Bio-synthetic fibres*

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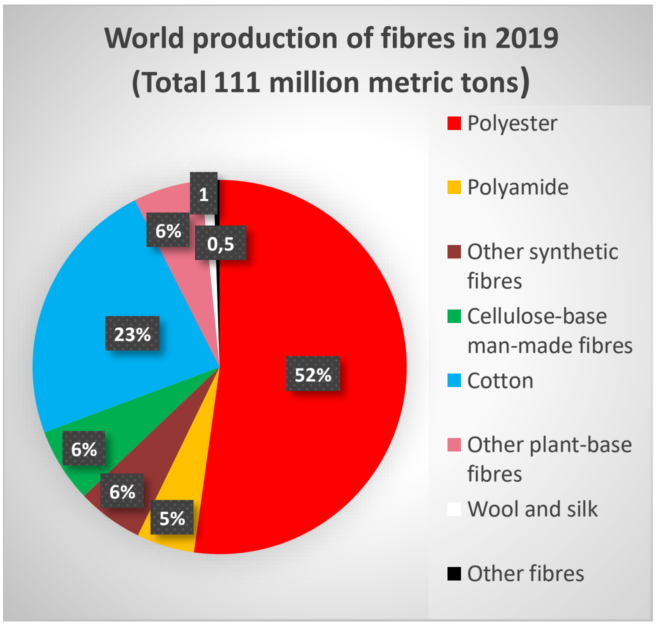
Synthetic fibre materials are produced and used in huge quantities around the world for clothing and non-clothing applications (in the form of furniture and household textiles, as well as technical and health applications). The huge importance of these fibres is shown by the fact that the total world production of fibres in 2019 (natural and man-made fibres combined) was 111 million tonnes, of which synthetic fibres accounted for 70 million tonnes, 63% of the total production.[1]

Synthetic fibre materials are nowadays usually produced from petroleum derivatives, simple organic compounds (monomers). From these, linear high molecular weight materials, polymer chain molecules, suitable for fibre formation, are produced chemically by polymerisation or poly-condensation. Fibre formation can take two forms. In one process, the polymer, which has been melted by heat, is pressed through tiny openings in the fibre-forming head and then stretched to a high elongation and solidified by cooling. Stretching causes the polymer chains that make up the fibres to arrange themselves, pair up in the direction of the fibre axis, forming bonds between them and thus gaining the desired strength. This is how, for example, polyamide and polyester fibres are made. In the other process, a suitable solvent is used to dissolve the polymeric material, and the fibres are formed by squeezing the liquid through small openings, which are then strengthened by evaporation of the solvent or by coagulation of the liquid jet in a precipitation bath, again with strong stretching. This process is used, for example, in the production of poly(acrylonitrile) and elastane fibres.[2]



The raw material for these fibre materials is fossil oil (the remains of plants and animals that decomposed in prehistoric times), which is in huge but dwindling supply around the world. Moreover, the extraction of petroleum and the production of the monomeric compounds that make up synthetic fibres is extremely energy-intensive and often polluting. Fibres and products made from fossil-based materials also have the disadvantage of being non-biodegradable or taking a very long time to degrade, and their non-recyclable waste is very polluting. Therefore, there is nowadays an increasing effort to develop processes that can produce the monomeric compounds needed for fibre production from other starting materials. Obviously, this is done by seeking as far as possible renewable sources in nature, which have been found in various plants, in particular maize, sugar beet, sugar cane, vegetable oils (e.g. soya, castor). Synthetic fibres made from these are called *bio-synthetic fibres*.

However, it should not be overlooked that these very plants also play a very important role in nutrition, they are the ones that fibre production has to compete with, and therefore other non-food materials, agricultural or forestry residues (from biomass), algae, fungi, bacteria are also used.

Unfortunately, only some of the bio-based synthetic materials are biodegradable (by living organisms, mostly microbes) in industrial composting facilities. Only about 40% of all currently produced biosynthetics are such – and unfortunately this does not include, for example, bio-polyester, bio-ethylene, bio-polyamide, i.e. the most commonly used types. These and the textiles made from them decompose over time by oxidative processes (a combination of sunlight and oxygen) into tiny particles at most, so they remain pollutants in the form of microplastics.

Promising results

One of the themes of the 7th Framework Programme announced by the European Commission is the development of bio-based synthetic textile fibres (bio-based elastane and polyester) by optimising industrial technology for the production of 100% bio-based chemicals from lignocellulosic raw materials (wood, plant residues, etc.): furfural, hydro-oxymethylfurfural (HMF), tetrahydrofuran (THF) and 2,5-furan-dicarboxylic acid (FDCA). The aim is to optimise the synthesis of furfural, which is a key phytochemical in the production of polyester and elastane fibres, to increase yields, reduce costs, recover solvents and acetic acid, upgrading cellulose to produce HMF and producing bio-carbon from lignin for in-plant combustion for thermal production. Furfural will be optimised for the synthesis of 100% bio-based THF, which accounts for 70% of the weight of the

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high elastic elastane fibre, and a new 100% bio-based polyester textile fibre will be developed from HMF.

