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Review Article

AN OVERVIEW OF ELECTRICALLY CONDUCTING TEXTILES

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ABSTRACT

Textiles are having evolution from being normal protective clothing to smart and technical textiles. Electrically conducting fabrics forms the backbone of being smart textiles. The smart textile combines electronics with textile structures, referred to as "textronics". One major challenge to the success of such wearable smart textile resides in the development of lightweight and flexible components, and fibrous structures with high electrical conductivity able to withstand the stresses associated with wearing and caring for the textile. Therefore, flexible, deformable, stretchable, and durable conductive textile materials are needed for durable smart fabrics that capture and convey information and enable computing while accommodating the drape and movement of the human body. In recent decades, numerous approaches have been made in research to address this challenge using the flexibility and versatility of textile structures, along with innovations in the field of particulate and fibrous materials. This review focuses on the methods of synthesis of electrically conducting textiles and their applications. Particularly, it summarizes textile based multi-functional devices and their potential applications for portable or wearable functional integrated electronics, energy conversion & storage devices, sensors and actuators. The methods of fabrication like incorporation of conducting polymers are briefly discussed.

Keywords: Flexible electronics, *In situ* polymerization, Conducting Polymer, Smart materials, Sensors, Biomedical.

1. INTRODUCTION

Clothes were known to be our second skin and now it is attaining the sensory functions also. The fundamental challenges in incorporating additional functionality is that the drapability and manufacturability of textile and clothes to be maintained. The digital era is expanding exponentially, and this time to the internet of things (IOT). Flexible electronics are the need of the era. Electrically conducting textiles form a resilient platform for the development of these types of flexible electronics. Apart from this, smart textiles have increasingly attracted interest in recent years by textile designers and technologists. Electrically conducting textiles forms the brain of smart textiles. These can be used in two ways; i) for developing flexible electronics which in turn can be used in smart textiles, ii) for integrating a smart property as such in textiles (*e.g.* conducting fabric can act as strain sensors, EMI shields etc). Textile materials as such are insulators with resistance in the range of $10^{10}\Omega/cm^2$ and many manmade textiles develop static electricity that causes a number of difficulties. Static electricity attracts dust, increases the risk of catching fire and paves way to uncomfortable clothing. Adding up low conductivity about $10^3\Omega/cm^2$ can clear of these hazards and commonly used in clean room carpets, technical clothing etc. In the early twentieth century, more useful blends of electrical functionality and textiles appeared, such as the electrically heated glove for drivers, and, after the discovery and development of conducting polymers in 1977, illuminated clothing and heated clothing [1]. Modern methods to produce electrically conducting filaments comprise conductive substrates, metal wires, metalized yarns and inherently conductive polymers.

This review focuses on the fabrication procedures and application characteristics of e-textiles with some implications on the challenges and future perspectives of multifunctional devices. Particularly, it summarizes textile based multi-functional devices and their potential applications for portable or wearable functional integrated electronics, energy conversion & storage devices, sensors and actuators.

2. METHODOLOGIES FOR THE FABRICATION

2.1. Metalized fibers

The conventional concept of electrical conductivity is conferred to metals. They can be drawn into fibers and incorporated in textiles for wearable electronics. But have high elasticity and bending resistance. Such metal conductive fibers were woven into a fabric, producing connections with rigid printed circuit board (PCB) electronics or used as pulse sensing electrodes [2]. Flexible highly conducting materials have been prepared by weaving thin wires of various metals such as brass and aluminum. The manufacture of filament size yarns of stainless steel allowed the manufacture of conductive yarns and fabrics.

Metallized fibers are obtained from textile fibers wound with thin metal strips, or adding a metalized coating directly to a core yarn. Many metallized fibers were obtained from silver-coated polyamide yarns or from polyester fibers with copper sulphide deposited to their surface. Electroless plating of metal such as nickel or copper also serves the purpose. Now carbon nanotubes or grapheme are used for the metallization.

2.2. Graphene and MXenes

Graphenes and MXene are very good 2D materials for electrically conductive coatings for flexible and stretchable electronics [3, 4]. The closest substitutes to the etched copper tracks are metal based conductive inks. Typically, these inks consist of metal (e.g., gold, silver, platinum, or copper) micro or nanoparticles, a binder to increase the inter particle bonding and adhesion to the substrate, and a solvent to carry the dispersion.

Semi-conductive materials have been produced by impregnating textile materials with conductive carbon. The aerospace industry uses 10.6% carbon filled yarns and fabrics. The incorporation of 40% carbon to allow percolation threshold causes a significant deterioration of mechanical properties. A wide range of processes are developed including vapour phase deposition, sputtering, reduction of complexed copper salts, electroless plating using metals to yield moderately conducting fabrics. Electroless plating of copper, nickel and silver was reported as early as 1986 [5]. Aluminium was spray coated on textiles to give a conductance of 500 S [6].

Yu *et al*. demonstrated that solution-exfoliated grapheme nanosheets (~5nm thickness) can be coated from solution on three-dimensional, porous textile support structures for high loading of active electrode materials and to facilitate the access of electrolytes to those materials. With further controlled electrodeposition of pseudocapacitive MnO_2 nanomaterials, the hybrid graphene/MnO_2 based textile yields high-capacitance performance with specific capacitance up to 315 F/g [7].

Electrically conductive yarns from carbon nanotubes (CNTs) and polyvinyl alcohol (PVA) were prepared by two different methods, wet-spinning and coating processes by Xue *et al.* For the wet-spinning process, the CNTs/PVA mixed solution was extruded into a coagulant bath, which contained high concentration of coagulating agent. The coating process was carried out on five common fibres, including natural fibres and synthetic fibres, by using a blend of CNTs and PVA. The conductive yarns were treated by an acetylisation process in order to decrease the solubility of PVA to water. The conductivity of the obtained CNTs/PVA composite fibre by the wet-spinning process was about tens kΩ/cm for 40 wt% of CNTs to PVA. Electrical conductivity of PVA/CNTs coated yarns varied with the substrates. It was found that the conductivity of the yarns by coating process is much higher than that of the composite monofilament, obtained by wet-spinning process, under the same CNT concentration [8].

