INTI Plásticos

ÉCOLE DES MINES D'ALÈS
Alès - Nîmes - Pau

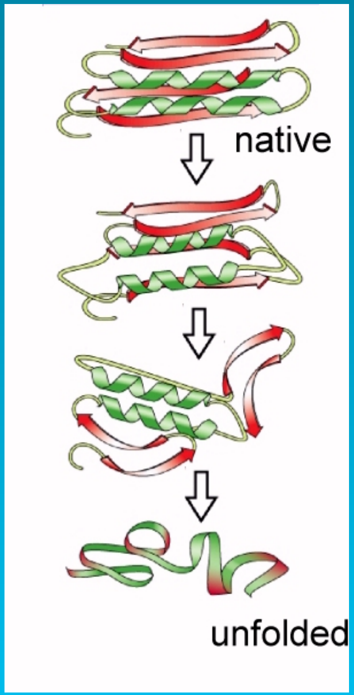
Technical feasibility of common polymer technologies applied to natural polymers

- Casting: *Paulo Sobral, FZEA-USP Brazil*
- Spread Coating: *Patricia Eisenberg, Plasticos-INTI Argentina*
- Extrusion and thermomoulding : *Laurent Ferry, EMA, France*

Introduction

Protein processing

« Wet technologies »	« Dry technologies »
Proteins	Proteins
Dispersion conditions	Melting, glass transition
Filmogenic solution	**Powders or granules**
Coacervation conditions	Processing conditions
Film or coating	**Film or rigid material**



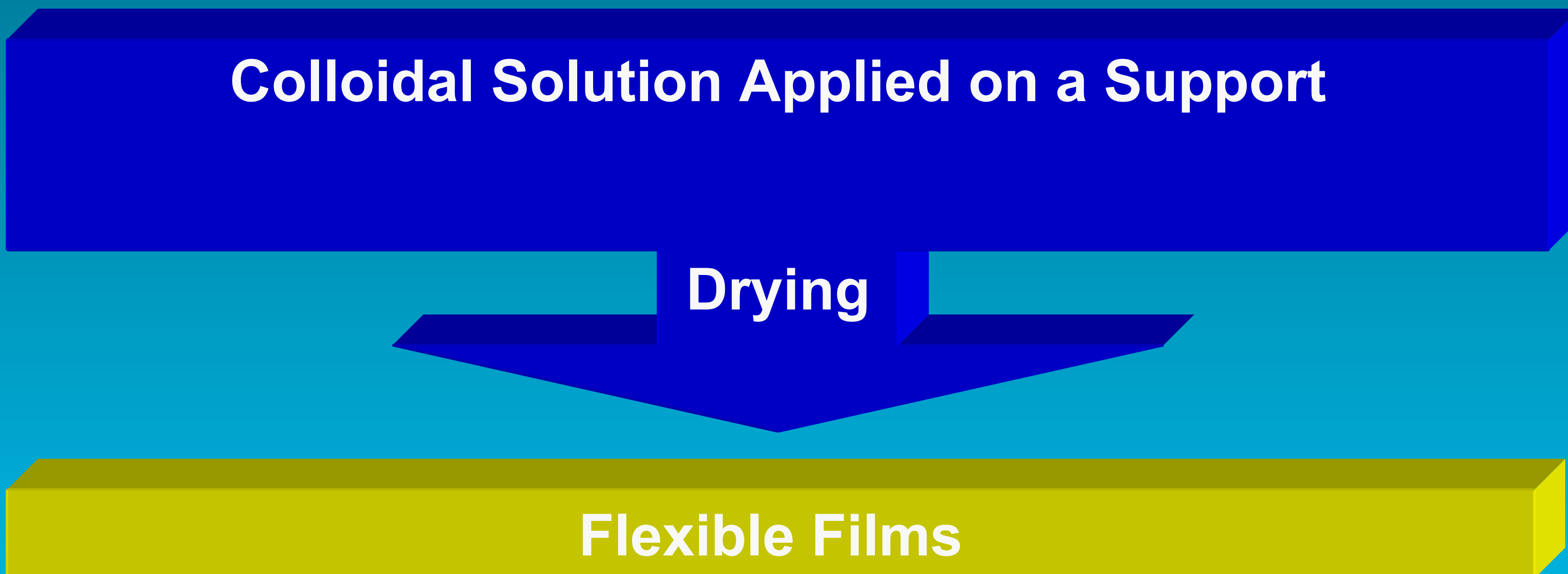
According to S. Guilbert GFP Volume 13, Chapître 8

Raw matter

- Cottonseed cakes
  - Complex materials
    - Composition
      - proteins, lipids, cellulose, sugars…
    - Different parts
      - Kernels, shells, linter
  - Effect of oil extraction process
    - Protein modification
- Delipidated glandless cottonseed flour

CASTING

Production of films by casting



Film forming solution

Basic formulation

- **COTPROT**
- **pH agent**
- **Plasticizer**
- **Crosslinking agent**

Film production steps

Extraction
pH, T, t

↓

COTPROT

↓

Glutaraldehyde addition with constant stirring
Glutaraldehyde/reactive lysine ration = 3
T = room temperature (22 to 25°C)
t = 60 min

↓

Plasticizer addition with constant stirring
Cplasticizer = 10, 20, 30, 40, 50 g/100 g DM)
T = room temperature (22 to 25°C)
t = 15 min

