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Nova vlakna za 21. stoletje

Povzetek

Članek obravnava najvidnejše razvojne dosežke na področju vlaken v zadnjih nekaj letih: nanovlakna, kemično pajkovo svilo, gensko spremenjen bombaž, vlakna iz polimlečne kisline, inteligentna vlakna, vlakna z negativnim Poissonovim številom, sojina vlakna, vlakna iz ptičjega perja in nova poliestrska vlakna z latentno elastičnostjo.

Ključne besede: nanovlakna, kemična pajkova svila, BioSteel, Bt bombaž, polimlečna kislina, PLA, sojina vlakna, vlakna iz ptičjega perja, optična vlakna, vlakna z negativnim Poissonovim številom, Corterra, Sorona, Securus, polibutilen tereftalat, PBT, politrimetilen tereftalat, PTT, triexta, elesterell-p, elastomultiester

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Novel Fibres for the 21st Century*

Abstract

The paper deals with the most prominent advances in the field of fibres in the last few years: nanofibres, man-made spider silk, genetically altered cotton (Bt- cotton), polylactide (PLA) fibres, intelligent fibres, auxetic fibres (negative Poisson's number fibres), soybean fibres, feather fibres, and new polyester fibres with latent elasticity.

Keywords: nanofibres, man-made spider silk, BioSteel, Bt-cotton, polylactide (PLA) fibres, soybean fibres, feather fibres, optical fibres, auxetic fibres, Corterra, Sorona, Securus, polybutylene terephthalate, PBT, polytrimethylene terephthalate, PTT, triexta, elasterell-p, elastomultiester

1 Introduction

The development of novel fibres and enhancement of existing ones in the last decade are based on novel technologies ranging from genetic engineering, biotechnology, nanotechnology to the microelectronics and informatics which together with the interdisciplinary approach to the science (Figure 1) create the opportunities for fibres with new potentials. First fibres produced by using novel technologies have been developed and some of them are already commercially available, such as nanofibres from various raw materials, genetically altered natural fibres (Bt-cotton), man-made fi-

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* The paper was first published in Tekstilec in the Slovenian language in vol. 47, 2004, no. 1/2, p. 13–25. However, according to fiber development in the last years, the authors have changed only some data.

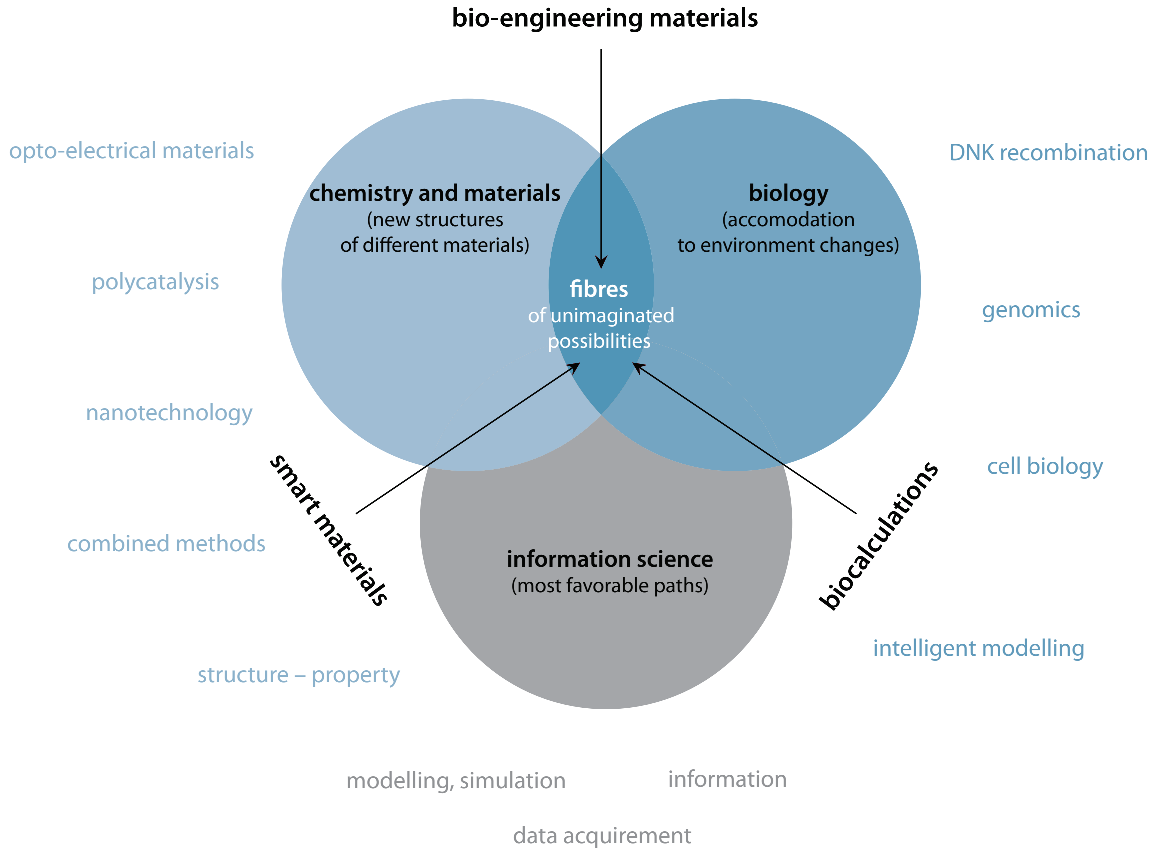

Figure 1: Interdisciplinarity of science will enable development of new fibres

bres made from naturally renewable raw materials (fibres from polytrimethylene terephthalate and polylactic acid, intelligent fibres, auxetic fibres (fibres with negative Poisson's number), etc. Novel technologies bring the opportunity to use by-products of some other industries, e.g. food industry, as the raw material for novel fibres (soybean fibres, feather fibres).

2 Nanofibres

Nanotechnology is a sophisticated technology, which will substantially affect the development of the entire textile technology as well as the type and applicability of products in the future. As expected, it will pave the way for more energy-saving, more efficient and cleaner textile industry. The impact and use of nanotechnology will be especially high in the production of fibres and dyestuffs. With completely new surface treatment processes, nanotechnology will impart multifunctionality to textiles by combining various properties, such as water repellency, antibacterial protection, mould protection, applicability for sensors and camouflage purposes, etc.

It is expected that the global market for nanofibres should reach US $ 176 million in 2012 and grow to US$ 825 million by 2017, according to BBC Research report [1].

Nanofibres [2, 3, 4] are ultra fine fibres with a diameter less than 100 to few 10 nanometres. The finest microfibres produced so far are only few micrometres in diameter; their fineness can be compared with that of degummed pure silk. The diameter of conventional fibres, e.g. cotton, wool and many other natural and man-made fibres, is from 10 to few 100 micrometres. Such extremely fine nanofibres excel in specific surface area, flexibility and tensile strength. These properties can be efficiently utilized for filtration, in biomedicine, for protective textiles, sails, nanocomposites and in the field of electronics and optics. By using nanofibres, it will be possible to develop materials which will be up to 10 times stronger and more durable than steel with the same weight.

