POLITECNICO DI MILANO

Master of Science in Materials Engineering and Nanotechnology

Trends in Man-made Fiber and Textile Industry

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Academic Year 2012-2013

Abstract

High level of competition is seen now in textile industry. A shift from mass-production to specialty products is one of the strategies to compete in the market. Textiles are acquiring new functionalities, becoming “smart” or responsive.

Scarcity of oil resources and legislation restrictions promote the development of biomaterials and sustainable manufacturing methods.

Innovations in textile can result in significant cost savings and reduce environmental impact.

The aim of this thesis work is to provide a general overview of trends in synthetic fibers and textile industry. Contemporary innovations in variety of industry fields are taken into attention and briefly described in the first part of the thesis report: materials, machinery, functional textile, smart/intelligent textile and applications.

Recent advances in bioplastics are given in the second chapter. Achievements in conductive, piezoelectric and photovoltaic fibers made in last years are presented in the following chapters.

Un alto livello di competizione è ora presente nell'industria tessile, e una transizione dalla produzione di massa a una produzione più specifica è una delle strategie per competere in questo mercato. I tessuti stanno sviluppando nuove funzionalità, diventando "intelligenti" o sensibili.

La carenza di risorse petrolifere e le restrizioni legislative incentivano lo sviluppo di biomateriali e di metodi di fabbricazione sostenibili.

Innovazioni nel settore tessile potrebbero avere come conseguenza significativi risparmi economici e una riduzione dell'impatto ambientale.

Lo scopo di questa tesi è fornire un quadro generale dei trend nell'industria tessile e delle fibre sintetiche. Le innovazioni in una vasta gamma di campi industriali saranno analizzate e brevemente descritte nella prima parte della tesi: materiali, macchine, tessuti funzionali o intelligenti e loro applicazioni.

I recenti progressi nel campo delle materie bioplastiche saranno trattati nel secondo capitolo. I risultati relativi alle fibre conduttive, piezoelettriche e fotovoltaiche saranno presentate nei capitoli successivi.

Table of contents

1 General information

1.1 Man-made fibers

Man-made or synthetic fibers are defined as fibers formed by chemical synthesis. Types and examples of man-made fibers are shown in the table 1.

Man-made fibers			
Natural polymers		Synthetic polymers	Inorganic sources
Cellulose based	Protein based		
Viscose Cupro Lyocell Modal Acetate Tencel	Aneroin Synthetic spider silk Casein Collagen Ardein Zein	Aramid Polyester Polyamide Polypropylene Acrylic Carbon PTFE	Graphit Stone wool Glass Slag wool Refractory ceramic fibers Metal

Table 1. Classification of man-made fibers

Around 83.5 million tons of fibers were manufactured in 2012. Man-made fibers account for 67.1% of all fibers produced worldwide with synthetic fibers (a share of about 60.9%) and man-made cellulosic fibers (approx. 6.2%) (fig. 1). Fiber market is expected to grow as a result of increase in population [1].

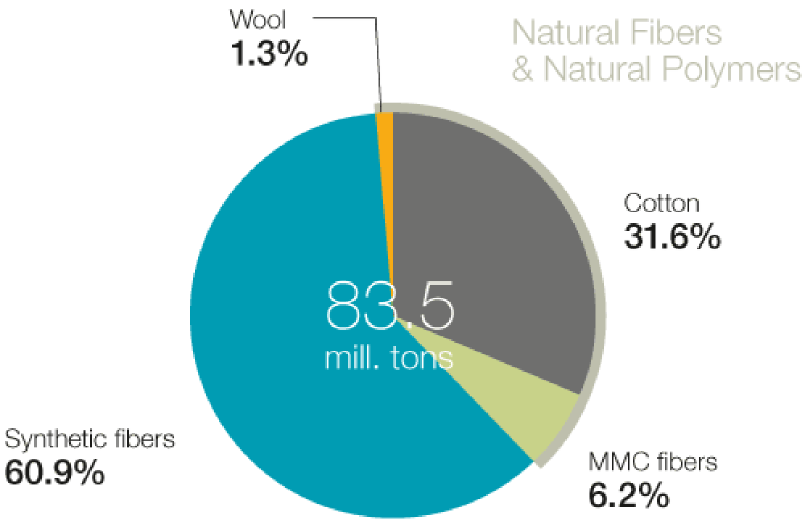


Figure 1: Global fiber market 2012.

Polyester fibers and threads have dominated in the textile raw market since 1970. As seen in the figure 2, 75% of all man-made fibers produced in 2012 were made from polyester. Percentage of other materials used in man-made fiber production such as cellulosics, polyamide, polypropylene and acrylic are 9, 7, 4 and 3 percent respectively.

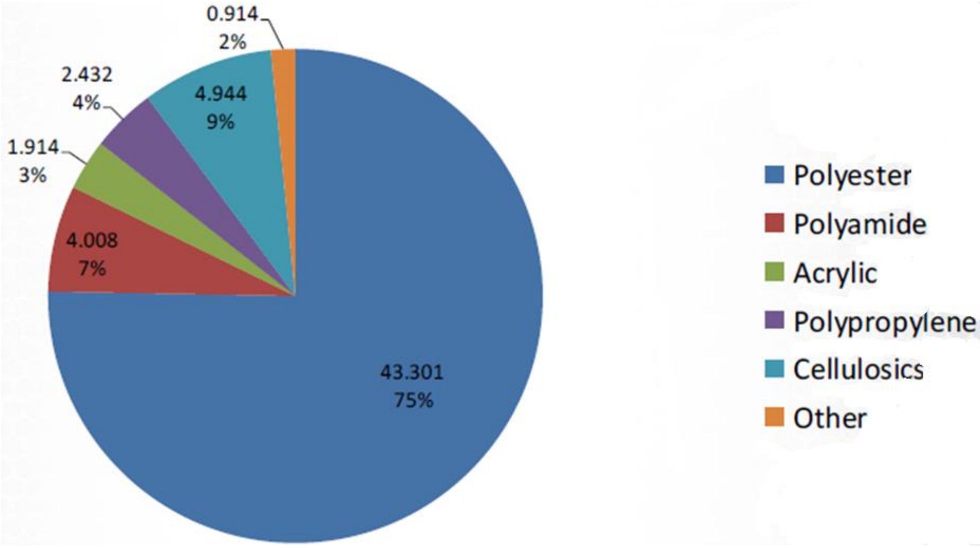


Figure 2: Man-made fiber productions by the type in 2012.

Textile industry is concerns with fiber, yarn and cloth (flexible woven, knitted, braided structures) production, dyeing and finishing, making up of clothing and household textiles, manufacture of technical textile products used in engineering, agriculture, medicine and other fields, and the distribution and retailing of textile products to personal and commercial markets. Today, clothing and textiles represent about seven per cent of world export.

1.2 Trends in made-made fiber and textile industry

It is difficult to grasp all innovations in man-made fiber and textile industry because of the size of the industry and variety of sectors. Trends and innovations described in this work were identified and classified through review of literature and materials of 52nd Dornbirn Man-made Fiber Congress held in September 2013.

Following trends are revealed:

- Sustainability
- Development of functional textile
- Development of smart textile
- Manufacturing innovations
- Materials engineering
- Unconventional applications

Environmental sustainability is now considered as one of the key drivers of innovations. Manufacturing methods are developed in accordance with environmental legislation and the share of biobased fibers is continuously increasing.

Continuing technological innovations are seen in machinery and synthetic fiber manufacturing. Improvement of fiber characteristics (tenacity etc.), decreasing production cost and environmental impact have been the major concerns in recent years. Seamless knitting, stitch-free seams, 3D weaving and 3D sewing technologies are examples of recent innovative processes.

1.2.1 Sustainability

One of the major trends in textile industry is sustainability. The textile industry is a large consumer of volatile chemicals and generator of pollutants and. The man-made fiber industry has to show that it respects the environmental in terms of:

- Raw material use
- Energy
- Emissions
- Water use
- Waste
- Employee and consumer health etc.

An increased attention has been given to involvement of bioplastics for man-made fiber production over the past years. Development of bio-based materials is seen in the following directions: bio-derived monomers for commodity polymers modified natural polymers and microbial synthesis. Renewably sourced polymers are described in the second chapter.

There is a growing trend to implementation of environmentally friendly industry processes in various fiber and textile production steps: spinning, dyeing, finishing etc.

Turning major wet textile processes into dry is one of the major concerns of industry nowadays.

Several techniques have been developed to increase sustainability of dyeing process. UV-curing enhances dyeability and can be used instead of mercerization pretreatment [2]. Spin dyeing instead of bath dyeing saves water, energy, amount of dyes. Dye pigments are added to spin-bath and then spinning dope is extruded trough a spinneret, resulting in colour inherent fibers.

Supercritical carbon dioxide has been proposed as an environmentally friendly replacement of water and organic solvents for fiber and textile finishing [3] and dyeing. Carbon dioxide is inexpensive, non-toxic, non-flammable and chemically inert. Its critical point is 7.31 MPa at 31°C. Dyeing in supercritical carbon dioxide not only reduces amount of dyes and results in no waste water with hazardous substanses but also decreases operation costs and batch time (up to 50%). To date, the coloration of synthetic fibers such as PET, PA6 and PA66 with disperse dyes in supercritical carbon dioxide is able to achieve commercial requirements. However dyeing of natural fibers is still under development due to low sulubility of polar dyes in hydrophobic supercritical carbon dioxides [4].

Turning pretreatment and finishing processes to "green" way is a big step to sustainability. Plasma, laser and ultrasound treatment, spray finishing, hotmelt coatings are examples of processes with reduced environmental impact.

Plasma technology can be explored in various areas of textile processing e.g. surface modification of fibers, removal of impurities, improvement of wettability and imparting functional finishing. Unlike conventional wet processes, which penetrate deeply into fibers, plasma only reacts with the fabric surface and doesn't affect the internal structure of the fibers [5]. Moreover, it is single step process with cleaning, activation and coating in the same system.

Spray finishing significally reduces of amount of water needed for textile finishing. Spray application makes new effects possible, for example, production of bifunctional textile with one side repellent and the absorptive (fig. 3).

Figure 3: Bifunctional textile obtained by spray finishing

The application of ultrasound power has a significant role in the concept of clean technology for textile processing. Ultrasound can improve effectiveness of a wide variety of chemical and physical processes:

- Thermal treatment (heat setting, finishing, dyeing)
- Wide range of further applications (welding and cutting, wet chemical finishing)

Ultrasound technique offers new opportunities for product design e.g. two side colouring (fig. 4).

Figure 4: Ultrasound assisted double side coloration

Thermoplastic hotmelt finishing and coating have energetic and environmental advantages as no water has to be removed by energy consuming evaporation.

Mass-production of textile led to decreasing prices and quality of garments. Thus the lifetime of the garment has shortened. The clothing industry is based on extremely fast cycles of fashion, which results in increasing amount of textile waste. The consumption of textile is not sustainable.

1.2.2 Functional textile

Functional textile is a textile with additional functionalities like

- flame resistance
- breathability
- thermo regulation
- stain resistant
- anti-microbial
- electro conductivity
- etc.

Functionalization along the textile chain can be implemented by polymer additives, spin finishes and finishing or coating of textile.

Functionalization with microcapsules has also gained popularity. Microcapsules are small capsules (1-100 µm diameters) of a polymeric membrane containing an active compound such as phase change materials, perfumes. They are used either to protect this active compound from external agents as humidity, temperature, light, and oxidation or to control its release rate.

<u>Stain repellence/Self-cleaning</u>

The structure of the textile surface has an important influence of the soiling and cleaning mechanism. One of the approaches is structuring of surfaces of fibers by using nano particles (minimising of the contact area between dirt and textile fibres). Inorganic nanoparticles made of silica (e.g. from tetraethoxysilane) and various clays have proved their effectiveness.

Titanium dioxide coatings have recently attracted attention because of their photocatalytic properties. It is reported that self-cleaning effect can be achieved by functionalization of textile substrate with TiO_2 nanosol [6].

Fire retardant

A great deal of effort has been invested in development fire retardant textile. A novel family of flame retardant polymeric coatings [7], synergistic systems [8] have been proposed.

Anti-microbial

Antibactarial textile is highly requred in medical textile and many other indoor and outdoor applications [9]. A variety of antimicrobial textile agents have been reported: organometallics, phenols, organosilicones, quaternary ammonium compounds, N-halamines, modified algae materials, silver nanoparticles and silver based compounds [10], chitosan.

Numerous studies demonstrated that TiO_2 nanoparticles immobilized onto textile materials provide desirable level of UV protection [11].

Conductive, photovoltaic and piezoelectric fibers are later described in this work.

1.2.3 Smart textile

Smart textile is textile that can sense and/or react to environmental conditions or stimuli from mechanical, thermal, chemical, electrical or magnetic sources.

There are three categories of smart fabric: passive smart fabric which refer to fabrics with a sensing function; active smart fabrics which add an actuating function and ultra-smart fabrics which include sensing, actuating and processing elements.

Types of smart textile:

- Electronic textiles
- Textile with phase change materials
- Textile with shape memory materials
- Chromatic textile
- Photovoltaic smart textile

Generations of smart textile:

- Adoption: textile as a platforms for embedded electronics devices
- Integration: electronic devices are to be seamlessly incorporated (e.g. embroidered)
- Combination: textile materials and structures with inherent electronic functionality (e.g. yarn transistor, fiber based circuits, photovoltaic fibers).

Electronic textiles

E-textiles or electronic textiles are fabrics with embedded electronic elements (fig. 5). They have a wide range of potential use: wearable electronics, medical monitoring and sensor networks [12], [13] etc. The spectrum of e-textiles ranges from common electronic devices built on textile substrate to novel components based on fibers and yarns.