2.3. Intrinsically conducting polymers

Textile materials that conduct electricity can be produced by the incorporation of intrinsically conducting polymers (ICP) such as polypyrrole, polyaniline and PEDOT on an appropriate substrate that provides the required characteristics of flexibility, strength and processability. Electrically conducting yarns/fabrics were also made from conducting polymers by direct intrusion or spinning. Polyaniline or polypyrrole was melt spun or wet spun and fibres were produced [9]. Electrospinning units also give new platform for fibre production. Conductive fibres were obtained using two experimental processes (melt spinning and coating process). In melt spinning process, polyaniline, polypyrrole and graphite were used in order to obtain conductive polypropylene based fibres with specific electrical and mechanical properties. Polyaniline was treated using dodecyl benzene sulphonic acid to improve the solubility and the dispersion in xylene. The electrical resistance and morphological characteristics of conductive yarns were investigated. These yarns are supposed to be used to create smart clothing, corrosion protection or conductive fabrics for electromagnetic shielding applications [10]. Fig.1 represents the types of electrically conducting textiles.

Among these ICPs, polyaniline, polypyrrole and polythiophenes have drawn considerable interest because of their economic importance, good environmental stability and satisfactory electrical conductivity when doped. Less soluble nature of this ICPs has limited their direct fibre formation. It is reported that many of the limitations of conducting polymers associated with process ability, low mechanical strength, and poor flexibility can be successfully overcome by adhering them to strong, flexible textile substrates. The application of conducting polymer loading technology on textiles or flexible supports is increasing with other areas of its applications. The coating of ICPs on textiles is achieved by the use of one of the following approaches.

3. COATING METHODS

3.1. Direct coating

Direct coating of polymer solution can be done by the techniques like spray painting, printing or brush painting. After spreading of the solution of polymer, solvent was evaporated out. The advantage is that large area can be coated. Another benefit of direct application of the conducting polymer solution is that neither the substrate nor the instruments are exposed to corrosive oxidizing agents. This method has practical difficulties because of poor solubility of many conducting polymer in nearly all solvents of practical interest. Besides that desired uniform coating on the surface is not often obtained. The problem of insolubility can be solved to some extend by using derivatives of parent conducting polymer structures. For example, the introduction of an alkyl chain into the 3rd position of pyrrole monomer, or of an alkoxy group into the ortho-position of the aniline monomer, yield upon polymerization the corresponding polymers that are more soluble in some organic solvents, whereas sulfonation of PANI enhances the solubility of the resulting polymer in water. Kaynak *et al.* has reported the direct polymerization of poly (3-decanylpyrrole) [11, 12], poly (α,-bis(pyrrolyl)alkanes) [13] and 3-(−)-/ 3-(+)-menthyl carboxylate [14] pyrrole on wool. They studied the electrical conductivity, abrasion resistance and other features of coatings. The distortion of the molecular structure of conducting polymer occurs upon such chemical modification, leading to a drastic decrease of the electric conductivity of the resulting polymers. In another study by their group, a series of conductive textiles were produced by the chemical polymerization of the *iso*-alkyl pyrroles using both solution and vapour polymerization techniques. Fabrics coated with poly-*iso*-alkyl pyrrole formed using the solution polymerization method had a lower surface resistance than those formed using the vapour polymerization method. These conductivity results were in direct contrast to those obtained for 3-*n*-alkylpyrroles on fabrics. A remarkable crystal-like growth on the surface of the textile fabric was observed when solution polymerization of 3-*iso*-pentylpyrrole was employed, reinforcing the notion that subtle changes in monomer structure can drastically affect bulk polymer properties [15].

3.2. *In-situ* chemical polymerization

Monomers are cationically polymerized *in-situ* on the surface of material (fabric, yarn or fibers), provided with relatively strong chemical oxidants like ammonium peroxydisulfate (APS), ferric ions, permanganate or dichromate anions, or hydrogen peroxide. These oxidants are able to oxidize the monomers, leading to chemically active cation radicals of the monomers used. The cation radicals thus formed react with monomer molecules, yielding oligomers or insoluble polymers. This chemical polymerization can also occur in the bulk of the solution instead of on the surface of material, and the resulting polymers precipitate as insoluble solids. The distribution of the resulting conducting polymer between the precipitated and in-situ coated depends on many variables and varies within a broad range. For efficient coating it is necessary to shift this distribution toward the surface of material and the bulk polymerization should be diminished as far as possible. This can be usually achieved by choosing the reaction conditions, like the concentration of solution components, the concentration ratio of oxidant to monomer, reaction temperature, and an appropriate treatment of the surface of the material to be coated by conducting polymer. Although a bulk polymerization cannot be suppressed completely, a reasonably high yield of in-situ coating on material surface can be achieved by adjustment of the reaction conditions.

Deposition of conducting polymers using an in-situ polymerization approach, wherein the polymer is formed in the presence of the textile to form a thin uniform adherent coating, was first reported by Kuhn and coworkers [12, 13]. The technique for the deposition of

OCPs on textile substrates in an aqueous system was pioneered by Milliken Research Corporation [14-16]. In principle it is a very straightforward approach: the reagents (ICP precursor, oxidant and additional dopant) and the textile to be polymer-coated are placed in a vessel and agitated for a period of several hours. The process is carried out in an aqueous system, and the reagent concentrations are relatively low. One typical example provided in US 4975-317 consists of a 1 .5 L volume containing 50g of fabric with 1 6.7 g iron (III) chloride (0.04 mol/L), 2 g pyrrole (0.02 mol/L) and 1 .5 g 37% HCI, resulting in a fabric with electrical resistance of about 3 k.Q/square. The relatively low reagent concentrations are typical of adsorption reactions, and the set-up is reminiscent of conventional textile dyeing procedures (which are also adsorption reactions). Dyeing apparatus is actually used in some examples, illustrating the relatively easy commercial scale-up that is possible with the system. Boutrois *et al.* [17] later reported a full-scale industrial process for coating entire rolls of fabric with polypyrrole by the technique. A special fabric rolling technique was used, to ensure good circulation of the reaction liquor and provide separation of the fabric layers. The reaction was carried out at < l° C for six hours.

If the reaction is carried out in solvents other than water, the polymerization occurs almost entirely in the solvent, with little deposition on the surface of the substrate. Water and reagent purity has no discernible effect, with the result in distilled water indistinguishable from that in tap water, and no benefit observed when precursor is distilled before use.

