Biotex* (Biotex, 2011) aims to develop a textile sensor (as a 'patch') for biochemical analysis of body fluids. Sweat is initially absorbed by the textile and conveyed using hollow fiber with a hydrophilic nature to a small area of the textile called the 'collector'. This storage area can increase the concentration of fluid at one point. The sensor on the surface detects the presence of a specific chemical such as sodium. Other sensors detecting potassium or chloride may also be inserted in the fabric. These sensors can be used to prevent the risks associated with obesity, diabetes and high level sport.

CPC and ICP are also developed for use as chemical sensors in the textile area. The aim of another European project *INTELTEX* (Inteltex, 2011) is to develop new textile structures based on CPC for several sensors types. Some of these are solvents (acetone or acetic acid) (Rentenberger *et al.*, 2011) or water vapor (Devaux *et al.*, 2011) detection in multifilament forms or woven structures.

A patent (Qi and Mattes, 2010) describes conducting-polymer based multifunctional sensing fabrics suitable for monitoring humidity, breath, heart rate, blood (location of wounds), blood pressure, skin temperature, weight and movement, in a wearable, electronic embedded sensor system. Conducting PANI fibers have been woven, knitted, stitched or braided into a fabric comprising non-conducting fibers, enabling the fabric with monitoring and detection abilities.

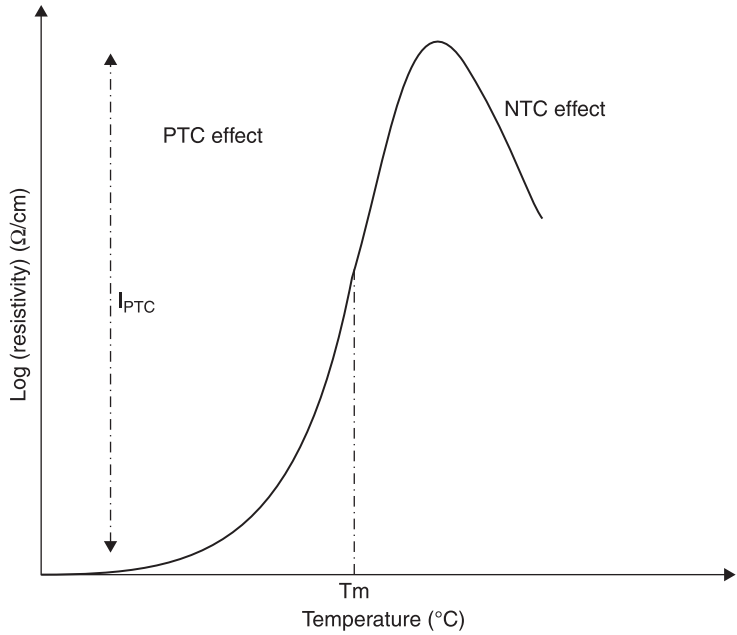
5.4 Temperature resistive sensors

As for most conductive materials, temperature plays a major role on the electrical conductivity of CPC or ICP. Of course, compared to mechanical and chemical, some other mechanisms are observed to produce temperature sensors based on the two families.

5.4.1 CPC temperature resistive sensors

For CPC, in 1945, Frydman introduced the positive temperature coefficient (PTC), defining the non-linear increase in electrical resistivity as a function of temperature (Fig. 5.6). Major contributions of temperature change on CPC electrical resistivity are:

- the rearrangement of the fillers;
- the volume expansion of the matrix (difference in expansion between the matrix and fillers).



5.6 Evolution of electrical resistivity versus temperature highlighting the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effects (I_{PTC}: intensity of PTC effect, Tm: melt temperature).

Other contributions, such as thermal expansion (α, playing a role in the dimensions of the materials S and L, see Eq. 5.1) and dependence of electrical conductivity (σ, i.e. $1/\rho$) according to temperature of fillers, are negligible.

