CATÓLICA PORTO
BIOTECNOLOGIA

Molecular mobility and the thermomechanical properties of chitosan films

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Why use Edible Films?

- Consumers' awareness of environmental issues related with packaging
- Limited availability of Petroleum

➢ Driving force to use of biodegradable biopolymers from renewable sources

- Consumers' demand for healthier and more convenient foods (e.g. minimally processed foods)
- Changes in retailing practices and/or in way of life force the development of convenient food products with longer shelf-life

➢ Driving force for the use of edible coatings/films

Why Molecular Mobility in Edible Films?

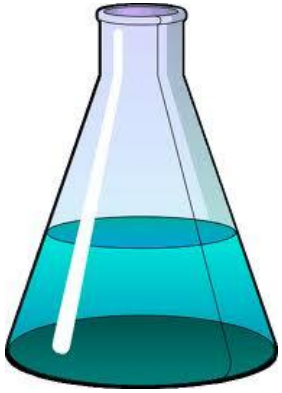
- Edible films are partially crystalline partially amorphous materials
  - Interesting physical properties
  - Good models for other food systems

- The molecular mechanisms that control functionality in polymeric films are poorly understood
  - Specially in edible materials where water plays an important role as plasticizer

Methodology – *preparation of films*

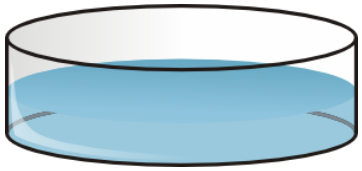
Chitosan
(1, 2 and 3% w/v)

Glycerol
(10, 50 and 90% w/w)



1% lactic acid solution

Solvent Casting



40º C until equilibrium

RH = 53% and T= 22ºC

FILMS Characterization

Methodology – *characterization of films*

Film Characterization

- *Water Content*
- *Water Activity*
- *Chitosan and Glycerol Content*

Thermal Analysis

Scan from -150 to 200ºC

20ºC/min

- glass transition temperature (Tg)
- Crystallinity (melting Δh)

DSC TA-60WS

NMR Measurements

Free Induction Decay and Spin Spin Relaxation

sample relaxation time was determined (**T2**) :

- glycerol component (**T2gly**)
- water component (**T2water**)

$$Y = A_1 \exp^{(-X/T2gly)} + A_2 \exp^{(-X/T2water)} + Y_0$$

Bruker AVANCE III
300 MHz

Mechanical Properties

ASTM D 882-91 (1991)

-elongation at break (EB)

- tensile strength (TS)

Instron universal
testing machine

Results – *characterization of films*

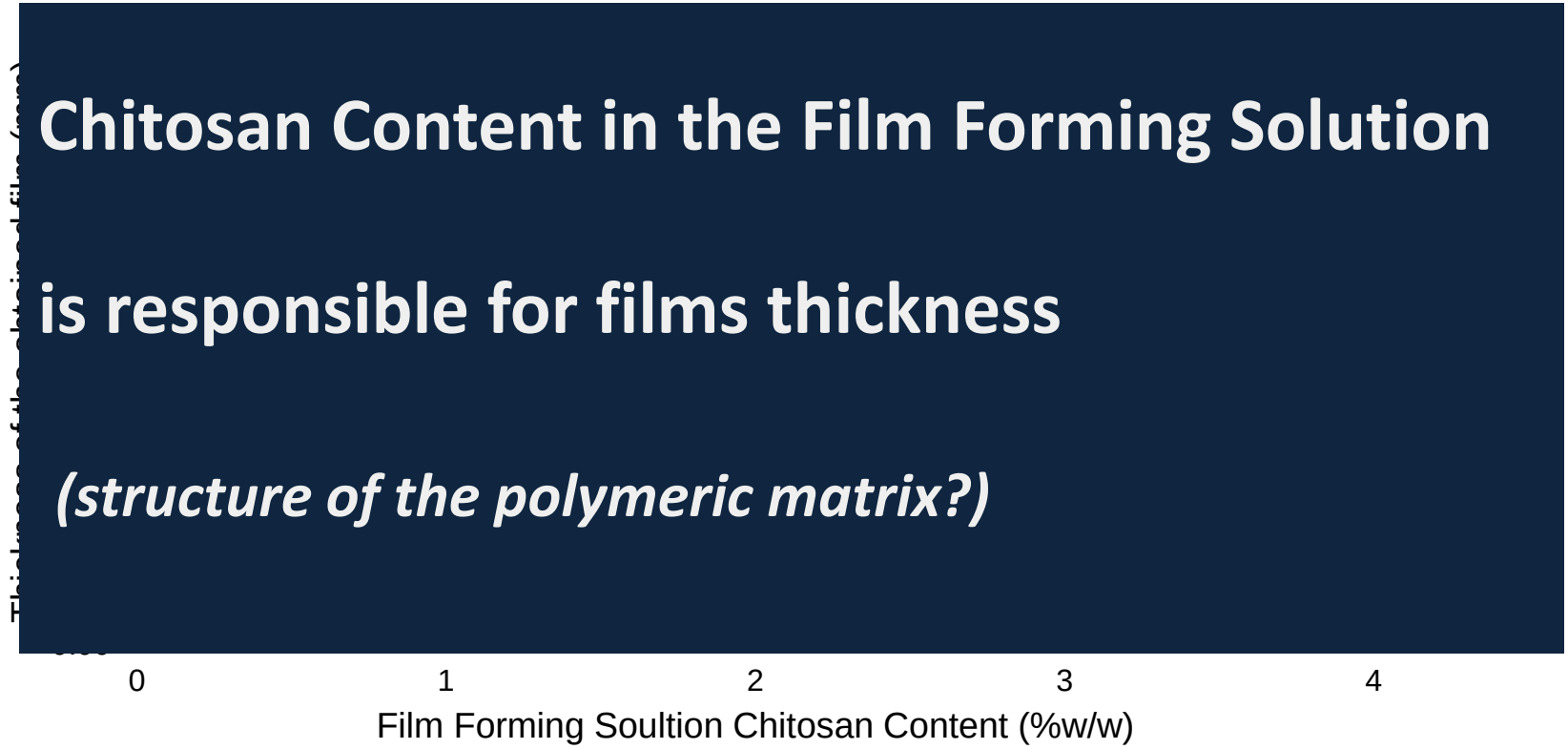
FFS	Films	
	Chitosan (mg/g film)	Glycerol (mg/g film)
1%10%		
1%50%		
1%90%		
2%10%		
2%50%		
2%90%		
3%10%		
3%50%		
3%90%		

