INCO COTONBIOMAT - WP5

Characterization of films obtained by dry technologies

Joël Grevellec, Laurent Ferry, ***Ecole des Mines d'Alès***

Alain Crespy, ***Université de Toulon et du Var***

Christian Aymard, Jérôme Lecomte, Catherine Marquié, ***CIRAD Montpellier***

Outlines

1. Introduction
2. Methodology
3. Processing
4. Study of plasticization
5. Hygroscopicity
6. Permeability
7. Mechanical properties
8. Conclusions

Introduction

- **Objectives**
  - Manufacturing of biodegradable materials from cottonseed cakes
    - Using dry technologies : extrusion, injection-moulding
    - Applications :
      - Films (mulching, silage,greenhouse)
      - Bags
      - Pots or other containers…
  - Understanding of molecular mechanisms governing processing, structure and properties of the materials

Introduction

- **Protein processing**

« Moist technologies »

« Dry technologies »

Proteins

Dispersion conditions

Melting, glass transition

Filmogenic solution

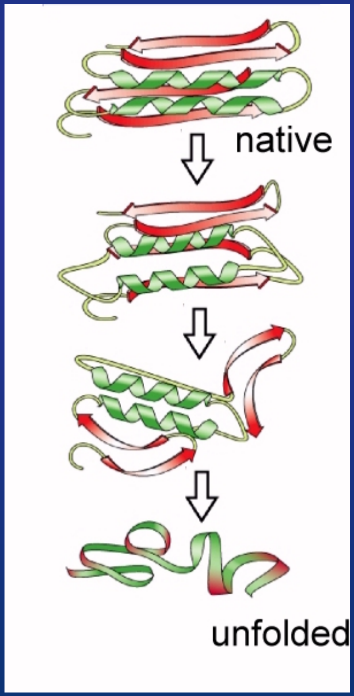
Powders or granules

Coacervation conditions

Processing conditions

Film or coating

Film or rigid material



According to S. Guilbert GFP Volume 13, Chapître 8

Methodology

- **Complex raw matter**

Cakes

proteins | **shells** | **lipids** | **gossypol**

Glandless seeds

→ **Delipidated flours / Delipidated flours + shells**

→ **Delipidated flours / Partially delipidated flours**

→ **Glandless delipidated flours / glanded delipidated flours**

Processing

- **Cakes or flours preparation**
    - Grinding
    - Sieving at 400 µm
- **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
    - **Internal mixer**
        - Incorporation of plasticizers at room temperature
        - Progressive heating up to 90°C
- **Film processing**
    - **Thermocompression**
        - P = 50 bars
        - T = 120°C