Nanofibres are usually produced by electrospinning (Figures 2 and 3), which is a cost-effective and simple method. Polymer liquid (solution or melt) in a syringe is exposed to high voltage. As soon as the voltage of polymer liquid is high enough to overpass the liquid's surface tension, a metallic nozzle or pipette ejects a liquid jet toward a metallic collector, which is the electrode of opposite charge and where the jet disperses into a multitude of fine and extra fine fibres. During the travel, the charged liquid jet undergoes bending and elongational deformations. The result is the thinning of fibres into fine fibres of nanometric crosswise dimensions. In order to be able to produce nanofibres of good quality with constant diameter and with even and smooth surface, it is necessary to optimise technological parameters, which means to choose suitable polymers (all polymers are not suitable for electrospinning of nanofibres), and optimal concentration and temperature of spinning liquid and voltage. Provided that suitable technological parameters have been selected, it is possible to directly produce porous fibres by electrospinning.

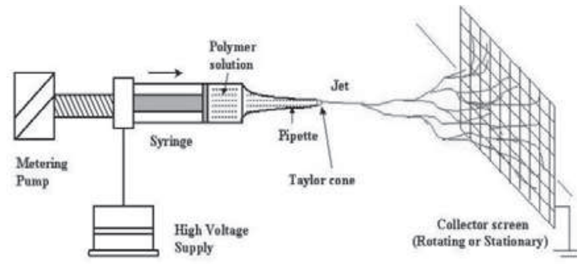

Figure 2: Scheme of electrospinning procedure

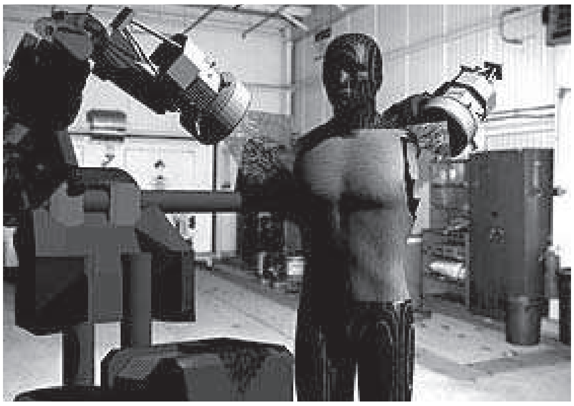

Figure 3: Direct depositing of nanofibres on the surface of a garment with an electrospinning process

The electrospinning technique can be also used for the production of nanofibres from polymers, which are soluble in volatile solvents, as well as from polymer melts. The morphology and properties of nanofibres, produced in this way, substantially differ from those of microfibres and conventional fibres. Due to their large specific surface area, low density and high porosity, nanofibres are very interesting for textile purposes. They surpass properties of microfibres, such as wind and water proofness.

Toray Industries Inc. from Tokyo has developed a polyamide nanofilament yarn Miramatte with total mass per unit length 44 dtex, containing more than 1.4 million nanofilaments with the fineness of individual filaments about 3 ntex and the diameter of individual fibres 20–200 nm. By using these fibres, Toray has manufactured a polyamide textile material with more than 1000 times larger surface area than that achieved by using conventional polyamide fibres. This novel textile material has outstanding capacity of absorbing unpleasant odours and 2–3 times higher capacity of absorbing moisture than standard polyamide textile materials, even higher than cotton! The fact, which is also very important, is that nanopolyamide fibres have high capacity of absorbing moisture on their outer surface (1000 higher than conventional polyamide fibres that practically bind the entire moisture in their interior). The ratio of the moisture bound on the surface to the moisture bound inside fibres is 1/1000 for polyamide fibres.

Miramatte fibres, which contain 3 times higher content of added inorganic particles than standard polyamide fibres, are opaque and impermeable for UV light, and are therefore suitable for the manufacture of thin fabrics. Inorganic particles are not arranged only in the interior of fibres, but also on their surface, which imparts them a special uneven surface with a characteristic touch similar to that of fine bird's feathers. The fibres will be used for clothing and various types of filters[5].

Based on the novel patented technology for the speciality fibres production, Toray will research the possibilities of producing nanofilament yarns from polyester (PES), polypropylene (PP) and new polymers, such as polylactic acid (PLA) by controlling nanostructure, i.e. molecular orientation at a nanoscale level, through optimisation of flow conditions [6].

Cellulose nanofibres for industrial nonwovens suitable for dry and wet filtration, for protective clothing, for agricultural products, such as pesticide and fertilizer absorbents, as well as for biodegradable composites are developed at the Cornell University in the USA. Novel cellulose solvents provide the possibility to produce high-strength nanofibres with the diameter less than 100 nm by using the electrospinning method; even wastes from cotton spinning mills can be used as raw material [7, 8].

Application of nanofibres on textile materials, the so-called nanocoating technique, makes such textile materials 100% waterproof. By applying nanofibres (nanowiskers) on cotton and synthetic materials, the American company Nano-Tex succeeded in making the materials water- and oil-repellent and at the same time steam-permeable, abrasion resistant and crease resistant. The textile material is dipped into the aqueous solution of nanofibres, which adhere to the material. An air cushion, which is formed above the flocked nanofibres surface, repels water and other liquid impurities. The mechanism is similar to that simulating water repellence by the geese plumage surface [9].

Carbon nanofibres are important for many various fields of application, such as filtration, composites, protective clothing, etc. The touch of carbon nanofibres is similar to that of cotton fibres only that their colour is black. Carbon nanofibres can be even more than 100 times stronger than steel. The invention of the hollow carbon nanofibres (nanotubes) production process (Figure 4) in 1991 prompted the development of carbon nanofibres. Nanotubes are used as fillers in composites to enhance their mechanical properties, for electrical cables, heat cables as well as for strong hook-and-loop fasteners (Velcro) (Figure 5) [10]. Nanotubes are extremely fine fibres with outstanding mechanical properties, high electrical and thermal conductivity, and chemical stability, which is the result of their chemical composition and perfect hexagonal arrangement of covalently bonded carbon atoms. Carbon atoms are arranged in concentrically shaped graphite layers (Figure 6).

