

# **Molecular Crystals and Liquid Crystals**



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# Quo vadis natural fibres in 21st century?

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#### **ABSTRACT**

The global production of natural fibres is evaluated at the level 35-40 million tons/year. It is expected that the global megatrends in population growth, prosperity growth, climate change and limited cotton supply, increase in fiber consumption will lead to a demand overhang for other cellulosic fibers, including new lately discovered natural fibres. There is fierce competition between natural and man-made fibres and also both types co-exist on markets mainly in terms of quality, sustainability and physiological influence in human body. The paper focuses on the novel trends in natural fibres processing and utilization, recently explored natural fibres and their potential.

#### **KEYWORDS**

Natural fibres; lignocellulosic fibres; protein fibres; textiles; non-textile applications; agro-fine-chemicals

## Introduction

Natural fibrous resources are valuable sources of lignocellulosic, protein and mineral fibres used not only in textiles [1, 2] but also in eco-friendly composites, nano fibres, nonwoven, geotextiles and their by products, but these resources also provide nutrients, food, animal feed, and added-value agro-fine-chemicals for cosmetics and pharmaceuticals.

The natural fibres are divided into several groups depending on the material they are derived from and classified as follows:

Bast fibres (flax, hemp, jute, kenaf, ramie) are extracted from stems, while leaf (sisal, abaca), seed (cotton, kapok), and fruit (coir, African palm, luffa) fibres are taken from other parts of plants, grass fibres (bamboo, totora) and wood fibres (hardwood and softwood) are extracted from different types of plants. There is also a wide group of animal fibers (wool, silk, hair), [3-6] and finally mineral fibers - asbestos, basalt, and volastonite - classification of natural fibers [7].

Fibrous plants have been known to humankind since around 7 000 BC. They can grow from Northern to Southern Arctic Circle. Different parts of lignocellulosic plants are valuable sources of fibres used in textiles and eco-friendly composites, nonwoven, and also sources of food, nutrients, animal feed, agro-fine-chemicals for cosmetics, pharmaceuticals and in other areas of application. Some of bast fibrous plants could be explored for reclaiming the soil polluted by heavy metals thanks to their ability to bind cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn).

Nowadays, an especially important advantage is that natural fibres and derived products are completely renewable, biodegradable and they recycle the carbon dioxide (CO<sub>2</sub>).

The lignocellulosic plants with high yield of lignocellulosic materials (like flax, hemp, kenaf, jute, ramie) can be also explored as source of energy by burning (combusting) or by transforming to bioethanol or biobuthanol [8, 9].

Special treatment and functionalization of the fibres, such as plasma, corona, mercerization, liquid ammonia, enzymatic and ultrasound (US) treatment, by applying dendrimers, and metal organic framework functionalization (MOF), nano-TiO<sub>2</sub>, protection against biodeterioration, transformation to nanofibres and super capacitors, provide new promising properties of the fibres, fabrics, nonwoven, geotextiles and also acoustic and 3D textiles [7–10].

Because of their natural elastic (e-) modulus, their lower mass in comparison to carbon and glass fibres, their UV protection most of natural fibres (including flax) have many advantages when compared to synthetic fibres [11].

Natural fibres, including lignocellulosic ones, have very important properties like: excellent air permeability, high hygroscopicity, high heat absorption, they do not release of substances harmful for health, they do not cause allergic reactions. They are also characterized with safer behaviour in flame and fire conditions as compared with man-made fibres [12, 13].

The new emerging method of genetic modification (GM) of the fibrous plants offers several opportunities for obtaining improved features of the fibres e.g. higher level of cellulose, or for creating polyhydroxy-alcanoate (PHA) and polyhydroxy butyrate (PHB), the latter two called natural polyesters [14].

The idea of novel fibrous plants containing nano-fibres is another alternative attracting considerable scientific attention. It is based on incorporating phosphate groups into cellulose in order to obtain modified cellulose with higher thermal resistance. Bio-silk, especially spider silk, fibres based on polylactic acid and other emerging new fibres for example based on fibroin and chitin are also very interesting directions in the area of natural fibres.

