Composites: materials of the future

Part 8: Bio-based composites

Definition

Even if, at present, bio-based plastics are gaining importance, the bio-based composites available on the market are generally regarded as such thanks to the use of reinforcements made from plant fibres, with, in most cases, their remaining matrix made from fossil fuels. Nevertheless, with, most of the time, the matrix representing more than half the mass of the composite, the trend is the use of matrices that are also bio-based so as to move towards a "100% bio-based" composite. Somehow, as is often the case, humankind once again seeks to copy what nature has been doing very well for millions of years: wood!
Composites with bio-based reinforcements, as defined above, represented a volume of 362 kT in Europe in 2010, which constitutes about 15% of the total production of composites, estimated at 2.5 million tonnes. This percentage is expected to reach approximately 30% in 2020 out of a total volume of composites of around 3.2 million tonnes, with the new trend being to replace the petro-based matrix with increasingly large quantities of bio-based polymers.

The main factors pushing the rapid growth of these materials are well known:

- Limited fossil fuel resources that are increasingly expensive
- Sustainable development and concerns about climate change at the heart of changes in European regulations
- European re-industrialisation based in part on the development of the bio-economy
- Consumer demands for more accountability vis-à-vis sustainable development and environmental protection

The main factor limiting the development of bio-based materials and their market penetration is the performance/cost ratio that seems to be lower than materials derived from petrochemicals, which is due to products that are less mature. The lack of rigorous data on the life cycle of these materials is also hindering their development.

Types of fibres

As shown in Figure 1, there are a large number of types of fibres available on the market.

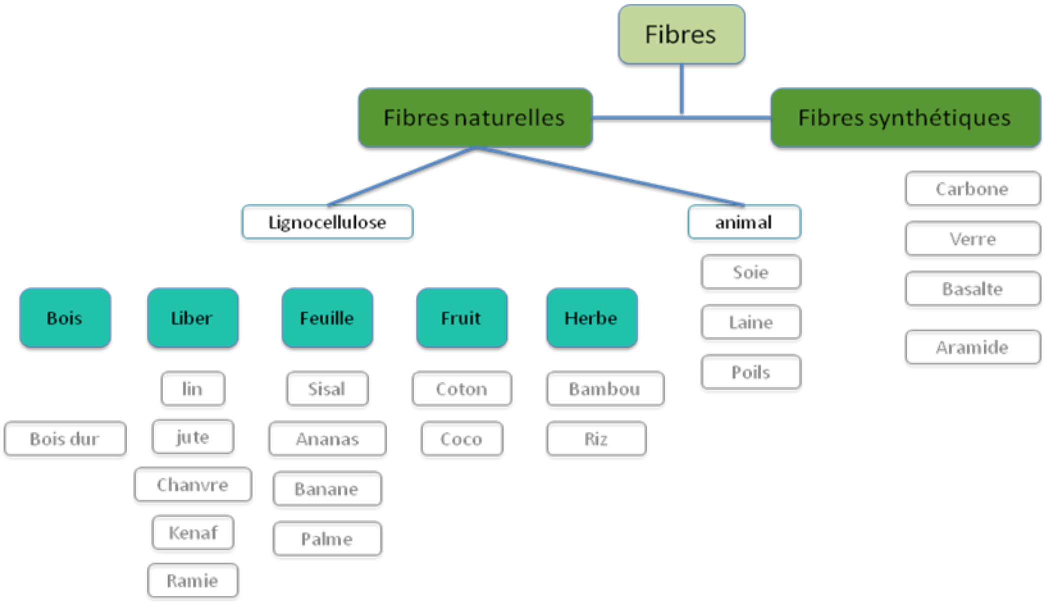


Figure 1 : Types of fibres available

Fibres fall into two main categories: synthetic fibres and natural fibres. The latter, leading to bio-based composites, can also be classified according to their origin: plant or animal. The main difference lies in their composition: Plant fibres are (mostly) composed of (ligno) cellulose and animal fibres are (mostly) composed of proteins.

A) Composition and Structure of plant fibres

Plant fibres are mainly composed of (ligno) cellulose, that is, cellulose (fig. 2), hemicellulose (fig. 3) and lignin (fig .4).

