TNO innovation for life

Source – History – Application of Nitrocellulose

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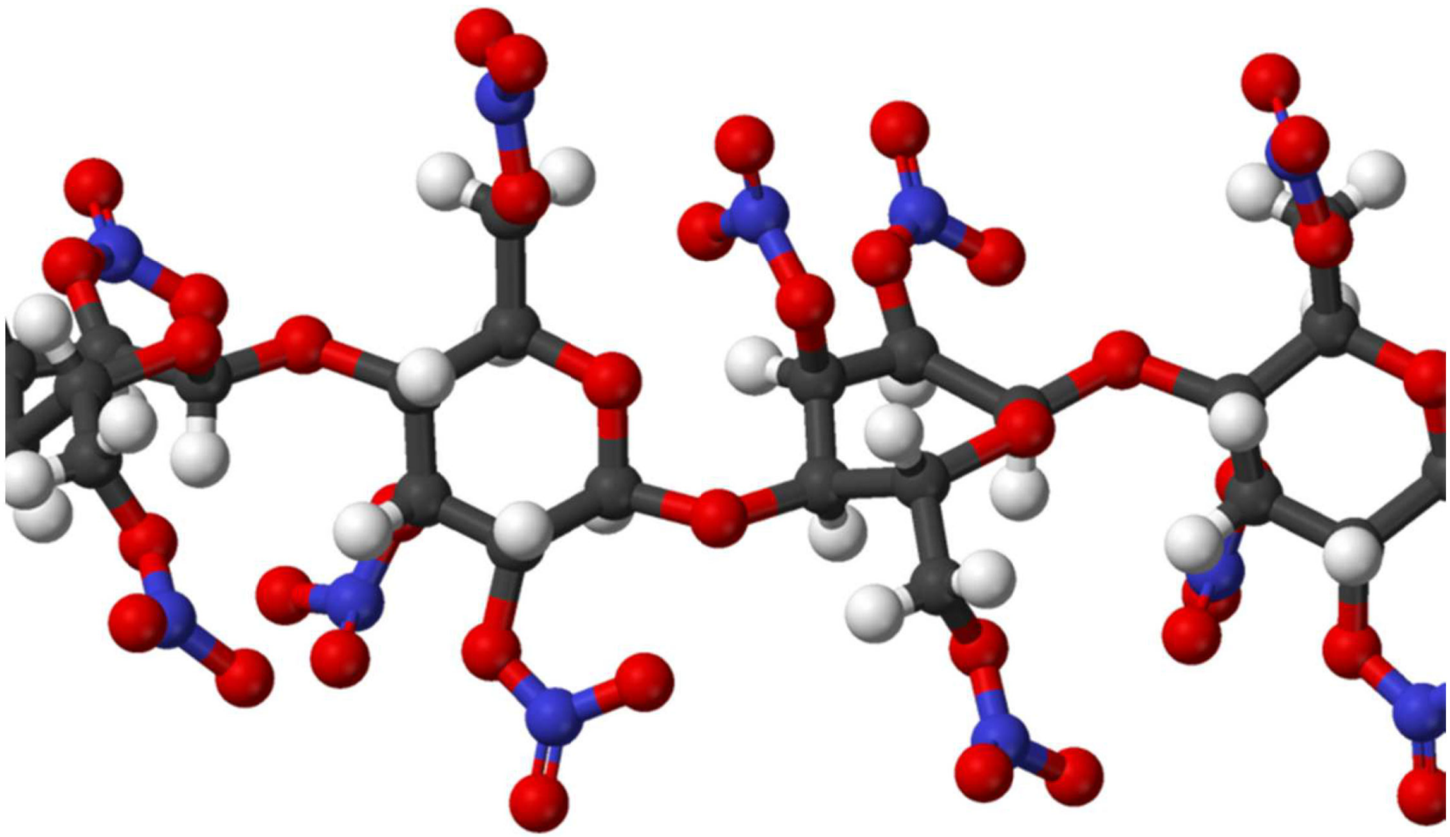
Material of interest......................