In 21st century the coexistence and competition between man-made and natural fibres is balanced in area of quality, sustainability and economy of their production. Natural fibres conduct heat, can be dyed well, can resist mildew action and have natural antibacterial properties, they block UV by nanolignin and it is easy to make them flame retardant [3–15]

They are ideal for the production of comfortable healthy clothing that provide UV protection for the body, decrease oxidative stress, increase the level of alpha-globulin in the body, thus improving the well being of users [12-16].

The facts mentioned above influence the position of natural fibres and stabilize their production levels thanks to the growing area of their applications.

Generally, natural fibres are miniature composites, formed from a 'reinforcement' of cellulose embedded in a 'matrix' of lignin and other polysaccharides e.g. hemicellulose. Cellulose molecules of lignocellulosic fibre have hydrophilic nature due to its hydroxyl group. It is worth emphasizing that pectin is a natural polymer present in plants, and like all natural polymers easily biodegrade [17].

New opportunities for bast fibres e.g. flax and hemp, apart from traditional orientation to textile applications in clothing and house goods, are created for technical applications.

The fibres offer unique advantages for eco-high-tech composite products – not only from ecological point of view, but also in purely technical terms [3–11].

In recent years textile materials have been used in various fields of economy other than apparel industry: space and aviation production, medical products, defence industry, automotive and transportation in general and other areas.

From niche material in the late 20th century, now in the 21st century, after improving technology and decreasing in the use of chemicals and water, and in the face of growing

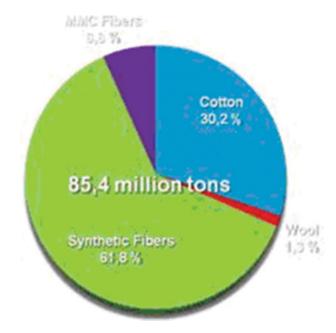


Figure 1. The global fiber market (Source: CIRFS, The Fiber Year, The Fiber Organon, Lenzing estimates).

environmental concerns, natural fibres have become a rediscovered products with stable perspective of use [13].

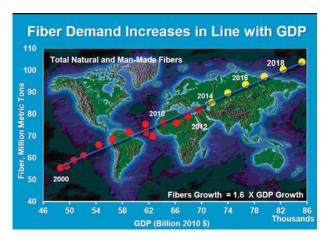
Recently, the American Chemical Society have announced that Cannabis Chemists have employed specialists conducting extractions and purification of hemp derived products. Now, representatives of 12 countries strongly support work in these areas development of novel products from hemp [18–21].

Production of natural fibres compared with other fibres is presented in Figure 1.

According to ICAC, CIFRS, The Fiber Year, The Fiber Organon, Lenzing the world fiber market with a volume of 89.4 million tons is dominated by oil-based synthetic fibers (a share of about 62.6%). Cellulosic fibers which consist of cotton with approximately 29.4% of volume and man-made cellulose fibers (approximately 6.7%) are coveted, high quality niche product, with partially better properties than cotton. The smallest share of the global fiber market had wool with approximately 1.3% of the total global fibre production [22].

Every 5 years, in the wide group of natural fibres and natural fibrous resources, more than 3 new types of natural fibers are discovered and investigated for their ability to yield fibres for industrial use. From 2012 to 2015 scientists described new cellulosic and protein fibres such as:

- **Screwpine** (*Pandanus utilis*) fibre, which is derived from leaves of a woody evergreen tree growing up to 20 m.
- **Snake plant** (*Sanseviera trifasciata*) produces fibres with the diameter of elementary fibre at  $10-26 \mu m$ .
- **Aibika** (*Abelmoschus manihot*) is the source of fibre with diameter of elementary fibre at 16–25 μm.
- **Kaori** (*Grewia Serrulata*) is another fibre yielding tree, a small one, with dainty, white flowers which bloom profusely. The tree is native to India.
- Yak (Bos grunniens) is an animal fibre with the diameter of coarse hair at 58.21  $\mu$ m, midtype fraction 36.52  $\mu$ m. [Results of INF&MP testing]



**Figure 2.** The world fibre demand with GDP (*Source: Ashish Pujari; Fibers: Capacity Explosion Hurting Growth Prospects; ITMF Annual Conference 2014; Beijing, P.R. China; IHS Singapore*).