Processing

Processing

- **Raw matter**

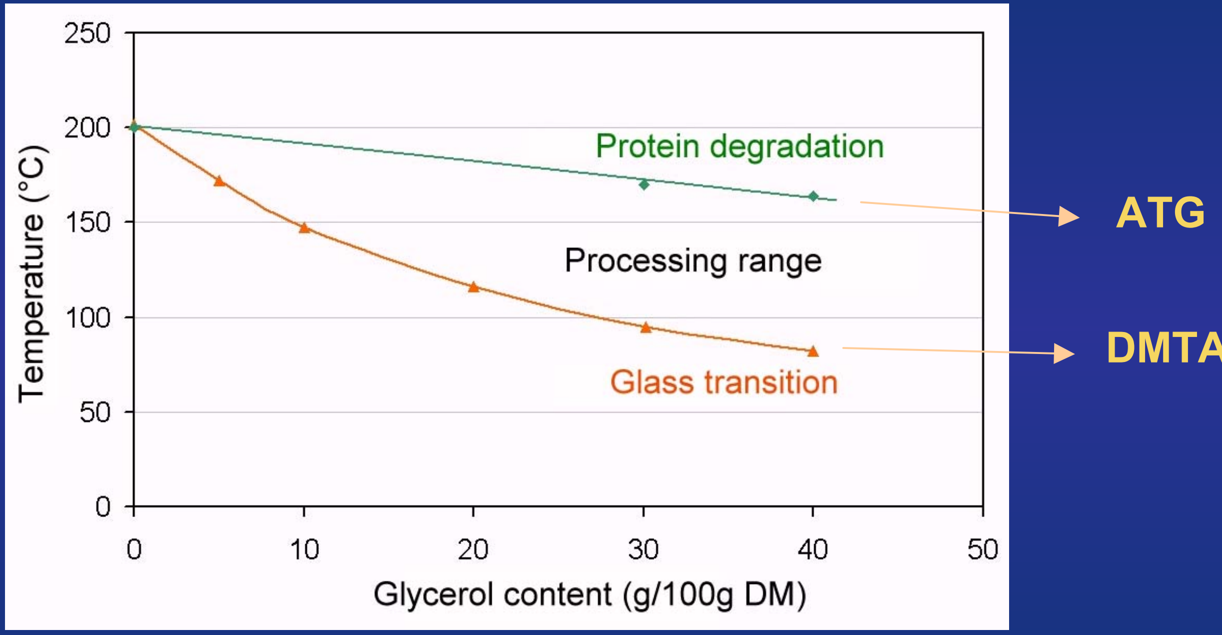
Flours

Cakes

- **Thermocompressed films**

Study of plasticization

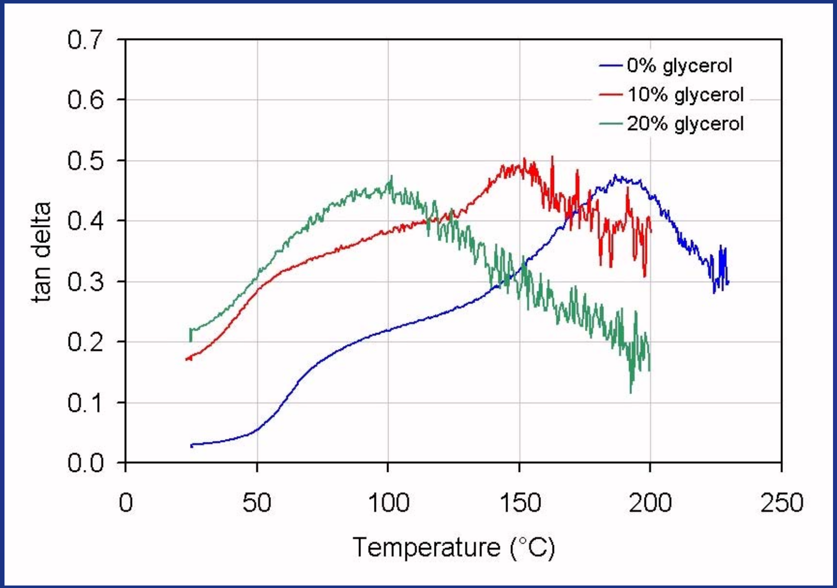
- **Results on cotton protein isolate**

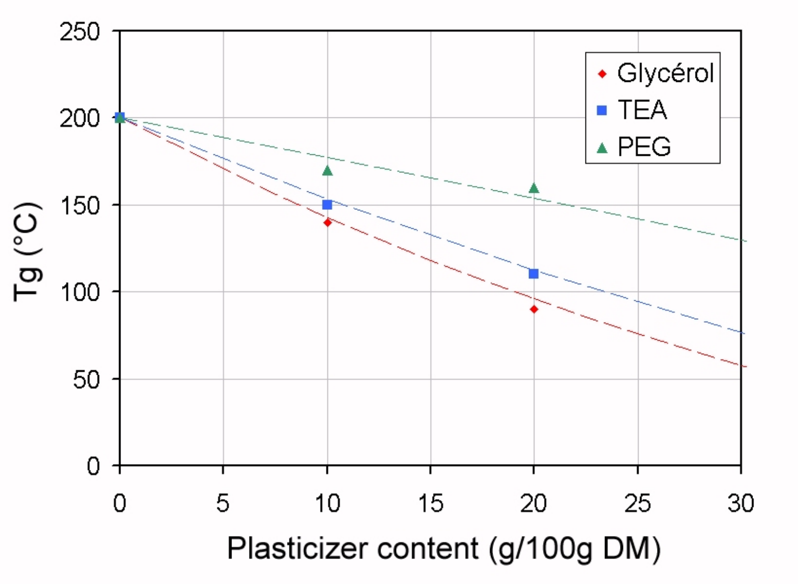


  - **Plasticization is necessary to obtain a large processing range**

Study of plasticization

- **Influence of plasticizer content**



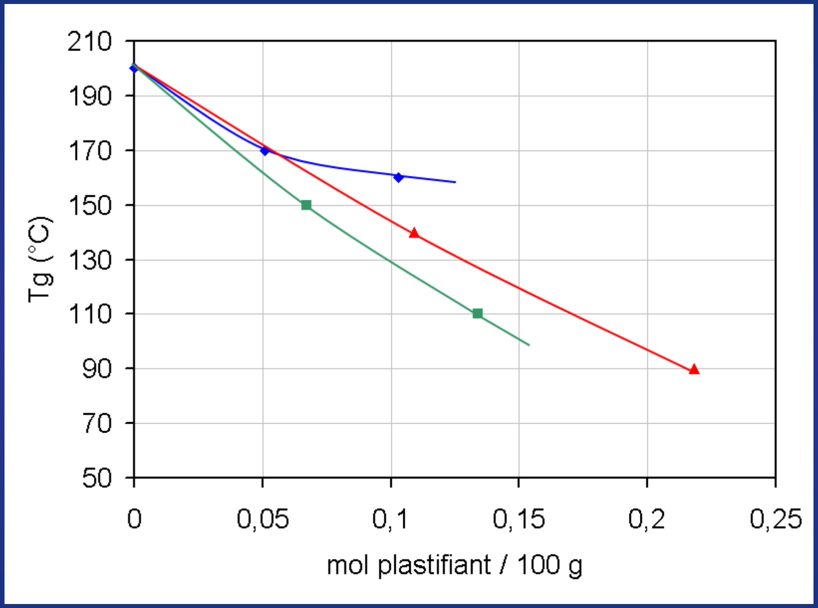


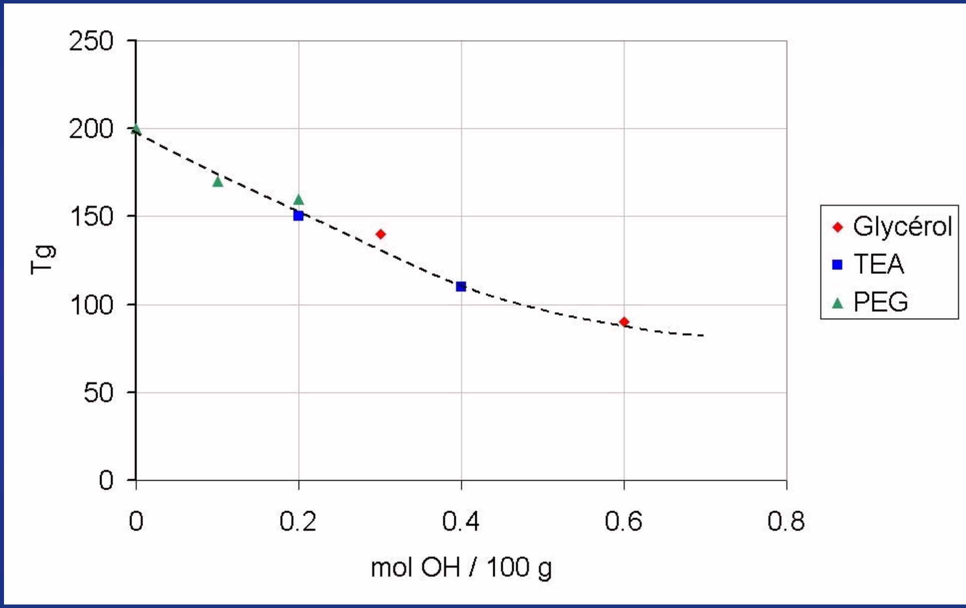
- **Plasticizing effect increases in the sense PEG, TEA, glycerol**
- **Evolution of glass transition well described by Couchman-Karasz relation**

$$Tg = \frac{x_1\,\Delta Cp_1\,Tg_1 + x_2\,\Delta Cp_2\,Tg_2}{x_1\,\Delta Cp_1 + x_2\,\Delta Cp_2}$$

Study of plasticization

- ## Influence of the plasticizer type



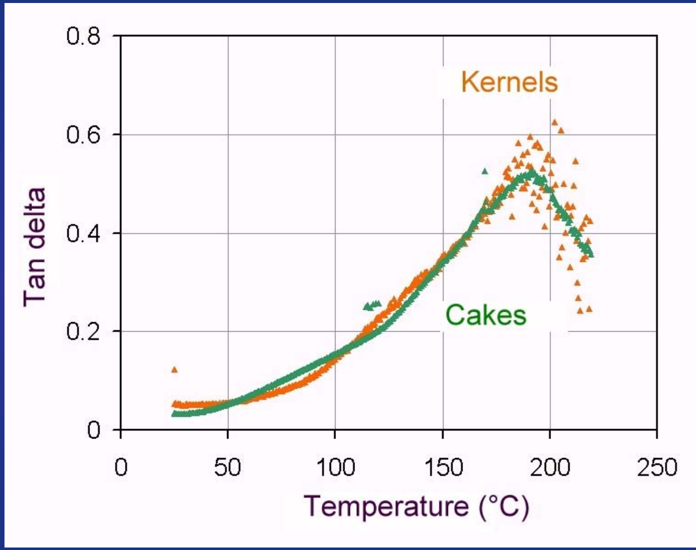


- **Plasticization is directly related to the number of hydroxyl groups supplied by the plasticizer**

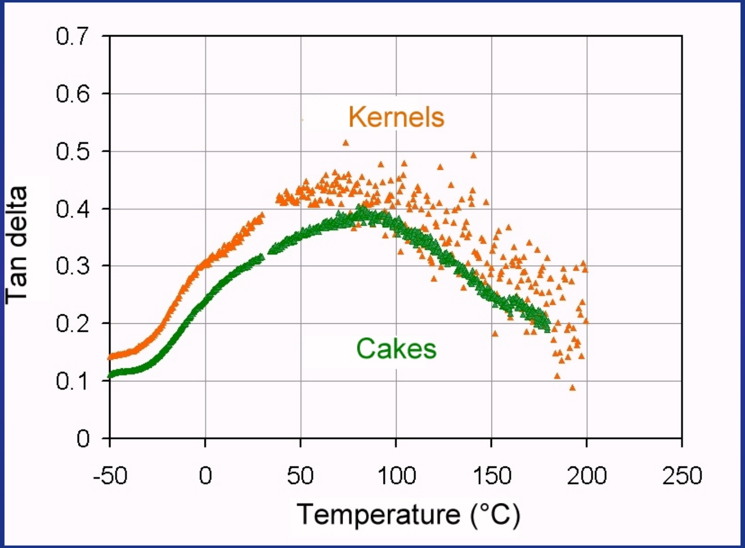
- **The native structure of proteins being stabilized by hydrogen bonds, its disorganization implies OH groups**

