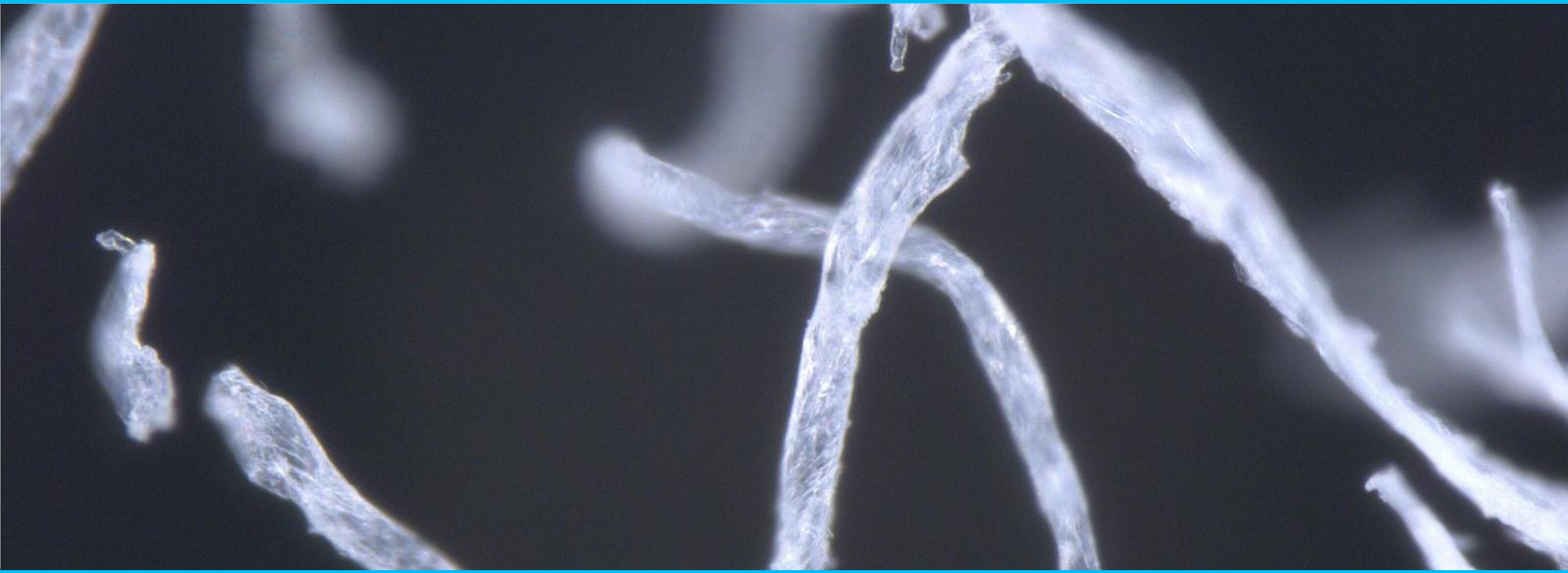
Nitrocellulose Degrees of Freedom



Chemico-Physical Effects on Mechanical Processing

7th NC Symposium, Canada, 31st May – 1st June 2016

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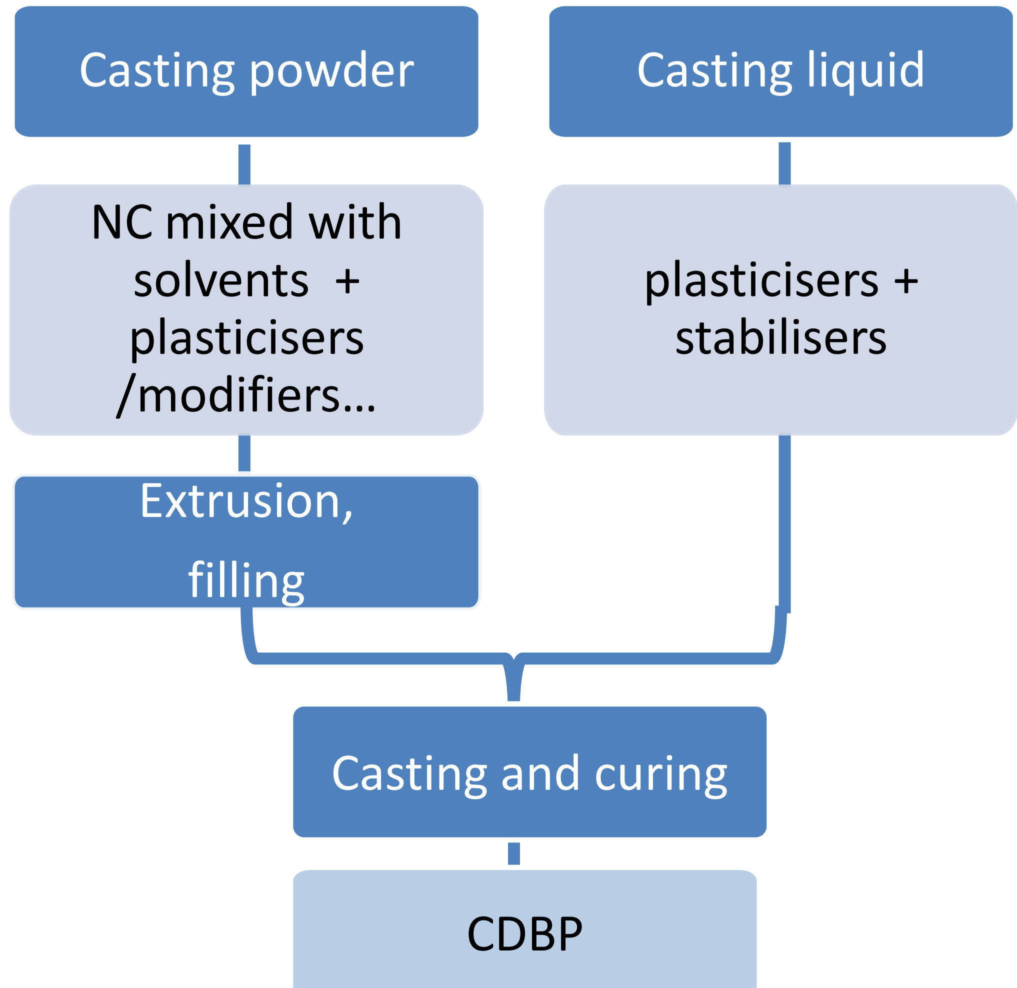
Nitrocellulose Degrees of Freedom

- **Introduction**
- **Fibre Properties**
- **Polymeric Properties**
- **Swelling and Gelling**
- **Conclusions and Future Work**