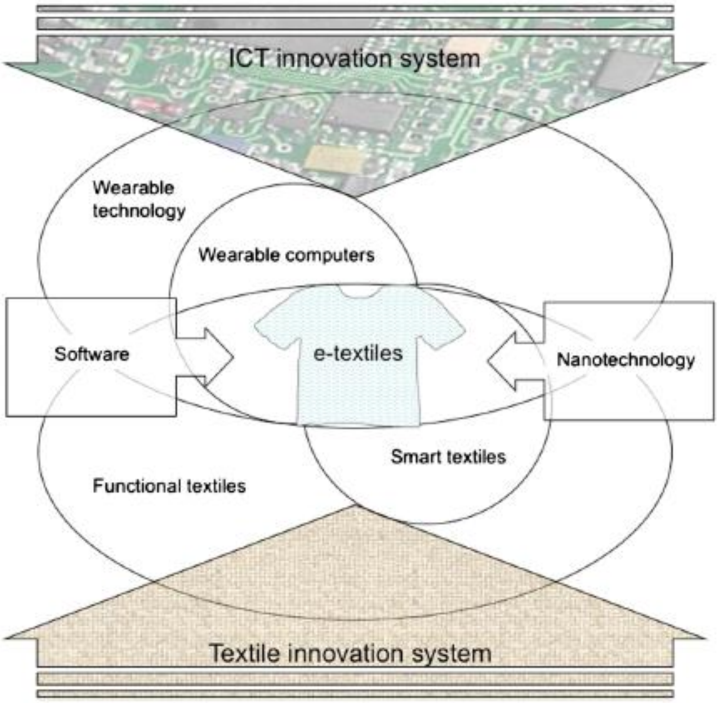


Figure 5: E-textiles in the converging innovation system of the textiles and electronics sector

Various fiber based devices have been developed: piezoelectric generators, photovoltaic solar cells, transistors. Conductive fibers are required for signal transferring in e-textile applications. Textile is a flexible, light and low cost substrate, which can be used as a platform for different electronic devices such as sensors or light emitting diodes. Example of embedded LED fabricated on the textile surface is shown in the figure 6.

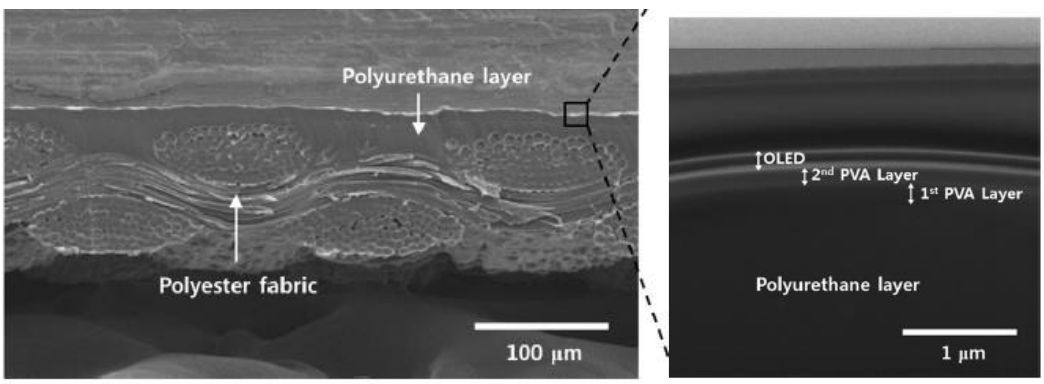


Figure 6: SEM image of the cross-section of the fabric-based OLED

Smart textile is an emerging industry and yet it is difficult to say how it will influence the environmental. Köhler describes concerning about end-of-life impact of e-textile and possible risks [14].

Textile-embedded electronic components contain small amount of scarce materials, such as silver, gold, and rare earth elements, which are scattered across large textile surface area and hard to recover [15].

1.2.4 Materials engineering

Bi-component fiber spinning has been known over the past 70 years. To date, multi-component filaments have attracted much interest [16]. Multicomponent spinning is offering opportunity of developing fibers which combine multiple functions (fig. 7). Moreover, it is an alternative way to produce fine fibers.

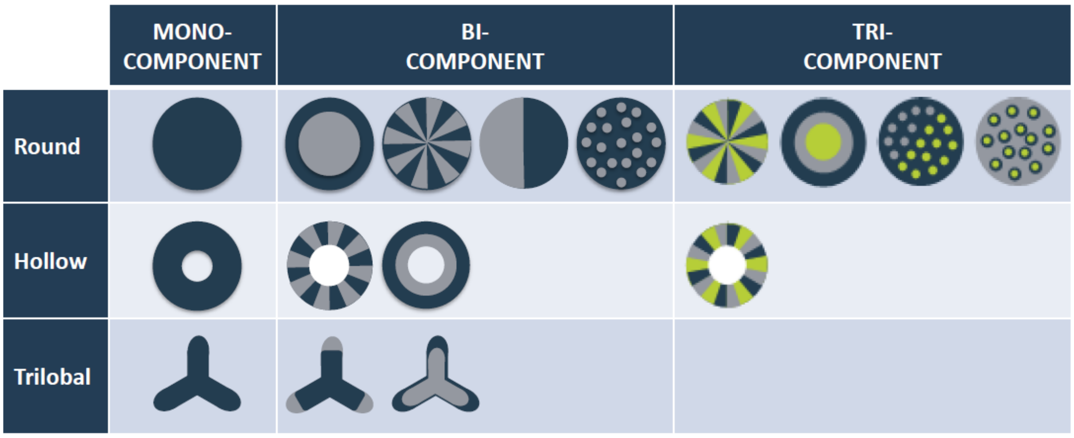


Figure 7: Cross-section geometries

Composite fibers have been extensively studied. Incorporation of nanoparticles in fiber matrix can provide remarkable morphological, thermal, mechanical or other properties. Some examples reviewed in the literature: nanocomposites of organoclay in PA6 or polypropylene [17], high density polyethylene and carbon nanotubes, electrospun nylon and TiO_2 nanoparticles [18], electrospun polyurethane and tourmaline nanoparticles [19] and so forth.

<u>3D printed textile</u>

3D printing technology can completely transform the textile industry. 3D printed product is deposited layer by layer of thermoplastic or other material. This process has no wastes, results in seamless structure and any shape can be manufactured. There are already prototypes of 3D printed fabric and garments in the market (fig. 8).

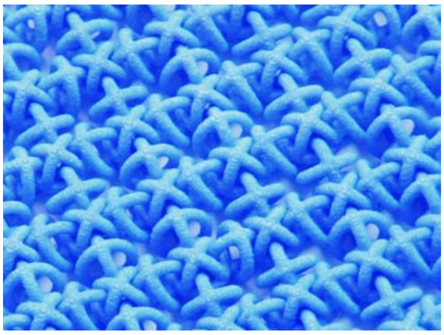


Figure 8: Example of 3D printed textile

1.2.5 Unconventional applications

Counterfeiting

Viscous fibers with embedded UV active particle create a high security feature against counterfeiting (fig.9).

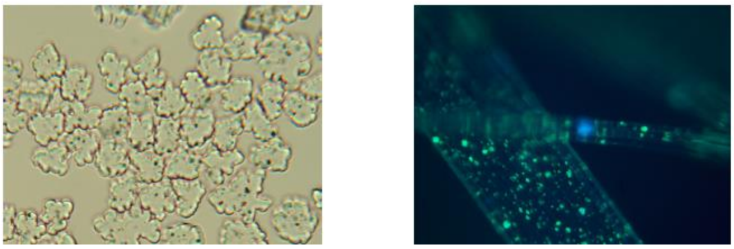


Figure 9: Counterfeiting fibers by Kelheim

Tiles

Novel application of carbon fiber reinforced composite for parquet application was proposed. Carbon parquet combines the natural wood look with the advantages of the robust composite (fig. 10).

Figure 10: Carbon parquet

Additional functionalities can be added to parquet structure: touch sensor, heating, lighting.

2 Bioplastic materials for man-made fibers

Scarcity of oil resources stimulates growing demand for renewable polymer products. Renewable and biodegradable materials are especially needed in textile industry where consumption is growing every year due to population growth.

Bioplastics are plastics derived from renewable biomass sources, which are abundant in nature. Man-made fibers can be produced from various polysaccharides: cellulose, starch, chitin and others or from protein sources such as silk, collagen, soy, casein.

There are three strategies of synthetic bio-based fibers production: modification of natural polymers, synthesising by microbial systems and synthesizing polymers from bio-based monomers.

Up to now, biopolymers contribute only to less than 1% of today's plastic production [20], but the bioplastics market is rapidly growing and increases by 30% every year [21]. The most dynamic development is foreseen for biopolymers, which are chemically identical to their petrochemical counterparts but at least partially derived from biomass.

"New generation" medical textile requires biomaterials with bioactive properties. Natural polymers such as proteins, silk fibroin [22] and polysaccharides have received growing interest in biomedical research as materials for wound dressing, scaffolds and tissue engineering. There are different strategies to produce bio-active fiber-based structures: direct spinning of natural bioactive polymer solution into fibers, coatings of conventional fibers or textiles with biopolymers [23], incorporation of bioactive molecules into the dope to be spun.

Bioplastics nonwovens have many potential applications in geotextile and filters production. Bioplastic fibers as well as bioplastic polymer matrixes have attracted attention in composites construction. When natural fibers and biopolymer matrix are mixed together, each component originates from renewable resources and such biocomposites may be compostable, making them attractive alternatives to glass-fiber-reinforced petrochemical polymers. Besides biodegradation, biodegradation, recycling of biocomposites makes them more interesting, extending their life cycle and reducing the global impact on the environment by lowering consumption of raw materials and saving carbon for a longer time. However, natural fibers (e.g. cellulose) have high hydroxyl content which makes them susceptible to water absorption and can affect the composite mechanical properties. Hence, surface modification is required.

Complete shifting from chemical raw material production to renewable resources is challenging. Land is required not only for growing biomass for biopolymers, but also for food and biofuel production. Intensified farming and deforestation can cause greenhouse effect worsening. Utilization of agricultural and forestry wastes as a feedstocks for bioplastics production was proposed.

Another alternative feedstock is carbon dioxide has recently attracted much attention. For example, polycarbonate can be produced by alternating copolymerization of carbon dioxide and epoxide.

Biodegradability is the ability of a substance to be broken down by bacteria so it can be returned to the environment without posing an environmental hazard. Term biobased doesn't mean that the plastic is biodegradable. Biodegradability of the plastics depends on the chemical structure and not on the source. For example, petroleum-based polymers such as PBAT (polybutyrate adipate terephthalate) and PCL (polycaprolactone) are biodegradable.

Utilization of renewable feedstock does not guarantee that a plastic is environmentally friendly over its entire life cycle. The sustainability benefits of using renewable feedstock may not be sufficient if the material cannot be recycled. Environmental impacts associated with the creation, use and disposal of biopolymers remains unclear.

The increased use of bioplastics and biocomposites may have serious implications for the recycled plastic industry in the near future, because of required separation of different kinds of plastic and development of recycling lines for new materials.

2.1 Modified natural polymers

2.1.1 Cellulose

Cellulose is an abundant and ubiquitous polysaccharide. It is the major structural component of plant cells and is found throughout nature. Structure of cellulose is shown on the figure 11. It consists of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units.

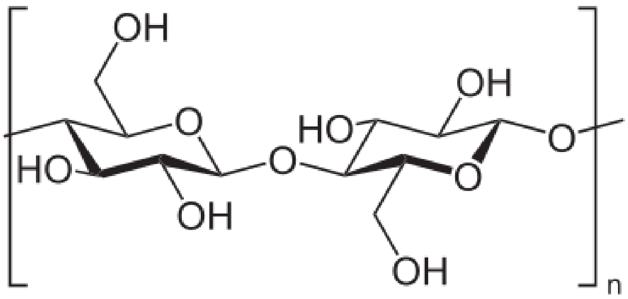


Figure 11: Structure of cellulose

Cellulose for synthetics fibers production is used in two forms: regenerated cellulose (known as rayon or viscose) and cellulose esters (acetate fiber). Viscose, the first man-made fiber, was introduced in 1894. Up to now, regenerated cellulose and acetate fibers have been extensively produced and have plenty of applications.

Recent advances in this field are addition to fibers functional additives and development of fibers with different cross-sections.

Cellulose is mostly produces from wood and cotton. Utilisation of agricultural byproducts from corn, wheat, rice, soy bean and sugar cane is proposed as a feedstock [24].

2.1.2 Starch plastics

Starch is a widely used bioplastic. This polysaccharide consists of two types of molecules: amylose and amylopectin. Starch polymers are present in large amounts in corn, potatoes, rice, barley, wheat and other plants. For example, 50-100 kg of starch can be obtained from one sugar palm tree.

Starch softening temperature is higher than its degradation temperature due to presents of many intermolecular hydrogen bonds. Plasticizers are used to reduce glass transition temperature. Starch can be electrospun in an propriate solvent [25]

Termoplastic starch (TPS) has lower mositure an temperature resistance. In order to decrease water solubility starch biopolymer is copolymerised with other polymers. TPS is biodegradable.

2.1.3 Regenerated proteins

Silks are natural fibers composed of proteins, which are polymers with 20 different possible amino acid monomers. Natural protein fibers have been in use for centuries.

Silk is poduced by many insects and consist of two proteins: fibroin and sericin. Production of regenerated silk fibers starts from production of the silk fibroin soluion that is regenerated and purified from natural silk cocoons. Fibroin exhibit good mechanical properties and processability and its fiber can be obtained by wet-spinning or electrospining. Regenerated silk fibers are mainly used in medical application.

The potential applications of silk fibroin in electrinics, photonics and optoelectronics are described in [26]. Silk fibroin is highly transparent (>90%) across the visible region of the spectrum, which together with it's robustness, biocompatibilty and biodegradability make it suitable for biophotonic devices. Silk optical waveguide was fabricated by printing fibroin wolution (fig. 12) [27].

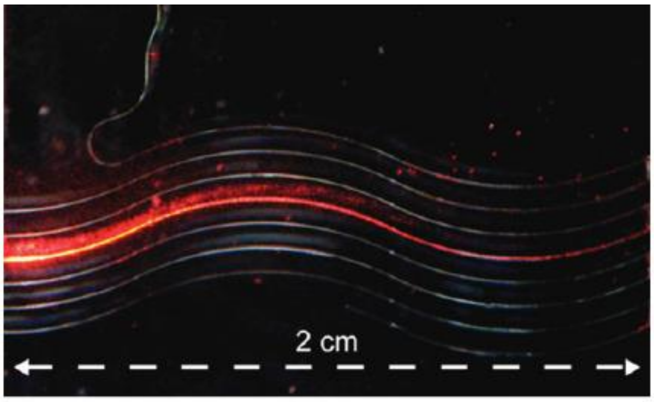


Figure 12: Optical image of wavy silk fibroin waveguide gaining light from He:Ne laser source

Milk fiber obtained from regenerated casein protein from wastes of milk production was recently introduced to the market. It has good physical and chemical properties, dyeability and moisture management.

Many other protein sources are found in nature, which can be used for bioplastic production: soy, peanut, corn and others.

2.1.4 Chitosan

Chitosan is a polysaccharide and a straight-chain copolymer composed of D-glucosamine and N-acetyl-D-glucosamine. Chitosan is produced commercially by N-deacetylation of chitin (fig. 13) from the shells of shrimp and other sea crustaceans [28].

