COMPOSITE MATERIALS MADE FROM COTTONSEED PROTEIN CONCENTRATE AND NATURAL FIBRES

Dra. Patricia Eisenberg
Tec. Guido De Titto
Dra. Mariana Mollo
Ing. Matias Segal
Tec. Marianela Speraggi
Tec. Pablo Rocci

INTI Plásticos

What are composite materials ?

Materials in which two or more separate materials have been combined to make a single construct with better properties

Fibers, or some type of linear structures, are bound tightly in a solid matrix, such as plastic.

The matrix material, while having its own strength and structural characteristics, serves primarily to hold the fibers or reinforcing structures in place

Natural Fibres

Subdivided based on their origins:

- plants
  animals
  minerals

Plants Fibres

Bast Fibres

- flax
- jute
- ramie
- kenaf
- hemp

Seed Fibres

- cotton
- coir (coconut)

Leaf Fibres

- sisal
- abaca (banana)
- palm
- henquen

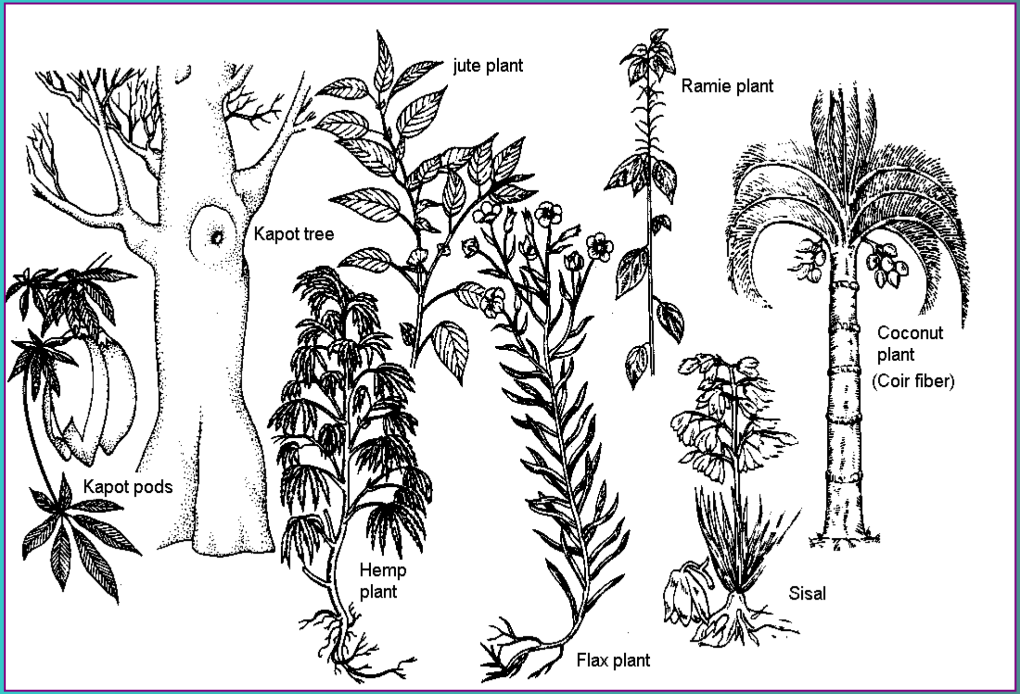
India, China & Bangladesh

jute

Philippines

abaca

hemp



Mexico

henequen

Brazil & Tanzania

sisal

Successful of Natural Fibers as reinforcements

- large quantities availability
- well-defined mechanical properties

Mechanical Properties of Natural Fibres

Compared to conventional reinforced fibres

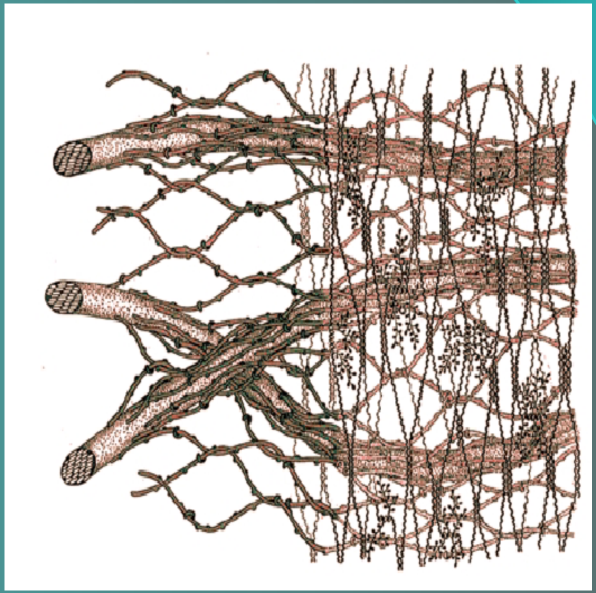
Fibre	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6
Jute	1.3	1.5–1.8	393–773	26.5
Flax	1.5	2.7–3.2	345–1035	27.6
Hemp	—	1.6	690	—
Ramie	—	3.6–3.8	400–938	61.4–128
Sisal	1.5	2.0–2.5	511–635	9.4–22.0
Coir	1.2	30.0	175	4.0–6.0
Viscose (cord)	—	11.4	593	11.0
Soft wood kraft	1.5	—	1000	40.0
E-glass	2.5	2.5	2000–3500	70.0
S-glass	2.5	2.8	4570	86.0
Aramide (normal)	1.4	3.3–3.7	3000–3150	63.0–67.0
Carbon (standard)	1.4	1.4–1.8	4000	230.0–240.0

A.K. Bledzki, J. Gassan / Prog. Polym. Sci. 24 (1999) 221–274

Components of Natural Fibres

With regard to the physical properties

- CELLULOSE
- HEMICELLULOSE
- LIGNIN
- PECTIN
- WAXES

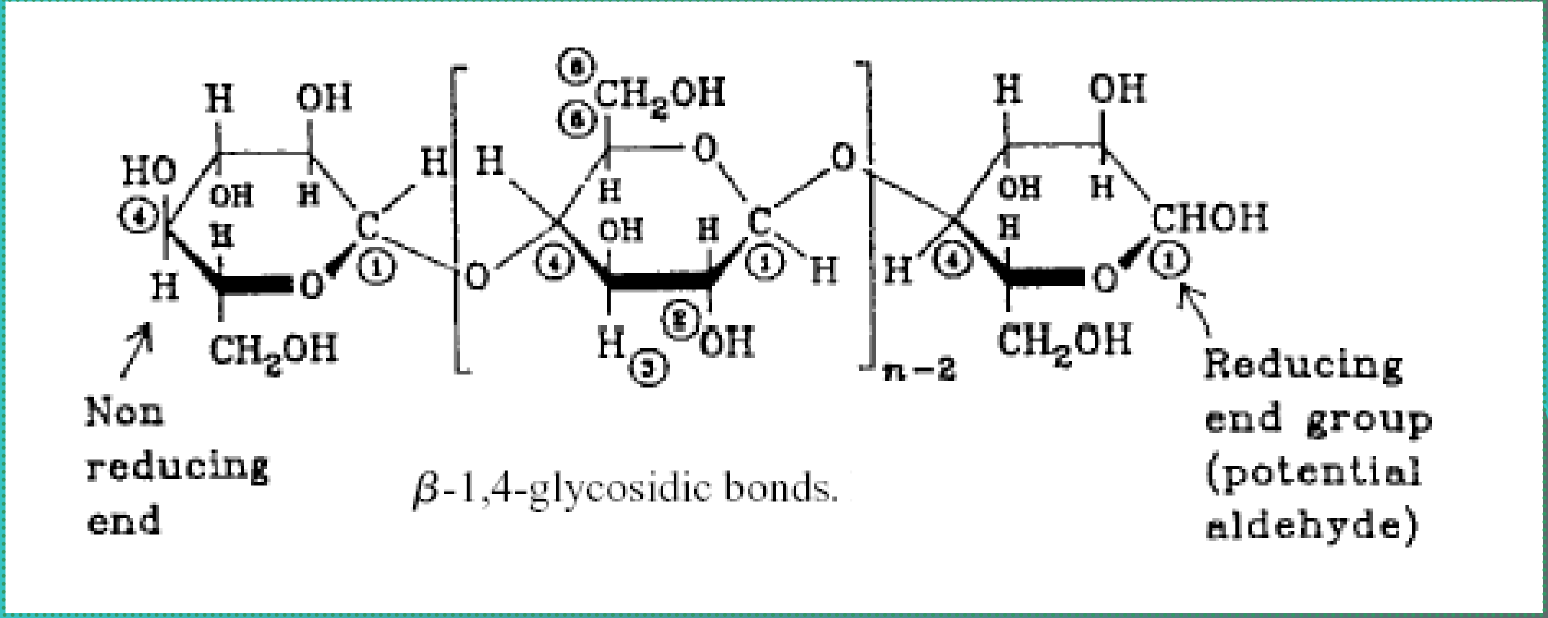


CELLULOSE

Major component of plant fibers

Linear condensation polymer

Repeating units: D- anhydroglucopyranose



Degree of polymerization ~ 10,000

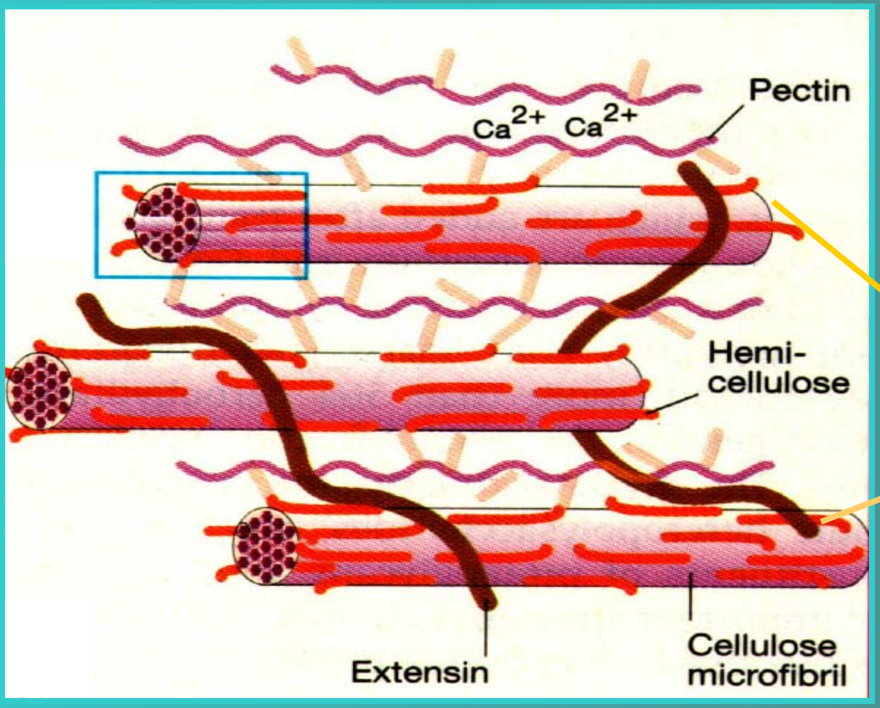
The mechanical properties of natural fibres depends on its cellulose type.

Each type of cellulose has its own cell geometry

The geometrical conditions determine the mechanical properties

HEMICELLULOSE

Compromise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed.



Forms supporting matrix for cellulose microfibrils

Hydrophilic and soluble in alkali

Difference with cellulose:

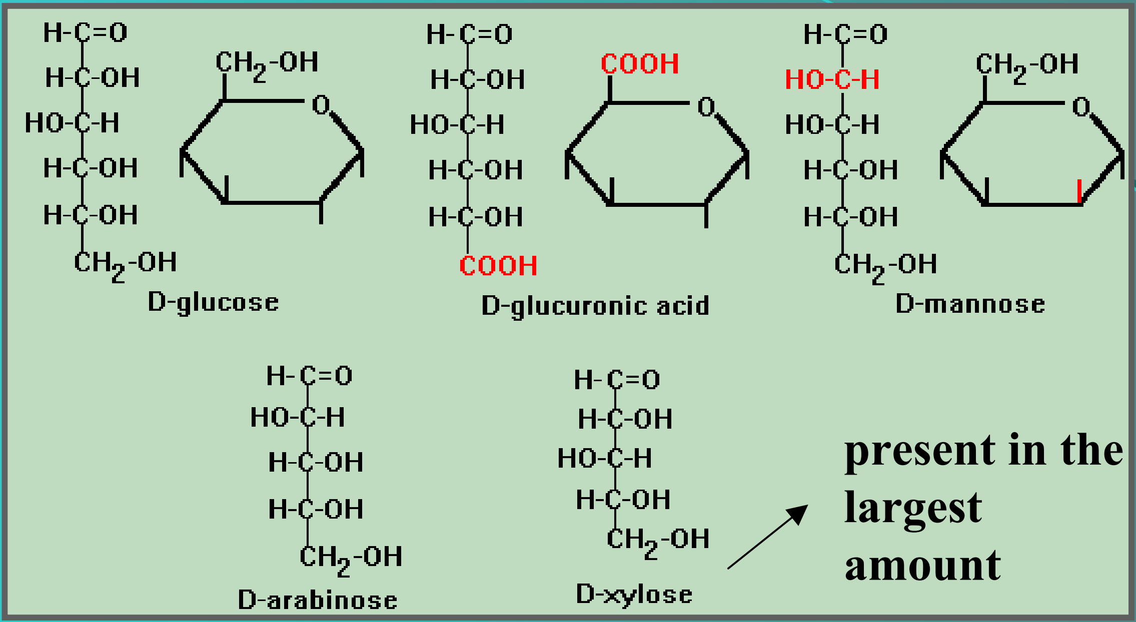
- CONTAIN SEVERAL SUGAR UNITS

(5-6 ring carbon ring sugars)

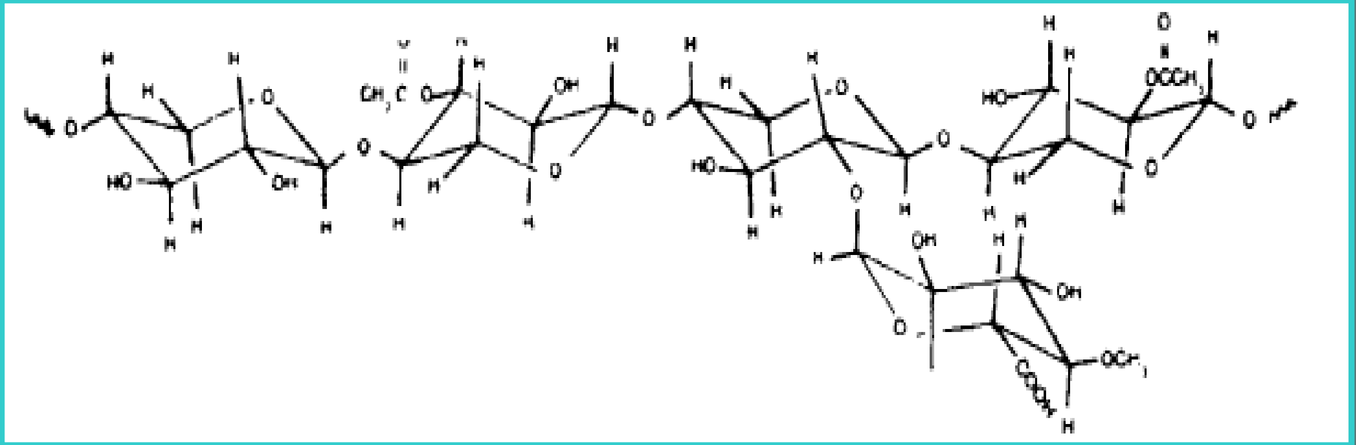
- EXHIBIT CONSIDERABLE DEGREE OF CHAIN BRANCHING

- DEGREE OF POYMERIZATION (DP) ~ 50-300

Unlike cellulose, hemicellulose differ from plant to plant



In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength.