Study of plasticization

- Influence of lipids



unplasticized

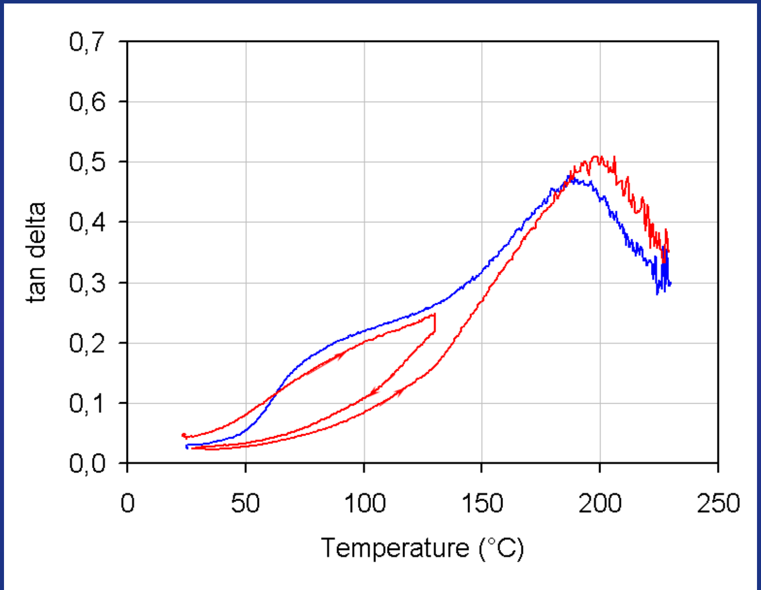


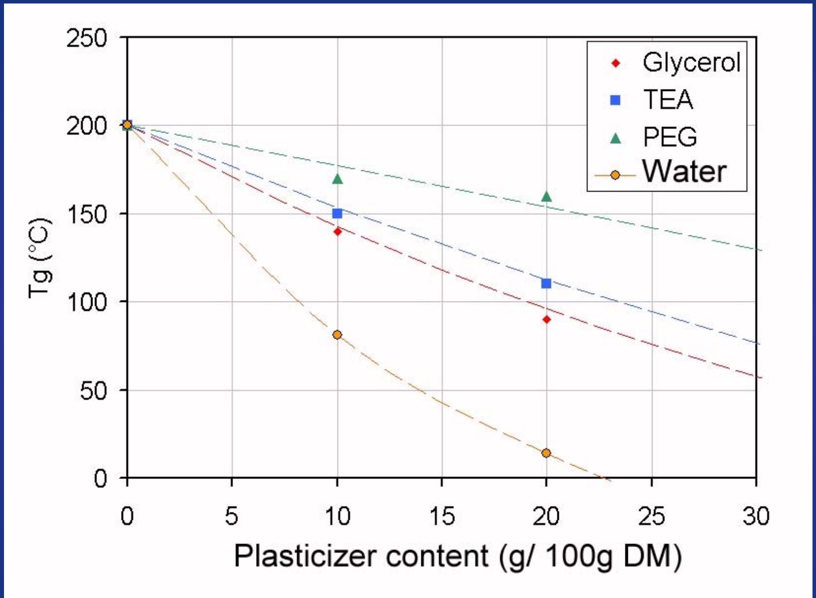
Plasticized by 20% glycerol

- No noticeable plasticizing effect related to the presence of lipids

Study of plasticization

- **Influence of humidity**

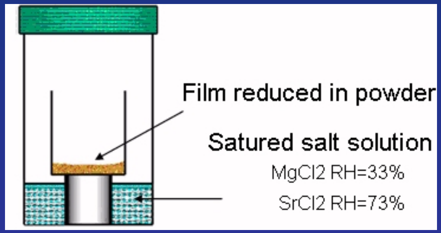


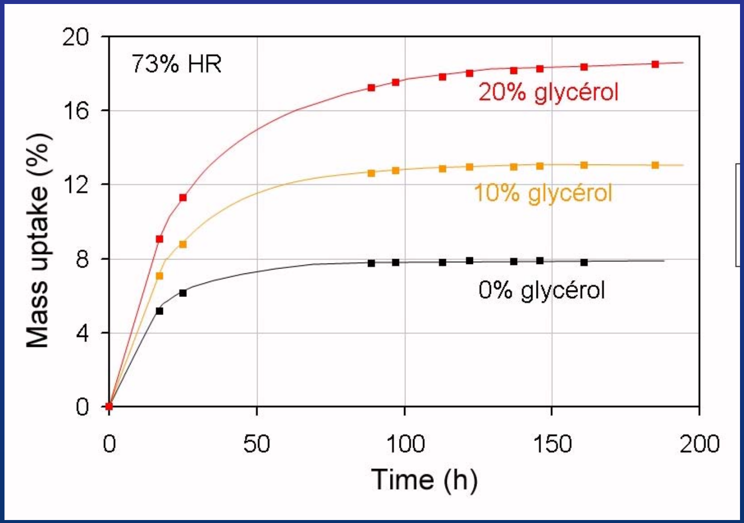


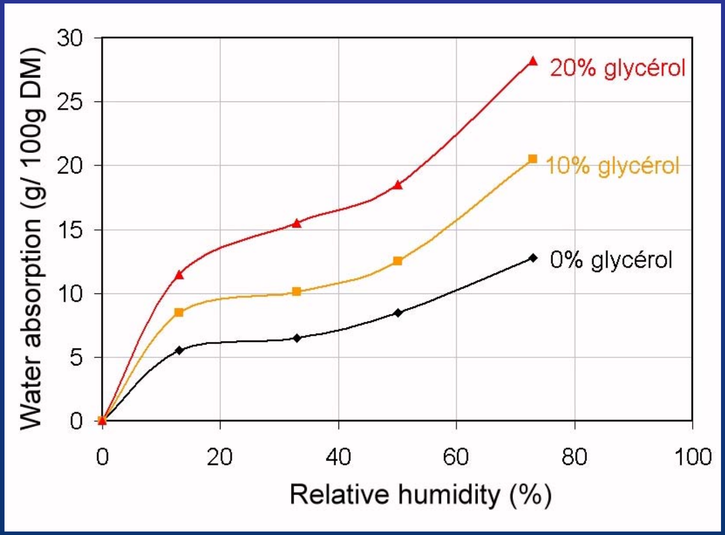
- **Presence of water**
  - **Due the polar feature of cottonseed protein**
  - **Contributes to plasticization**
  - **Non ideal plasticizer because water content varies with RH and T**

Hygroscopicity

- **Experimental Set up**
  - **Films are ground and dried**
  - **Conditioning in humidity-controlled hermetic container**
    - **Saturated solution of LiCl 13% HR**
    - **Saturated solution of $MgCl_2$ 33% HR**
    - **Saturated solution of $SrCl_2$ 73% HR**
  - **Weighing of samples versus time**



