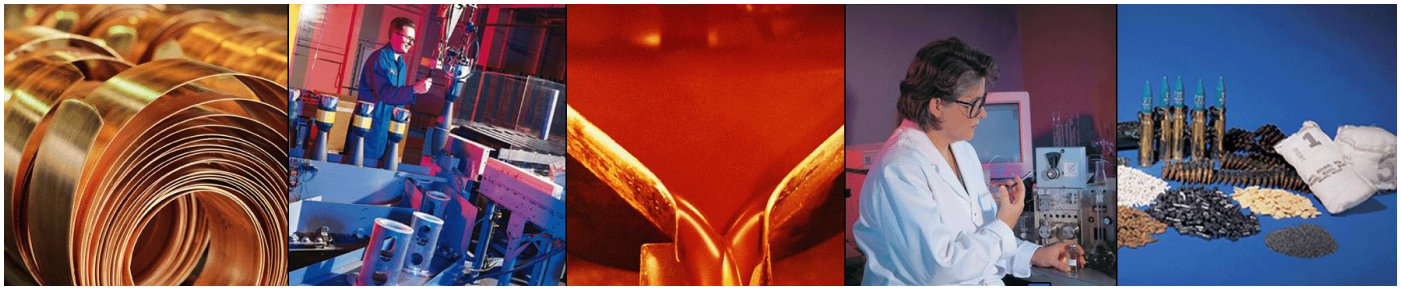
GENERAL DYNAMICS

Ordnance and Tactical Systems–Canada Valleyfield



Review of the fibre structure of cotton/wood cellulose and nitrocellulose and effect on nitration and solvent reactivity

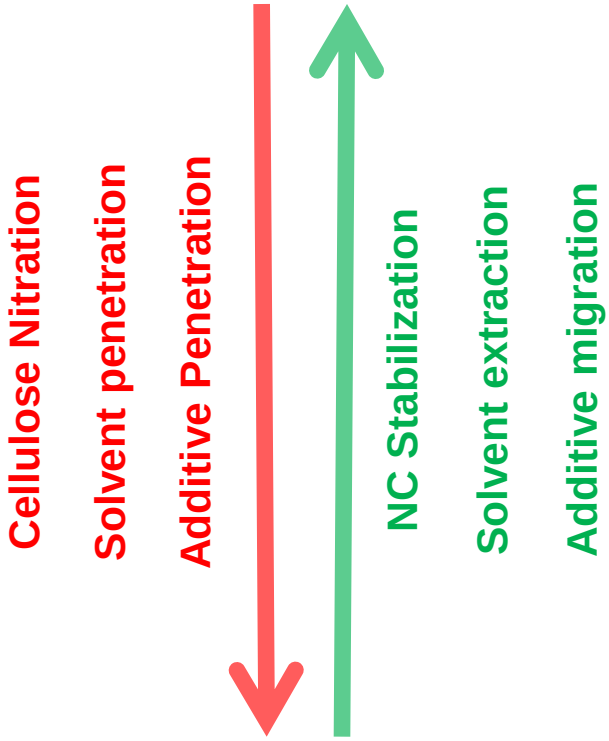
Prepared by Mario Paquet

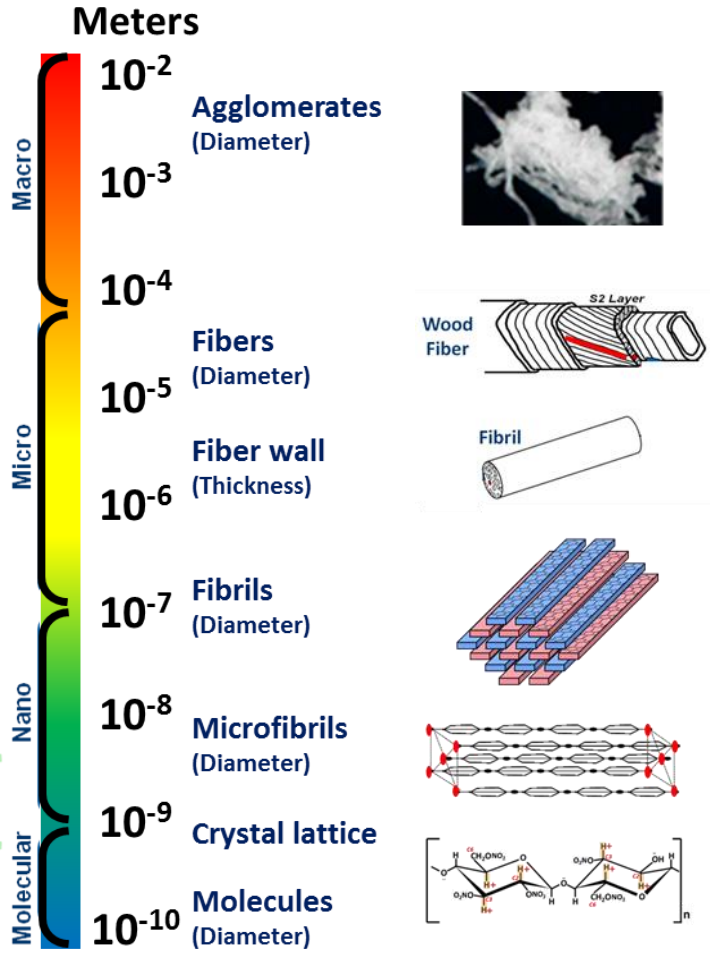
8th International Nitrocellulose Symposium
Bergerac France
June 5-6 2018

NC based material for extruded propellant

Shaping NC for propellant → forming a gel structure

Penetration and extraction of chemical additives: essential in processing Cellulose/NC

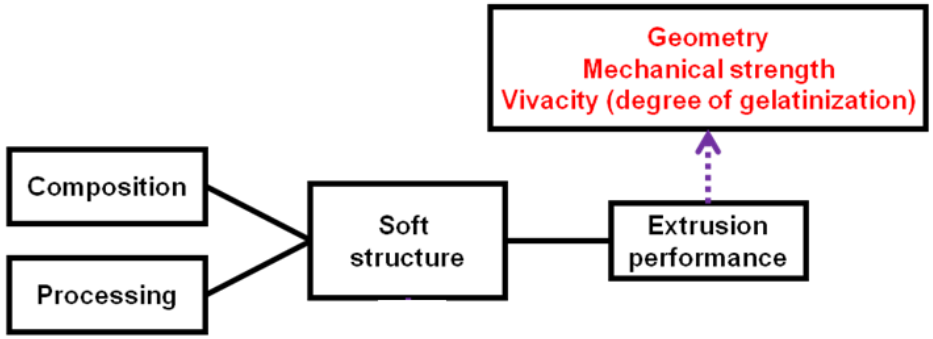




NC based material for extruded propellant
Shaping NC for propellant → forming a gel structure

For propellant at extrusion

Effect of soft material (dough) on performance



Propellant dough in a mixer

Extrudable paste using NC/solvent system

Solid → Addition of a gelatinizer/solvent → Semi-solid → Addition of a solvent → Liquid

Soft Matter System

Material in different physical states which are easily deformed by stresses/thermal fluctuations at/near room T°C or near required processing T°C

NC based materials in semi-solid form depending on processing conditions, can be a **homogeneous** or a **heterogeneous** gel system

NC based material
from a historical perspective

Cellulose → *Nitration $HNO_3 + H_2SO_4$* → **Cellulose nitrate**

1845 Schönbein
Importance of sulfuric acid in nitration

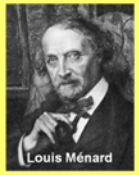
Paints

1882 Stevens Pyroxylin Lacquers

Importance of Amyl Acetate (rate of evaporation for quality of coating and hygroscopicity for clarity)

Collodions

1846 Ménard Collodion



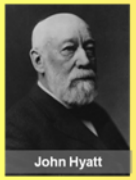
1851 Archer Photography

Ability of NC to form film

Plastics

1856 Parkes Parkisine

1869 Hyatt Celluloids



Importance of plasticization and importance of Camphor and Castor Oil as plasticizers

Explosives

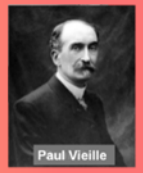
Propellants

+ NG → **Spherical Powder**
1933 Olsen

+ NG + NQ → **Triple Base**
1937

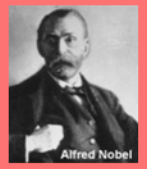
+ NG → **Double Base**
1875 Nobel Ballistite
1891 Abel/Dewar Cordite

Single Base
1884 Vieille Poudre B



Blasting

+ NG → **Dynamites**
1865 Nobel Gel Dynamite



Combustible Cases

1940

Homogeneous Gel

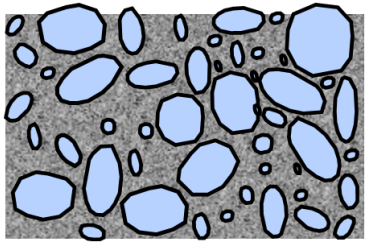
Heterogeneous Gel

Fibers

NC based material for extruded propellant

Types of gel structure vs physical structure of propellant

Heterogeneous (or Composite) Propellant



Homogeneous Propellant

Propellant NC base

Propellant NC base: gel

Triple Base

Single Base

Double Base

Spherical Powder

Homogeneous NC Gel

Heterogeneous NC Gel

Combustible Cases

NC Fibers

Propellant classified by the presence or absence of pieces of solid material imbedded within the NC propellant base

NC propellant base made of a mix crystalline and amorphous NC molecules

Macroscopic Homogeneity versus Mesoscopic Homogeneity

NC based material for extruded propellant

Types of gel structure is related to fiber structure

An NC based propellant may be formed on a gel system that is either, relatively:

- **homogeneous**
- **heterogeneous**

A **homogeneous** gel system: NC molecular chains without other level of structure *therefore a molecular material*

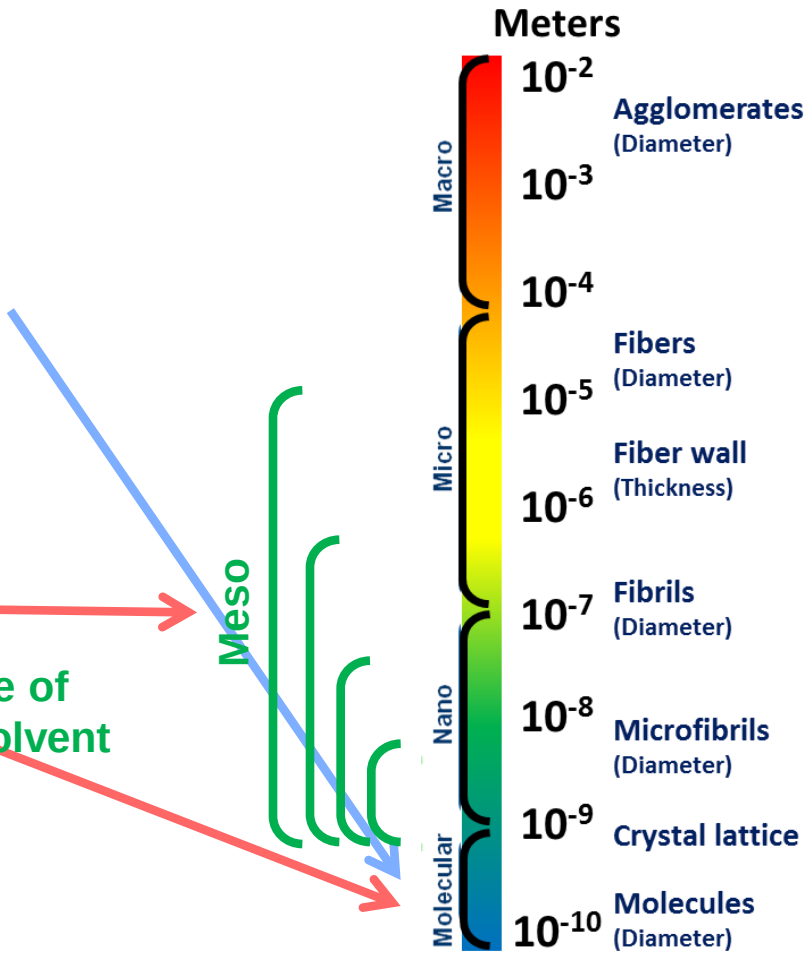
A **heterogeneous** gel system: a mixture of NC retaining some of the NC higher levels of structure (*fibrillar type of material)* in addition to NC in molecular form.

The mesoscopic range is affected by type of cellulose/NC, processing conditions and solvent system.

General tendency for NC heterogeneous gel:

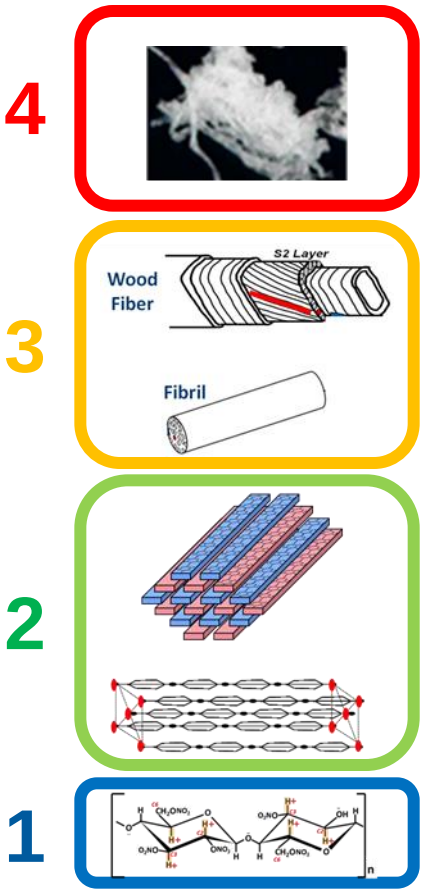
-Mechanical strength → improved

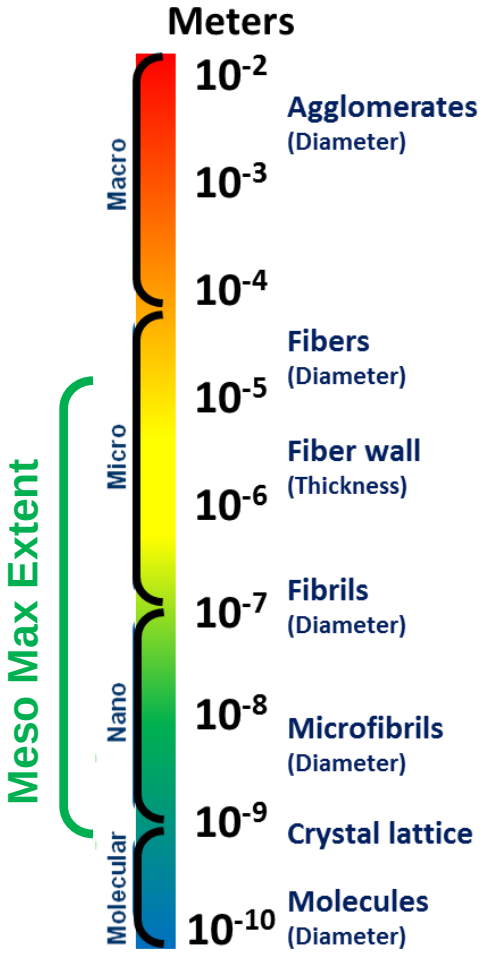
-Combustion → faster burning rate



NC based propellant structure

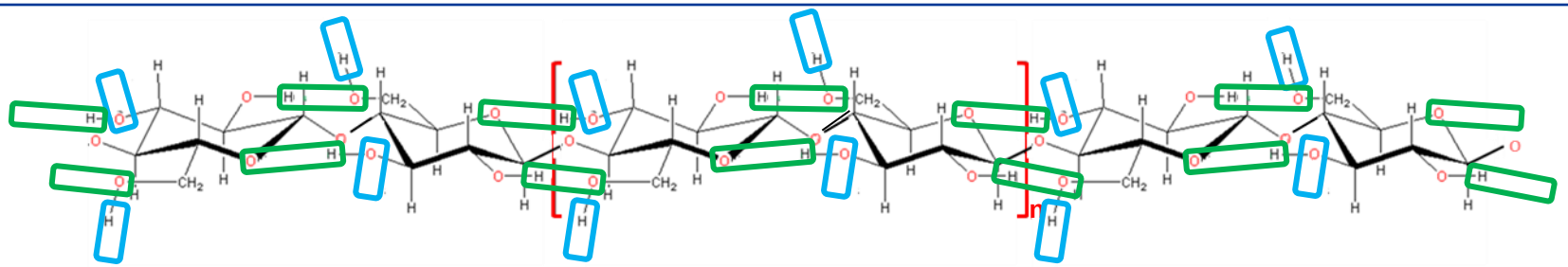
Types of gel structure: Soft material systems