↓

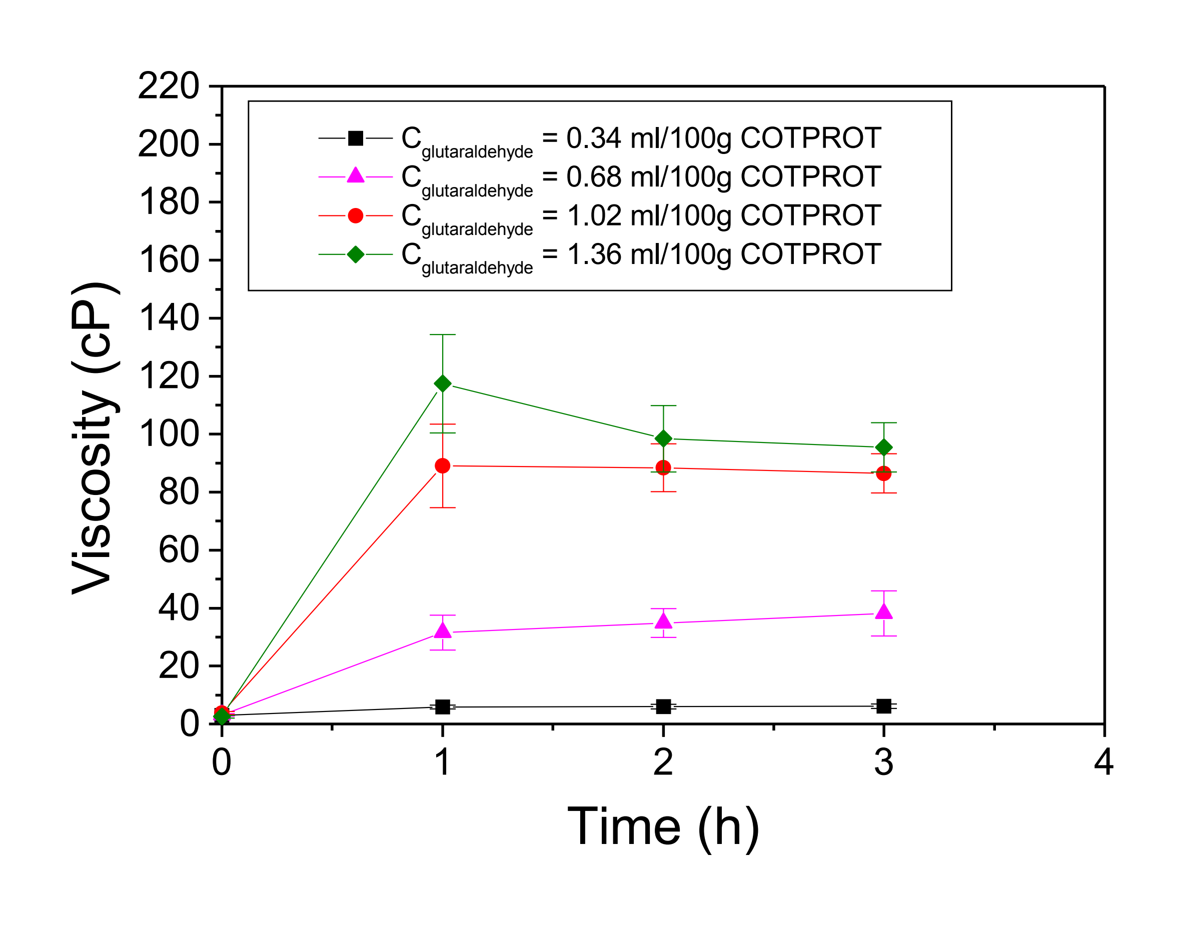
Spreading in plexiglass plates

↓

Drying
1st step = 12h at room temperature
2nd step = 60°C (7h)