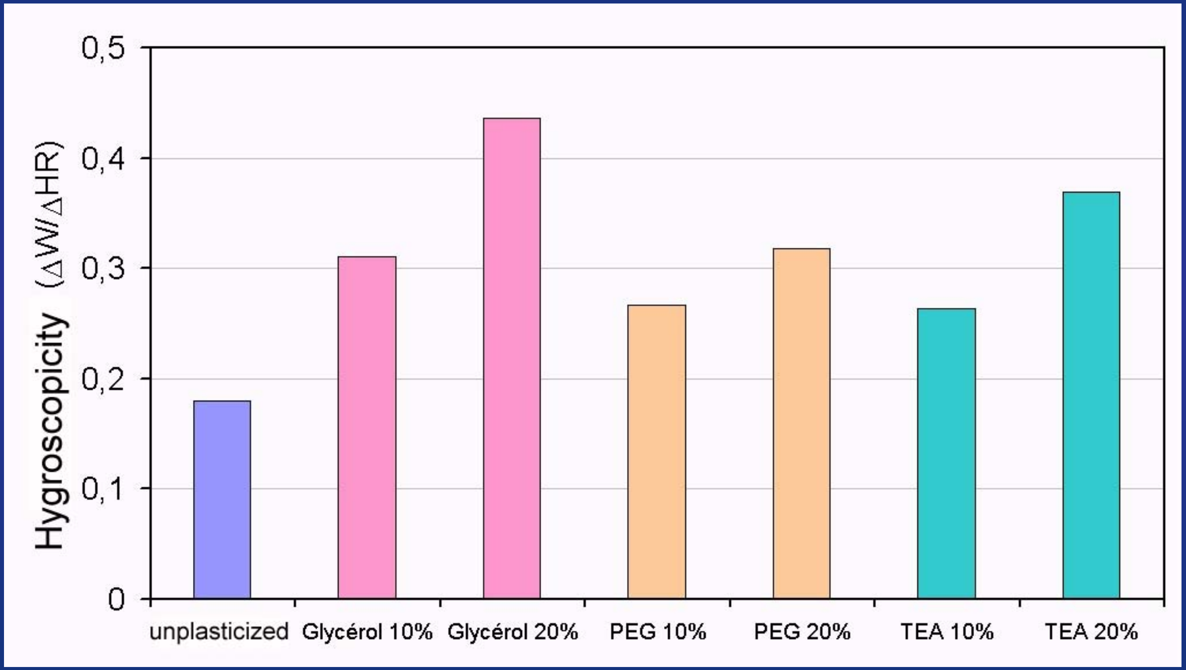




Hygroscopicity = $\dfrac{\Delta W}{\Delta HR}$ **ΔHR = 73%-33%**

Hygroscopicity

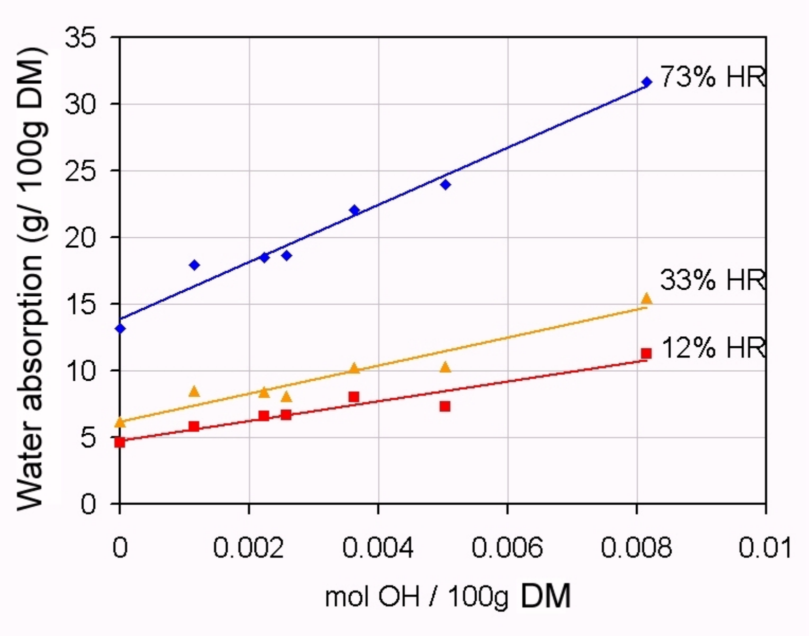
- **Influence of plasticizer**



  - **Hygroscopicity increases with increasing plasticizer content**
  - **Hygroscopicity increases in the sense PEG, TEA, glycerol**

Hygroscopicity

- **Influence of plasticizer**

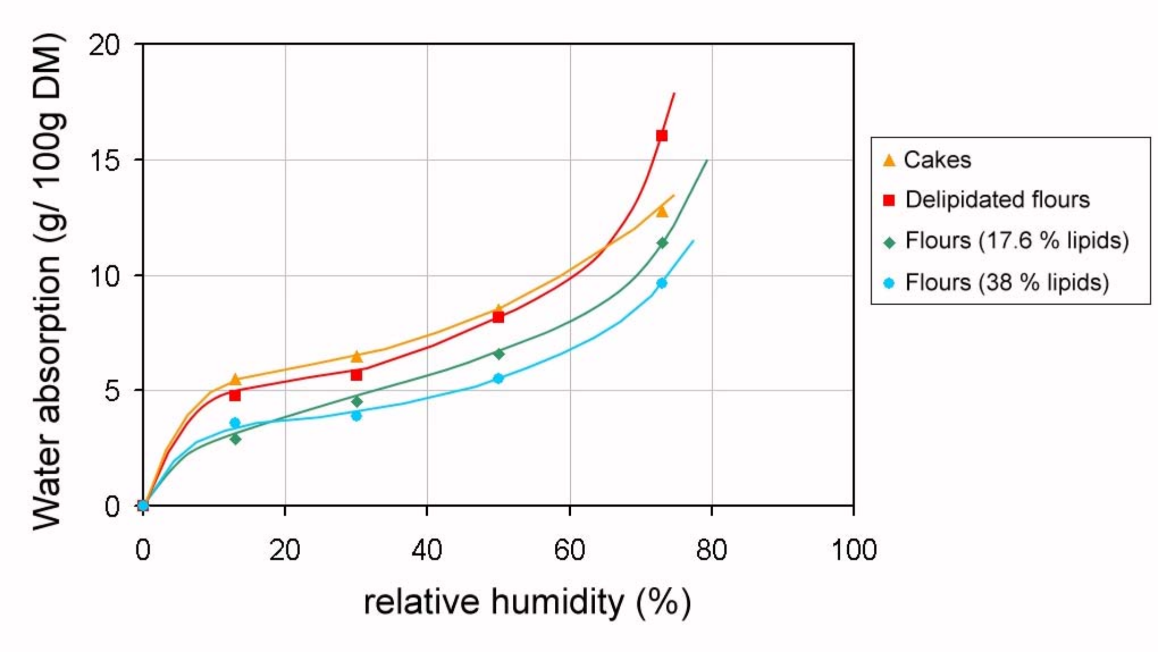


- **Hygroscopicity is directly related to the amount of hydroxyl groups supplied by the plasticizer**