Thereafter, several researchers successfully prepared conducting textile materials using *in-situ* technique. The coating thickness was controlled by adjusting the reactant concentrations. The researchers report that thickness of the coating initially increased rapidly followed by a steady increase when the concentration of pyrrole (Py) was larger than a concentration of approximately 0.4 mg/mL. The surface resistance of coated PET decreased from 10^6 to $10^3\Omega$ with increase in pyrrole concentration within 0.2 mg/ml until the concentration reached a value of about 0.4 mg/mL, above which the rate of decrease diminished. The effect of initial treatment with monomer or oxidant prior to polymerization reaction with regards to thickness and surface resistance was minimal. The immersion time of the textile into the monomer solution prior to polymerization reaction did not have a significant effect on the abrasion resistance [18].

Conducting textiles were prepared embedding polypyrrole in natural and manmade cellulose-based fibres, such as cotton, viscose, cupro and lyocell by means of *in-situ* polymerization. Chemical vapour phase deposition of polypyrrole is a suitable process for producing electro-conductive composites in two steps: (a) fabric impregnation with an aqueous solution of oxidant and dopant and subsequent drying; (b) exposition to pyrrole vapour and polymerization. Comparative morphological and structural analysis was carried out on the conducting viscose prepared with both vapour and liquid phase processes and some significant differences in the structural, calorimetric and electrical properties were highlighted, due to the different methods of preparation. Vapour phase prepared fabrics show a high uniform polypyrrole coating on the fibre surface and its partial penetration inside the amorphous zones of the fibre bulk. The vapour deposition method produces fibres with a uniform conductive layer, while cellulose samples prepared with liquid polymerization show PPy aggregates on the fibre surface. The electrical properties decrease by 70-80% in 2 weeks due to atmospheric ageing, after this time the conductivity is substantially unchanged. The application of siliconic oil as a coating on the conductive fibres sensitively slows down the resistance increasing [19].

Loose wool fibres were also coated with electrically conducting doped polypyrrole (PPy) by *in-situ* chemical oxidative synthesis from an aqueous solution of pyrrole. PPy coated wool fibres were spun and knitted using conventional industrial machinery. Electrical and thermal properties of the fabrics were studied using simulated ageing tests, with the aim of evaluating the performances decay during the processing stages and the final use of the products. The results show that fabrics made of PPy coated wool fibres have an acceptable conductivity decay with respect to most of the stress that textile products are usually subjected to, but low fastness was found to washing, probably due to alkali dedoping of conducting PPy coating, although an excellent resistance to organic solvents allows conventional dry cleaning treatments [20].

Highly conductive polymers (polypyrrole, polyaniline or poly-3,4-ethylene-dioxythiophene)/silk fibroin composite fibers were also fabricated successfully and expediently by in situ polymerization without any modification of silk fibroin surface. Polypyrrole/silk fibroin (PPY/SF), polyaniline/silk fibroin (PANI/SF), and poly-3,4-ethylene-dioxythiophene/silk fibroin (PEDOT/SF) composite fibers exhibited varied conductivity in the range of $3.8\text{-}4.2 \times 10^{-1}$, $0.9\text{-}1.2 \times 10^{-2}$ and $4.9\text{-}5.2 \times 10^{-3}$ S cm^{-1}, respectively. Improved thermal stability of silk fibroin fiber via coating process was observed from thermogravimetric analysis (TGA) results. Structural analysis indicated that the interactions including hydrogen-bonding and electrostatic attraction existed between silk fibroin macromolecules and conductive polymers. The peptide linkages bearing on silk fibroin macromolecules played an important role in the in situ polymerization by attracting conjugated cation radicals. These composite fibers still possessed former fibrillar morphology and strength properties [21].

As to avoid bulk polymerization, the material surface is enriched either with a monomer, or an oxidizing agent, and after that is treated with a solution of either oxidizer or monomer, respectively. A major advantage of this process is that the polymerization occurs almost exclusively at the surface. For some polymer materials, the surface can be enriched with a monomer by its sorption from solution. DPMB, DPSB.

Conductive fabrics were prepared by immersing the nylon 6 fabrics in 100% aniline or an aqueous hydrochloride solution of aniline followed by initiating successive polymerization in a separate bath (DPSB) or in a mixed bath (DPMB) of oxidant and dopant solution with aniline. In each case, the polymerization conditions were optimized to obtain the maximum quality of polyaniline (PANI) on the fabrics. The higher conductivity of composite fabrics, whose value reached up to 0.6 X 10^1 S/cm, was obtained by the DPMB process. Moreover, this method induced the least decrease in the degree of crystallinity as compared to the DPSB process. The serviceability of the PAN–nylon 6 composite fabrics was also evaluated. No significant changes in the conductivity were observed after abrading the composite fabrics over 50 cycles and multiple acid and alkali treatment. The stability of conductivity was slightly decreased by less than 1 order after exposure to light for 100 h, but it was significantly decreased after washing with detergent. The result shows the diffusion controlled process DPSB is less efficient. But it eliminates the wastage due to polymerization in solution [22]. But another study by Jin and Gong reports that monomer diffusion has an important role to produce durable coatings. They also show HCl dopant to be more effective than other dopants [23]. Aniline was polymerized on cotton using DPSB process and tested for EMI shielding [24].

The enrichment of the surface by an oxidizer can occur either by ion-exchange mechanism or by the deposition of an insoluble layer of oxidizer. The disadvantage of this process is that it is limited by materials that can be covered or enriched with a layer of either monomer or oxidizer in a separate stage, preceding the polymerization. Vapour phase polymerization can also be considered as modified chemical polymerization.

A vapour phase polymerization method was used to coat cotton threads [25]. Xue and Tao used vapour polymerization to coat polypyrrole on polycaprolactam and polyurethane (Lycra) fibres [26].

Wool and alpaca fibers were coated with polypyrrole by vapour-phase polymerization method. The changes in frictional and tensile properties of the single fibers upon coating with the conductive polymer were studied. Coating a thin layer of polypyrrole on the alpaca and wool fibers results in a significant reduction in the fiber coefficient of friction as the conducting polymer layer smoothen the protruding edges of the fiber scales. It also reduces the directional friction effect of the fibers. Depending on the type of fiber, the coating may slightly enhance the tensile properties of the coated fibers [27].