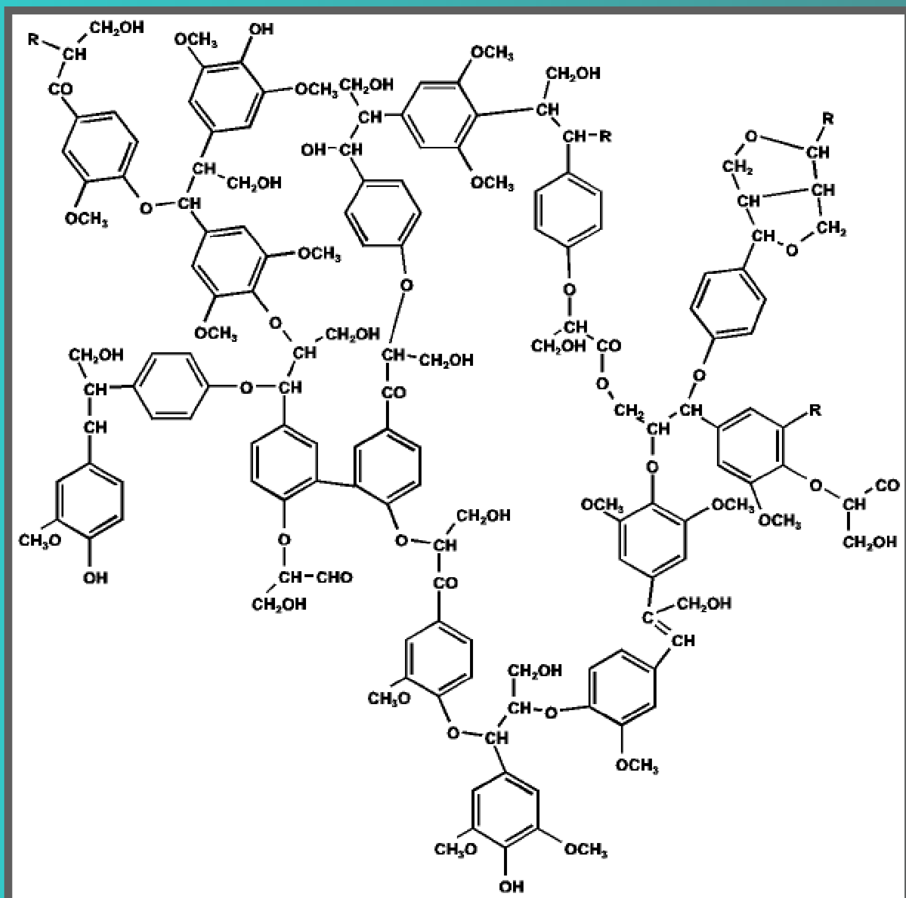


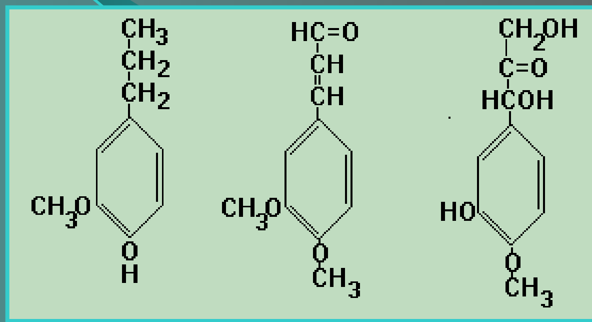
It is easily hydrolyzed by dilute acid or base

LIGNIN

Complex hydrocarbon polymer with aliphatic and aromatic constituents.

Very high MW





Monomer units are various ring-substituted phenyl-propanes linked together

Gives rigidity to the plants

PECTIN

Heteropolysaccharides essentially polygalacturon acid.
Soluble in alkali

WAXES

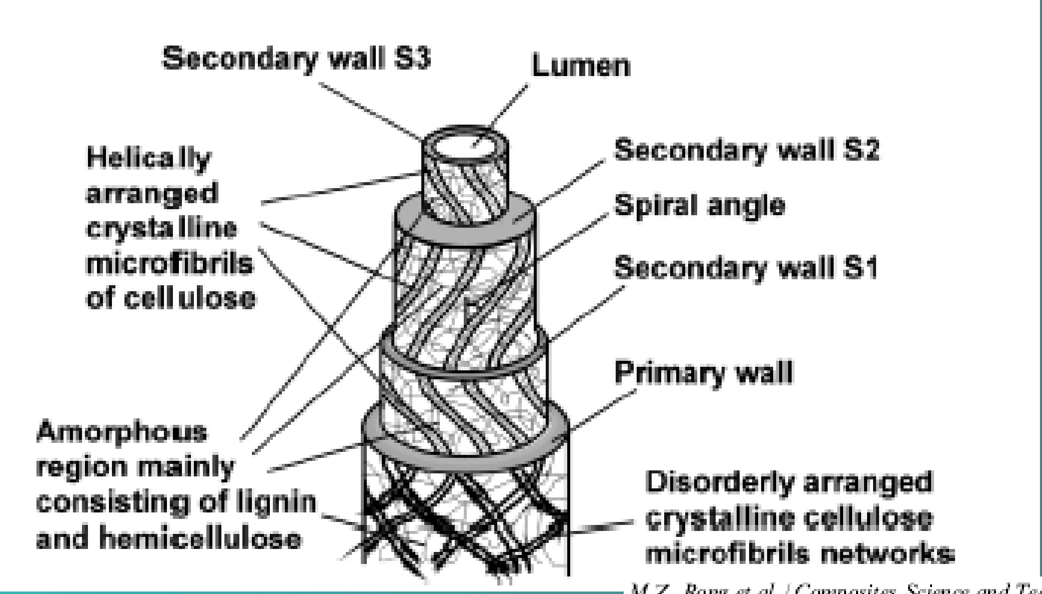
Different types of alcohols, acids (palmitic acid, oleaginous acid, stearic acid)

Physical structure of natural fibres

Single fiber formed out of crystalline microfibrils based on cellulose, connected by amorphous lignin and hemicellulose.

Multiple cellulose-lignin/hemicellulose layer in one primary cell and three secondary cell walls stick together to a multiple-layer-composite:

THE FIBRE CELL.



M.Z. Rong et al. / Composites Science and Technology 61 (2001) 1437–1447

Fiber Treatment and Modification

Performance of composite materials depends on the properties of the individual components and their interfacial compatibility

For technical oriented applications fibres have to be specially modified

- homogenization of fibre 's properties
- increase degrees of elementarization and degumming
- control degree of polymerization and crystallization
- promote good adhesion between fibre and matrix
- control moisture

Natural Fibers , Biopolymers, and Biocomposites. Ed. Mohanty, Misra & Drzal, 2005.

Several noncellulose components have to be removed to assure the compatibility of plant fibers to surronding polymer matrix

Alkalinization

Washing or boiling fibers in a 2% sodium, potasium hydroxide solutions

Removal unwanted fiber components

Increase ability fiber separation

Protein Extraction from cottonseed pellets at Pilot Plant Scale (INTI-Cereales)

Pellets Production

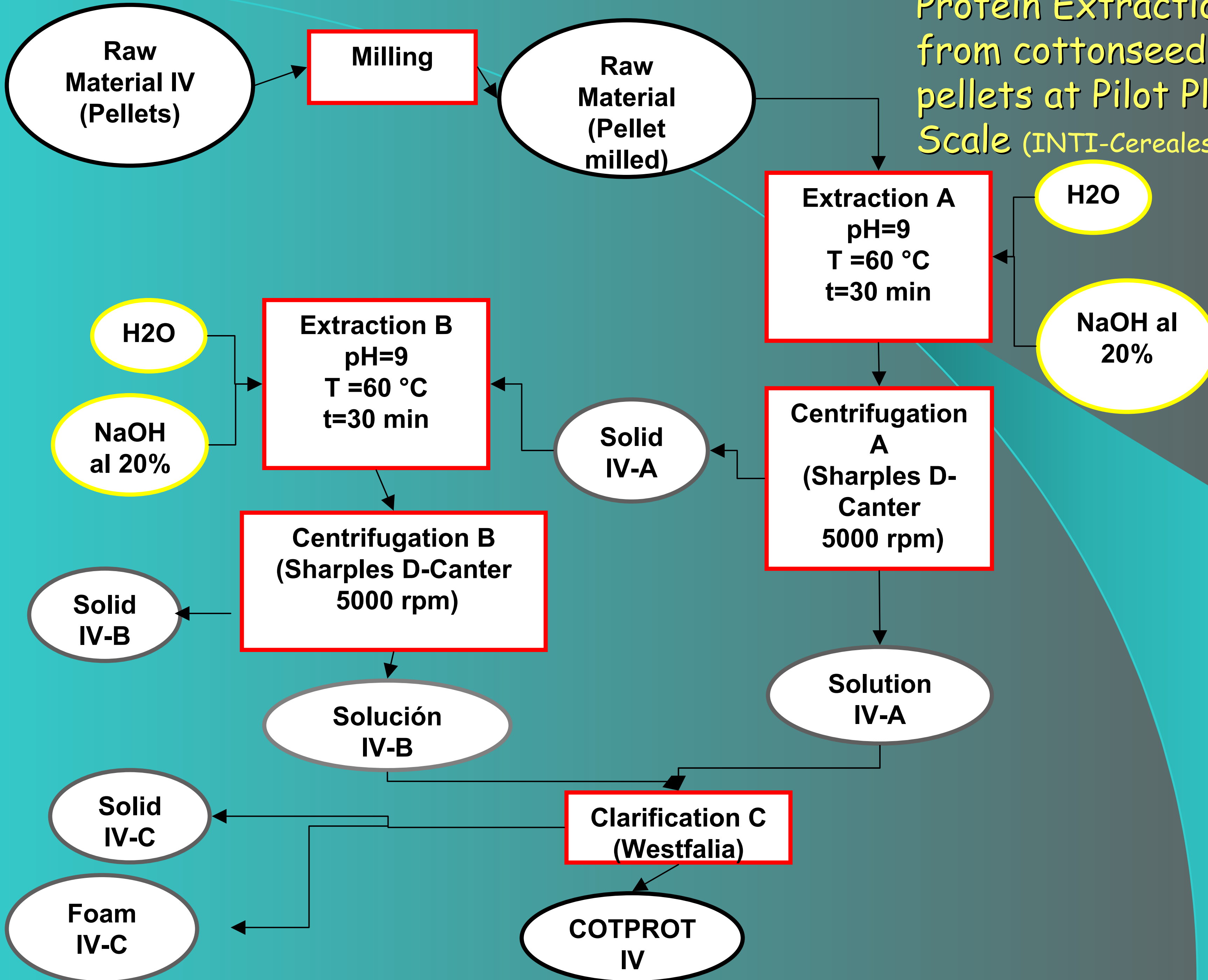
Oil extraction
(VICENTIN)

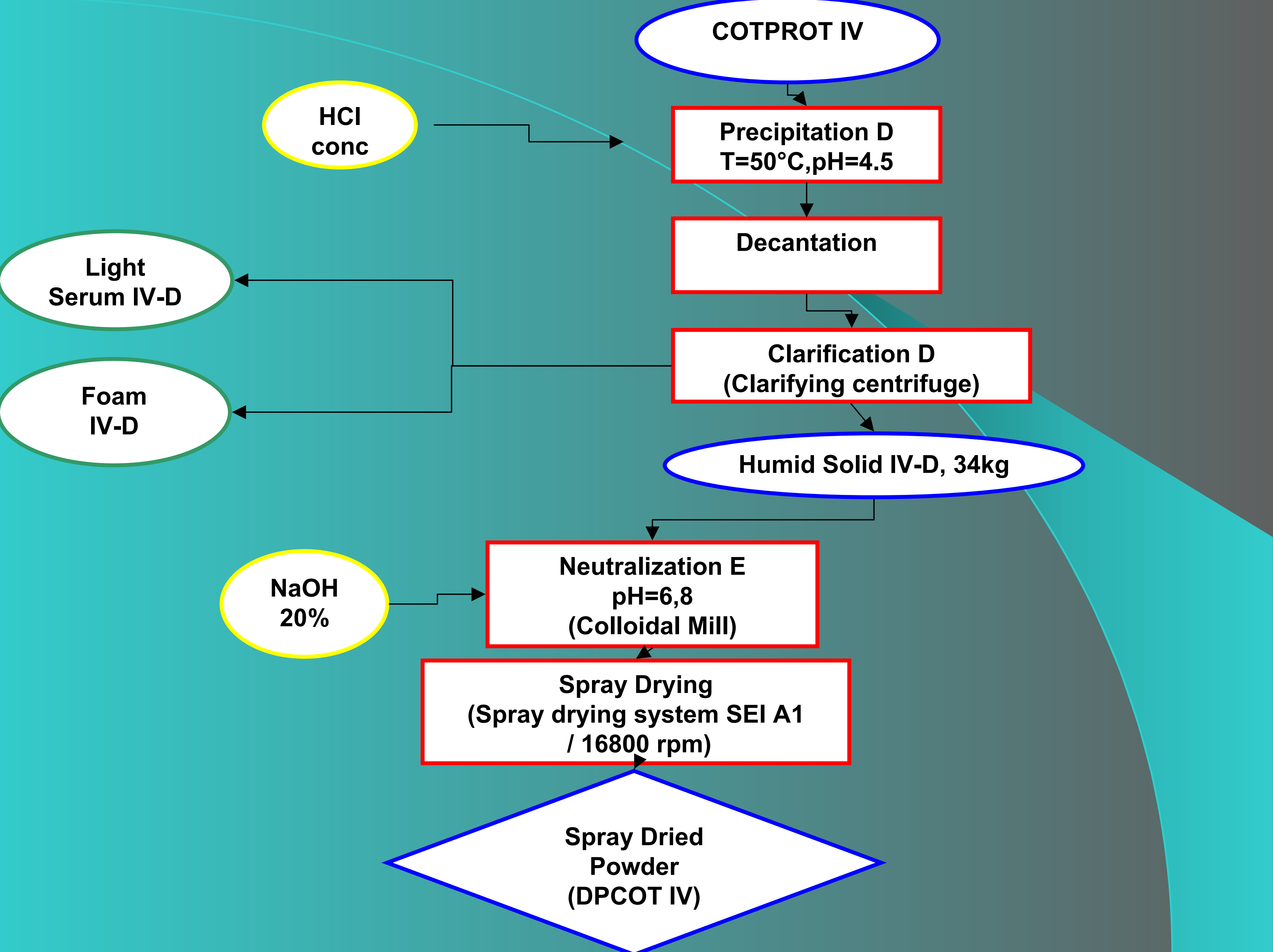
- Pressing (90°C)
- Hexane extraction (60 °C)
- Solvent elimination (90°C)
- Granulation (pellets)

Pellets Characterization

- Protein Content (g/100 g DM) — 40.8
- Fats Content (g/100 g DM) — 6.6
- Total gossypol content (g/100 g DM) — 0.3
- Ash content (g/100 g DM) — 9.2
- Reactive Lysine content (g/100 g DM) (CIRAD, France) — 0.85

Protein Extraction from cottonseed pellets at Pilot Plant Scale (INTI-Cereales)




COTPROT IV
HCl conc
Precipitation D T=50°C,pH=4.5
Decantation
Light Serum IV-D
Foam IV-D
Clarification D (Clarifying centrifuge)
Humid Solid IV-D, 34kg
NaOH 20%
Neutralization E pH=6,8 (Colloidal Mill)
Spray Drying (Spray drying system SEI A1 / 16800 rpm)
Spray Dried Powder (DPCOT IV)

500 liters stainless steel tanks with automatic temperature control

Horizontal centrifuge SHARPLES (model P-600)

Clarifying centrifuge WESTFALIA (model SA –1)