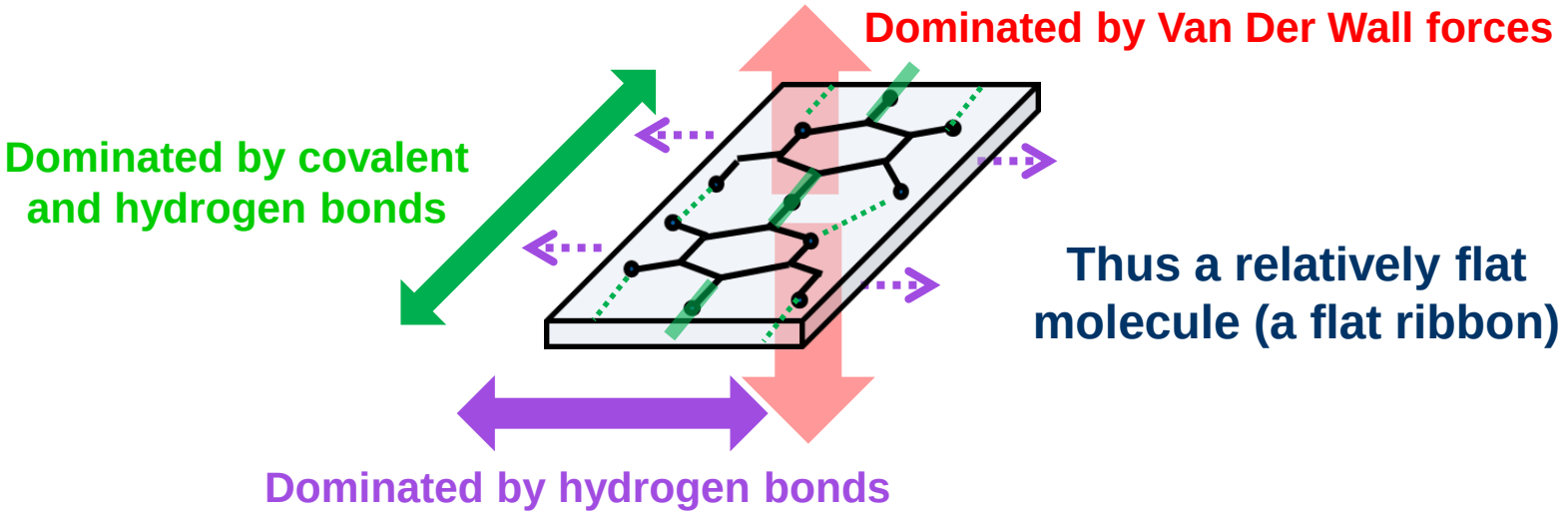


Cellulose and NC structure

Several layers of structure: Basic cellulose structural unit

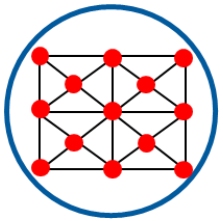


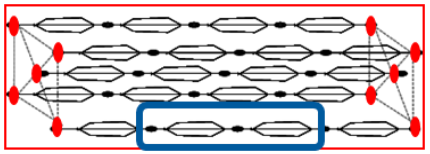
Cellulose is a linear polymer of β-(1→4)-D-glucopyranose units.
Long and rigid ribbon like molecule by **intramolecular hygrogen bonding**.
Intermolecular hydrogen bonds extend in the plane of the molecule

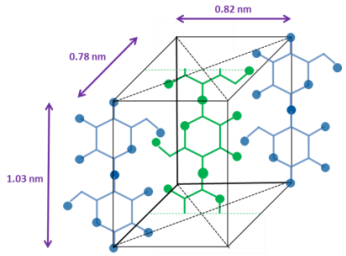


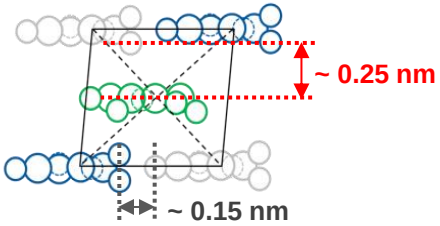
Cellulose multi-molecular structure

Crystalline areas basic structure within fibril





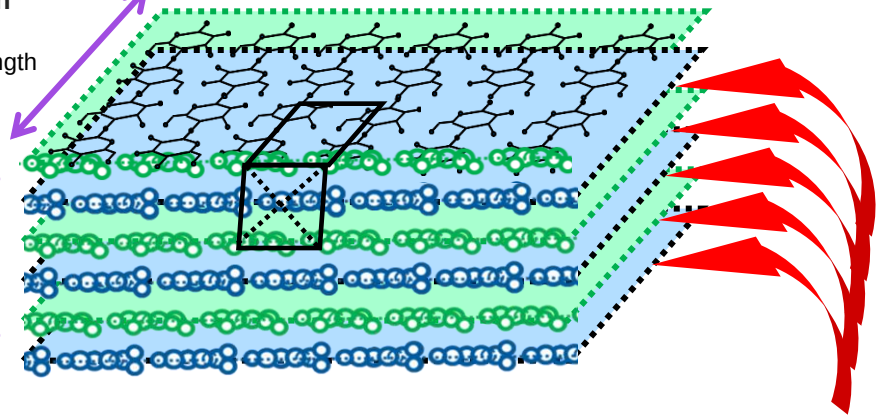




Dominated by intramolecular covalent and hydrogen bonding
High Relative Strength

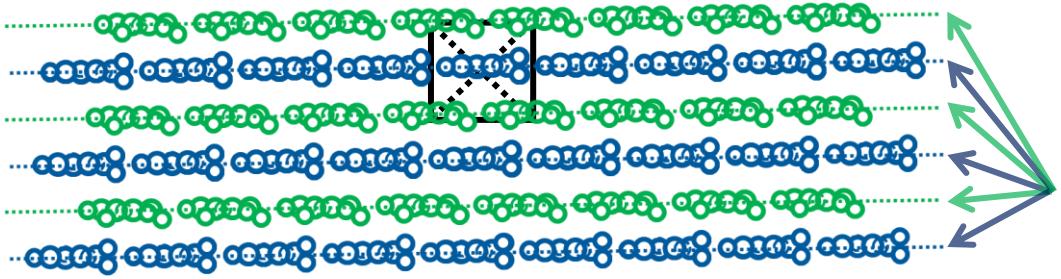
Dominated by intermolecular hydrogen bond
Intermediate Relative Strength

Dominated by intermolecular Van Der Wall bonding
Low Relative Strength



Main penetration pathway (Only: small and compatible molecules)

The cellulose crystallite molecular arrangement can be seen has a multi sheet structure

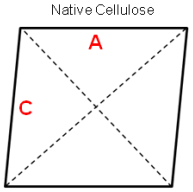


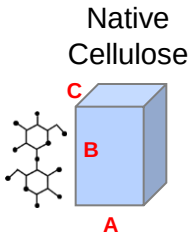
Antiparallel Sheets

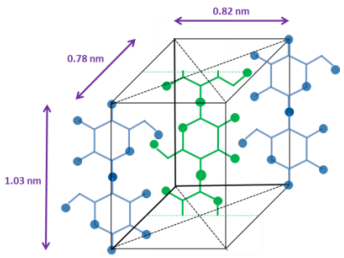
Cellulose multi-molecular structure

Crystalline areas basic structure within fibril

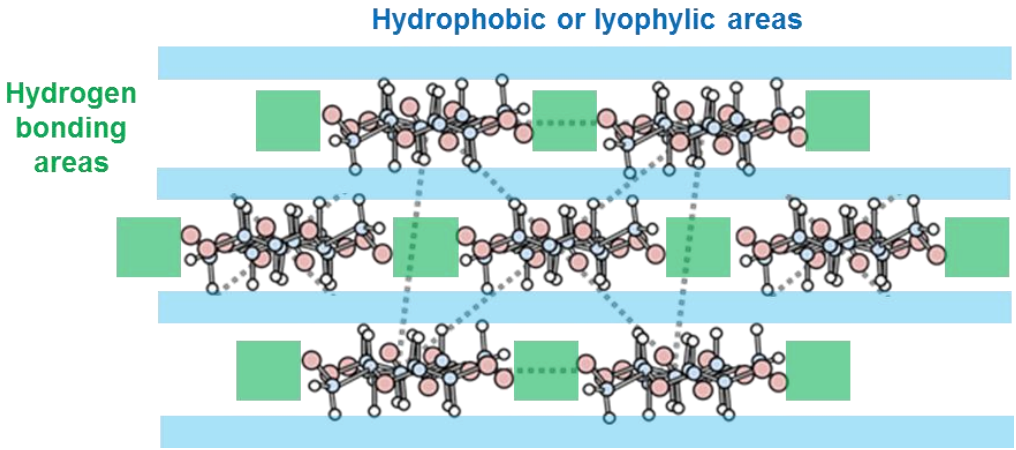
	A	B	C	β
	Angstom	Angstom	Angstom	Angle °
Native cellulose	8.2	10.2	7.8	84.5
Di nitrocellulose	13.9	10.3	8	90
Tri nitrocellulose	12.3	25.4	9	90

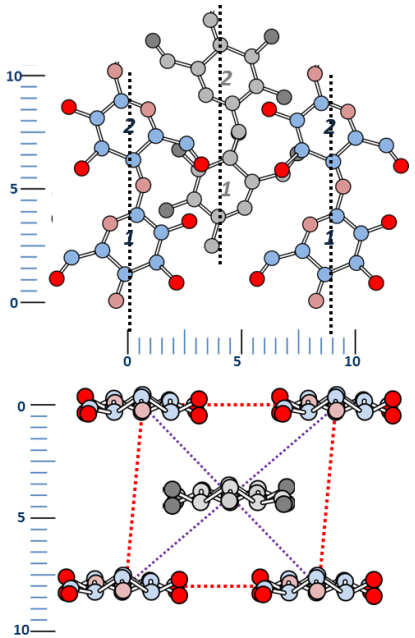






Native Cellulose





Nitrocellulose multi-molecular structure

Crystalline areas basic structure within fibril

	A	B	C	β
	Angstom	Angstom	Angstom	Angle °
Native cellulose	8.2	10.2	7.8	84.5
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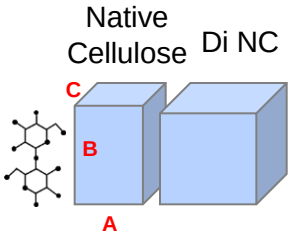
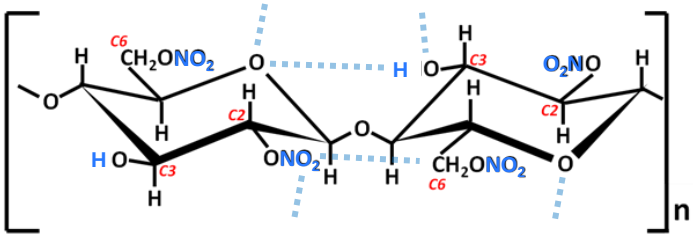
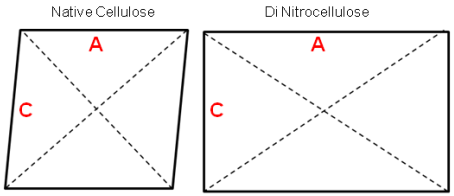
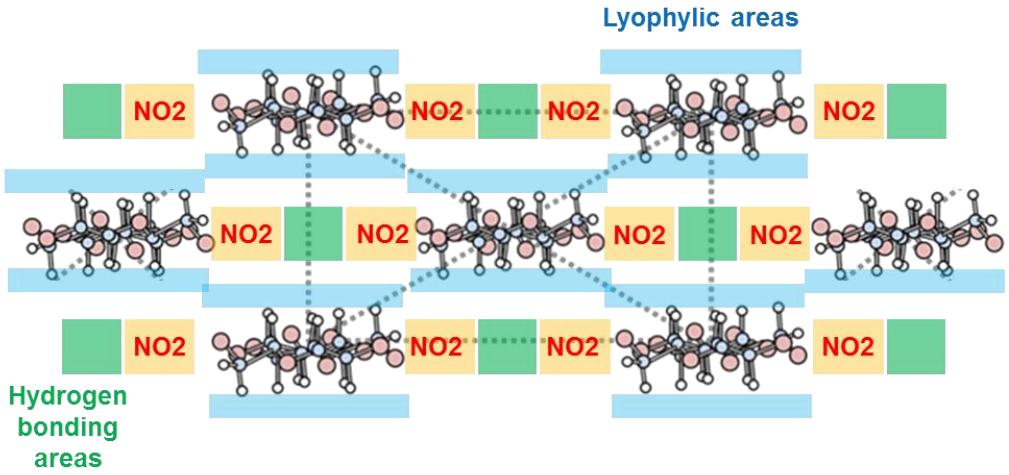
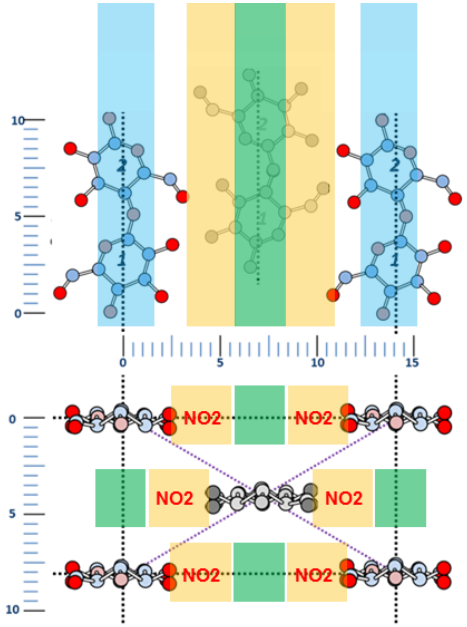




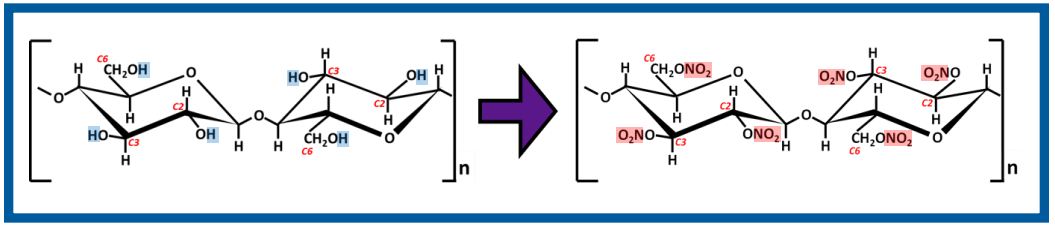


Di NC





Cellulose nitration



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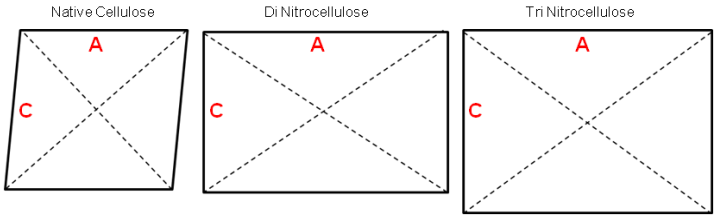
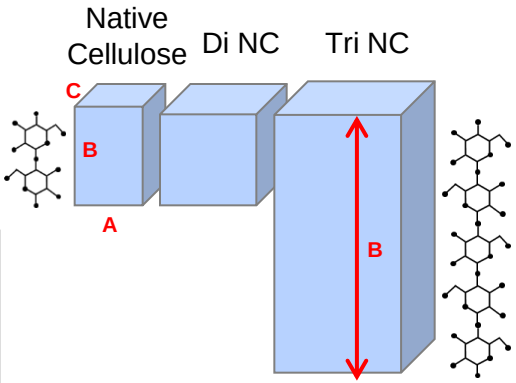




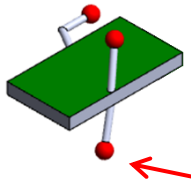
An important structural change occurs with formation of trinitrate