The conductive polymer-coated fabric based on PPy prepared by the method of vapour phase polymerization gave a promising flexible strain sensor with very high sensitivity. The polymerization temperature has a great effect on the sensitivity and the sensing reproducibility. The environment temperature and humidity also affects the conductivity of the conductive fabrics so prepared [28].

The electrical resistivity of wool yarns obtained in continuous vapour polymerization (0.43kΩ/mm) was much lower than other conducting polymer coated yarns [29].

3.3. Template process (admicellar polymerization)

G.G. Wallace *et al.* reported a molecular template (a sulfonated polyaniline) to facilitate integration of a complementary conductive polymer (polyaniline) into wool-based textiles. The efficiency of the polymerization/coating process is enhanced since the template localizes the reaction within the textile. The presence of the molecular template results in the formation of an adherent, uniform and stable conducting polymer layer. The poly(2-methoxyaniline-5-sulfonic acid) (PMAS) molecular templated fabric had a surface resistivity of 28 MΩ/Square, but after the integration of polyaniline the surface resistivity decreased to 342 kΩ/Square. The integration of polyaniline also improved the electrochemical reversibility of the coating [30, 31].

Conductive textile yarns were prepared by a continuous vapour polymerization method. Application of polypyrrole by the continuous vapour polymerization method used is designed for the easy adaptation into industrial procedures. The resultant conductive yarns were examined by longitudinal and cross-sectional views, clearly showing the varying levels of penetration of the polymer into the yarn structure. It was found that for wool the optimum specific resistance was achieved by using the 400 TPM yarn with $FeCl_3$. For cotton yarn, the optimum specific resistance of $1.53\Omega/cm^2$ was obtained with 80 g/L of $FeCl_3$ solution [32].

As another version surfactants was used as template and technique is called admicellar polymerization. Conductive PPy/cellulose composites were prepared with flax substrate by using admicellar polymerization. In admicellar polymerization, thinner PPy layer would be formed by a surfactant template. The optimum preparation condition was studied and deduced as follows: pyrrole concentration 0.3 mol/L, $FeCl_3$ concentration 0.3 mol/L, adsorption time 150 min, PVA to pyrrole weight ratio 2%, polymerization temperature 0°C, polymerization time 9h. The surface resistivity of conductive composite fabric almost linearly increased with the prolongation of storage time. The stability of the conductive composite is the best when PVA/pyrrole are 2% [33].

3.4. Electropolymerization

White and coworkers introduced a novel approach to enable electrochemical deposition of conducting polymers on non-conducting fibres such as kevlar or polyester [34-36]. Good conductivity and electroactivity were obtained, however, the mechanical properties and the handle of the fibers was inevitably compromised. Bhadani *et al.* also used an electrochemical approach to coat cotton, silk and wool fibres [37]. The potentiostatic and galvanostatic polymerization were tried on aniline and pyrrole. The potential sweeping technique gave more adherent films [38]. In all cases fires were wound tightly on anode and polymerized. But when this winding comes to fabric is not practically applicable.

Subianto *et al.* fixed the textile materials to anode by adhesive and reported to be more efficient. Cotton fabric was attached to the anode by means of a water-based adhesive (Henkel Pritt stick) with a second layer of adhesive applied to the external surface of the fabric. Electropolymerization of pyrrole was carried out for 4-6 h [39].

Kim *et al.* prepared polypyrrole/PET conducting fabric by electrochemical polymerization after chemical polymerization to improve the conducting ability of their composite fabric [40].

After that Molina *et al.* also polymerized pyrrole chemically and electrochemically on PET fabrics with AQSA and polyoxometallates as dopant. For electrochemical method the chemically polymerized fabric was taken as substrate. It gave smooth and uniform coatings. The counter ion has a significant influence in the polypyrrole conductivity films. The more planar the structure of the counter ion, the more conductive film is obtained [41].

The cotton fixed on stainless steel electrodes was electrochemically coated with polypyrrole micro-structures and compared with that obtained by chemical polymerization. The conductance, smoothness and electrical properties were better for electrochemically coated cotton [42].

Polyaniline (PANI) has been electrochemically polymerized on conducting textiles of polyester covered with polypyrrole (Ppy)/anthraquinonesulphonic acid (AQSA), obtaining a double conducting polymer layer. Electrochemical syntheses have been performed by means of cyclic voltammetry (CV) and potentiostatic methods. PANI morphology varies with the method of synthesis as it has been corroborated by scanning electron microscopy. EDX analyses have been performed to study zonal composition of the samples. Surface resistivity measurements have been carried out with a 4-point probe equipment. Electrochemical impedance spectroscopy (EIS) and CV have been employed to characterize the electroactivity of the samples in solutions with different pH values. X-Ray photoelectron spectroscopy (XPS) was employed in order to determine the doping level of polyaniline films and the oxidation state of the sample. With the potentiodynamic synthesis the doping level was higher than that obtained with potentiostatic synthesis; however, polymer overoxidation appeared [43].

4. INFLUENCE OF SUBSTRATE PROPERTIES

Milliken researchers consistently reported that fibre type (for example, whether the fabric used was made from polyester or cotton) had little effect [44]. This is somewhat surprising, as in an adsorption reaction, it is logical that the chemical and physical properties onto which reagents are being adsorbed will be relevant (the somewhat analogous process of dyeing is highly fibre type-dependent). Other researchers have examined the influence of the substrate surface properties in more detail, for example *Avlyanov et al.,* who established that the hydrophobicity of the substrate influenced the conductivity and durability of the textile-ICP composite produced [45]. For hydrophobic surfaces the conductivity was higher, while adhesion of the polymer was better on hydrophilic substrates.

In another study that focused more on the polymerization reaction kinetics, Ferrero et al. used a range of synthetic fibre types (polyester, nylon 6, polypropylene and acrylic) [46, 47]. They found that generally the lowest resistance resulted with nylon 6, and highest with polypropylene. An HPLC analysis of monomer and dopant adsorption by the fabrics indicated that nylon had high adsorption of monomer (presumably due to the presence of amide groups to which the slightly polar pyrrole molecule may have an affinity) and moderate adsorption of dopant, while polypropylene had particularly low adsorption of the dopant. The adsorption is presented in terms of the amount per unit area of fabric - this is because the resistance measurement is surface resistance, rather than resistance of the bulk material. Thus it is polymerization on the surface of the fabric that is most relevant.