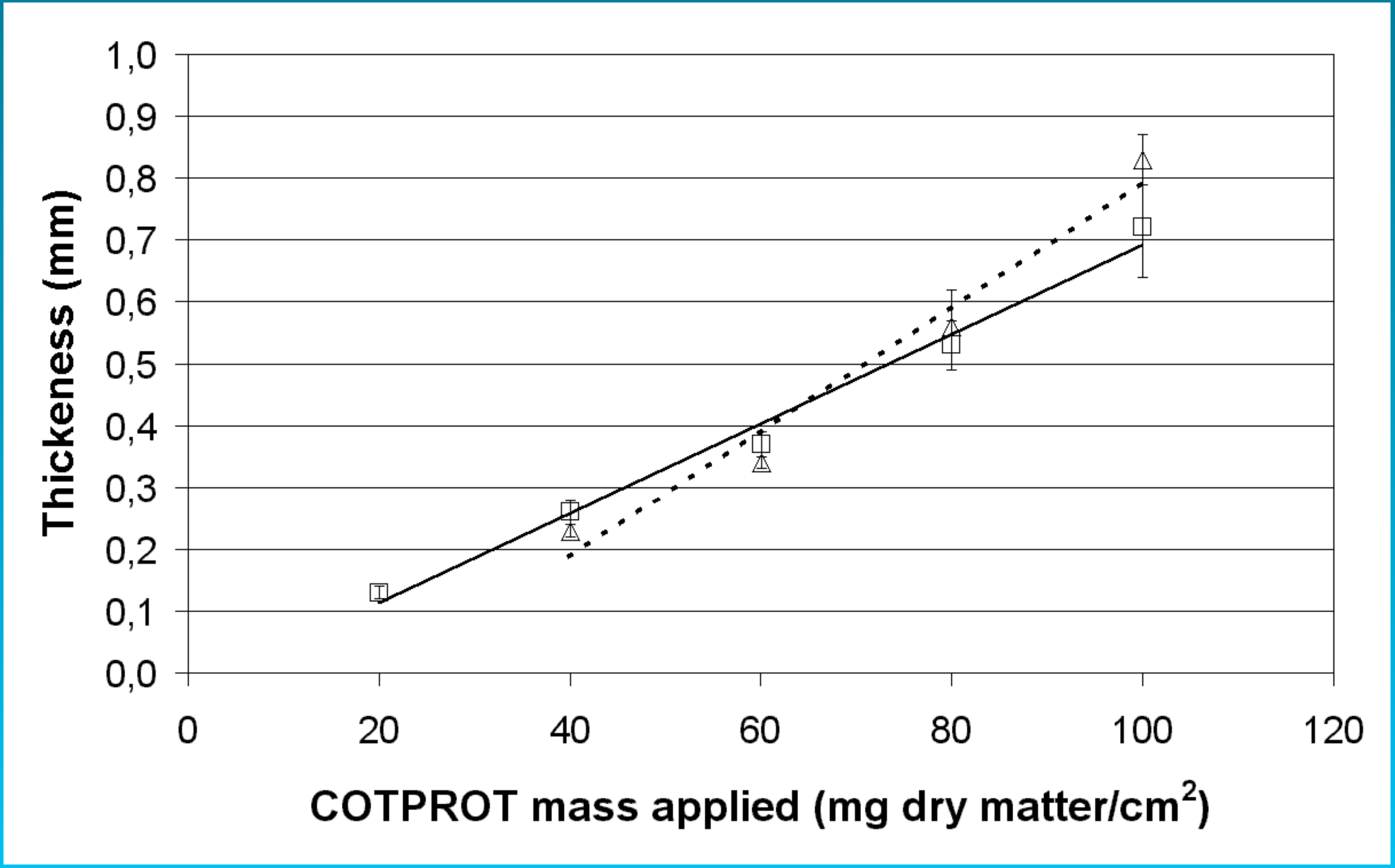
Controlling the cast processing

Viscosity of the solution




Controlling the cast processing

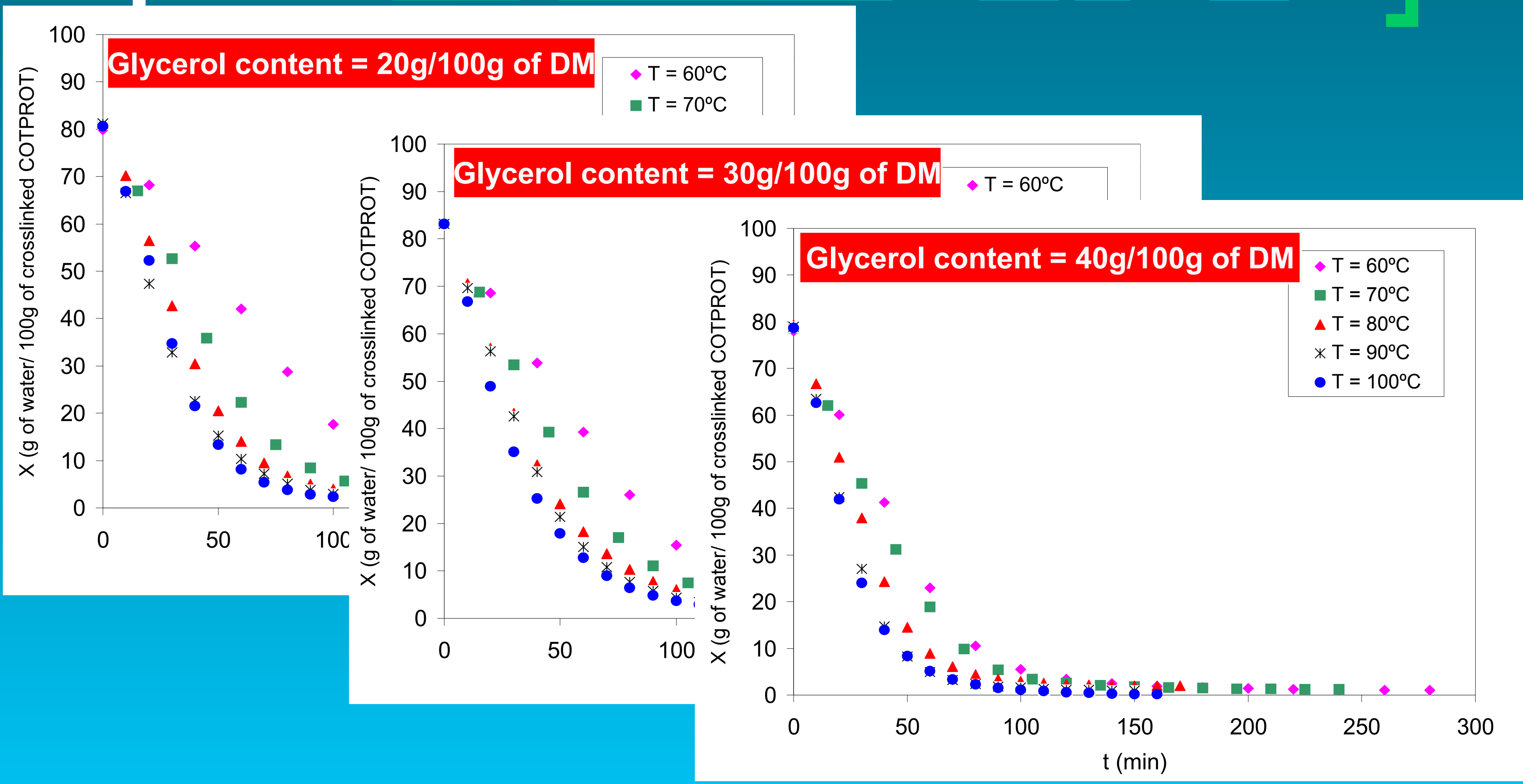
Control of thickness of films



Glutaraldehyde/reactive lysine molar ratios of 6 (◊) and 3 (Δ)

Choice of the support

Drying the solution



Characterization of films

SPREAD COATING

INTI Plásticos

Spread Coating equipment

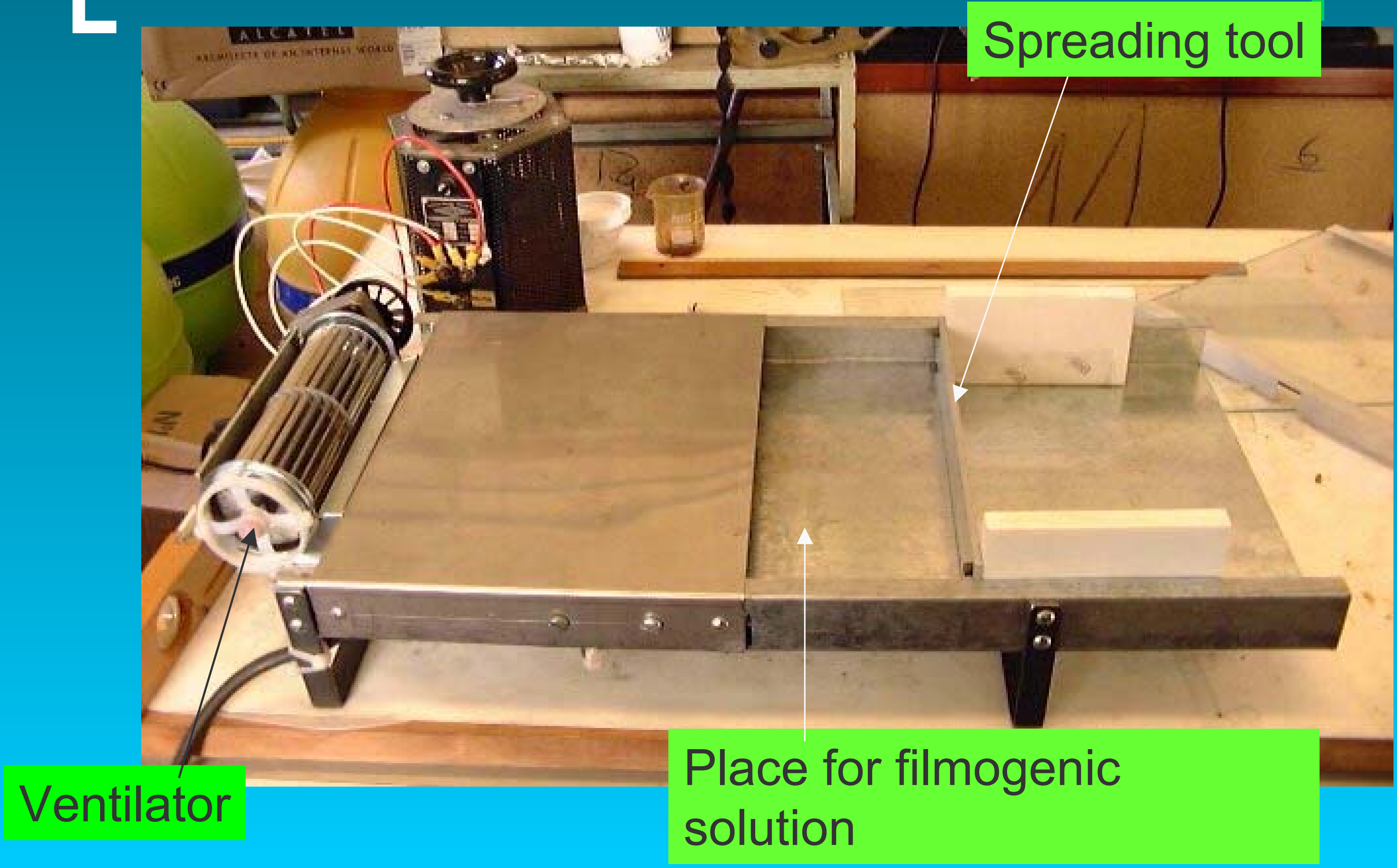
Design and Construction

Raw Material

- High viscous COTPROT solution adequate formulated

A prototype of the equipment was built in order to evaluated the film forming conditions.