Nitrocellulose Degrees of Freedom

Cellulose source

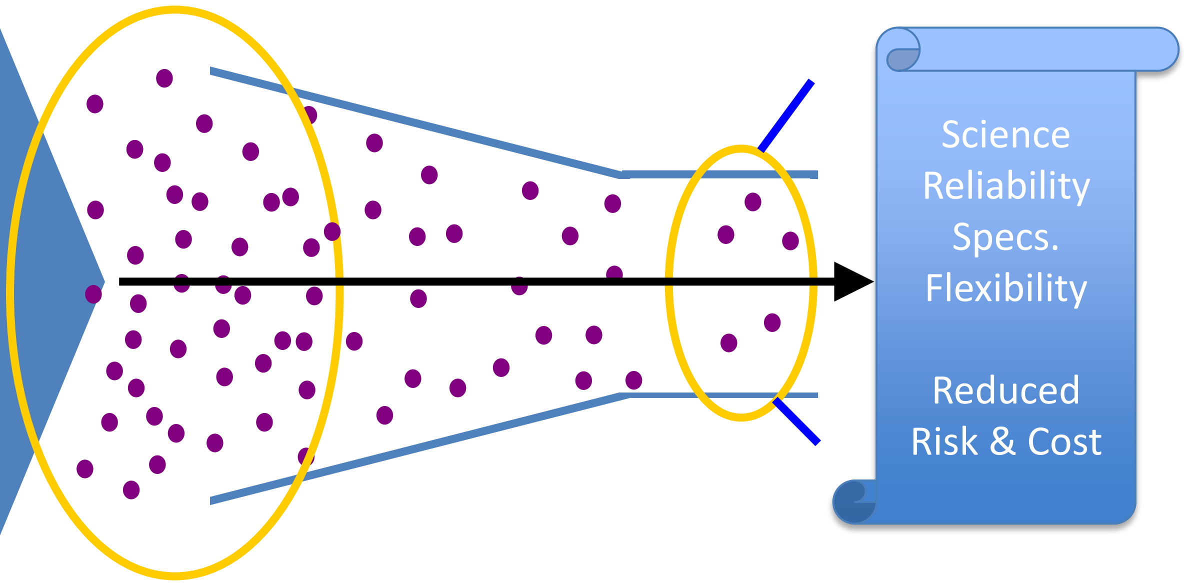
Fibre technology: nano/micro/macro-scale structure and crystallinity of cellulose/NC
Pre nitration treatments (flock vs sheet, bleaching, cutting, thrashing)

Nitrocellulose manufacture

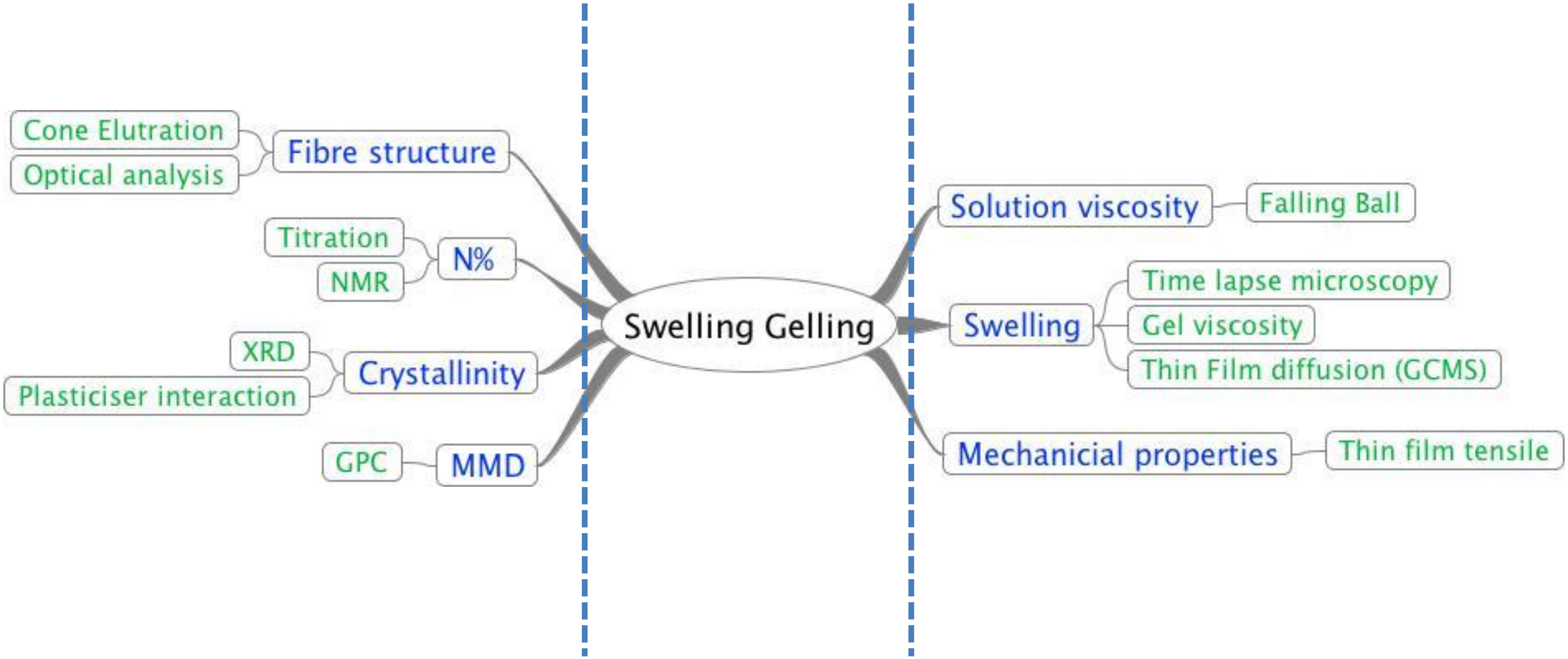
Total N%, N distribution
Molecular Mass Distribution, dispersity
Fibre length distribution
Water/solvent retention, Viscosity

Propellant manufacture

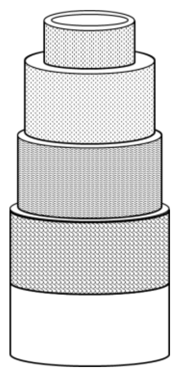
Gelation, solubility, bonding
Chemical stability
Ballistics
Chemical stability
Mechanical properties