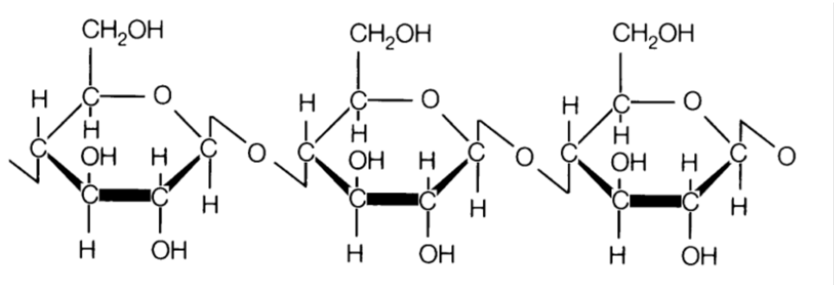


Fig. 2: chemical structure of cellulose.

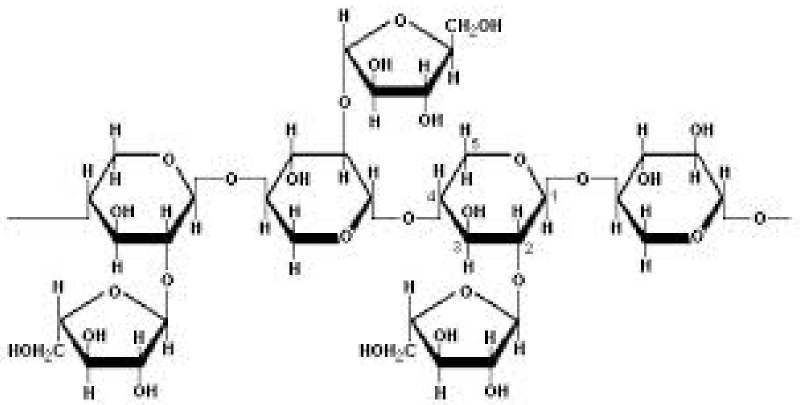


Fig. 3: chemical structure of a hemicellulose.

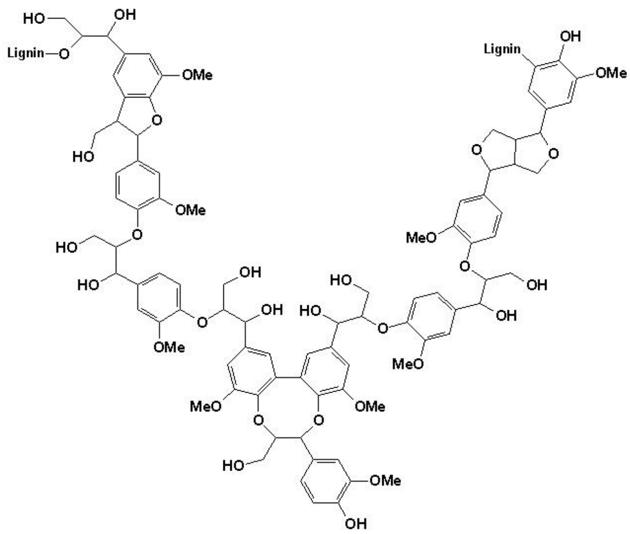


Fig. 4: chemical structure of lignin.

These macromolecules are present in all plant fibres, but in different proportions. Table 1 shows a series of plant fibres with their composition.

Fibres	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Banana	65	-	5
Coconut	43	0.15-0.25	45
Cotton	82.7	5.7	-
Flax	71	16.7	2
Hemp	78	17.9-22.4	0.6
Sisal ***(Henequen)***	60	28	8
Jute	63	12	11.7
Kenaf	50.5	-	17
Ramie	68.6	13.1	0.7
Sisal	70	12	12
Bamboo	60.8	-	32.2

Table 1 : composition of various plant fibres

The proportion of these various components gives each plant fibre its specific properties.

B) Composition and Structure of animal fibres

A family of animal fibres are protein-based; silk produced by the silkworm (*Bombyx mori*) is an example. It is predominantly composed (70% - 80%) of a high molecular weight protein called fibroin (fig.5) whose fibres are agglomerated by means of the other component, sericin (20% - 30%). It includes, in addition, some other minor components.Sericin is a protein with much lower molecular weight, mainly composed of serine.

