Unit - Chemistry of Garments: Cellulose Fibres

For some background material see the Free Text book
The Basics of General, Organic, and Biological Chemistry by David W. Ball, John W. Hill, Rhonda J. Scott.
Chapter 16, section 7

Polysaccharides

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as homopolymers because each yields only one type of monosaccharide (glucose) upon complete hydrolysis.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. (Irish) Potatoes are often considered as a "starchy" food, yet other plants contain a much higher percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%-8% by weight of tissue) and in skeletal muscle cells (0.5%-1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

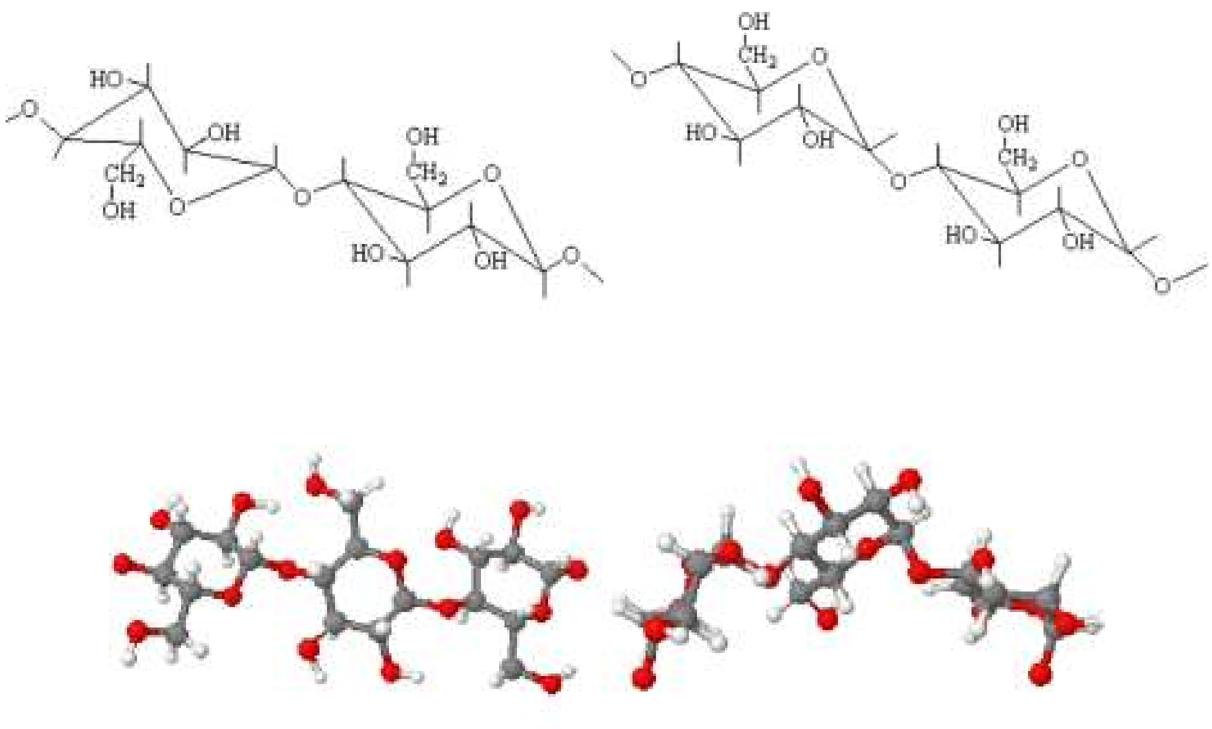
Note.
About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%-20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Cellulose and starch are based on the same monomeric unit (D-glucose). The properties of these polysaccharides however are very different.