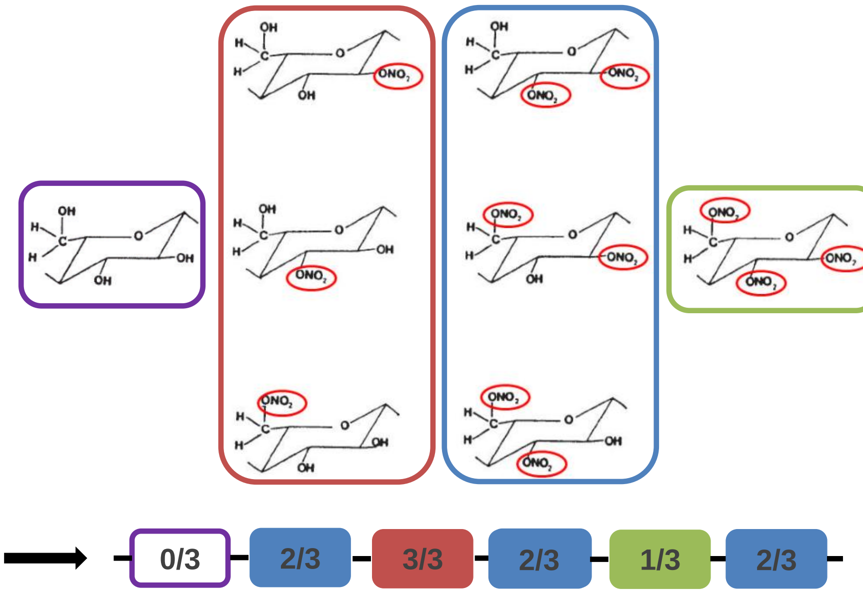


Key Parameters



Fibre Properties





Macro-structure
Fibre length and $Đ_{fib}$

Micro-structure
Nitrogen content and distribution

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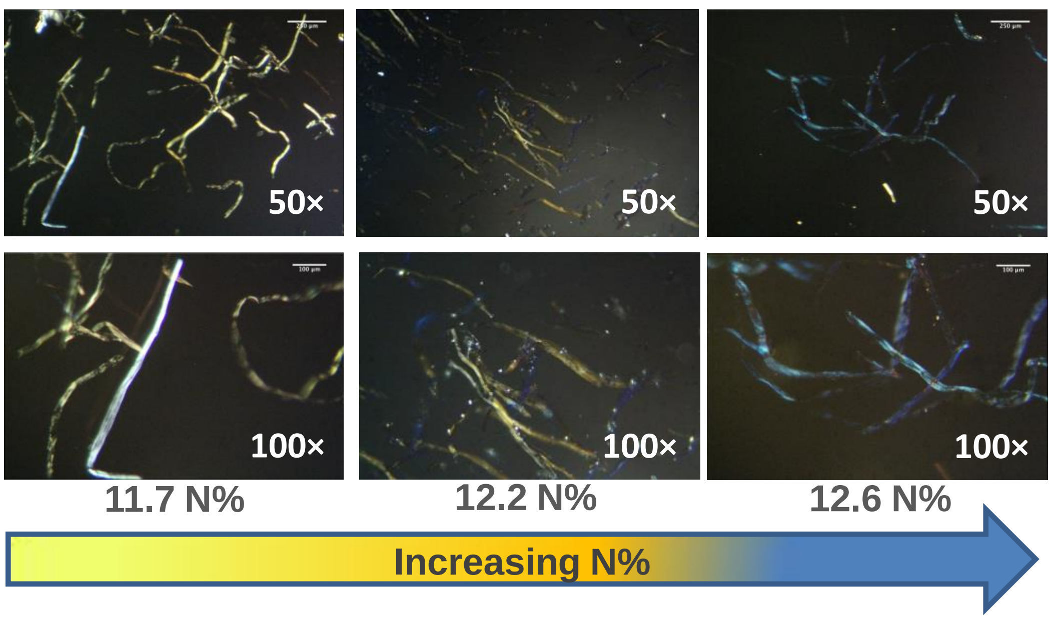
Nitrogen Content

- Variation in N-content affects NC crystallinity > different polarisation colours



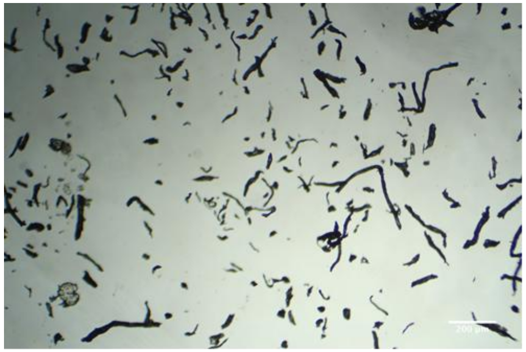
N-Content (%N)	Colour
11.0	Grey white
11.5	White
11.7	Yellow white
12.0	Yellow
12.2	Orange
12.3	Red orange
12.4	Red
12.5	Violet
12.6	Blue
12.8	Blue white
13.1	Pale grey
13.2	Grey
13.4	White
13.5	Intense white

- Polarisation colours correlate with titrimetric values
- Nitration of fibres appears to improve at higher N-content

*Kohlbeck, J. A., Bolleter, W. T., Polarization Colours of Nitrocellulse, J. App. Pol. Sci., 20, 153-156 (1976)

Fibre Length and Dispersity

- Fibre length varies with nitrogen content;
  - Guangrao linter and Tembec wood derived samples increase in fibre length
  - Temmings and Buckeye derived samples decrease



11.7 N%
96 µm
Đ$_{fib}$ = **1.7**

12. 2 N%
127 µm
Đ$_{fib}$ = **1.4**

12.6 N%
244 µm
Đ$_{fib}$ = **1.3**

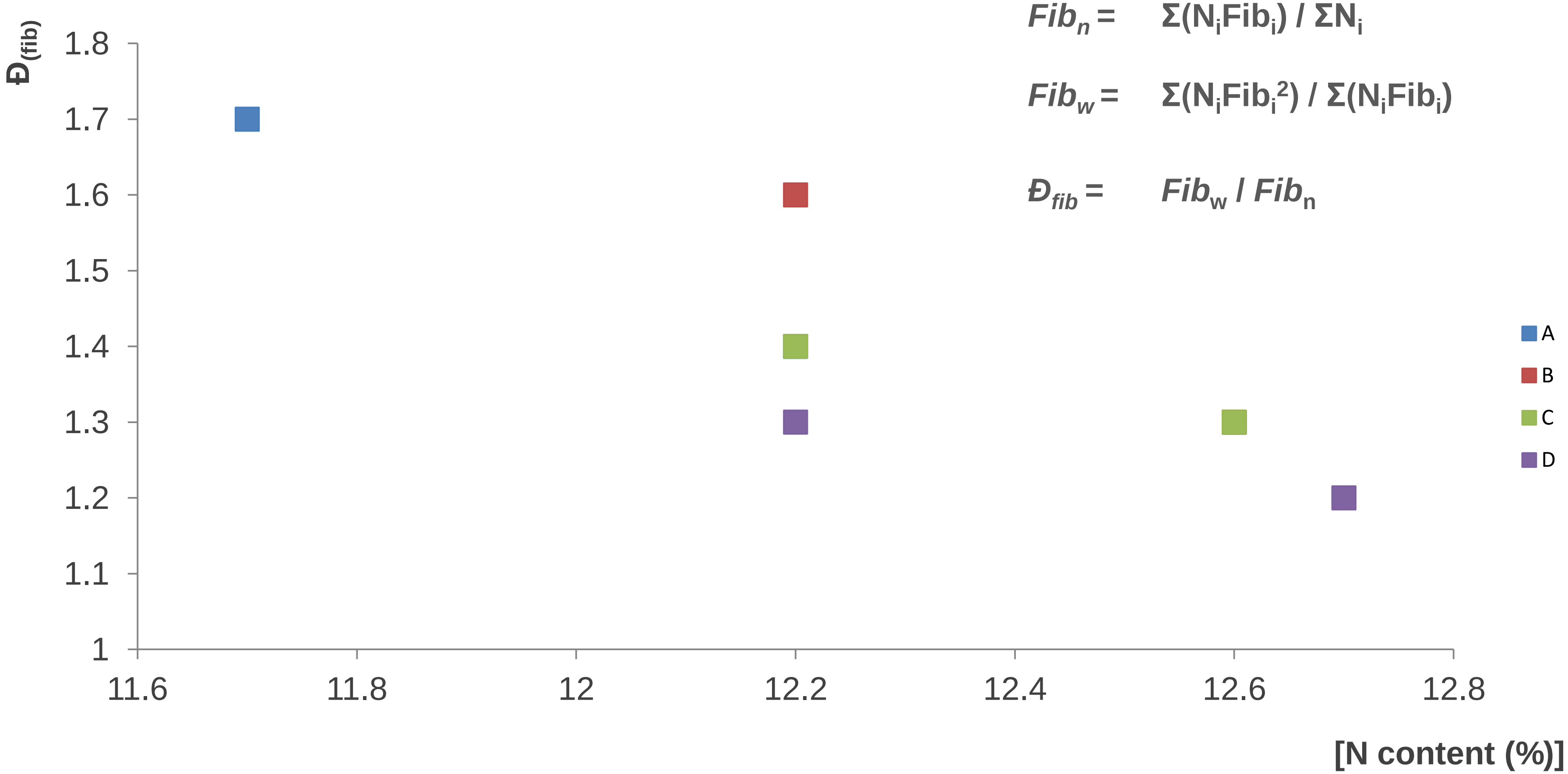
- The dispersity of fibre length (Đ$_{fib}$) decreases in all cases with increasing nitrogen content
  - Improved fibre length homogeneity in high nitration

