# Functional cellulose

**Cellulose is a natural polymer of glucose that is available in various forms and functionalities. A still larger variety of natural cellulose sources becomes available will new crops are grown and processed. These special functionality are still largely unexplored. The variety in functionalities can be further adjusted by chemical and/or biocatalytic modification, leading to potential new (high) added value applications.**

*Natural functionalities*

Cellulose is worldwide the most available natural polymer, occurring in the structural cell walls of all higher plants and some algae. Also some bacteria can produce cellulose[1]. Annually the natural production of cellulose is billions of tons and appears in a large variety.

Only a small part of the cellulose produced by nature is used by the existing industries as cellulosic fibre feedstock, in particular wood and fibre crops such as cotton, flax, jute and coconut.

Native cellulose-fibres are widely applied in papermaking, textiles, composites etc.

Cellulose is a complex polymer, that is available in a large variety of different qualitative properties depending on its origin and processing. Current applications are mostly based on largely available cellulose that was naturally present as lignocellulose in the 'load-bearing' parts of the plants (wood, flax, straw, hemp). Other widely used fibres are cotton cellulose, a pure cellulose that grows in a boll to protect the seeds of the cotton plant.

Cellulose produced by bacteria is chemically pure (free of lignin and hemicellulose) and exhibits a high level of crystallinity and high degree of polymerization, which is mainly used in medical applications.

The upcoming biobased and circular economy reveals a larger variety of more special cellulose sources that are available in smaller amounts, eg. citrus peels, beet pulp. These sources have functionalities that are quite often still unexplored.

*Table 1 Overview of the most relevant properties of native cellulosic fibres*

| **Composition of the fibres** | **Fibre Dimensions** | **Cellulose properties** | **Cellulose Quality parameters** |
|---|---|---|---|
| • Polysaccharides<br>• Cellulose<br>• Hemicellulose<br>• Pectins<br>• Lignin<br>• Other plant components (e.g. proteins) | • Fibre length<br>• Diameter<br>• Lumen<br>• Cell wall thickness<br>• Morphology | • Cellulose fibre strength properties<br>• Microfibril orientation<br>• Density<br>• Polymerisation degree<br>• Molecular mass distribution<br>• Swelling<br>• Solubility in alkali / ionic liquids | • Purity<br>• Degree of Polymerisation<br>• Crystallinity / amorphous phase |

[1] On nutrient media containing glucose.

| | | | |
|---|---|---|---|
| | | • Flexibility | |

*Cellulose functionalisation*

Chemical and/or biocatalytic modification of natural cellulose can lead to further differentiation in functionalities. Modified cellulose based on wood or cotton cellulose has already been on the market for a long time for both plastic and non-plastic applications. It was used as a basis for polymer production starting in the 19th century e.g. for films and fibres (cellulose acetate, cellulose hydrate). Esterification of cellulose (cellulose acetate, propionate and butyrate, and mixes thereof) was performed to make cellulose dissolvable or fusible , so that it becomes suitable for thermoplastic processing. Quite some cellulose applications were replaced by low cost petrochemical-based plastics, as cellulose modification until now was costly, requiring harsh and quite often less sustainable processing conditions. Although there have been improvements recently in regenerated cellulose technology (e.g. Lyocell, Celsol, Modal), cellulosics still only finds applications in niche (high-end, low volume) markets.

Cellulose is also derivatised to deliver more commodity type of polymers that are used as a natural structuring agent[2] in foods, laundry, human health care, paints, home and personal care (emulsions, foam, thickener)., like CMC (carboxymethylcellulose), EHEC (ethyl hydroxyethylcellulose) and MEHEC (methyl ethyl hydroxyethylcellulose). Also cationic cellulose is being produced at large scale.

**Future opportunities in fibre functionalities**

Due to the recent increasing public awareness on climate change and environmental issues, as well as concerns regarding the depletion of fossil fuel resources, cellulose products have started to regain market attention due to their renewable and natural origin.

Many of the recent cellulose-based innovations break down natural cellulose fibres into smaller building blocks, such as glucose, alcohols and acids, and then rebuild to synthesize polymeric materials. These polymerscan be spun into fibres, though with other properties compared to the natural fibres. In fact, old functionality is destroyed and new functionality is created in new polymers. When the natural fibre structure could be retained and functionalised at low costs and low environmental impact, the options for new sustainable ànd economically attractive biobased materials will increase significantly.

The underlying initiative aims for the sustainable production of functionalized cellulosic fibres with low consumption of energy and water, low environmental impact (non-toxic chemicals, green solvents), at low cost, exhibiting multi(functional) properties in high end (high value) market applications (unmet needs).