Furan and certain furan derivatives such as furfural are used in the manufacture of plastics. Furfural is found in pine and beech tar, in bran and can also be produced from agricultural waste. It can be used in the production of bio-based polyester and elastane fibers. The development, called *EcoLASTANE*, is being carried out by a consortium of a French, a Spanish and a Czech chemical company, in collaboration with several research institutes, and is produced from ligneous cellulose. The promising trials have resulted in very high quality elastane and polyester fibres for textile pilot processing.[3,4,5].

Bio-synthetic polyesters

Polyester is the most widely produced synthetic fibre, accounting for about 52% of total fibre production, making it a very important material. Only about 1% of this is currently produced in the form of bio-polyester, but this is increasing.[6].

The conventional fossil-based polyester material is poly(ethylene terephthalate). Poly(trimethylene terephthalate) (PTT) and polylactic acid (PLA) are fibres with approximately similar properties.

For example, DuPont's *Sorona* polyester fibre is made from poly(trimethylene terephthalate), which is produced from 37% renewable plant material. The main component is 1,3-propanediol (PDO). While fibre-grade PDO is traditionally produced by petrochemical processing, DuPont has developed a new method for this. Glucose (sugar) is extracted from starches derived from corn or biomass and fermented by the addition of microorganisms. The result is PDA obtained by a naturally derived PDA, to which petroleum-based terephthalic acid (TFA) is added to produce the macromolecule needed to make the fibre. Sorona fibre is recommended for the production of clothing and furnishing textiles, including car upholstery. According to the manufacturer, its production requires 30% less energy consumption and produces 63% less greenhouse gas emissions than conventional polyester fibres.[7].

Ingeo, a product of NatureWorks LLC, is made from polylactic acid, which is produced from sugar beet, wheat, corn or other starch-containing plants. The starch (glucose) is extracted from the plant. Enzymes are added to convert the glucose by hydrolysis into dextrose, which is fermented by microorganisms into lactic acid. In the next process, the lactic acid molecules are converted into lactide rings and polymerized to form the long polylactide chain molecules, the material of Ingeo PLA.[8]

The Japanese company Toray markets its bio-polyester-type fibre material under the name *Ecodear PET*, which is produced by polymerisation and melt spinning of ethylene glycol extracted from sugarcane molasses and petroleum-derived terephthalic acid.[9]

The fibrous material known as *PLA* is made from polylactic acid and is at least 85% vegetable in origin: a material containing lactic acid ester obtained from sugar beet, wheat, maize or other starch-containing plants by converting starch into sugar and fermenting it. The fibre is produced by melt fibre formation. Its mechanical properties are similar to those of polyethylene and polyester. Chemically, it belongs to the polyester family. Its production requires about 65% less energy than petroleum-based synthetic fibres. It also has the advantage of being degradable in humid media and at temperatures above 60°C; it represents about 19% of degradable synthetic fibres and is therefore a significant source.[10,11,12] It is used in the production of textiles for housing, technical (e.g. furniture and car upholstery), health (bandages) and hygiene (e.g. nappies).

Toray is marketing its PLA fibre material under the *Ecodear PLA* brand, while Kanebo, also from Japan, is marketing its PLA fibre material under the *Lactron* brand.

Biosynthetic polyamides

Different types of polyamide fibres account for 5% of the world's total fibre production.[13]

Bio-polyamides are derived from vegetable fats or oils. Most of them are based on sebacic acid, except for polyamide 11, which is produced from aminoundecanoic acid obtained from castor oil. Sebacic acid-based polyamides are prepared by the stepwise polymerisation of a diacid with a diamine, for example hexamethylene-diamine containing 6 carbon atoms and decamethylenediamine containing 10 carbon atoms, to give polyamide 6.10 and polyamide 10.10. Polyamide 11 is prepared by first brominating the double bond of undecylenic acid containing 11 carbon atoms and then reacting with ammonia to give 11-aminoundecanoic acid, which is then polymerised to polyamide 11.