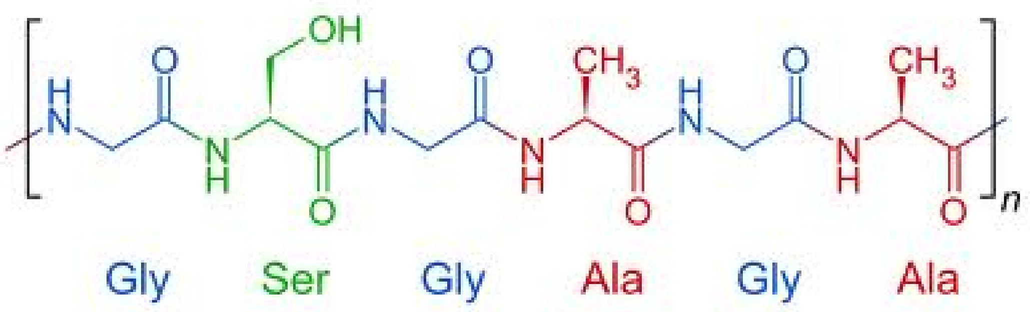


Fig. 5: Chemical structure of fibroin

It should also be noted that it is possible to extract the fibres of origin from the outer cuticle of some insects, fungi and yeasts, the shells of crustaceans or cephalopods[1] a chitin-based material, whose molecule structure (Fig. 6) is similar to cellulose.

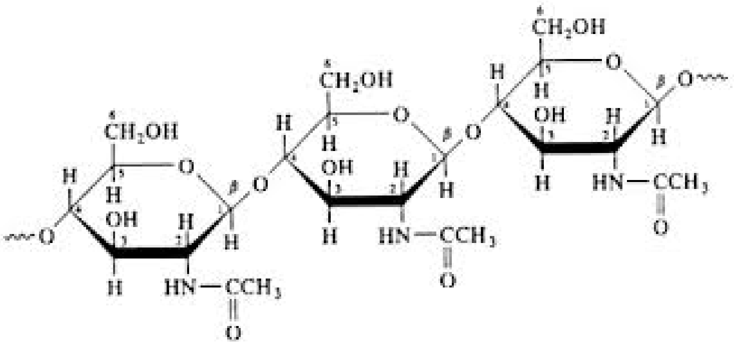


Fig. 6: Chemical structure of chitin

C) Influence of external parameters

An important parameter of plant and animal-based fibres is the variability of their compositions, therefore, to a certain extent, their properties, depending on external parameters such as climatic conditions, age of the plant or animal, etc. Humidity directly influences their properties at the time of use.

[1] Wikipedia

Constitution of plant fibres

The internal composition of plant fibres is complex (Fig. 7). They generally consist of, like wood, cells which contain microfibrils in their walls, which themselves consist of cellulose molecules. Microfibrils are nanofibres and much research aims to use them in nanocomposites.

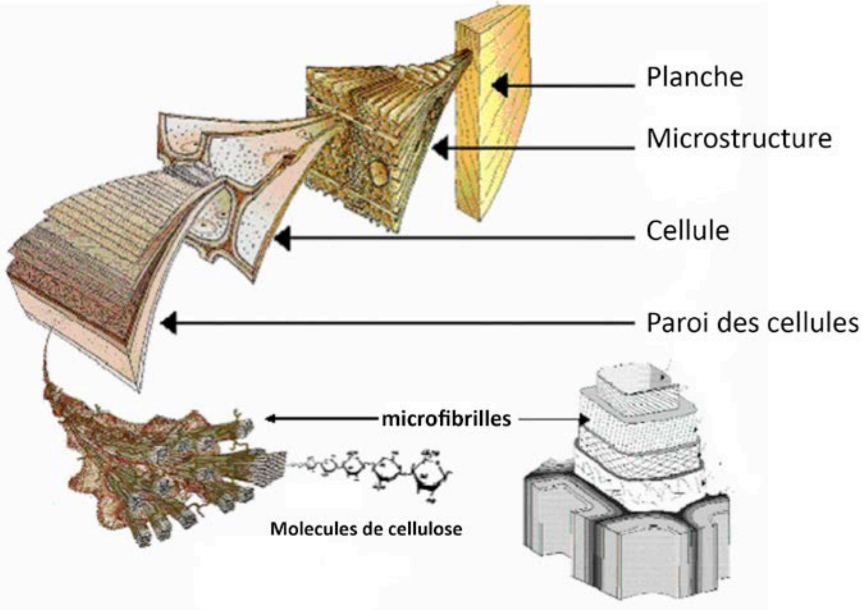


Fig. 7: Structure of wood, showing the cells and microfibrils.