Man-made cellulosic fibers should benefit from the cellulose deficit, resulting from limited cotton supply. Whereas the global fiber market is expected to expand by about 2.9% per year until the year 2020, the growth of the man-made cellulose fiber market is predicted by 9.1% per year. [CIRFS, The Fiber Year, The Fiber Organon, Lenzing estimates]

The world fibre demand is presented in Figure 2.

It will increase along with the gross domestic product (GDP) up to 2018.

The global population is growing and moving to urban regions, where cities are growing larger. Only in India and China there will be 265 million more urban residents by 2020. Investments in infrastructure will be required for urbanization in these regions. A growing middle class will want clothing like in western regions for different occasions (e.g. sports, work, and leisure). The demand for textile machinery will also increase.

Differences in per capita consumption worldwide are presented in Figure 3 (growth potential is observed especially in China & India) [22].

All market segments within textile industry are expected to grow, with the highest growth rate (absolute value and %) for technical textiles. Technical textiles are suitable for other industries and will substitute traditional materials as steel, cement and wood as they are. light weight, flexible, durable, cost effective, and multi-functional materials for application from building to transportation. New technologies with fewer manufacturing steps will improve cost efficiency of nonwovens compared to woven textiles [23].

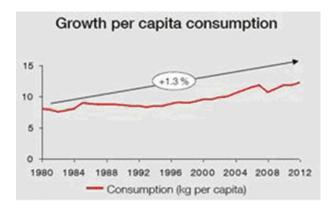
Some data about increase in production and share of technical textiles by 2030 is presented in Figure 4.

Lignocellulosic fibres can be described as composites made of three compounds.

The main chemical components of lignocellulosic fibres are: cellulose from 26% (e.g. bamboo) to 99% (e.g. cotton, ramie), lignin from 0.5% (flax, ramie) to 31% (bamboo) and pectin and hemicelluloses from 4% (henequen, nettle, cotton).

Fineness is connected with diameter of elementary fibre. For natural fibres it is between 2  $\mu m$  (spider silk) to - 50  $\mu m$  (lama, luffa cylindrical). Diameters of main representatives of natural fibres was presented by Ryszard Kozłowski *et al* [7].

Now, we are convinced that the fibres of the 21st century are: spider fibres, nanocellulosic fibres and fibres from carbon nanotubes, including bucky paper, and hollow basalt fibres which are applied for composite structure.



**Figure 3a.** Differences in per capita consumption worldwide (Source: *The Fiber Year 2013*; PCI World Synthetic fibers Supply/ Demand Report 2012; UN; Oerlikon: Analyst & Media Briefing OMF).

#### **Biosilk**

One of the new fibres is biosilk, production of which has just been announced. The fibre is made either from GM potatoes and as AMSilk is a registered trademark of biosilk in the European Union.

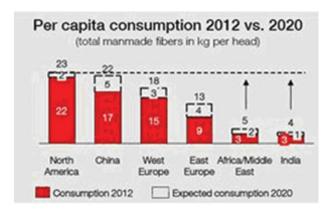
## **Carbon fibers**

The excellent carbon fiber properties will branch out into new markets and increasingly substitute traditional materials. Restricted to strategic applications like aviation, space and defense, new end-uses have emerged due to improved technical knowledge and higher availability.

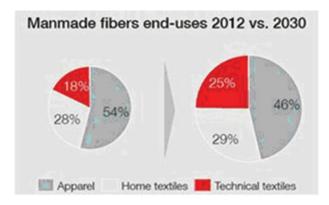
The most important factors determining the physical properties of carbon fiber are degree of carbonization and orientation of the layered carbon planes (the ribbons). Fibers are produced commercially with a wide range of variations in crystalline and amorphous contents.