Spray Dryer

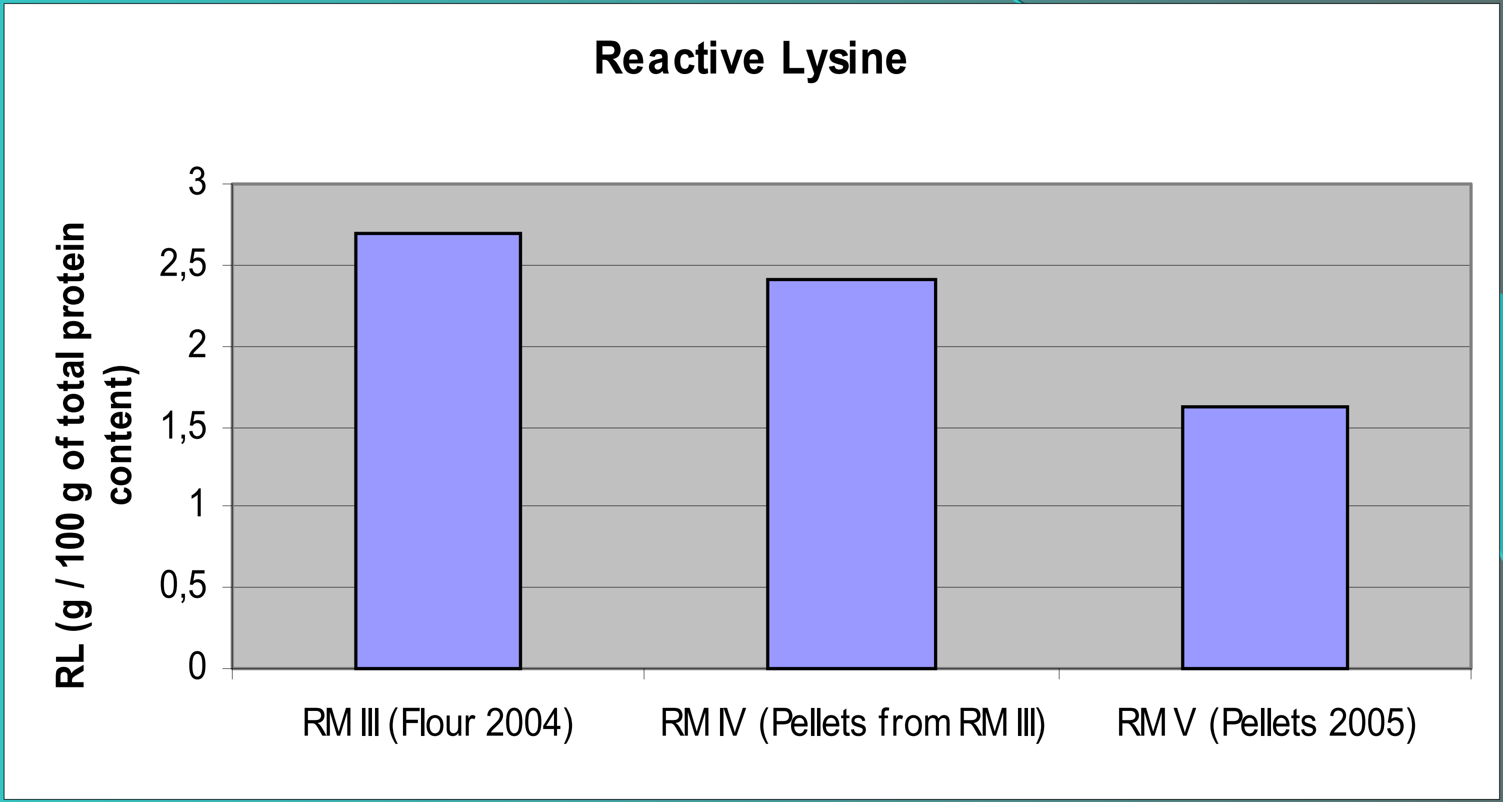
with an atomizer rotor

(16800 rpm), fed with a peristaltic pump

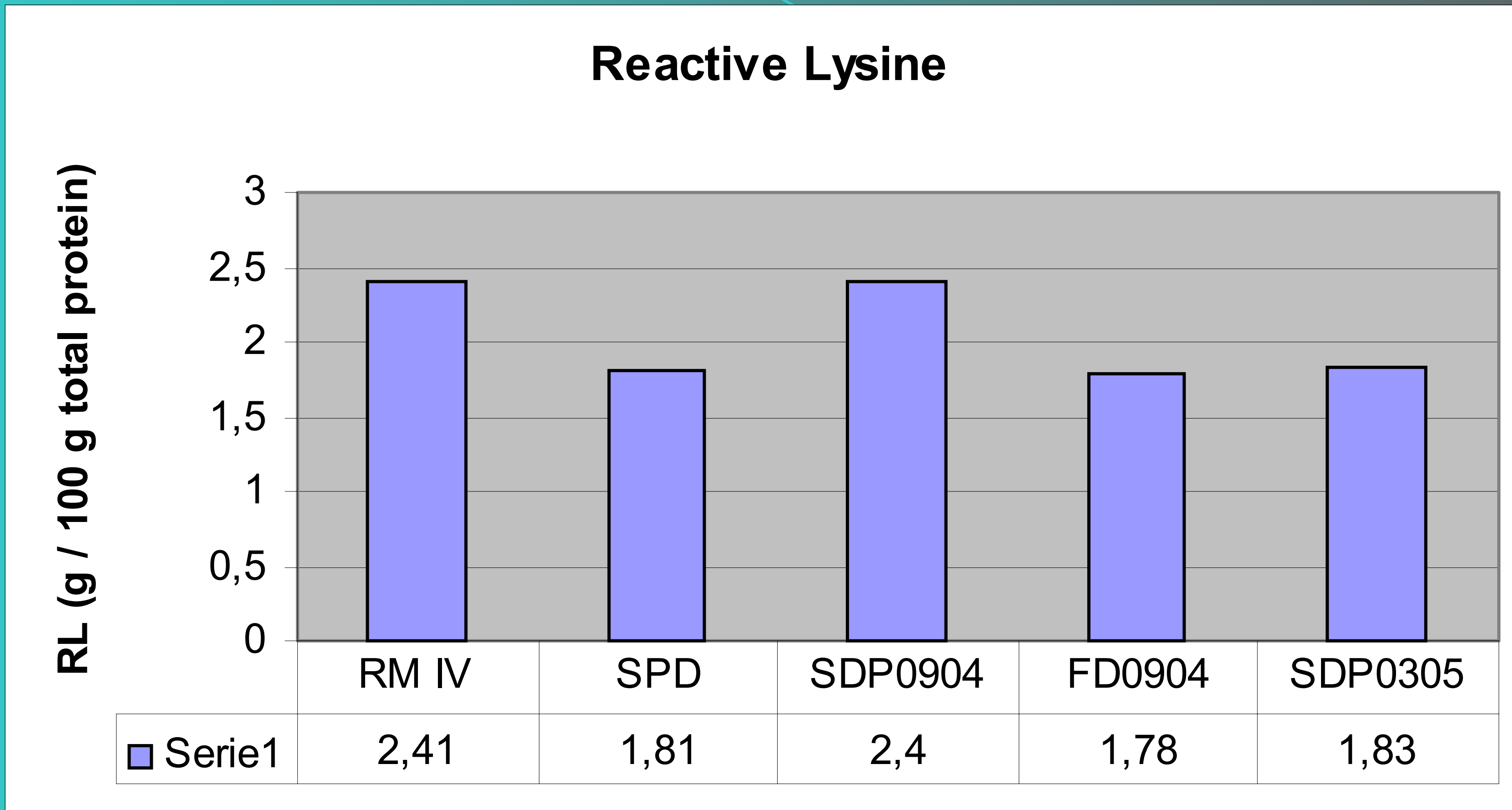
DPCOT Characterization

- Protein Content (g/100 g DM) **56.2**
- Fats Content (g/100 g DM) **2.5**
- Total gossypol content (g/100 g DM) **0.6**
- Ash content (g/100 g DM) **5.7**
- Reactive Lysine content (g/100 g DM) (CIRAD, France) **1.35**

Raw Material Reactive Lysine content



Reactive Lysine content after protein extraction process



FD904: Laboratory extraction process with TEA, freeze dried

DPCOT

Water

30 min, 30 °C
500 rpm
pH = 10 ,TEA

Plastizacer

15 min
30 °C
500 rpm

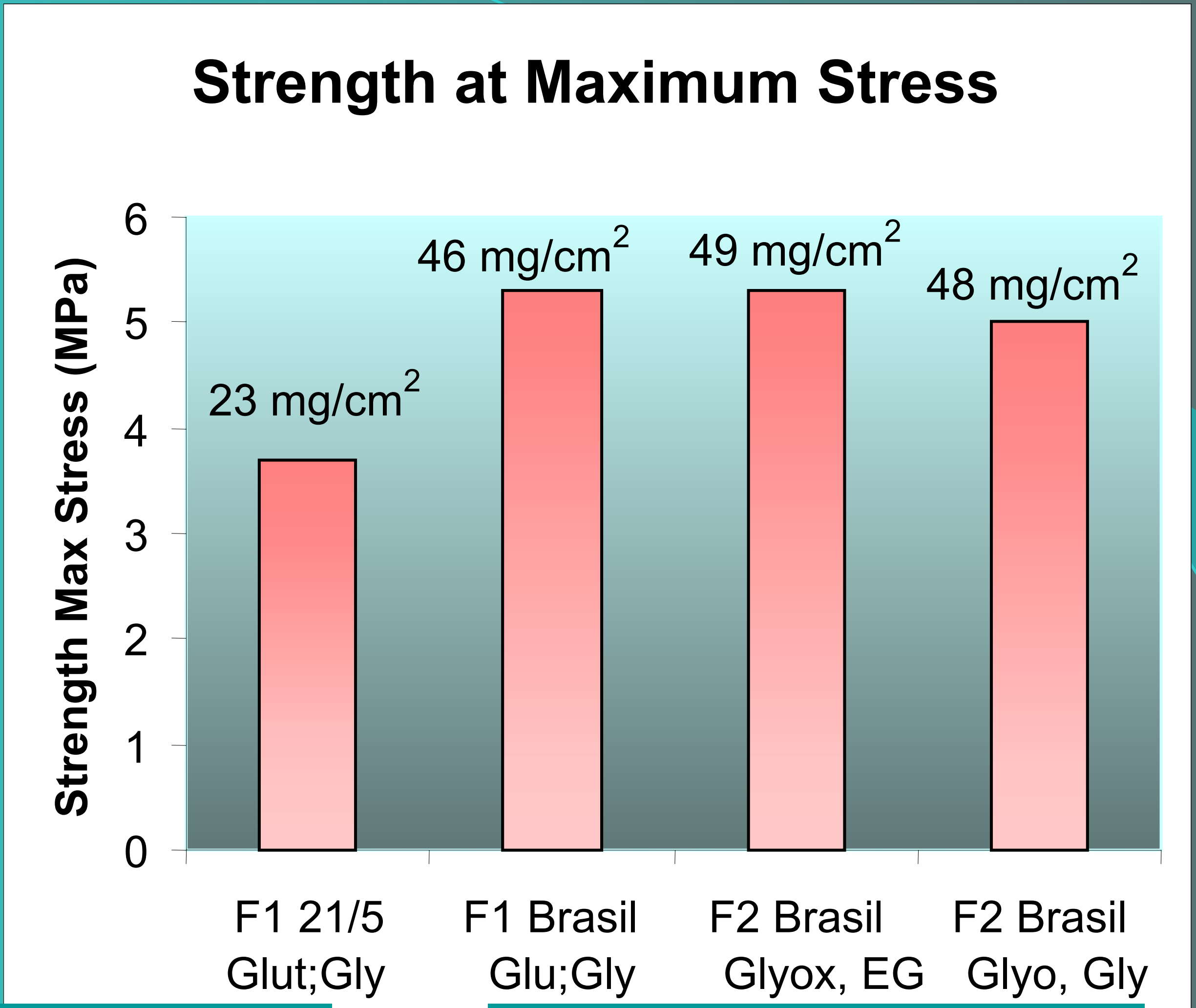
Crosslinking agent

15 min
30 °C
500 rpm

Degasification

Filmogenic Solution

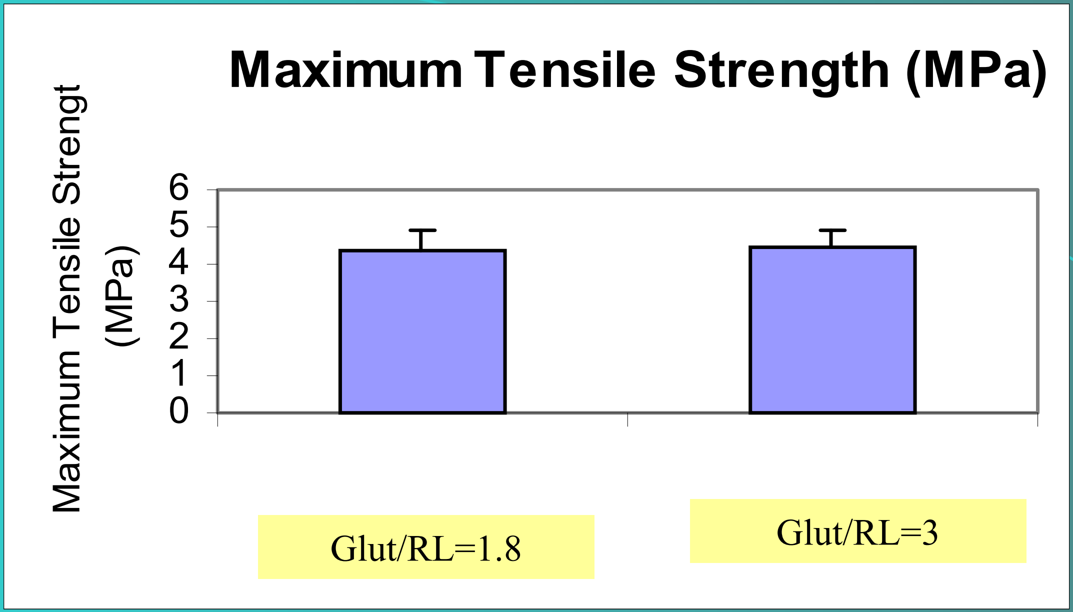
Film Mechanical Properties



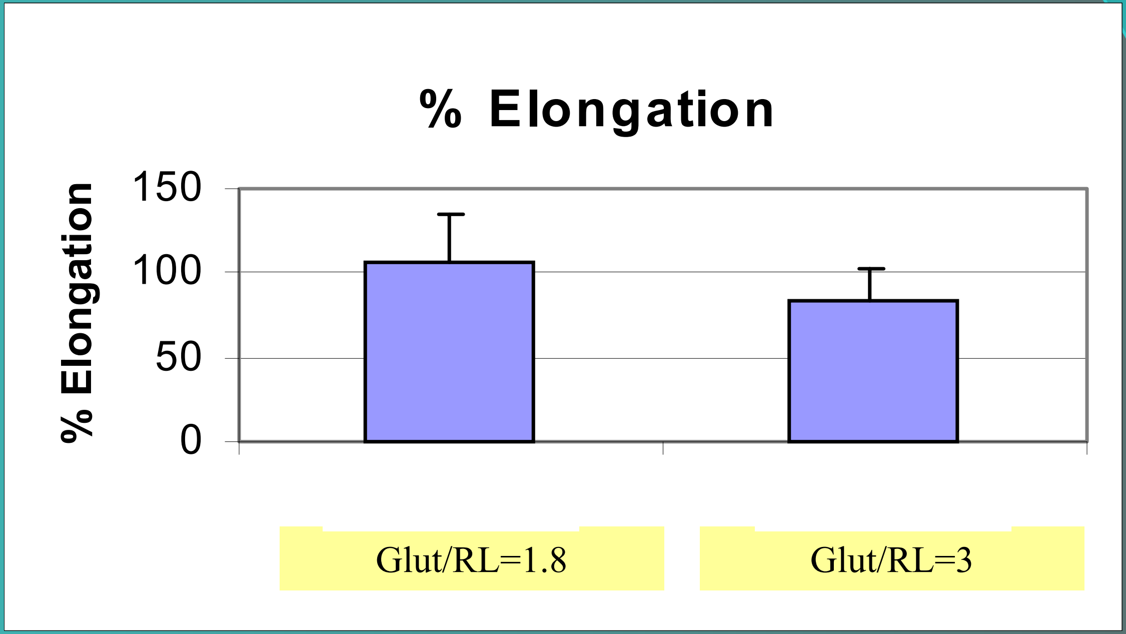
Raw material: pellet

Raw material: flour

Mechanical Properties vs glutaraldhyde / RL ratio



Casting film fabrication



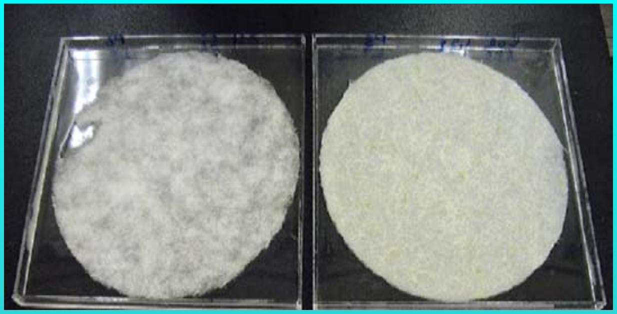
Reinforced Films Preparation

Fibre Incorporation

Fibre incorporation into the filmogenic solution

- Inhomogeneous fibre distribution (clusters)
- Fibre decantation
- Very difficult solution degasification