Gunpowder-1

- **Gunpowder**, also known as **black powder**, was the first chemical explosive and the only one known until the mid-19th century. It is a mixture of sulfur, charcoal and potassium nitrate (saltpeter)—with the sulfur and charcoal acting as fuels, while the saltpeter works as an oxidizer.

- Because of its burning properties and the amount of heat and gas volume that it generates, gunpowder has been widely used as a propellant in firearms and as a pyrotechnic composition in fireworks.

- Gunpowder was, according to prevailing academic consensus, invented in the 9th century in China

Gunpowder-2

- Gunpowder is classified as a low explosive because:
  - relatively slow decomposition rate
  - low brisance

- Gunpowder's burning rate increases with pressure, so it will burst containers if contained but otherwise just burns in the open.

- Ignition of the powder packed behind a bullet must generate enough pressure to force it from the muzzle at high speed, but not enough to rupture the gun barrel. Gunpowder was widely used to fill artillery shells and in mining and civil engineering to blast rock roughly until the second half of the 19th century, when the first high explosive (nitro-explosives) were discovered.

Gunpowder => Guncotton

- For many centuries **gunpowder** was the world's only explosive, and was not superseded until the discovery of **guncotton.**

- So long ago as 1832 Bracon discovered that woody fiber could be turned into an explosive by the action of concentrated nitric acid; and a few years later a French inventor, Dumas, tried to make cartridges of paper treated in similar fashion.

- If he had succeeded these would have been the first smokeless cartridges, but he failed; and it was not until 1845 that Schonbein, a German chemist, hit upon the proper method of treating cotton wool with nitric and sulphuric acids, so as to turn it into guncotton

Guncotton

- 1846 invention of nitrocellulose by Schonbein and Pelouze
- Known as an instable material => many accidents
- First improvement => purifying the process by Sir Abel (1865)

Nitrocellulose

- Nitrocellulose had many properties that made it an important material apart from its use as a propellant. Since it forms a plastic material when dissolved in organic solvents like ether-alcohol or acetone, it can be made into many different forms that maintain their shape when the solvents evaporate. It can also be hot-formed and will retain its shape when cooled.

- The manufacturers of military explosives experienced several instances of extremely high production during the late 19th and early 20th centuries caused by large-scale wars. When peace was reached, there was an enormous excess of production capacity and raw materials with which nitrocellulose could be made. In order to utilize this glut of resources, gunpowder manufacturers began to develop civilian uses for this material.

2

Gunpowder manufacturers such as E. I. du Pont de Nemours and Company developed the first commercially available plastics for these reasons.

Collodio In all reality, the use of excess gunpowder manufacturing capacity for the production of consumer products was the beginning of the commercial plastics industry. One of the primary compounds that was developed into plastics was collodion and it is simply guncotton with a lower nitrate constituent, less than 12%. This material is also known by the trade name **Pyroxylin** and it was developed into many different consumer products such as artificial leather,

Application

Pyroxylin-type plastics began to be replaced by less flammable plastics in the 1920s and 1930s. Nevertheless they did not disappear. Better chemical manufacturing techniques reduced the incidence of detonation in later years. Celluloid plastics are still used in a few applications such as Ping-Pong balls.

Stability

- Second improvement => adding stabilizer DPA by Nobel (1889)
- Third improvement => adding centralites EC/MC (1906) by Germany
- During turn of century – production of very stable materials, some of them still in stock in Swedish Navy

Stability (2)

- General rule is the natural saponification of nitro esters, so also for nitrocellulose and nitroglycerine

- This process is accelerated by nitrogen oxides in combination with heat, moisture, light etc.

- On-going process, natural process

- First generation of stabilisers;
  - Aromatic amines (DPA)
  - Urea derivatives (centralites)
  - Urethanes
  - Double-bond compounds (vaseline, nitroguanidine)
  - Gelatizers (camphor, nitrobenzene, dinitrotoluene)

Smokeless powder - 1

Smokeless powder - 2

Smokeless powder is the name given to a number of propellants used in firearms and artillery which produce negligible smoke when fired.