Fibre Length and Dispersity

$$Fib_n = \Sigma(N_i Fib_i) / \Sigma N_i$$

$$Fib_w = \Sigma(N_i Fib_i^2) / \Sigma(N_i Fib_i)$$

$$Đ_{fib} = Fib_w / Fib_n$$



A, B, C, D, E

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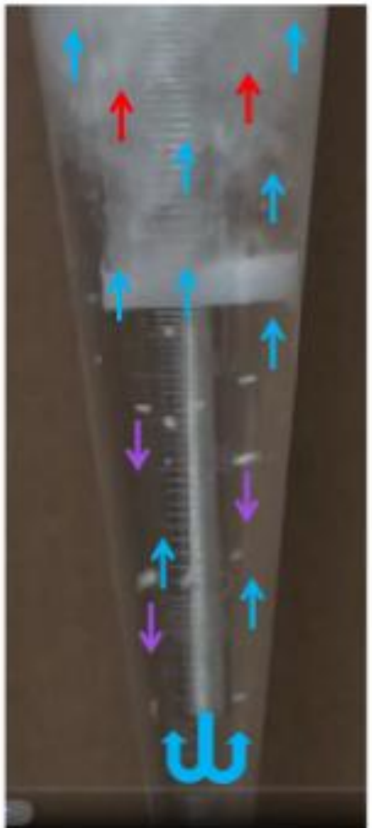
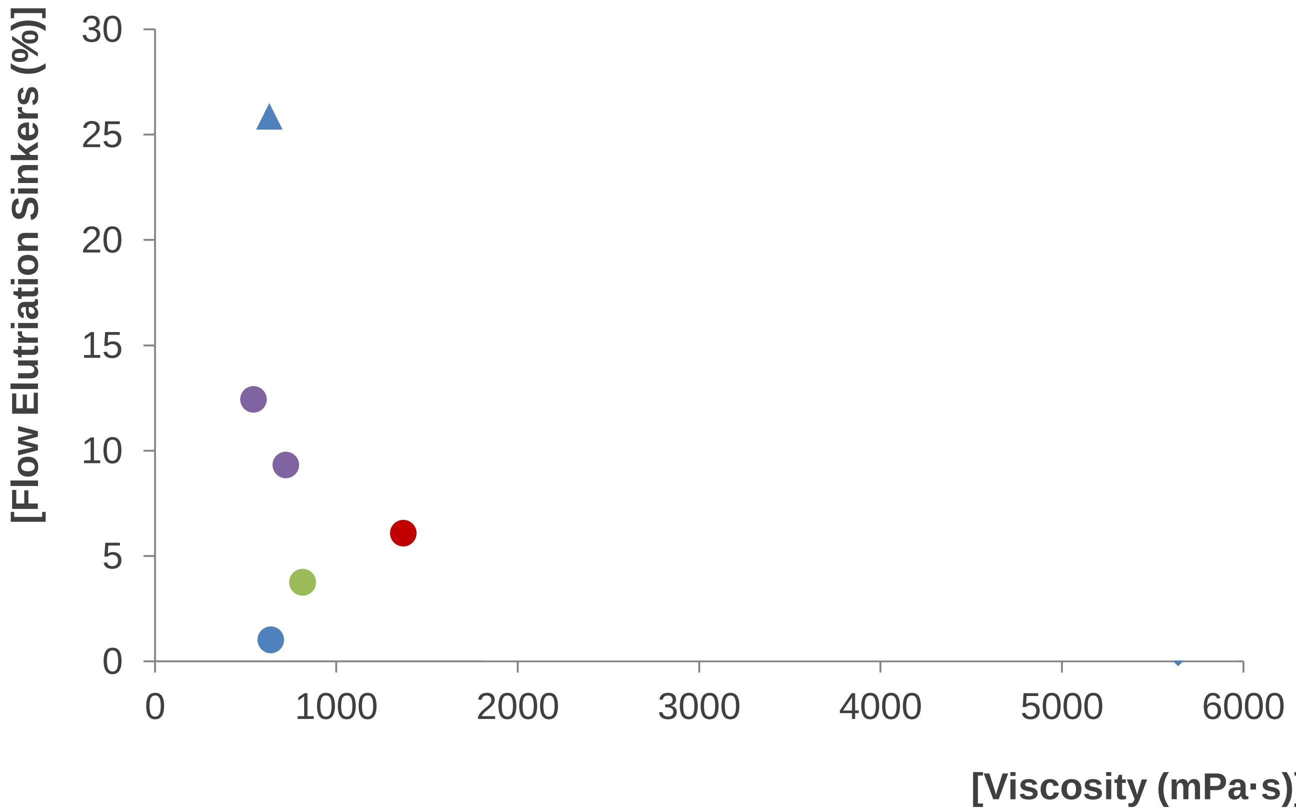
Fibre Elutriation





▲= 11.7 %; ●= 12.2 %; = 12.6 %; ■ = 12.7 %

A, B, C, D, E

*Paquet, M. & Cossette, N. Measuring the Quality of Fiberization of NC. in *5th International NC Symposium* (2012)