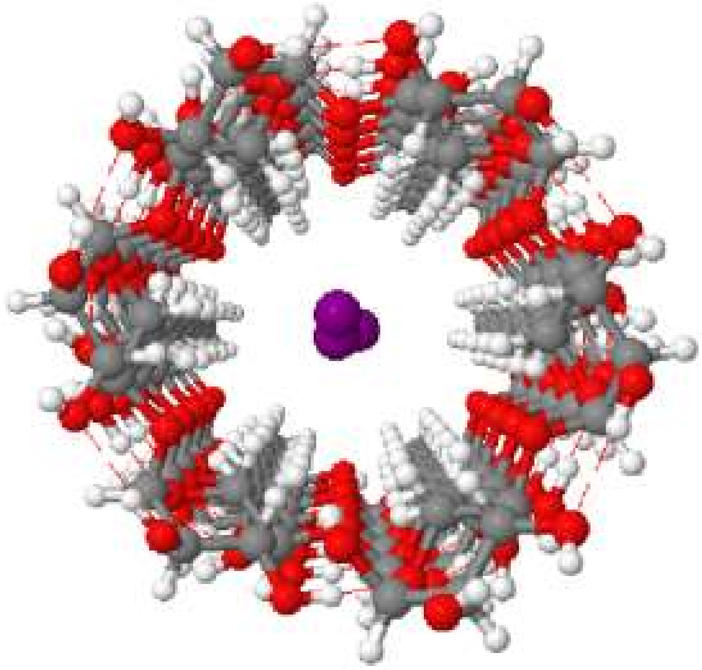
- The orientation of the 1,4-glycosidic linkages is beta and alpha respectively between the repeating glucose units. For cellulose, this results in the neighbouring units being rotated by 180° with respect to each other and produces a long, straight, rigid molecule.
- There are no side chains in cellulose as there are in starch. The absence of side chains allows these linear molecules to lie close together.
- The presence of the -OH groups, as well as the oxygen atom in the ring, provides many opportunities for hydrogen bonds to form between adjacent chains. These hold the chains firmly together side-by-side to form microfibrils with high tensile strength. This strength is important in plant cell walls, where the microfibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells.



beta and alpha 1,4- links between glucose units in cellulose and starch

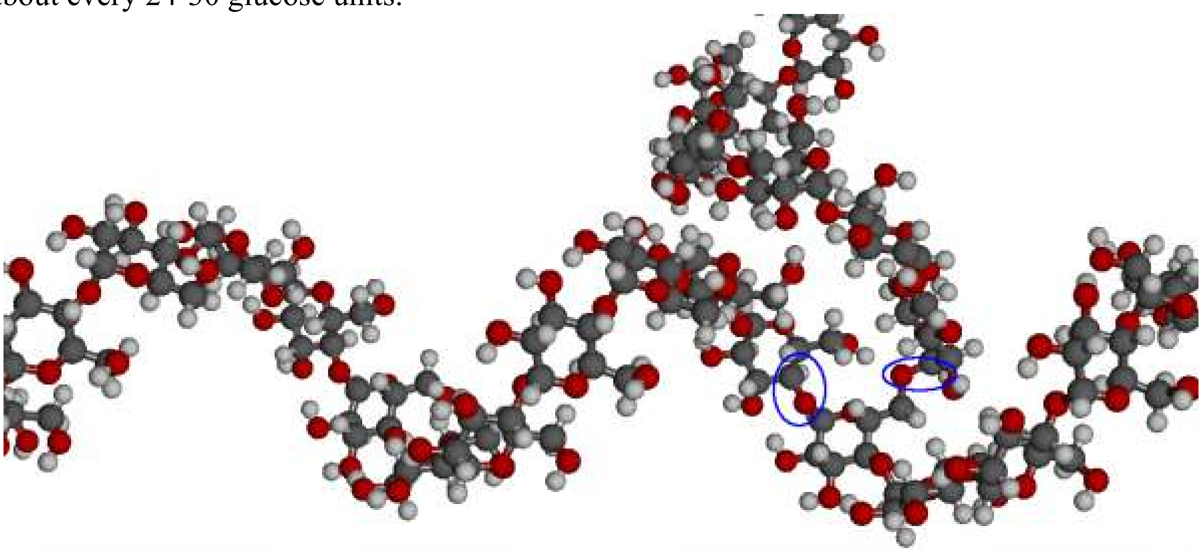
The resulting polymeric structures are such that cellulose gives rise to linear arrangements while starch is non-linear and branched.