Glycerol Content in the Film Forming

Solution is responsible for the Chitosan

Content on the obtained film!

Results – *characterization of films*



90%
50%
10%

Results – *characterization of films*

Films with same composition have significantly

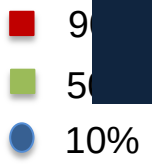
different thickness!

Structure of the polymeric matrix?

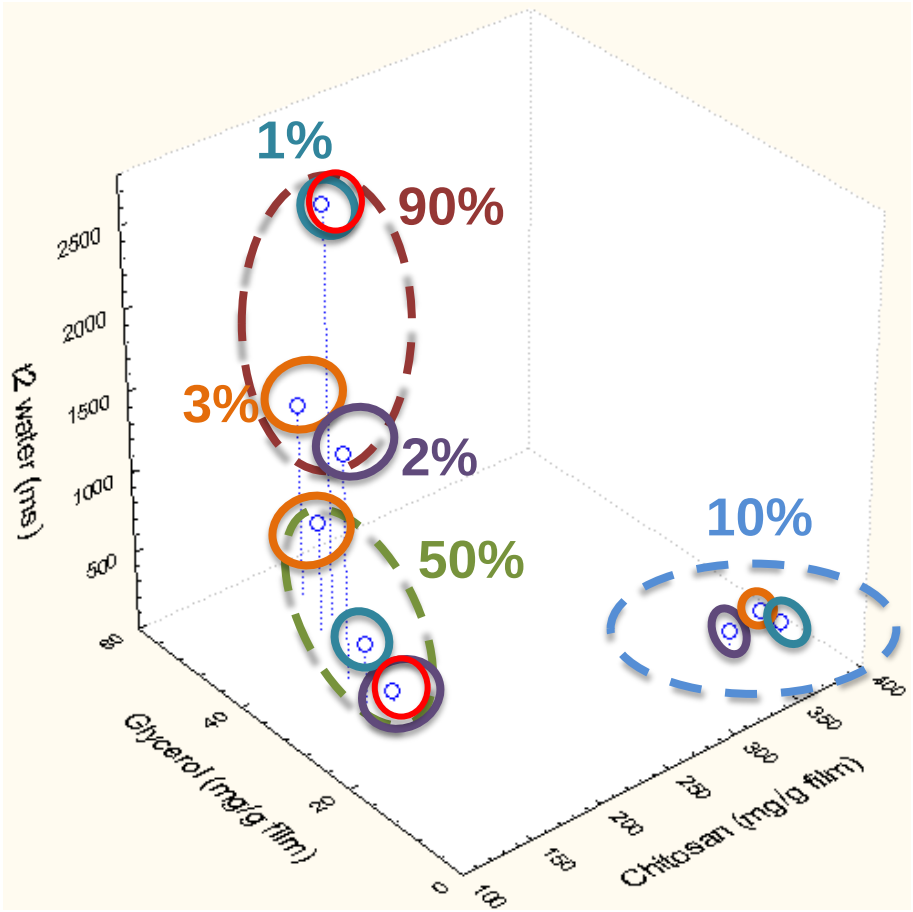
- Crystallinity

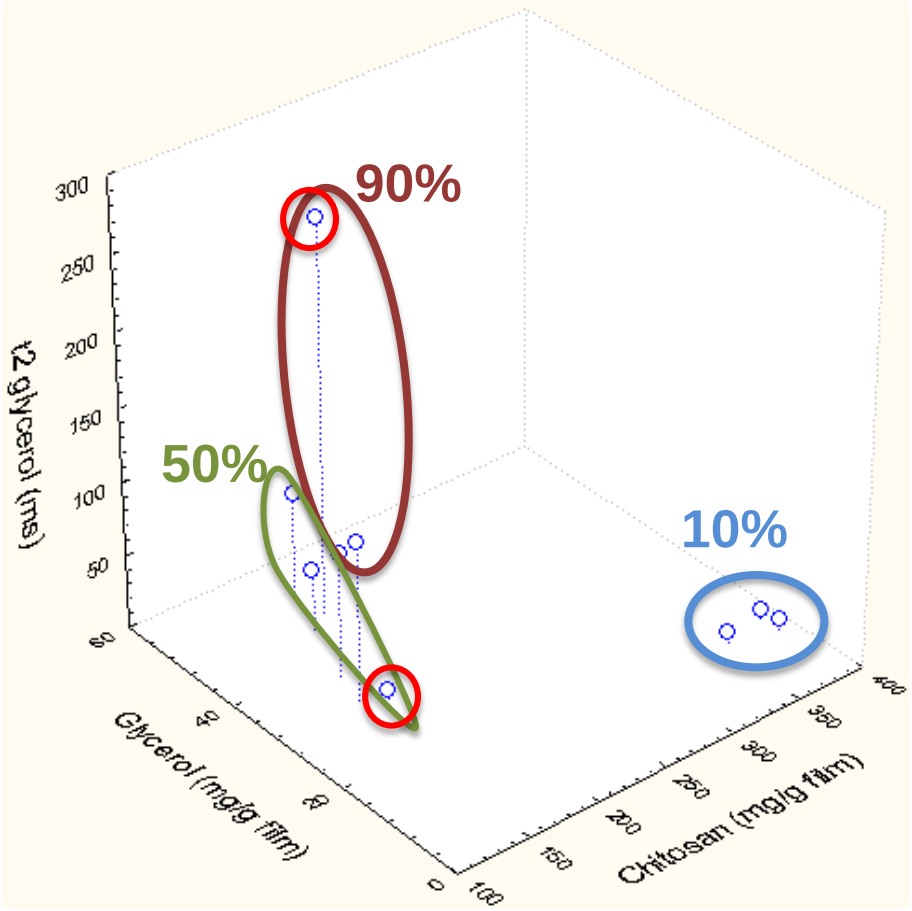
- Water Content

- Free Volume



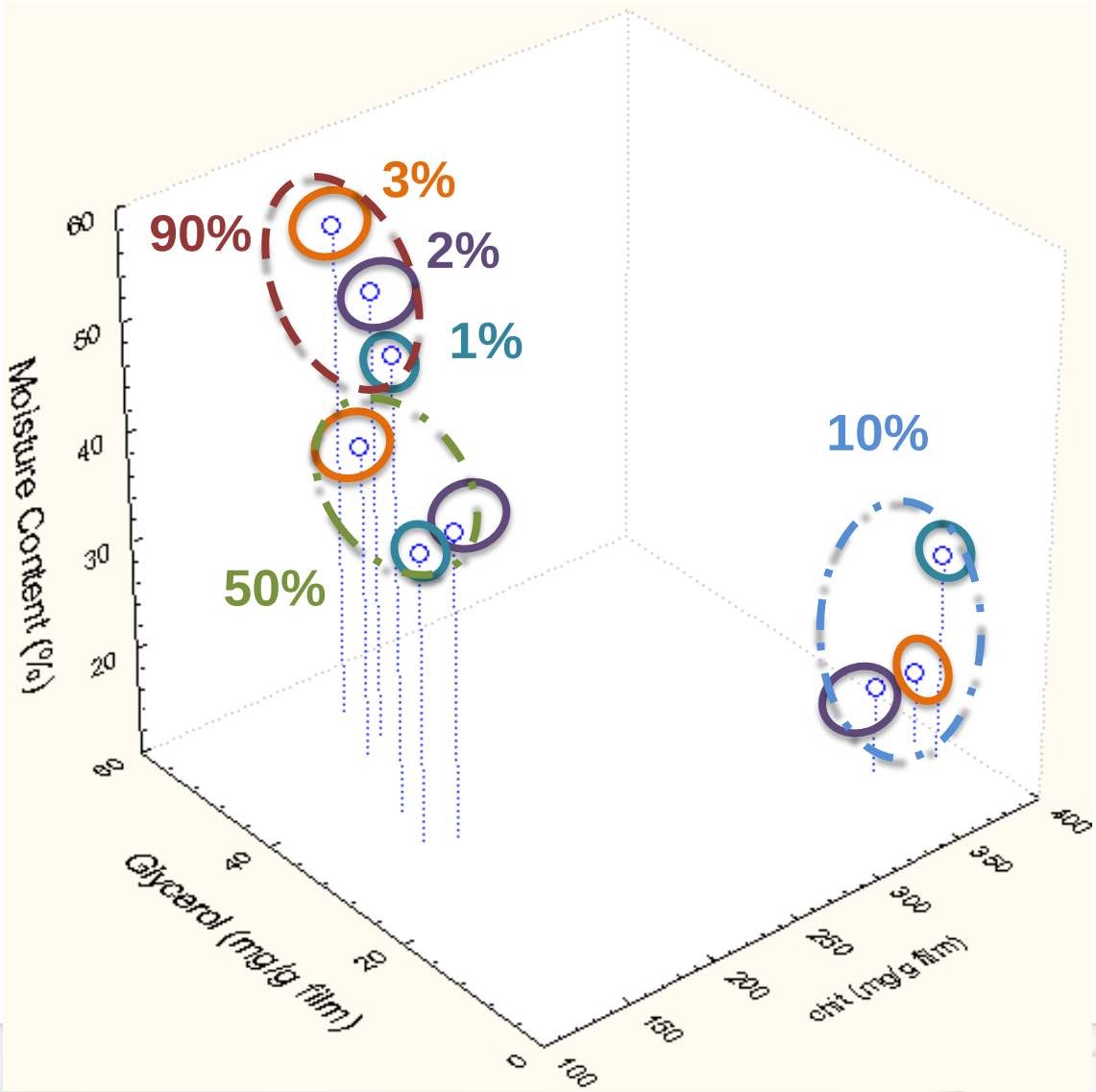
Results – *NMR water and glycerol mobility*