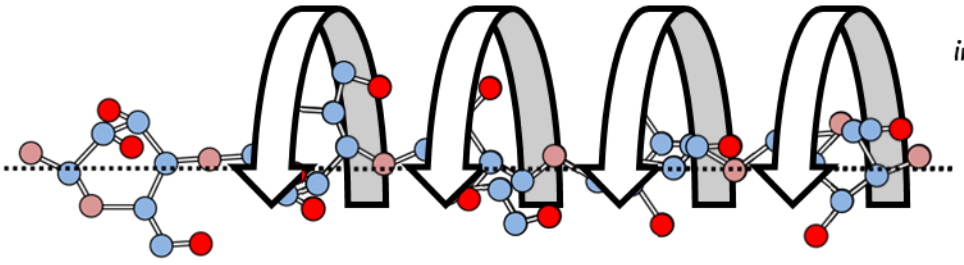
The basic crystal structural unit is not 2 but now 5

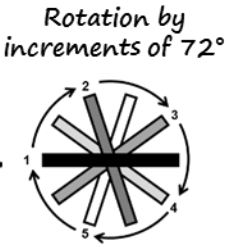
To accommodate the bulky nitrate groups:
No longer a flat molecule but change of conformation from chair to half-boat

Tri NC

Rotation along axis







Oxygen carrying a nitro group

Nitrocellulose multi-molecular structure

Crystalline areas basic structure within fibril

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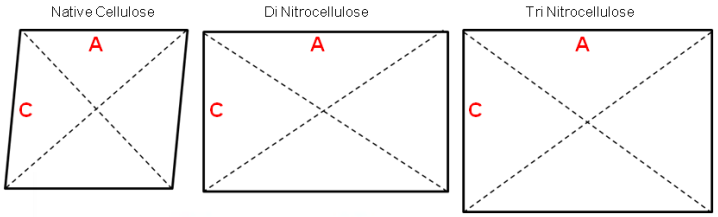
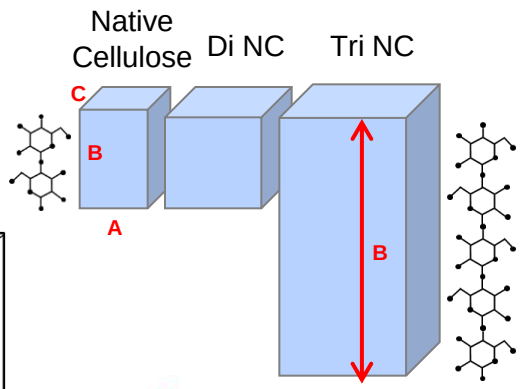
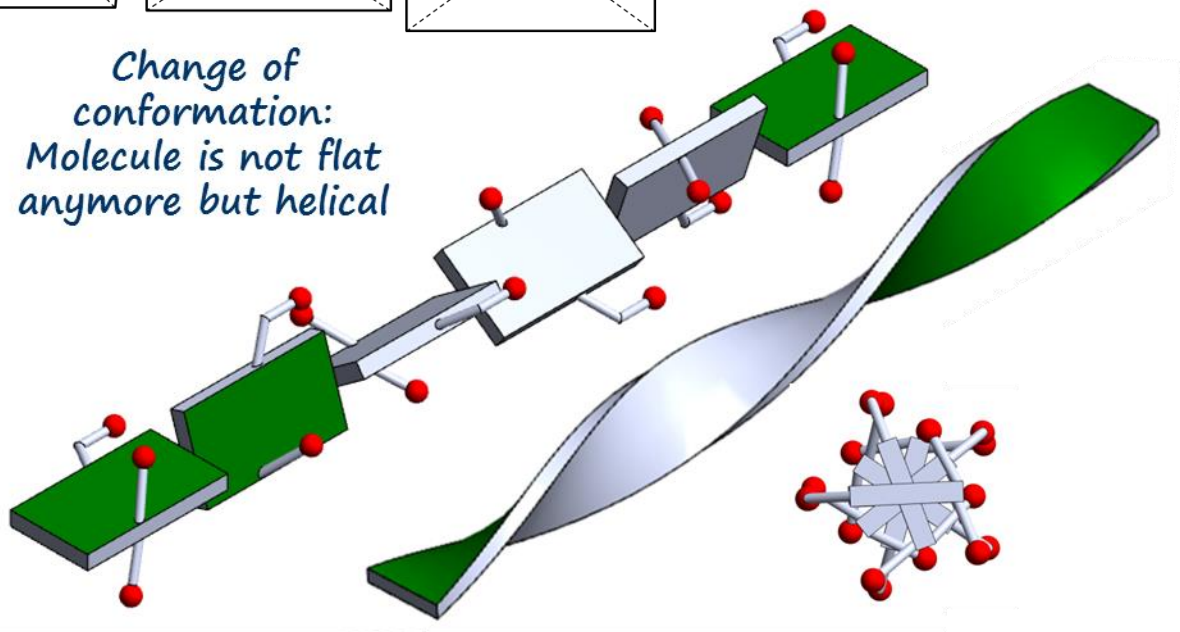
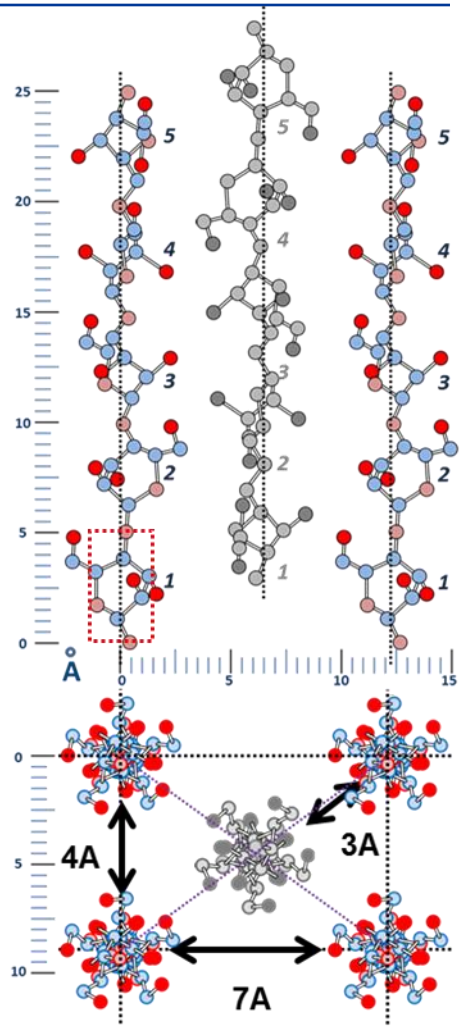
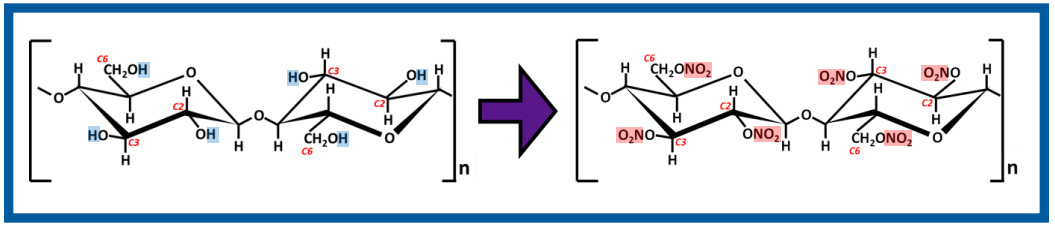




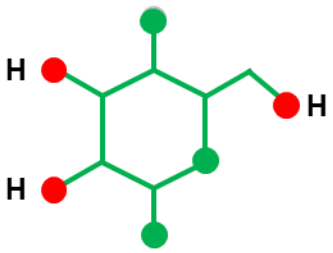




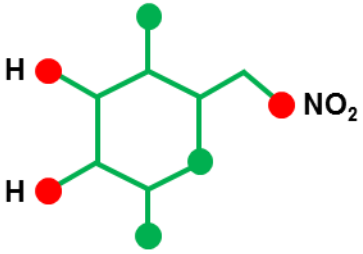
Cellulose nitration



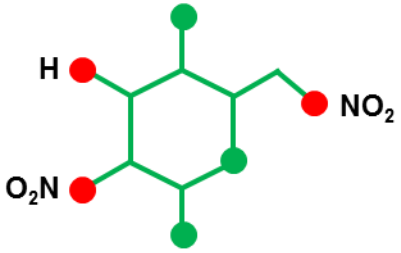
The nitration may be express as average substitution per pyranose ring



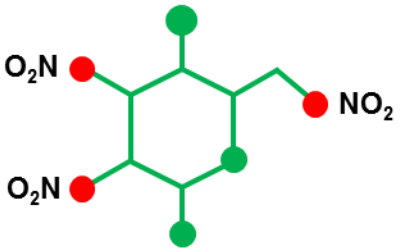
C0



C1



C2



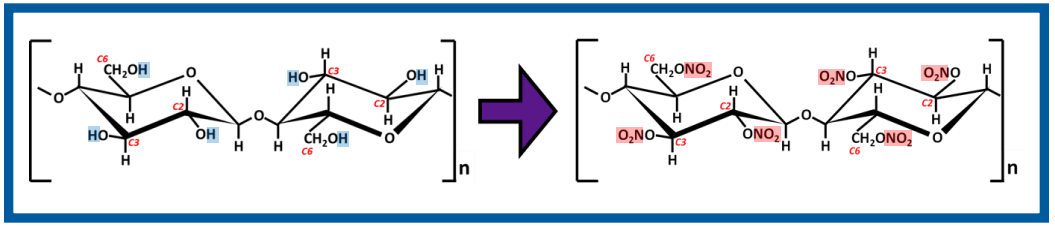
C3

Label	# of Nitro Group	% Nitrogen	Molecular Weight
C0	0	0.0	162
C1	1	6.8	207
C2	2	11.1	252
C3	3	14.1	297

NC usually divided by nitrogen content ranges or DS (Degree of Substitution):

- -10.5% to 11.1% (DS # 1.9) → plastic and lacquers
- -11.2% to 11.7% (DS about 2.1) → lacquers
- -11.8% to 12.3% (DS about 2.3) → lacquers, coated fabrics, dynamites and blasting gelatine
- -12.0% to 13.5% (DS about 2.5) → Smokeless power
- -13.5% to 14.1% (DS about 2.9) → Propellant and special apps

Cellulose nitration



Accessible zones | **Cristalline zones**

0.0% | **7.5%** | **14.1%**

12.8%

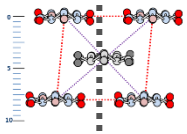
Nitration of accessible zones

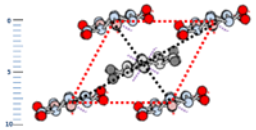
Mercerization of crystalline zones (not nitrated)

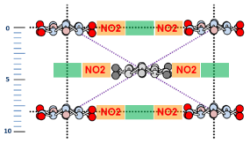
Nitration of crystalline zones

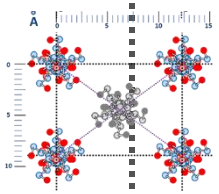
Native cellulose

Mercerized cellulose





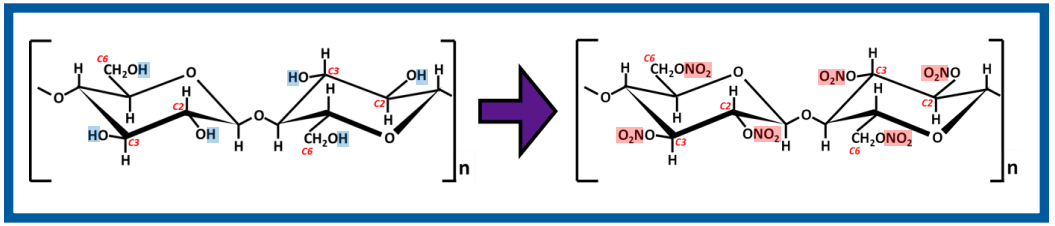




0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

% Average Nitrogen

Cellulose nitration



Nitration of accessible zones | **Nitration of cristalline zones**

0.0% %Accessibility: near 53% **7.5%** **14.1%**

14.14%N max x 53% = 7.5%N

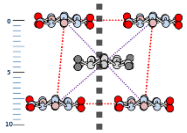
Typical	% Crystallinity	% Amorphous	% Accessibility
For wood:	60%	40%	60%
For cotton	70%	30%	50%

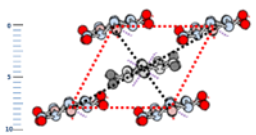
10.8% *12.8%*

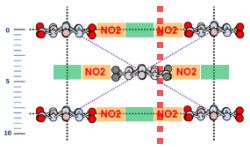
Nitration of crystalline zones

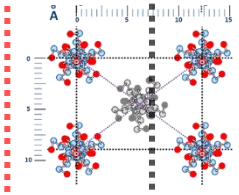
Native cellulose

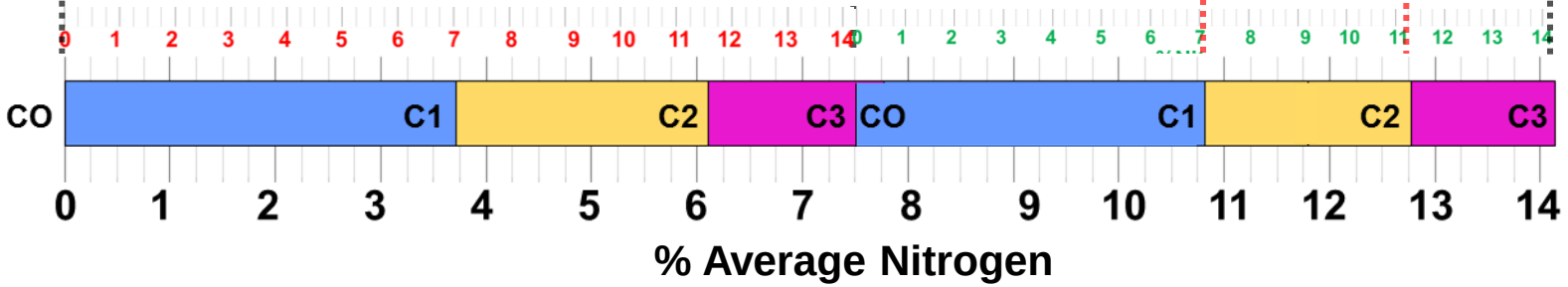
Mercerized cellulose



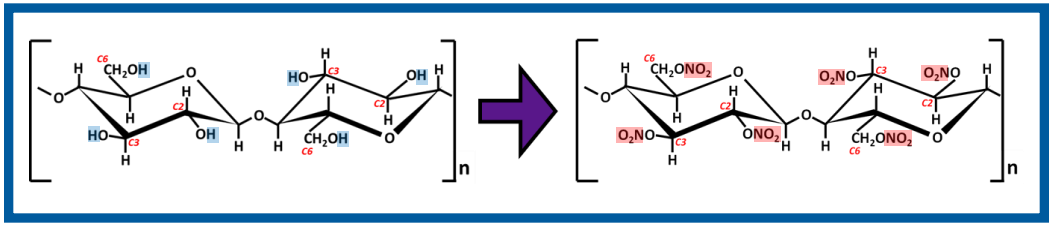








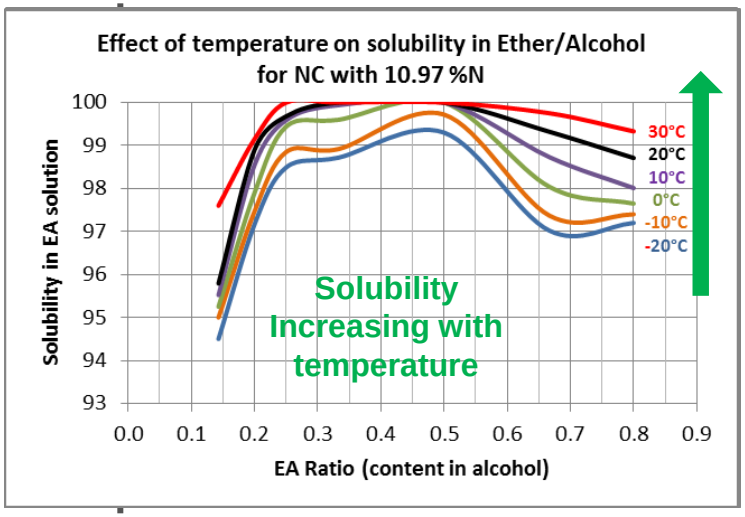
Cellulose nitration

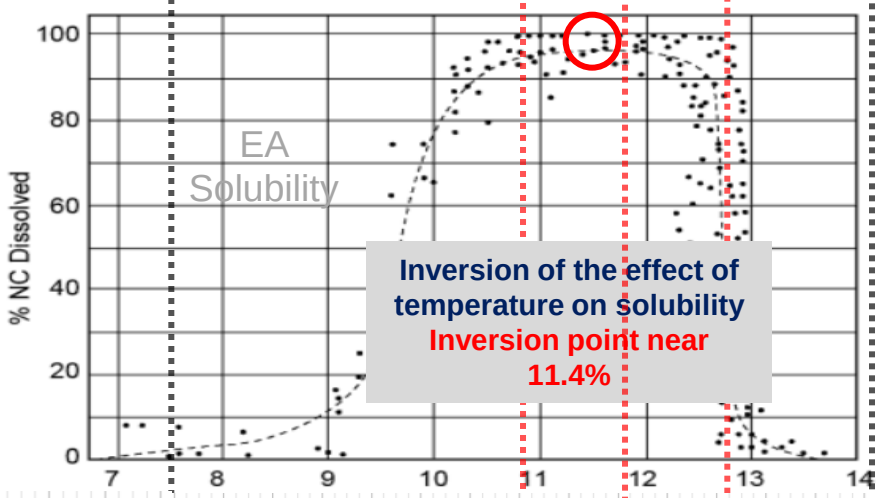


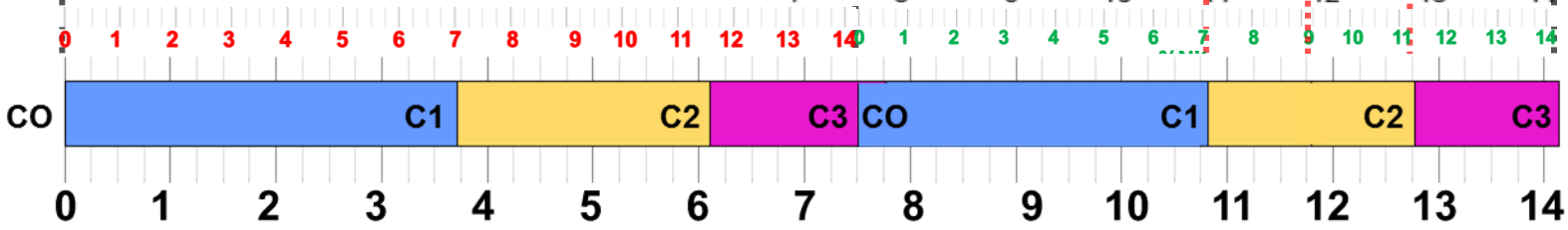
Nitration of accessible zones | **Nitration of cristalline zones**