Properties of natural fibres

The main mechanical properties of natural fibres are shown in table 2.

Material	Stiffness (GPa)	Strength (MPa)	Extensibility	Resilience (MJ/m3)
Silk	7 - 10	75 - 110	0.2 – 0.3	70
Wool (100% RH)	0.5	20	0.5	60
Flax	50 - 70	500-900	1.5 – 4.0	
Hemp	30 - 60	350 - 800	1.6 – 4.0	
Kenaf	25 - 50	400 - 700	1.7 – 2.1	
Jute	20 - 50	300 - 700	1.2 – 3.0	
Bamboo	30 - 50	500 - 740	~ 2.0	
Sisal	10 - 30	300 - 500	2.0 – 5.0	
Coconut	4.0 – 6.0	150 - 180	20 - 40	
cellulose nanofibrils	*140 - 220*[2]			

Table 2: Some properties of natural fibres

[2] Wikipedia

Thermal properties of natural fibres

One of the major problems with plant-based natural fibres is their limited temperature resistance. The TGA thermogram shown in Figure 8 shows that the cellulose degrades at temperatures above 250°C. Lignin degrades very significantly from 180°C. In fact, discolouration and loss of weight are also observed on cellulose from 200°C[3].

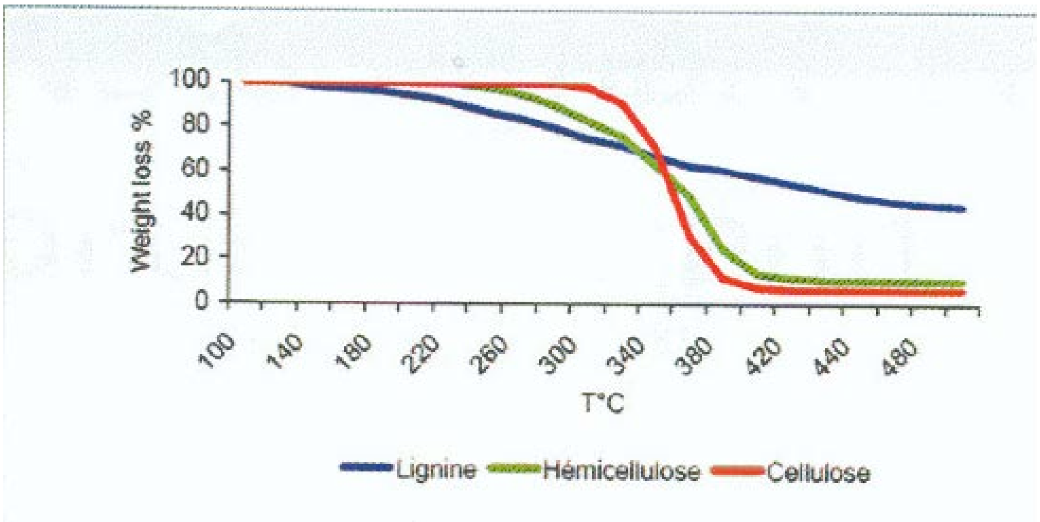


Fig. 8: TGA thermograms (weight loss) of plant fibre components

All plant fibres are heat sensitive. The most resistant are cotton, kenaf and hemp. The low resistance of plant fibres to any rise in temperature limits their use as reinforcements for thermoplastic matrix composites with low melting points (<200°C) like HDPE, PP and PLA.