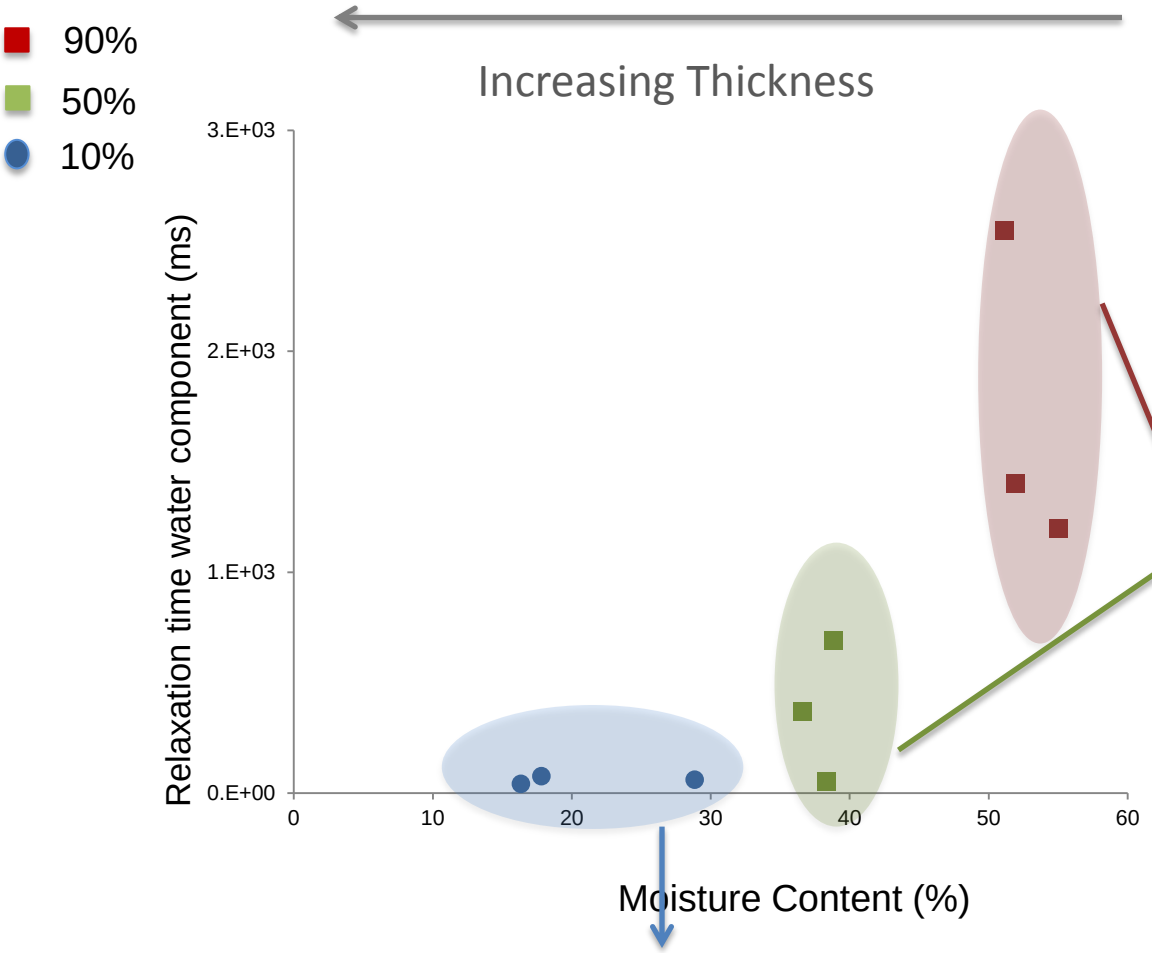


Results – *Characterization of films*

Moisture content



Results – *Mobility vs Moisture Content*



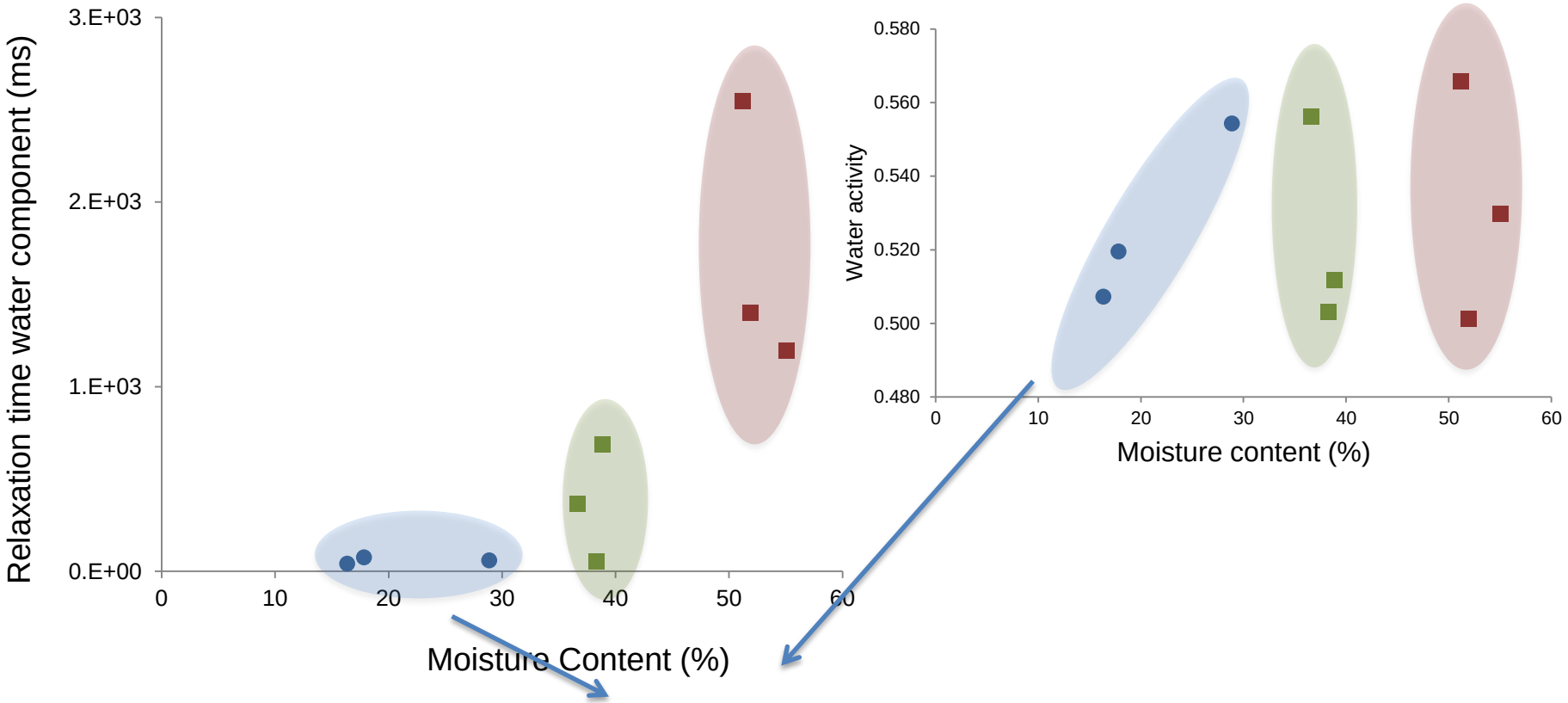
Same Composition different mobility:

differences in the film structure?

Different Moisture Content and same mobility:

Water is linked to polymer chains and cannot move?