Conductivities of silk, cotton, polyester and wool fibers electrochemically coated with polypyrrole ranged between 0.2-16 S/cm, with the silk and polyester fibers showed the highest conductivity [48]. In another study, conductivity of wool and polyester yarns coated with polyaniline were considerably less than cotton, acrylic and nylon [49]. Poly(ethylene terephthalate) fibres coated with polyaniline (2 wt%) had surface resistivities of 3×10^5 Ohm/square whereas with fibres coated with polypyrrole, resistivities in the order of 10 Ohm/square have been obtained [50].

The PPy coated with PA6 possessed much better coating qualities and electrical conductivity that with lycra. The relationship between $\Delta R/R^{\circ}$ and applied strain is linear in PA6 as it depends on changes in fiber dimensions, but not linear in case of lycra as the strain damages coating [51].

Conducting polymer-fibre composites of polypyrrole with cellulose (paper) and protein (wool) fibres respectively have been successfully produced. The polymer coating comprises 100-200 nm spheres which are fused together in a continuous sheet that fully encapsulate and bond to the fibre surface. Conducting polymer-cellulose fibre composites using individual wood fibres produced from bleached P. radiate. Kraft pulp was prepared by dispersing about 0.5 g of the dry pulp in 500 cm^3 of water to give a fully dispersed suspension of individual cellulose fibres. The suspension was filtered and the fibres redispersed with effective stirring in a solution of pyrrole (0.5 M) and p-dodecyl benzyl sulfonate (0.05 M) in water (500 cm^3) for about 1 h to allow the pyrrole to absorb onto the surface of the individual cellulose fibres. The fibres were then filtered and washed with further pyrrole solution (0.5 M) and added to a solution of ferric chloride (0.5 M) as the oxidant to effect polymerization. The progress of polymerization was noted by the change in colour of the fibres from brown/orange to dark green to black over a period of about 5 min. However the suspension was left stirring for a further 3 h to ensure complete polymerization [52].

When aniline was polymerized on paper the porous structure of paper was retained. The hydrogen bonding between cellulose and polymer was suggested [53]. The electro-mechanical properties of Pani-PET conductive yarns indicate that many applications such as fibrous sensors, connection devices in smart clothing, electromagnetic shielding devises are possible [54].

Polyaniline (PANI)/Nylon-6 composite films were prepared by oxidative polymerization of aniline inside host Nylon-6 film. Such a composite had the desired electro-active and mechanical properties to serve as a self-standing functional unit. Comparative studies on sorption of aniline by Nylon-6 matrix from various media were conducted revealing superior aniline uptake from neutral solution in water. Aniline content was measured to be as high as 12%. Spectroscopic measurements showed that hydrogen bonding seemed to play important role in aniline sorption by Nylon-6 matrix. Polymerization was monitored using atomic force microscopy and conductivity measurements. The morphology studies showed the appearance of PANI nanodomains on Nylon-6 surface in the early stages of the polymerization. Eventually the domains coalesced during polymerization forming a continuous PANI layer. The conductivity measurements confirmed the change of the morphology from isolated islands to continuous conducting surface by drastic increase in conductivity [55].

Polymerization occurred only at the surface level and not in the bulk. Actually, silk behaved like synthetic fibers, polyester, and polyamide, which showed the formation of an outer layer of conductive polymer. In the case of wool, another protein fiber like silk, a partial penetration of the polymer inside the fiber matrix was observed because the scaled surface structure of wool allows paths for penetration and diffusion of relatively small molecules like the Py monomer. When cellulose-based regenerated fibers like viscose and Lyocell were used as substrate, the polymerization proceeded in the bulk of the fiber, owing to the easy penetration of the monomer into the fiber matrix during the initial step of the process. These results provide strong evidence of the key role played by morphological and structural features of the fiber substrates in determining the nature and extent of the PPy-fiber interaction, which may range from nanodispersion of PPy into the fiber matrix, as in the case of cellulose fibers, to formation of skin-core composite structures, as for silk and synthetic fibers [56].

The PPy-polycaprolactam fibres had much higher conductivity (initial resistance 9 kΩ/cm) than the polyurethane fibres (initial resistance 10 times higher). The electrical properties and environmental stability varied widely depending upon the processing conditions. The desirable electronic properties of the polymer coating are combined with the mechanical properties of the fabric. The surface resistivity is dependent on the coating thickness, typically 0.1-1 Ω/m, can be prepared.

Polymerization of pyrrole was carried out in the presence of wool yarn at various concentrations of the monomer and dopant anion. The changes in tensile, moisture absorption and electrical properties of the yarn upon coating with conductive polypyrrole are reported. Coating the wool yarns with conductive polypyrrole resulted in higher tenacity, higher breaking strain, and lower initial modulus. The changes in tensile properties are attributed to the changes in surface morphology due to the coating and reinforcing effect of conductive polypyrrole. The thickness of the coating increased with the concentration of p-toluene sulfonic acid, which in turn caused a reduction in the moisture regain of the wool yarn. Reducing the synthesis temperature and replacing p-toluenesulfonic acid by anthraquinone sulfonic acid resulted in a large reduction in the resistance of the yarn [57].

Electropolymerization of pyrrole in the presence and absence of acrylamide was accomplished. Conductivity of polypyrrole and poly(pyrrole-acrylamide) free-standing films show a conductivity of 90 and 1.0 S/cm, respectively [58].

5. MODIFICATIONS/ IMPROVEMENT

Several independent methods were experimented in order to improve the conductivity, strength and other mechanical properties. Some of them are described below

Alkali reduction pretreatment of the PET fabric before the polymerization of aniline onto the fabric and the introduction of squeezing with laboratory padder on the fabric to push the reagent into the inner part of the fabric and short immersion time of the aniline-absorbed fabric in oxidant solution improved the washing fastness [59].

The fibres were treated especially under super critical carbon dioxide in order to improve the adhesion. This development is reported to produce wear resistant conductive polyamide, polypyrrole and polyester, polyaniline having $1x10^3$ to $3x10^4$ and $9x10^4$ to $3x10^5$ Ω/cm respectively. Washing fastness tested according to SFS-EN ISO 6330 7A gave good result in conductivity within ESD standards [60].