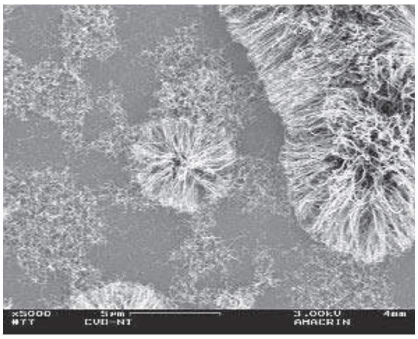

Figure 4: Fibres from hollow carbon nanotubes

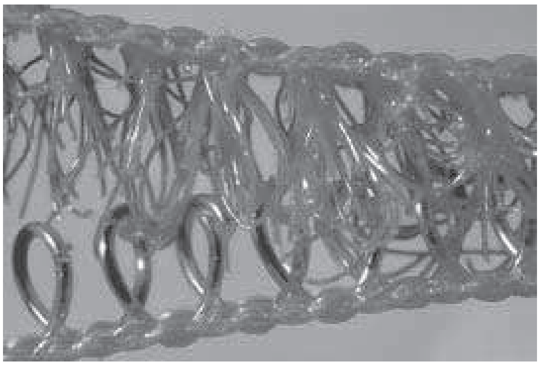

Figure 5: Touch and close fasteners from nanofibres

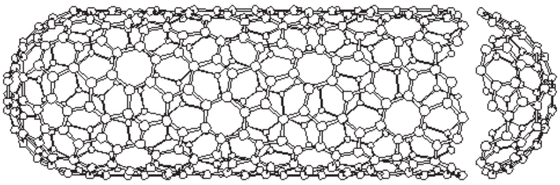

Figure 6: Structure of hollow carbon nanotube

3 Development of fibres by using genetic engineering

3.1 Genetically altered cotton

In the 80s of the previous century the American multinational corporation Monsanto began to develop cotton, which was supposed to be pest –resistant, by using genetic engineering [11] (Figure 7). Genetically altered cotton, i.e. Bollgard cotton or Bt cotton, was created by injecting the cry-1Ac gene insecticidal protein isolated from a bacterium Bacillus thuringiensis into cotton seeds to give them enhanced resistance to pests. Bacillus thuringiensis is a gram-positive aerobic soil-dwelling bacterium, which is capable of producing four types of toxins in a crystal proteinaceous form among which the most important is δ-endotoxin. In the USA, Bacillus thuringiensis was registered as a microbial pesticide in 1961. The development of genetic engineering created the opportunity to isolate an active gene and to transfer its sequences into the genetic material of some other organism, even cotton. Genetically altered cotton contains the cry1Ac gene in its genome and is therefore capable of producing its own crystal toxic protein. When a bollworm attacks cotton plant and consumes any of its parts, it also swallows the mentioned toxin, which causes its death. Toxin is non-toxic to bees, neuropterans and ladybirds. It protects cotton plants from specific species of caterpillars, but not from leaf lice.

50% lower amount of pesticides required for cultivation of Bt cotton means lower pollution of soil, water and air. In the long term, lower consumption of pesticides will appease allergic reactions of farmers [12]. The Bt cotton yield is by approximately 10–15% to even 25–30% higher than that of non-Bt cotton with the same hybrid.

As a result of lower need for pesticides and higher yield, Bt cotton has been widely accepted by farmers [13,14]. Since 1996 it has been planted in the USA, Argentina, Australia, China, Mexico and South Africa. The world share of Bt cotton-growing area was as low as 12% in 1996, 23% in 1998, and already as high as 39% in 2000.

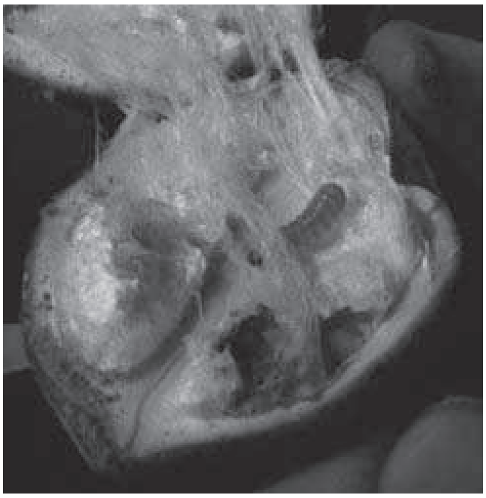

Figure 7: Opened cotton boll with a caterpillar of cotton's moth Pectinophora gossypiella inside

3.2 Man-made spider silk BioSteel®

In the year 2002 the Canadian company Nexia Biotechnologies Inc. and the US Army Soldier Biological Chemical Command succeeded in developing the first man-made spider silk protected under the trademark BioSteel® (Figure 8) [15,16,17,18]. The industrial process of BioSteel® fibres spinning has been developed by Acordis Speciality Fibres Ltd., Coventry, Great Britain.

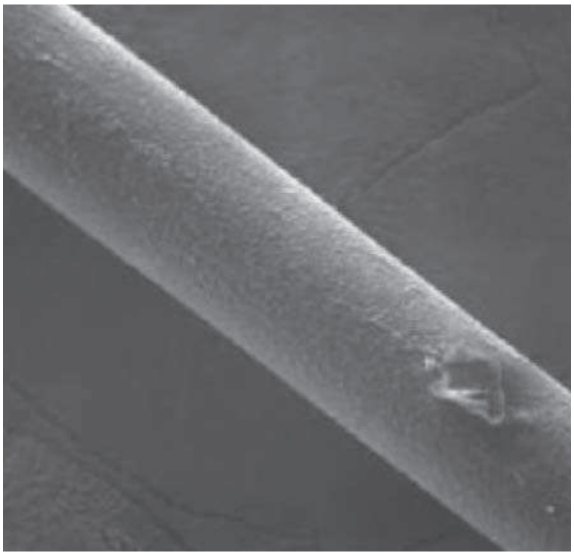

Figure 8: Longitudinal view of BioSteel® fibre

The production of man-made spider silk is based on genetic recombination technology. The DNA segment that controls the production of spider silk protein was introduced into the genome of mammary gland cells of goats. Mammary glands adopted silk-making genes and began to produce the desired proteins in milk. At a later date, individual spider genes were introduced into a single cell of a goat egg by using the in vitro injection method. In this way a transgenic goat was generated whose milk contained spider silk proteins. From the aqueous solution of recombinant spider silk proteins they extruded fibres with Young's modulus and toughness comparable with those of natural spider silk, but more elastic and by about 50% less strong (Figure 9). In addition to the recombinant DNA technology, certain modifications have been introduced into the fibres spinning process. In this way fibres of unequal lengthwise thickness and with various additions were obtained.

BioSteel® fibres are highly strong and elastic with Young's modulus from 40 to 50 GPa, tough, with low density and insoluble in water. They are flame and UV-stabilized. During a tensile test they behave stiffly under the initial stress as a result of high Young's modulus similar to that of aramid fibres, but as soon as they approach the yield point they become very elastic and their resistance to elongation diminishes; finally, the breakage occurs at the elongation, which is comparable to that of polyamide (PA 6.6) fibres.

BioSteel® fibres have outstanding mechanical properties and, which is very important they are biodegradable. All these properties coupled with their biocompatibility make them suitable for use in medicine for surgical microsutures, surgical meshes, artificial ligaments and sinews (BioSteel®-M products). It is estimated that BioSteel® sutures will improve surgical sewing by producing safer seams than those currently produced by using silk, polyamide or polypropylene sutures, but still strong enough, and by minimizing wound scars.

For technical applications BioSteel® fibres must be additionally protected in order to preserve their properties for as long period of time as possible. For this purpose the fibres will be embedded into proper matrixes that will protect them from undesirable environmental impacts. Bicomponent fibres consisting of a BioSteel® core and protective xylan coating for manufacture of fishnets are under development. It is expected that BioSteel® fibres, due to being extremely tough, will be also used for the manufacture of bullet-proof vests for military purposes.