Results – *Mobility vs Water Activity*



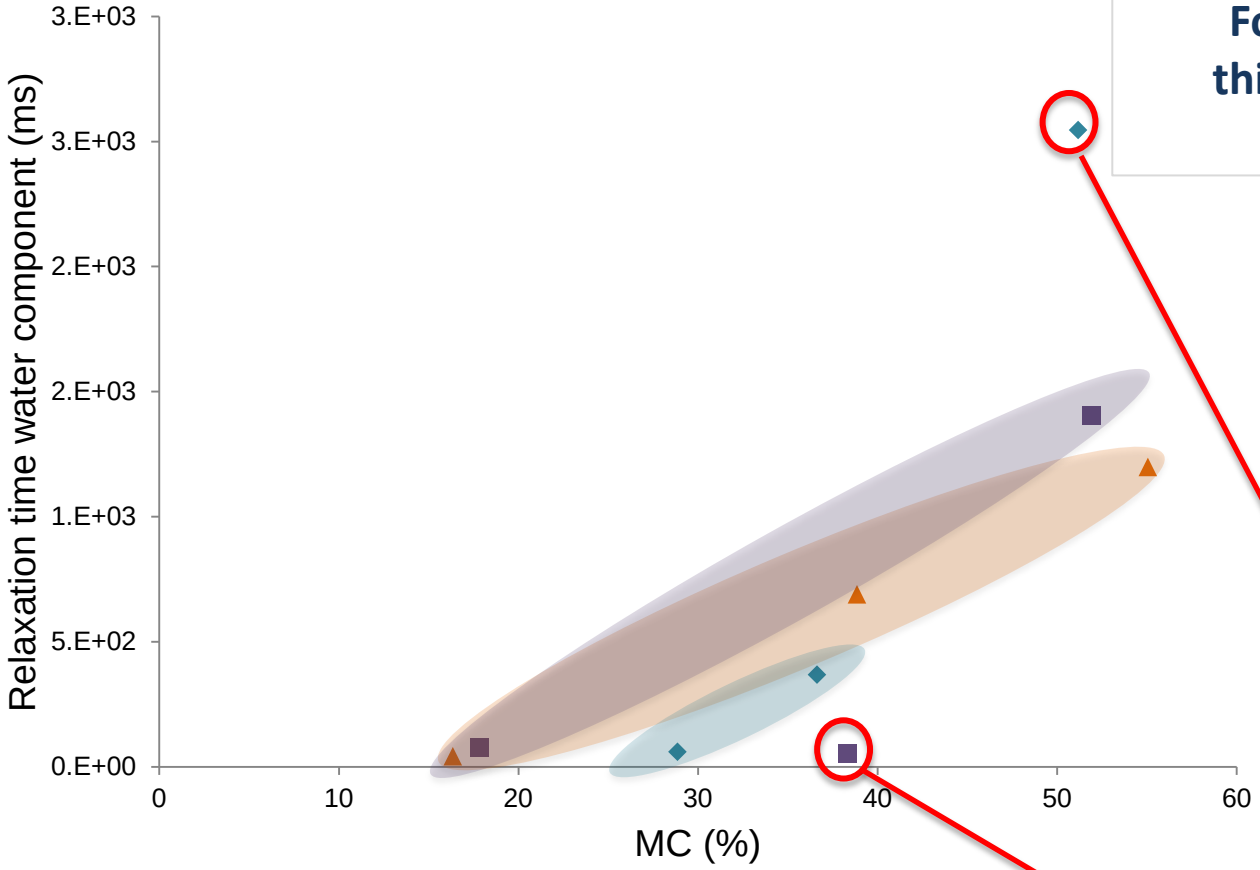
Constant T2 for different aw

90%
50%
10%

Samples with high Chitosan and very low Glycerol content. Lower crystallinity

Water in the amorphous polymer chain?