The fabrics were first functionalized with triethoxysilane in order to improve the properties of polypyrrole coatings. The presence of triethoxysilane (SP) along with polypyrrole (Ppy) at the highest initial concentration leads to slightly better conductivity than that of composite modified only with polypyrrole. This could be due to covalent binding of polypyrrole layers through SP and also due to some displacement of polymerization from solution to the surface of fibres. Stronger, thicker and adherent outer polypyrrole layers are created, and the conductivity of washed viscose 0.2 SP/25Ppy is about 3×10^{-5} S/square, while that of /25Ppy is only 2×10^{-6} S/square. The increase in the number and size of adherent polypyrrole islands, which can withstand washing, is evident [61].

Attempts were made to plasma deposit an oriented π-conjugated polymer of pyrrole on paper surfaces in order to produce electrically conductive layers. The N/C atomic ratio of 0.13-0.24 was observed for all treatment conditions. This implies the nature of the deposit formed on the paper surface via pulsed plasma is different from that of pyrrole monomer alone. An increase in conductivity of all pyrrole-plasma treated papers was observed. The paper sample exposed with 50W RF-power plasma for 5 min showed 8.15×10^{-9}S/cm conductivity. The conductivity measurements indicated that plasma enhanced ring-opening reaction mechanism of pyrrole [62].

An oxidative pre-treatment of wool fibers enhances the deposition of the conducting polymer. NDS is used as dopant because of its stability with the oxidant ($FeCl_3$). The dopant/monomer ratio controls the electrical conductivity and the adhesion of the polymer layer; a small excess of oxidant is needed to increase the conductivity and to lead to a complete polymerization; and the monomer concentration in the polymerization bath above 2 g/l provides the highest conductivity [63].

A pretreatment was done on cellulosic fibers (cotton) and protein fiber (silk), after going for activation stages. These were coated with conductive polymers such as pyrrole and aniline by two methods: Vapour and liquid phase. The conductivity of conductive fibers was comparable with normal conductive polymers. Physical properties of two groups of fibers have been investigated together, such as, crude fibers and coated fibers by PPy. The tensile strength of the coated fibers in comparison to the crude fibers was increased [64].

Solvent-based preliminary treatments were carried out on polyamide fabrics to be coated with a thin layer of electrically conducting doped polypyrrole, with the aim of improving the adhesion of the conducting layer to the fibre substrate. Polyamide fabrics were treated with dilute formic acid, pure tetrachloroethylene and ethanol/water at different temperatures and times. After the treatments, the fabrics were coated with polypyrrole by *in-situ* chemical oxidative polymerization. The adhesion of the PPy layer was evaluated by means of surface resistivity measurements, SEM investigation and ATR FT-IR analysis after Martindale abrasion tests. The adhesion of PPy layer on the fibre surface was strongly improved by the solvent treatments, in particular with ethanol and tetrachloroethylene. The surface resistivity of the ethanol-treated fabrics did not change after more than 200 abrasion cycles and the PPy layer linked to the fibre surface was observed by SEM and ATR FT-IR also after 4000 abrasion cycles [65].

Electrically conducting PET textile/PPy composite was prepared by chemical and electrochemical polymerization of PPy on a PET fabric in sequence. The chemical polymerization at lower temperature using FTS as an oxidant with PVA as a surfactant produced the best quality of PPy coating on the textile and the highest electrical conductivity. When the composite was prepared using 0.5 M aqueous solutions of FTS and pyrrole with PVA at 0°C, the specific volume resistivity of the composite was as low as about 1 Ω/cm at only 7 wt % of PPy content. The increase of EMI SE with the electrical conductivity results dominantly from shielding by reflection rather than absorption. Shielding efficiency by reflection (R_e) increased with decrease of the specific volume resistivity, while shielding efficiency by absorption (A_b) decreased. The increase of R_e must be due to shallower skin depth of the composite with higher electrical conductivity. An important advantage of the composite prepared for a particular application, relative shielding efficiency by reflection and absorption can be easily controlled by the electrical conductivity [66].

The interaction at the liquid/solid interface was used to self assemble a layer of the conductive polymers at the surface of the textiles. The mechanism of adsorption of the conducting polymer onto the surface of the textiles is thought to be physical adsorption followed by polymerization in the plane of the liquid/solid interface [67]. The process results in a smooth coherent film of conducting polymer on the surface of the fibres. The rate of polymerization was enhanced in presence of textile substrate.

6. EFFECT OF DOPANTS

The films produced utilizing AQSA as the dopant demonstrates an extremely smooth morphology when compared to the PTSA and Cl doped materials. The Cl doped sample is significantly more rough and porous; although the surface is much smoother than the solution side of electrochemically grown thick films of polypyrrole. Because the typical doping levels for these materials is 0.30, and because of the high molecular weight of aryl sulfonates, the dopant comprises as much as 50% of the polymer film mass. The planar ring system of the dopant is therefore expected to contribute significantly to the morphology of the polypyrrole film. The relative stability of the AQSA film, particularly during the initial stages of conductivity loss, is due in part to the smooth surface which inhibits oxygen penetration. The more porous morphology of the films produced using other dopants contributes to the relative instability of their film [68].

For a given voltage, the current obtained is higher for the AQSA doped PPy coated sample than the others, hence the power per unit area is higher. Anthraquinone-2-sulfonic acid (AQSA) sodium salt monohydrate, naphthalene-2-sulfonic acid sodium salt, p-toluenesulfonic acid monohydrate and sodium perchlorate monohydrate were used as dopants. The best conductor is the fabric coated with AQSA doped PPy. Lower the initial resistance of a sample, higher is the temperature increase achieved during the experiment. The AQSA system shows the highest temperature increase [69].

Wool shows an interaction with organic dopants during polymerization. The interaction plays an important role on the resulting properties. FT-IR and EDX analysis show that the organic dopant is preferably absorbed by wool, whilst chlorine is preferably embedded onto the conductive PPy coating as counter-ion. On the other hand, loss of chlorine from the PPy/wool composite was observed after washing, leading to an increase of the surface resistivity of the fabrics; nevertheless, the presence of naphthalene disulphonicacid in the polymerization bath enhances the final electrical conductivity [70].