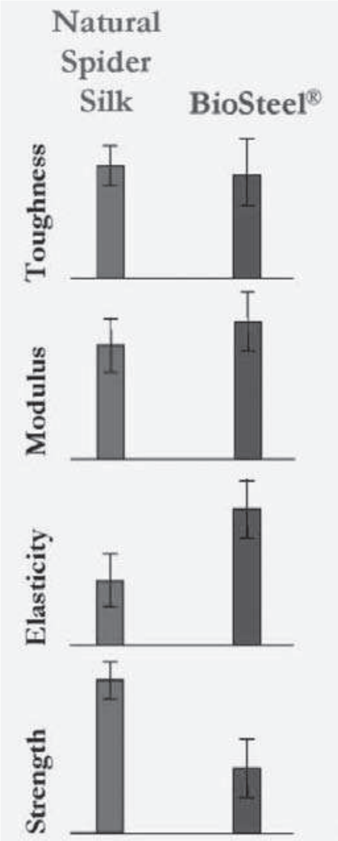

Figure 9: Natural spider silk properties in comparison to fibres BioSteel®

3.3 Triexta fibres from polytrimethylene terephthalate polymer Corterra® and Sorona®

The production of polyester fibres made of polytrimethylene terephthalate (PTT) started at the end of the 90s. Although the polymer was synthesized and patented already in 1941, its production was not possible due to expensive 1,3-propanediol, the basic raw material for PTT. At the end of the 90s Shell Chemicals developed the method for preparing qualitative 1,3-propanediol by continuous hydroformilation of ethylene oxide. The process is accomplished by the treatment with high pressure and at high temperature in a blend of ethylene oxide, hydrogen and carbon monoxide in solvent. The intermediate product 1,3-hydroxypropanol is converted into 1,3 propanediol (Bio-PDO) which gives the polytrimethylene terephthalate polymer during polycondensation with pure terphthalic acid (Figure 10). Polymer contains also 2.5–3% of low molecular oligomers among which the content of non-volatile cyclic dimmer is the highest. Shell Chemicals is currently producing PTT polymer and PTT fibres under the trademark name Corterra. Fibres are extruded from Corterra polymer by melt processing.

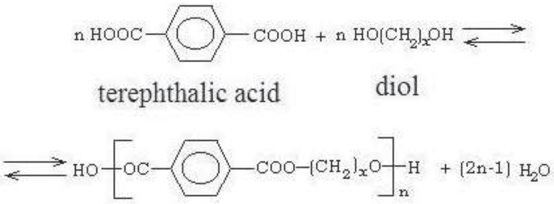

Figure 10: A polycondensation reaction for synthe sis polyester from terephthalic acid and diol:
Diol: x = 2 /ethylenediol/, x = 3 /1,3-propanediol/, x = 4 /1,4-butanediol/
Polyester: x = 2 /polyethyleneterephthalate (PET) or 2GT/, x = 3 /polythreemethyleneterephthalate (PTT) or 3GT/, x = 4 /polybuthyleneterephthalate (PBT) or 4GT.

Chemical resistance of Corterra fibres is similar to that of polyester fibres made of polyethylene terephthalate. They are dyed with disperse dyestuffs without carriers. Some properties are presented in Table 1 [19, 20].

Corterra fibres are produced as POY yarns; commercially available are smooth, textured, highly strong filament yarns and spinning materials. They are used for the manufacture of sportswear and recreational clothing, carpets, nonwovens for upholstery of furniture and cars. Products made of Corterra fibres are distinguished for their easy care, high stretch, softness, pleasant touch and brilliant colours. They combine good properties of PA 6 fibres (good elastic recovery, similar burning behaviour) and PET fibres (similar chemical resistance). Their good elastic properties make Corterra fibres suitable for the production of core spun yarns where they compete with elastane yarns (Lycra), because they develop elasticity at high temperatures, e.g. during dyeing.

DuPont is currently developing a PTT polymer and fibres under the trademark name Sorona. In 2003 it started to close the production of 1,3 propanediol (3GT) based on petrochemical raw materials (naphtha), and in 2004 it started to market 1,3 propanediol produced by using a biochemical method of cornstarch fermentation, similar to winemaking (Figure 11). DuPont has developed the biosynthesis of 1,3 propanediol in a long cooperation with Genencor International. A monomer has been protected under the trademark name Bio-PDO™.

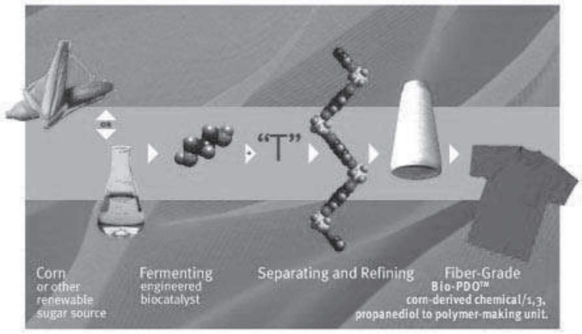

Figure 11: Biochemical synthesis of 1,3 propanediol - Bio-PDO™

Table 1: Comparison of properties of fibres from different polyester polymers: PET, PBT, PTT in bicomponent elasterell-p (elastomultiester) fibres.

Property	PTT	PET	PBT	T 400
Density of fibres (g/cm^3)	1.35	1.39	1.32	1.36
Density of amorphic regions (g/cm^3)		1.335	1.286	
Density of chrystallic regions (g/cm^3)		1.455	1.390	
Glass transition temperature (°C)	50	74	20–40	65
Melting point from DSC (°C)	228–230	253–255	221–226	229
Temperature of thermofixation (°C)	160	177–188	182–188	160–177
Dyeing temperature (°C)	100	125–130	100	100–130
Spec. tensile breaking stress (cN/dtex)	2.29	3.795	2.38	3.35
Breaking elongation (%)*	41	16,5	37	27
Elastic elongation (%)	27	21	28	37–68
Modulus of elasticity (cN/dtex)	13.24	42.36	16.42	35.3
Yarn crimp extension (%)**	246	213	233	275
Crimp form	irregular	irregular	irregular	regular, spiral
Yarn liveliness	twisting	twisting	twisting	stil

* elongation after decrimping

** Decrimping was measured by ASTM D1774 method: skein of linear density 5000 den was first treated at boiling to develop crimps. After that a linear density was measured at load of 2.5 g (L2.5). After cyclic loading of skein 3-times up to mass, that caused decrimping (up to 1030 g) the length of yarn was measured again (L1030). Crimpness = (L1030 – L2.5)/(L2.5)*100 (%).

Biochemical synthesis involves the use of microorganisms whose enzymes convert the cornstarch into 1,3-propanediol. In that case, the raw material for the synthesis of PTT is natural, renewable and no more dependent on naphtha [21].

In March 2009 Federal Trade Commision (USA) approved a new class of fibres with a generic name triexta fibres that are made from PTT polymer which base on BIO-PDO.

3.4 Polylactide fibres (PLA)

Polylactic acid is a natural, biodegradable organic substance, which is harboured in the bodies of animals, plants and microbes. Polylactic acid as such cannot be found in the nature but should be industrially prepared by lactic acid polymerisation. Lactic acid used for the synthesis of polylactic acid is derived from genetically altered corn grains (Figure 12). PLA is a thermoplastic polymer with the melting point at about 175°C. It is produced by Cargill Dow LLC (Nature Works®), Mitsui Toatsu Chemical (Lacea®), Shimadzu Chemical (Lacty®), Unitika (Terramac®).