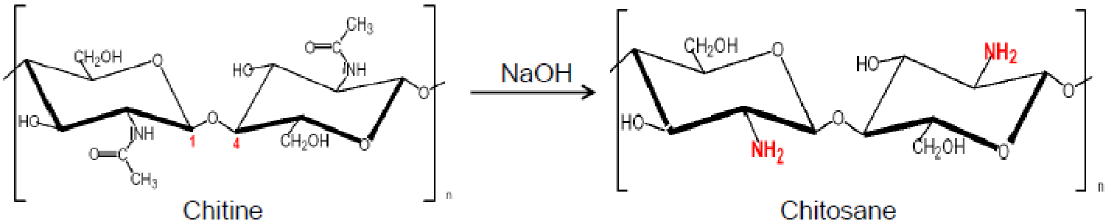


Figure 13: N-deacetylation of chitin

Chitosan fibers are produced by wet, pseudo-dry, gel and dry-jet spinning through coagulation of aqueous chitosan solutions in alkali media. Chitosan fibers obtained by these methods have low tenacity value of around 2 g/denier, which result to some difficulties in post operations such as weaving or knitting.

M. Desorme et al. demonstrated that chitosan fibers spun through hydroalcoholic solutions show improved mechanical properties [29].

Electrospinning of chitosan is performed with tetrahydrofuran (THF) and acetic acid solvents [30].

Chitosan has intrinsic antimicrobial activity and thus is used for permanent antimicrobial finish of textiles [31]. Excellent biocompatibility of chitosan with cells, biocompatibility and biodegradability makes it promising material for tissue engineering.

2.2 Polymers synthesised from biobased monomers

The use of bioderived monomers for polymers synthesis is gaining popolarity. “Green monomers” make synthetic polymers renewable without impairing their properties.

Fermintation of glucose can be used to produce a great variety of bio-based monomers. Starting from glucose and plant oils, it is possible to obtai various essential monomers. Figure 14 shows the most important pathways from biomass to building blocks to polymers [32].

For example, bio-polyethylene synthesis consists of the following steps: first, ethanol is produced by fermentation of glucose; then ethylene is obtained via ethanol dehydration and finally, PE is polymerized.

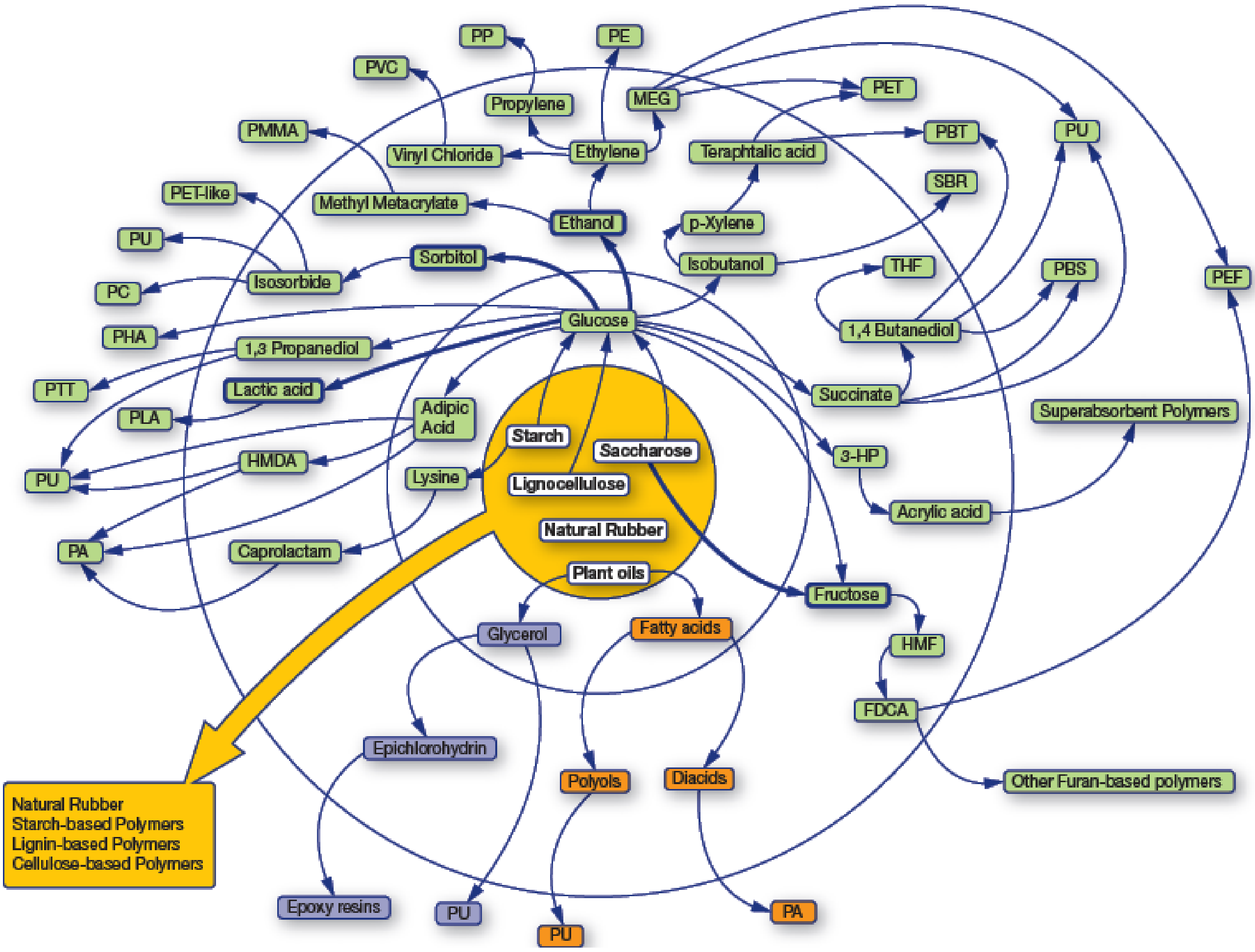


Figure 14: From biomass to biopolymers

As illustrated in figure 15, novel families of 100% bio-based plastics can be derieved from citrus fruits and carbon dioxide. Extraction of orange peels is an industrial process for producing limonene oils, which are then oxidized to form to form mono- as well as difunctionam epoxides. Subsequent catalytic copolymerization of limonene monoxide with carbon dioxide affords thermoplastic polylimonene carbonates with properties resembling those of polystyrene. Limonene-based polyesters were prepared by copolymerization of limonene monoxide with dicarboxylic acid adhydrides such as succinic anhydride. Novel limonene dicarbonates, produced from limonene dioxide, enable chemical fixation of 34 wt% carbon dioxide. They were cured with polyfunctionam amines, such as citric aminoqmides, to produce a wide variaty ofcrisslinked terpene-based green polyurethanes without requiring the use of isocyanates. Because it uses wastes from orange juice oroduction, the production of limonene-based polymers does not interfere with food production.

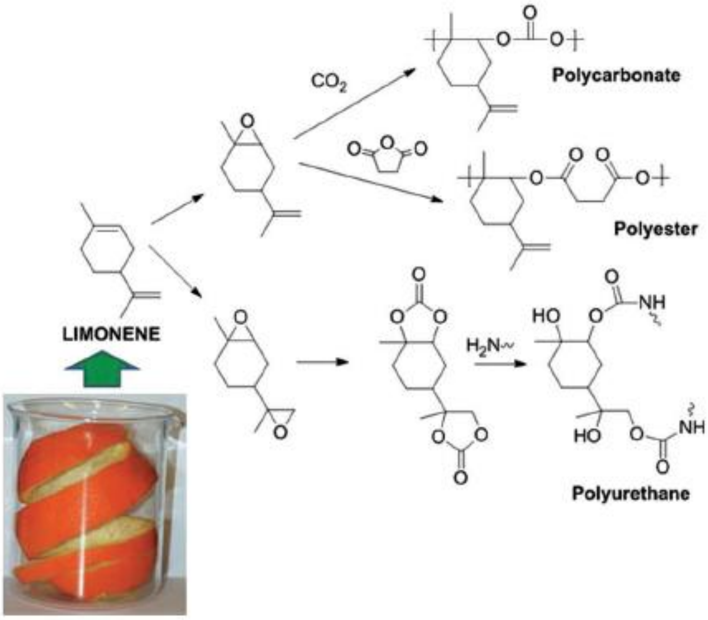


Figure 15: Bio-based polymers derived from orange peel

Further step in this field is exploring new feedstocks from which biomnomers can be synthesized such as byproducts and waste materials.

2.2.1 Biobased polyesters

Polylactic acid

Polylactic acid or polylactide (PLA) is one of the most widely used bioplastics. PLA (fig. 16) is based on lactic acid, a natural acid, which is mainly produced by fermentation of sugar or starch with the help of microorganisms.

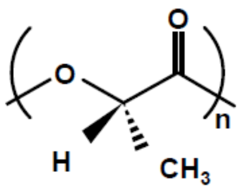


Figure 16: Chemical structure of PLA

PLA is obtained either by ring opening polymerization of lactide or by direct polycondensation of lactic acid. The monomer lactic acid is a chiral molecule and exists as D- and L- lactid acid. Steriochemistry controls the physico-chemical and mechanical properties of PLA. As a function of the stereoisomer composition, PLA can be amorphous or crystalline, melting at temperatures up to 185°C.

PLA is amorphous polymer with low impact resistance and low thermal stability, whereas PLLA (poly-L-lactid acid) is semi-crystalline and shows a high mcganical strength. Blending PLA with other polymers improves its mechanical properties.

There are asome attempts to improve properties of PLA fibers through incorporation of additieves [34].

PLA is one of the most studied bioplastic regardung recyclability. PLA is biodegradible at the presence of oxigen and moisture.

Study on the reprocessing of PLA (containing 92% L-lactide and 8% D-lactide) showed that only the tensile modulus remains constant with thermomecanical cycles up to seven injection mouldings while other mechanical properties such as hardness and modulus decrease. The viscosity of PLA decreases greatly after only one injection cycle [35]. The degradation of PLA is attributed to chain scission during processing.

Two main processes have been used for chemical recycling of PLA. The first one is hydrolysis of PLA at high temperatures to obtain lactic acid, and the second one is thermal degradation of PLA to prepare L,L-lactide, which is a cyclic dimer and can be used for polymerisation of new PLA.

Industry is concerned about the potential contamination of the PET recycling stream by PLA products. It is believed that PLA at even low contents can act as contamination and seriously affect the properties of the recycled PET. Life cycle assessment (LCA) of PLA is given in [36].

Nature Work LLC is the world’s largest producer of PLA under Ingeo trademarked brand name [37].

Sorona (PTT)

Sorona is brand name of bio-based polyesters produced by DuPond.

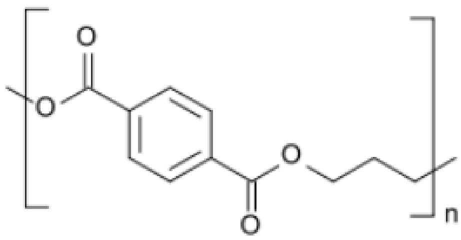


Figure 17: Chemical structure of Sorona

Sorona (fig. 17), poly(trimethylene terephthalate), is a co-polymer of 1,3-propanediol (obtained by fermentation) and petroleum-derived terephthalic acid (TPA) or dimethyl terephthalate (DMT) [38]. This biopolymer is used for textile production and is claimed to be durable and stain resisrant.

2.2.2 Biobased polyamides

Rennovia has developed a 100% bio-nylon-6,6 (PA 6,6) produced from bio-based hexamethylenediamine (HMD) and adipic acid. Both HMD and adipic acid are sinthesised from glucose.

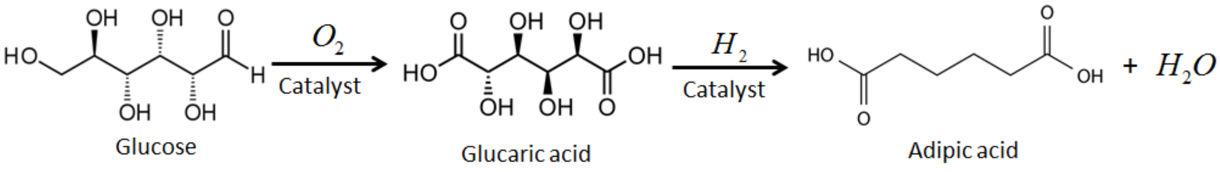


Figure 18: Production scheme of Adipic acid

Synthesis of Adipic acid composes of two heterogeneous catalyst process steps: aerobic oxidation of glucose to glucaric acid and hydrodeoxygenation of glucaric acid to adipic acid (fig. 18).

Hexamethylenediamine (HMD) is obtained by hydrodeoxygenation of glucose to key intermediate and subsequent amination of it (fig. 19).

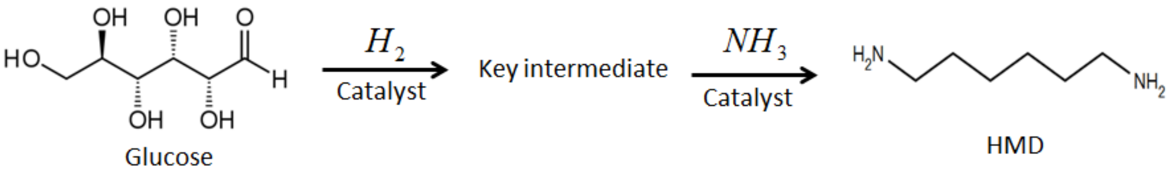


Figure 19: Production scheme of HMD

RadiciGroup is offering a polyamide 6,10 *(RADIPOL® DC)* made with 64% renewable source material. This polymer is produced by polycondensation of bio-derived sebacic acid (1,10-decanedioic acid) and oil-derived hexamethylenediamine.

Sebacic acid is a substance of biological origin obtained from castor oil plant (Ricinus communis) seeds. The plant is cultivated in arid areas and it does not compete with agricultural products for human consumption. Castor cultivation is concentrated in India, China and Brazil.

2.3 Polymers produced by microbial systems

Today not only fibers, but also raw materials for their production can be synthetically made. With the advent of genetic engineering, technology has reached a stage where sustainable biomaterials can be synthesised by the use of genetically modified microorganisms rather than by use of plant resources or oil (fig. 20).

Biopolymer properties can be adjusting from the very beginning by modification of biosynthesis process such as fermentation conditions, nutrition media and even genetic modification of microorganism. Producing sustainable raw materials equipped with new functionalities is already within reach.

Figure 20: Schematic representation of fiber production from biosynthesised materials

In recent years, considerable attention has been given to biopolymers produced by microbes: various proteins, bacterial cellulose, PHAs and many others.

Hohenstein [39] in collaboration with others developed biotech alginate and chitosan fibers, which have constant quality (controlled monomer sequence, no heavy metals, no endotoxins). They produced chitosan from zygomycetes. Those organisms can be grown in sustainable way on waste products from food production and directly produce a high chitosan –not chitin-content in their cell.