Natural starches are a mixture of two polymers: amylose (10%-30%) and amylopectin (70%-90%). Amylose is not branched and is coiled like a spring, with six glucose monomers per turn. When coiled in this fashion, amylose has sufficient room in its core to accommodate the tri-iodide ion. The characteristic blue-violet colour that appears when starch is treated with iodine is due to the formation of the amylose-tri-iodide complex. This colour test is sensitive enough to detect even minute amounts of starch in solution.



tri-iodide ions inside coils of glucose in amylose, see BioTopics

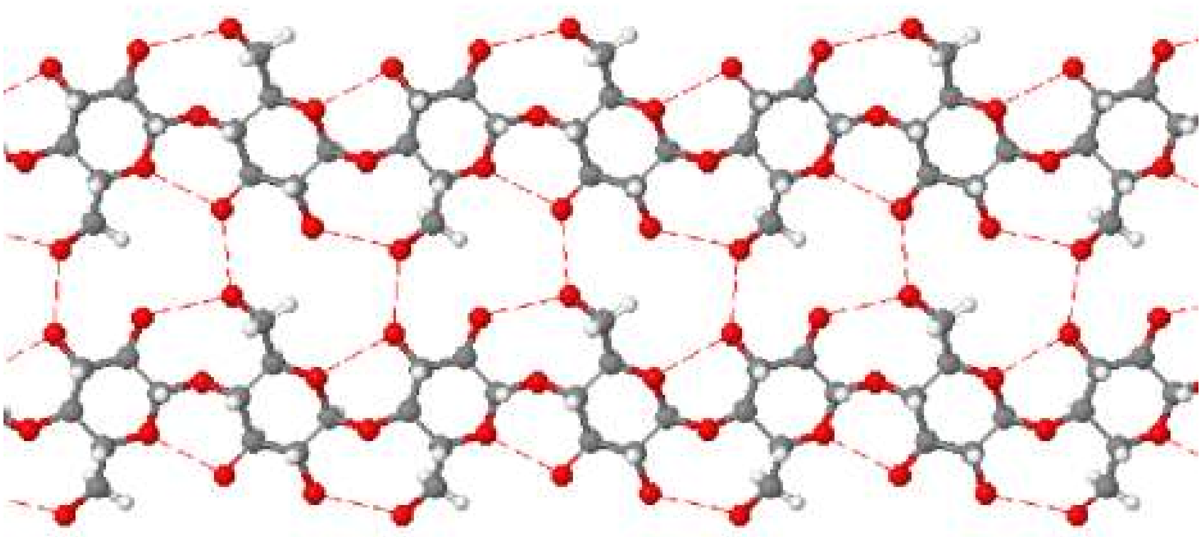
Amylopectin on the other hand is a branched-chain polysaccharide where in addition to the α-1,4-glycosidic bonds there exist the occasional α-1,6-glycosidic bonds, which are responsible for the branching. Branching occurs about every 24-30 glucose units.



Since the helical structure of amylopectin is disrupted by branching, the reaction of iodine with amylopectin does not produce the deep blue colour but instead a less intense reddish brown colour.

Cellulose fibres.

The presence of linear chains of thousands of glucose units linked together allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into cellulose fibers. As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Since cellulose does not have a helical structure like amylose, it does not bind to iodine to form a coloured product.



Strands of cellulose

Note.
Humans are unable to metabolize cellulose as a source of glucose since our digestive juices lack the enzymes that can hydrolyze the glycosidic linkages. So although we can digest potatoes, we cannot process grass. However, certain microorganisms can digest cellulose because they contain the enzyme cellulase, capable of catalysing the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet.

While on the subject of the digestion of saccharides, there has been much debate about the use of high-fructose corn syrup (HFCS) and the increase in the number of people with obesity.

Vegetable Cellulose Fibres

1. fibre occurring on the seed (raw cotton, java cotton)
2. phloem fiber (flax, ramie, hemp, jute)
3. tendon fibre from stem or leaves (manila hemp, sisal hemp etc)
4. fibre occurring around the trunk (hemp palm)
5. fibre of fruit/nut shells (coconut fibre - Coir)

cotton and linen are the most important among them and are forms of cellulose.

Cotton

Cotton has been used as a textile fibre for thousands of years with India being generally considered as the birthplace of cotton cloth. Cotton is a hair attached to the seed of several species of the genus Cossypium, a shrub up to 2 metres in height, indigenous to nearly all tropical regions but growing best near the sea, lakes or large rivers where there is a warm humid climate and sandy soil. Cotton or cotton mixed with synthetic polymers provides most clothing in the world. It is used in making the finest garments suited to hot or cold weather, bed-sheets, and for worldwide popular jeans. Each cotton fibre has 20-30 layers of cellulose built up in an orderly series of spring- like spirals. These fibres bring out certain characteristics like absorbency wet-strength, softness and durability in cotton clothing.