0.0% | 7.5% | 11.8% | 14.1%

10.8% | 12.8%



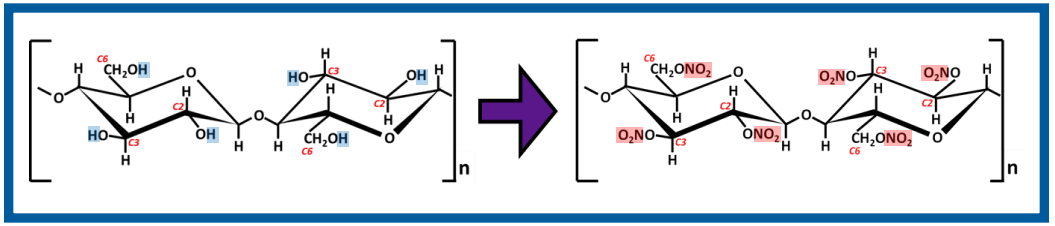




0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

% Average Nitrogen

Cellulose nitration



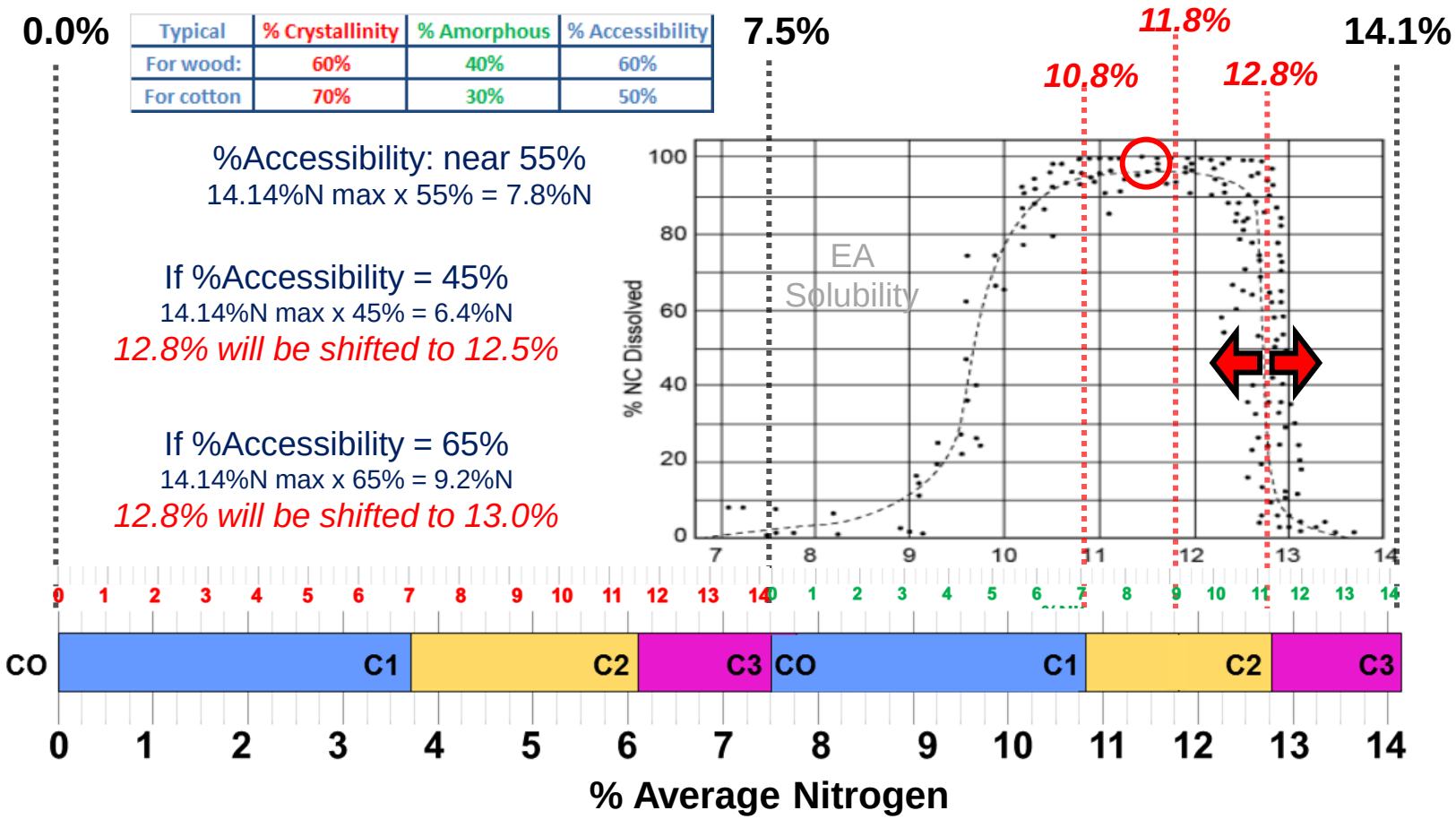
Nitration of accessible zones | **Nitration of cristalline zones**

Typical	% Crystallinity	% Amorphous	% Accessibility
For wood:	60%	40%	60%
For cotton	70%	30%	50%

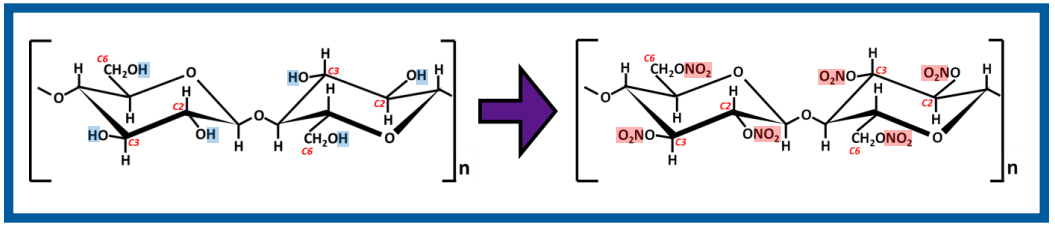
%Accessibility: near 55%
14.14%N max x 55% = 7.8%N

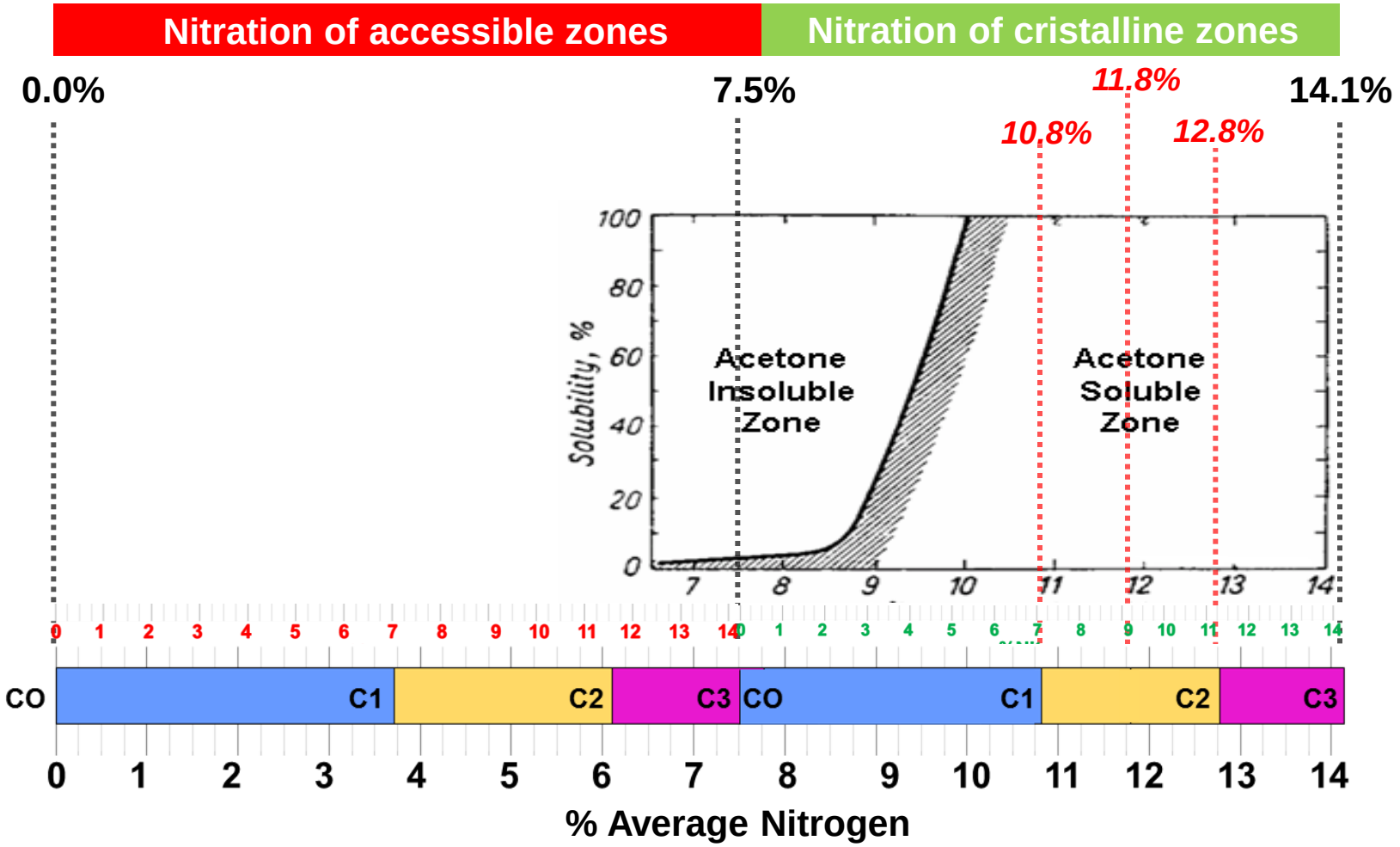
If %Accessibility = 45%
14.14%N max x 45% = 6.4%N
12.8% will be shifted to 12.5%

If %Accessibility = 65%
14.14%N max x 65% = 9.2%N
12.8% will be shifted to 13.0%

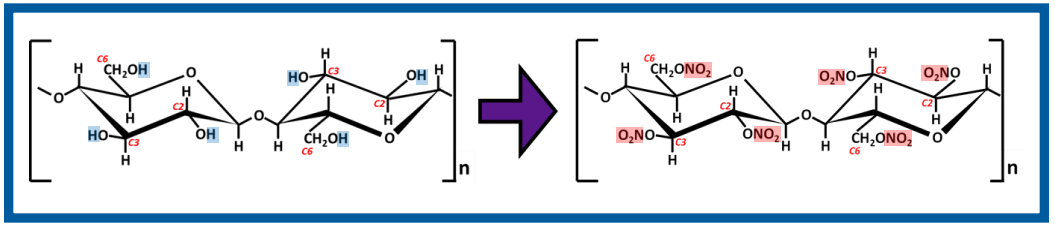


Cellulose nitration





Cellulose nitration



Nitration of accessible zones | Nitration of cristalline zones

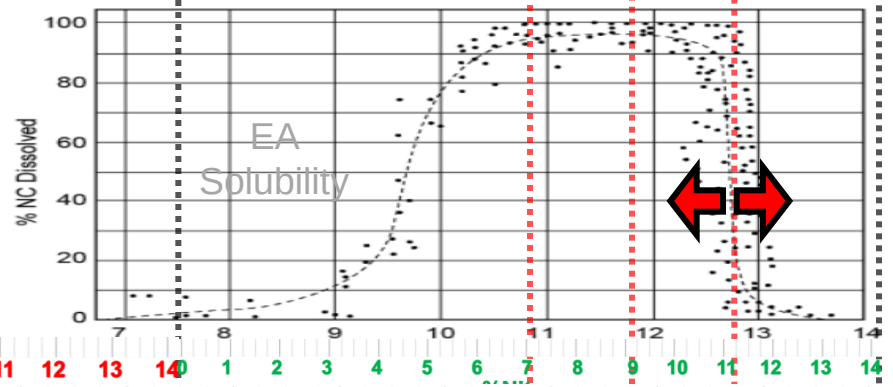
0.0% | 7.5% | 10.8% | 11.8% | 12.8% | 14.1%

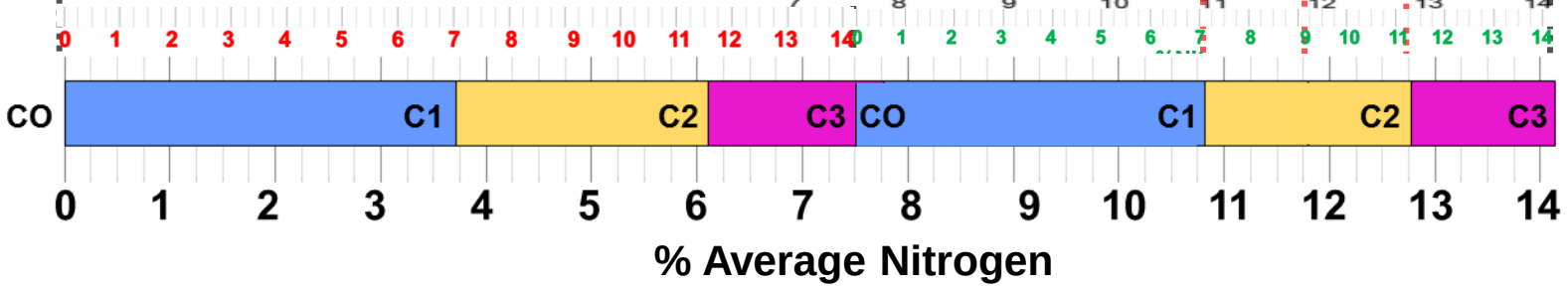
Higher Crystallinity — *Lower Crystallinity*