Short fibres Non-woven fabrication



HEMP FORMIE

Fibers chemical treatment

Achieve a good cohesion between fibers for optimun non-woven fabrication

Natural Fibre
2% Non Ionic detergent solution
Na_2CO_3

60 min, 70 °C
800 rpm

Drying
24 hs
60 °C

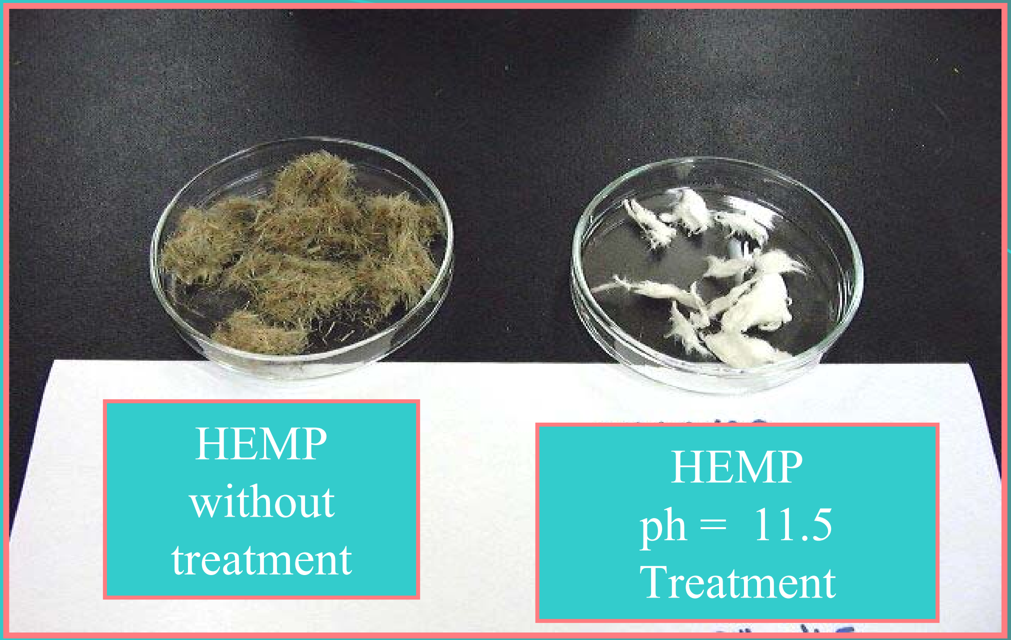
Washed Fibre

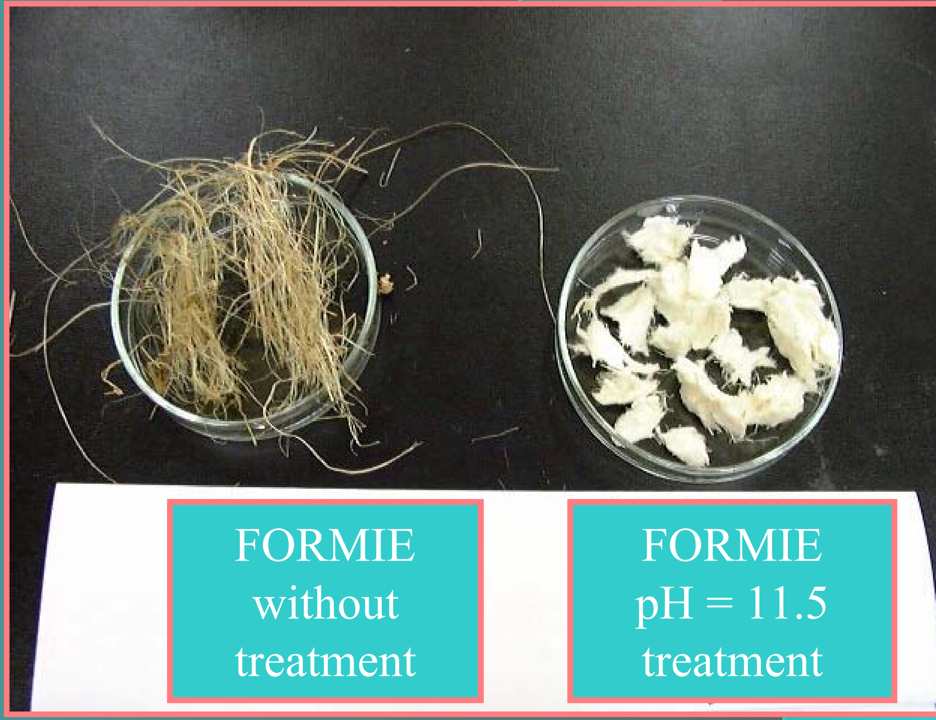
2% H_2O_2

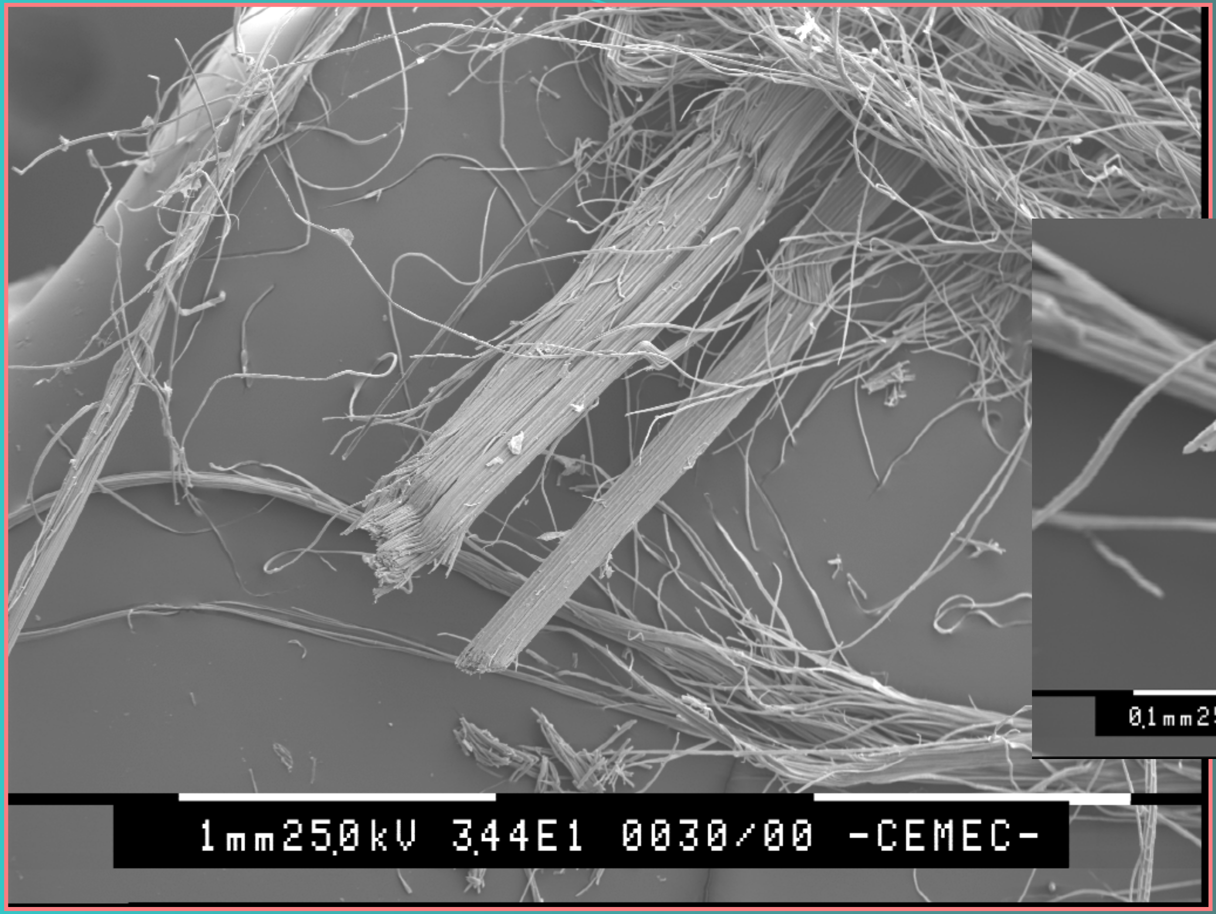
Dispersion 240 min
30 °C
800 rpm, pH: 11.5

Drying
24 hs,60 °C

Washed & Whitened Fibre


HEMP without treatment
HEMP ph = 11.5 Treatment

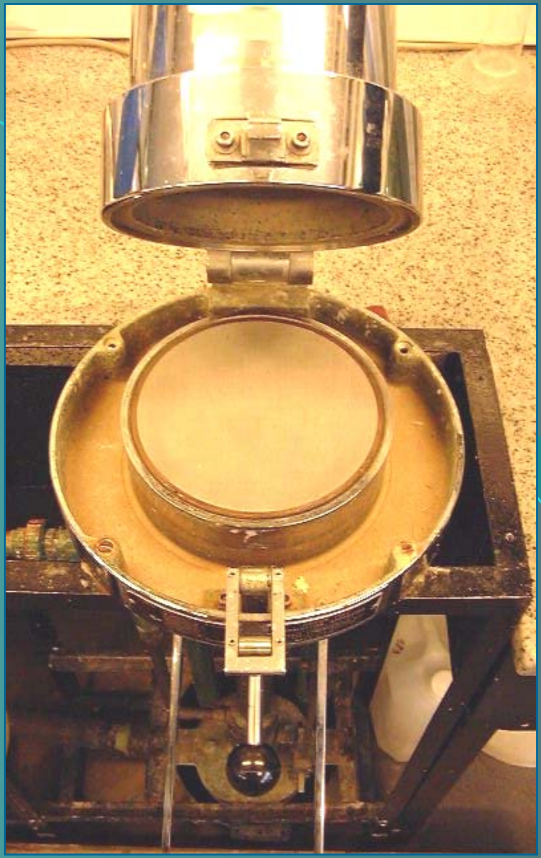

FORMIE without treatment
FORMIE pH = 11.5 treatment

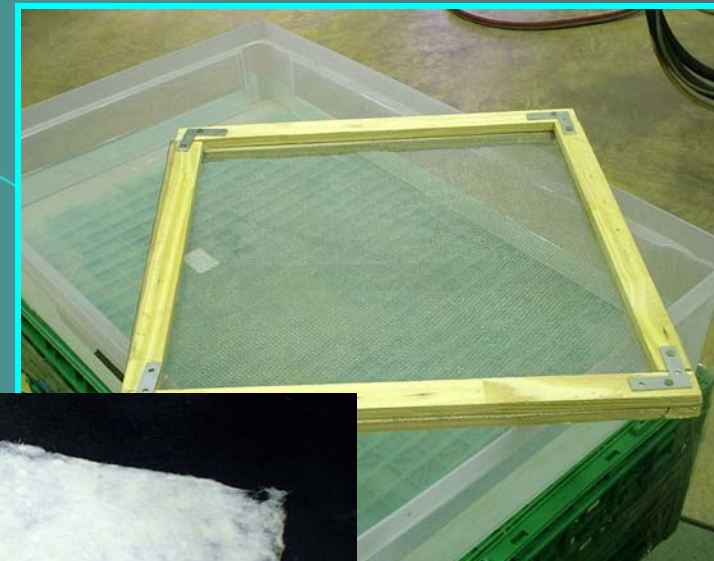


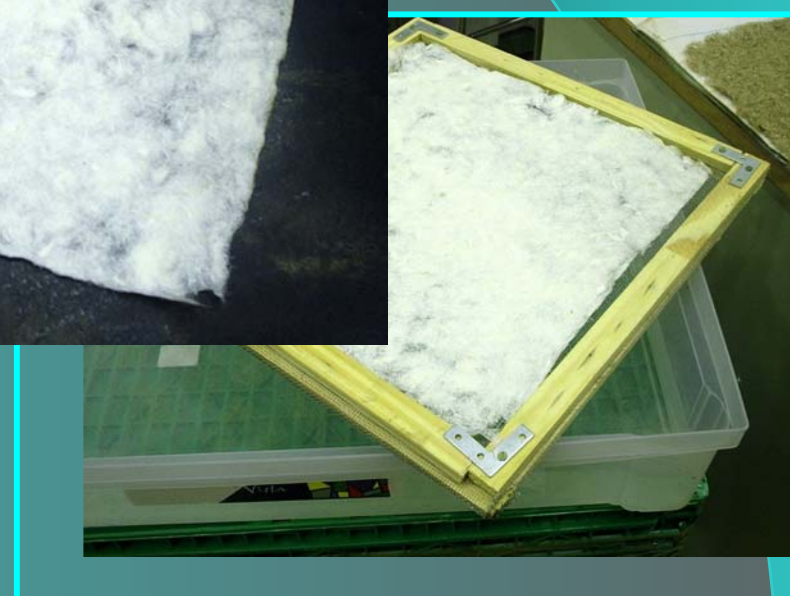
Formie fibers basic treated

Short fibres Non-woven fabrication

(Paper maker equipment, TAPI)



Impregnation of Fibres

Non-woven fabrication

A better combination of fibre and polymer could be achieved by fiber chemical treatment and fiber impregnation.