See textile manufacturing for the steps involved from growing cotton to the production of cloth. The finishing-processing of textiles involves:

Desizing
Depending on the size that has been used, the cloth may be steeped in a dilute acid and then rinsed, or enzymes may be used to break down the size.

Scouring
Scouring, is a chemical washing process carried out on cotton fabric to remove natural wax and non-fibrous impurities (eg the remains of seed fragments) from the fibres and any added soiling or dirt. Scouring is usually carried in iron vessels called kiers. The fabric is boiled in an alkali, which forms a soap with free fatty acids (saponification). A kier is usually enclosed, so the solution of sodium hydroxide can be boiled under pressure, excluding oxygen which would degrade the cellulose in the fibre. If the appropriate reagents are used, scouring will also remove size from the fabric although desizing often precedes scouring and is considered to be a separate process known as fabric preparation. Preparation and scouring are prerequisites to most of the other finishing processes. At this stage even the most naturally white cotton fibres are yellowish, and bleaching, the next process, is required.

Bleaching
Bleaching improves whiteness by removing natural coloration and remaining trace impurities from the cotton; the degree of bleaching necessary is determined by the required whiteness and absorbency. Cotton being a vegetable fibre will be bleached using an oxidizing agent, such as dilute sodium hypochlorite or dilute hydrogen peroxide. If the fabric is to be dyed a deep shade, then lower levels of bleaching are acceptable, for example. However, for white bed sheetings and medical applications, the highest levels of whiteness and absorbency are essential.

Mercerising
A further possibility is mercerizing during which the fabric is treated with caustic soda solution to cause

swelling of the fibres. This results in improved lustre, strength and dye affinity. Cotton is mercerized under tension, and all alkali must be washed out before the tension is released or shrinkage will take place. Mercerizing can take place directly on grey cloth, or after bleaching.

Many other chemical treatments may be applied to cotton fabrics to produce low flammability, crease resist and other special effects. Some important non-chemical finishing treatments include dyeing and printing.

Linen

Linen is woven from yarn made from the fibres of the flax plant, a member of the genus Linum in the family Linaceae. The flax plant has blue or white flowers and grey-green stems, and it grows to a height of about 1 metre. It grows well in temperate and fairly equable climates, free from very heavy rains, although moist winds during the growing season are good.

The following comment is taken from BelovedLinens.net

The various processes employed in the preparation of the plant in Egypt are admirably depicted on the enduring walls of their ancient palaces, temples, and tombs, by the skilful hand of the artist. Drawings of the various implements employed; of the people in the act of sowing the seed; pulling the plant; carrying water to fill wooden vats, evidently for the purpose of steeping the Flax; putting it through the several processes requisite to produce the fiber; spinning it into yarn; and weaving the yarn into cloth, are all distinctly portrayed.

This depiction is from the Theban Tomb located in Deir el-Medina, part of the Theban Necropolis, on the west bank of the Nile, opposite to Luxor. It is the burial place of the Ancient Egyptian official, Sennedjem and his family. He is seen pulling the flax out by hand (rather than cutting), after which it is tied in bundles and carried off the field on the back of oxen.

The steeping and the subsequent process of beating the stalks with mallets shown on the walls of the tombs, illustrates the following passage of Pliny upon the same subject:-*" The stalks themselves are immersed in water, warmed by the heat of the sun, and are kept down by weights placed upon them; for nothing is lighter than Flax. The membrane or rind, becoming loose, is a sign of their being sufficiently macerated. They are then taken out and repeatedly turned over in the sun until perfectly dried, and afterwards beaten by mallets on stone slabs. That which is nearest the rind is called tow, inferior to the inner fibers, and fit only for the wicks of lamps. It is combed out with iron hooks, until all the rind is removed. The inner part is of a whiter and finer quality. Men are not ashamed to pre-pare it. . . . After it is made up into yarn it is polished by striking it frequently on a hard stone, moistened with water. When woven into cloth it is again beaten with clubs, being always improved in proportion as it is beaten."*