OH Base Crystallites | **Amorphous Mix OH-NO3** | **NO3 Base Crystallites**

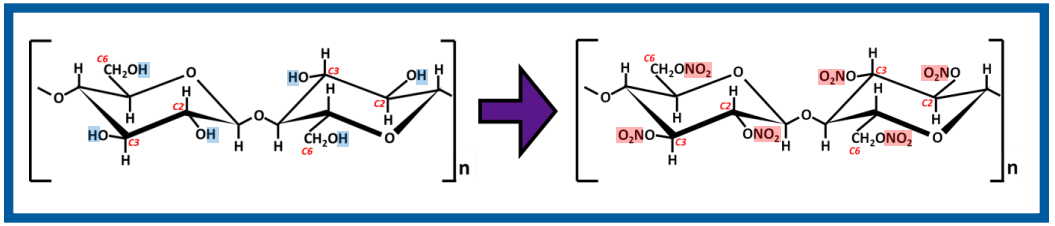
Obtained with ideal cellulose and nitration conditions

Nitration conditions can also shift this curve





Cellulose nitration

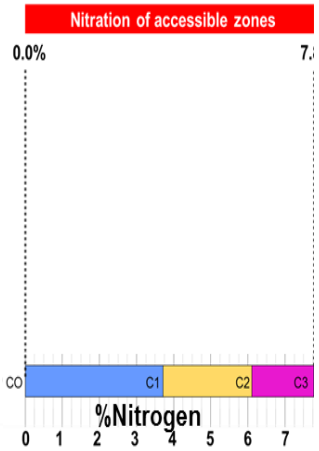


Nitration → speed of penetration

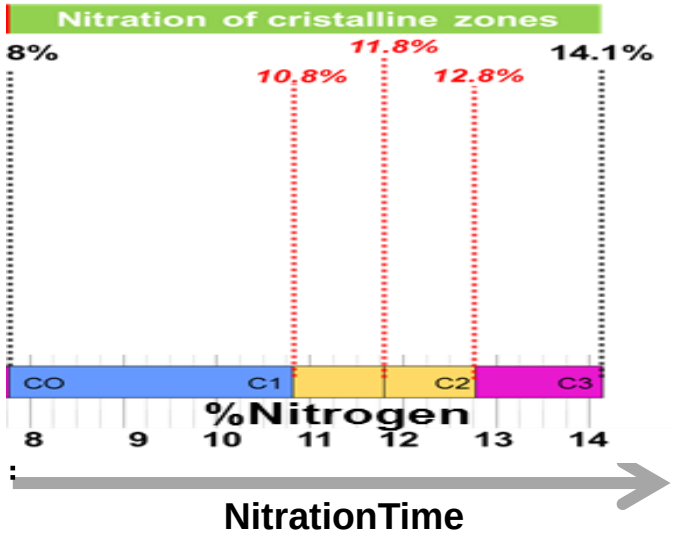
Average %Nitrogen of NC

Rapid nitration targeting a specific average %Nitrogen of NC can yield high disparity in nitrogen content between Accessible and Crystalline zones

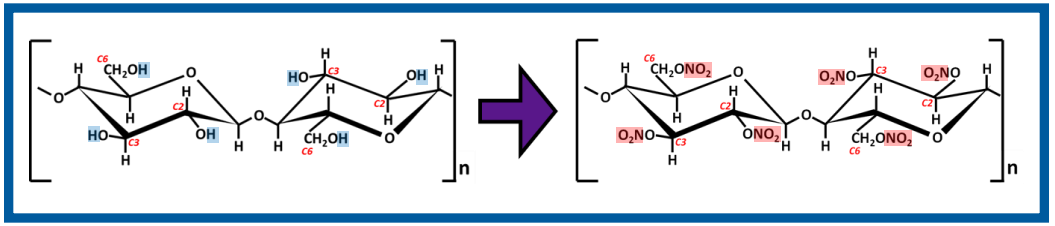
Average %Nitrogen of Accessible zones



Average %Nitrogen of Crystalline zones



Cellulose nitration



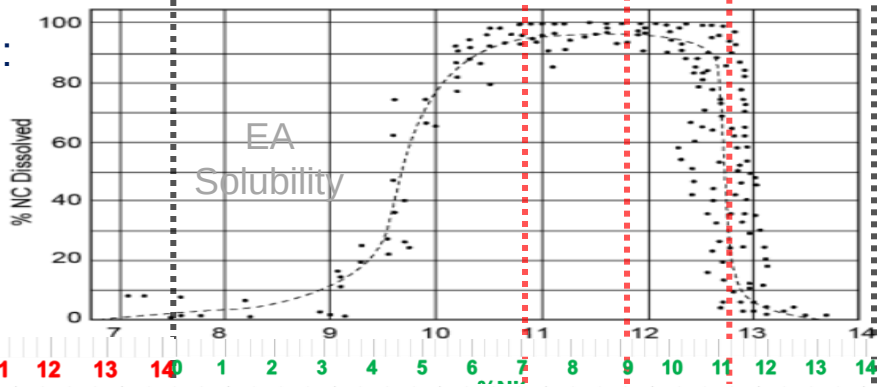
Nitration of accessible zones | Nitration of cristalline zones

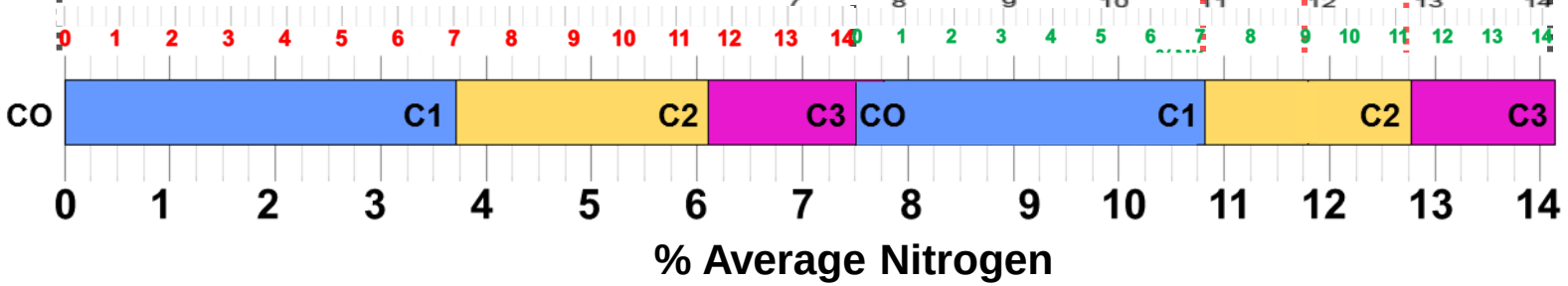
0.0% | 7.5% | 10.8% | 11.8% | 12.8% | 14.1%

Higher Crystallinity — *Lower Crystallinity*

OH Base Crystallites | **Amorphous Mix OH-NO3** | **NO3 Base Crystallites**

A striking feature of this curve:
An asymmetrical curve

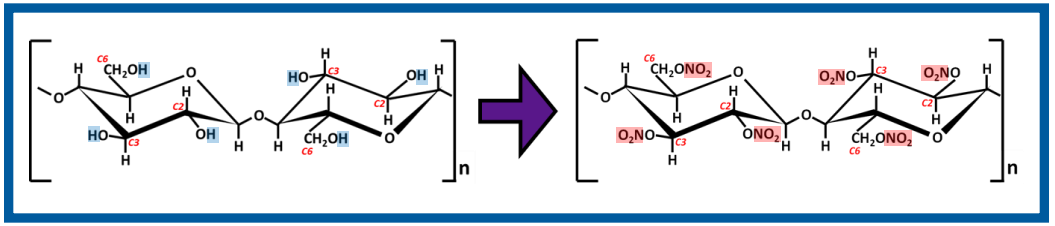




0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

% Average Nitrogen

Cellulose nitration



Nitration of accessible zones | **Nitration of cristalline zones**

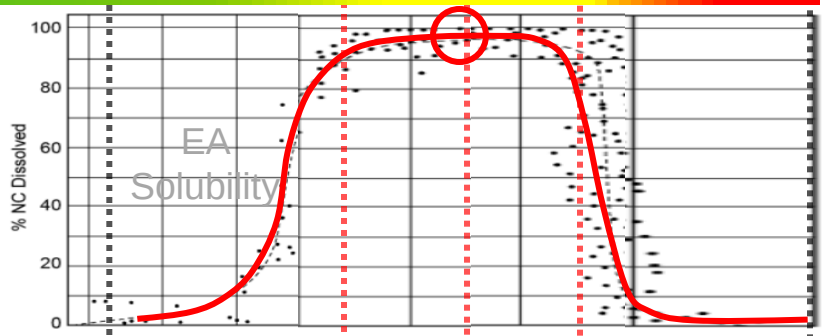
0.0% — *Higher Crystallinity* — **0.0** — **1.0** — **1.5** — **2.0** — **3.0** *Lower Crystallinity*

OH Base Crystallites | **Amorphous Mix OH-NO3** | **NO3 Base Crystallites**

In fact it is nearly **symmetrical**

The effect is due to conversion between DS and %N

(The Mw of cellulose at C0 = 160 g/mole)

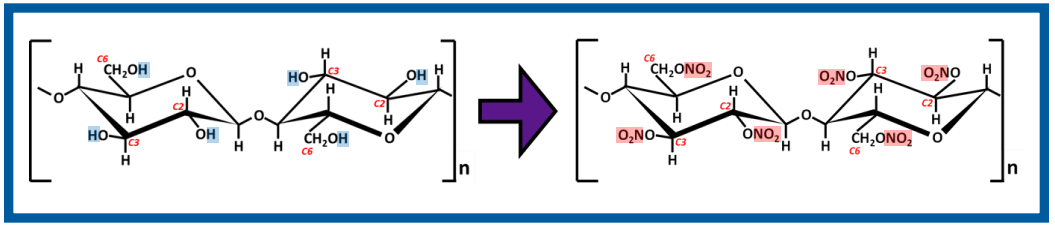


CO | C1 | C2 | C3 | CO | C1 | C2 | C3

0 1 2 0 1 2 3

Average degree of substitution (DS) of NC — **Average degree of substitution (DS) of NC**

Cellulose nitration

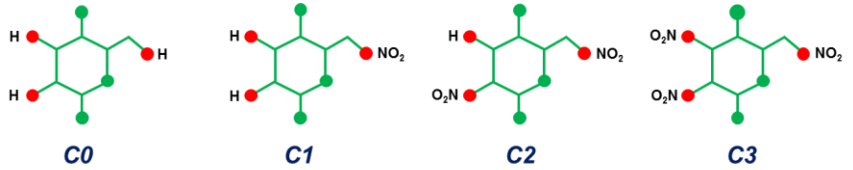


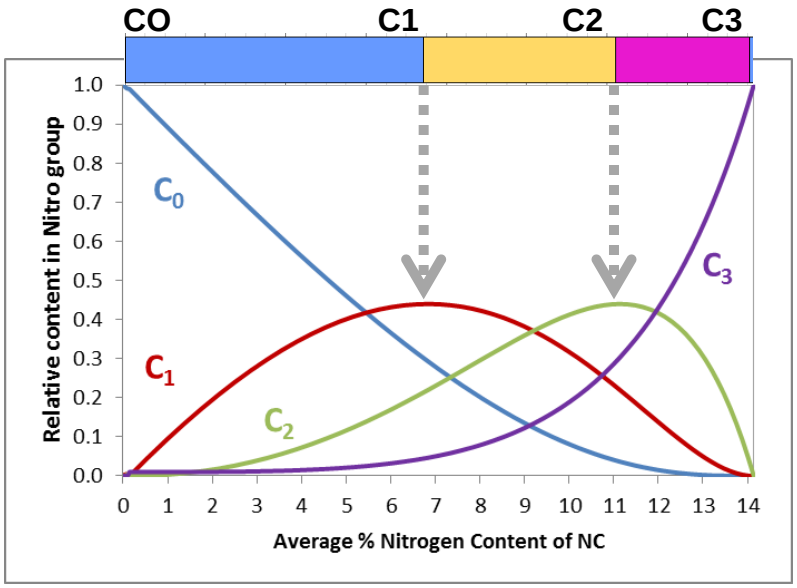
Theoretical arrangement of substituents in cellulose

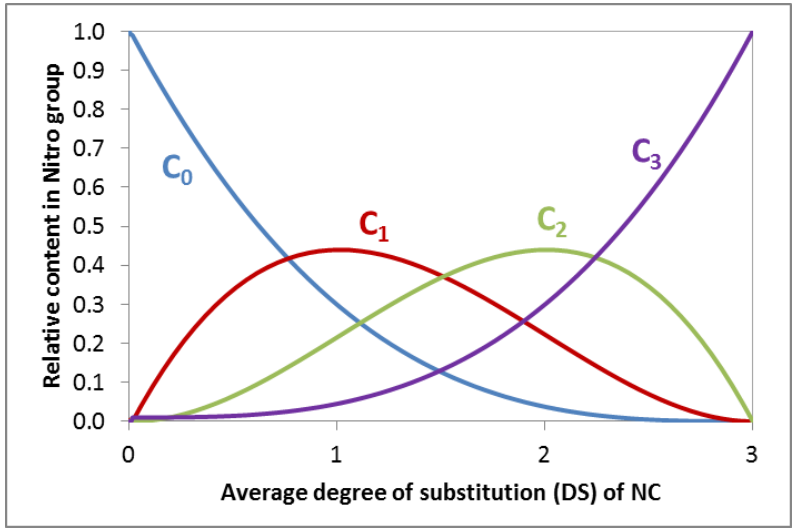
On the basis of:

- -availability of all anhydroglucose is equal
- -no interference between hydroxyl groups
- -reaction rates constant
- -end group effects negligible

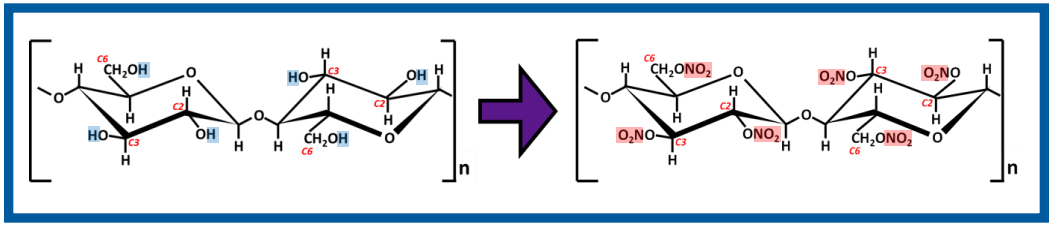
Label	# of Nitro Group	% Nitrogen	Molecular Weight
C0	0	0.0	162
C1	1	6.8	207
C2	2	11.1	252
C3	3	14.1	297







Cellulose nitration



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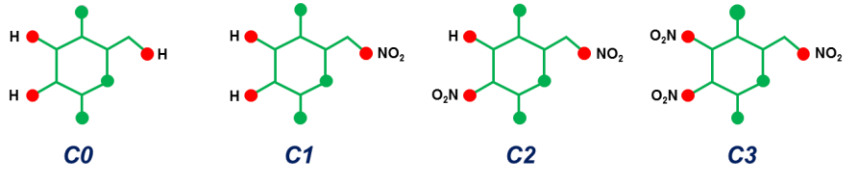
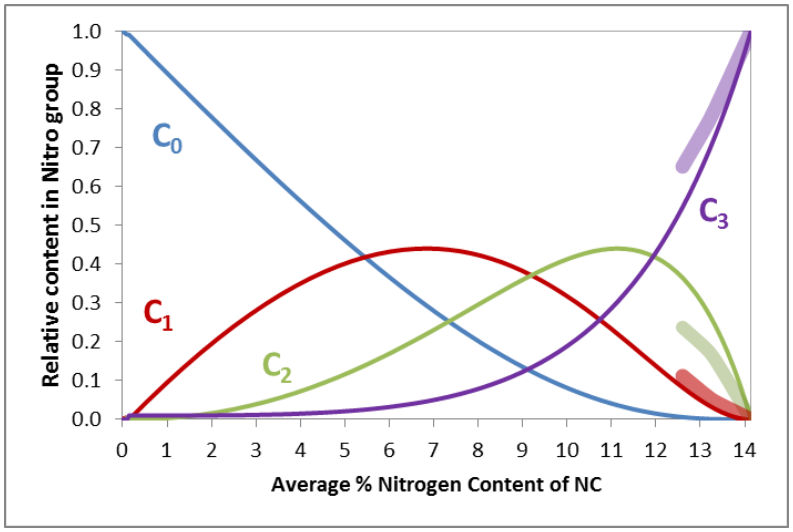
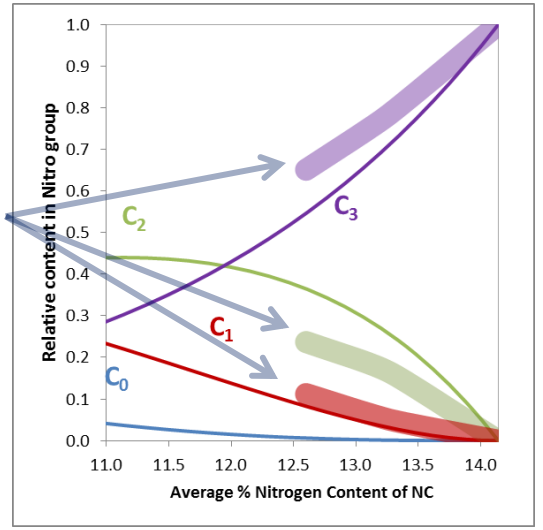
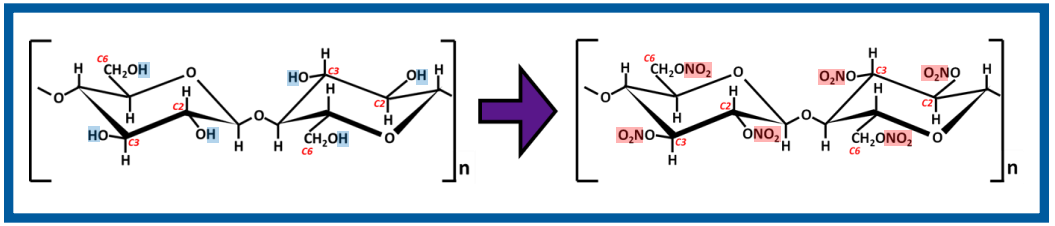