Filmogenic solution of low viscosity was used

Washed & Whitened Fibre

Dispersion 30 min

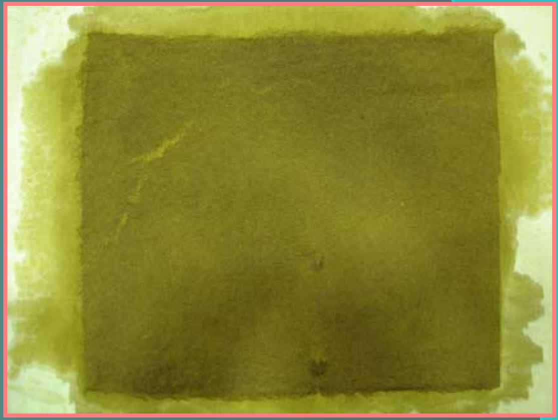
1500 rpm

Fibre non woven mat

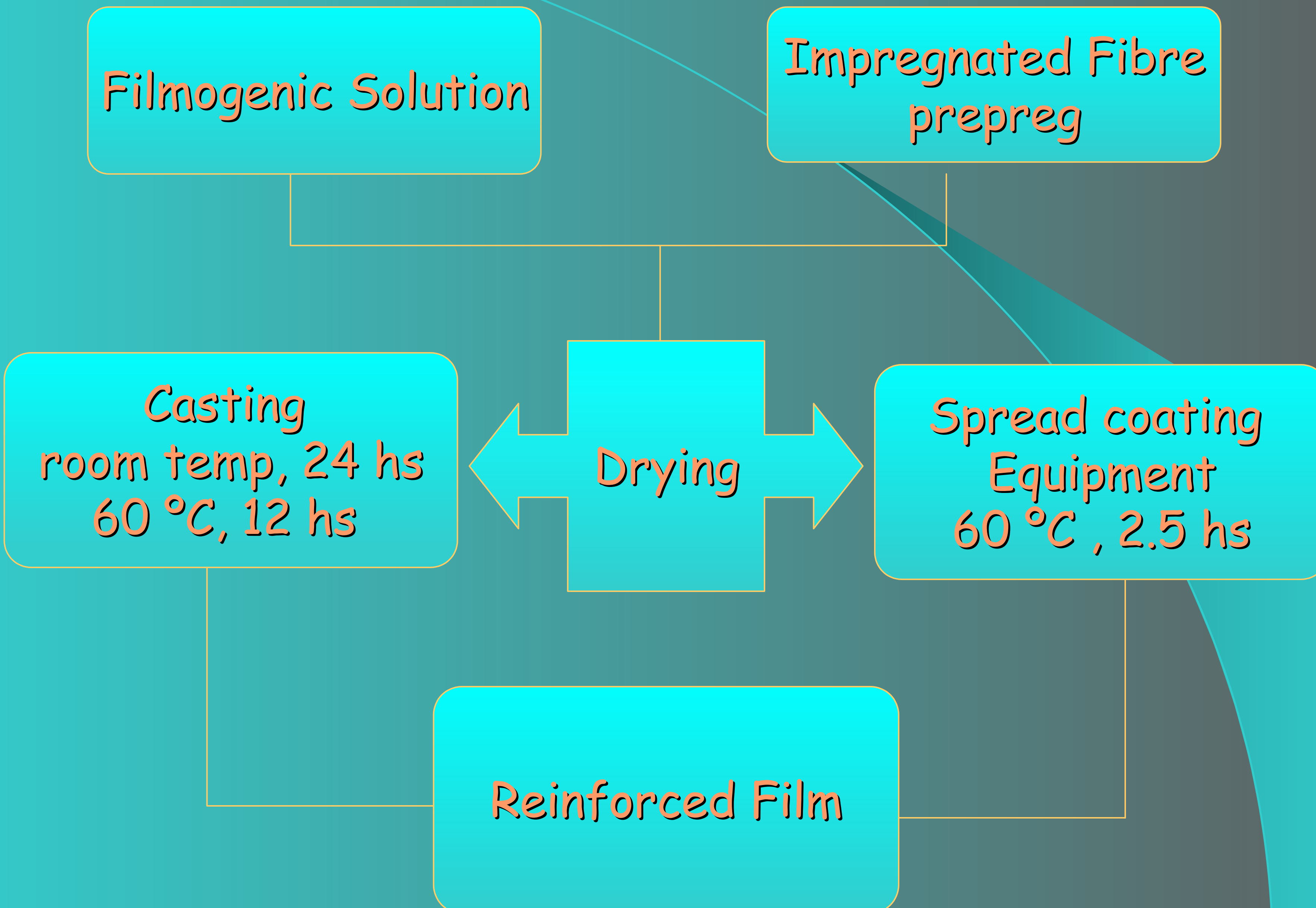
Drying
24 hs
60 °C

Filmogenic Solution

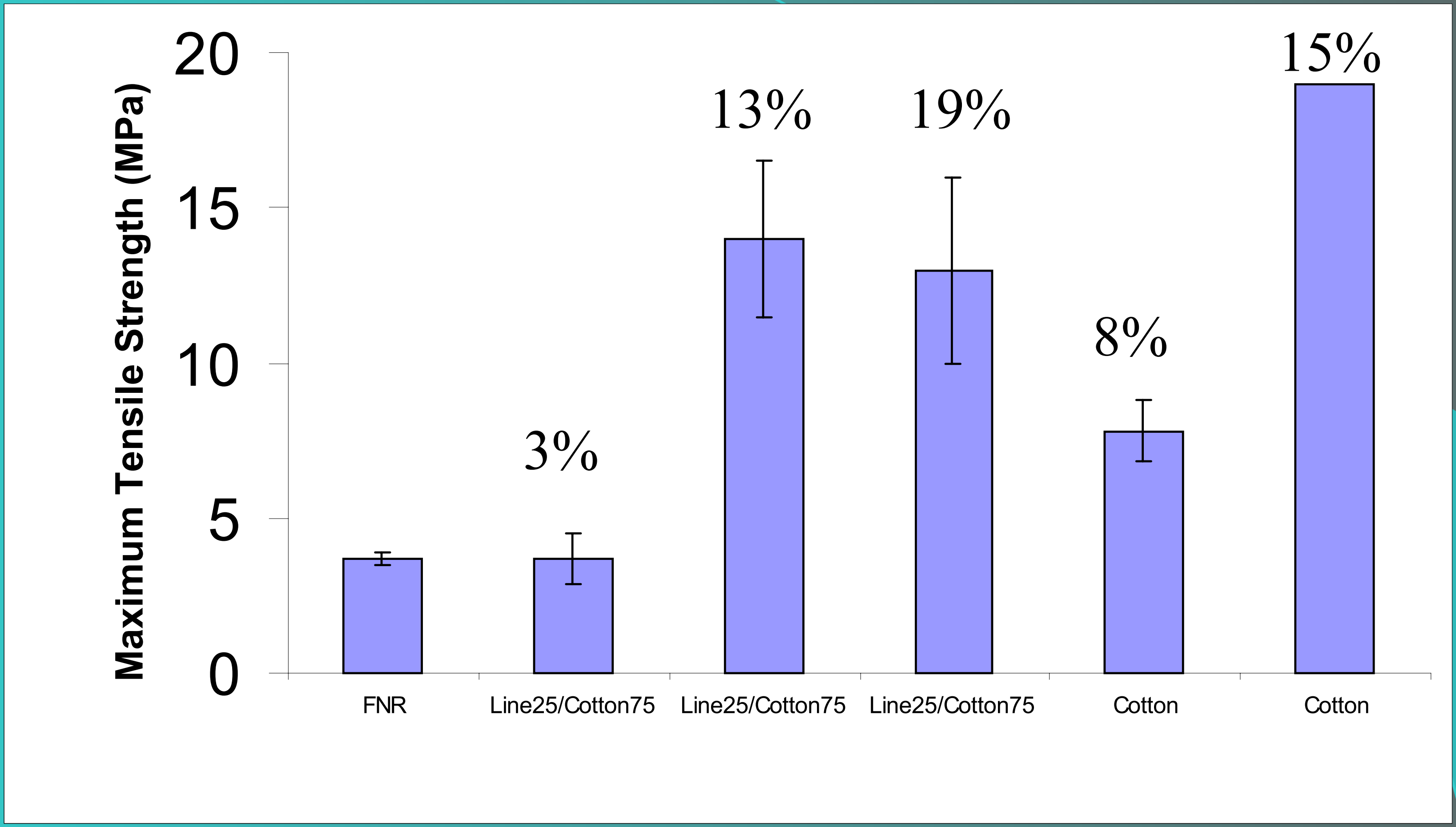
Fibre non woven mat
Impregnation



Reinforced Films Preparation

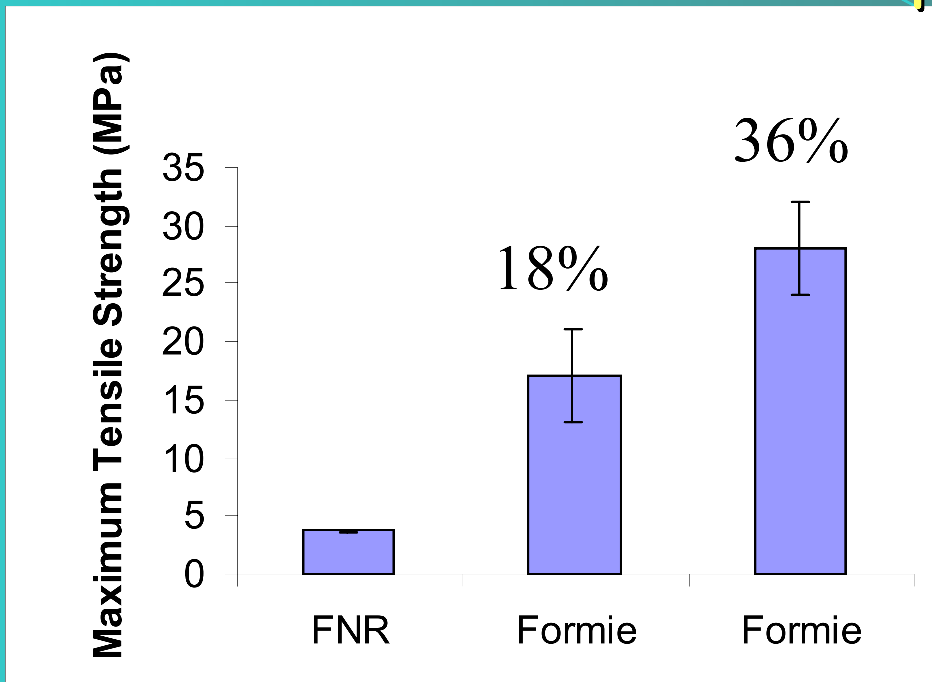


Reinforced Films Mecanical Properties



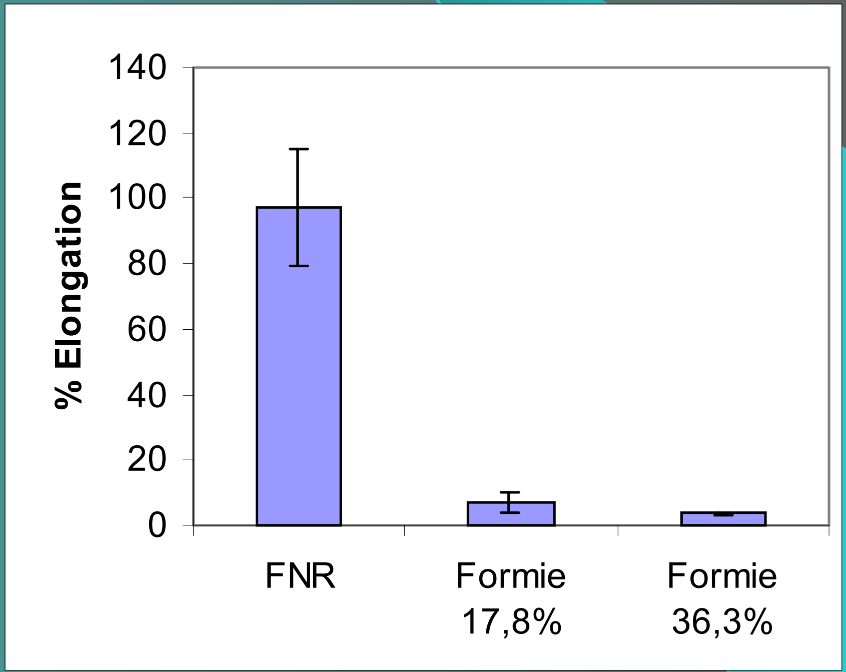
Veils from CIRAD Cotton Lab

Reinforced Formie Films Mechanical Properties



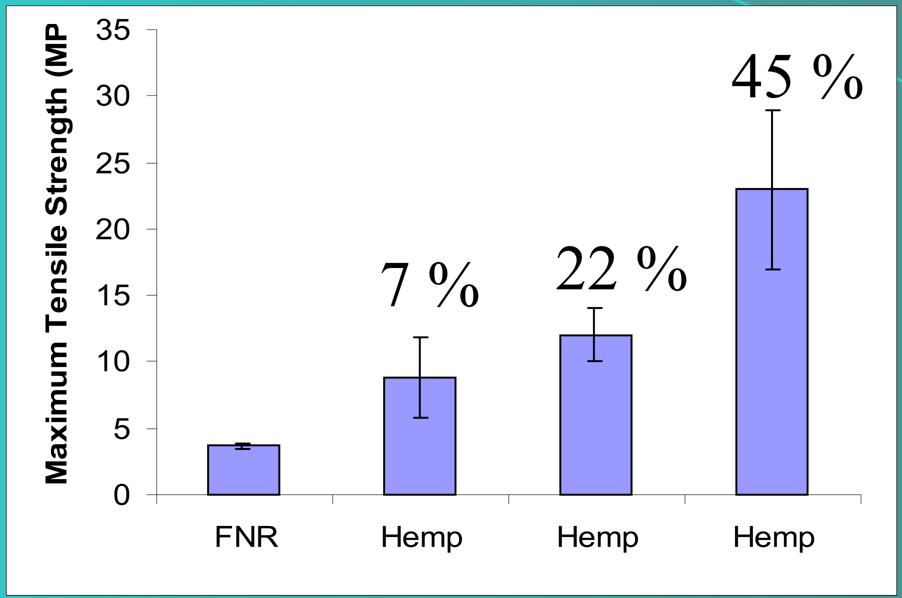
18 % fiber content produce ~ 460% increase in MTS
& 93% in % elongation lost

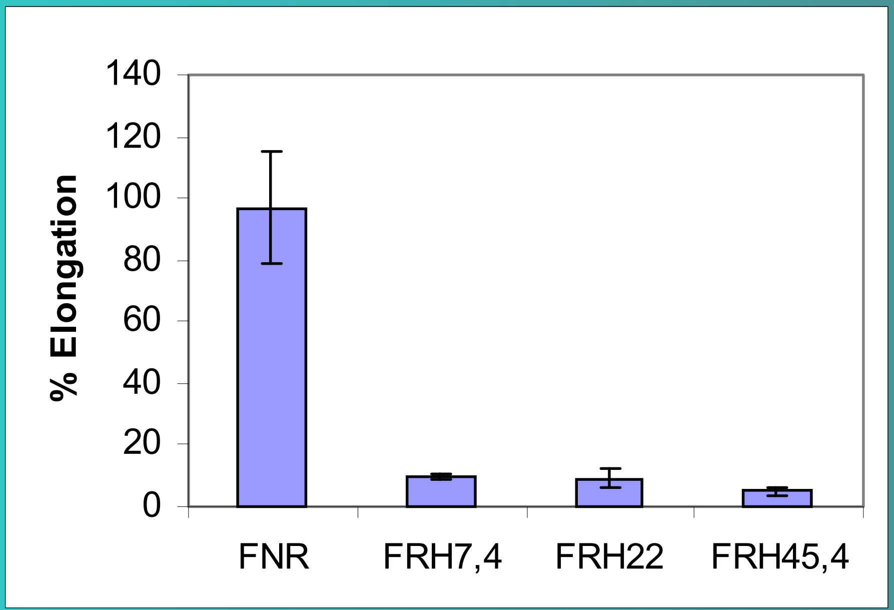
36% fiber content produce ~ 750 % increase in MTS
& 96% in % elongation lost



Short fibre non woven (Paper maker equipment TAPI)

Reinforced Hemp Films Mecanical Properties





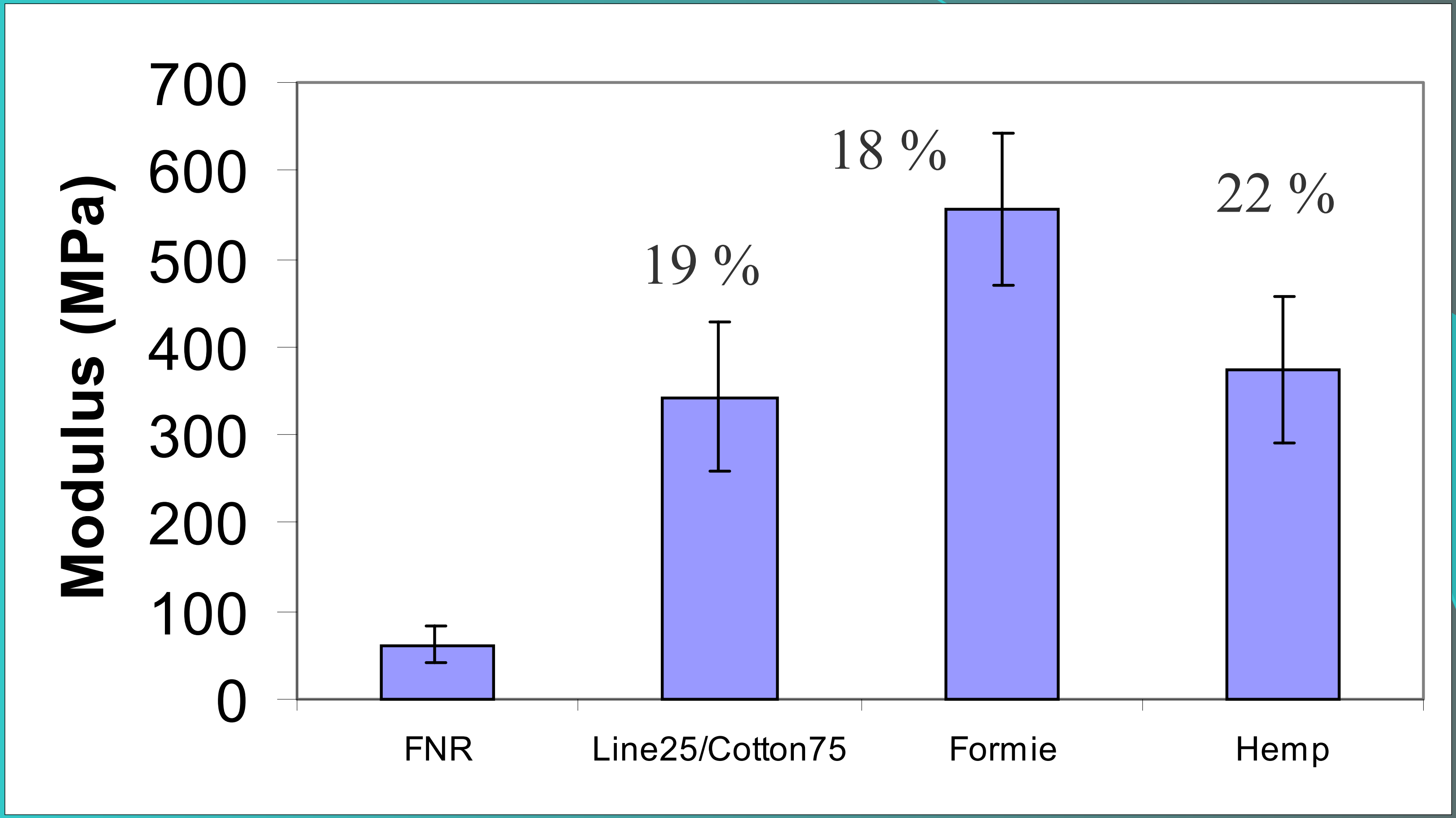
45% fiber content produce ~ 621% increase in MTS
& 95% in % elongation lost