Canadian video showing the processing of flax to linen

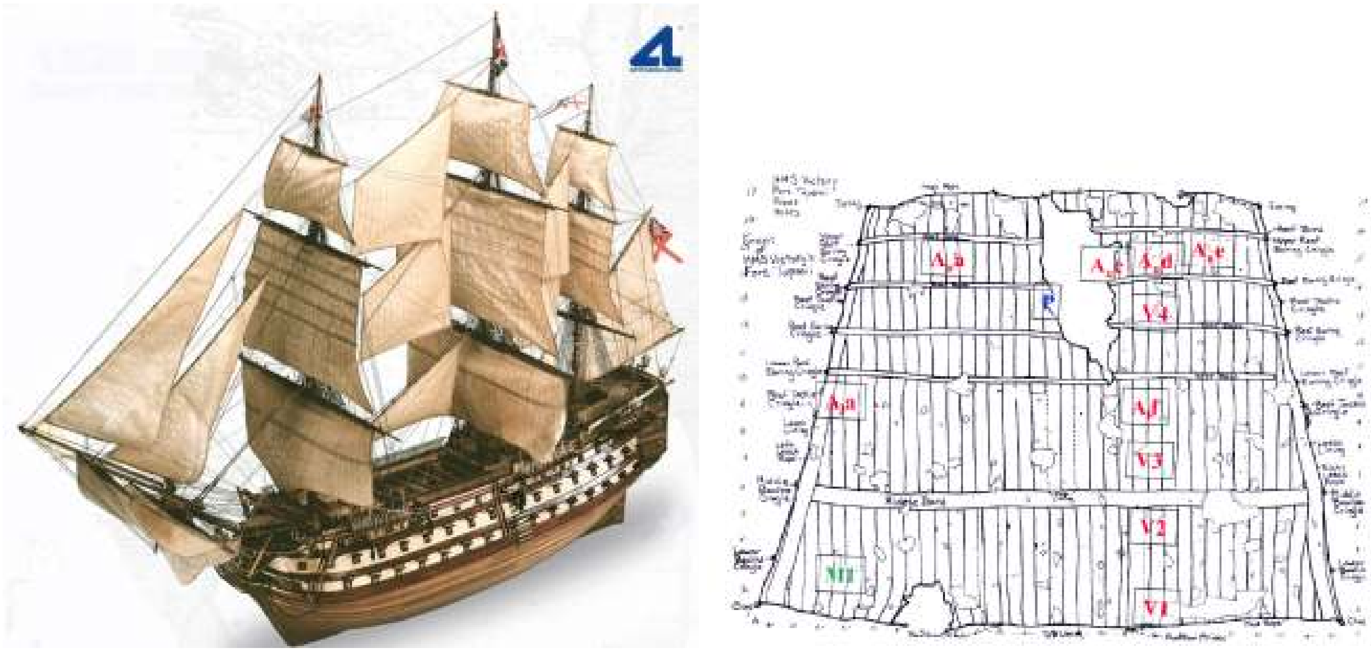
Irish Linen production

Apart from clothes, linen has been used in the making of tea towels, bath-towels and linen because of its strong capacity to absorb moisture.

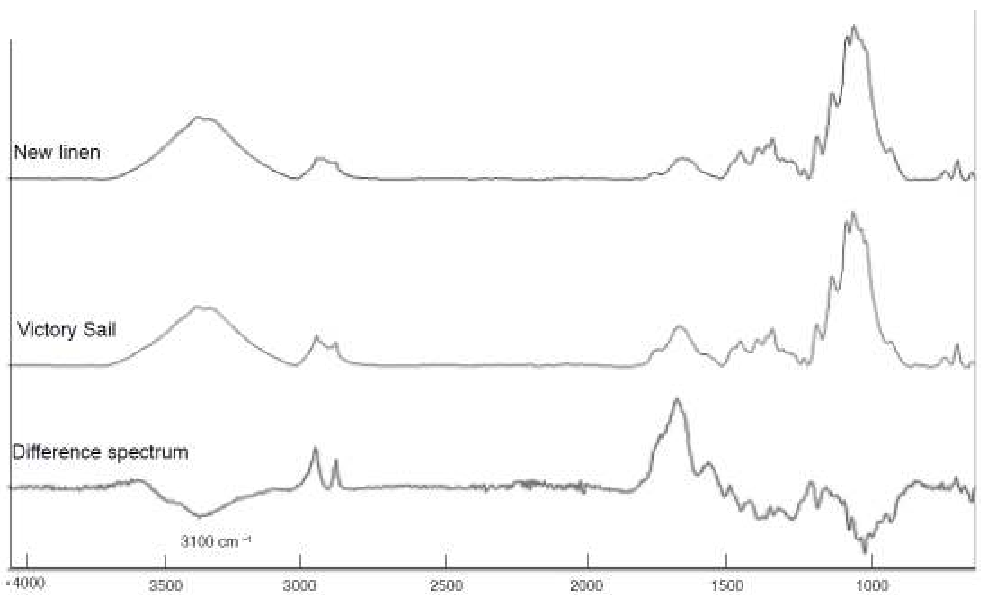
The largest single artefact left from the Battle of Trafalgar is the fore-topsail of HMS Victory, the flagship of Admiral Lord Nelson. Measuring 24m (80 ft) at its base, 17 m (54 ft) at the head and 17m (54 ft) deep, the sail covers an area of 336 m^2 (3,618 square feet) and weighs roughly 360 kg.