Spread coating equipment prototype



Spread coating equipment prototype (results)

- The spread coating process was suitable for our formulation
- The formulation spread facility needs careful viscosity adjustment
- Drying conditions (time and temperature): the drying process needs to be very slow, at low temperature, in order to obtain a good film surface quality.

Spread coating equipment prototype (results)

The results obtained with the prototype spread coating equipment allows us to determine:

- Pilot plant equipment dimensions (equipment length)
- Endless rubber blanket: design, material type and velocity regulation
- Drying system: type of system, conditions (air velocity)

Film obtained with the prototype spread coating equipment

Film formulated with SDP; glutaraldehyde, glycerol and Polyvinyl alcohol (1.0 % w/w). Dried with the prototype spread coating equipment at 40ºC , 1 h, 60ºC 30 min

Casting vs spread coating Film fabrication

Filmogenic Solution (FS)	Mass Area (mg/cm2)	Water content (%)	Thickness (mm)	Maximum Tensile Strength (MPa)	Maximum elongation (%)
DM:10%, Gly:20% Glu/RL:3.6 Casting	31.1	9.8 (SD=0.2)	0.27 (SD=0.04)	4.5 (SD:0.8)	51 (SD:22)
DM:10%, Gly:20% Glu/RL:3.6 Spread Coating	-	10.3 (SD=0.1)	0.17 (SD=0.01)	4.5 (SD:0.4)	84 (SD:19)