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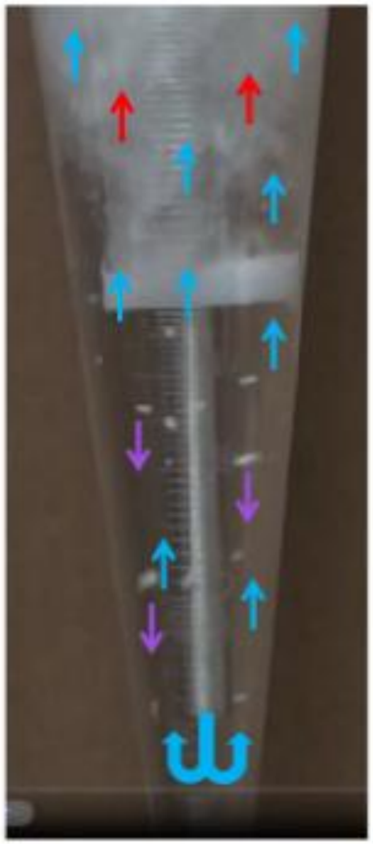
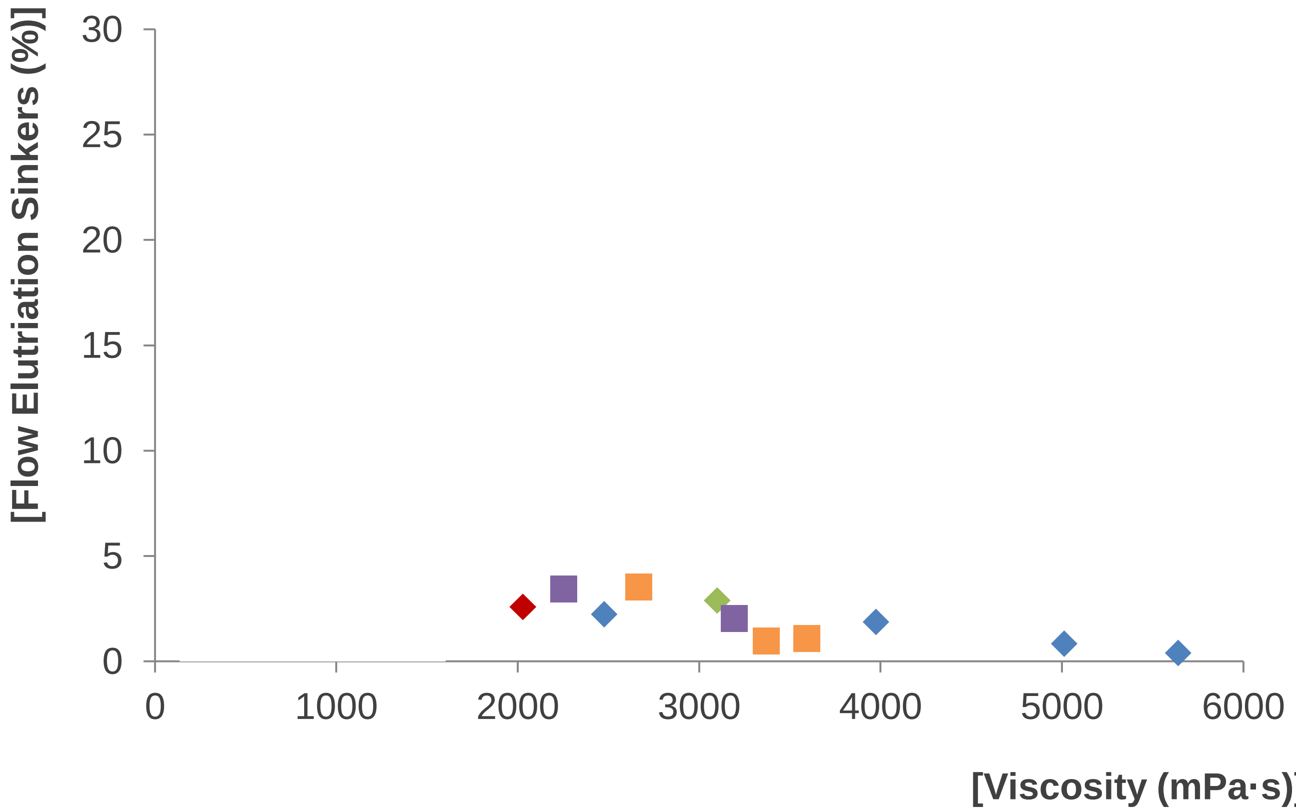
Fibre Elutriation





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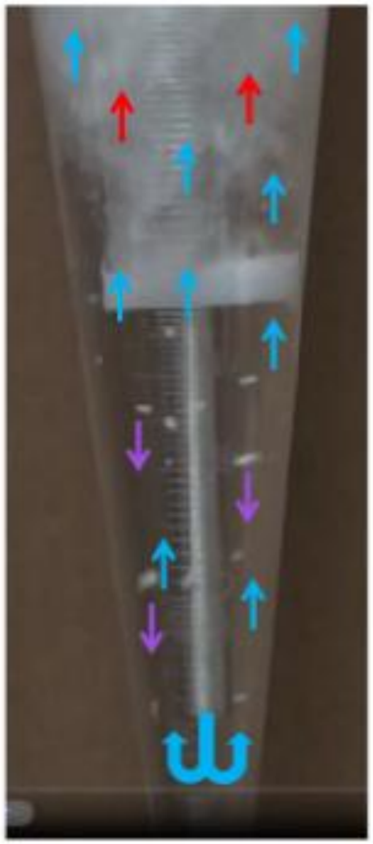
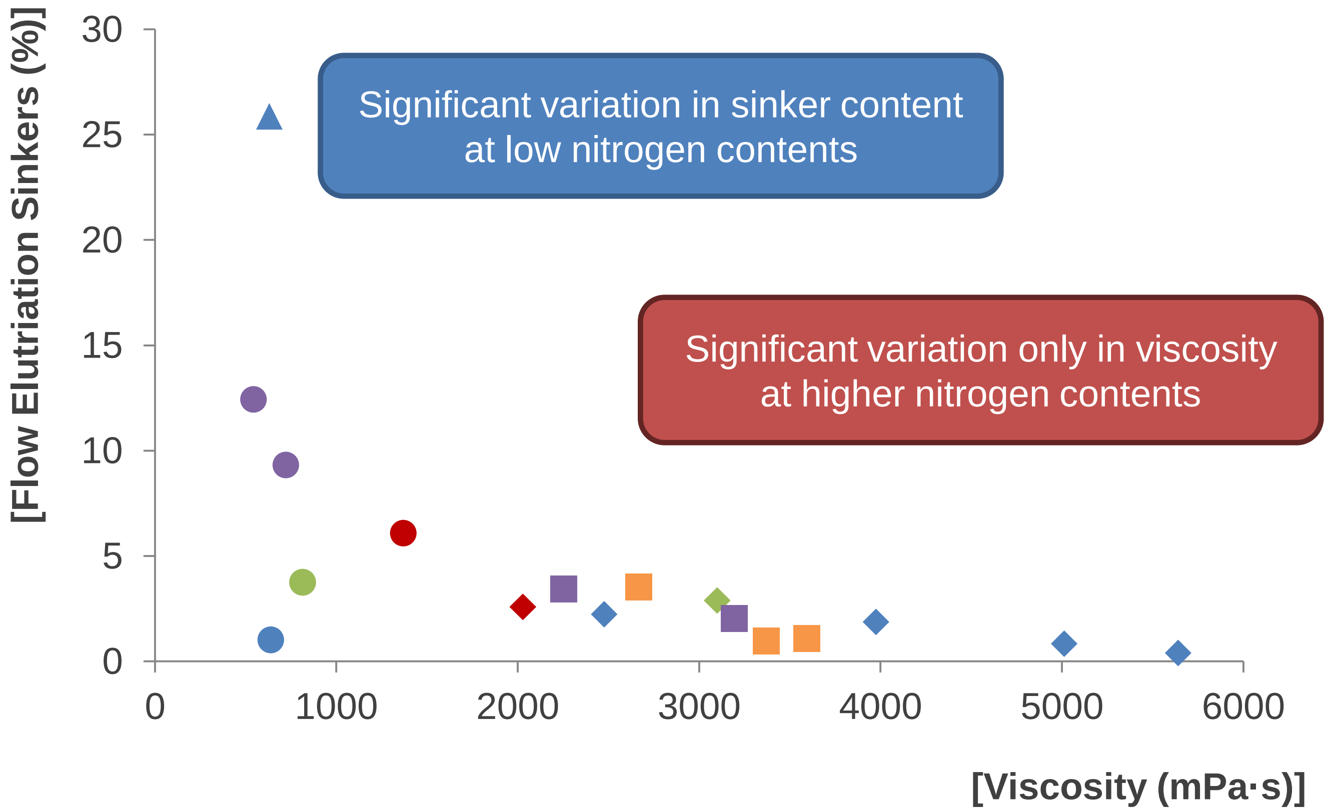
A, **B**, **C**, **D**, **E**