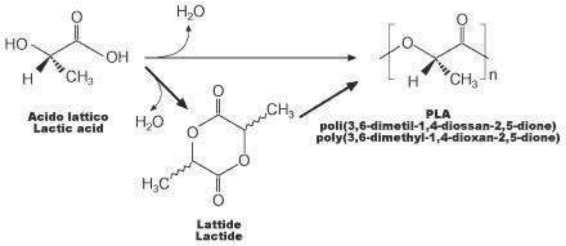

Figure 12: A synthesis of polylactic acid (PLA)

Cargill Dow LLC patented the production of fibres from PLA polymer in 1997 under the trademark name Ingeo^{TM} [22]. The fibres are currently produced by the Japanese company Toray and the American company Fiber Innovation Technology, Inc. (F.I.T.). Kanebo is producing PLA fibres under the trademark name Lactron® [23].

The fibres are produced by using the conventional melt-spinning method. They have round or profiled (trilobal) cross section, and high-to-medium lustre. The production includes also bicomponent fibres of the sheath/core type composed of synthetic polymer and PLA.

Physical properties of PLA fibres are similar to those of PA 6 and PES fibres. Their tensile strength is 45–55 cN/tex, elongation at break 20–35%, Young's modulus 7.5–9 GPa. At the 19% elongation their elastic recovery is 64%. Their contraction in boiling water is 8–15%, absorption of air moisture is about 80%. The melting point of PLA fibres is 175–180°C and the glass transition temperature 58°C. The density of fibres is 1.25–1.27 gcm^{-3} and their weight is lower than that of PES/PET fibres.

4 Intelligent fibres

Intelligent or smart fibres are the fibres made of special, stimuli-sensitive polymers or nanocapsules that react to the environment by changing their microstructure and properties. They react to the changes of temperature, mechanical force, light, concentration of electrolytes and pH as well as to the changes of the electric and magnetic field. Intelligent fibres help regulate body temperature or provide invisibility to IR detection, prevent staining of products, induce self-cleaning properties (e.g. floor coverings), prevent odour absorption, provide safety (e.g. during car driving), provide anti-ballistic protection, they are biologically active (bioactive), electro-conductive, etc.

Intelligent fibres are most frequently manufactured by coating fibres with polymers sensitive to external stimuli or by embedding such polymers into fibres by using the plasma process.

4.1 Fibres with PCMs (Phase Change Materials)

Most developed polymers, which recognize the environmental conditions, are sensitive to the change of temperature. At a certain temperature they undergo the process of phase change and are therefore classified as PCMs or Phase Change Materials. The potentials of the fibres containing PCMs are in the field of protection against cold and heat, sportswear, medical and hygienic products. The PCMs technology has been developed and patent protected by NASA. The use of PCMs in fibres was tested for the first time in 1987.

PCMs have superior capacity to absorb latent heat than fibres. The capacity of paraffin PCMs to absorb latent heat is about 200 kJ/kg without changing their temperature, whereas the temperature of 1 kg of standard fibres rises for 1 degree when only 1 kJ of latent heat is absorbed. With the absorption of heat, intermolecular links in PCMs break and PCMs convert into liquid state.

PCMs help to regulate body temperature by dynamic storing and releasing heat within the skin temperature range, i.e. from 29 to 35°C, through the changes of their aggregate state from solid to liquid phase and reversely from liquid to solid phase. We speak about various paraffin waxes: licosane, octadekane, heptadecane, hexadecane [24]. Fibres, textile materials and foams with embedded PCMs store the released body temperature and return it to the body as soon as the body needs it in dependence of its physical activity or outdoor temperature so that the body keeps constant body temperature all the time. The only fibres with embedded PCMs, which are commercially available, are PAN and PES fibres. Gateway Technologies Inc. has protected the PCMs technology. In most cases PCMs are spread over the surface of fibres (the protected trademark name Outlast) (Figure 13).

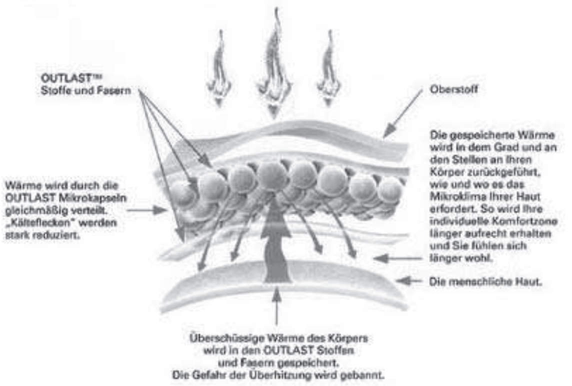

Figure 13: A cross-section of a textile phase change material (PCM) with a layer of Outlast in the middle

4.2 Shape Memory Fibres

Polymers, which change their shape in response to external stimuli (temperature, pH, etc.), are identified as SMPs (Shape Memory Polymers):

- Dimensional changes of some SMPs, such as poly-N-isopropylacrylamides (PNIPAAm), are induced by the change of temperature. At a certain balance temperature the polymer absorbs water from the environment and swells substantially, converts to gel and increases its dimensions. When the temperature rises, gel discharges water and shrinks.
- Ionic polycarboxyl polymers (PAA) with bound weak carboxyl groups sensitive to pH electrolytes are also classified as SMPs. When pH value is reduced, carboxyl groups lose their charge (bind hydrogen proton). Repulsion between polymers becomes less intensive which leads to shrinkage of gel (collapse). Addition of salt to the gel makes the effective distance of repulsive forces activity shorter the consequence of which is again the shrinkage of gel (collapse).

By using the existing technology, SMPs are spread over the surface of fibres as a film, which should not be damaged if we want to achieve good reversibility.

- Third generation of developed SMPs are polyethyleneglycols (PEG), which appear in a rubber-like state and never crystallize abundantly. Unlike PNIPAAm and PAA polymers, PEGs are, as a result of their elasticity, capable of withstanding tensions during swelling without any risk of surface cracks. PEGs applied on cotton, polyester or other fibres provide adaptation to a predefined temperature and reversible contraction of fibres or textiles.

The use of SMP materials for controlled delivery of drugs, food, perfumes and herbicides, for medical and hygienic textiles, such as baby diapers, healing underwear, which helps heal wounds, compression dressings, plasters, incontinence diapers, sanitary towels, socks, agrotextiles, etc. is under investigation. At contact with liquids (water, blood, etc.) SMPs shrink, e.g. SMP materials used as compression dressings shrink at contact with blood and bleeding stops [25].