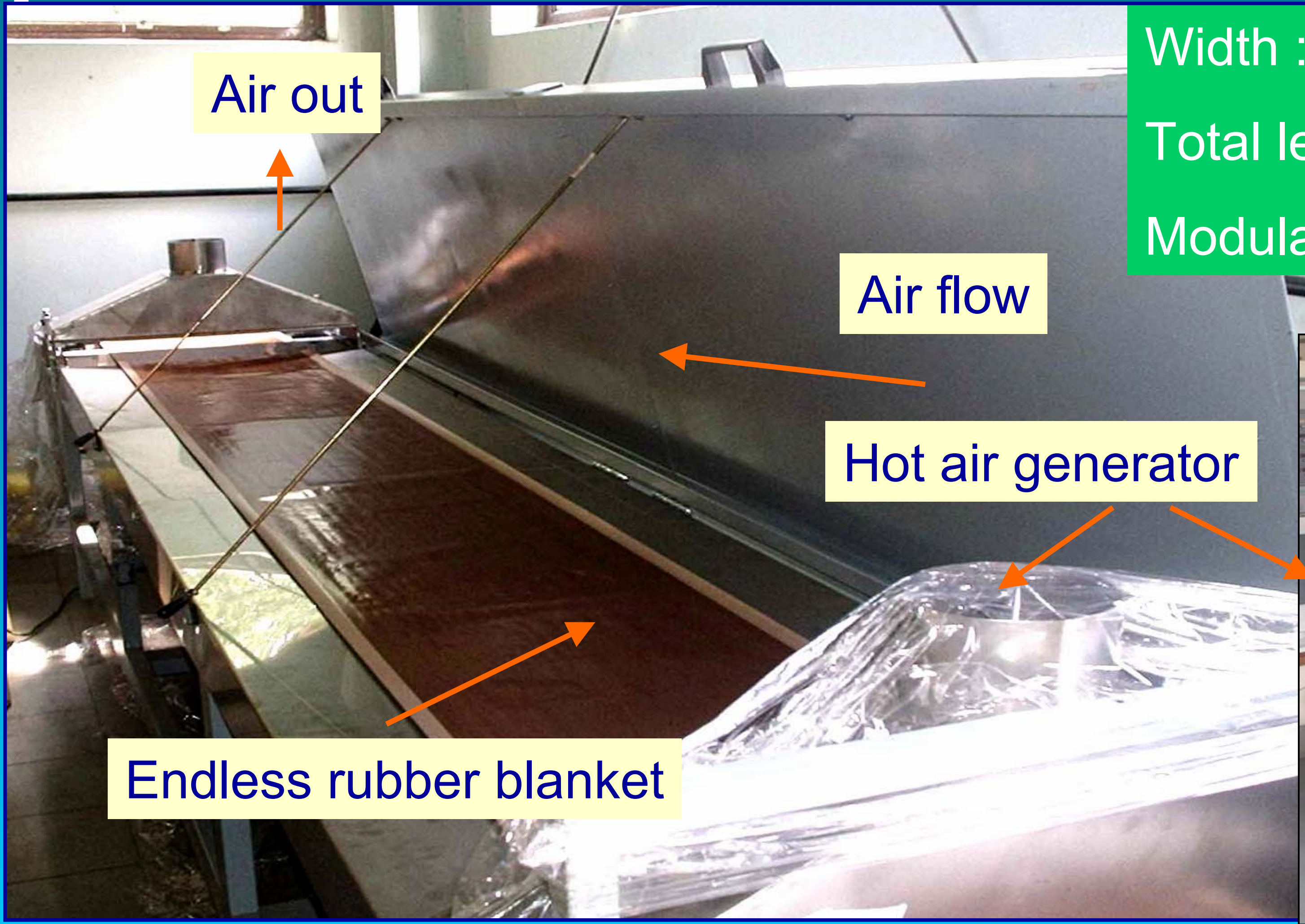
Pilot plant
spread coating equipment

Pilot plant
spread coating equipment

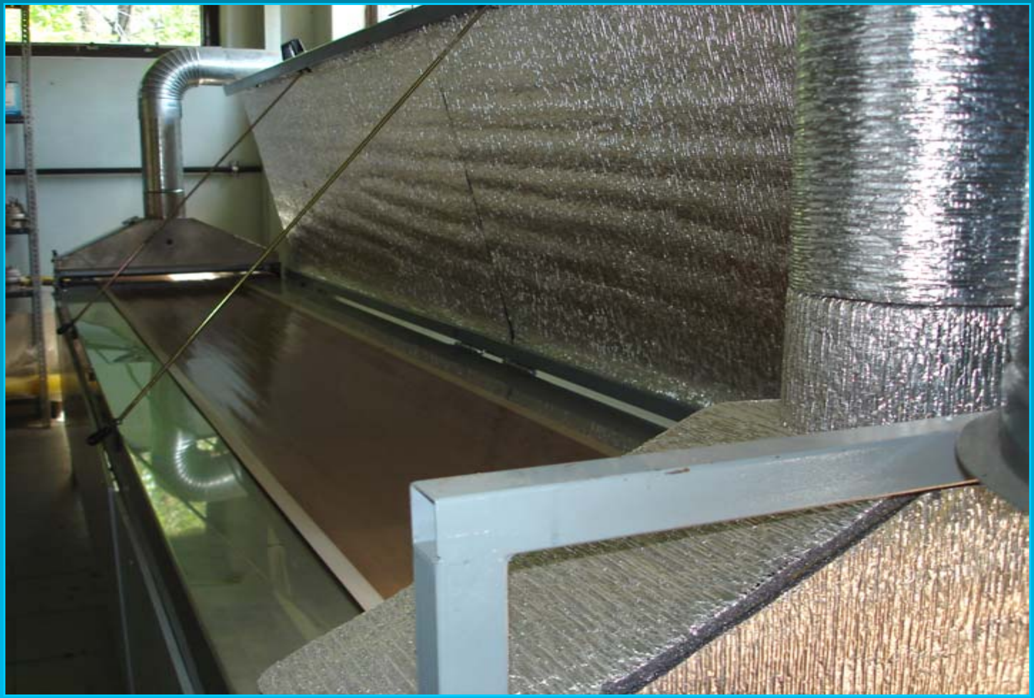
Width : 400 mm

Total length: 6 m.

Modular design.