NMR Data on Degree of Substitution of NC



Cellulose nitration



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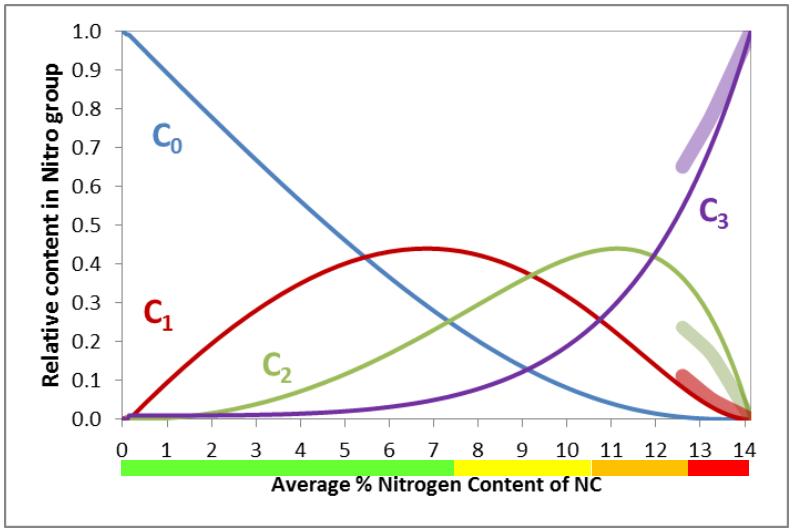
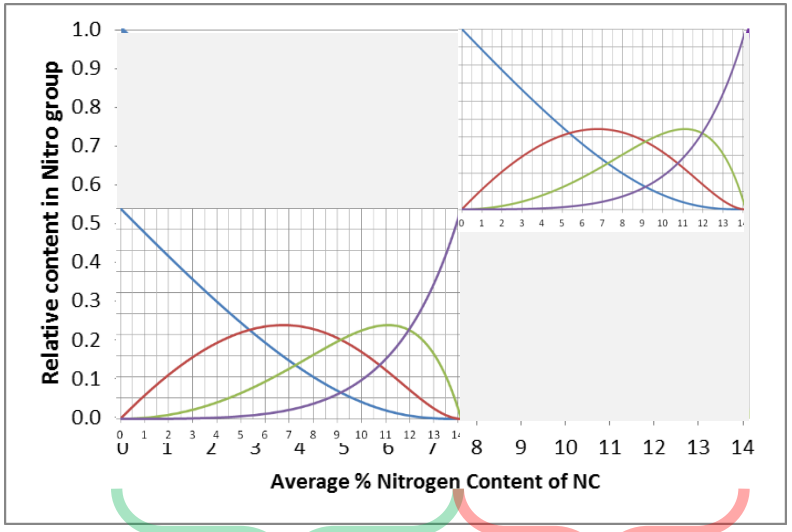
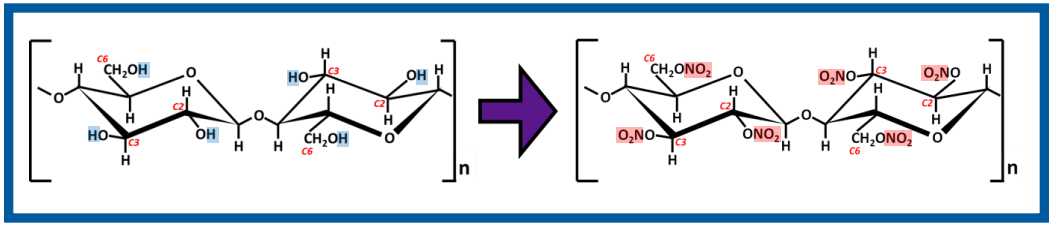




Nitration of amorphous areas of cellulose

Nitration of crystalline areas of cellulose

Cellulose nitration



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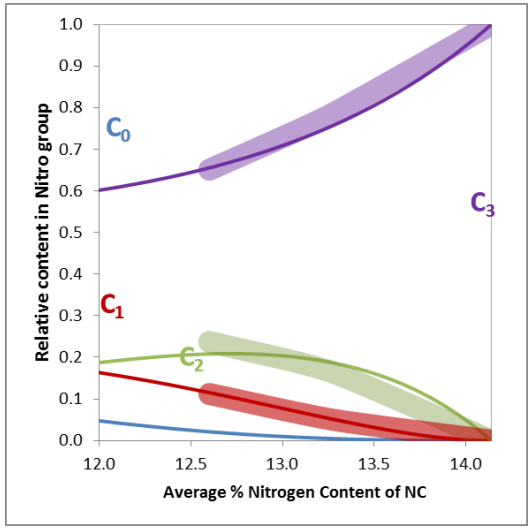
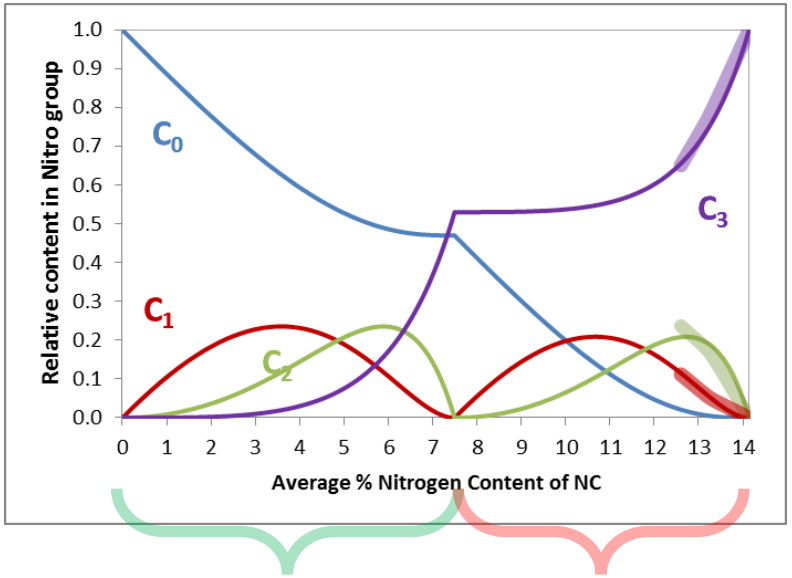
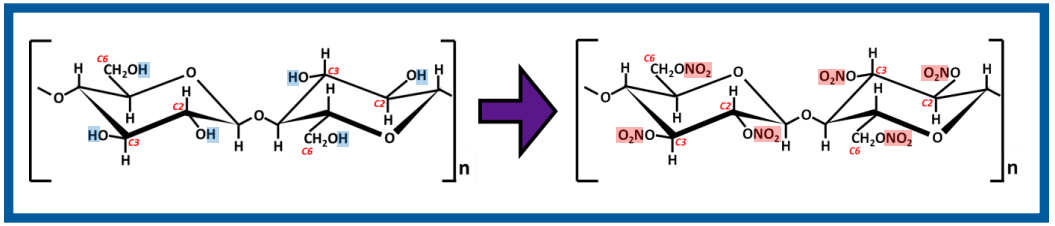




Nitration of amorphous areas of cellulose

Nitration of crystalline areas of cellulose

Cellulose nitration

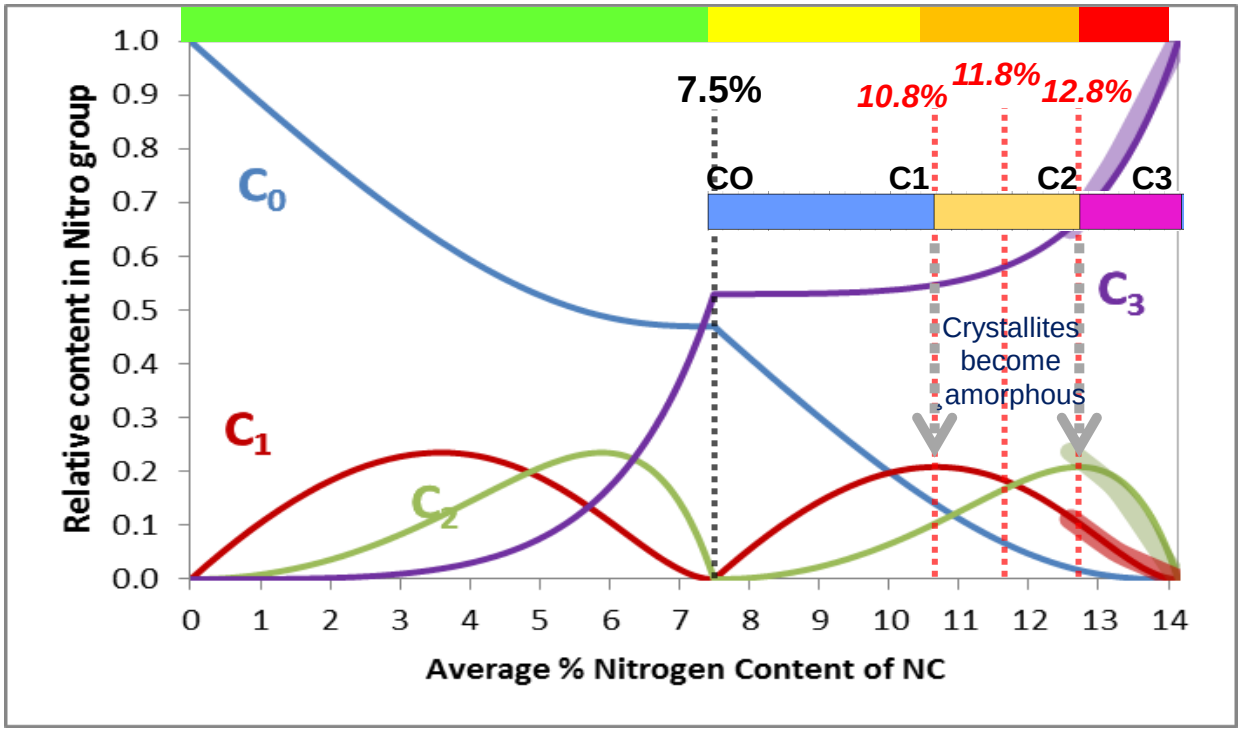


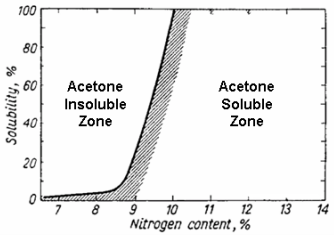
Impervious to most solvent — More solvent solubility — Limited solvent solubility

Higher crystallinity

OH Base Crystallites — Amorphous Mix OH-NO3 — NO3 Base Crystallites

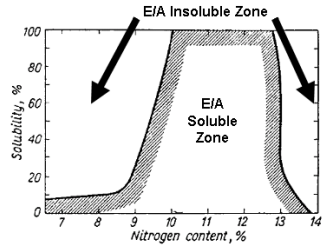
Lower crystallinity





Solubility of NC in acetone solution against nitrogen content

Gray line = Typical acetone solubility curve



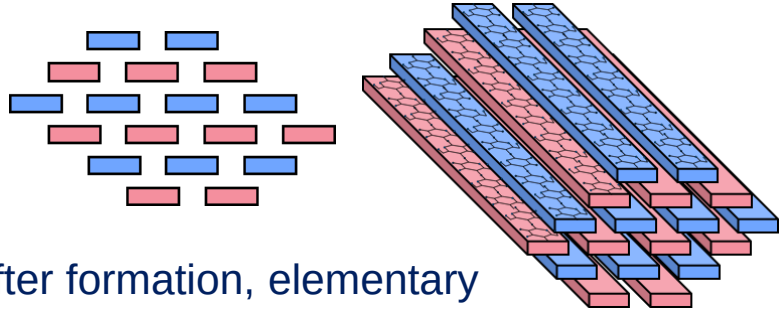
Solubility of NC in 2:1 ether-alcohol solution against nitrogen content

Gray line = Typical EA solubility curve

Cellulose /Nitrocellulose microfibril structure

Nanofibril basic structure: Size of crystallite and formation on microfibrils

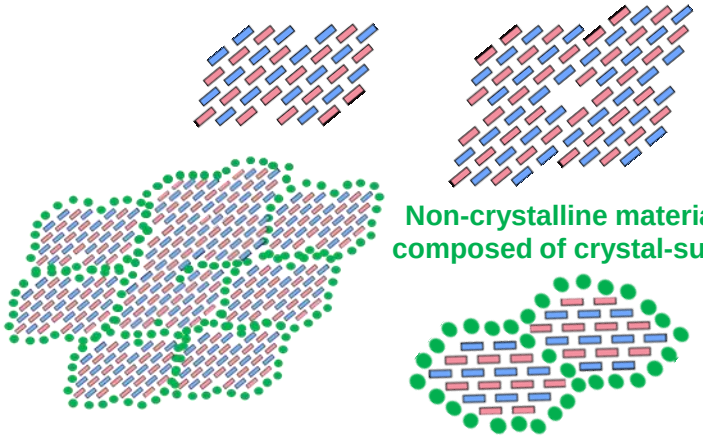
Elementary microfibrils are about 3 nm in diameter



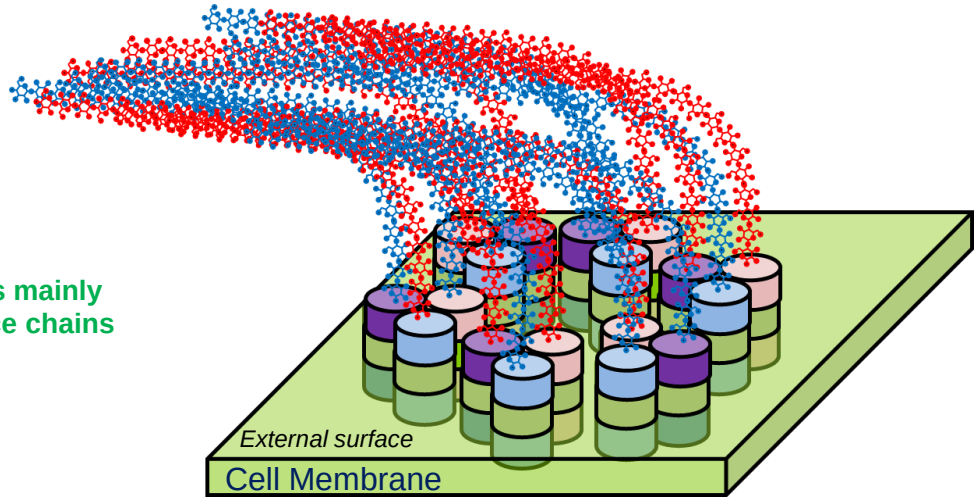
Rosette containing 6 groups of 3 synthase units producing 1 cellulose chain each.
A total of about 18 cellulose chains per elementary microfibril.