The term is unique to the United States and is generally not used in other English-speaking countries, which initially used proprietary names such as “**Ballistite**” and “**Cordite**” but gradually shifted to "propellant" as the generic term.

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Cotton to Cellulose

Cotton - 1

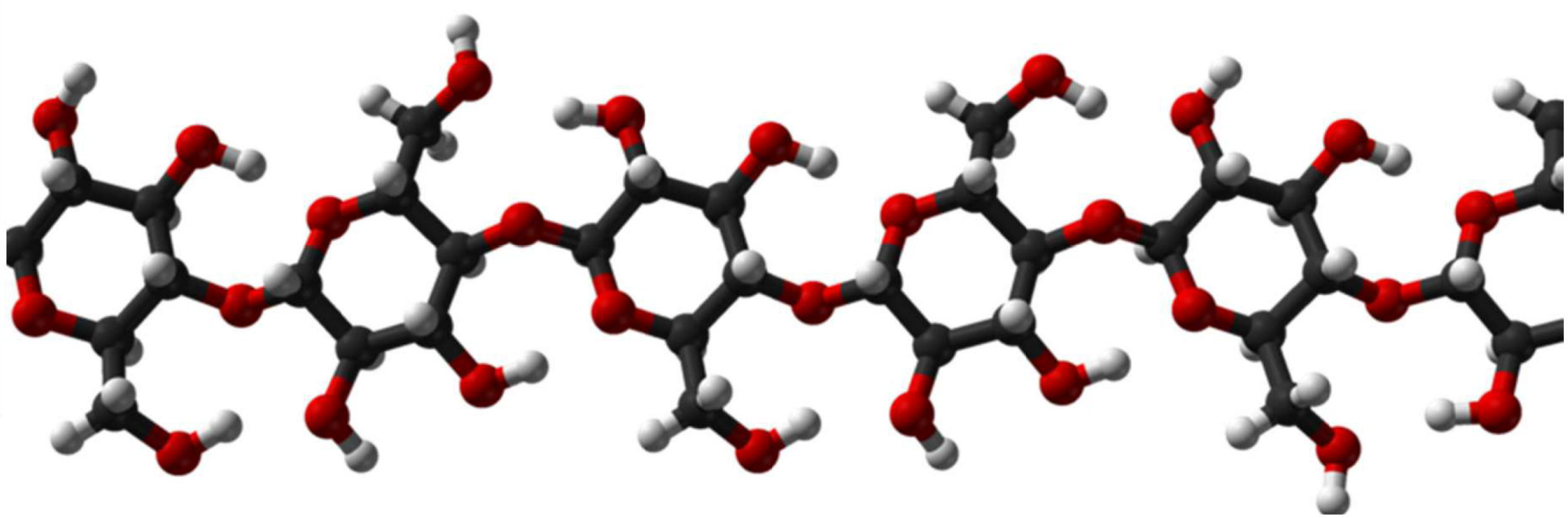
Cotton is a soft, fluffy staple fiber that grows in a boll, or protective capsule, around the seeds of cotton plants of the genus Gossypium. The fiber is almost pure cellulose. Under natural conditions, the cotton bolls will tend to increase the dispersion of the seeds.

Cotton => cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is an important structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms. Cellulose is the most abundant organic polymer on Earth.[5] The cellulose content of cotton fiber is 90%, that of wood is 40–50% and that of dried hep is approximately 45%.

Cellulose - 1

Cellulose is mainly used to produce paperboard and paper. Smaller quantities are converted into a wide variety of derivative products such as cellophane and rayon. Conversion of cellulose from energy crops into biofuels such as cellulosic ethanol is under investigation as an alternative fuel source. Cellulose for industrial use is mainly obtained from wood pulp and cotton



Cellulose - 2

Paper products

Cellulose is the major constituent of paper, paperboard, and card stock.