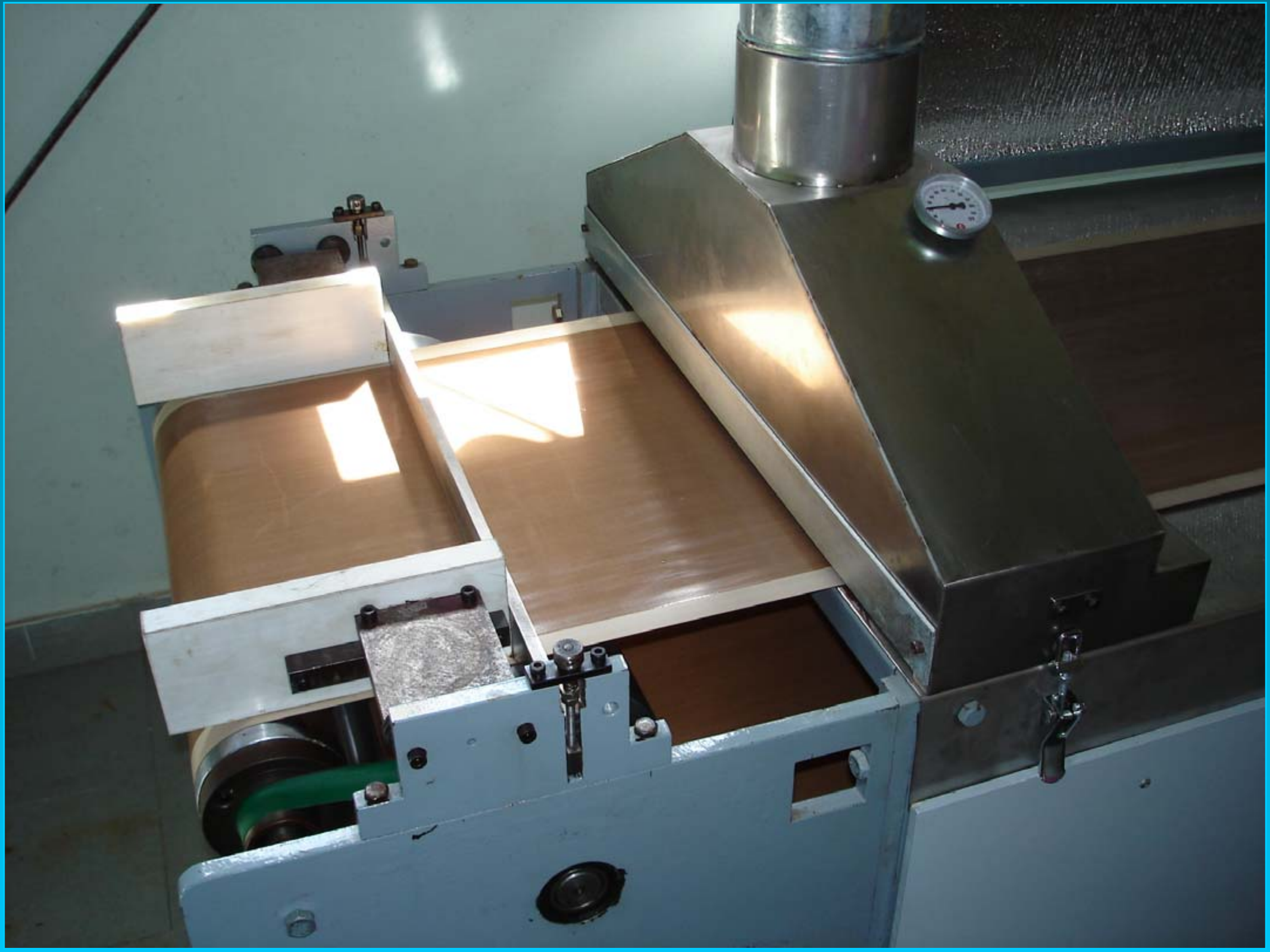


Pilot plant
spread coating equipment



Pilot plant
spread coating equipment

Spread coating equipment
Spreading the film-forming solution



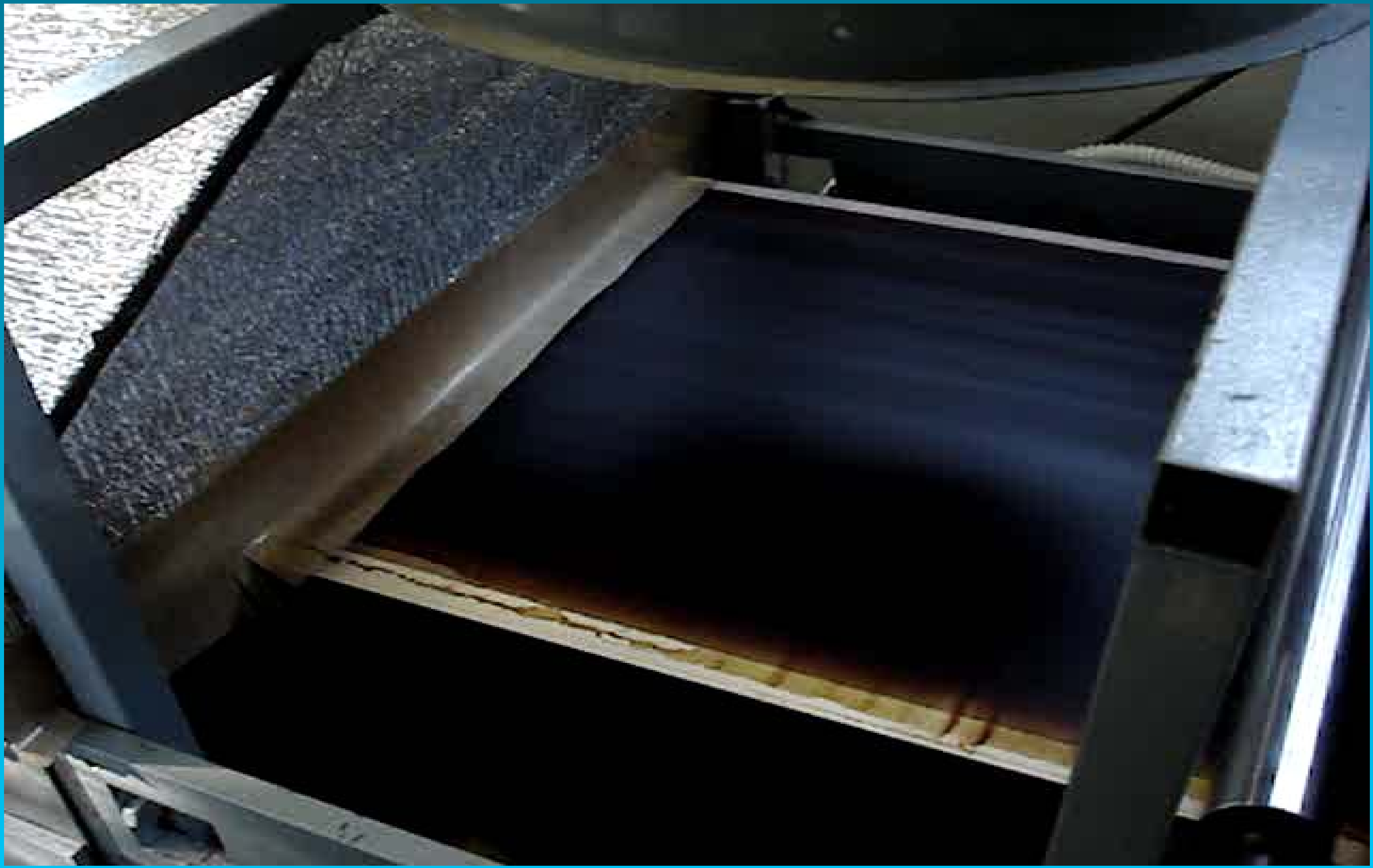
Spread coating equipment
Spreading the film-forming solution

Spread coating equipment
Non reinforced film fabrication

Film coming out from the drying zone

Film in the rolling system

Spread coating equipment
Non reinforced film fabrication



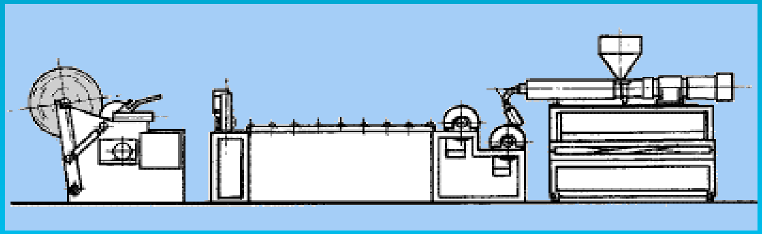
Spread coating equipment
Non reinforced film fabrication

EXTRUSION – THERMOMOULDING

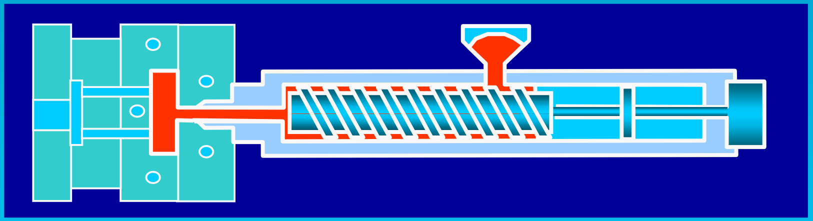
ÉCOLE DES MINES D'ALÈS
Alès - Nîmes - Pau

Dry technologies

- Melt processing techniques
  - Thermoplastic polymers
  - Temperature and mechanical forces induce polymer flow
  - Molten polymer is pushed :
    - Through a die (extrusion)
    - Into a mould (injection-moulding)