2.3.1 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are the family of thermoplastic biopolyesters which are totally synthesized by microorganisms such as Cupriavidus metallidurans bacteria under conditions with limited essential growth components (N, Mg, S, K, O_2) (fig. 21). Composition and properties of PHA depend on carbon sources (starting materials). Around 150 bilding blocks of PHA are already described and synthesized. Bacteria are able to produce copolymers and thus turn properties of obtained bioplastics. PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) is a copolymer of PHB (polyhydroxybutyrate) and PHV (polyhydroxyvalerate) has better mechanical properties and lower melting temperature in comparison with PHB.

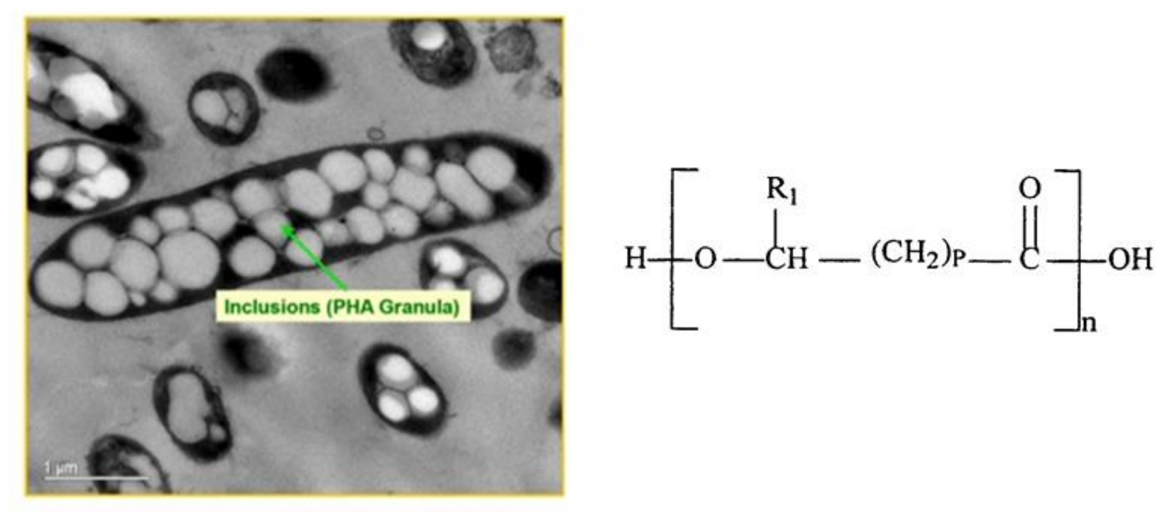


Figure 21: PHA granules inside bacteria and general chemical structure of PHA

Carbon sources that are used as bacteria nutrition media: glucose, fructose, sucrose, plant oils, waste materials like whey lactose and water sludge. PHA is biodegradable and it is claimed that it can be mechanically recycled without sufficient loss of molecular weight and mechanical properties.

Up to now, production cost of PHA is higher than that of petrochemical polymers. Another obstacle that limits application of PHAs is use of toxic solvents while extraction of biopolymer from the cells.

2.3.2 Protein-based plastics

It is proved that all natural silks are chains of iterated peptide motifs and the composition and length of repeated units define mechanical properties of the fibers. The sequences of amino acids of silkworm silk and spider silk have been extensively studied. By knowing those fibers with a diverse range of properties can be designed.

Spiders can produce silk proteins with a tensile strength similar to Kevlar (table 2) and very high degree of elasticity.

Material	Strength, $\frac{N}{m^2}$	Elasticity, %	Energy to break, $\frac{J}{kg}$
Dragline silk (major ampullate)	4×10^9	35	1×10^5
Flagelliform silk	1×10^9	>200	1×10^5
Minor ampullate	1×10^9	5	3×10^4
Kevlar	4×10^9	5	3×10^4
Rubber	1×10^6	600	8×10^4
Tendon	1×10^9	5	5×10^3
Nylon, type 6	7×10^7	200	6×10^4

Table 2: Comparison of mechanical properties of spider silk with other materials

By using genetic engineering, proteins with defined strength and elasticity can be designed. After the construction of the synthetic silk genes, they are expressed into a suitable production organism: bacteria, yeast or others.

Several research groups are working on development of artificial spider silk. The Japanese company named Spiber announced the opening of the pilot plant by the 2015 [40].

Recently novel silk-like protein called aneroin was generated from sea anemone and its fibers were successfully produced by both electrospinning and wet-spinning [41].

2.3.3 Bacterial cellulose

Bacterial cellulose is produced by some spices of bacteria such as Acetobacter, Sarcina ventriculi and Agro bacterium. The properties of bacterial cellulose differ from the conventional. It has high crystallinity, high degree of polymerization and high wet tensile strength.

Carbon sources utilized in fermentation process for bacteria cellulose production include monosaccharides (such as glucose and fructose), disaccharides (such as sucrose and maltose), and alcohols (such as ethanol, glycerol, and mannitol).

It is proved that textile waste of cotton and regenerated cellulose fabric can be used as a feedstock for bacteria cellulose synthesis. This innovative strategy can save natural resources and reduce the cost of the cellulose production [42].

3 Piezoelectric fibers

Piezoelectric effect is the ability of some materials to generate a voltage when a mechanical stress is applied to them. If pressure is applied, a voltage is induced across the material (direct piezoelectric effect). The effect is reversible, so if a voltage is applied, mechanical change will happen (reverse piezoelectric effect), e.g. a change in the shape.

Piezoelectricity was discovered in 1880 in crystals of tourmaline, quartz, topaz and Rochelle salt. Since then the list of piezoelectric materials was supplemented with many natural and synthetic materials and they have found numerous applications: microphones, frequency standards, power sources, sensors, ignition systems and others.

The materials that exhibit a significant and useful piezoelectric effect are divided in three groups:

- Minerals and synthetic crystals (quartz, Rochelle salt, topaz, berlinite etc.)
- Organic materials (collagen, silk, wood, dentin, PVDF etc.)
- Ceramics (lead zirconate titanate, barium titanate etc.)

One common feature of all piezoelectrics is occurrence of dipole moment either in crystalline materials without the center of symmetry or in organic materials with special orientation of molecular groups.

To date, research on piezoelectric fibers is mainly based on lead zirconate titanate (PZT), ZnO nanowires and polyvinylidene fluoride (PVDF).

Piezoelectric properties are dependent on the size of the material and may change significantly [43]. It is found that electrospun PVDF fibers have larger (about twice) piezoelectric coefficient d_{33} than that of PVDF thin films due to fewer defect and smaller domain wall motion barrier in PVDF. Another example of the effect of geometrical shape is 0.3 PZN-0.7PZT metal core piezoelectric fibers that have inferior piezoelectric properties than bulk ceramic fibers of the same material [44].

Piezoelectric fibers have some advantages over conventional monolithic wafer. They are lightweight, more flexible, can conform curved or irregularly shaped surfaces and withstand large deflections. In addition, the surface area offered by piezoelectric fibers is greater than that offered by a film, improvement in piezoelectric performance

3.1 Piezoelectric ceramic fibers

Piezoelectric ceramics are polycrystalline ferroelectric materials with a perovskite crystal-type structure. Ferroelectrics have spontaneous electric polarization below a certain phase transition temperature called the Curie temperature.

Above the Curie temperature the ceramic crystallites have a simple cubic symmetry, below –tetragonal symmetry, which has luck of symmetry and thus dipolar moment (fig. 22). Piezoelectric ceramics have the general formula of $A^{2+}B^{4+}O_3^{2-}$. The letter A represents a large divalent metal ion such as barium or lead, and B is one or more tetravalent metal ion such as titanium or zirconium or manganese.

Each crystallite has own domains orientation which results in weak net polarisation of the whole material. The piezoelectric properties of the ceramics can be enhanced by applying a large electric field at an elevated temperature. This technique results in alignment of dipoles and is called poling.

PZT is a solid solution of lead zirconate $PbZrO_3$ and lead titanate $PbTiO_3$ and it has outstanding piezoelectricity. An electric polarization of PZT can shift up/down of Zr/Ti atom and remain their positions after applying and removing an external electric field for the piezoelectric property.

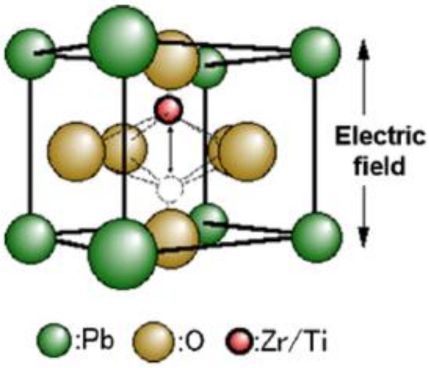


Figure 22: Schematic diagram showing crystalline structure of PZT

Ceramics are brittle materials, but the polymer coating improves the mechanical properties of rigid ceramic fibers and makes them more suitable for textile integration. Hollow PZT fibers with protective polymer cladding proved good flexibility and are suitable for fabric integration (fig. 23). Application of PZT in the form factor of nano wires also makes it more strength.

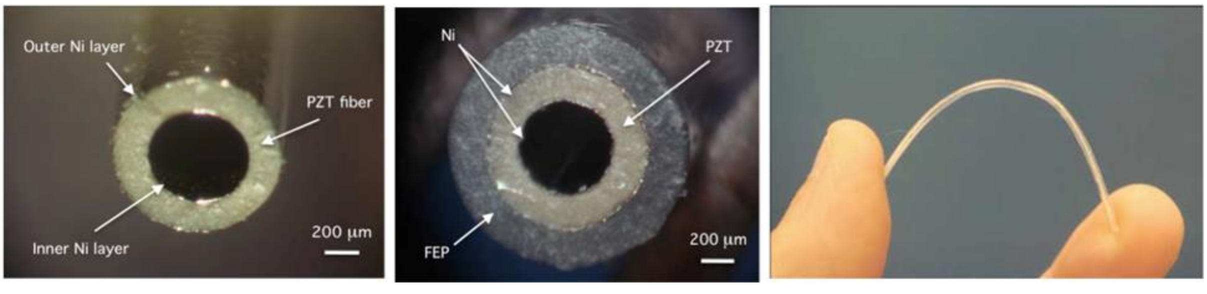


Figure 23: Hollow PZT fiber without and with polymer coating

Several methods of PZT fibers production are reported in the literature. One of them is electrospinning of a sol-gel based solution and subsequent sintering. However, excess of solvent can lower the density of the PZT, which decreases overall energy conversion efficiency. Other methods include template synthesis and magnetron sputtering.

3.2 Piezoelectric polymer fibers

Although piezoelectric polymers experience weaker piezoelectric effect than piezoelectric ceramics, polymer based piezoelectrics offer more flexibility in design and processing. Moreover, due to their flexibility, piezoelectric polymers are not susceptible to fatigue crack when subjected to high frequency cyclic loading like piezoceramics.

PVDF is well known piezoelectric polymer and it used in many applications. This semicrystalline polymer can be found in different phases depending on chain conformations. PVDF is a thermoplastic fluoropolymer with low melting temperature of around 177°C. Curie transition temperature of PVDF is 170 °C.

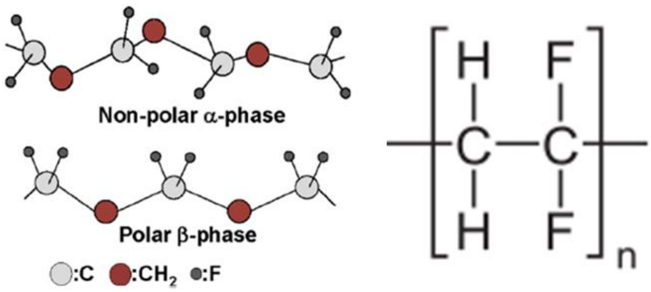


Figure 24: Chemical structure of PVDF and its α and β phases.

PVDF is usually found in non-polar α phase (fig. 24) with random orientation of dipole moments, because this phase is more energetically favourable. The β phase shows the highest polarity of all crystal forms due to it polar structure with oriented CF_2 groups.

The phase of the processed material depends on the condition of the crystallization. Application of electric field and/or careful optimization of the process parameters such as polymer flow rates and drawing ratios allow alignment of the polymer chains and conversion of the α crystal phase to the β piezoelectric crystal phase.

It is reported that addition of multi-wall carbon nanotubes reinforce PVDF fibers and facilitate the growth of the β-phase thus improving piezoelectric properties [46].

Inclusion of $BaTiO_3$ ceramic nanoparticles of different size (10, 100, 500 nm) to PVDF doesn't have piezoelectric contribution to final composite response [47].

Several techniques of fabrication PVDF fibers and optimization of their piezoelectric properties have been described in the literature.

K. Magniez et al. obtained PVDF fibers containing a high piezoelectric β-phase content of up to 80% by melt spinning and consequent drawing at 120 °C between 25 and 75% of their original length [48].

Bicomponent melt spinning allows simultaneous integration of the inner electrode. Lund et al. produced melt-spun piezoelectric Bicomponent fiber with PVDF sheath and carbon black/HDPE composite core [49].

Efficient orientation of dipole moments in PVDF is achieved by poling. The poling technique can be held in two modes: contact and non-contact (so called corona poling (fig. 25). Poling conditions such as time, temperature and voltage influence the piezoelectric properties of the fibers. Studies show that typical electric field strengths required for permanent polarization are in the range 50-300 MV/m [50]. Heating the polymer increase the mobility of molecular chains. The results show that high piezoelectric effect is achieved when the poling voltage is high as possible and the poling temperature is between 60 and 120.

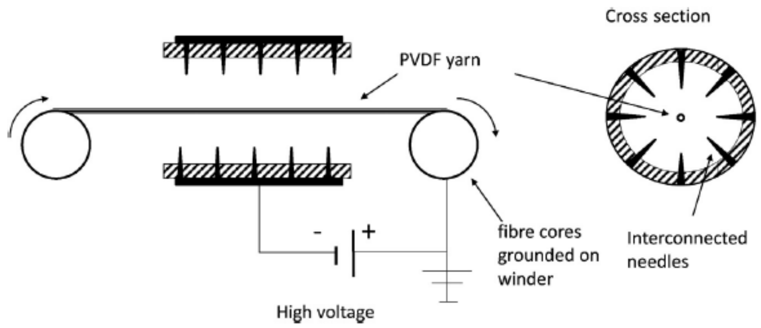


Figure 25: Equipment for corona poling

Continuous process which combines melt extrusion, drawing and poling has been demonstrated for production of PVDF fibers (fig. 26) [51].