If you want to build your own 16m replica you can get the plans from HobbyNuts

The linen sail was severely damaged and has since suffered significant natural deterioration. As the only extant early 19th century sail in the world, it is a unique artefact and arguably Britain's foremost maritime textile treasure. Prior to its display at the bicentennial exhibition in 2005, the sail was analysed by Infra-red and Raman spectroscopy and conservationists did some repair and preservation work. Complementary tensile tests were completed on loose yarn from around the damaged areas. The mechanical data and Raman spectral comparisons suggested a good correspondence between the historic sailcloth and surrogate specimens.



Model of HMS Victory and sketch of the fore-topsail showing damage.



FTIR of sample from the HMS Victory fore-sail compared to new linen.

The deterioration over the years has come in part from the aerial oxidation of the alcohol groups to carboxylic acids. This can be seen in the difference spectrum calculated from the IR spectrum of fresh linen compared to that of the sail. The band at 1720 cm^{-1} being due to acid formation (C=O) and the negative band at ~3100 cm^{-1} showing the loss of the OH groups. The two bands at 2930 cm^{-1} and 2850 cm^{-1} show that the sail has gained some oils or waxes that were not originally present.

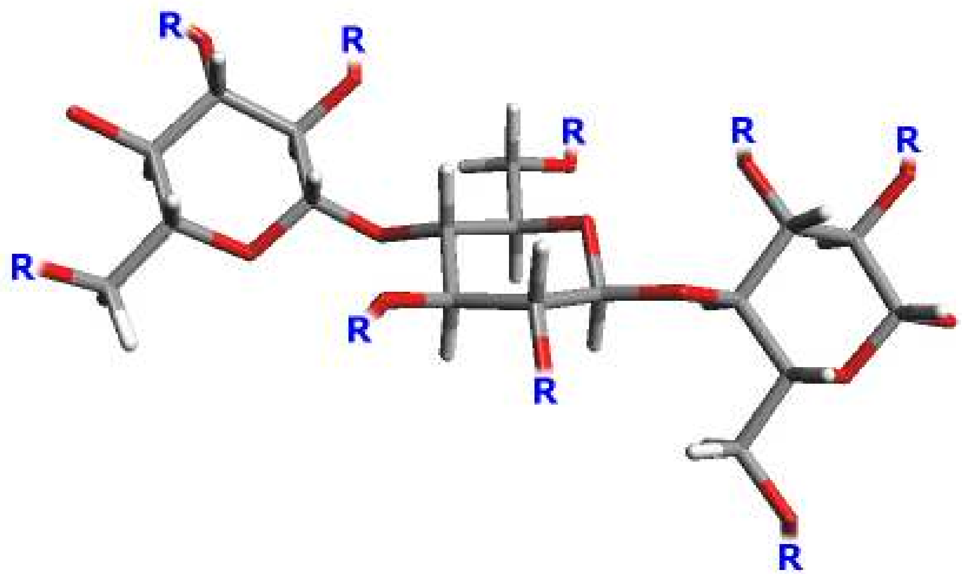
Semi-synthetic cellulose based fibres

Artificial silk

Artifical silk is frequently used as a synonym for rayon.
The first successful artificial silks were developed in the 1890s from cellulose fiber and marketed as "artificial silk" or "viscose", a trade name for a specific manufacture. In the U.S.A. in 1924, the name of the fiber was

officially changed to rayon, although the term viscose continued to be used in Europe. The term "viscose rayon" refers to the same material.

Prior to that "nitro-cellulose" had been prepared but was found to be impractical due to its instability and flammability. It has alternatively been called "guncotton" and is not a nitro compound but has nitrate groups replacing three of the OH groups.