## Corn-based PLA fiber

Polylactic acid (PLA) is a polymer similar to polyester that can be melt-spun into fiber for textiles, also by electrospinning. PLA is made from annually renewable resources and under



**Figure 3b.** Differences in per capita consumption worldwide (Source: *The Fiber Year 2013*; PCI World Synthetic fibers Supply/ Demand Report 2012; UN; Oerlikon: Analyst & Media Briefing OMF).



**Figure 4a.** Production and share of technical textiles by 2030 (Source: The Fiber Year 2013; PCI Dorbrin Conference 2011; Oerlikon: Analyst & Media Briefing OMF).

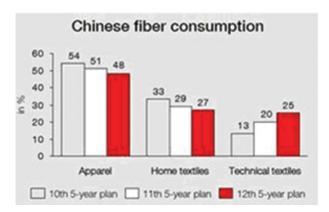
certain circumstances is biodegradable. The PLA used to produce textile fibers is typically derived from conventionally grown, commodity corn, and it will biodegrade only under ideal conditions in an industrial composting facility [24].

Polylactide is aliphatic polyester derived from lactic acid. It has similar mechanical properties to polyethylene terephthalate, but it has a significantly lower maximum continuous use temperature. PLA products can be recycled after use either by remelting and processing the material for the second time or by hydrolyzing to lactic acid, a basic chemical.

Corn is a versatile, natural, biodegradable and renewable resource that has many commercial applications from plastic containers to clean-burning ethanol. Chemical and biotechnological processes on corn have led to the development of a wide range of products, from polymers to biofuels and vitamins. In the past decade, numerous consumer products based on the results of research demonstrated the potential of bio-renewable sources being used instead of petroleum-based products [24].

# New generation of fibrous plant are obtained by genetic modification (GMO)

By genetic modification of plants it is possible to increase biomass and amount of oil from the seeds and leaves, to decrease lignin content in order to make the fiber more delicate and to



**Figure 4b.** Production and share of technical textiles by 203 (*Source: The Fiber Year 2013; PCI Dorbrin Conference 2011; Oerlikon: Analyst & Media Briefing OMF*).



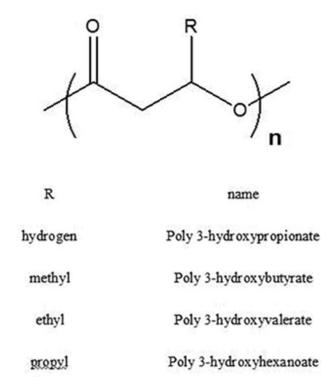


Figure 5. Polyhydroxyalkanoate polymers chemical formula.

facilitate degumming of fibre and to obtain more homogeneous fibres. GM cotton is resistant to pests and tolerant to Roundup [25].

# Biotechnological engineering also allows for the production of PHA and

PHB in statu nascendi in genetically engineered plants and sources for natural fibres.

• Oilseed crops like rapeseed, sunflower, soybean, linseed are also considered as good targets for seed-specific PHA (polyhydroxy alkanate) and PHB (poly(3-hydroxybutyrate) production. The other plants currently in use for PHA production are cotton and maize. Starch producing crops seem to be more advantageous than oil crops in terms of yield (kg/hectare). Yet, the diversion of acetyl-CoA towards PHB synthesis is likely to be more complex in starch crops. Advantages of PHA synthesis in fibrous plants, in order to modify properties of plant fibres, are linked the use of non-food crops (flax/linseed, hemp, cotton, kenaf) and them being a source of renewable and eco-friendly polymers for production plastic goods, packing foils, bottles, single-use products. The advantages of PHB (Polyhydroxybutyrate) also result from its high molecular weight (2 million g/mol), obtaining by bacterial fermentation of organic sources and its purity [26, 27].

Current trends trends in natural cellulosic fibres finishing processes include for example plasma treatment applied in bleaching, printing and dyeing and corona treatment, the latter is used mainly for improvement of hydrophylicity. Application of nano Ag and nano-TiO2 aims at stain removal, endowing the textiles with UV and other radiation barrier properties and with self-cleaning and bacteriostatic functions. Moreover, the fibres are treated for improvement of their fire retardancy and for protection against bio-deterioration protection. New methods of degumming have been developed, for example with the use of ultrasounds and



enzymes (bio-scouring). The fibres can be functionalized by reaction with polyoxometalate (e.g. molybdenum and cooper polyoxymetalate) and by dendrimers for improvement of dyeability, antibacterial effect, as special finishing of fibers and fabrics in biomedical applications and finally by metal-organic frameworks (MOFs) for application in special and military fabrics. Natural dyestuffs and liquid ammonia treatment are also used to natural fibres in modern processing for improvement of their properties [28].