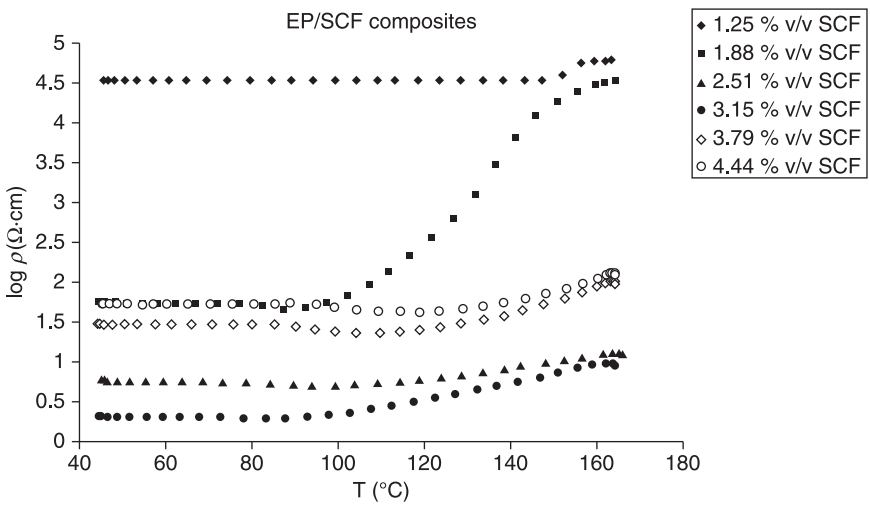
The matrix volume expansion leads not only to a reduction of the metallic conduction but also to tunneling and hopping conductions. This phenomenon is due to an increase in the distance between particles, until the current flow is cut (Feller, 2011). The disconnection of fillers conductive paths ranks CPC temperature sensors amongst electrical percolation type temperature sensors (EPTTS). The polymer phase transition temperatures (melting temperature T_m and glass transition temperature T_g) and the crystallinity degree are predominantly responsible for the PTC effect. Indeed, when increasing the temperature, the crystalline regions melt and become disorganized, causing a dilution of the particles that are localized in the amorphous phase if their size does not permit their intercalation into the crystalline phase. This leads to an increase in the distance between fillers and global resistivity (Zhao *et al.*, 2003). In Fig. 5.6, beyond the melting temperature of the polymer matrix, the NTC effect (negative temperature coefficient) appears. It corresponds to a diminution due to fillers reorganizing in the molten state, due to a molecular mobility, which in turn increases interparticle interactions.

The PTC effect is difficult to model because many factors can influence the passage conductor/insulator, such as being near the percolation threshold. The PTC is dependent on all parameters that influence the fillers percolation. As shown by Feller *et al.* (2002(a,b)) in Fig. 5.7, when short carbon fibres (SCF) are introduced, whether in a polyester matrix or poly (epoxy) (Fig. 5.7), the PTC intensity (I_{PTC}, defined in Fig. 5.6) has a greater amplitude before the percolation threshold (1.88 vol.% of SCF). Beyond an excessive fillers content (>1.88 vol.%), SCF tend to agglomerate and form nodes, which reduce the number of contact paths. The disconnection is efficient (i.e. has a significant effect on electrical resistance) if the ratio between disconnected conductive path and connected conductive path is high. It is necessary in this case to be slightly above the percolation threshold for easy disconnection.

The list of influent parameters is difficult to establish, especially as the various experimental results on different systems are sometimes contradictory. Some parameters influencing the sensing response can be:

- the influence of molar mass (Zhang *et al.*, 2005);
- the adhesion work between fillers and the polymer matrix (Park *et al.*, 2005);
- the electrical fillers migration from amorphous to crystalline phase (Zhao *et al.*, 2003);
- the cycle numbers thermal cycles (Meyer, 1974; Tang *et al.*, 1993).

Concerning the kinds of electrical fillers, carbon fillers (He, 2005; Ni, 2006; Lisunova *et al.*, 2007) are commonly used in CPC temperature sensing. Metallic fillers have also been implemented (Rybak *et al.*, 2010). The choice of conductive fillers is also



5.7 Influence of filler content on the intensity of the PTC (Feller *et al.*, 2002).

an influential factor, which modifies the temperature response. As an example, the amplitude I_{PTC} is higher in a nanocomposite based on polyethylene (PE) with CB than with CNT. This behavior is explained by the high level of contact in the CNT network, which is more stable during matrix volume expansion (Lisunova *et al.*, 2007).