The R groups replacing the OH's, might be nitrate, CS_2Na, acetates or other substituents

Rayon

For some background reading see the J Chem Educ article by Prof G.B. Kauffman, Rayon - the first semi-synthetic fibre product

Rayon is a manufactured regenerated cellulose fiber. Because it is produced from naturally occurring polymers, it is neither a truly synthetic fiber nor a natural fiber; it is a semi-synthetic or artificial fiber. Rayon is known by the names viscose rayon and artifical silk in the textile industry.

Most linear celluloses can be dissolved in solvents capable of breaking the strong hydrogen bonds, such as aqueous inorganic acids, calcium thiocyanate, zinc or lithium chlorides, dimethyldibenzylammonium hydroxide, ammoniacal cadmium hydroxide, and ammoniacal copper hydroxide (Schweizer's reagent). Only high-molecular weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide and which is called α-cellulose, can be used in producing rayon. The only materials containing a high enough percentage of α-cellulose for making rayon are cotton (plants of the genus *Gossypium*) and some types of wood pulp.

In 1857, the Swiss chemist, Matthias Eduard Schweizer, discovered that **copper(II) ammonia solutions** could dissolve cellulose. He reported that...

This possesses to an extraordinary degree the power to dissolve plant fiber at ordinary temperature.

If purified cotton is covered with the blue solution, it soon assumes a gelatinous, slippery state, the fibers separate and disappear. and after some working up with a glass rod everything is converted into a slimy liquid..... If an insufficient amount of solution is used, a portion of the fibres still remains visible; however, if an excess of the solution is added and shaken, an almost clear blue solution is obtained, which, after it has *been diluted with water, can be filtered.*

If the filtered solution is supersaturated with hydrochloric acid, a voluminous white precipitate is formed, which, collected on a filter, has the exact appearance of moist aluminum hydroxide. This substance, unorganized, to be sure, but not changed essentially in its chemical nature, appears to be cellulose. If the gelatinous precipitate, freed completely from salts by washing, is dispersed in water, and potassium iodide and afterward some chlorine water is added, the substance is colored brown [not blue], proof that it is neither starch nor a starch-containing substance.

On being dried on a water bath, the precipitate shrinks together strongly and leaves behind a horny, translucent, brittle mass, which is similar to dried paste but has no taste at all and does not stick to the teeth. Heated in the air, the substance burns without leaving a residue.. . .

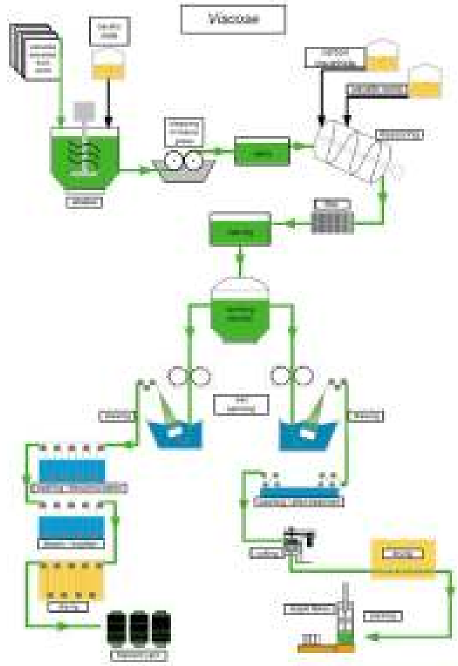
If the fiber solution is painted on a glass plate and allowed to dry on it, a thin, bluish white coat remains, which adheres solidly to the glass....

Production method for Viscose Rayon
Regular rayon (or viscose) is the most widely produced form of rayon. This method of rayon production has been utilized since the early 1900s and it has the ability to produce either filament or staple fibers.
The process is as follows:

1. ***Cellulose***: Production begins with processed cellulose
2. ***Immersion***: The cellulose is dissolved in caustic soda: $(C_6H_{10}O_5)_n + nNaOH \rightarrow (C_6H_9O_4ONa)_n + nH_2O$
3. ***Pressing***: The solution is then pressed between rollers to remove excess liquid
4. ***White Crumb***: The pressed sheets are crumbled or shredded to produce what is known as "white crumb"
5. ***Aging***: The "white crumb" aged through exposure to oxygen
6. ***Xanthation***: The aged "white crumb" is mixed with carbon disulfide in a process known as Xanthation, the aged alkali cellulose crumbs are placed in vats and are allowed to react with carbon disulfide under controlled temperature (20 to 30°C) to form cellulose xanthate: $(C_6H_9O_4ONa)_n + nCS_2 \rightarrow (C_6H_9O_4O\text{-}SC\text{-}SNa)_n$
7. ***Yellow Crumb***: Xanthation changes the chemical makeup of the cellulose mixture and the resulting product is now called "yellow crumb"
8. ***Viscose***: The "yellow crumb" is dissolved in a caustic solution to form viscose
9. ***Ripening***: The viscose is set to stand for a period of time, allowing it to ripen: $(C_6H_9O_4O\text{-}SC\text{-}SNa)_n + nH_2O \rightarrow (C_6H_{10}O_5)_n + nCS_2 + nNaOH$
10. ***Filtering***: After ripening, the viscose is filtered to remove any undissolved particles
11. ***Degassing***: Any bubbles of air are pressed from the viscose in a degassing process
12. ***Extruding***: The viscose solution is extruded through a spinneret, which resembles a shower head with many small holes
13. ***Acid Bath***: As the viscose exits the spinneret, it lands in a bath of sulfuric acid, resulting in the formation of rayon filaments: $(C_6H_9O_4O\text{-}SC\text{-}SNa)_n + \frac{1}{2}nH_2SO_4 \rightarrow (C_6H_{10}O_5)_n + nCS_2 + \frac{1}{2}nNa_2SO_4$
14. ***Drawing***: The rayon filaments are stretched, known as drawing, to straighten out the fibers
15. ***Washing***: The fibers are then washed to remove any residual chemicals
16. ***Cutting***: If filament fibers are desired the process ends here. The filaments are cut down when

producing staple fibers

More information is available from the CIRFS: European Man-Made Fibres Association on Viscose



Steps involved on the production of Viscose Rayon

In 2010 the Federal Trade Commission (FTC) issued a statement concerning the advertising of fabric as being derived from bamboo with the implication that they were environmentally friendly.
see Bamboo-zled by bamboo
Rayon is made from plants and trees, bamboo included, but it must go through a chemically-intensive process that results in a considerable amount of pollution -- a fact that runs contrary to the environmentally-friendly claims of bamboo clothing.

Clothing made using bamboo fibers is not of the same silky smooth consistency as those made with rayon, the FTC said. Once bamboo or any other tree is turned into rayon, it is misleading to claim it is anything other than rayon because of the chemical bath used to convert the material from a natural product into rayon. It can be called "rayon made from bamboo," which isn't misleading as long as you understand there's nothing environmentally friendly about rayon.

Cellophane
Cellophane is a thin, transparent sheet made from (viscose) regenerated cellulose by extruding the solution through a narrow slit into an acid bath. It has low permeability to air, oil, grease and bacteria which makes it useful for food packaging.

Cellulose triacetate
Cellulose triacetate (CTA) was first commercially produced in the USA in 1954 and is derived from cellulose by acetylating cellulose with acetic acid and/or acetic anhydride.

Characteristics of textiles containing CTA

- Shrink resistant
- Wrinkle resistant

- Easily washable
- Generally washable at high temperatures
- Maintains creases and pleats well

In late 2010 Eastman Chemical Manufacturer announced a 70% increase in output to supply increasing demand for the chemical's use as an intermediate in the production of polarized films for liquid crystal displays (LCD)s.

Cellulose acetate phthalate

Cellulose acetate phthalate (CAP) is commonly prepared by the reaction of a partially substituted cellulose acetate (CA) with phthalic anhydride in a solvent such as acetic acid, acetone, or pyridine in the presence of a basic catalyst. The basic catalysts employed are anhydrous sodium acetate when the solvent is acetic acid, amines when using acetone, while pyridine is able to act as both solvent and base.

The structures obtained result in about half of the hydroxyls being esterified with acetyls, a quarter are esterified with one or two carboxyls of a phthalic acid, and the remainder are unchanged.

Recently (CAP), a pharmaceutical excipient used for enteric film coating of capsules and tablets, was found to inhibit infection by the human immunodeficiency virus type 1 (HIV-1) and several herpesviruses. See Pub Med for a copy of the article.

Acknowledgements.
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