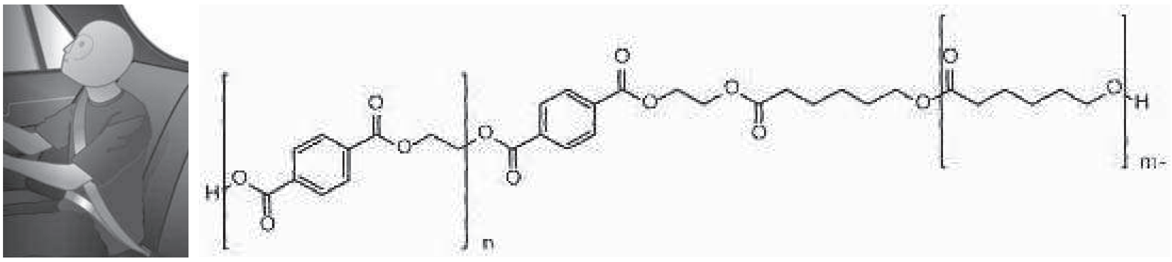

Figure 14: Intelligent fibres Securus for saftey belts and a blockcopolymer PET-PCL

It is expected that SMP fibres will be used for clothing which will not need ironing as they will revert, at the pre-programmed temperature, to their initial shape and dimension after having been stretched and subjected to deformations. The company European Space Agency has developed a shirt, which recovers from wrinkles at body temperature during wear [26].

Patented Securus fibres (Honeywell) [27, 28] also belong to the group of shape memory fibres. These fibres are the first high performance fibres with engineered properties of that kind. They are designed for car seat belts (Figure 14).

Securus fibres are block copolymer fibres made of polyethylene terephthalate and polycaprolactone (PET-PCL). They are extruded from a PET-PCL copolymer melt by using a special reactive extrusion technology. In addition to high strength and high Young's modulus, these fibres are capable to quickly absorb impacts. Seat belts made of Securus fibres can absorb 3 times more energy than currently used conventional seat belts. The "intelligent" reaction of Securus fibres provides that seat belts extend to a determined value within a pre-defined range of loading. Securus fibres deliver three-step restraint reaction to tension within the tension range 0–24 cN/tex or within 0–15% extension. At lower tensions to about 8.8 cN/tex (to about 2% extension) high Young's modulus of fibres enables that seat belt holds occupants tightly in position. This function of holding occupants in position is very important in a traffic collision as it triggers the seat belt locking mechanism. In this first step Securus fibres behave similarly as conventional polyester fibres. The second step represents the range of higher tensions from 8.8–13.2 cN/tex (2–9% extension) when Young's modulus of fibres is extremely reduced and enables balancing of load. In this stage an occupant's controlled forward movement is possible by which the force imposed on the occupant is reduced. In the third step in which the tension exceeds 13.2 cN/tex (above 9–15% extension) Young's modulus substantially increases and holds the occupant in position as long as the fibres succeed in absorbing the entire energy released at impact in a traffic collision.

The Securus seat belts with their programmed behaviour provide higher protection for occupants than conventional polyester seat belt restraint systems by minimizing the force exerted on an occupant's chest and also on the head of smaller persons and children.

4.3 Fibres sensitive to UV rays (chromic materials) and to X-rays

The group of colour active intelligent fibres involves the fibres, which change their colour reversibly in dependence of external conditions (chameleon fibres). These are the fibres, which change their colour, and the fibres, which become invisible. They can be sensitive to heat [29], light (visible or UV) and other electromagnetic radiations [30], electric energy, pressure and solvents or other liquids.

- Fibres that absorb visible light and change their colour accordingly contain specific organic dyestuffs (photochromic dyestuffs). The UV-sensitive spiropirane induces the fibre colour percentage phenomenon in dependence of the absorbed UV light wavelength.
- Fibres made from stainless steel that are coated with thermochromic ink, when connected to the power supply, can change their colour in dependence of the heat released by conductive fibres. Wall curtains, which are programmed to change the colour of the integrated conductive fibres, are the example of such use.
- Acordis Speciality Fibres has developed a PP multifilament yarn named Micropake, which is made from PP with the addition of a concentrate containing more than 60% of $BySO_4$. Fabrics made from Micropake are "visible" for X-rays. The yarn's properties are superior to those of PVC monofilament that has been used for this purpose so far.

4.4 Optical fibres

One of the applications of optical fibres is for optical sensors used to measure temperature, stress/strain, gases, biological substances and odours [31]. Since glass optical fibres are capable of transmitting light signals over long distances, they have been used for optical fibre cables in telecommunications for quite a long time. Organic polymer optical fibres are made from polymethylacrylate (commercially available for about 25 years), polystyrene and polycarbonates. They can be used for data transmission over short distances up to few ten metres and can be incorporated into clothing. Novel perfluoro polymers have low absorption capability and are as such suitable for making optical fibres for communication appliances [32].

The use of optical fibres in combination with electronics and information technology, which includes computers, telephone sets, etc. is connected with the development of intelligent textiles. Sensatex [33] was the first company, which manufactured and marketed "a smart T-shirt" (Figures 15, 16) with integrated organic polymer optical fibres connected to a processor. A smart T-shirt emits light in 256 colours in dependence of critical level of vital life functions – by measuring blood pressure, pulse, blood sugar, etc.

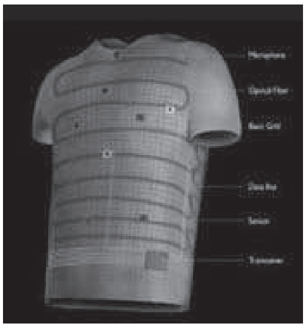

Figure 15: Smart shirt – scheme

Figure 16: Sensatex: a smart shirt

In order to achieve various colour effects, to transfer motion pictures on textiles, etc., light emitting diodes (LEDs) powered by unnoticeable batteries have been developed. Fibres are integrated into clothing together with microchips and switches [34]. At France Telecom such optical fibres were additionally perforated along the length so that they emit light over the entire length and not only at the ends.

The use of the mentioned organic polymer optical fibres in the field of technical textiles will pave the way for the development of sophisticated systems in which the information technology integrated into textile materials (floor coverings, automotive textile, curtains, etc.) will be less noticeable and more comfortable.

5 Auxetic fibres (negative Poisson's ratio fibres)

When axially stretched, fibres extend in lengthwise direction ($+\Delta l/l$) and contract in transversal direction ($-\Delta d/d$) at the same time. Poisson's ratio (μ) expresses the ratio of longitudinal strain to transversal strain. A classical elasticity theory of isotropic materials predicts the values of Poisson's ratio values from −1 to +0.5. Since the volume of fibres does not change or perhaps only slightly increases ($\Delta V \geq 0$) at stretching, the Poisson's ratio is less than 0.5, typically from +0.2 to +0.4 (Figure 17). Most fibres behave in this way when stretched. Only a small number of natural and synthetic materials exhibit the opposite phenomenon, which means that they become thicker when stretched and thinner when compressed (Figure 18). These materials have a negative Poisson's ratio. They are known under the name auxetic, anti-rubber or dilational (expanding) materials [35]. The word auxetic is derived from the Greek word auxesis meaning "increase". This term is used in biology to describe the cell volume enlargement at growth prior to its division.