All three polyamides have excellent mechanical properties: high tensile strength, elasticity, toughness, abrasion resistance, good chemical resistance – valuable competitors to the well-known polyamide 6 and polyamide 6.6 fibres.[14]

Polyamide 6 (PA 6) is a very widely used fibre material. The biotech company Genomatica Inc. of California and the Italian fibre producer company Aquafil SpA have successfully completed the first pilot production of plant-based polyamide 6. They produced the first few tons of plant-based caprolactam, a monomer of the polyamide chain molecule, converted it into PA 6 polymer and started large-scale pilot production at Aquafil's plant in Slovenia to evaluate the product's behaviour and properties in apparel and carpet yarns.[15]

Rilsan brand polyamide 11, manufactured by Arkema, is produced from aminoundecanoic acid derived from castor oil. It is suitable for the production of both apparel and technical textiles. It stands out for its low density of 1.04 g/cm^3, good mechanical strength and excellent resistance to chemicals.[16]

Biosynthetic elastane fibre

The main property of polyurethane elastane, known as spandex in American English, is its high elastic elongation, which makes it suitable for replacing rubber threads in many applications.

Lycra, produced by Invista, is one of the best known types of elastane fibre. Its bio-based version is produced from a derivative of its main component, 1,4-butanediol (BDO), derived from corn.[17]

The bio-based elastane fibre, *Creora Bio-Based*, from the South Korean company Hyosung TNC, is said by the manufacturer to reduce carbon dioxide emissions by 23% and water consumption by 39% compared to conventional production methods.[18]

Fibres of chitin origin

Chitin is a long polymeric chain molecule that occurs in many places in nature: in the cell walls of fungi and as a sub-cellular constituent of the exoskeleton of arthropods (crustaceans, insects). In the fibre industry, chitin, derived mainly from the shell material of crustaceans, is used to produce chitosan by chemical means. This is the raw material for fibres. Chitosan is soluble in acetic acid and can be used to form fibres in the dissolved state, which are precipitated in sodium hydroxide. *Chitosan fibre* has strong antibacterial properties, good absorbency and, importantly, is biodegradable. On the downside, its strength is relatively poor, which limits its application potential. Therefore, it is mainly used in combination with other fibres, such as viscose, marketed as *Crabyon* by Swicofil, for the production of lightweight textiles for clothing, bedding, household, medical and cosmetic applications.[19]

Biosynthetic fibres from algae

Fibres produced from algae with a high cellulose content that grow in seas and lakes are biodegradable and can be easily dyed with natural-based pigments. They have the advantage of being available in large quantities and multiplying very rapidly. Dried and powdered seaweed (alginate) is used to form an aqueous gel into which a natural dye, such as insect carapaces, is mixed and from this coloured gel fibres are formed which can then be processed into textiles. These fibres are strong, flexible and flame-resistant, making them suitable for imitation leather, for example. When mixed with cotton, they are used to make underwear.[20, 21]

Casein fibres

The use of milk casein protein as a raw material for the production of textile fibres is not new, having been known since the 1930s. It was very popular in the 1930s and 1940s, but was later superseded by the spread of polyamide. It is produced by coagulating milk with acids and dissolving it in caustic soda to obtain a pulp suitable for fibre pulling, which is in fact a regenerated protein at the end of the post-treatment process. Its good absorbency and antimicrobial properties make it a preferred raw material for underwear and bedding. In recent years it has been reintroduced and, with the modernisation of the production process, is now produced under the name *Qmilk* by the German company Qmilch GmbH. It is made from milk that would otherwise be lost in the production and trade of dairy products.[22, 23]

Synthetic spider silk

Spider silk has excellent mechanical properties that rival those of steel and the para-aramide type Kevlar, while being much lighter. It has good heat resistance, is acid and alkali resistant, and has good medicinal properties (anti-haemorrhagic, promotes wound healing).

All these properties can be very important for technical and medical textiles, so it is understandable that a lot of scientific work is being done to produce spider silk synthetically, since „harvesting" natural spider silk in commercial quantities would be a hopeless undertaking.

The Japanese biotech company Spiber Inc. produces a spider silk fibre called *Brewed Protein*, a molecular structure fibre made from sugar beet and corn sugar and microbes, using fermentation.[24] The Californian company Bolt Threads' *Microsilk* fibre is also a craft spider silk, whose protein is produced by fermentation using yeast, sugar and water.[25] The Israeli company Seewix has genetically engineered a unique DNA sequence and uses a fermentation process using bacteria, sugar, yeast and water to produce a material that mimics the natural process of spider silk formation and its properties. The product is marketed under the name *SVX*.[26] The German institute Kraig Biocraft Laboratories has developed a silk-like fibre produced by genetically modified silkworms: the fibres are made from the protein of the silkworm, naturally produced by the silkworm, but derived from the silk. *Dragon Silk* is thus made from a unique combination of the silk protein of the silkworm and the silk protein of the silkworm.[27]

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