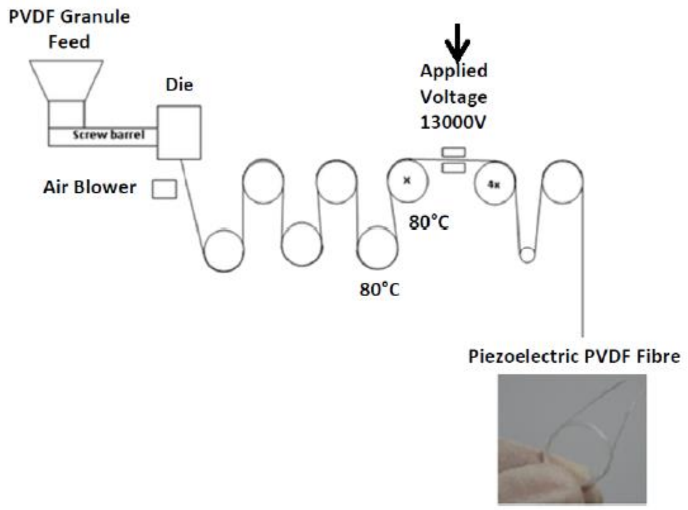


Figure 26: The continuous process of making piezoelectric PVDF fibers using a custom melt extruder and high voltage power supply

This innovative strategy together with availability of inexpensive PVDF makes possible large scale production of energy harvesting devices.

The use of electrospinning in piezoelectric fiber production has gained popularity. Electrospinning is a process for producing nano fibers by forcing viscous solution through a spinneret subjected to an electric field (fig. 27).

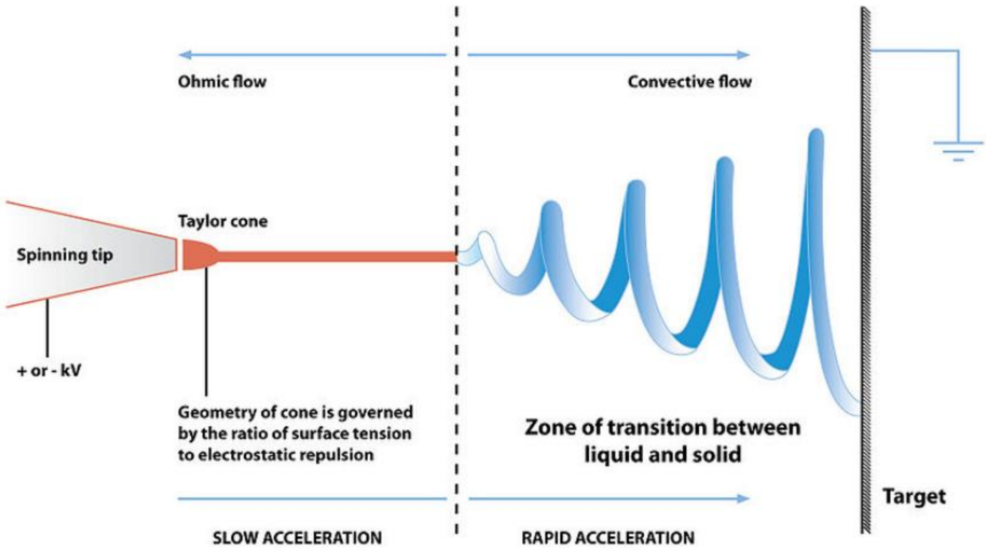


Figure 27: The diagram of the electrospinning process

High electric field during the electrospinning process aligns the dipole moments and cause piezoelectric effect of the electrospun fibers. The morphology and polarization intensity of piezoelectric fiber can be controlled by adjusting the travelling velocity , DC-voltage, and the gap between the needle and collection plate.

Conventional electrospinning process results in formation of non-woven fiber mat. Near-field electrospinning (NFES) is more controllable process. This method reduces the electrode-to-collector distance, which is typically on the order of 10 cm in the conventional electrospinning process, to less than 1 mm. In addition, NFES only needs a small electric field to produce continuous fibers with fine diameters.

Figure 28 illustrate the schematic diagram of the process of NFES with in situ electrical poling and a SEM image of PVDF fiber obtained [52].

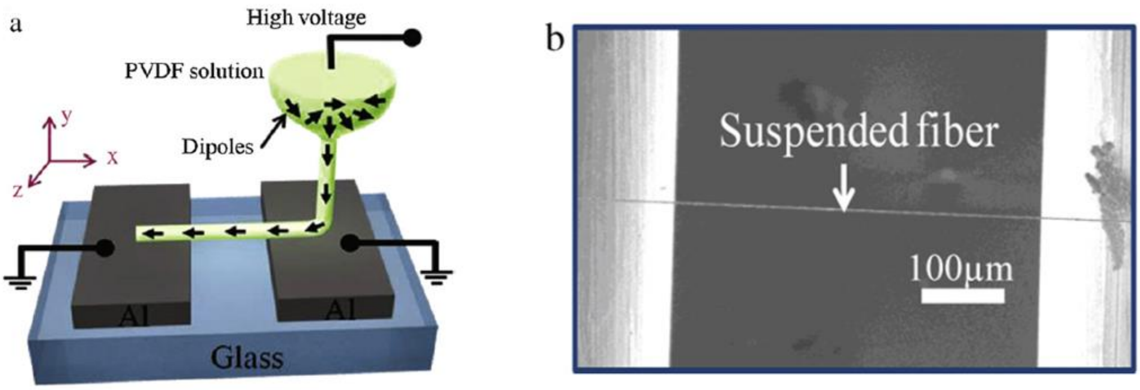


Figure 28: a) Schematic diagram of the electrospinning process with in situ poling
b) SEM image of a suspended PVDF fiber with diameter of 2.6 μm and length of 500 μm

M. Lee et al. manufactured hybrid piezoelectric fibers composed of two piezoelectric materials - zinc oxide nanowires and PVDF polymer [53]. Zinc oxide nanowires not only enhance the adhesion of PVDF polymer but also affect piezoelectric properties of PVDF while poling process.

Producing of piezoelectric fibers by thermal drawing from preform simultaneously combining a multiplicity of solid materials in single fiber trough simple and scalable process has some difficulties. The requirements that make production of multimaterial fibers challenging:

- All materials must flow at a common temperature
- All materials should exhibit good adhesion/wetting in the viscous and solid states without cracking.

The latest advances in this field have led to the development of P(VDF-TrFE) based piezoelectric fiber with carbon-loaded poly carbonate/ indium electrodes and polycarbonate cladding [54]. Cross-section of this fiber along with other piezoelectric fiber structures found in the literature is given in the appendix A.

Vinylidene fluoride-trifluoroethylene (VDF-TrFE) is another polymer with piezoelectric properties, which crystallizes spontaneously into its piezoelectric β-phase. However, PVDF-TrFE fibers are not applicable in large scale for two reasons: the low production rate and high price of the material.

There are a limited publications about piezoelectric fibers synthesised from biopolymers, although many of them exhibit piezoelectricity: proteins, polynucleotides, polysaccharides and poly(glutamate)s [55].

3.3 Piezoelectric ZnO nanowires

The origin of the piezoelectricity of ZnO is due to non-symmetrical crystalline structures of its two possible hexagonal and zincblende polymorphs, in which the oxygen and zinc atoms are tetrahedrally bonded (fig. 29).

ZnO exhibit both piezoelectric and conductive properties that can form the basis for electromechanically coupled sensors and transducers. Moreover, ZnO nanowires have excellent mechanical properties and are more sensitive to small mechanical agitation.

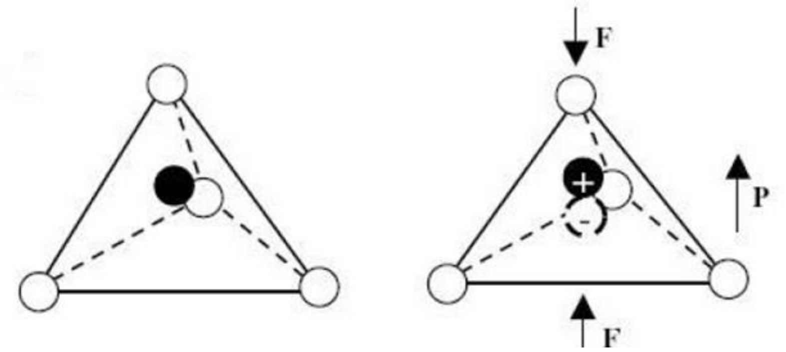


Figure 29: Schematic drawing of the piezoelectric effect of the ZnO

ZnO nanowires are grown by chemical vapour deposition or by electrodeposition mechanism on the metallic fibers in order to obtain piezoelectric fibers.

3.4 Piezoelectric fiber composites

Piezoelectric fiber composites (PFC) consist of piezoelectric fibers embedded in polymer matrix. Compared to traditional piezoelectric ceramic bulky devices PFC composed of piezoceramic fiber, polymer matrix and integrated electrodes is characterized by robustness, flexibility and high actuation energy densities [57]. Piezoelectric fiber composites can be moulded to different geometries and integration in glass or carbon fiber reinforced composites [58].

However, PFCs have limited temperature operating range, which is defined by melting temperature of polymer matrix. Both composites with ceramic and polymeric piezoelectric fibers have been demonstrated.

3.5 Applications of piezoelectric fibers

Piezoelectric fibers have a fascinating application in generators, harvesting energy from environmental (vibrations, human motion, wind etc.) and transferring it to electrical energy. A lot of electrical energy can be obtained by integration of fibers into sails, floors and many other structures.

Wearable generators can be produced by combination of flexible piezoelectric fibers with conventional fibers and conductive electrodes within the textile weave [59]. Piezoelectric fabric can power portable electronic devices instead of bulky and short lifetime batteries. Generators with fibers, nano fibers, and non-woven structures are reported in the literature [60].

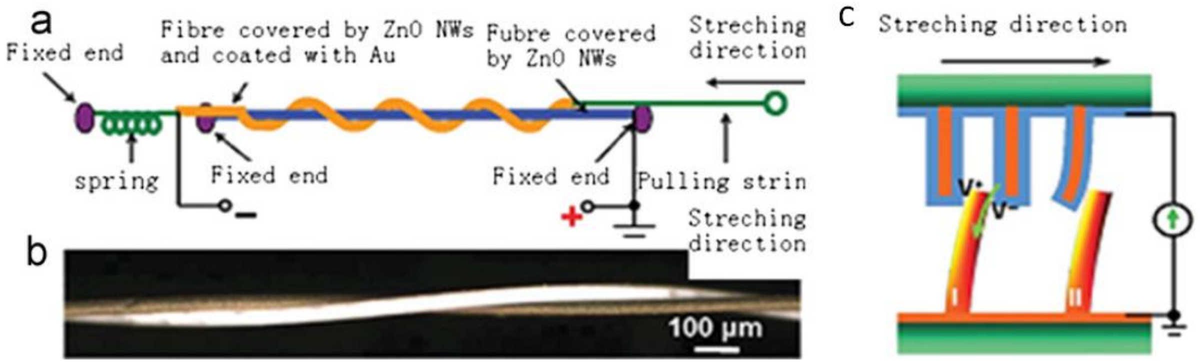


Figure 30: Design and electricity-generating mechanism of the fiber-based nanogenerator driven by a low-frequency, external pulling force

A novel approach for fiber-based piezogenerators was proposed [61]. Device is composed of two entangled fibers covered with zinc oxide nanowires (fig. 30). One of the fibers is covered with metallic layer and collect piezo-generating voltage when fibers are pulled relative to each other.

Broad range of applications of piezoelectric fibers and composites also includes sensors, actuators and transducers.

Various kinds of sensors can be performed on the basis of piezoelectric fibers and PFC, because of their sensitivity to vibrations, sound, acceleration [62].

Two different structures of force sensors are possible. Figure 31 shows fiber composite sensor, which incorporate solid-core PZT fibers with diameter of 250µm inside a passive polymer matrix with integrated electrodes [63]. This device structure combines the mechanical flexibility of polymers with the large transduction capabilities of ceramics.

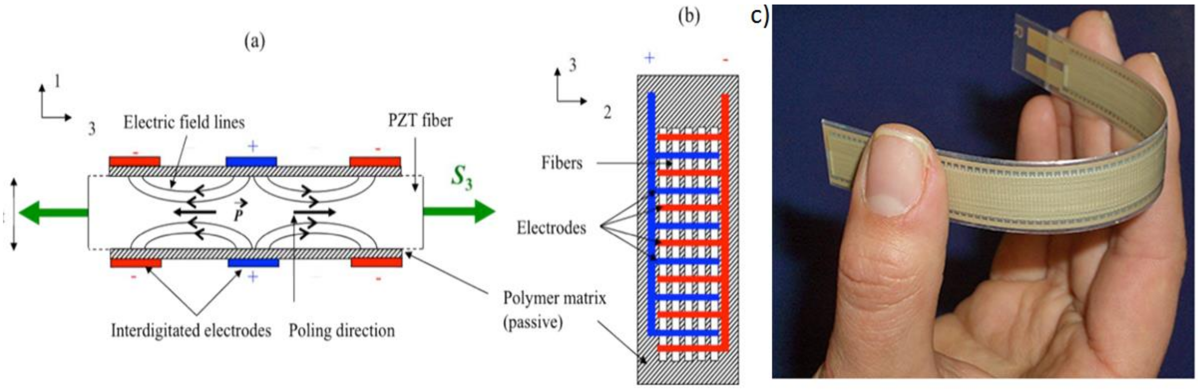


Figure 31: Piezoelectric fiber composite sensor from Advanced Cerametrics Inc.
a) Cross-sectional view illustrating the electric field used to pole the PZT material and the result net polarization along the length of the fibers b) Top view of PFC sensor c) Photo image of the PFC sensor

The force sensor presented in the figure 32 implies continuous electrodes attached to PFC.