Examples of auxetic materials can be found among polymers, metals and ceramics. Some natural ma-

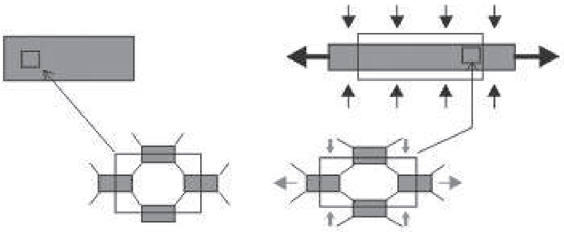

Figure 17: A model of stretching a fibre with a positive Poisson's ratio

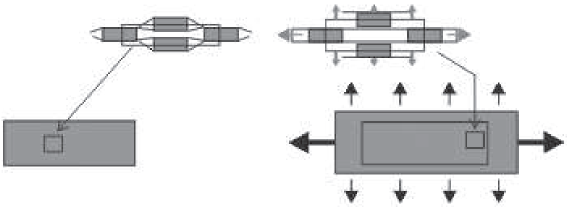

Figure 18: A model of stretching a fibre with a negative Poisson's ratio

terials have a negative Poisson's ratio at a molecular level. This untypical property has a significant influence on their mechanical properties, such as shear modulus, puncture and indentation resistance, impact resistance, thermal shocks and sound absorption.

In 1987 R.S.Lakes [36] manufactured the first synthetic material exhibiting a negative Poisson's ratio. By using high pressures, he succeeded in compressing standard polyurethane foam consisting of honeycomb-shaped air-filled hexagonal cells in such a way that it adopted "re-entrant" behaviour and was, when normally stretched, capable of extending to a certain extent even in transversal direction. The behaviour of such structure when stretched is presented in Figure 19.

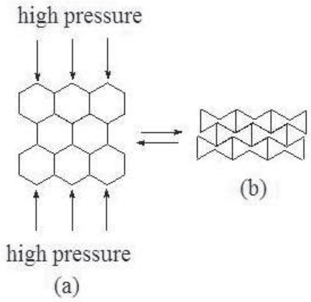

Figure 19: A model of hexagonal structure (a) that at high pressure lead to a structure with a negative Poisson's ratio (b)

In 1988 K.E.Evans found out that the thickness of conventional polytetrafluoroethylene (PTFE) film increased when stretched. It is the so-called nodule-fibril microstructure which, when stretched in the direction of fibrils, creates a lattice-like structure which expands also in transversal direction (Figure 20). Evans applied this model of microstructure to other polymers, including PE and PP [37, 38]. Scientists at the Bolton Institute produced auxetic fibres by using polyethylene of ultra high molecular weight (PE UHMW) in powder form. The process was based on conventional melt-spinning method but with novel processing conditions required to produce the nodule-fibril microstructure. After sintering, PE powder partially melted and gave rise to fibrillation. The obtained PP filaments have diameters to 1 mm and Young's modulus ranging between 0.2 and 2 GPa [39].

Figure 20: A model of nodule-fibril microstructure after Evans

The development of a continuous manufacturing process for such materials in fibrillar monofilament or multifilament form as well as fabrics woven or knitted from such materials, has created the opportunity to use unique properties of auxetic materials, such as pull-out resistance, toughness, energy absorption compression and indentation resistance, impact resistance, release of entrapped particles, wear resistance and microporosity. The fibres can be used for composites, protective clothing (helmets, jackets, sportswear), filters, for mechanical lungs (microporous hollow materials), ropes, cords, fishnets, upholstery, in biomedical industry, for medical bandages and fibrous seals.

6 Novel man-made protein fibres

6.1 Soybean fibres

Soybean fibres [40] (Figure 21) are the only commercially available man-man protein fibres. The raw material for soybean fibres is soybean proteins that remain after extraction of soybean oil and are produced by a novel bioengineering technology. Firstly, the protein globulin is distilled from the soybean cake and refined (about 400 kg of globulin are obtained from 1 tonne of soybeans) and, secondly, under the functioning of additional chemical reagents and biological enzymes, the globular and spherical structure changes in such a way that it can be processed into fibres. Fibres are extruded from the spinning solution confected from soybeans, by using the wet-spinning method. Cable-shaped regenerated fibres are stabilized by acetalizing in acid bath prior to being cut into short staples. Antibiotics (against

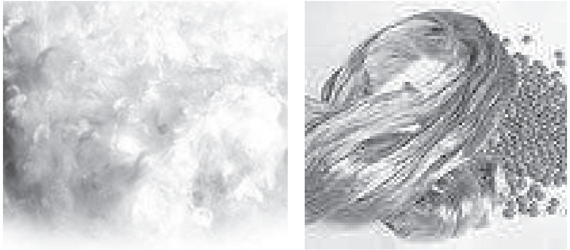

Figure 21: Soyabean protein fibres – raw (left) and bleached (right)

coli bacillus, staphylococcus aureus and candida albicans bacteria), anti inflammatory agents and UV protection agents are added during the spinning process.

The company Swicofil [41] is currently producing soybean fibres with length 38–76 mm and fineness 0.9–3 dtex. Their specific breaking tension in dry is 38–40 cN/tex, and in wet 25–30 cN/tex, elongation at break from 18 to 21%, elastic recovery 55%, density 1.29 g/cm^3. They have fine lustre.

At increased temperatures the properties of fibres substantially change. At 160°C their colour turns to light yellow and at 200° to intense yellow. With the rise of temperature, the fibres begin to carbonise at 300°C and become brown. As these changes occur at relatively low temperatures, the fibres must be treated and dyed at temperatures below 100°C. At the temperatures above 100°C the fibres become hard to the touch, however, washing in soap water at the temperature higher than 60°C makes them soft again.

In boiling water and hot air the fibres undergo contraction by 2.2%. Ironing of products made from soybean fibres is not necessary. Soybean fibres have good resistance to electrostatic charging which contributes to higher wear comfort of clothing. They have high UV-resistance. Soybean fibres can be used especially in the blends with cashmere fibres, silk, cotton, bamboo and elastane fibres. They are used for personal underwear and bed linen, shirts, evening dresses, children's clothing, towels and sportswear.

6.2 Feather fibres

Using bird's plumage, particularly that of turkeys and chickens, also means solving the problems related to by-products of food industry which arose after the BSE outbreak when processing of bird's plumage into stock forage was forbidden. Only in the USA, the production of bird's plumage amounts to about 1–2 million tonnes. Fibres from bird's plumage (Figures 22 and 23) are rich in keratin, highly crystalline, with good mechanical and thermal resistance. Turkey feathers give fine downy fibres and rough fibres. Downy fibres originating from the basal part of a feather quill shaft are about 40 mm long, their fineness is about 55 dtex, strength about 3 cN/tex and elongation at break about 17%. Rough fibres originate from the upper part of a feather quill shaft and are about 50 mm long, their fineness is about 140 dtex, strength about 7 cN/tex and elongation at break about 8%.