Natural fibre-based composites

A) Composites with thermosetting matrices

As with all composites, one must distinguish between thermosetting matrix composites and thermoplastic matrix composites. It is obviously possible, and currently practised industrially, to strengthen conventional thermosetting resins, which are petroleum-based, by means of natural fibres, particularly, plant fibres. However, some techniques must be adapted. For example, it is not possible to obtain "rovings" of continuous natural fibres, such as is the case with synthetic fibres. Nonetheless, provided that their processing temperature does not exceed 150°C, "conventional" "epoxy", polyurethane or "polyester" type resins can be used.

However, a bottleneck is still observed as far as the availability of adequate, bio-based thermosetting resins is concerned. During the *"On the road to a bio-based economy*" event that was held on 27 October 2011 in Elewijt, Belgium, bio-based

[3]QUIEVY N., Melt processing and characterization of cellulose fibre based composites and nanocomposites, Thèse, Louvain-la-Neuve, 2010

thermosetting resins based on furan were presented. The furfuryl alcohol used to manufacture it is, in fact, 100% bio-based.

On the commercial side, a few years ago, SICOMIN already launched a range of GREENPOXY "green" resins[4] proclaimed to be more than 50% of plant origin.

In the race towards bio-based epoxy resins, the marketing of a bio-based epichlorohydrin (EPICEROL®)[5]is an important step.

Research is on-going to achieve mechanically effective epoxy resins based on epoxidized natural oils. Other studies aim to replace the styrene in polyester resins with bio-based resins, particularly *isosorbide*® based[6].

B) Composites with thermoplastic matrices

The main problem in producing composites with bio-based thermoplastic matrices is the resistance of natural fibres in the high-temperature processing step. PLA is interesting because it's commercially available and relatively inexpensive. Thermoplastic starch is also a bioplastic that can be selected as a natural fibre matrix because its processing temperature is low. These bio-based polymers often have inadequate mechanical properties and require reinforcement. Since they are semi-crystalline, reinforcing them with natural fibres is ideal because it increases the material's ratio of bio-based material.

Natural fibres have some advantages and problems to report:

Advantages during implementation: Natural fibres are not abrasive on extrusion screws or other metal parts.
Fibre/matrix adhesion problems: Compatibilizers are usually necessary considering the hydrophilic nature of the fibres and, in most cases, the hydrophobic nature of polymer.
Problems of bulk density: Natural fibres have a low bulk density and, therefore, have difficulty flowing into the processing machines' feed hoppers, thus requiring pre-granulation, when possible. .
Viscosity problems: Natural fibres increase the viscosity of the polymer
Odour problems: The degradation processes of plant fibres release odours depending on their nature and their preparation method as well as the processing temperature.

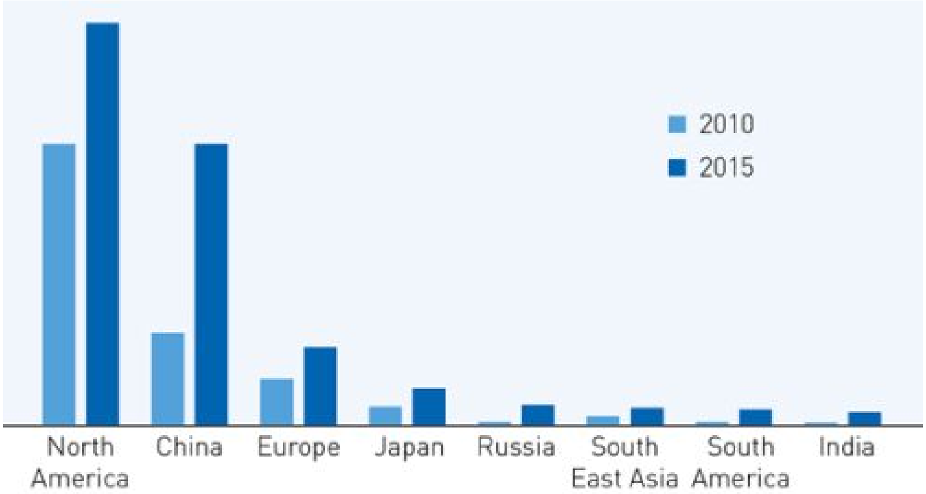
[4] http://www.sicomin.com/produits/systemes-epoxy/vert
[5] www.solvaychemicals.com
[6] www.roquette.fr

Wood Polymer Composites (WPC)[7]

WPC - wood polymer composites - continue to rise, especially in the USA and China, in the construction, automotive and injected products industries.