Fibers

Cellulose is the main ingredient of textiles made from cotton, linen, and other plant fibers. It can be turned into rayon, an important fiber that has been used for textiles since the beginning of the 20th century. Both cellophane and rayon are known as "regenerated cellulose fibers"; they are identical to cellulose in chemical structure and are usually made from dissolving pulp via viscose. A more recent and environmentally friendly method to produce a form of rayon is the Lyocell process.

Cellulose - 3

Consumables

Microcrystalline cellulose (E460i) and powdered cellulose (E460ii) are used as inactive fillers in drug tablets and as thickeners and stabilizers in processed foods. Cellulose powder is, for example, used in Kraft's Parmesan cheese to prevent caking inside the tube.

Science

Cellulose is used in the laboratory as a stationary phase for thin layer chromatography. Cellulose fibers are also used in liquid filtration, sometimes in combination with diatomaceous earth or other filtration media, to create a filter bed of inert material.

Cotton pulp - 1

Cotton pulp is a base product used to manufacture a range of fiber products such as high-quality paper and filter materials. Cotton-based pulps are preferred for these applications, as they contain none of the acids and lignin present in wood pulp. The pulp is predominantly produced from cotton linters harvested from cotton plants or cotton waste, such as rags and off-cuts. The cotton pulping process involves “cooking” the finely-chopped cotton fibers with various chemicals and water. During this process, the pulp slurry is subjected to several cleaning stages prior to being formed into finished products or half-stock sheets destined for further processing by end users.

Cotton pulp - 2

Cotton is one of the purest forms of cellulose found in nature. Pulps produced from cotton are free of almost all lignin, acid, and non-cellulose contaminants common to wood pulps, making products manufactured from them more stable, reliable, and robust. These characteristics make paper produced from cotton far more desirable as archival-grade bases for artwork and documents, as they do not degrade under artificial light as quickly. Cotton pulp, due to its lack of lignin, is also inherently brighter than wood pulp, thus requiring very little bleaching.

Comparison of typical feedstocks used in pulping

Component	Wood	Nonwood
Carbohydrates	65–80%	50–80%
Cellulose	40–45%	30–45%
Hemicellulose	23–35%	20–35%
Lignin	20–30%	10–25%
Extractives	2–5%	5–15%
Proteins	<0.5%	5–10%
Inorganics	0.1–1%	0.5–10%
SiO_2	<0.1%	0.5–7%

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Application of Nitrocellulose

Wim de Klerk (TNO - NLD)

Application - lacquer

- Nitrocellulose lacquer was used as a finish on guitars and saxophones for most of the 20th century and is still used on some current applications.

- Manufactured by (among others) DuPont, the paint was also used on automobiles sharing the same color codes as many guitars including Fender and Gibson brands, although it fell out of favor for a number of reasons: pollution, and the way the lacquer yellows and cracks over time.

Application - film

Nitrocellulose plasticized by camphor was used by Kodak, and other suppliers, from the late 1880s as a film base in photography, X-ray films and motion picture films; and was known as *nitrate film*. After numerous fires caused by unstable nitrate films, safety film started to be used from the 1930's in the case of X-ray stock and from 1948 for motion picture film

Application - billiard

Because of its explosive nature, not all applications of nitrocellulose were successful. In 1869, with elephants having been poached to near extinction, the billiards industry offered a $10,000 prize to whoever came up with the best replacement for ivory billiard balls. John Wesley Hyatt created the winning replacement, which he created with a new material he discovered called camphored nitrocellulose—the first thermoplastic, better known as celluloid. The invention enjoyed a brief popularity, but the Hyatt balls were extremely flammable, and sometimes portions of the outer shell would explode upon impact. An owner of a billiard saloon in Colorado wrote to Hyatt about the explosive tendencies, saying that he did not mind very much personally but for the fact that every man in his saloon immediately pulled a gun at the sound

Different Sizes – smaller……

Smaller NC Particles

- **Macro => Micro => Nano**

➢ Microcrystalline nitrocellulose (MCNC) – Patent US2007/0068610

➢ Nanocrystalline cellulose (NCC)

➢ Bacterial cellulose (BC), is produced through fermentation. The structure is similar to plant cellulose. Thickness is about 100 times smaller than plant cellulose (~ 0.01 micrometer).
Finally synthesized also NBC.