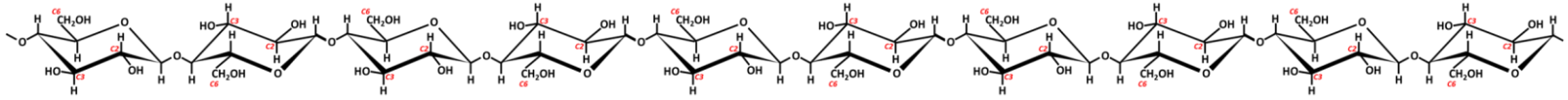
Immediately after formation, elementary microfibrils can fuse or aggregate into bigger microfibril

For cotton and wood: about 80 chains/microfibril



Non-crystalline material is mainly composed of crystal-surface chains





Solubility of Nitrocellulose

Five (5) possible types of response to a solvent system of NC molecules and microfibrils

-Wetting
-Swelling (intercrystalline) *Amorphous zone*
-Swelling (intracrystalline) *Crystalline zone*
-Gelatinization
-Dissolution (+ *very significant change in viscosity*)

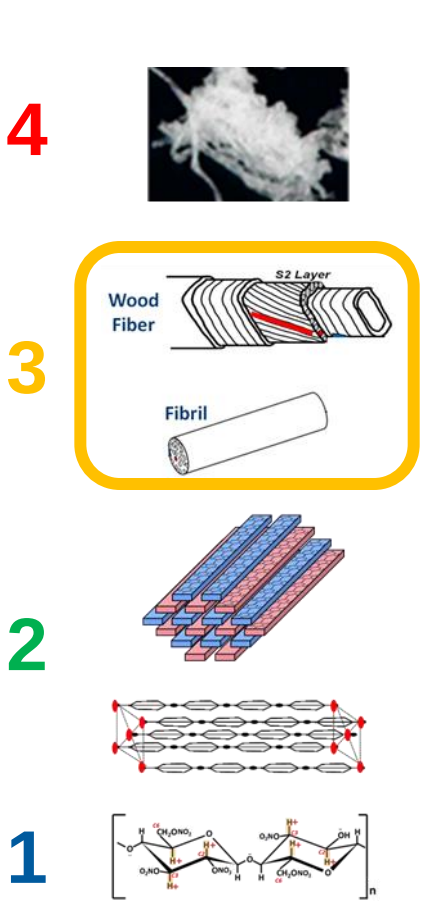
Solvent system can be adjusted to end the solvent intake process at any of these stages.

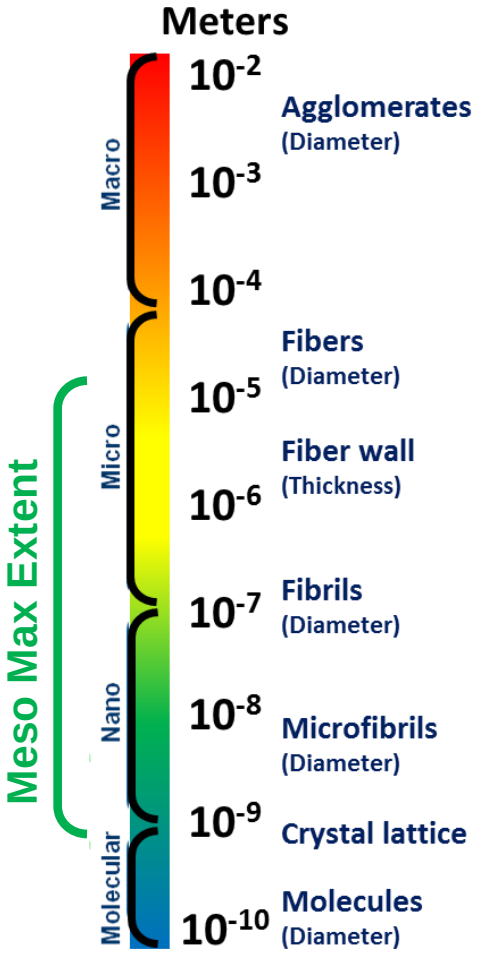
The solvent intake process can also be ended by limiting the solvent content.

For NC in fiber form:
Extra descriptions are required to account for additional levels of structures.

NC based propellant structure

Types of gel structure: Soft material systems

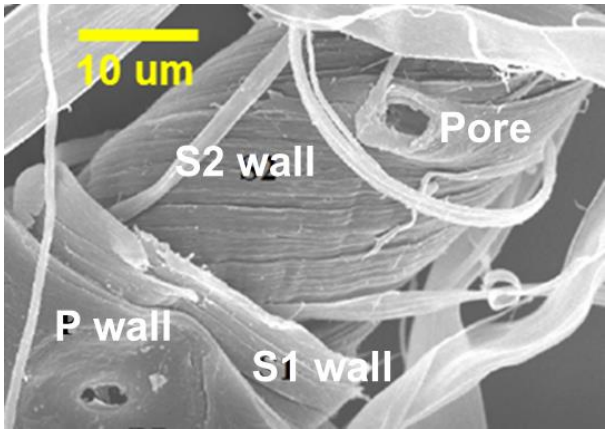


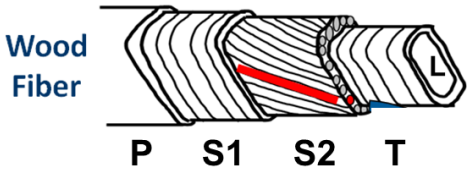


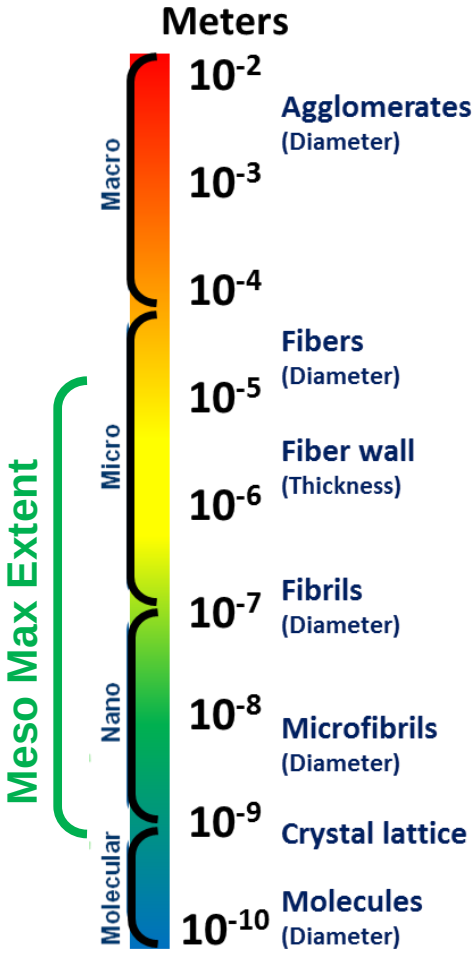
Cellulose / Nitrocellulose fiber structure

Multiple wall assembly

Wall layers







Wood
Primary wall (P)
1st Secondary wall **(S1)**
2nd Secondary wall **(S2)**
Tertiary wall **(T)**
Lumen **(L)**

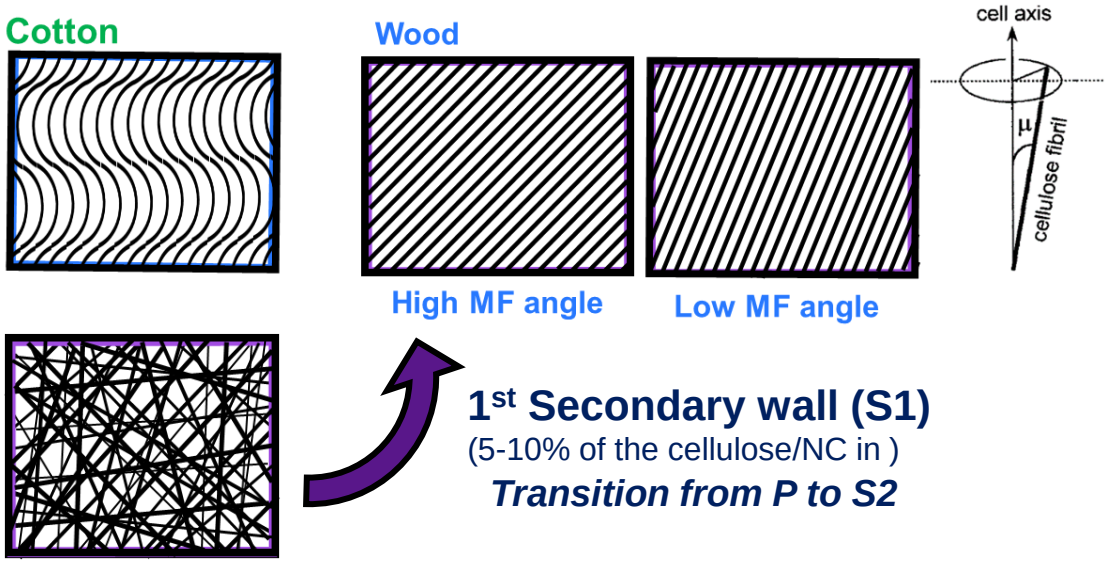
Cotton
Cuticle
Primary wall (P)
1st Secondary wall (S1)
2nd Secondary wall (S2)
Lumen

Cellulose / Nitrocellulose fiber structure

Multiple wall assembly: Wall fibrillar structure

2nd Secondary wall (S2)
(80-90% of the cellulose/NC fiber)

Primary wall (P)
(5-10% of the cellulose/NC fiber)



1st Secondary wall (S1)
(5-10% of the cellulose/NC in)
Transition from P to S2

S2 wall: contains most of the cellulose, microfibrils in fairly parallel with dense alignment. Usually easily penetrated by nitrating acids in cellulose and compatible solvent system in NC. Designed for structural support.

P wall: The thinnest but most complex wall. Designed to resist expansion of interior components (*turgor pressure of the original xylem cell*). Microfibrils with complex alignment. Also designed to ***resist bursting*** *and accommodate extension of cell.*

S1 wall: Transition between P and S2, change in chemical composition and structure.

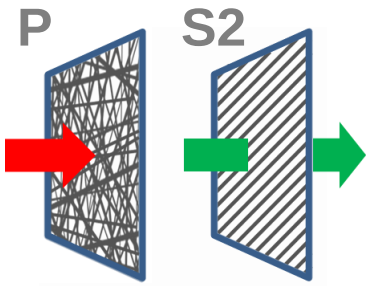
Cellulose / Nitrocellulose fiber structure

Multiple wall assembly: effects on solvents absorption

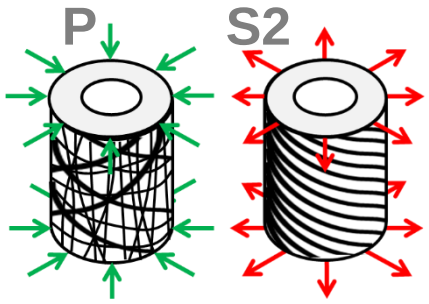
Swelling and dissolution of the P, S1 and S2 walls are very different

P wall fairly impermeable vs S2 wall
(delaying/preventing solvents absorption)

P wall usually the most nitrated portion of the fibre *–except in contact areas within agglomerates*



P is constructed to limit fiber swelling
(limiting solvents absorption)



Fiber with P and S2 layers

Fiber with S2 layer only

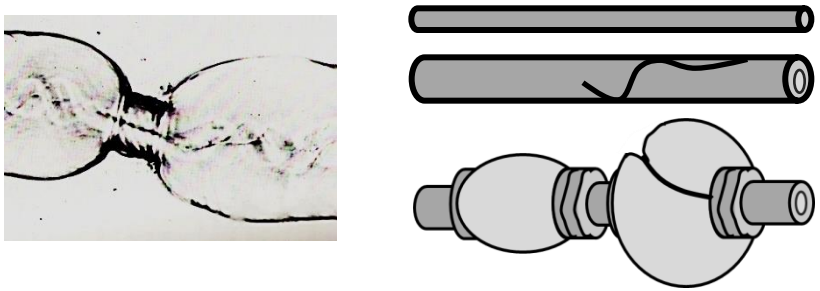
Cellulose / Nitrocellulose fiber structure

Multiple wall assembly: swelling and ballooning

Ballooning

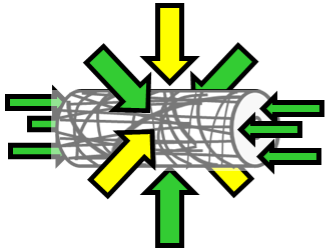
The fast swelling S2 wall rips apart the P and S1 walls which rolls up increasing the strength of these walls in unswollen sections.

Swelling and ballooning



Cotton P wall

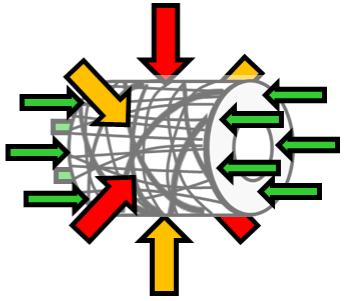
Somewhat permeable



Radial and axial penetration

Wood P wall

Fairly impermeable



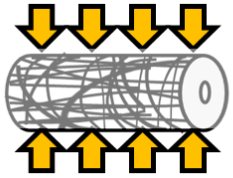
Axial penetration

Four possible types of response to a solvent system from NC fibers:

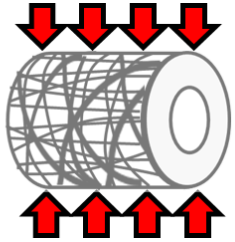
- -Rapid dissolution and disintegration (fragments)
- -Swelling by ballooning and slow dissolution
- -Swelling by ballooning and no dissolution
- -Limited swelling and no dissolution

Else no swelling and no dissolution

Weaker



Stronger



Note: Generally, a distribution of responses is obtained

NC based material for extruded propellant

Forming a gel structure: **Molecular, Intermolecular and Surfaces Forces**

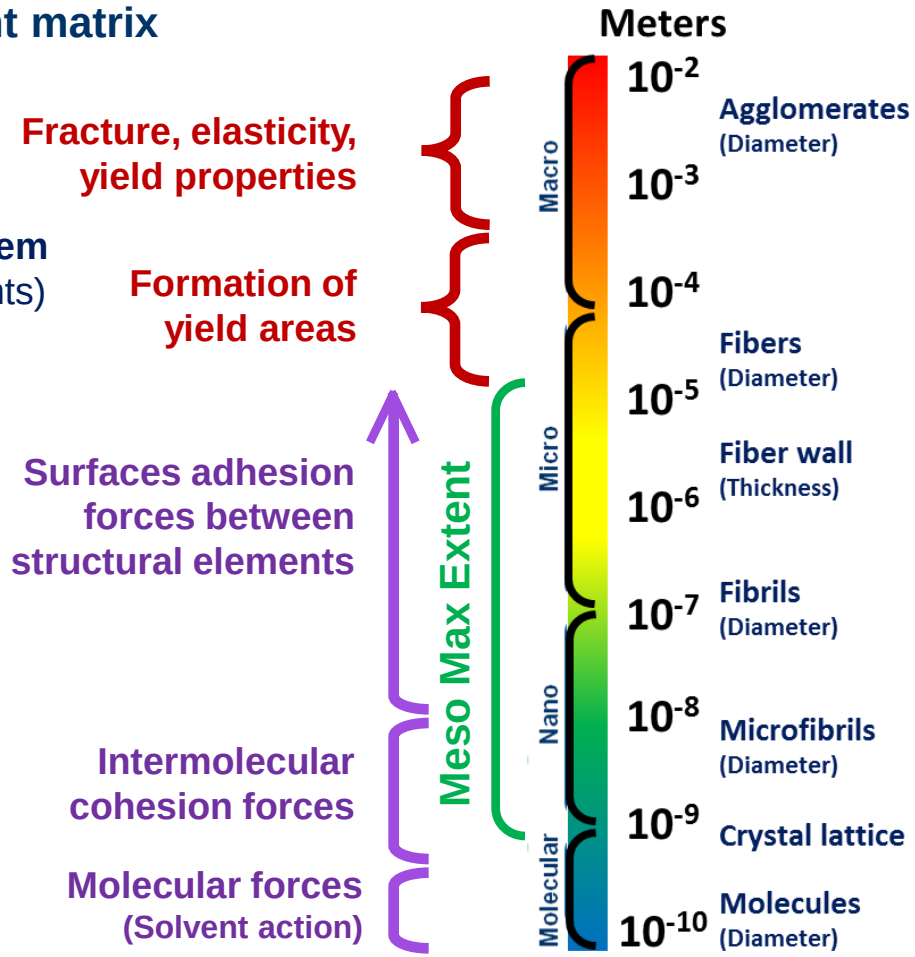
Gel structure of NC based propellant matrix