Results – *Mobility vs Moisture Content*



For films with the same thickness, water mobility correlates with MC!

Water with high mobility: Looser polymeric network?

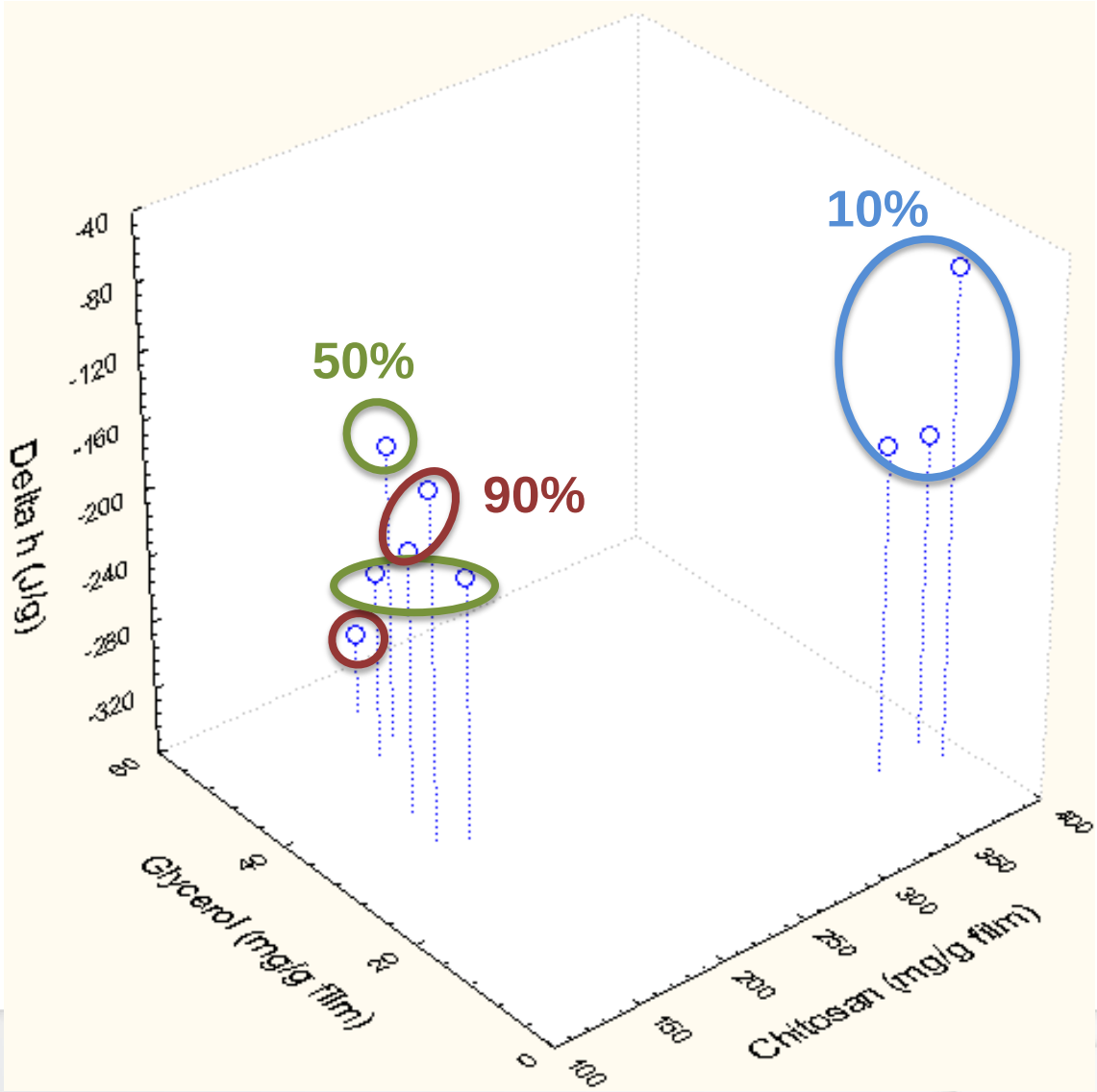
Increase strength of the polymer-water bonds?