# Biodeterioration of natural fibres and prevention against biodeterioration

Natural fibers, nonwovens and fabrics are susceptible to biodeterioration caused by microorganisms. Fungi and bacteria decompose lignocellulosic substances and reduce strength properties. Therefore antimicrobial finishing of natural textile products is necessary so that their area of applications can be braodedned to include medical materials, shoe lining, packaging products, non-wovens for insulation and goods for defense and military applications [29].

Protection of natural fibres against biodeterioration focuses on replacing old and not always environmentaly safe compounds with new more ecological ones. This is of special importance because of the REACH system introduced in EU, which specifies the principles of using chemical substances in order to increase environmental safety and eliminating health hazard. (New Regulation on Biocidal products, applies from 1st September 2013, replaces the former Directive 98/8/EC). The latest Biocidal Regulation (BR) states that from 1 September 2015 companies may only use marked biocidal products, if the respective product is included in the Article 95 (list for the products type to which the active substance belongs) [29].

More data about protection of natural fibres against biodeterioration are presented in the book Polymer Green Flame Retardants [30, 17].

Natural fibres should be considered not only for their technical parameters but also for their effect on human health and comfort, their effect on the environment, and last but not least social impact, especially in rural areas of the globe [13].

# Healthful aspects of clothing

Natural fibers still dominate among clothing types due to their comfort providing properties and positive physiological effect on human organism. Research confirmed that they reduce oxidative stress, do not cause allergic reactions, ensure high levels of alfa-globulin in body and excellent feeling. Therefore great majority of underwear and bedding textiles in the market are made of natural fibres [12].

#### Acoustic textiles

The use of textiles for noise reduction is based on two major advantages: low production costs and small specific gravity. As the recyclability is one of the main drivers for automotive industry, especially in Europe, a deeper insight has been given to natural, renewable resources. It is possible to design thin light weight textiles that can effectively replace the bulky materials traditionally used in the past. An acoustic textile must have acoustic properties in its own or it must be specifically engineered to absorb sound as light weight compact woven and nonwoven textiles that behave as porous screens [31].



#### Geotextiles

The main man-made polymer materials used to make geotextiles are polypropylene and polyester, but for some applications, natural fibers such as coir or jute are used [32].

Natural-fiber-based erosion-control geotextiles are subject to decomposition and have a limited useful life before their inherent durability suffers. Onsite use of natural-fiber blankets degraded in this way can result in an ineffectual installation [13].

Different fibers will degrade at different rates - for example, coir geotextiles degrade in two to three years, and jute in one to two years. Coir is therefore useful in situations where vegetation will take longer to establish, and jute is useful in low-rainfall areas because it absorbs more moisture.

The application of geotextiles is manifold. Used as reinforcements, filter and drainage elements or separation layers, they find employment in road construction [33].

There are diverse applications for woven geotextiles. In the form of sturdy geogrids, they are included in road construction. Geogrids are also widely used to reinforce asphalt.

Compared to traditional construction methods, the strong fibres are particularly beneficial in terms of their uncomplicated processing, what has a positive impact on budget [34].

### Cosmetic textiles

Cosmetic textiles is new sector which has commercially evolved in past decade.

Microencapsulation is the technology used in the manufacturing cosmetic textiles. This is a new concept of transfer or release of active cosmetic substance from clothing to the human body. The principle is achieved by imparting the cosmetic and pharmaceutical ingredients into the fabric of the clothing, so that with the natural movements of the body, the skin is slowly freshened and revitalized for a period of time [35].

Cognis is a Germany based company that developed a microencapsulation based cosmetic treatment for textiles known as Skintex \*. A series of products are marketed with moisturizing, cooling, energizing, relaxing, anti-heavy legs and mosquito repellent properties [36].