***Paquet, M. & Cossette, N. Measuring the Quality of Fiberization of NC. in *5th International NC Symposium* (2012)**

Fibre Elutriation





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A, B, C, D, E

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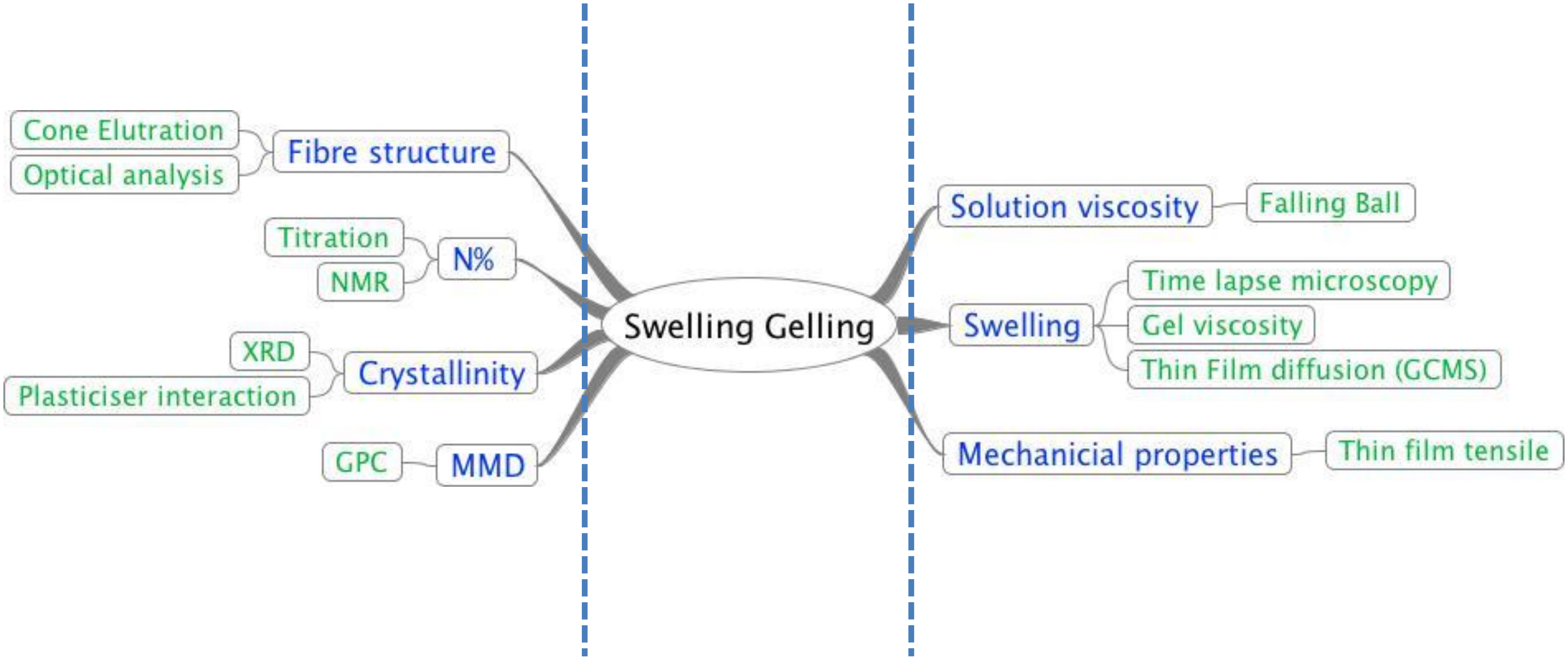
Solvent Processing