3%
2%
1%

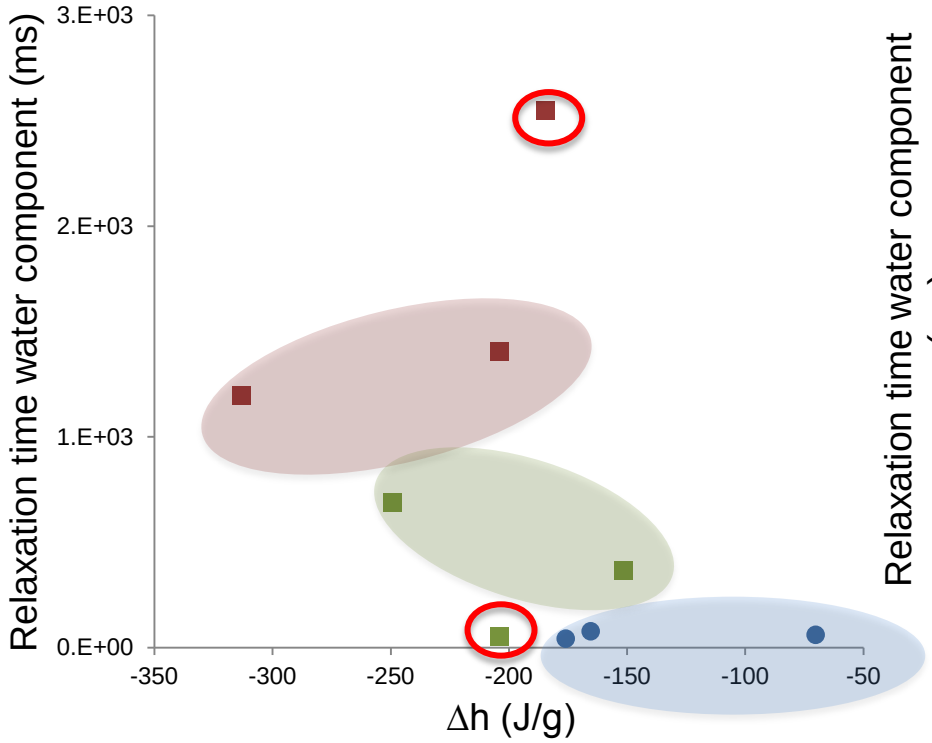
Increasing Chitosan

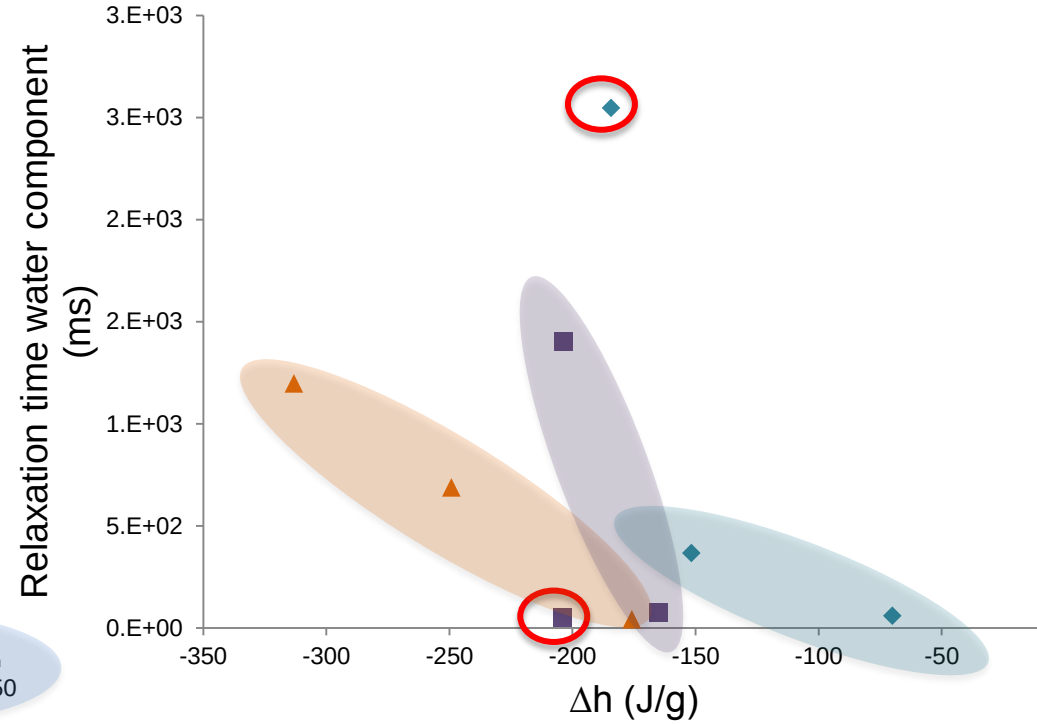
Results – *Characterization of films*