Cast extrusion

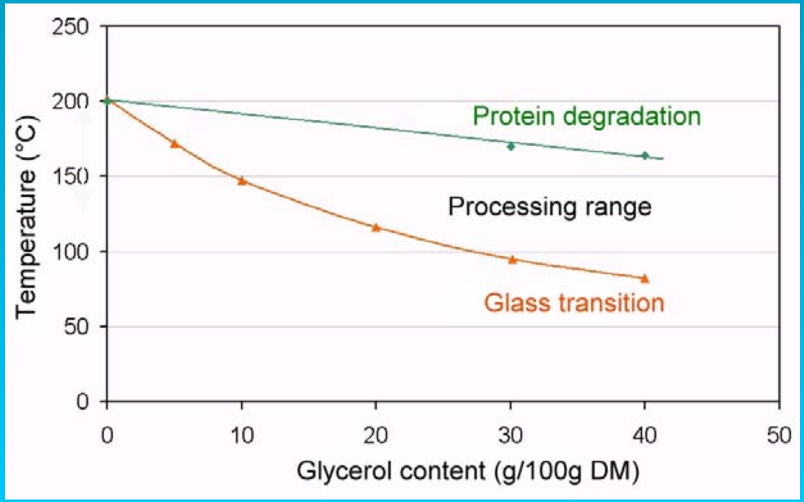


Injection moulding

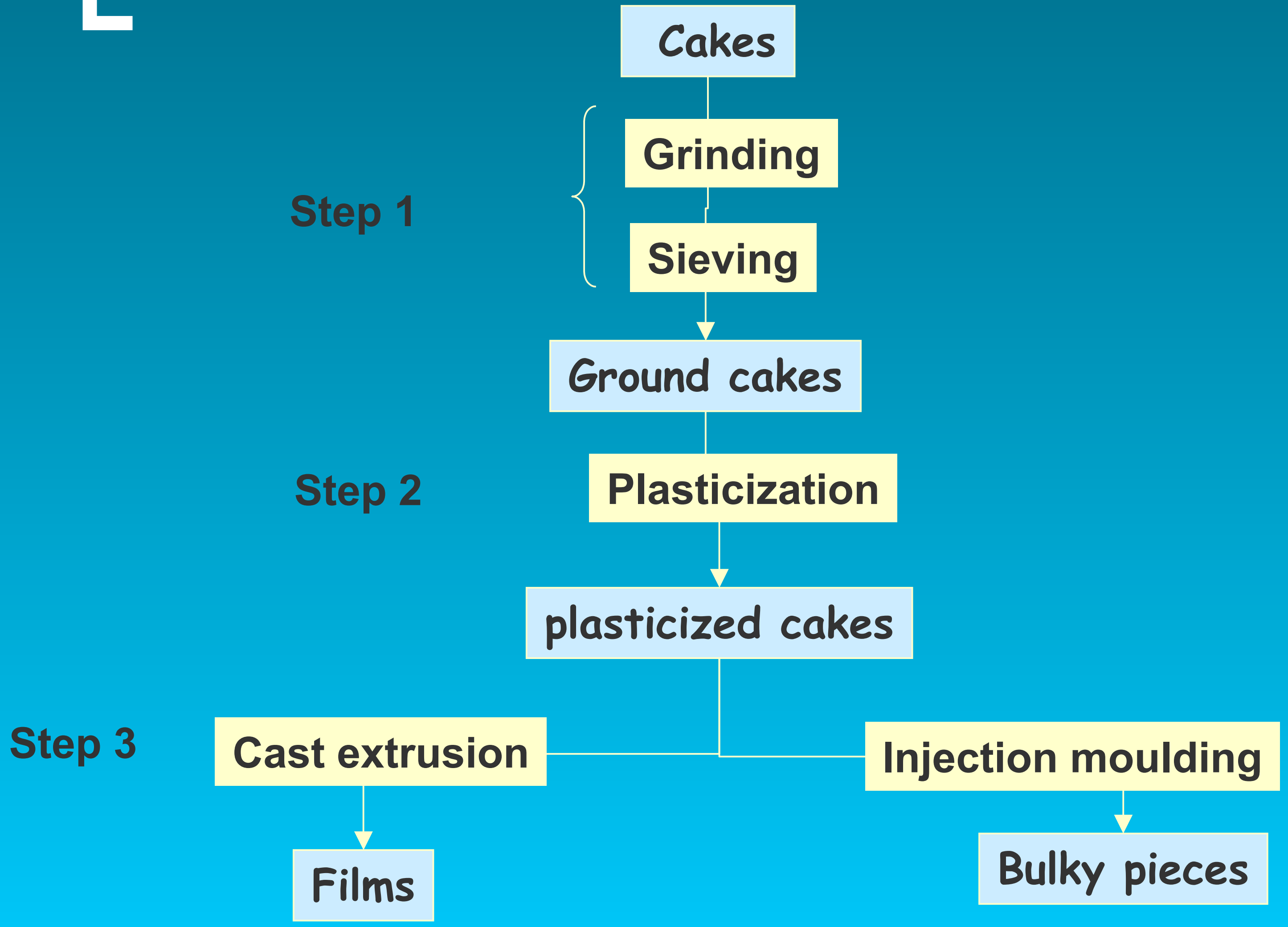
Processing proteins

- Requirements for dry processing
  - Reach the « molten » state (T > Tg)
  - Avoid protein degradation

- Necessity to use plasticizers to enlarge the processing range

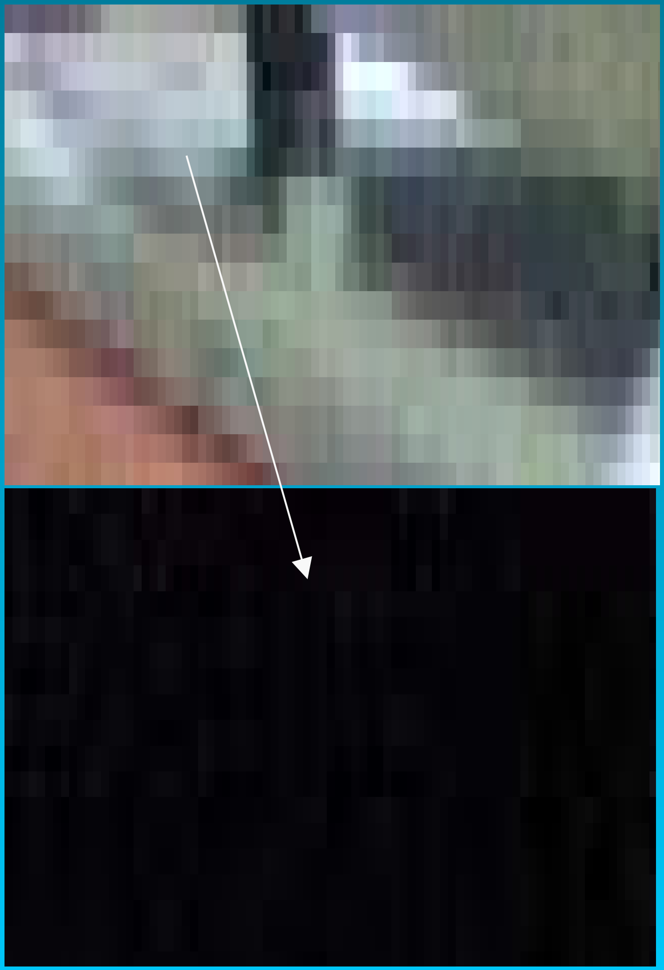


Scheme of the process



Step 1

- Grinding
  - Obtaining of fine powder to favorize further plasticization
- Sieving
  - Obtaining a calibrating powder
  - Elimination of shells and linter



Step 1

- Protein enrichment
  - Delipidated Cakes

	Proteins	Lipids	Cellulose
Raw matter	**33.23**	**0.93**	**19.09-20.18**
Ground, sieved at 400 µm	**41.68**	**1.84**	**12.90-12.81**

(g/100g DM)

Step 2

- Plasticization
  - 3 plasticizers
    - Glycerol ($C_3H_8O_3$) 92 g/mol
    - Triethanol amine ($C_6H_{15}NO_3$) 149 g/mol
    - Polyethylene glycol ($HO\text{-}(CH_2CH_2O)_4\text{-}H$) 194 g/mol
    - 0, 10, 20% w/w
- Processing at laboratory scale
  - Internal mixer (Haake)
    - Plasticizer is introduced at room temperature
    - Progressive heating up to 90°C
  - Thermocompression
    - P = 50 bars
    - T = 120°C

Step 2

- Main results (presented tomorow)
  - Glycerol gives the best plasticizing effect
  - 20% g/100 g DM content
  - Presence of lipids in the powder must be avoided
  - Presence of shells must be avoided
  - Necessity to combine temperature and pressure to unfold cottonseed proteins

Step 2

- Compounding at pilot scale
  - Device
    - Twin-screw extruder
    - Peristaltic pump to introduce glycerol
  - Processing conditions
    - Screw profile
    - Temperature profile
    - Screw rotation speed

Step 2

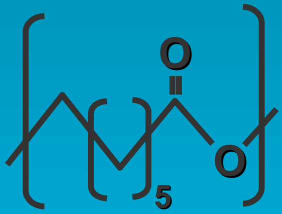
Step 3

- Cast extrusion
  - Devices
    - Single screw extrusion
    - Flat die
    - Calender
  - Processing conditions
    - Temperature profile
    - Screw rotation speed
    - Roll temperature