#### Nonwoven products

New applications of nonwoven include: solar, insulation and irrigation textiles, filter textiles and nonwovens protecting against flood, wind, heat, cold, erosion etc.

New nano, plasma and laser technologies are increasingly employed in nonwoven production and finishing. Today the percentage of man-made fibres in nonwovens is more than 85% worldwide. One of the newest development concerns spunlace nonwoven made from bast fibres e.g. flax which is extremely tear-resistant, durable and robust, with a relatively low production costs. This implementation of the new invention proves that there are more and more cases when natural fibres come back to the market. One of the examples is Norafin (France) that was successful in the commercial production of spunlace flax nonwovens (SFN) with varying surface mass, texture and finishes. Norafin has ventured into flax fiber processing and introduced the material into its hydroentangling process. For interior decoration SFN are transformed into slats for sunblind and shutters.

Hydrophobic-equipped SFN are an advantageous alternative to synthetically produced plastic membranes for roofing substructures [37].

Fiber	Density g/cm <sup>3</sup>	Tensile strength N/m <sup>2</sup>	Young's modulus GPa	Specific modulusGPa/g/cm <sup>3</sup>	Elongation to break%	Moisture absorption %
E-Glass	2.55	2400	73	29	3	_
Flax	1.40	800-1500	60-80	26-46	1.2-1.6	7
Hemp	1.48	550-900	70	47	1.6	8
Jute	1.46	400-800	10-30	7–21	1.8	12
Ramie	1.50	500	44	29	2	12-17
Coir	1.25	220	6	5	15-25	10
Sisal	1.33	600-700	38	29	2-3	11
Abaca	1.50	980	_	_	_	_
Cotton	1.51	400	12	8	3–10	8–25

**Table 1.** Mechanical properties of natural fibers compared to glass fiber [14].

# **Composites**

Composite is a material that contains at least two different components, clearly separated one from another and uniformly filling its volume, and produced in order to create particular properties.

Lignocellulosic natural fibres are excellent raw materials for production of a wide range of composites for different applications. Composite materials for lightweight construction and coatings are two areas of application with great potential [38].

The innovation in bio-based composites has been growing a lot for the last decade. It focuses on the use of natural fibers as reinforcement, on the development of increasingly biobased resins and finally on the interactions between the natural fibers and the matrix. The great advantage of bio-composites is biodegradability [39, 40].

Lignocellulosic natural fibres have not been fully exploited yet. New types of pre-forms are also needed in the world of composites, such as those made of "non-twist" fibres and sheets of unidirectional fibres that are not suitable for textiles, but are fundamental within that of composite. The vegetable world is full of examples where cells or groups of cells are 'designed' for strength and stiffness. Tensile strength depends strongly on the type of fibre, and its occurrence in a bundle or a single filament.

Main mechanical properties of natural fibers compared to glass fiber are presented in Table 1 [41].

# Agro —fine chemicals

Flax and hemp, as raw materials of bast fibrous plants, are rich sources of several valuable compounds including unsaturated fatty acids of omega-3 (alpha linolenic, stearidonic) and omega-6 (linoleic, gamma linolenic) groups. These plants also contain lignans that act as phytoestrogens, soluble fibre fraction found in mucilage in seeds, cyclolinopeptides, natural waxes, vitamins, mineral, squalene and essential oils [11–13].

#### **Conclusions**

Natural fibres, with their long history in the service of humankind, are finally gaining recognition as welcome and user-friendly materials, both in clothing and for other end uses. They are also carbon neutral: they absorb the same amount of carbon dioxide as they produce. During processing, they generate mainly organic wastes and, at the end of their life cycle, they are 100% biodegradable. Natural fibres are a renewable resource, par excellence. In the era of rising fossil fuel and energy prices, using annual plants to produce renewable bio-fibre materials makes economic and environmental sense. After a period of dynamic development for man-made fibres and of lowered production for natural fibres in the last decade, a more stable coexistence between both types of fibres may be observed now. In the 21st century research has opened new highly promising areas of applying natural fibres.

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