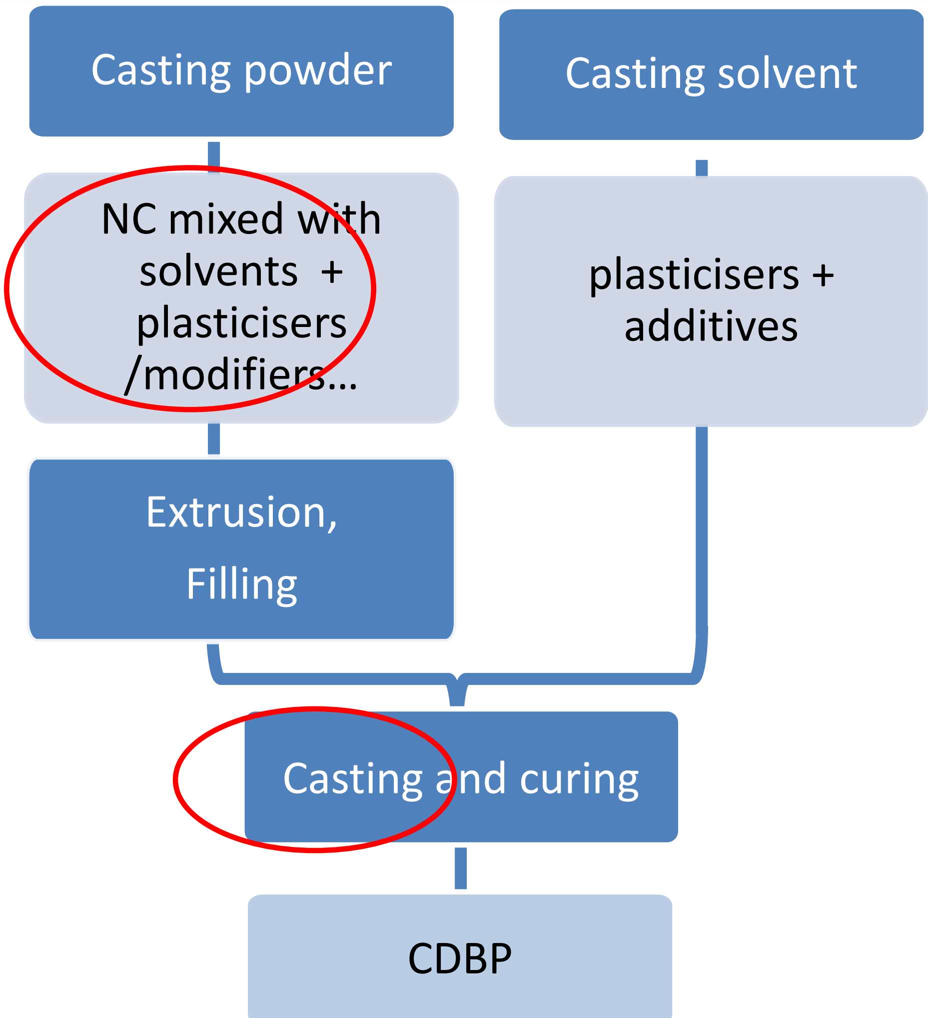
Diffusion and Swelling

- Rate and uniformity of swelling = critical for determining cure conditions and properties of the propellant. Difficult to predict

- Swelling of NC fibres: Sorption of solvents/plasticisers into NC fibre structure → change of volume and physical properties

- Diffusion and swelling mechanisms:
  - Case I swelling: swelling occurring after an initial diffusion phase
  - Case II swelling: diffusion and swelling occurring simultaneously
  - Case III swelling: swelling occurring into material which has already undergone at least one sorption-desorption cycle

Manufacture of CDBP



- Swelling occurs during:
  - Initial step of manufacture of casting powder ➔ NC fibres swollen in solvents (Case II swelling)
  - Addition of casting solvent to casting powder➔ NC has already been processed (Case III swelling)

NC fibres swelling

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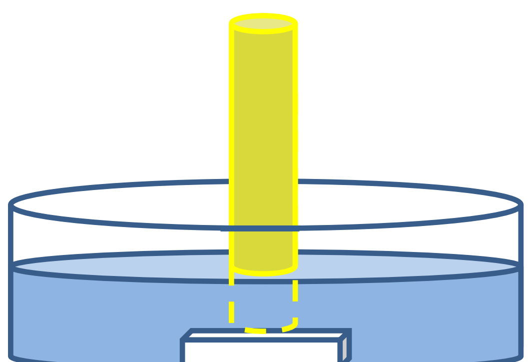
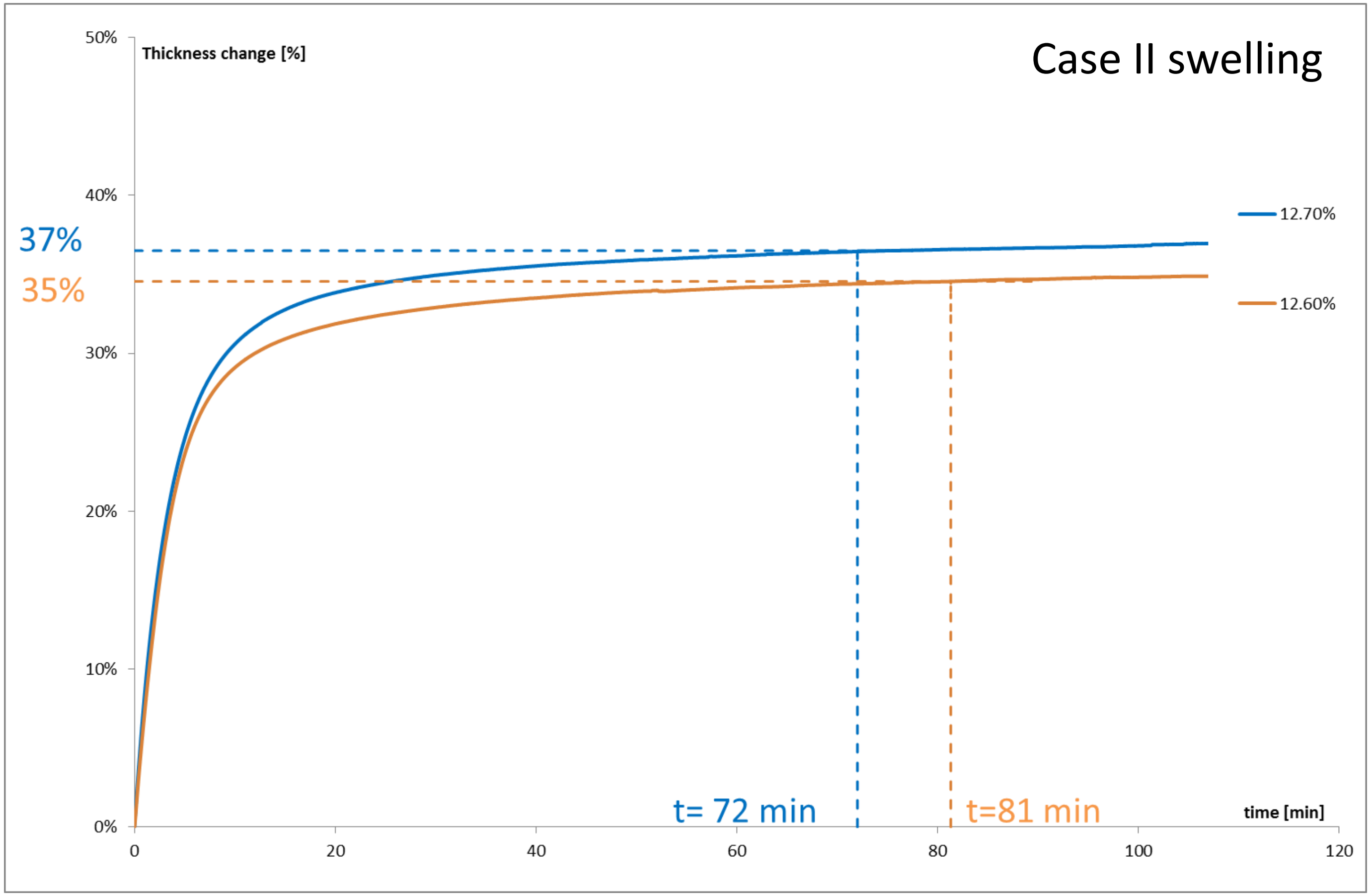
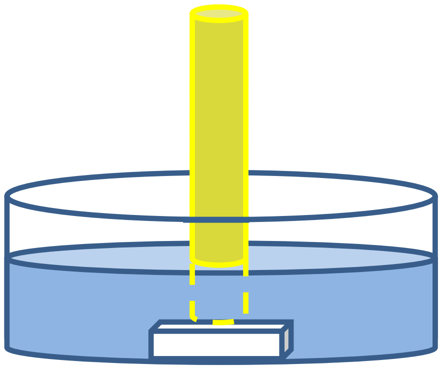
- In initial casting powder processing, raw NC exists in the form of fibres.
- Swelling previously studied on cast NC films ➔ not representative
- NC fibres pressed into discs (2KN), dried and immerged in excess of solvent/plasticisers @ 20^{0}C
- Changes in disc thickness over time measured with TMA