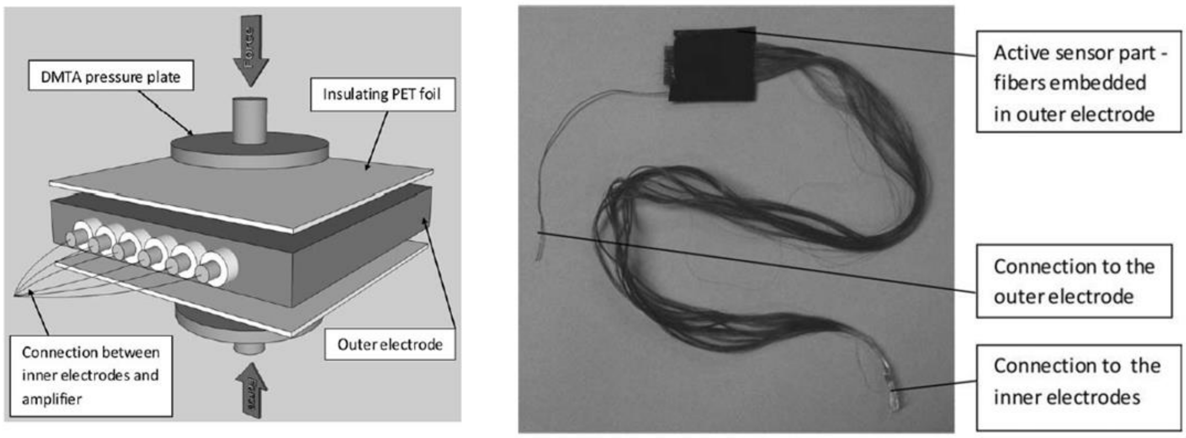


Figure 32: Schematic and photograph of the force sensor

Piezoelectric fiber composites imbedded into structures are used for health control, providing real time monitoring and not-destructive testing [65]. So, catastrophic and brittle failure can be avoided. PFC can provide early warning and prolong the service life of the components. PFC demonstrated their superior sensitivity and better performance over the traditional strain gauges. Strain gauges, conventional strain/force measuring devices, are mostly used to measure static forces. The disadvantages of the strain gauges include low sensitivity at low strains and require signal conditioning/amplification. On the other hand, piezoelectric sensors are passive and doesn't require external excitation source.

Piezoelectric fibers are capable of acoustic emission and detection over a broad range of frequencies, from the tens of Hz to the tens of MHz [66]. Fiber curvature defines the shape of the acoustic wave front (fig. 33). One of the interesting features of fiber transduces is that they can be assembled in dense arrays and woven into fabric thus resulting flexible large-active-area piezoelectric transducers.

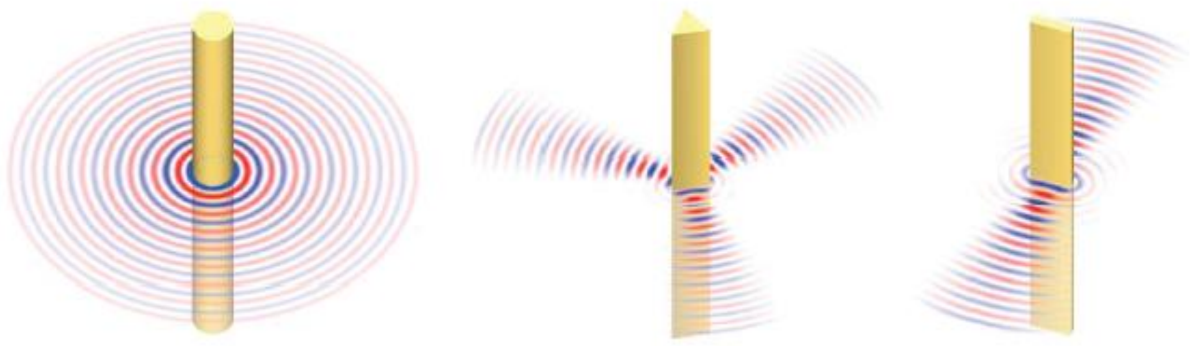


Figure 33: Near-field pressure patterns of the acoustic emissions from a circular fiber, a triangular fiber and a rectangular fiber with cross-sectional dimensions about 2 mm.

There are several approaches to design piezoelectric fabric. Piezoelectric fibers can interconnect with the conductive electrodes in a number of ways. Direct contact with electrodes maximizes capacitance and piezoelectric coefficient. Electrodes are not only used for signal transfer but also for poling.

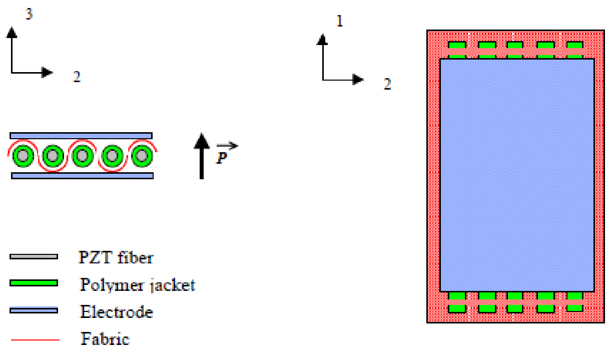


Fig. 34 Schematic representation of an energy harvesting textile sensor

Figures 34 and 35 represent two ways of signal detection: by adding electrodes on the top and the bottom of the piezoelectric fibers or by mixing conductive fibers with piezoelectric fibers in one woven structure.

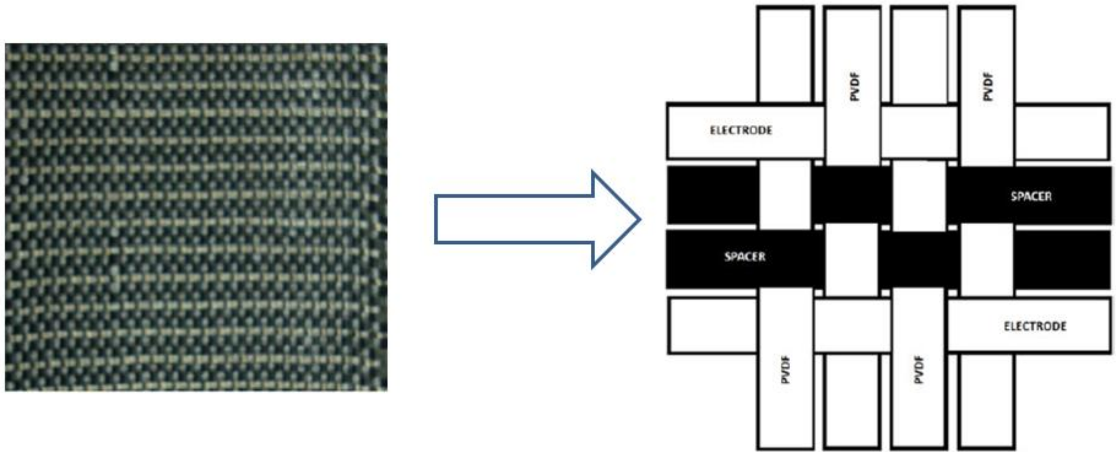


Figure 35: Configuration of the 2D flexible piezoelectric woven sensor

Development of piezoelectric fibers is the emerging field of smart textile. Piezoelectric properties of fibers synthesised from a limited number of piezoelectric materials were explored. Fabrication of fiber-based multi-energy devices consisting of piezogenerators, supercapacitors and photovoltaic fibers is the next step in piezoelectric fiber application field.

4 Photovoltaic fibers and textiles

A search for renewable low environmental impact alternative energy sources is considered one of the top priorities of today's society. Solar power is one of the most promising candidates among renewable energy resources.

Fiber-shaped solar cells offer lightweight, foldability and greater light condensation rate. These factors increase the mobility of devices and adaptability to power wearable, mobile or stationary electronic devices.

Photovoltaic devices generate electricity directly from sunlight. Current studies of fiber-shaped photovoltaic (FPV) or fiber-shaped solar cells are primary focused on dye-sensitized solar cells (DSSCs) and organic thin film solar cells [61].

4.1 Dye-sensitized solar cells

Conventional DSSC is composed of a porous wide band gap semiconductor layer (TiO_2 or ZnO) covered with molecular dye, electrolyte solution and two electrodes, one of which is conductive. Dye-molecules are attached to titanium dioxide by chemical bond and this interaction is called sensitizing, which gives name to this type of solar cell

Dye molecules absorb light and inject electrons into TiO_2 conduction band (fig. 36). Then electrons are transported through the load and reach counter electrode. Electrolyte transports the electrons back to the dye molecules.

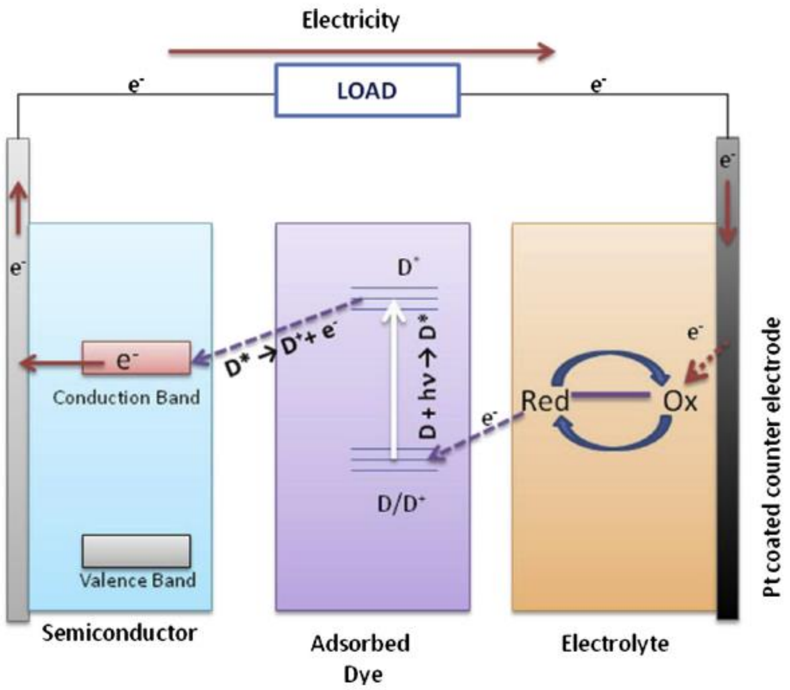


Figure 36: Schematic representation of working of dye-sensitized solar cells

Although the efficiency of DSSCs with liquid electrolyte is higher, there are some difficulties in utilization liquid electrolyte in fiber-shaped collar cell because of temperature stability problem, possibility of leakage and low processability.

Latest advances in research on fiber- based DSSCs imply porous polymer electrolyte membrane and solid electrolytes [67].

M. J. Uddin et al. developed flexible solid-state dye-sensitized photovoltaic micro-wires by depositing TiO_2 film on Ti-wires along which carbon nanotubes yarn was twisted with photoconversion efficiency of 0.1959% (fig. 37) [68].

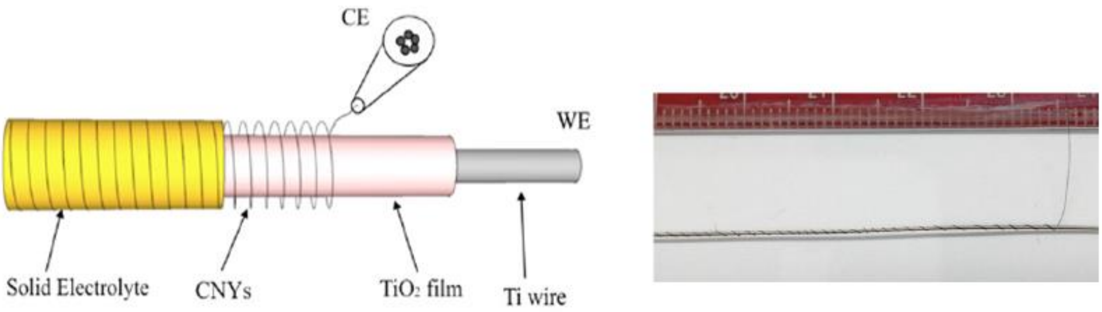


Figure 37: Schematic view and optical image of all-solid DSSC

Utilization of carbon nanotube yarns in both electrodes in previously described device structure increase photoconversion efficiency due to excellent catalytic properties and low electrical resistivity of aligned carbon nanotubes [69]. Wire electrode made of carbon nanotube yarn has increased interaction with electrolyte and large surface area [70].

Maximum conversion efficiency for the wire-shaped photovoltaic devices (8.45%) was achieved in DSSC with solid electrolyte, titania nanotubes layer and electrodes based on fibers spun from graphene [71].

All-solid DSSCs composed of ZnO nanorod array vertically grown on stainless steel wire were woven with Pt-coated wires to produce flexible solar textile (fig. 38) [72]. The efficiency of this novel photovoltaic textile with 10x10 wires is 2.57% at 100 mW/cm.

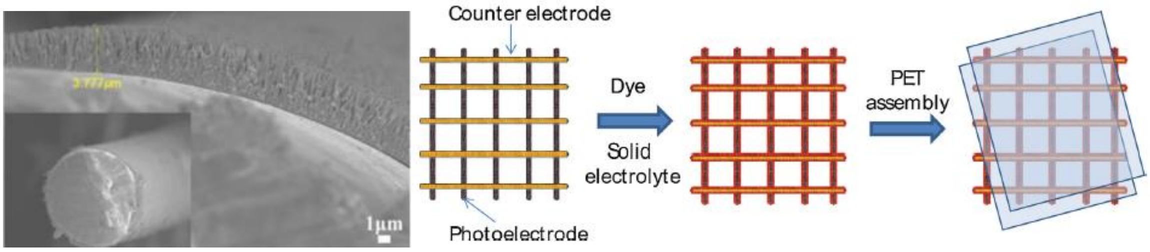


Figure 38: SEM image of ZnO nano rods on stainless steel wire and solar textile fabrication method

Different approach of fiber DSSC structure implies spring-shaped optical anode (fig. 39).

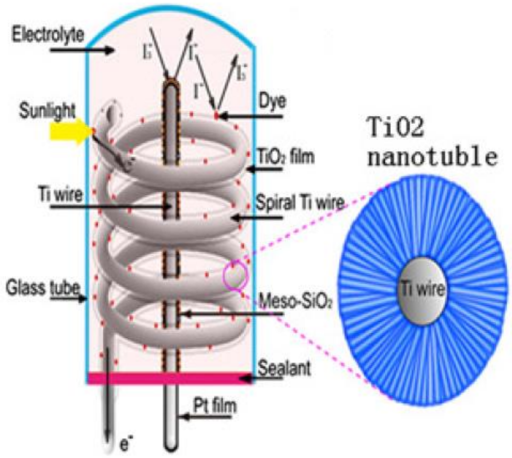


Figure 39: Spiro-photoanode –based DSSC

Synthesis of high-efficient flexible fiber-shaped solar-cells with solid state electrolyte together with long-term stability and reproducibility remains a great challenge.

4.2 Organic thin film solar cells

Organic photovoltaic cells use conductive organic polymers or small organic molecules for light absorption and transport to covert solar radiation into electricity. Organic photovoltaic cells are based mainly on multilayer structure or bulk heterojunction.

Bulk heterojunction solar cells are preferable to multilayer solar cells because they combine the advantages of easier fabrication and higher conversion efficiency due to the considerably extended donor/acceptor interface [73].

In bulk heterojunction a blend of donor and acceptor molecules is placed between two electrodes (fig. 40). During light absorption, an electron moves from the highest occupied molecular orbital (HOMO) of a donor molecule into the lowest unoccupied molecular orbital (LUMO) of an acceptor molecule, leaving behind a positively charged "hole" on the donor molecule. The electron and hole move in opposite directions toward the two electrodes. Electrons are collected by the cathode and holes by the anode [74].