22% fiber content produce ~ 320% increase in MTS
& 91% in % elongation lost

7% fiber content produce ~ 240% increase in MTS
& 90% in % elongation lost

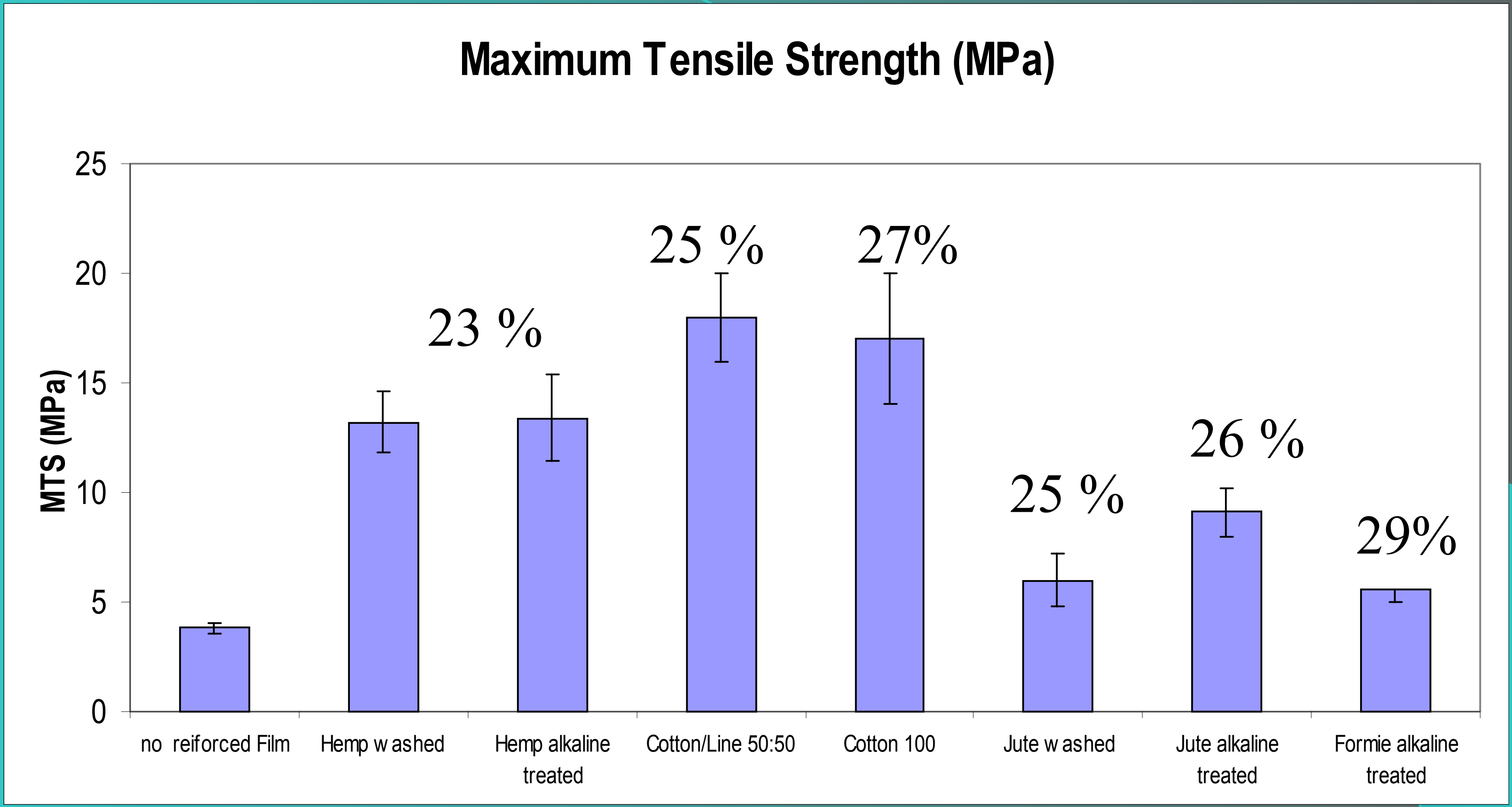
Short fibre non woven (Paper maker equipment TAPI)

Reinforced Films Mecanical Properties



Short fibre non woven(Paper maker equipment TAPI)

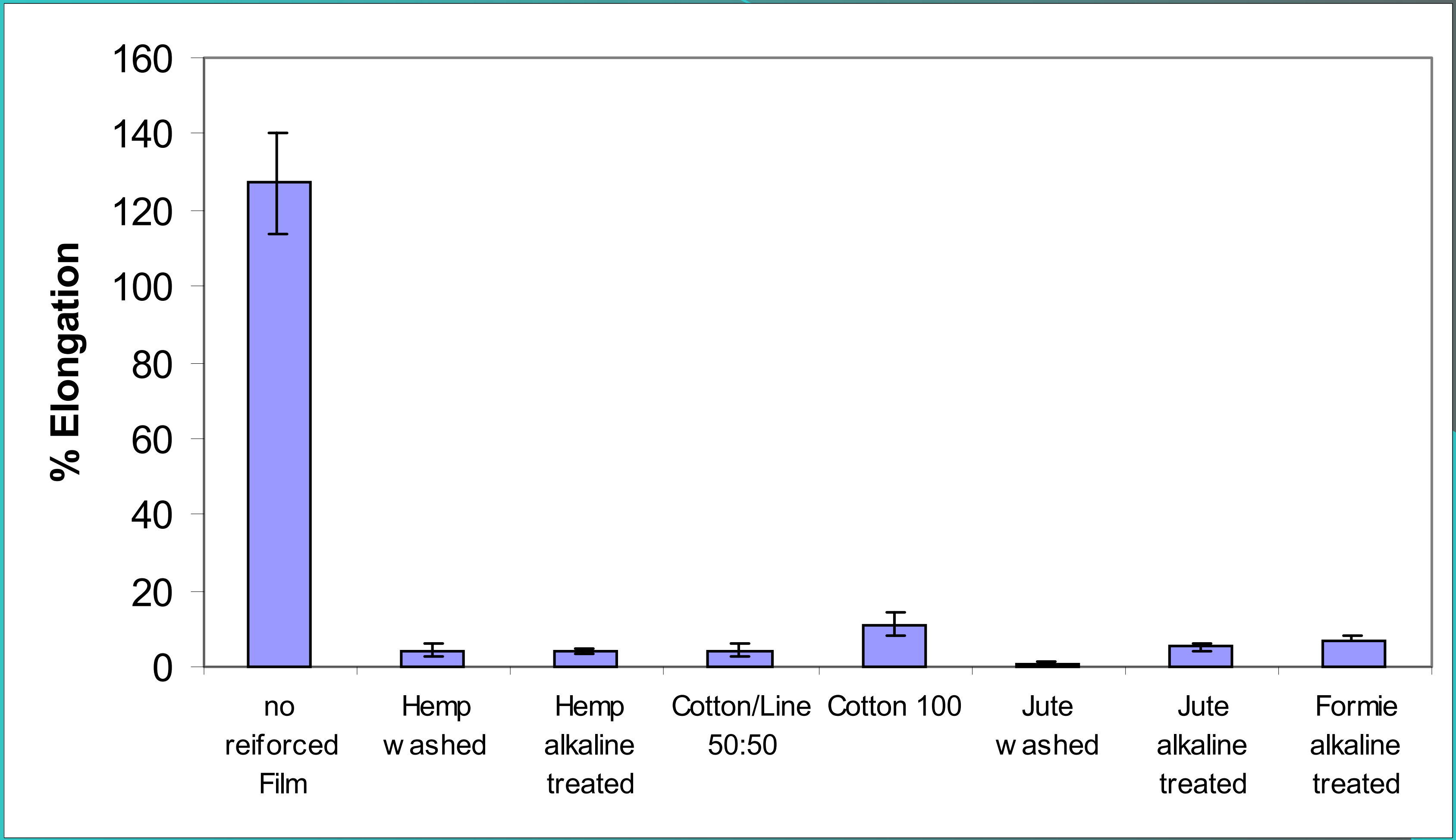
Composite Mechanical Properties
Effect of fibre chemical treatment



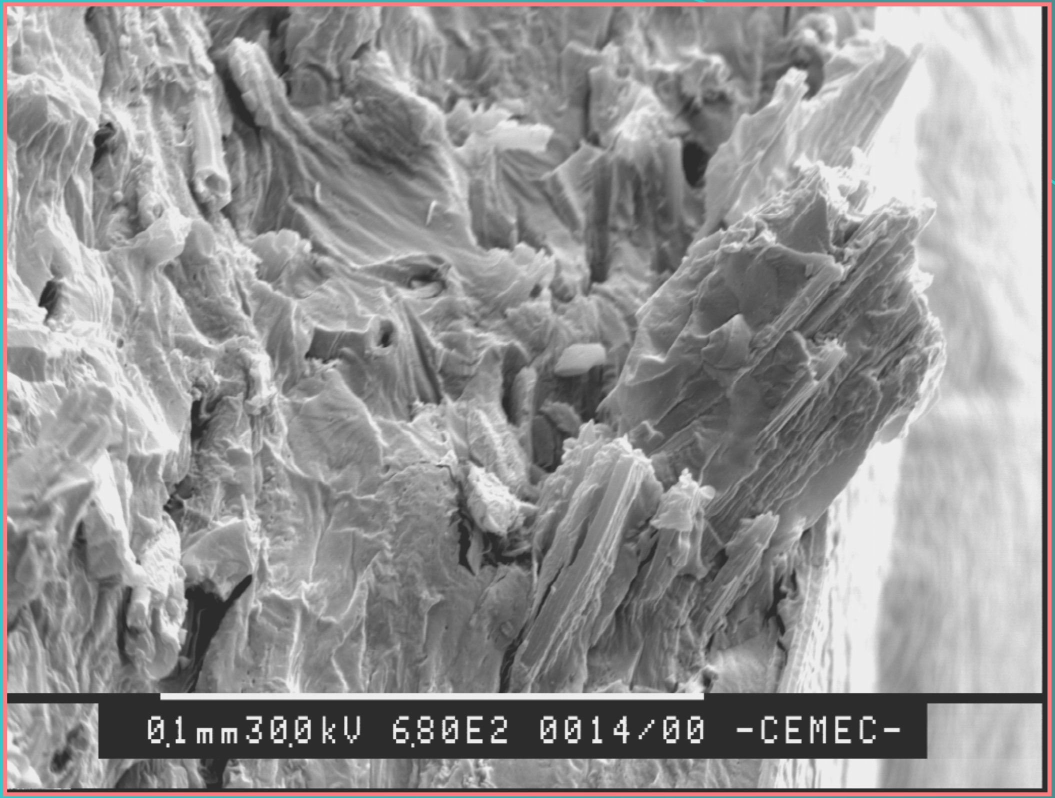
Filmogenic solution: DM = 6.46%, Glycerol = 20.2%, Glut / RL = 1.86

Formie without chemical treatment did not produce a non woven mat

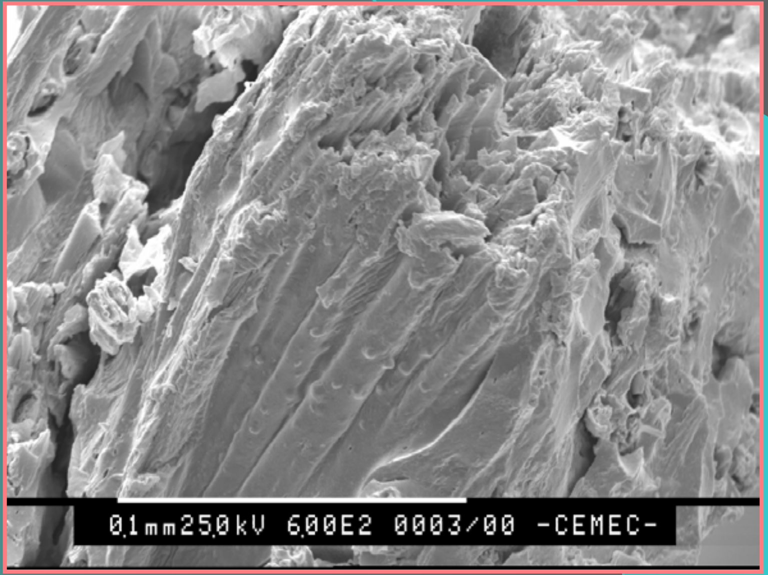
Composite Mechanical Properties
Reduce in Elongation at Break



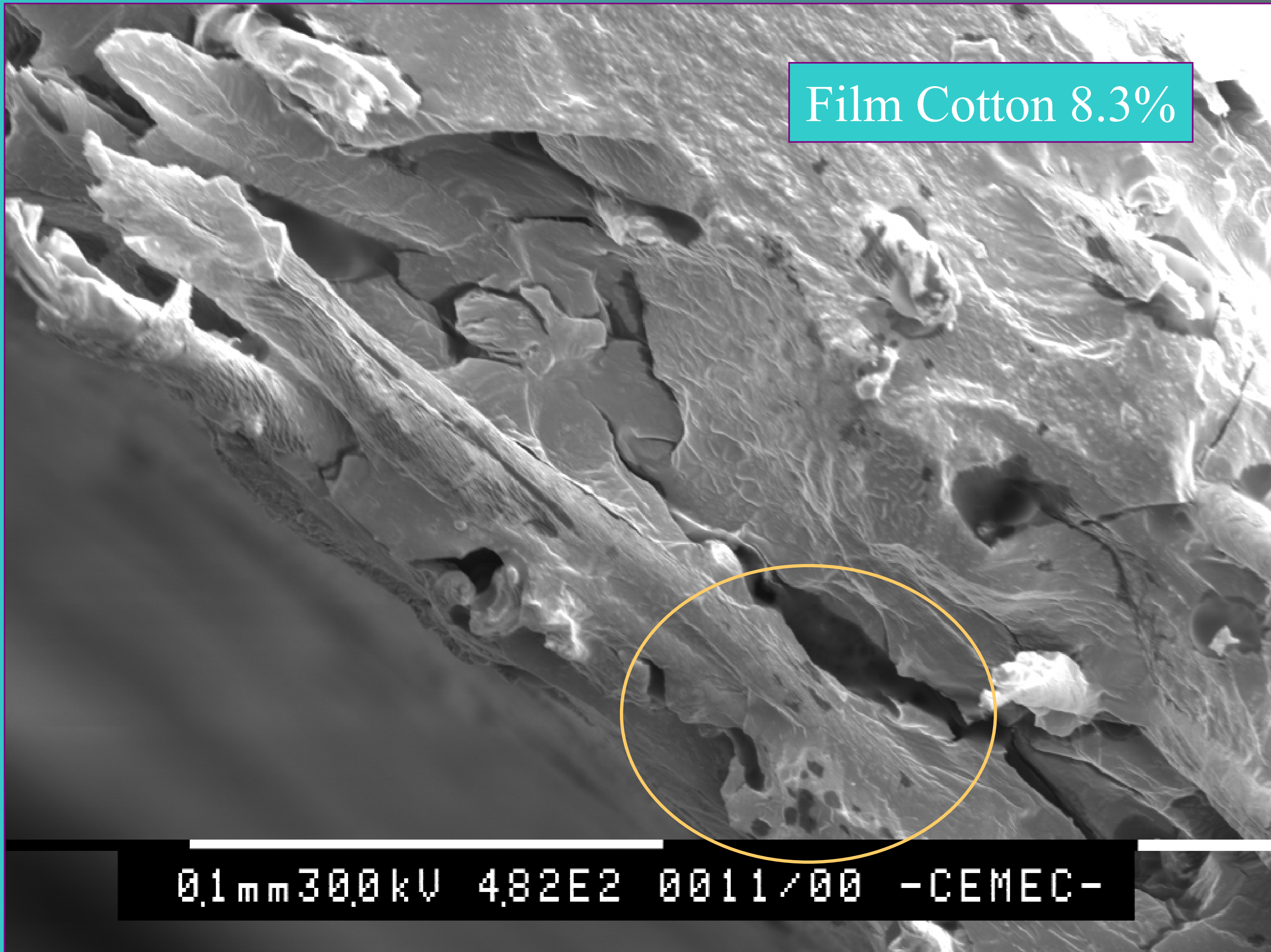
Scanning electron micrograph (SEM) of reinforced film