WPC have been on the market for over 30 years. In 2010, their global market reached 1.5 million tonnes of extruded WPC, which, at an average of 50% fibre, is 750,000 tonnes of wood, i.e. only a fraction of this material's market.

Other analyses suggest a total of 2.5 million tonnes WPC in 2012, all techniques taken together. China is experiencing the fastest growth (25% per year): it reached 900 000 t/year and is poised to dethrone the USA (1.1. million t) as the world's number one producer. In 2015, China will produce 33% of the global market. Southeast Asia, Russia, South America and India are emerging markets.



	2010	2015	growth % p.a	global share in 2015
North America	900000	1300000	8	48%
China	300000	900000	25	33%
Europe	150000	250000	11	9%
Japan	60000	120000	15	4%
Russia	10000	70000	48	3%
South East Asia	30000	55000	13	2%
South America	10000	50000	38	2%
India	5000	40000	52	1%
Total	1450000	2695000	13	103%

Fig. 9: WPC production worldwide (© *Nova Institute.eu 2013*)

Car interiors are a large consumer of natural fibre composites, including wood (38%) for the rear shelf, boot trim, spare wheel compartments, door interiors, etc. We can calculate that the average European passenger car contains 1.9 kg of wood fibres and 1.9 kg of other natural fibres. These 4 kg could rise to 20 kg in coming years.

[7] Partially taken from Techniline©, Sirris, 28/4/2014

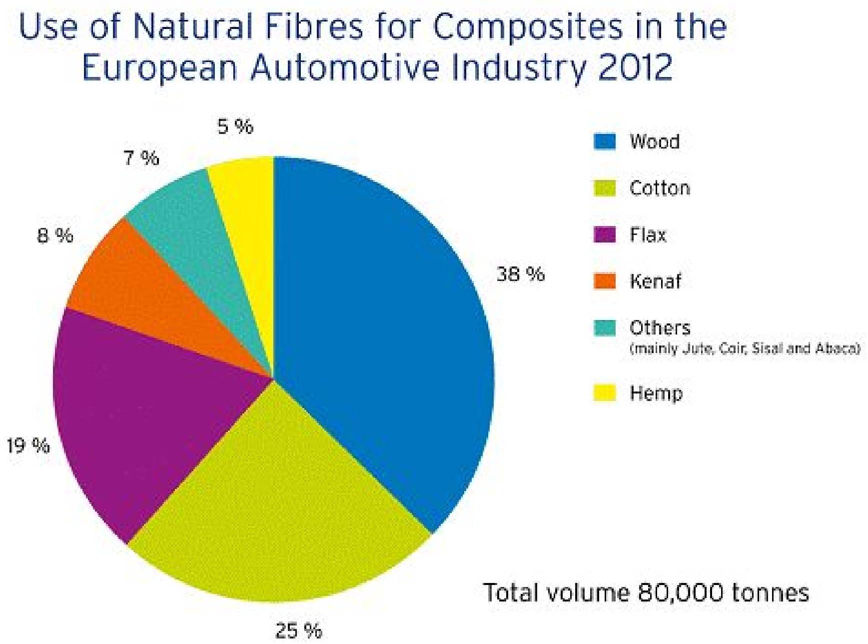


Fig 10 Use of natural fibres in the automotive industry (© Nova Institute.eu 2013)

The most commonly used materials are PE and PVC, but PP is also interesting, particularly in Europe and especially for injection moulding. Most WPC compounders are located in Germany. According to a study by Nova Institute, the total production of WPC in Europe was 260 000 t in 2012, of which 90 000 t were natural fibre composites (for the automotive industry).
Bioplastics play a minor role and are introduced only in niche applications. For 15 years, Tecnaro (DE) has offered lignin or PLA based WPC. Fasalex extrudes profiles containing starch for door frames in Austria. Ravensburger injects 100% organic compounds for toys.
The load is usually softwood, but rice hulls have priority in some regions such as China.

In conclusion, natural fibre composites have many advantages on mechanical, environmental and economic levels.

The use of bio-based matrices should, in the future, increase the durability of natural fibre based composites even more.