Four response of NC fibers to a solvent system

-Rapid dissolution and disintegration (fragments)
-Swelling by ballooning and slow dissolution
-Swelling by ballooning and no dissolution
-Limited swelling and no dissolution
Else no swelling and no dissolution
Note: a distribution of behavior is obtained

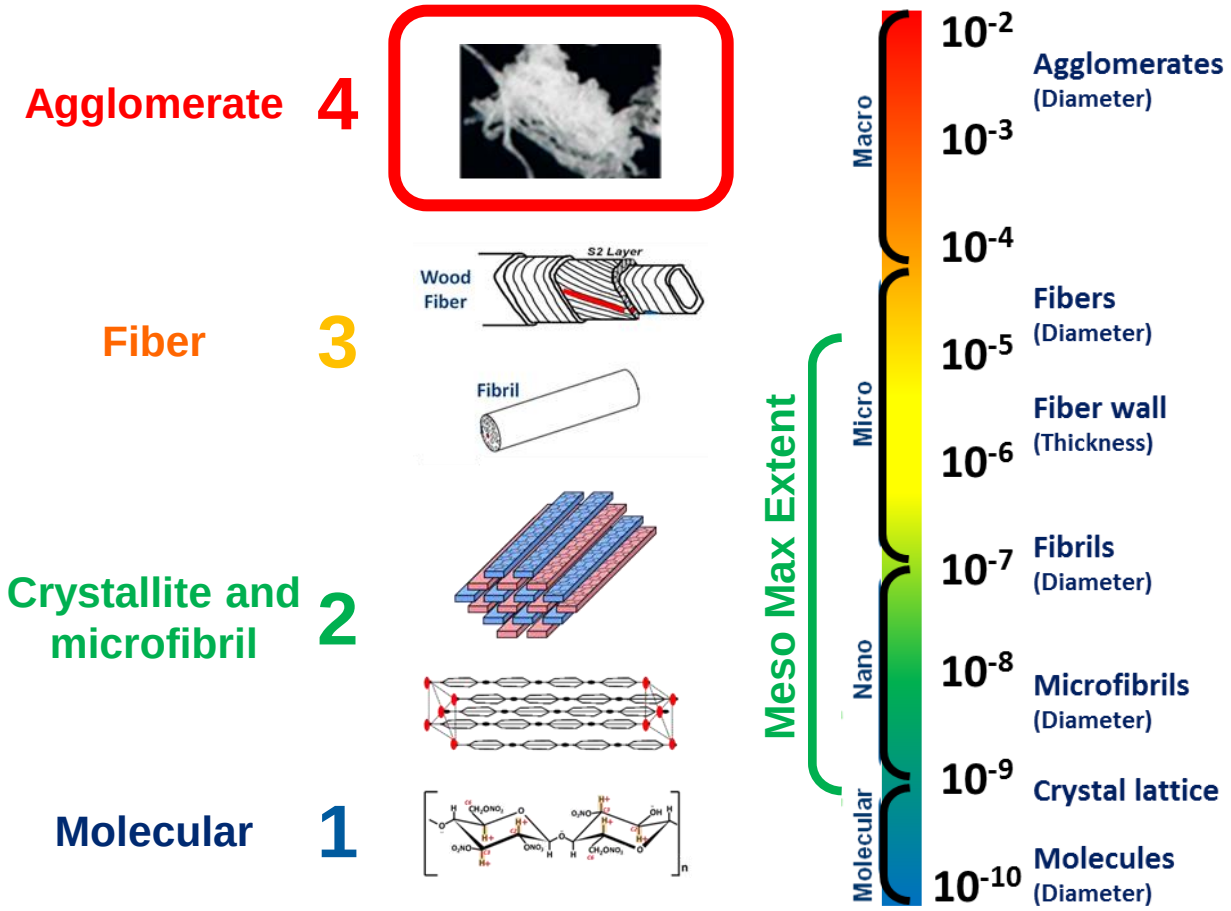
Five responses of NC molecules and microfibrils *to a solvent system*
(or for polymers in general)

-Wetting
-Swelling (type 1) *Amorphous zone*
-Swelling (type2) *Crystalline zone*
-Gelatinization
-Dissolution (+ *high viscosity*)

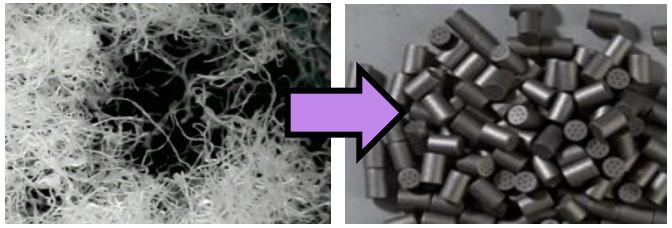


Nitrocellulose multi-level structure
Fibers agglomerates

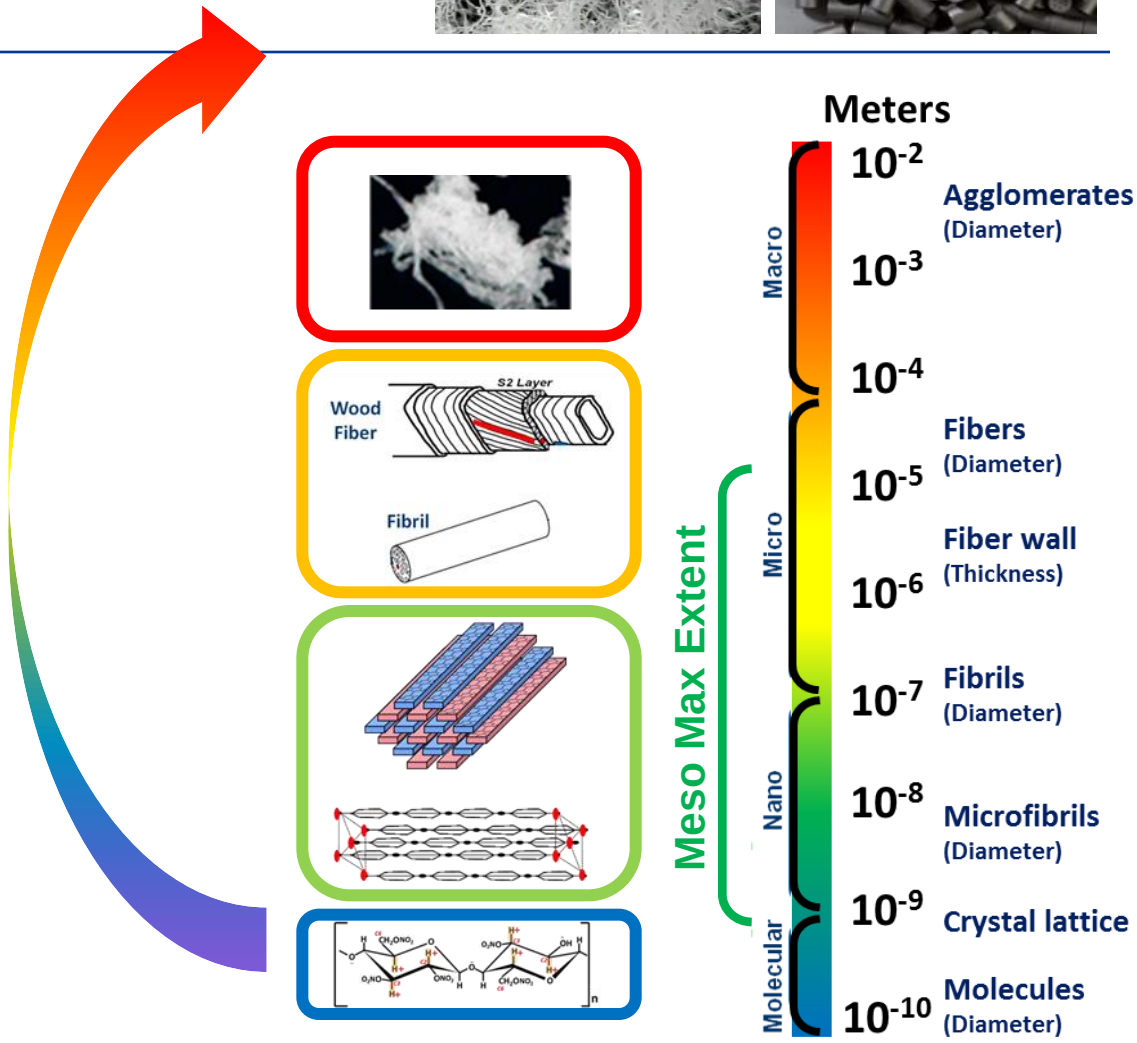
NC fiber agglomerates add another level of structure which bring another set of rules regarding dissolution of NC. Fiberboard density and type for cellulose preparation for nitration are important variables



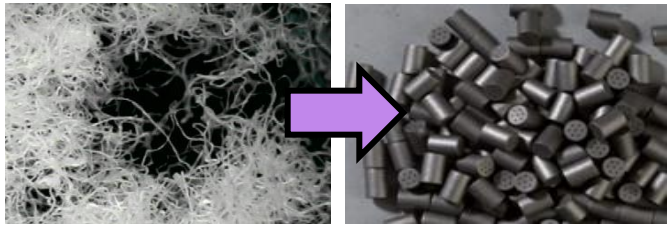
Nitrocellulose multi-level structure



Traditionally for propellant, the main strategy for understanding material properties is by attempting to relate propellant dough and/or final propellant quality with molecular properties of NC

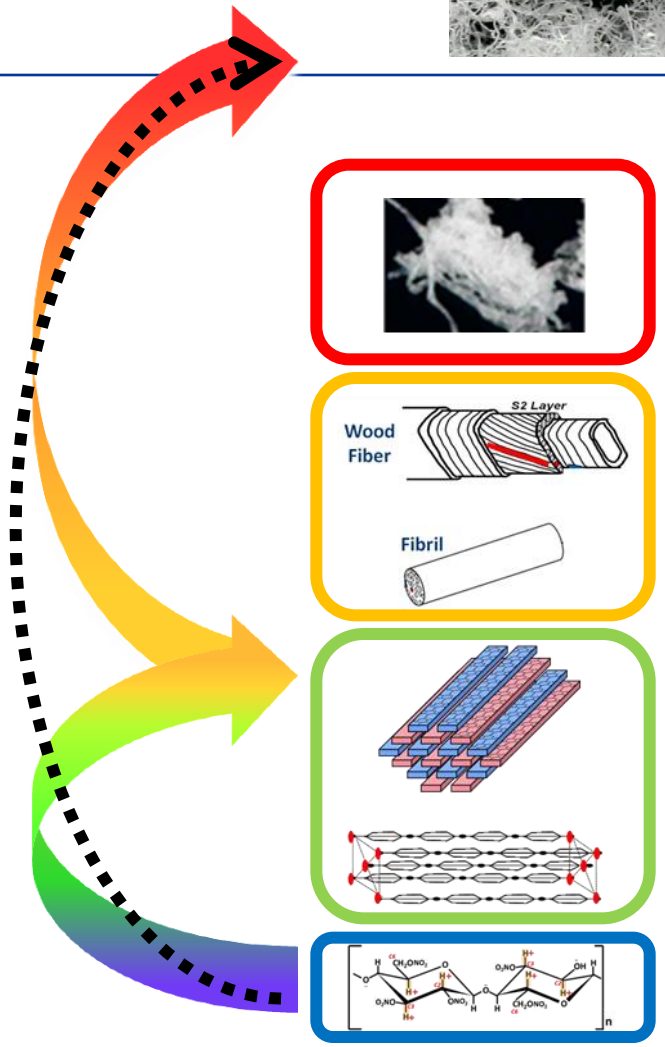


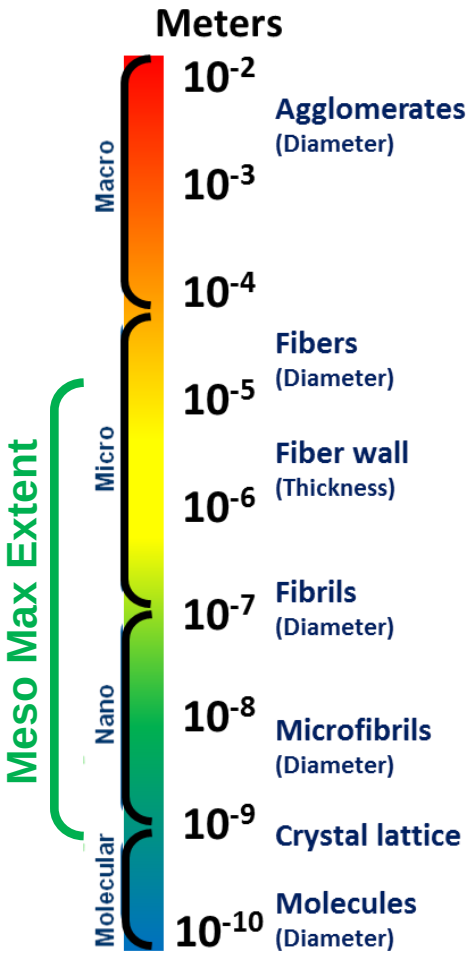
Nitrocellulose multi-level structure



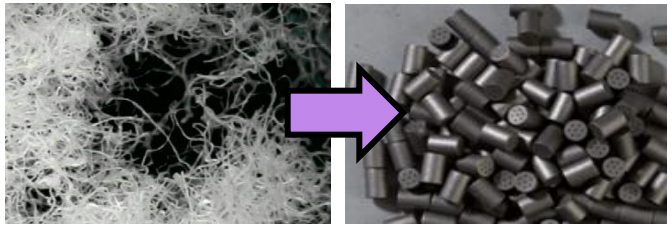
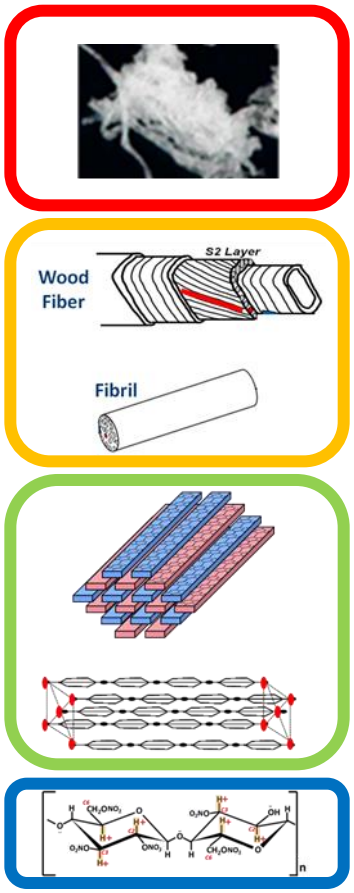
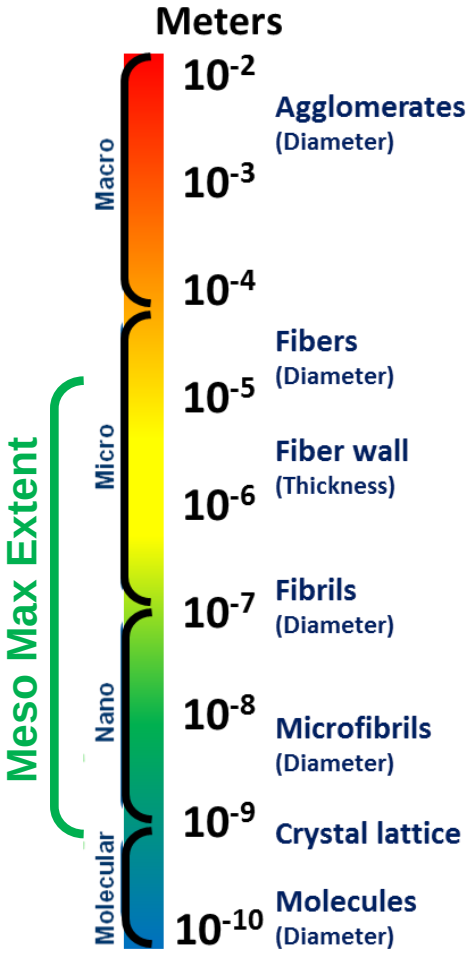
Properties of the mesoscopic structures determine much of the macroscopic behavior of NC based material.

The mesoscopic structures are related to the molecular structure, the chemistry of NC and the conditions under which it was generated and transformed by processing.





Nitrocellulose multi-level structure



This is obviously a very crude simplification of what is actually a highly complex system obtained from biological material that has evolved for hundreds millions of years.