- **Use of another family of plasticizers ?**

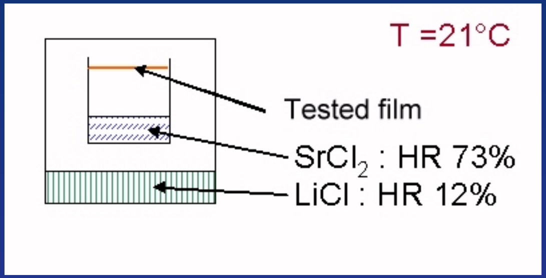
Hygroscopicity

- **Influence of lipids**

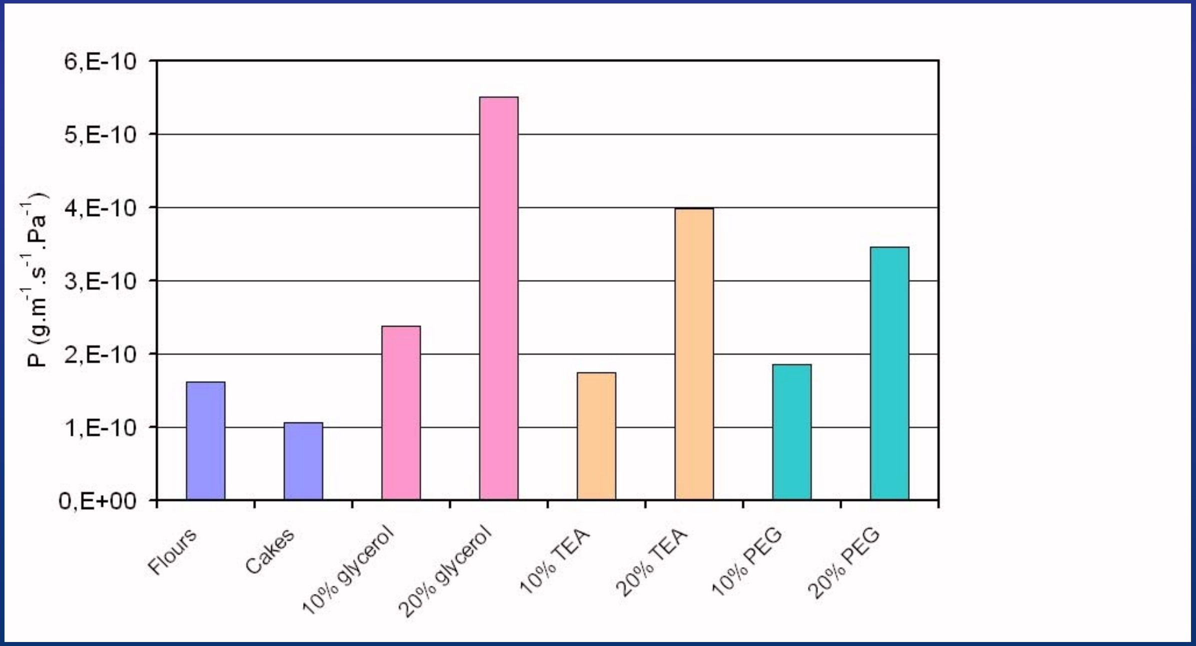


  - **Hygroscopicity decreases when lipid content increases**

Permeability to water vapor

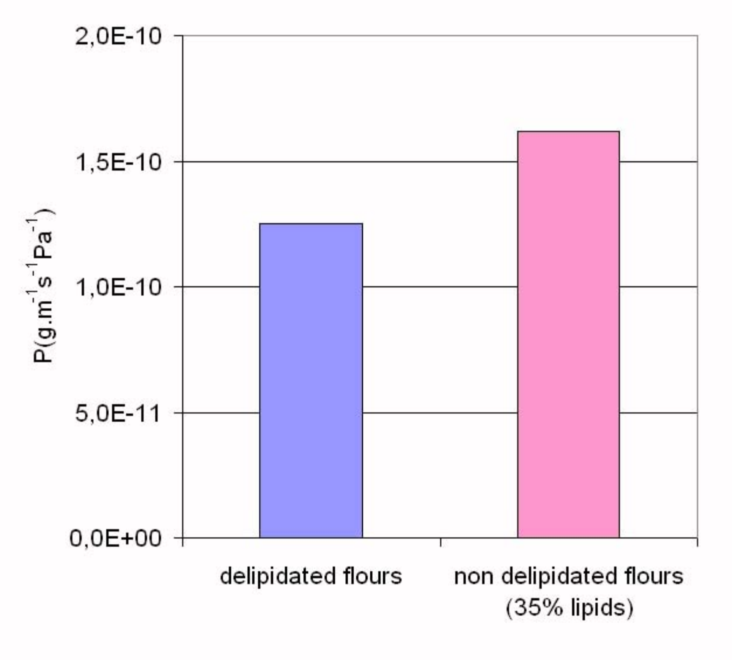


$$\text{Permeability} = \frac{\Delta W(g) \times e(m)}{A(m^2) \times t(s) \times \Delta P(Pa)}$$



Permeability to water vapor

- **Influence of lipids**

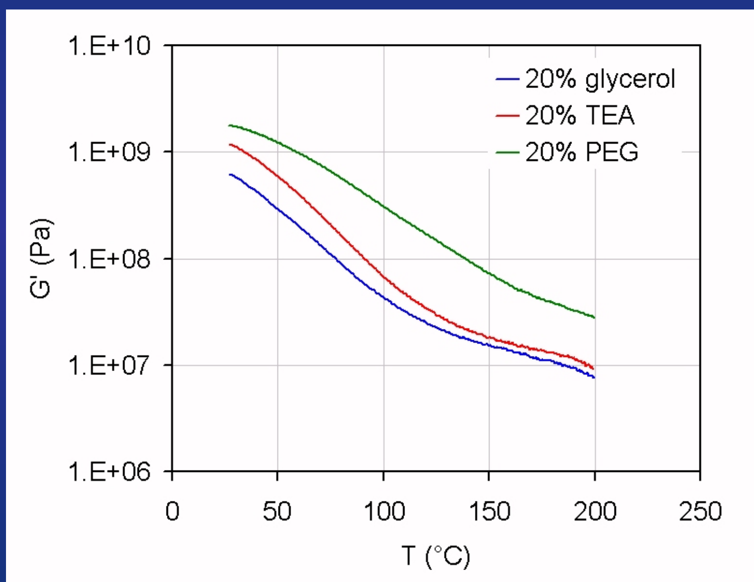


Film from non delipidated flours (35%lipids)

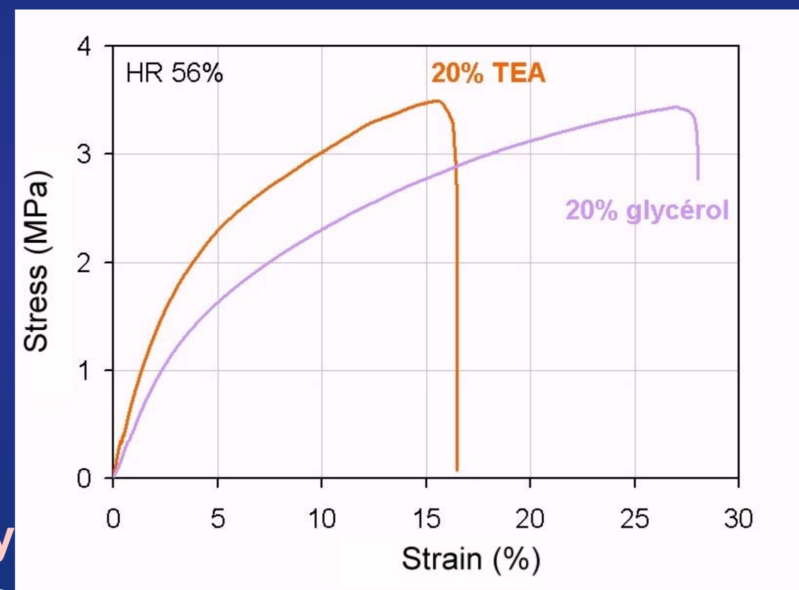
Mechanical properties

- Influence of plasticizers

DMTA



Tensile test

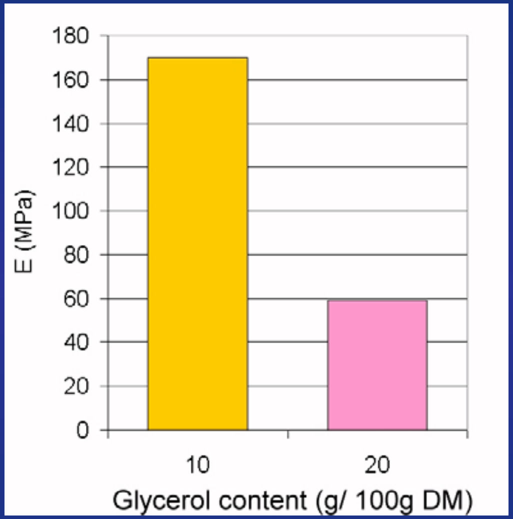


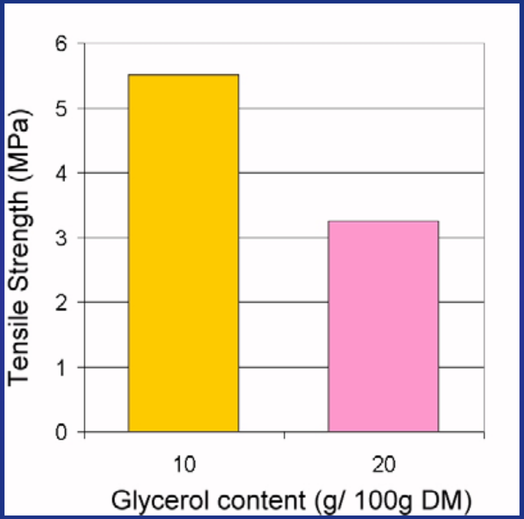
- Elasticity modulus decreases
- Tensile strength decreases
- Elongation at break increases