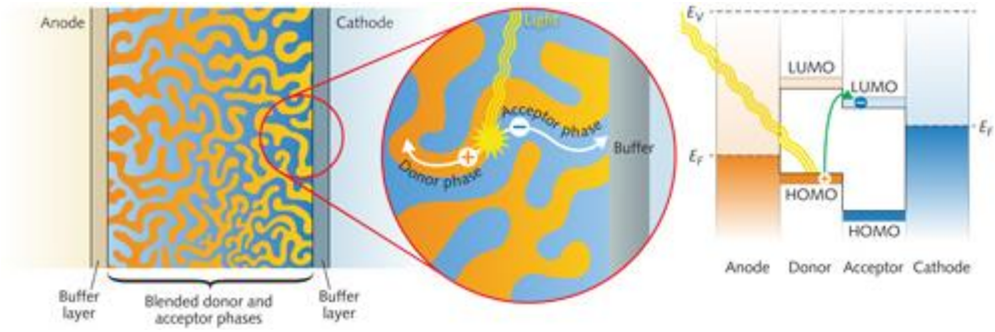


Figure 40: Bulk-heterojunction organic photovoltaic design

The preparation of efficient fiber-shaped organic photovoltaic cells (FOPV) face many difficulties compared with that of FDSSs. Indium tin oxide (ITO) – most widely used transparent hole collecting electrode material – can't be used in fiber-based photovoltaic cells, because it is brittle and require high annealing temperatures during manufacturing. There are some ITO-free alternative approaches, such as using carbon nanotube layers, PEDOT-PSS (fig. 41), graphene films, random networks of metallic nanowires or nano/micro-metallic grids.

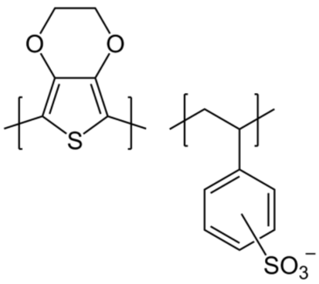


Figure 41: Structure of PEDOT:PSS

Example of organic fiber-based solar cell structure is given in the figure 42. Core fiber is coated consequently with polymer-based anode, two polymers in heterojunction blend and a semi-transparent cathode [22].

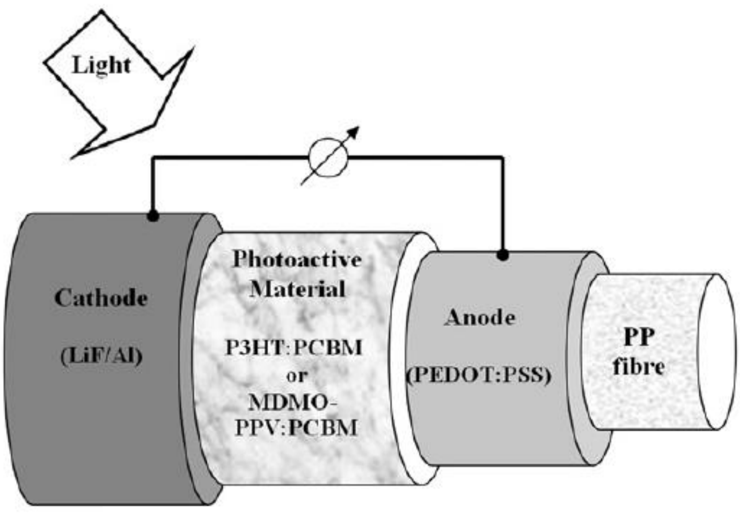


Figure 42: Schematic drawing of a photovoltaic fiber

Table 3 shows the materials which are widely used in bulk heterojunctions blends.

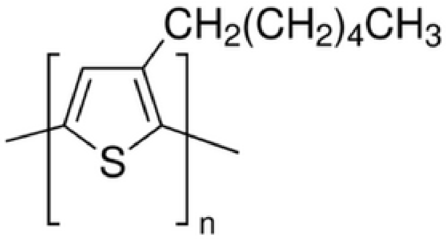
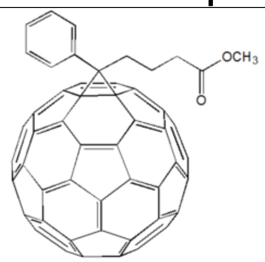
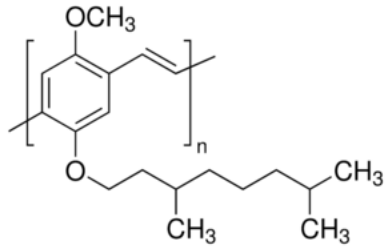
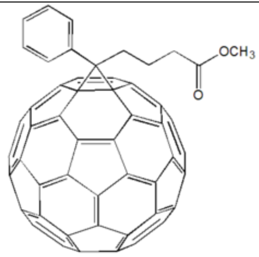
Material pair	Electron donor	Electron acceptor
P3HT:PCBM	 **P3HT** Poly(3-hexylthiophene-2,5-diyl)	 **PCBM** [6,6]-phenyl-C_{61}-butyric acid methyl ester
MDMO-PPV:PCBM	 **MDMO-PPV** Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]	 **PCBM** [6,6]-phenyl-C_{61}-butyric acid methyl ester

Table 3: Possible manufacturing method for photovoltaic fibers

To date, commercially applied organic semiconductors are materials with wide energy gap. These result in limited amount of photons, which organic photovoltaic can absorb. So, stable small band gap conjugated polymers are highly required.

The efficiency of photovoltaic device is not only defined by photoactive polymers. Geometry and thickness of the active layer play an important role in device characteristics [75], [76]. With the donor/acceptor blend film thickness increasing, the light absorption increases, but charge carrier mobility decreases.

Although fiber-shaped solar cell has three dimensional architecture and thus enhanced light capture, a large portion of photons is absorbed in upper electrode. Transmission of alternative to ITO transparent conductive electrodes is not so good.

So called “energy fiber” has developed [77]. It is a new concept of flexible energy storage and harvesting device (fig. 43), which can find many applications in smart textile. Polymer solar cell and electrochemical supercapacitor are produced on the same wire. Similar device with DSSC showed luck of mechanical strength and is under development.

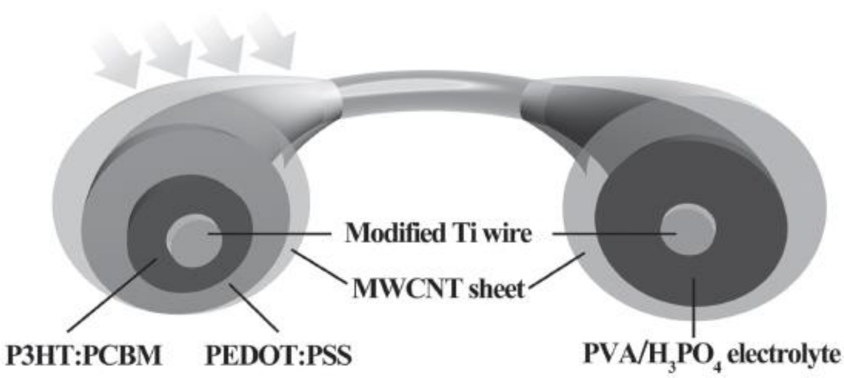


Figure 43: Structure of “energy fiber”

A possible industry-scale manufacturing technique for photovoltaic fibers derived from textile finishing processes has been proposed (fig. 44). This method is called “cup to cup”. Coating layer by layer is achieved consequently while travelling from one solvent or solution bath to another. The thickness of the layers can be controlled by solution concentration and dipping time. This method is under development but raises expectations of simple and low cost fabrication process.

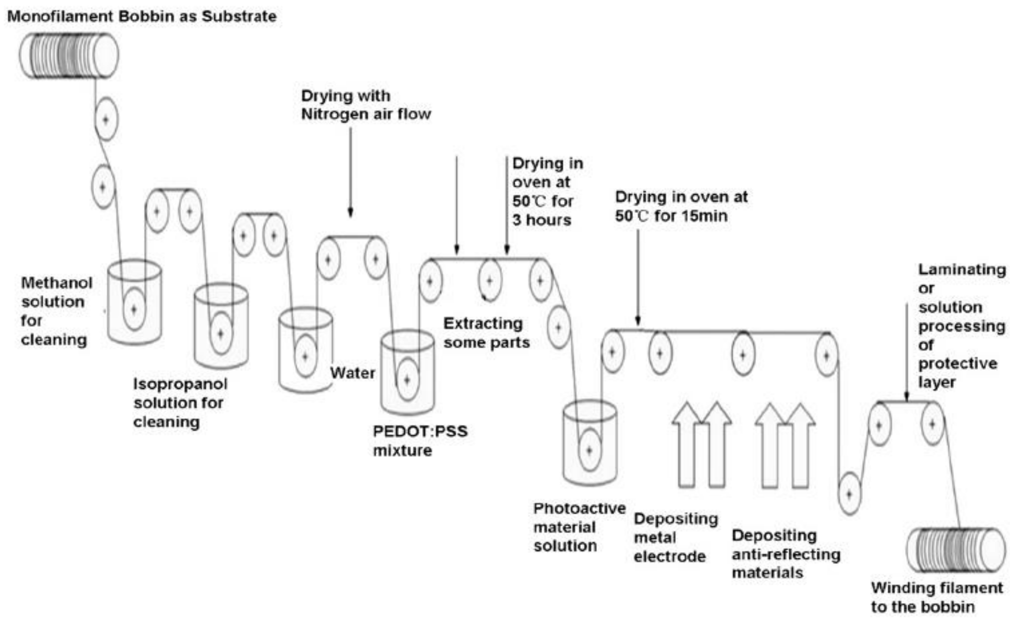


Figure 44: Possible manufacturing method for photovoltaic fibers

4.3 Silicon p-i-n junction fibers

Silicon-based photovoltaic devices are more efficient than organic polymer cells, but have some difficulties in production devices on flexible substrates. Semiconductor photovoltaic fibers can be produced via drawing or high pressure chemical vapour deposition (HPCVD). Drawing semiconductor solar cells is not that easy due to low melt viscosities, migration of oxygen etc. Appropriate morphology is obtained via high-pressure chemical vapour deposition in capillary template (fig. 45) [78].

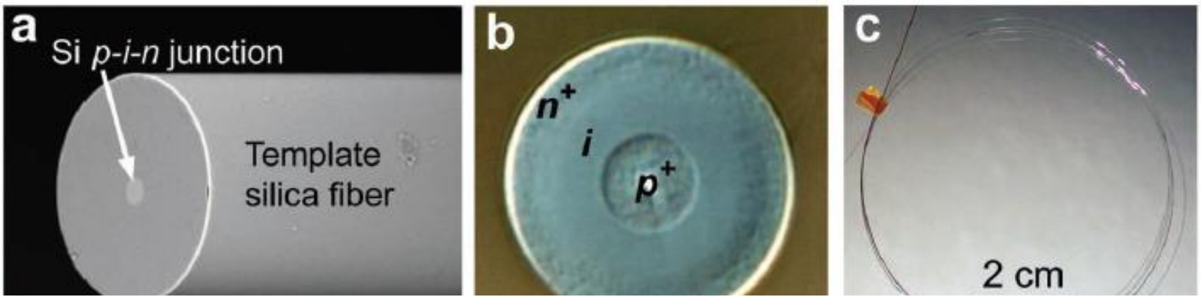


Figure 45: a)SEM of p-i-n deposited structure b) DIC optical micrograph of p-i-n deposited structure c)Photograph of silicon p-i-n junction fiber

Obtained silicon photovoltaic fibers have 400 micron bend radius, which breaks stereotypes of rigidity of conventional silicon-based solar cells. Silicon solar fibers can compete with the polymer ones until they will reach scalable production and high efficiency.

5 Conductive fibers

Conductive fibers are highly required to signal transferring to electronic devices imbedded into fabric, heating, protection from electromagnetic interference and electrostatic discharge and others. Moreover, the number of electronic devices based on fibers or woven structures are continuing increasing: photovoltaic solar cells, fiber-based transistors, power generators, sensors etc.

5.1 Types of conductive fibers

Conductivity in textile can be achieved in the following ways:

- Use wires
- Coatings with conductive substances
- Additives to the fiber
- Inherently conductive fibers

<u>Use wires</u>

Metal strands or metallic fibers (2-100 µm) mixed with textile fibers can be used to made textile electroconductive. However, application of metals and semiconductors is limited because of their stiffness, cost and weight with comparison to polymer fibers. Incorporation of metallic fibers can also give fabric undesirable handle.

Metallic filaments often suffer from unstable electrical properties, for example, change of electrical resistance induced by cyclic deformation, washing, stretching. Conductive yarns in textile applications are subjected to additional stresses like bending folding and pulling. Hence, mechanical robustness of metallic yarns should be considered while designing electronic textile. Figure 46 shows the fatigue failure of copper-based conductive yarns used to drive embedded LEDs into textile substrate [79].

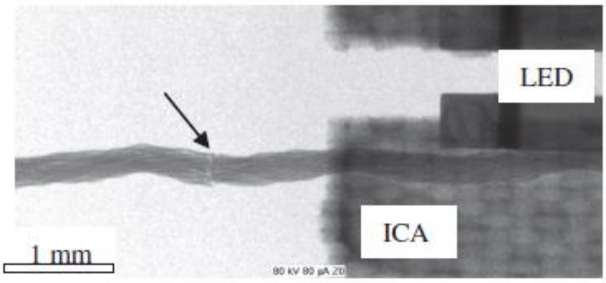


Figure 46: X-ray image of copper yarn fracture

Reliability and endurance of electro-conductive metallic yarns can be improved by twisting them around elastic core yarn (fig. 47) [80].

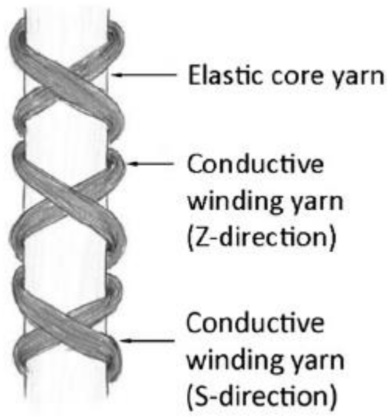


Figure 47: Scheme of twisting metallic wires with elastic polymer fibers

Coating with conductive substances

Coating normal textile with intrinsically conducting polymers, carbon black, carbon nanotubes, metal nanowires or metal-based powders is another way to impart conductivity.

Following techniques are used for yarns and textile metalizing:

- Vacuum metallizing
- Dip-coating
- Spraying
- Electroplating
- Metallisation
- Sputtering

The most commonly used conductive polymers include polythiophenes (such as PEDOT), polypyrrole (PPy), polyaniline (PAn) and polythiophene (PT). Several methods are available to coat a conducting polymer on textile substrate: in situ chemical polymerization, electrochemical polymerization and chemical vapour phase polymerization.