Cellulose sources

Source	*L*, nm	*d*, nm	Technique	References
Bacterial	100–1000	10–50	TEM	Araki, Wada, and Kuga (2001)
Tunicate	1160	16	DLS	de Souza Lima, Wong, Paillett, Borsali, and Pecora (2003)
	100–some 1000	15–30	TEM	Kimura et al. (2005)
Valonia	>1000	10–20	TEM	Revol (1982)
MCC	ca. 500	10	AFM	Pranger and Tannenbaum (2008)
Cotton	255	15	DLS	de Souza Lima et al. (2003)
	100–150	5–10	TEM	Araki et al. (2001)
Cotton linter	25–320	6–70	TEM	Elazzouzi-Hafraoui et al. (2008)
	300–500	15	AFM	Li et al. (2009)
Softwood	100–150	4–5	AFM	Beck-Candanedo, Roman, and Gray (2005)
Hardwood	140–150	4–5	AFM	Beck-Candanedo et al. (2005)
Wheat straw	150–300	ca. 5	TEM	Dufresne, Cavaille, and Helbert (1997)
Rice straw	117 ± 39	8–14	TEM	Ping and Hsieh (2012a)

Nanocellulose - 1

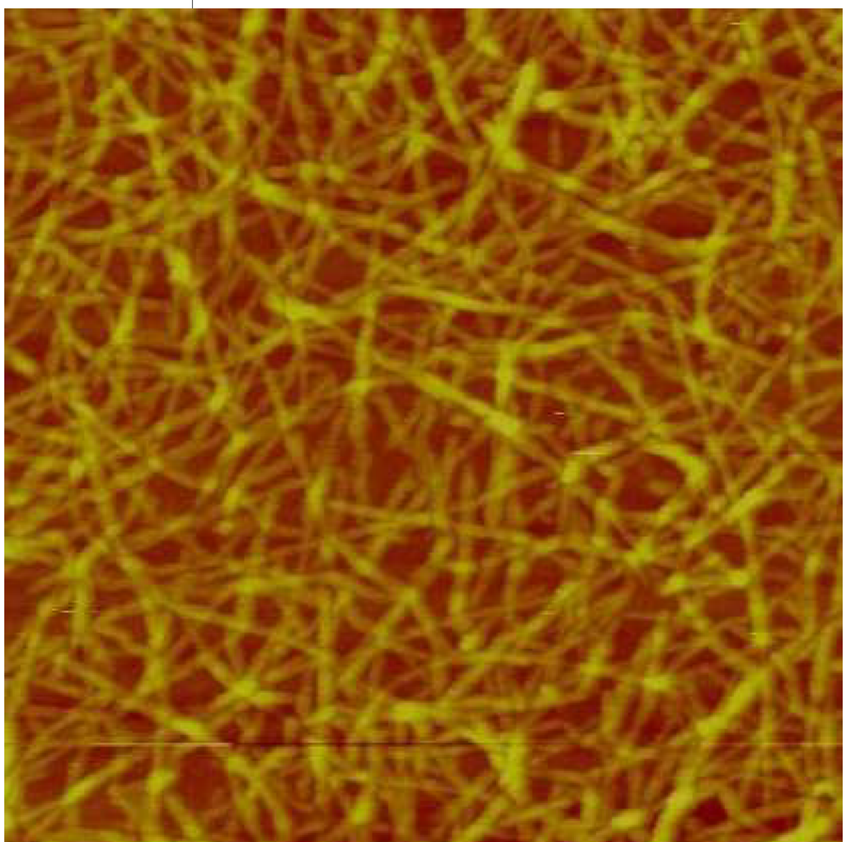
Nanocellulose, or **microfibrillated cellulose** (MFC), is a material composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). Typical lateral dimensions are 5–20 nanometers and longitudinal dimension is in a wide range from tens of nanometers to several micrometers. It is pseudo-plastic and exhibits the property of certain gels or fluids that are thick (viscous) under normal conditions, but flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed. This property is known as thixotropy. When the shearing forces are removed the gel regains much of its original state.