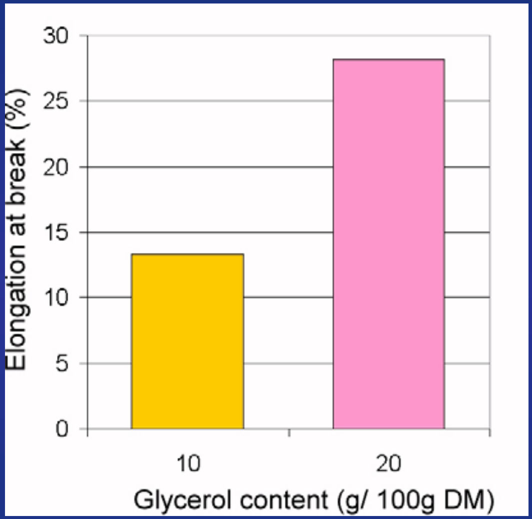
Mechanical properties

◆ **Influence of plasticizers**

Conditioning RH= 56%





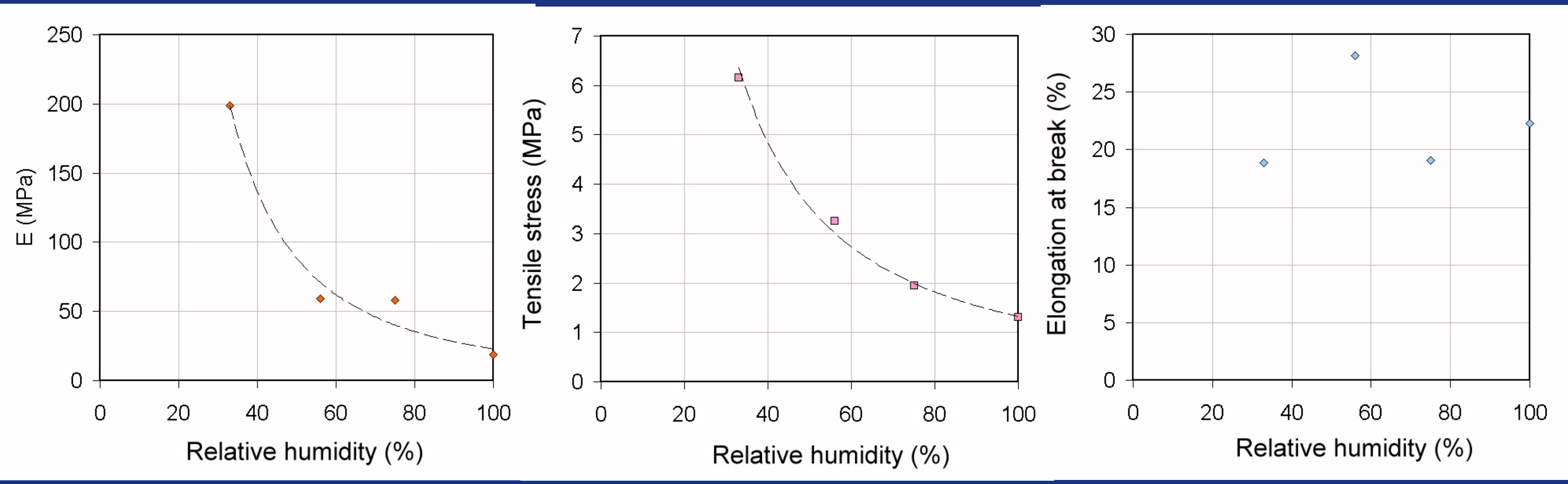


- **When plasticizer content increases**
  - **E decreases**
  - **Tensile strength decreases**
  - **Elongation at break increases**

Mechanical properties

- Influence of humidity

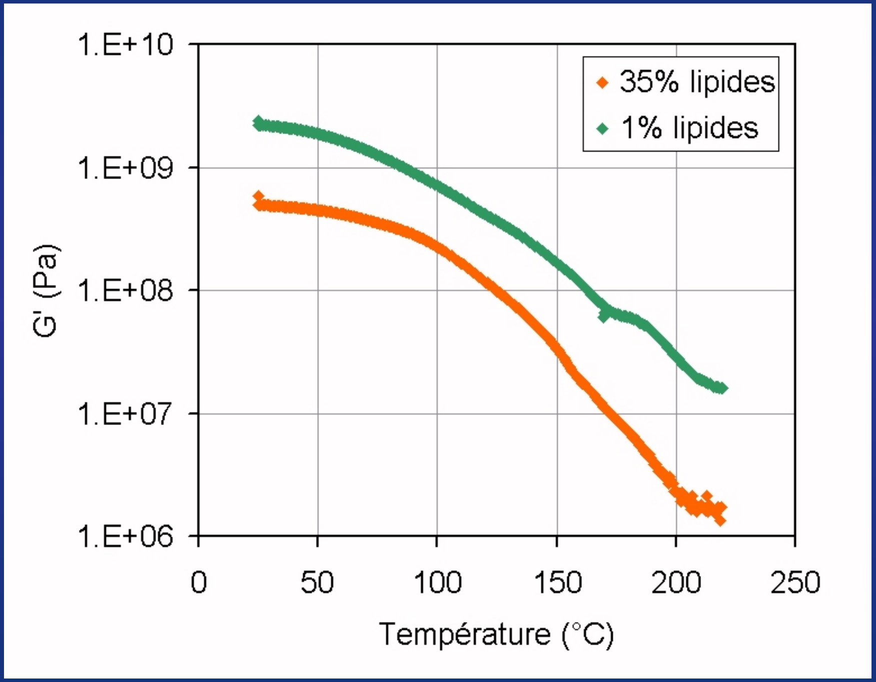
20% glycérol



- **When RH increases :**
  - E decreases
  - Tensile strength decreases
  - Elongation at break is not strongly affected but remains lower than 30%