Kaynak *et al.* investigated effects of short term heating on conductivity and stability of Polyethylene terephtalate - polypyrrole (PET-PPy) textile complexes incorporating different anionic dopants, heat treated at 60°C, 80°C, 105°C, 125°C and 150°C. In most cases heat treatments below 80°C did not significantly change the final resistance of the conducting textiles. Only the anionic dye-dopant Indigo Carmine acted in a heat-stabilizing manner during treatment at 150°C, while all samples containing other anionic dopant underwent some degradation. A treatment temperature of 125°C was the most effective for lowering the final resistance, with sulphonic group containing dopants being particularly effective in improving conductivity and stability. A 29% decrease in the final resistance of a PET-PPy/para-toluene-2-sulphonic acid (pTSA) sample was achievable after 900 s at 125°C [71].

7. EFFECT OF OXIDANTS

Mild oxidizing agents like ferric chloride, and strong Ammonium persulphate, potassium iodate are used as oxidating agents. Ferric chloride works well for polypyrrole but not suitable for polyaniline. Ferric P toluene sulfonate was used for PEDOT. In most cases monomer: oxidant ratio was above 1:1. Mostly the optimum ratio was 1:1.5 and above it led to over-oxidation and hence reduction in conductivity.

White *et al.* achieved free-standing and supported thin films of polypyrrole and poly(N-methyl pyrrole) using a selection of aqueous oxidants including polyoxometallates. The vapour growth method was chosen as an alternative to a sometimes expensive electrochemical growth method. Silk was successfully coated by these polymers [72].

PANI was selectively formed on wool in the case of polymerization of aniline, using potassium iodate (KIO_3), as an oxidizing agent in the presence of wool. IR spectrum of PANI-wool composite formed using KIO_3 showed the presence of cysteic acid units (Cy-SO_3H) resulted from the oxidation of cystine bonds (Cy-S-S-Cy) in wool. Selective formation of PANI on wool was considered to occur by a concentration of aniline on wool bearing cysteic acid units. It became apparent by IR analysis of oxidized wool that the oxidized layer of the wool textiles was thicker and cystine bonds in wool were converted into more cysteic acids by oxidation, using KIO_3 than using $(NH_4)_2S_2O_8$ and $K_2Cr_2O_7$. Therefore, formation of PANI on wool occurred remarkably in the case of polymerizing aniline using KIO_3 [73].

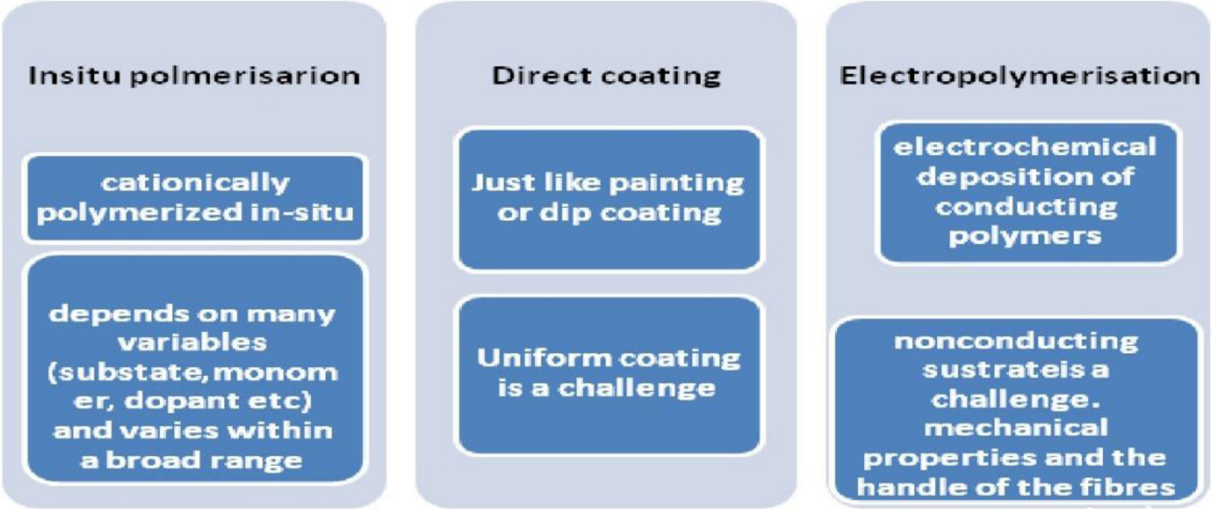

Fig.1. Types of electrically conducting textiles

Polypyrrole formation on the surface of cellulose fibres could only be obtained under extremely aggressive polymerization conditions; fibres were initially immersed for 30 min in concentrated $FeCl_3$ solutions where the pH ranged between 1.8 and 2 and during the subsequent 20 h polymerization pH never exceeded 3. This induced the erosion of the fibre surface, the generation of fine elements and a drop in the polymerization degree of cellulose. Iron is adsorbed on cellulose fibres in $FeCl_3$ solutions as multivalent ferric compounds, thereby inducing fibre cationization. Pyrrole polymerization on cellulose fibre was possible only when the $FeCl_3$ concentration in the impregnation solution was higher than 0.5mol/l when an impregnation/thickening procedure was applied. A direct correlation was observed between $FeCl_3$ concentration in the impregnation solution and the electric resistance of modified cellulose pellets. It is possible to use an impregnation/thickening sequence to promote pyrrole polymerization on cellulose fibres for the formation of a low-electric resistance cellulose/polypyrrole compound. There are many books and reviews in the area of conductive polymer coating [74].

Thus the conducting polymer coatings can be summarized as in the fig.1.

8. APPLICATIONS OF ELECTRICALLY CONDUC-TING TEXTILES

8.1. As flexible electronics

The electrically conducting fibers and yarns provide opportunity in electronic textiles such as a textile interconnector of light emitting diodes, flexible textile heaters, and touch gloves for capacitive touch sensors [20, 21]. These textiles are used in the world of fashion, wearable electronics etc.

8.2. As Smart textiles

Smart textiles are materials and structure that sense and react to environmental conditions or stimuli, such as those from mechanical, thermal, chemical, electrical, magnetic or other sources in Fig.2. Smart textiles are no longer a science-fiction fantasy. According to the manner of reaction, smart textiles can be divided into passive, active and intelligent.