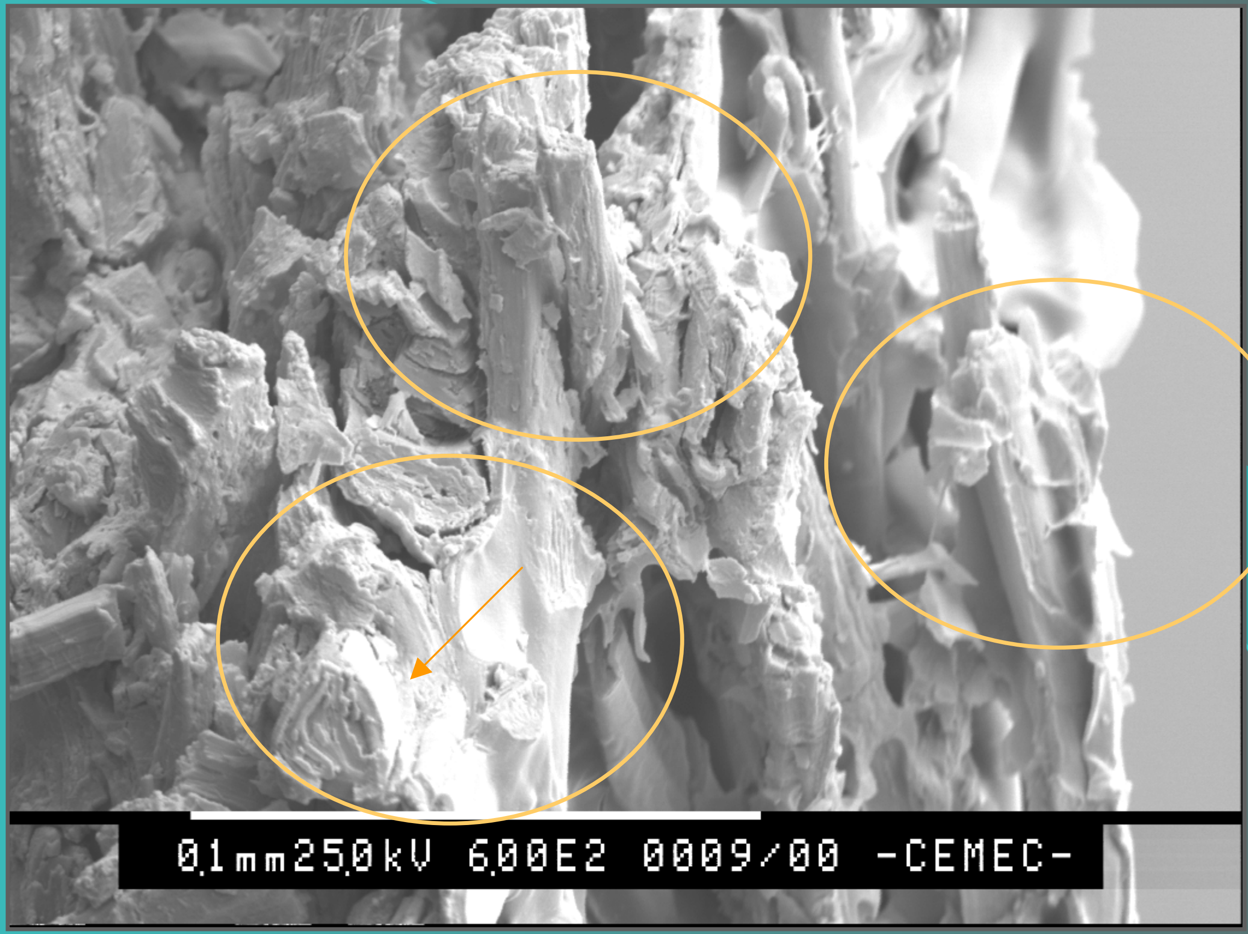


SEM of Film reinforced with formie non woven fiber mat 36.3% w/w



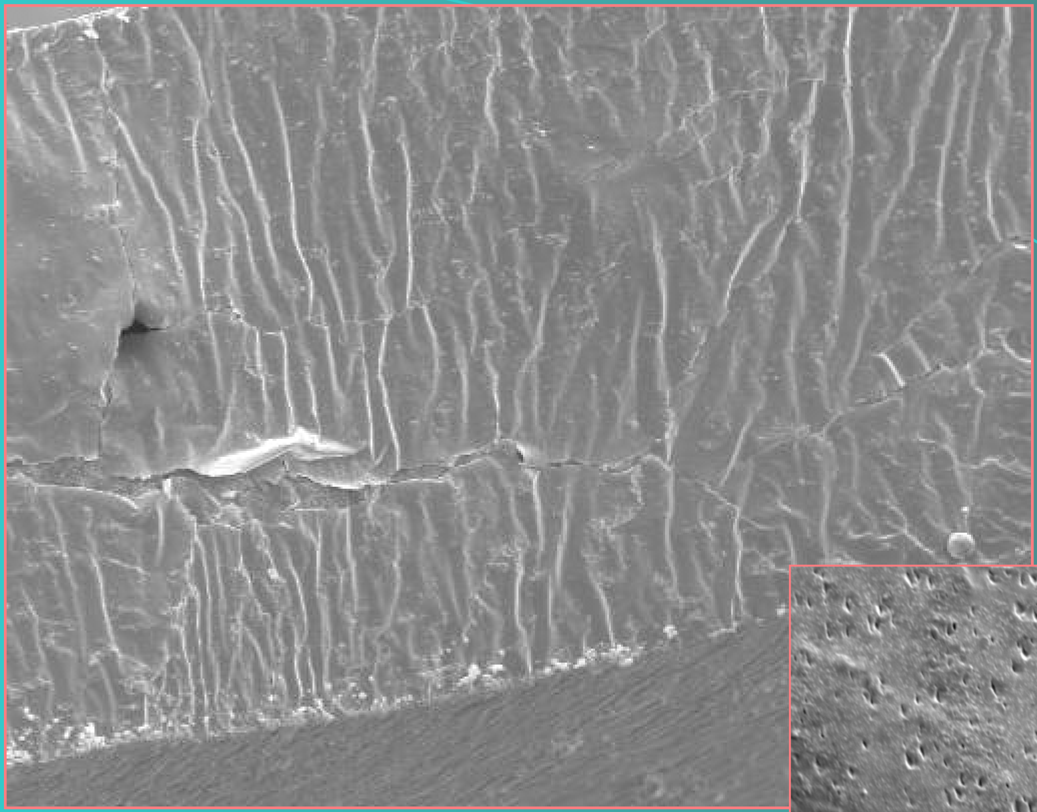
Film Line/Cotton 25/75, 12.8%

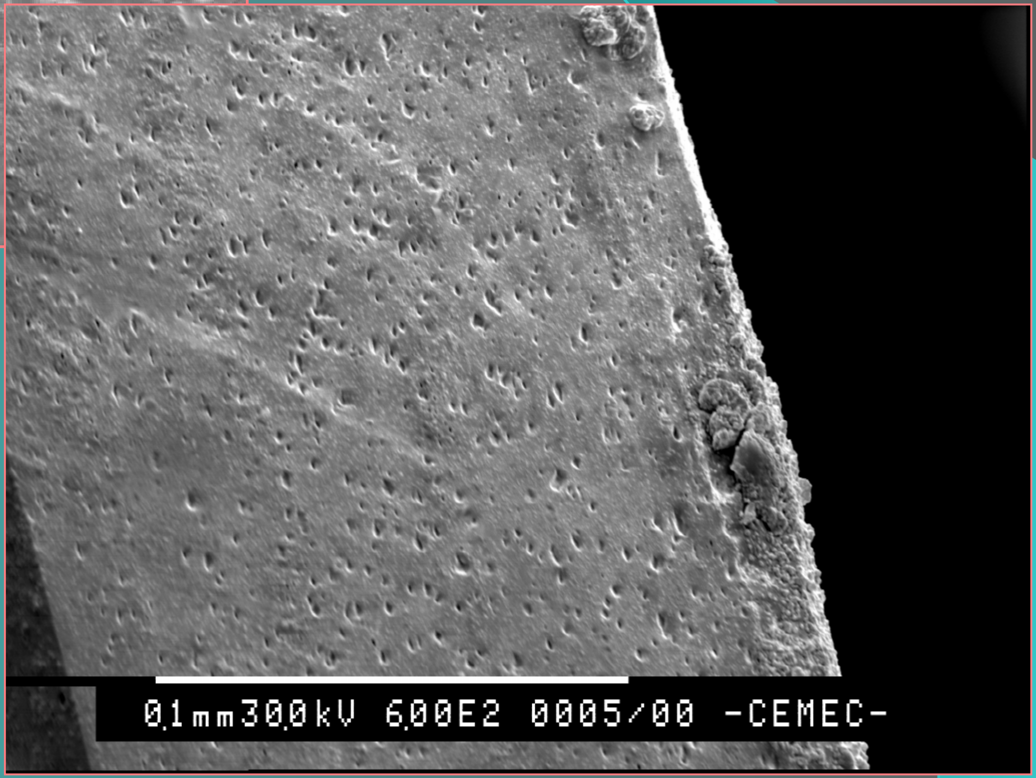

Film Cotton 8.3%
0.1mm30.0kV 4.82E2 0011/00 -CEMEC-



SEM of Film reinforced with hemp non woven fiber mat 45.4% w/w

Scanning electron micrograph of non reinforced films





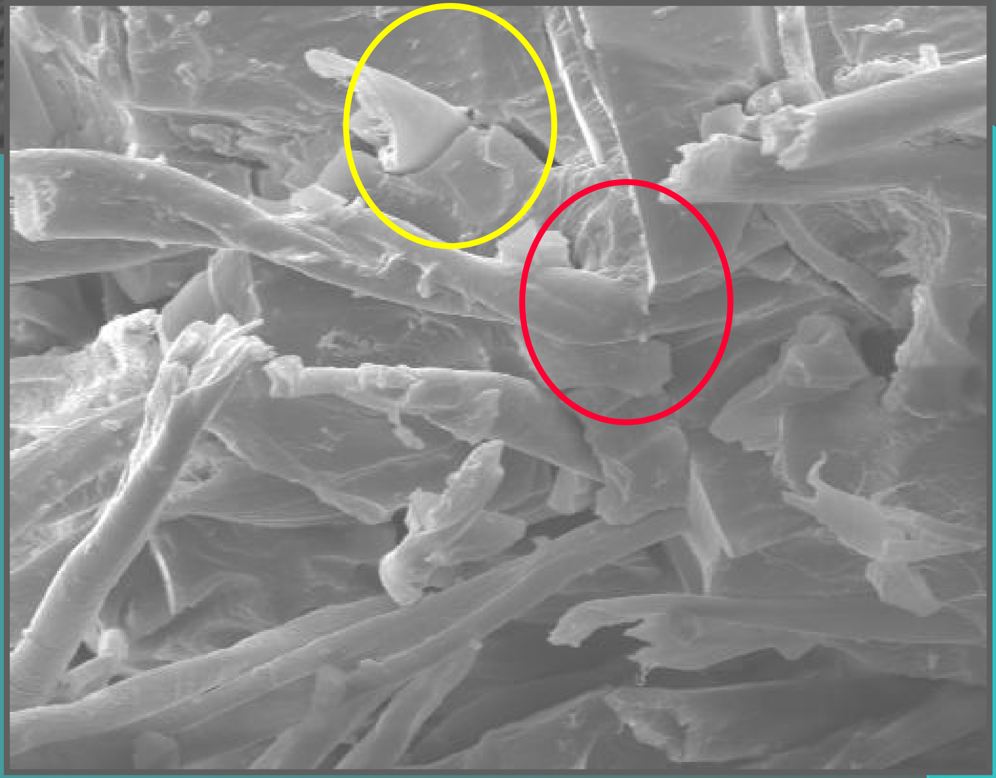
Films fabricated from Impregnated Fibre prepreg

- Mechanical properties measured for this films showed much lower values than those obtained with fibers non woven reinforcements (paper maker equipment TAPI).

  - Low matrix penetration and high inhomogeneous fiber distribution was observed.

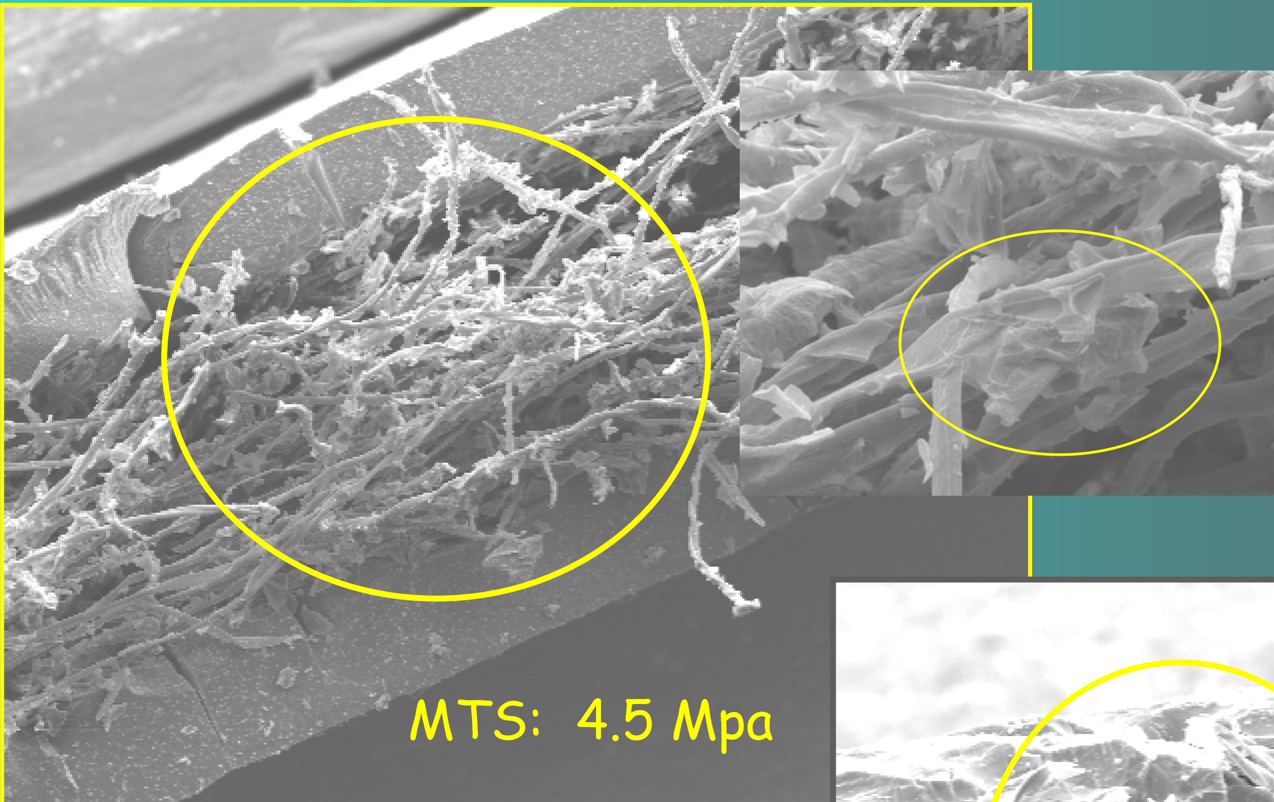
- As the filmogenic solution for the impregnation process was formulated with the crosslinking agent, low fiber prepreg interaction with the matrix could be atributed to the formation of the crosslinked network on the fiber surface.