5.4.2 ICP temperature resistive sensors

The ICP temperature dependence of resistance depends on the conduction regime (metallic or semi-conductor) of the polymer. With an increase in temperature, two types of behavior can be observed:

- If IPC has metallic conduction, they behave like metal and the resistivity increases in a large temperature range and a PTC effect can be observed (Lee *et al.*, 2006).
- If IPC is semi-conductor (hopping or tunneling effect) the resistivity decreases in a large temperature range, near room temperature, and an NTC effect can be observed (Bowman and Mattes, 2005).

In both cases, electrons–phonon interactions can play a key role. First, electrons–phonons interaction, due to thermal agitation, disturbs electrons movement. Consequently, for metallic type conduction, an increase of resistivity is noticed with temperature. Second, with the hopping or tunneling conduction, phonons excite loose electrons, which can move through the material (via π bond and hold, see Introduction), providing a kind of semi-conduction.

5.4.3 Textile applications of temperature resistive sensors

Regarding the effect of heat on CPC, only observations of change in conductivity as a function of temperature are studied (PTC, NTC). However, some studies are clearly oriented in the detection of a threshold temperature. According to Boiteux *et al.* (2007), the application prospects of their system (polypropylene/polyamide filled with iron particles) would be in smart materials: temperature sensors, 'circuit breakers', but also as thermistors, or as self-regulating heating elements.

In the field of textile techniques, CPC are used in temperature sensors in the *INTELTEX* project (Section 5.3.3). The elaboration of textile sensors is ensured by the incorporation of CNT in one or more polymers. The final goal of this work is integration into personal protective equipment (PPE) for firefighters; a new textile composite based on the use of innovative nanofillers enables them to be alerted to a critical elevation of the surrounding temperature (Cayla *et al.*, 2009). Concerning ICP, Mattes (2005) has developed a fiber (*PANION*) created from the conductive polymer PANI. Similarly, *SENSATEX* has developed a T-shirt (SmartShirt: Sensatex, 2011) to monitor the vital signs of the wearer, such as body temperature, by patented conductive fiber.

Some temperature sensors are already used in the textile field and show that temperature measurement is a real need. The European project PROeTEX (Proetex, 2011), amongst others, uses thermocouples to achieve a required fire fighter's coat integrating multiple physiological sensors to position, as well as environmental (temperature, presence of toxic gases). Another example is *thermochromic* material, which changes color due to changes in temperature (only temperature threshold detection in this case). For instance, in 2003, the American company Wickedglow Industries (Bodyfaders, 2011) launched a T-shirt range that changed color with heat from the body, or from contact.

5.5 Conclusion and future trends

Future advances will follow three directions:

1. improvement of existing sensors materials;
2. transfer from research to practical application; and
3. textile integrated components (electronic, sensor, actuator and energy).

The work on existing sensors materials will improve general reliability of sensors (number of supported cycle, range of detection, etc.) in all areas of application. Of course, these improvements will also result in the creation of new textile sensors to detect and quantify another solvent, detect another physical value (light, acceleration, etc.) or detect simultaneously temperature and solvent (*all in one* sensor), for instance.

The transfer from research (not only on textile materials) to textile public application by realizing more integrated textile components will see the achievement of fine fibre sensors (not only film or rod sensors) and/or woven, knitted, non-woven or braided sensors structure. This transfer to consumer application requires the development of low cost and reliable industrial production devices (spinning, printing and inkjet printing of CPC or ICP). The aim is to open sensor textile technologies to new business sectors and find application for existing textile sensor devices.

Long-term research and development will focus on the integration of electronics into textile materials (or in/on structure), in order to make fully integrated intelligent textile systems. The future integrated electronic devices are general components (resistor, capacitor e.), integrated circuits, non-textile sensors (i.e. optical sensors), actuators (mechanical, optical (screen) or chemical (molecules, drug, etc.)) and energy devices (electricity production, electrical (capacitor) or chemical (cell) storage). Thus, textile sensors plus fully integrated electronic components will be more efficient and 'invisible' to users.

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