Composites of intrinsically conductive polymers with inorganic nanoparticles show improved electrical, mechanical, optical and catalytic properties. Composites of PANI with different inorganic semiconductors such as ZnO, Fe3O4, MnO2, TiO2, ZrO2 have been reported. Y.-P. Zhao et al. prepared PET fabrics coated with PANI-ZnO composite.

Plasma treatment results in surface etching, cleaning and activation which improves interaction between fiber or textile surface and coating.

Low pressure oxygen and argon plasmas were used to pre-treat nylon fabric coating with single walled carbon nano tubes (SWCNTs) by dip-drying process [81].

Another strategy to improve coating adhesion is pre-dyeing. Pre-dyeing the nylon fabric with poly(2-methoxyaniline-5-sulfonic acid) prior to chemical polymerization of polypyrrole coating significantly improved the surface and coating properties [82].

Continuous conductive coating can be achieved while fiber fabrication by bi-component spinning. Polyacrylonitrile - polyacrylonitrile/carbon nanotube bi-component fibers were produced and exhibited good mechanical and electrical properties (fig. 48) [83].

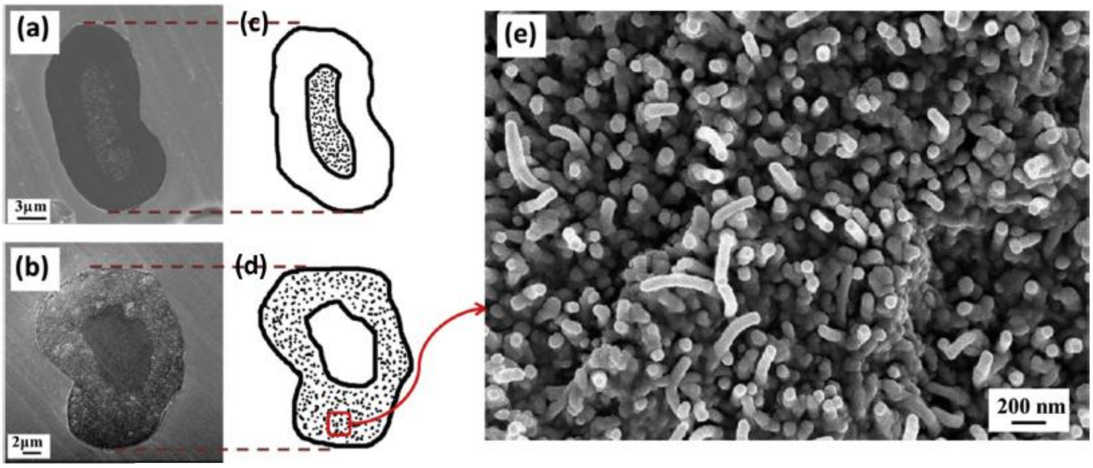


Figure 48: SEM images and cross-sectional schematics of bi-component fibers

Incorporation of conductive particles

Conductivity of fibers can be tuned by adding fillers like metal particles of carbon nanotube (CNts) in the spinning solution. However, high levels of conducting particles in polymeric threads can affect mechanical properties.

Inherently conducting fibers

Inherently conductive polymers or conjugated polymers have been extensively studied. Unfortunately, utilization of majority of conductive polymers is limited by low processability and environmental stability. One of the most used inherently conductive polymers for fiber production is Polyaniline (PANI).

Carbon and carbon nanotube fibers are widely used as conductive fibers. Carbon nanotubes yarn is produced by drawing from vertically aligned carbon nanotube array grown by chemical vapour deposition (fig. 49).

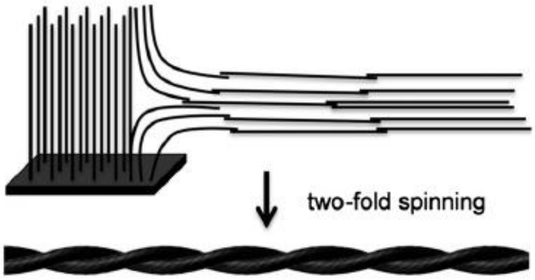


Figure 49: Schematic illustration of fabrication process of carbon nanotube yarn

However, production of carbon fibers requires sophisticated processes and high technology. To date, there is no factory with full and complete manufacturing process.

5.2 Applications

Sensors

Dependence of resistivity on various external stimuli, including gases, chemical vapour, temperature, pressure, light, liquid, pH and strain can be used in sensor development.

Integrated textile sensors in medical wound dressing systems for monitoring of wound healing process have been demonstrated (fig. 50).

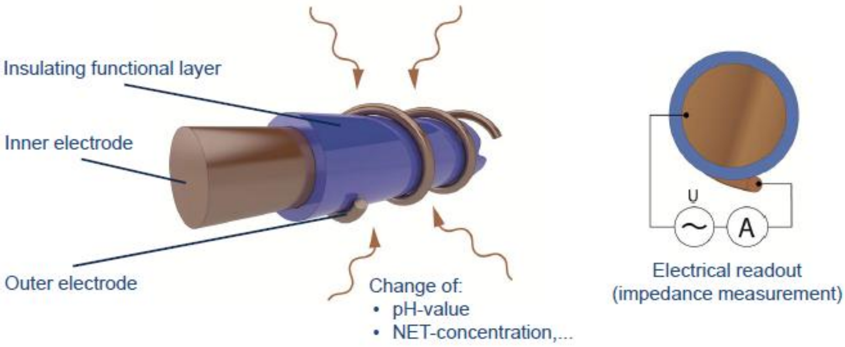


Figure 50: Wound condition sensor

In this type of sensor, pH value in wound influence resistivity and thus electrical output.

A strain sensor takes advantage of the physical property of electrical conductance and its dependence on the conductor's geometry. Good strain sensing capability and reversibility reported in yarns coated with thermoplastic polyurethane/carbon nanotube conductive polymer composite [84].

Integration of conductive fibers into textile-reinforced composites makes possible to provide information about strain within the structure in real time via electronical measurement (fig. 51).

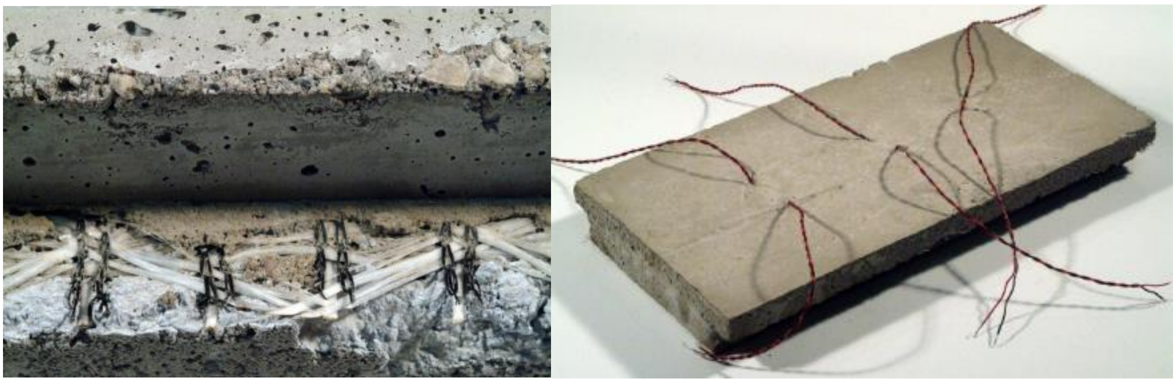


Figure 51: Example of fiber-based strain sensor in concrete monitoring

Conductive silver coated polyether ether keton (PEEK) filament yarn has shown significant promise as a strain sensor in structural health monitoring in textile reinforced composites [85].

Electrodes

Textile electrodes for the collection of bioelectric signals and for the stimulations of muscles and nerves have been widely studied in recent years. Textile-based electrodes are more comfortable for the patient and capable of monitoring during longer periods. However, there are dome challenges to overcome:

- The spatially resolved stimulation of nerves with low frequencies are not possible
- Artefacts by motion even with adhesives electrodes
- Displacements of the electrodes during movement
- Contact impedance – long term stability of electrical contact between skin and electrode

Among electrode preparation methods are embroidering and sewing with conductive threads, plating of conductive particles or utilization of conductive textile.

Example of sewed electrode made of silver-plated nylon conductive tread that is used for electrocardiogram (ECG) signal monitoring is shown in figure 52 [86].

Figure 52: Textile-based electrode for ECG recording

Development of long-term stable and wash-resistant dry electrodes for therapeutic and diagnostic applications are under development.

Conductive textile has found new application as supercapacitor electrodes. Supercapacitors utilize high surface area electrode materials and thin electrolytic dielectric (fig. 53) and have some advantages over other energy sources: high power and energy densities, ability to recharge in seconds, long life span and high reliability. Supercapacitors invoke great expectations as the power sources for new flexible consumer electronics and smart textile.

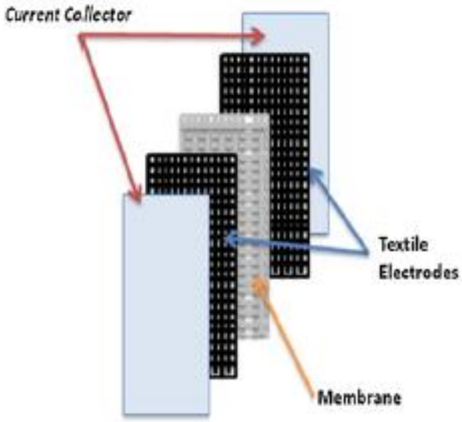


Figure 53: Unit cell of supercapacitor

Fiber and textile-based electrodes are a good choice because of their large surface area, flexibility and light weight.

Carbon materials in various forms (powder, fiber, fabric, web, nanotubes, carbon nano fiber/graphene composite [87], [88]) conducting polymers, metal oxides proved their suitability as supercapacitor electrode material. Utilization of conducting polymers has gained popularity due to low cost, high coping-dedoping rate during charge-discharge, high charge densities and ease of synthesis.

K. F. Babu et al. demonstrated the performance of polypyrrole (PPy)-coated PET and viscose rayon textile electrode in supercapacitor application [89].

To date, textile electrodes are also used in fuel cells. A new anode material for glucose-gluconate fuel cells prepared by electrodepositing gold nanoparticles onto carbon nanotube covered polyester substrate was proposed in [90].

Weavable high capacity electrodes made from Si-carbon nanotube yarn proposed as an anode material for lithium ion batteries [91]. The choice of these materials is due to mechanical durability and high electrical conductivity of carbon nanotubes and highest theoretical capacity for Li ions of Si.

Heating textile

Heating of conductive material is due to resistive heating - the process by which the passage of an electric current through a conductor releases heat. The amount of heat released is proportional to resistance and square of the current.

Among applications of heating textile is protective clothing, tiles with heating function, medicine.

Active heating garments can be developed by weaving conductive materials into fabric (fig. 54) [92] or over sewing (fig. 55).

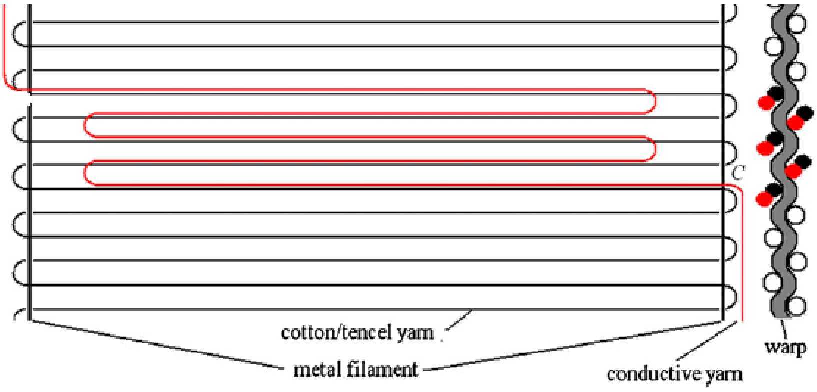


Figure 54: Example of intermittently weaved filaments into plain fabric

Tibtech developed stretchable heating narrow bands which give flexibility in designing heating garments [93].

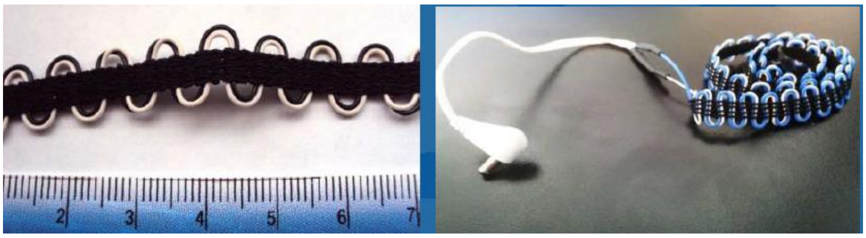


Figure 55: Heating elements of Tibtech

Conclusions

Textile industry is transforming into a dynamic, innovative, knowledge-driven competitive and sustainable sector. It is no more limited with only fibers and cloth production. To date, fibers and textile are used as a substrate to various devices: photovoltaic, conductive, light emitting, piezoelectric etc.

Several types of fiber-based solar cells have been recently introduced to the market: dye-sensitized solar cells, ZnO nanowires solar cells and organic thin film solar cells. Photovoltaic fibers allow production of lightweight and flexible photovoltaic devices. Although fiber-based photovoltaic devices have undergone significant advancements, they are still in development phase in meeting the criteria of cost, efficiency and stability.

Many efforts have been made to develop piezoelectric fibers from PVDF and PZT materials due to their significant promise in application as piezoelectric generators in conversion of waste mechanical energy into electrical energy. Piezoelectric fibers have other potential applications such as sound transducers and sensors.

The smart textile innovation cluster is still at a nascent stage of its formation as an industrial sector. Most of the reported fiber-shaped devices are a long way from fulfilling their final applications but invoke great expectations.

The need of sustainability makes man-made fiber and textile industry searching bio-based materials and developing environmentally friendly processes. Various techniques have been implemented to replace wet and hazardous procedures: plasma and ultrasound treatment, UV curing, spraying etc. Advances in bioplastics decrease utilization of petrochemicals for fiber production. More and more commodity polymers are synthesised on the base of bio monomers. Microbial production is still expansive but invokes great expectations because material properties can be genetically engineered.

Technical textile is rapidly developing and widening a range of applications such as reinforcement of composites, protective clothing, medical applications and filters.

Manufacturing innovations such as 3D seamless weaving and 3D printing together with development in smart textiles can have a remarkable influence on fashion and apparel in near future. Technology is rapidly beginning to be woven in textile.

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Appendix A: Piezoelectric fiber profiles found in the literature