Mechanical properties

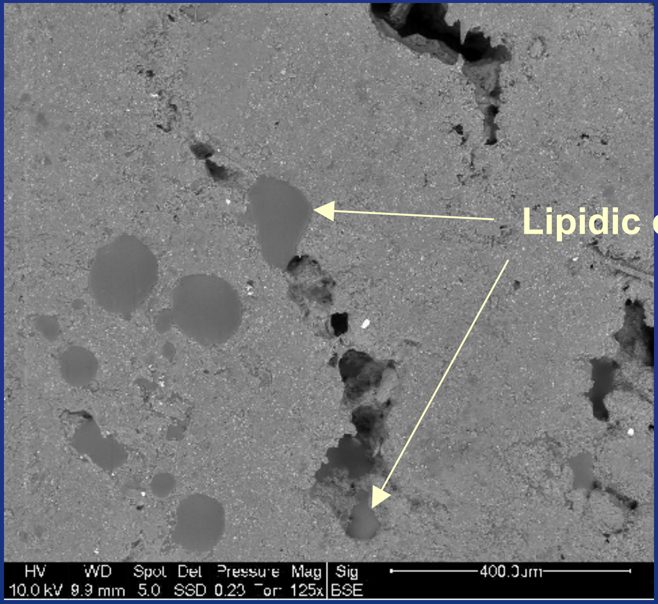
- Influence of lipids



- In the presence of lipids
  - Low value of elasticity modulus ➔ Poor cohesion

Mechanical properties

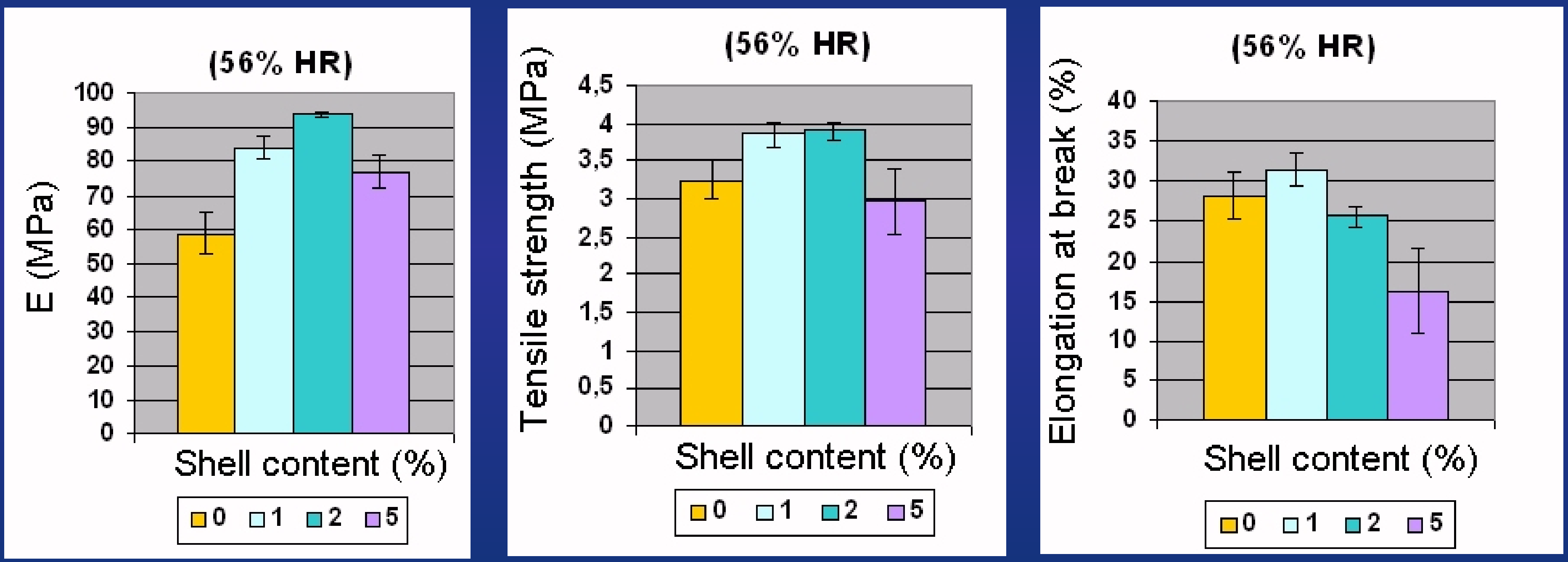
- **Influence of lipids**
  - **ESEM observations**



- **Films are porous due to a phase separation (lipid-protein) induced by T and P during processing**
  - **Low elastic modulus**
  - **High permeability**

Mechanical properties

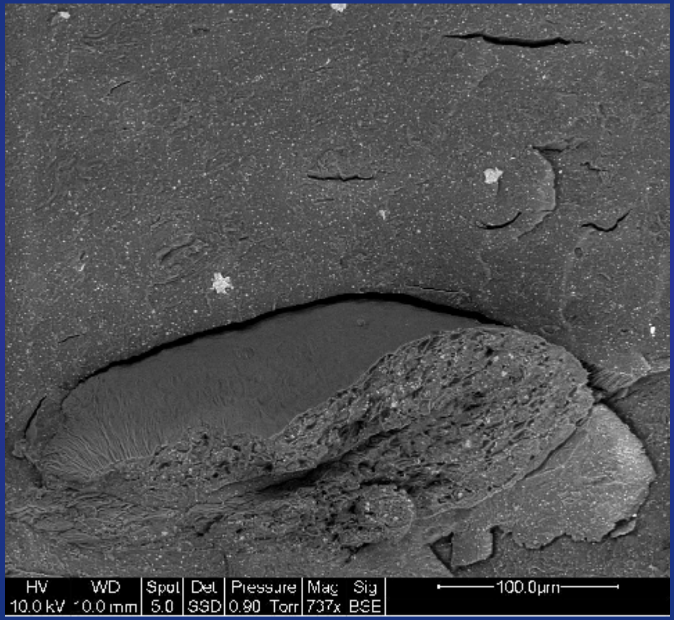
- Influence of shells

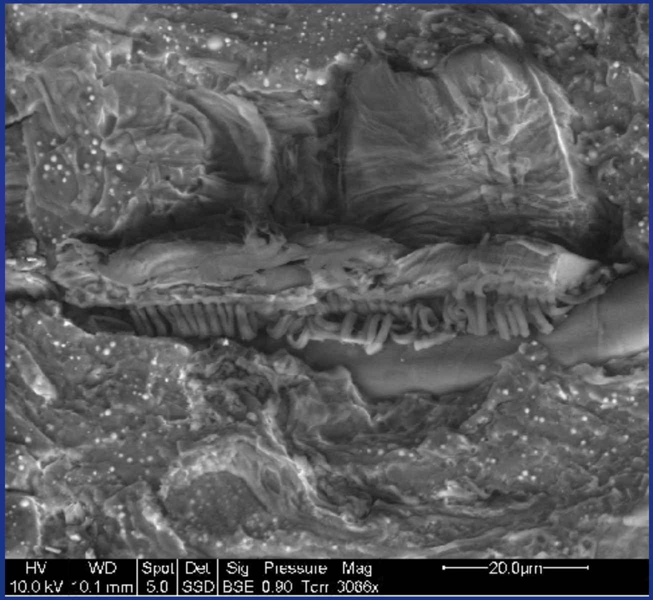


- Above 2%, shells cause a decrease of mechanical properties

Mechanical properties

- Influence of shells



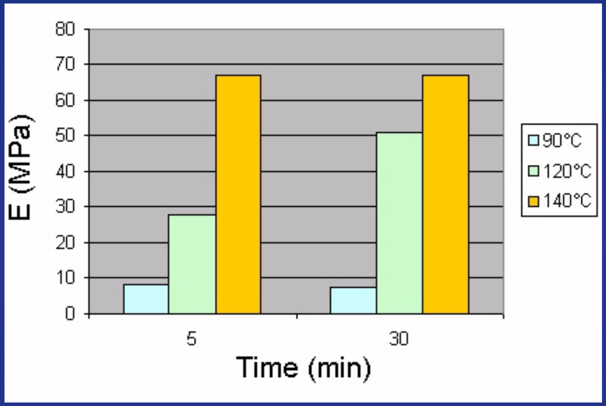


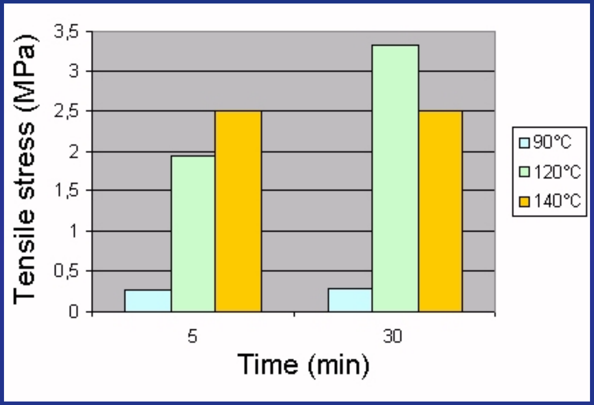
  - Shells induce weak points where the fracture is initiated
  - Mechanism similar to that observed with mineral fillers in synthetic polymers