NC fibres swelling

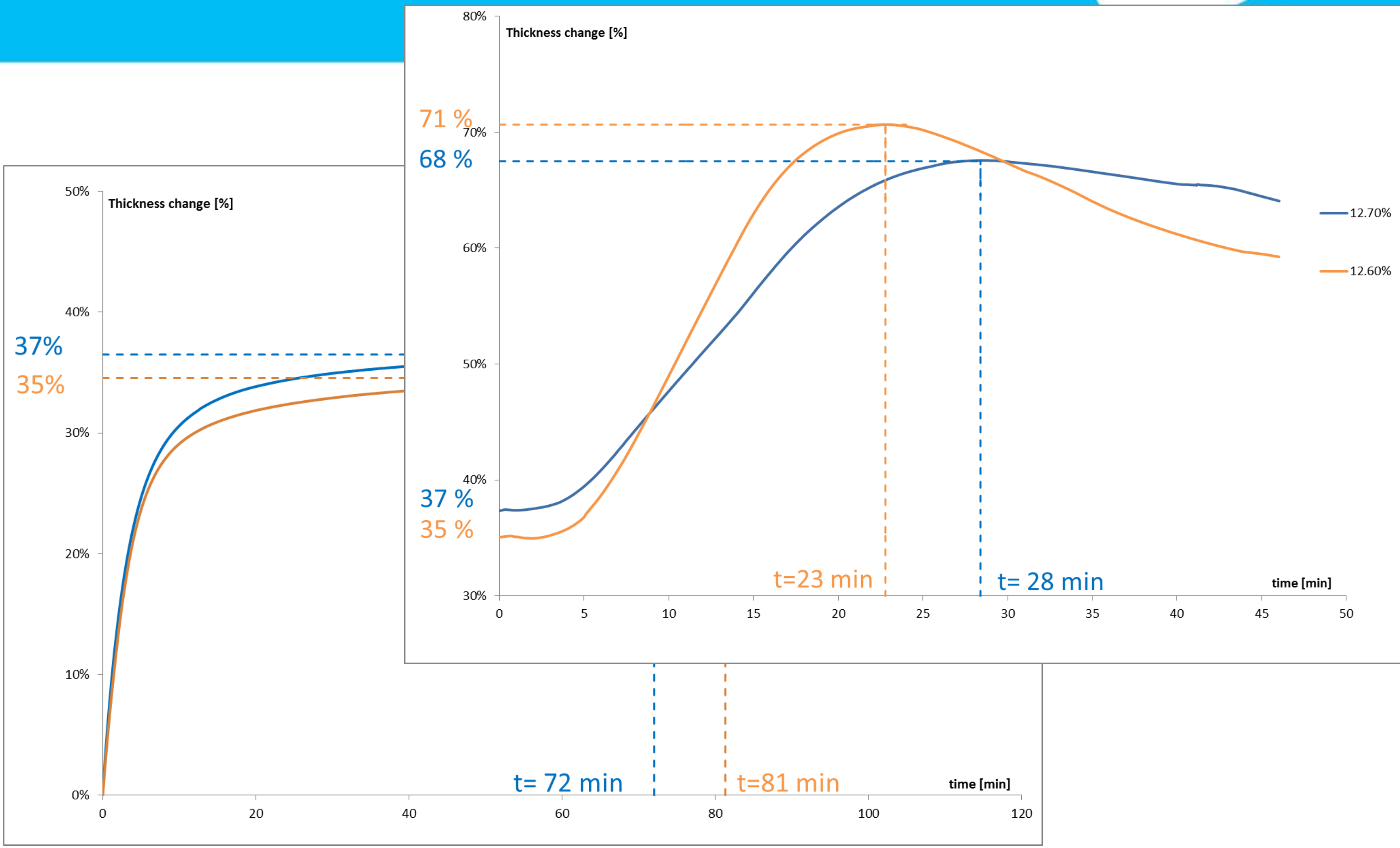
Ethanol





NC swelling

Ethanol-Acetone



Conclusions and Future work

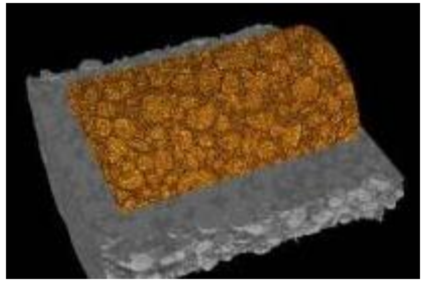
- Analysis of a number of NC key parameters with STANAG methods and novel techniques
  - Fibre length and distribution varies between supplier
  - Viscosity varies significantly at high N% while agglomerate/aggregate content varies significantly at low N%

- Early stage of swelling shows different kinetics which alters with
  - Nature of solvent
  - Temperature
  - Solvent ratio…

- Understanding the NC swelling kinetic will help understand the initial step in the CDBP process

Acknowledgements

- UK MoD - Weapons Science and Technology Centre
- ROXEL (UK Rocket Motors) Ltd
  - Bob Wall
- Cranfield University

Centre for Defence Chemistry

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Fibre Length and Dispersity

Manufacturer	N%	Fib_n	Fib_w	$Đ_{fib}$
A	11.7	96.5	159.9	1.7
A	12.2	128.1	182.8	1.4
A	12.6	243.1	309.3	1.3
B	12.2	205.0	327.3	1.6
B	12.6	164.7	216.1	1.3
C	12.2	134.0	185.6	1.4
C	12.6	241.3	311.2	1.3
D	12.2	332.8	426.1	1.3
D	12.7	203.0	253.3	1.2
E	12.7	241.6	301.9	1.2

$$Fib_n = \Sigma(N_i Fib_i) / \Sigma N_i$$

$$Fib_w = \Sigma(N_i Fib_i^2) / \Sigma(N_i Fib_i)$$

$$Đ_{fib} = Fib_w / Fib_n$$

Fib_n = Number average fibre length

Fib_w = Weighted average fibre length

N_i = Number of fibres of specific length

Fib_i = Fibre length of specific fibre

$Đ_{fib}$ = Fibre length dispersity