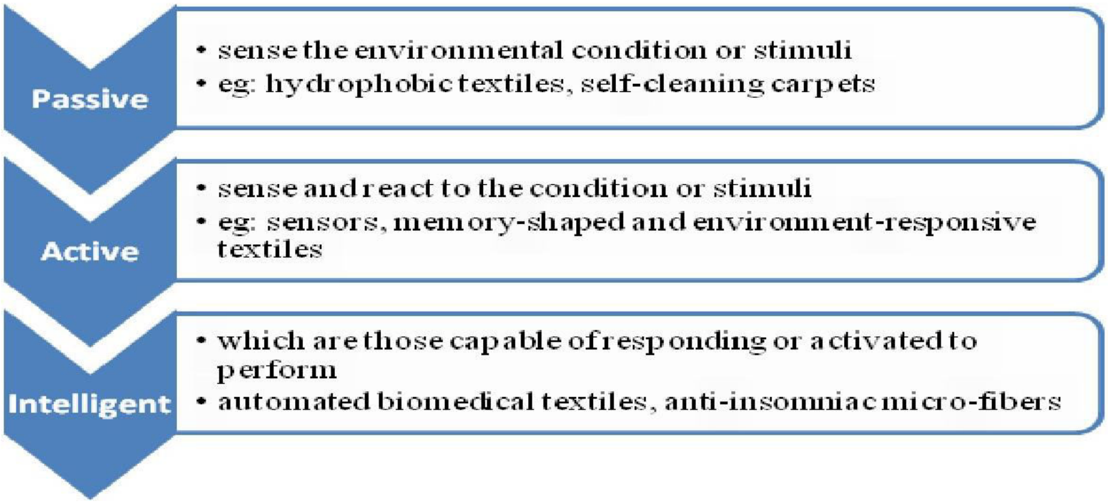

Fig. 2: Reaction of Smart Textiles

The research community is actively advancing in the field of sensors and actuators such as photo-sensitive materials, fibre optics, conductive polymers, thermal sensitive materials, shape memory materials, intelligent coating materials, chemical responsive materials, micro-capsules, micro- and nano-materials. The signal transmission, processing and control: neural networks and control systems, cognition theory and systems will be helping hand in hand for the development of smart textiles. Further integration of processes and products are such as wearable electronics and photonics, adaptive and responsive structures, bio-mimics, tissue engineering, chemical/drug releasing pave way for the completion of intelligent textiles.

In 1940, Ventile fabric [75] operated by the swelling ability of cotton yarn hindering water to penetrate beyond the amount was used as a waterproof protecting layer. It was not until the 1980s that textiles-especially garments were “discovered” as a potential arena for enrichment by other kinds of technologies such as sensorics for measuring the wearer as well as monitoring the surrounding. These have inter-changeably been denoted as smart textiles [76], intelligent textiles, or electronic textiles. This “(re) discovery” of textiles as an interesting field for new technical developments is in parallel with the “(re) discovery” of paper, which, although started later moved at a faster pace and printed electronics, paper electronics or smart papers now have emerged as branches on their own. Both textiles and papers are polymeric, fiber-based, cheap, pliable, flexible, large area (semi) 2D materials that take part in everyday activities of humans and by this being ubiquitous ever present.

8.3. Smart textiles for biomedical application

Garments having the ability to monitor bio-signals and communicate with the environment can provide continuous information about a person's state of health. Smart and wearable textile systems are also intended to improve the quality of life by enhancing the wearer's functionalities. The recent surge in using wearable personalized devices has made it increasingly important to have flexible textile-based sensor alternatives that can be comfortably worn and can sense a wide range of body strains. Textile strain sensors offer a new generation of devices that combine strain sensing functionality with wearability and high stretchability. Thus, wearable computing sketches future electronic systems to be an integral part of our everyday outfit. Such electronic devices have to meet special requirements concerning wearability. The first generation of intelligent clothes used conventional materials and components, which tried to adapt the textile design in order to fit in the external elements. Here, the electronic components are embedded into clothing. These garments contain conventional cables, miniaturized electronic components and special connectors. But now by combining one of humankind's oldest technologies-textile processing, and new advanced materials, such as electroactive polymers, a new kind of textile actuators (textuators) are being developed. The fibers or textiles have excellent flexibility and can follow many intricate motions of the human body. Besides, fibers crossed in fabrics will prevent the crack propagation that occurs in solid films or bulks, thereby improving their long-term use. In addition, the textiles have a comfortable appeal and can be "breathable" or keep the subject warm. Therefore, the fiber or textiles are the most suitable platform to fabricate. An overview of smart fibres, fabrics and clothing in biomedicine and in several health focused disciplines such as bio-monitoring, rehabilitation, telemedicine, health- professional support and sport medicine is available in the literature. For example knee scaffold for sports man to record speed, warble goniometers, soft electrodes for ECG measurement and textile materials for cardiopulmonary monitoring [77].

8.4. As Electrochemical textiles

Li ion batteries can be made flexible by using conducting textile based electrodes. Pu et al. made Ni coated conductive textiles and developed flexible batteries and a nanogenerator for wearable electronics [76]. CNT based conducting textiles, conducting cotton materials all tried for flexible batteries. Electrochromic property of ICP can be used for making electrochromic textiles which will be highlyuseful for defense [78]. Flexible solar cells can be made and put over the jacket /overcoat which can supply charge when needed.

9. CONCLUSION

The electrically conducting textile materials made the following impact:

- Flexible electronics gave a positive proposal for the advancements of internet of things.
- Textile intelligent systems, which comprises conducting textile structures (wires and electroconducting structures) present a dynamic behavior which favors the self-regulation of the thermal insulation and vapour permeability with the purpose to maintain the thermo-physiological balance; the integrated clothing assembly has as an option the module for monitoring the biologic potential, used only in critical situation (ex. accidents, falling down in a precipice etc.)
- Smart clothing is no longer science-fiction or fantasy. Even if they are still the prerogative of some special social categories such as sportsmen, informatics specialists, businessmen or researchers, the explosive expansion of the mobile communications and of the computation technique, will bring them into every body's wardrobe. The textile smart system represents a challenge that one has to be able to scope with every day.

Conflict of interest

None declared

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