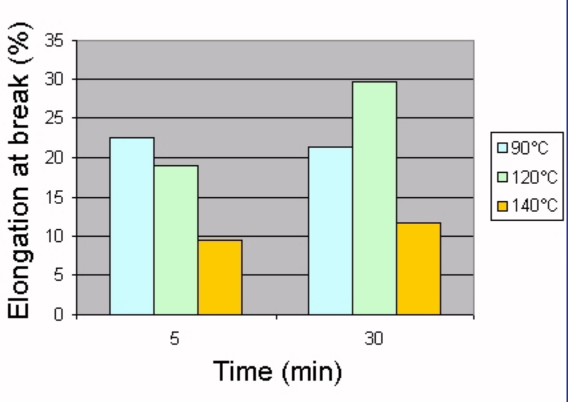
Mechanical properties

- Influence of processing conditions

P = 50 bars



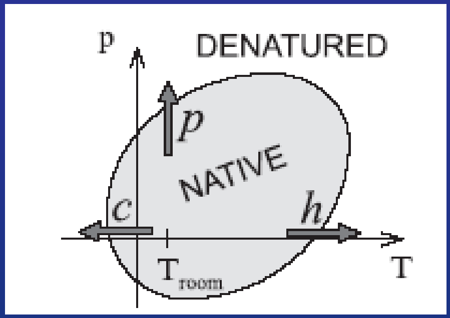




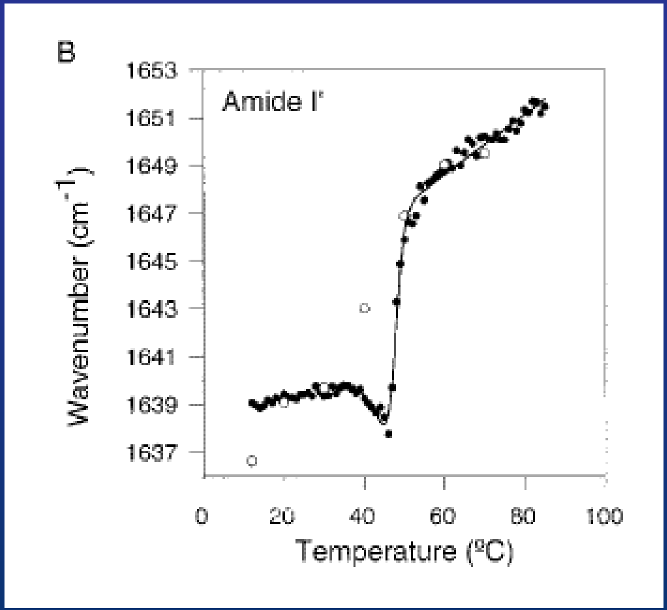
- Above 90°C, cohesion of films is better
- At 140°C; elongation at break decreases

Relation structure-processability

- **Evolution of protein structure during processing**
  - **Temperature and Pressure play a role in protein unfolding**
  - **IR spectroscopy may highlight protein structure changes**
    - **Amide I band is sensitive to globule-coil transition**



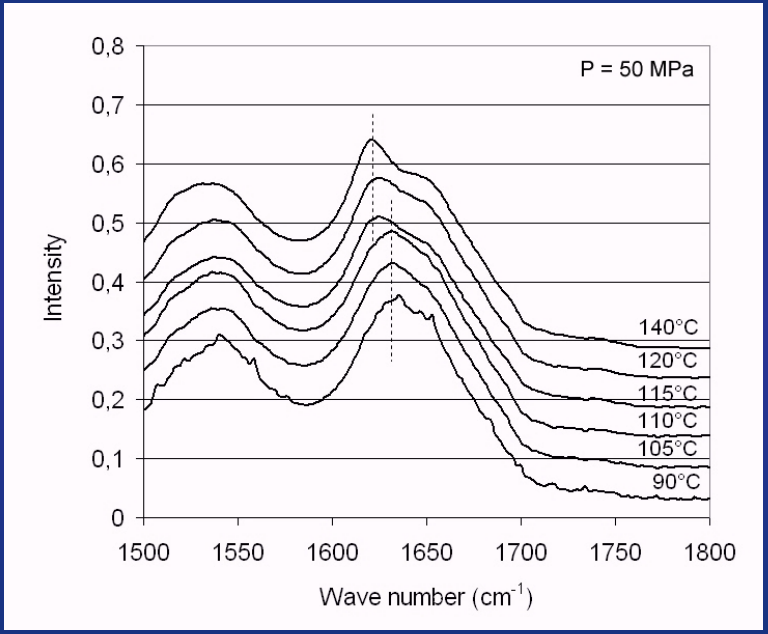
Smeller L.
Biochimica et Biophysica Acta, 1595 (2002) 11-29

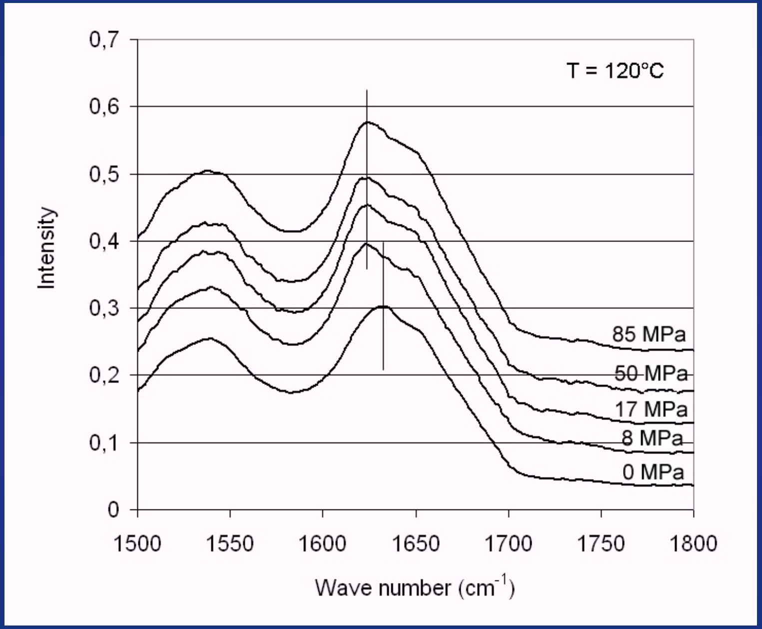


Torrent J., Rubens P., Ribo M. Heremans K., Vilanova M.,
Protein Science Vol. 10, (2001)725–734

Relation structure-processability

- **Results**





- **Necessity to combine pressure and temperature to obtain films with a good cohesion**

Conclusion

- Processing cotton protein films using dry technologies
  - Destructuration of proteins using plasticizers
  - Efficiency of plasticizers depends on the number of OH groups supplied by the plasticizer
    - Glycérol > TEA > PEG 200
  - No evident plasticizing effect of lipids
  - Necessity to combine pressure and temperature

- Functional properties
  - Hygroscopicity
    - Increases with the amount of OH groups supplied by the plasticizer
      - Glycérol > TEA > PEG 200
    - Is reduced in the presence of lipids
  - Mechanical properties
    - When plasticizing efficiency increases, E decreases and Ar decreases
    - The presence of lipids induces a poor cohesion in films
    - Elongation at break remains low compared to LDPE