Scanning electron micrograph of Film reinforced with carded cotton veil



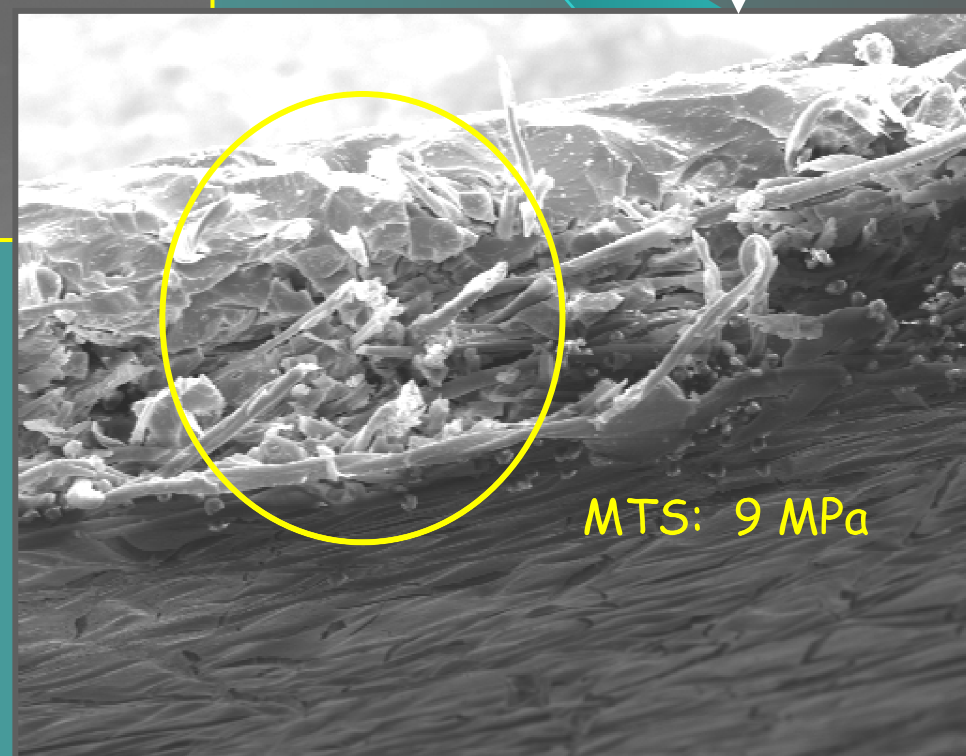
SEM
film reinforced with carded cotton veil

Prepreg: Filmogenic solution over veil

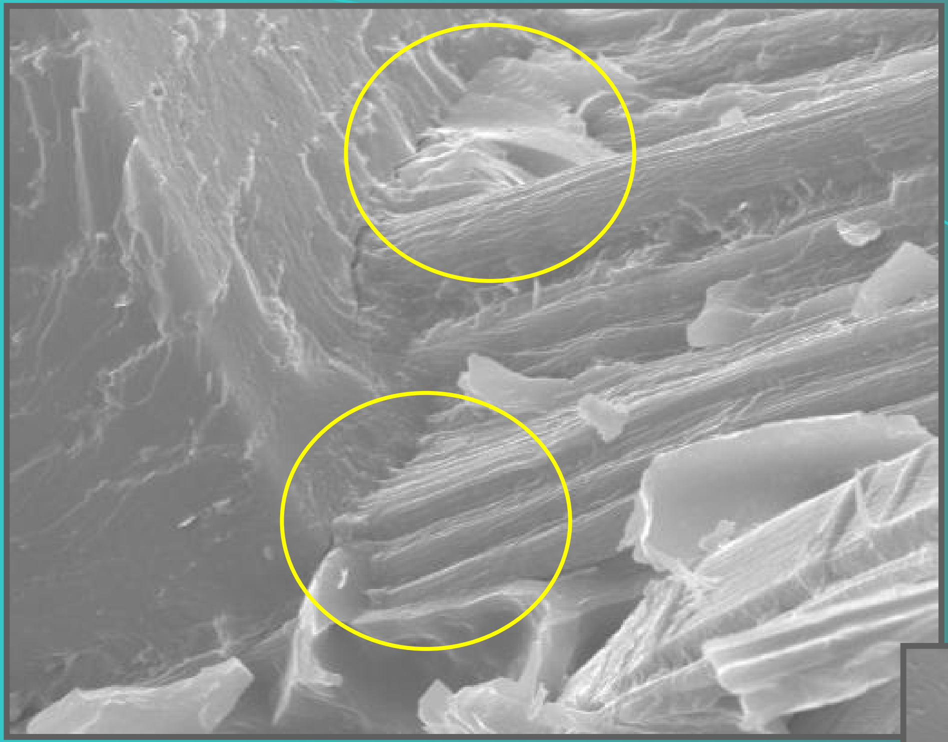


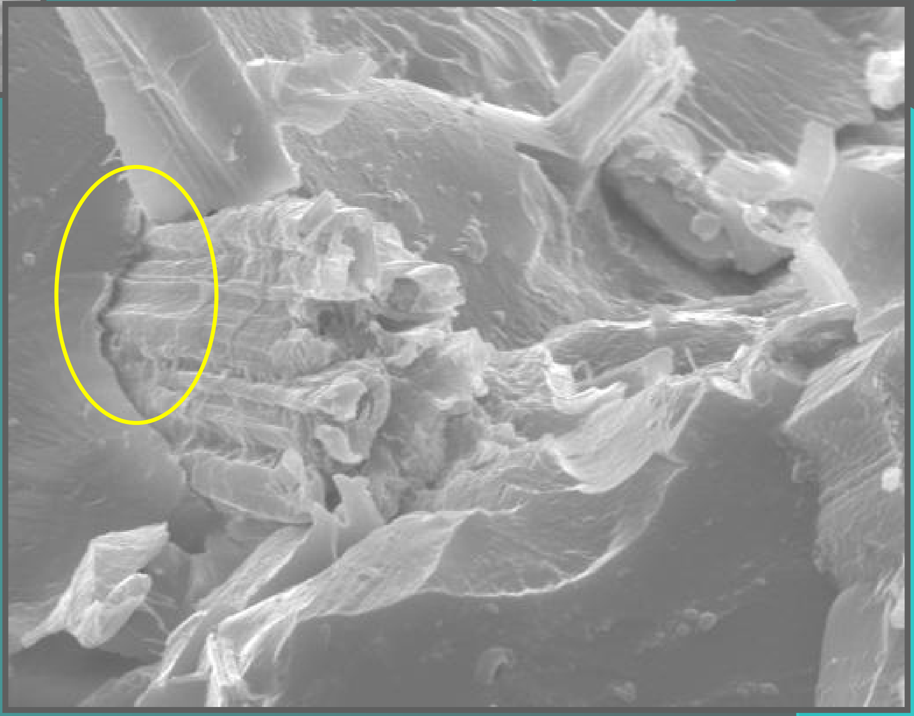
fabricated with spread coating technique

cast



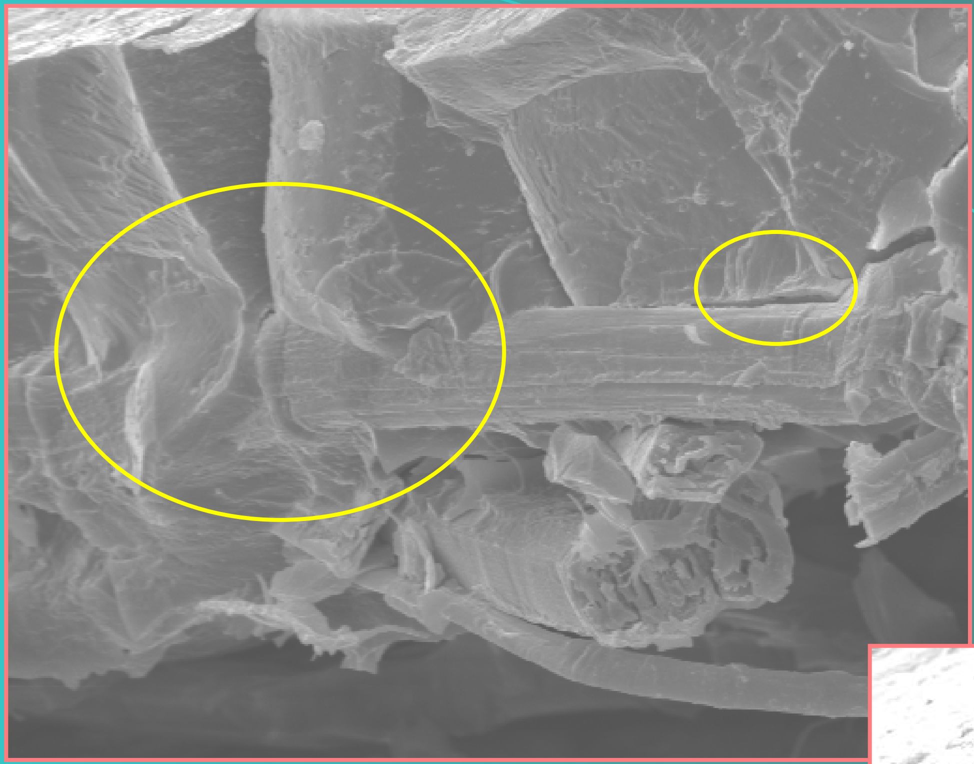
SEM: Film reinforced with hemp prepreg

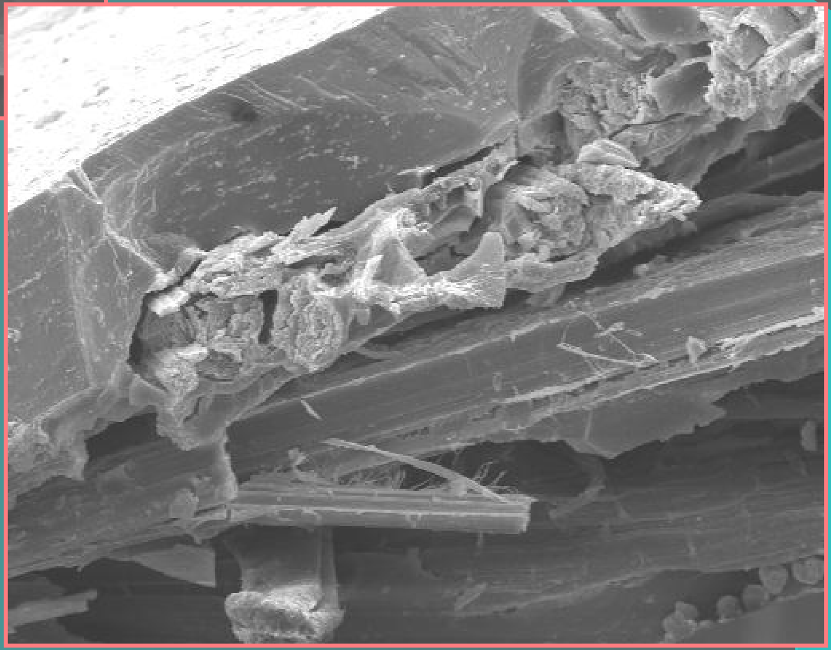


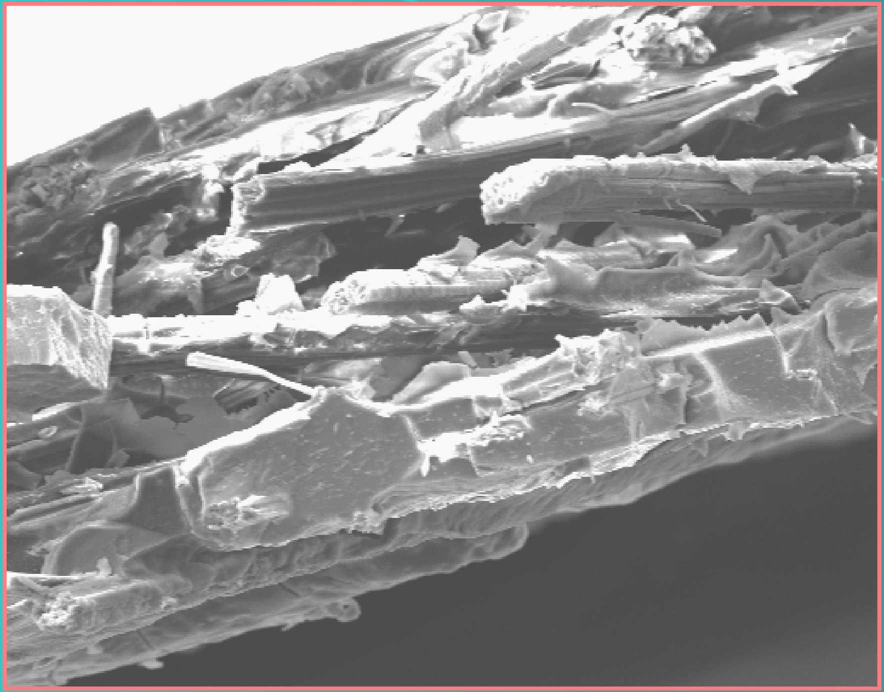


200% increase in MTS hemp prepreg
Vs
325% increase in MTS for short hemp fibre non woven
(TAPI)

SEM: Film reinforced with hemp prepreg

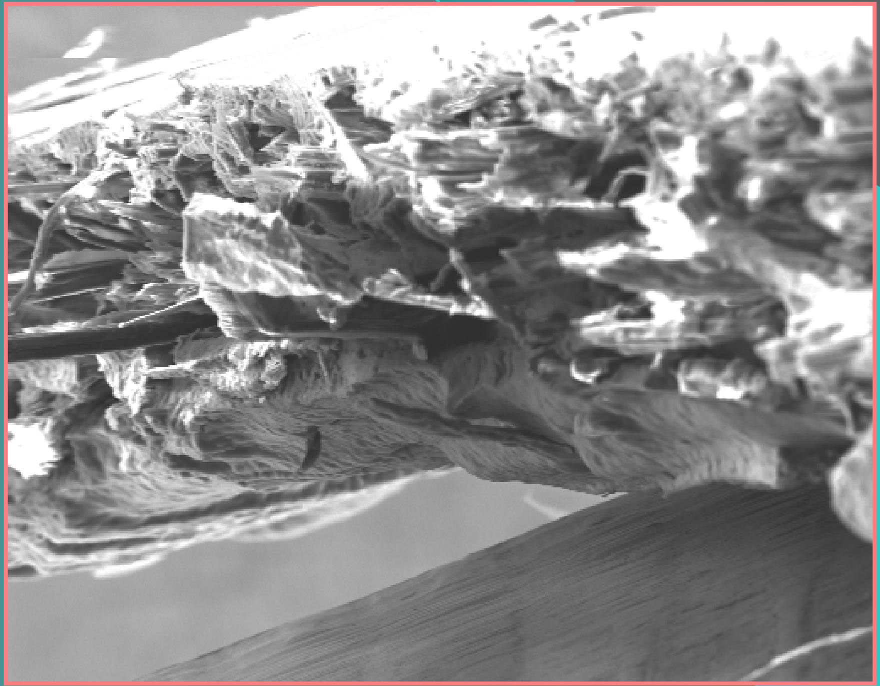






SEM: film reinforced with jute prepreg

200% increase in MTS jute prepreg
Vs
270 % increase in MTS for short jute fibre non woven
(TAPI)



Remarkable Results

Raw Materials considerations

Protein extracted from cottonseed pellets (SDP) have good film forming properties.

The films obtained from SDP showed similar mechanical properties to films obtained from proteins extracted from cottonseed flour.

Remarkable Results

Natural Fibres

Chemical Treatment

Natural fibres , used as reinforcement for SDP, were chemical treated in order to allow better non woven mat preparation and fibre impregnation.

An improvement in composite films mechanical properties was observed, in most of the studied fibres.

Remarkable Results

Composite Films

Veils of line/cotton and cotton used as film reinforcement showed the best mechanical properties.

A two to four-fold increased in maximum tensile strength and an average of about seven-fold increase in tensile modulus was observed for formie, jute, and hemp non woven mat, and for line/cotton veils.

Remarkable Results

Composite Films

An increase in the tensile strength was observed as the fibre content increase, at the studied range

SEM Microscopy showed good matrix-fibre interaction for short fibres non woven reiforcements studied.

Remarkable Results

Composite Films

No significant difference was observed in the mechanical properties using formaldehyde and glutaraldehyde as crosslinking agents.

For hemp fibres the tensile strength of films crosslinked with for formaldehyde was 12 MPa, and for the same fibre content the tensile strength value was 13 MPa for glutaraldehyde

To improve and develop

- Systematic studies on the chemical and enzymatic fibers treatment and their influence in composite performance

- Better formulation and process development for fibers impregnation

- Composite films fabrication, at the pilot plant spread coating equipment was not successful yet.

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