Nanocellulose - 2

The fibrils are isolated from any cellulose containing source including wood-based fibers (pulp fibers) through high-pressure, high temperature and high velocity impact homogenization (see manufacture below).

Nanocellulose can also be obtained from native fibers by an acid hydrolysis, giving rise to highly crystalline and rigid nanoparticles (generally referred to as **nanowhiskers**) which are shorter (100s to 1000 nanometers) than the nanofibrils obtained through the homogenization route. The resulting material is known as **nanocrystalline cellulose** (NCC).

Nanocellulose - 3



Crystalline cellulose has interesting mechanical properties for use in material applications. Its tensile strength is about 500MPa, similar to that of aluminium. Its stiffness is about 140–220 GPa, comparable with that of Kevlar and better than that of glass fiber, both of which are used commercially to reinforce plastics. Films made from nanocellulose have high strength (over 200 MPa), high stiffness (around 20 GPa) innovation for life

Sources

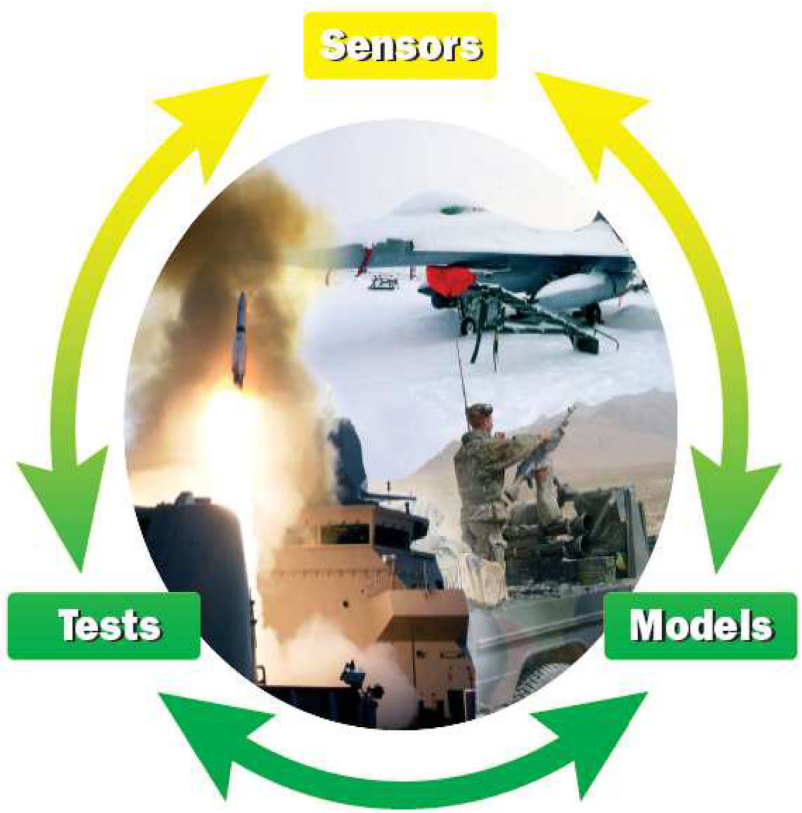
Influences

- Trees (age, location, direction of sunshine…)
- Soil (acidity, period of dryness, temperature ….)
- Preparation (wet, dry, cutting, mechanical stress, ……)

⇒ All influence the quality, fiber length of the cellulose, and after treatment also the stability of nitrocellulose

Questions?

Center of Expertise for Ammunition Safety



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