*How?*

In essence, the structure of the cellulosic fibres is to be retained (remains intact). Either we search for and make use of the natural available functionality in special cellulose sources. Or we use the presence of the available functional groups in regular cellulose to allow modification to introduce

[2] As a result of its surfactant properties (emulsions in water and oil).

new functional groups, either via a chemical or biocatalytic[3] process, in a controlled way. For a successful market introduction it is of course also important to identify the market opportunities of these cellulosic materials and companies willing to produce and commercialize these new functionalized cellulosic fibres.

A lot of research is already being conducted into sustainable processes for cellulose processing and valorisation, as well as into further functionalisation, either by chemical treatment (to produce e.g esters or ethers) or by surface modification such as metallization or coating. Moreover, the innovation potential has increased enormously as a result of toolbox development in both the chemo- and bio-catalytic synthesis . Especially the latter development enables the (regioselective) introduction of functional groups. Quite some progress has been booked in the functionalization of polyhydroxyalkanoates and polysaccharides (such as starch, chitin and chitosan) and animal and vegetable proteins (such as casein and gelatin). It is believed that the used approaches in functionalization of polysaccharides and proteins may also be applicable for cellulose. Bacterial cellulose is a well-defined polymer and would be the preferred candidate for such future developments, but also other pure (purified) cellulose varieties could be interesting candidates.

**The activities**

Three main activities can be distinguished

1. Identification of special sources of cellulose from (waste) streams from agriculture, forestry or food processing industry, e.g. sugar beet pulp, soya, fruits, vegetables, tea leaves, potato peels, tomatoes, hop, grains, corn, used malt[4];
2. Functionalization of cellulosic polymers (starting with well-defined cellulose as raw material), Examples are:
   - Controlled introduction of hydrophobic and hydrophilic domains (e.g. controlled hydrophilicity as function of temperature);
   - Crosslinking cellulose polymers or oligomers to created new 3-dimensional structures with enhanced functionality.
   - Controlled introduction of hard and soft segments enabling a change in topology; under the influence of an external trigger (e.g. by controlled crystallization of blocks).
3. Identification of market needs, followed by application development and creating market opportunities. How to sustainably synthesize functionalized cellulose-based materials, fine-tuned for specific applications? Establishing the structure-property relationship is key in developing these smart (high performance) materials obtained by functionalization of cellulosic fibres.
   - Possible applications: switchable surfaces, controlled change of surface roughness (as a function of temperature); self-healing coatings; responsive materials (like sensors) via

[3] Via enzymatic or fermentative processes.
[4] Lignified cellulose (lignocellulose) needs to be treated to remove the lignin, hemicellulose and potentially pect in and protein to obtain the cellulose fibre

controlled shape change by an external trigger, such as light, electricity, pH, temperature; membranes by controlled (switchable) permeability change.[5]

With many different existing types of cellulosic fibres and combined with a range of possibilities to functionalize, a range of new high performance and high value cellulose-based materials can be designed.

**What are next steps?**

Propose the approach for drafting a work program/project proposal:

- Who? Identify potential partners in the value chain, Identify a project/problem owner
- What? Smart aim of the project
- When? Timeline.
- Where? NL or EU or WW?

5 In composites, the traditional reinforcing glass and carbon fibres can be substituted by natural fibres, such as cotton fibres. This application is not within the scope of this paper.

**Glossary**

**Dissolving pulp** is a bleached wood pulp that has a high cellulose content;

**Viscose** is a solution of cellulose xanthate made by treating dissolving pulp with aqueous sodium hydroxide and carbon disulfide.

**Cellophane** is a transparent film that is obtained from a viscose solution, by extruding it through a slit into a bath of dilute sulfuric acid and sodium sulfate to reconvert the viscose into cellulose.

**Rayon** is a fiber of regenerated cellulose; it is structurally similar to cotton. Like cellophane rayon is also produced from a viscose solution, but by using a hole (spinneret) instead of a slit. Rayon is applied a.o. in tires.

The polluting effects of carbon disulfide and other by-products of the process used to make viscose have contributed to a decreasing sales of viscose-based produced. Though, cellophane and rayon itself are 100% biodegradable.

**Lyocell** is produced from cellulose that is dissolved in N-methylmorpholine N-oxide. The cellulose solution is then pumped through holes (spinnerets) to produce fibres. 98% of the amine oxide is typically recovered, making this process is relatively eco-friendly. However, it uses a substantial amount of energy, and uses an organic solvent of petrochemical origin. Lyyocell is commonly sold under the brand name Tencel®, which is made by Lenzing AG. Lyocell is more expensive to produce than cotton or viscose rayon.