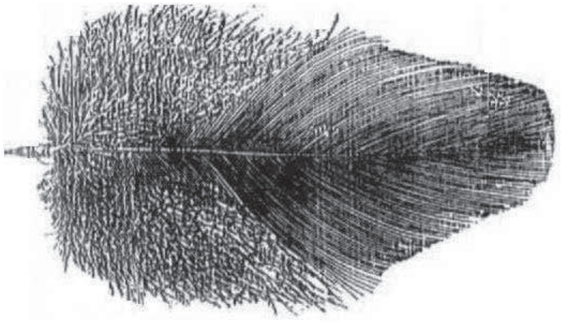

Figure 22: Turkey feather

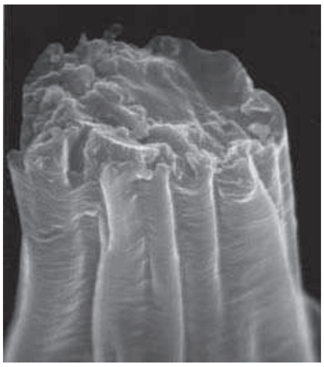

Figure 23: A magnified fibre taken from a turkey feather

Addition of 40% maximally of turkey feather fibres to other fibres improves heat insulation capacity of the products. So far the use of turkey feather fibres has been investigated in the blends with polyamide, polyester and cellulose fibres for heat insulators and for nonwovens used to reduce soil erosion [42]. The potentials of feather fibres are also in the field of absorption of heavy metals during the water and other systems cleaning process. Since the absorption of heavy metals depends on pH, proteins, as being amphoteric substances, are highly appropriate. The combination of nanofibrillar structure and active functional groups in bird feather fibres provides ideal biosorption capacities in technologically highly developed filters for absorption of heavy metals [43].

7 Polyester fibres with latent elasticity for stretch products

The development of latent-elasticity fibres, which are capable of developing outstanding elastic properties with recovery after elongation exceeding 100% during a finishing process (e.g. dyeing), has created the opportunity for novel applications. Their elasticity and elastic recovery rank the textured multifilament yarns made from these fibres among highly stretchable elastane fibres (EL) and less stretchable polyamide (PA) and polyester polyethylene terephthalate (PES/PET) textured yarns.

7.1 Polybuthylene terephthalate fibres (PBT)

Polybuthylene terephthalate (PBT) fibres are polyester fibres synthetized from terephthalic acid and 1,4 butanediol (butylene glycol). Polybuthylene terephthalate was synthetized for the first time in 1968. Absence of large side groups, flexibility of segments between benzene rings and regularity of chemical structure in the main chain provide good crystallization of molecules, so that PBT is considered a highly crystalline substance, which significantly affects its properties. Contrary to polyamides, PBT molecules are low-polar and absorb only a small amount of water. Longer exposure of PBT to hot water or steam leads to depolymerization of molecules. Due to high crystallinity, PBT has excellent chemical resistance to most organic solvents. It is also wear resistant. PBT fibres are wear resistant, they can be dyed at the boil without carriers, their colour -fastness is good, they do not change dimensions and are chlorine resistant even in wet. They excel at very soft touch, much better elasticity and elastic recovery than PA 6,6, Pa 6 and PES (PET). Elasticity of PBT yarn develops during treatments at higher temperatures, e.g. during dyeing. Some properties of PBT fibres are presented in Tables 1 and 2.

Despite high prices of raw materials and high production costs, which were higher than those of PET fibres, PBT fibres, due to their special properties (superior elasticity), were successfully used for floor coverings already in the 70s of the previous century. In Europe, the company Hoechst produced the PBT spinning material Boden Trevira® for yarns from which carpets and carpet runners with perfect elastic recovery were manufactured.

Today, PBT multifilament yarns are produced by Gruppo Bonazzi Aquafil, Trevira, Elite® yarn by Nylstar, Elastil® yarn by Miroglio Group, Elas-Ter® yarn by Teijin, etc.

The use of Elite® yarn is diverse: for underwear, swimwear, sportswear and recreation wear. In Japan, polybuthylene terephthalate fibres were used particularly for the manufacture of swimsuits and fine ladies' underwear. In the USA, the yarn was produced for stretch jeans and sportswear. Not long ago, Italian companies Miroglio and Montefibre started with the production of a modified PBT multifilament yarn Mirhon WE for sportswear (100%) and for the blends with polyester (PET), viscose, polyacrylonitrile fibres, cotton, flax and wool. In addition to high elasticity, the Mirhon WE yarn excels at good dyeability at the boil with disperse and also alkaline dyestuffs without carriers, at single-bath dyeing of PBT/PAN and PBT/WO blends and at achieving two-tone effects in PBT/PET blends [44].

7.2 Elasterell-p (USA) or elastomultiester (EU) fibres

Elasterell-p is the name of a new class of polyester fibres, which have high stretch properties in common. In 2002 they were classified by the US Federal Trade Commission as polyester fibres formed of two or more chemically distinct polymers (of which none exceeds 85% by weight) containing ester groups as the dominant functional units (at least 85% by weight in the total polymer content of fibre) and which, if stretched for at least 100%, quickly revert to their initial unstretched shape after the tension is removed [45]. In European Union these fibres are classified as elastomultiester fibres that is a new generic name formed by interaction of

two or more chemically distinct linear macromolecules in two or more distinct phases (of which none exceeds 85% by mass) which contains ester groups as dominant functional unit (at least 85%) and which after suitable treatment when stretched to one and half times its original length and released recovers rapidly and substantially to its initial length [46].

DuPont Textiles & Interiors (DTI), today DuPont INVISTA, has developed the first elasterell-p fibre T-400, previously named DP 0002. The fibre is marketed under the Lycra® brand. T-400 fibre is a bicomponent textile fibre made of polyethylene terephthalate (PET) and polybuthylene terephthalate (PBT). It differs from a pure PET fibre also in the degree of polymerisation and related properties as well as in helical crimp, which is induced by differences in the shrinkage of two distinct polymers present in a fibre. As a result of this phenom-

Table 2: Elastic elongation of the yarn T-400 in comparison to other polyester yarns.

Properties	T400	PES (PET)	PES (PBT)	PES (PET)/ elastane (91/9)
Yarn elastic elongation (%)	37	21	28	38
Fabric elongation (%)	23	10	9	21

enon, T-400 fibre is self-crimping, its stretch properties are not mechanically induced by texturing, it is inherently elastic. Its stretch properties are superior to those of textured polyester yarn with false twist from PET, PTT and PBT, which is under 35% (Table 1). T-400 yarn outstandingly preserves its stretch properties, which do not deteriorate with normal maintenance (washing, dry cleaning) as is the case with textured polyester yarns. According to DuPont, the stretch properties of T-400 have remained unchanged after repeated washing at 40 ± 5°C with water, detergent and a dose of chlorine bleaching agent, and drying at 65–70°C. They have softer touch than PET textured fibres.

A clothing is comfortable if the fabric provides at least 20% stretch. According to DuPont a highly comfortable product is manufactured from the yarn having the elastic elongation above 35% while the yarn with 28% elastic elongation (PBT) still does not impart high quality stretch to a product.

DuPont compared the elastic elongation of textured yarn made from PET, PBT and T-400 fibres with the yarn made from the combination of elastane and PET textured yarn (9% EL, 44 dtex, and 91% PET, 167 dtex) (Table 2).

8 Conclusion

The development of novel fibres is proceeding at a rapid pace. In many cases it is driven by the needs of a specific field of application, most frequently for military and aerospace purposes, for protective clothing as well as for top level and extreme sports.

The development of novel fibres is oriented toward multifunctionality, engineering of fibres with tailored properties, production of fibres based on renewable raw materials, ecologically clean production processes which do not additionally burden the environment, low energy consumption, recycling potentials and simple, above all biological degradation.

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