Step 3

Step 3

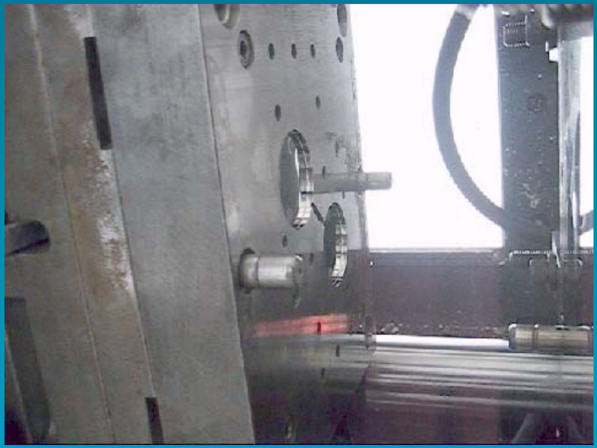
- Results of processing
  - Possible with plasticized flours
  - Difficult with plasticized cakes
  - Interesting results by mixing plasticized cakes with PCL



Polycaprolactone (PCL)

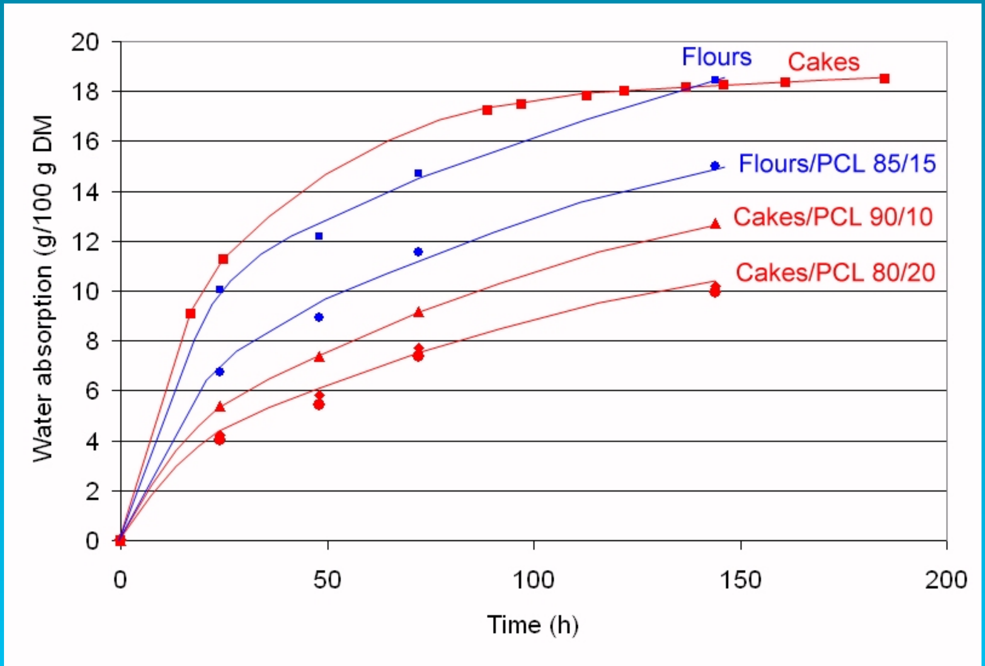
Step 3

- Injection moulding
  - Device
    - Sandretto Press (95 t)
    - Mould : disk
  - Processing conditions
    - Barrel temperature
    - Mould temperature
    - Pressure
    - Cycle time



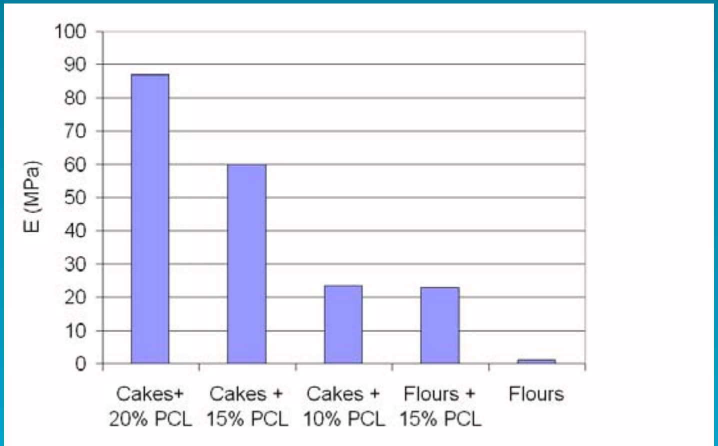
Film properties

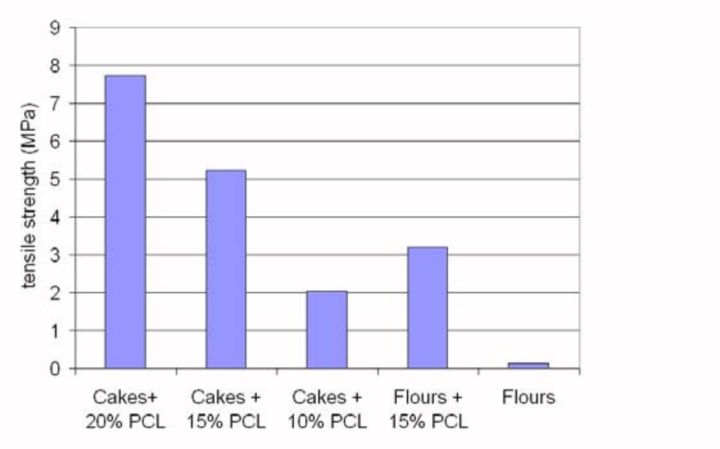
- Hygroscopicity

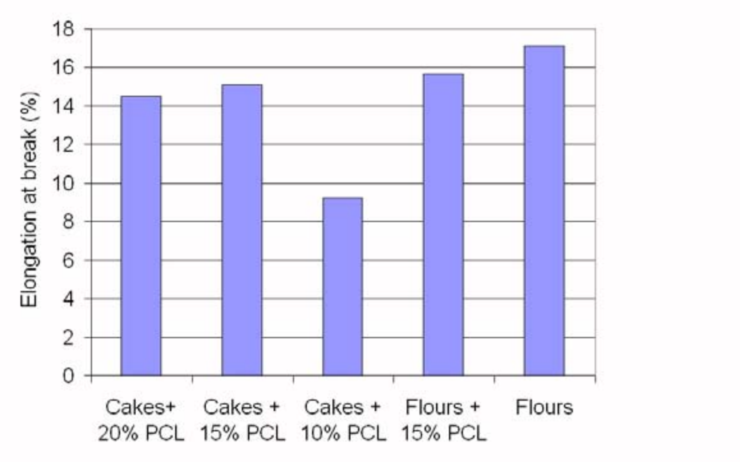


Film properties

- Mechanical properties







Conclusions

- Using different raw matters (cakes, flours) we showed the feasibility of making films and sheets by standard polymer processing techniques :
  - Casting
  - Spread coating
  - Extrusion

Conclusion about spread coating

Necessity :

- to adjust viscosity in order to obtain good film processability
- to obtain homogeneous film thickness

Conclusion about extrusion and injection moulding

- Necessity to improve plasticized cakes cohesion (adding PCL)
- Necessity to decrease shell content
- Necessity to use delipidated matter (solvent extraction)