Thermal properties – Δh



Results – *Mobility vs Crystallization*





Increasing Thickness

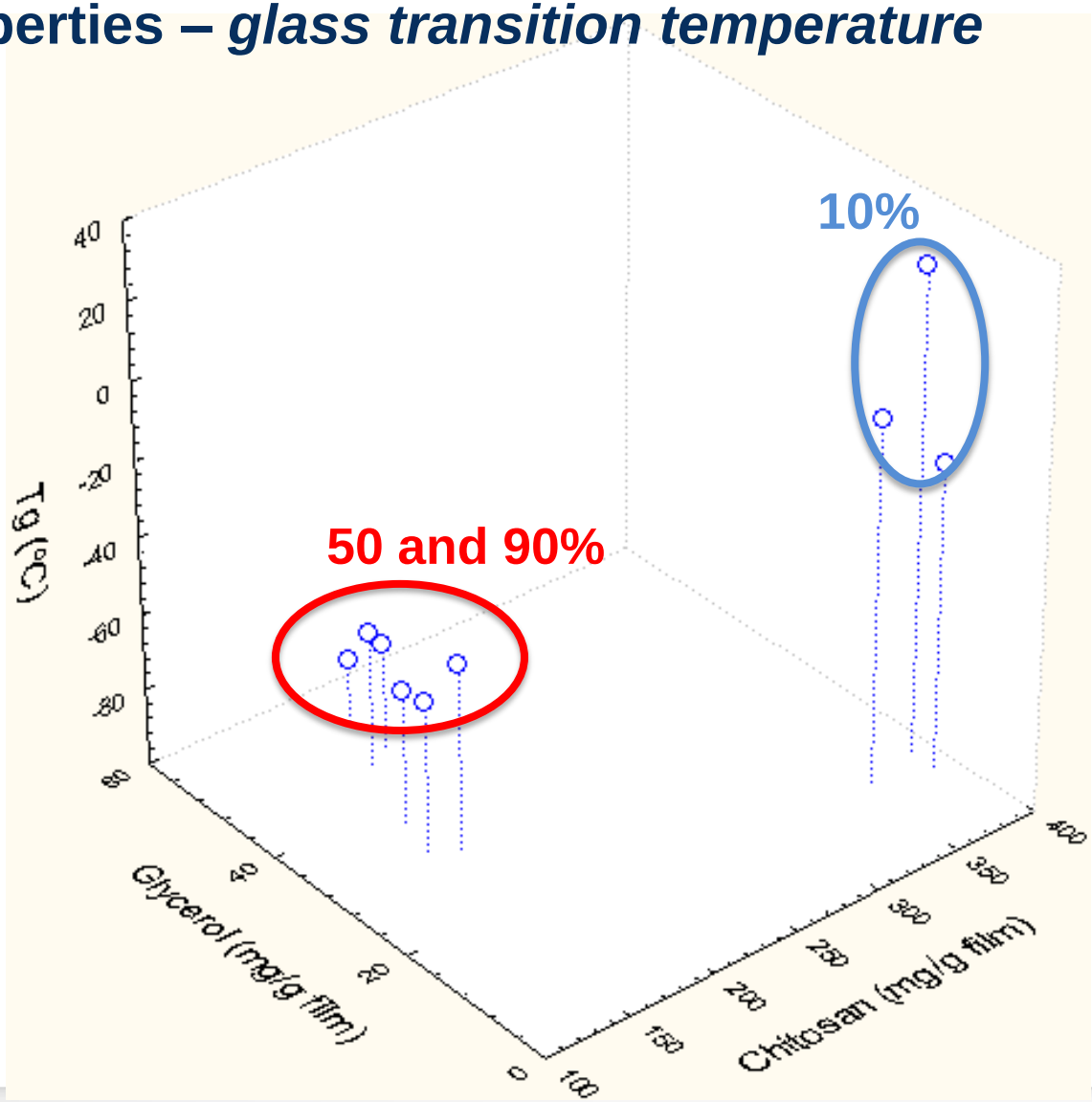
90%
50%
10%

Increasing Chitosan

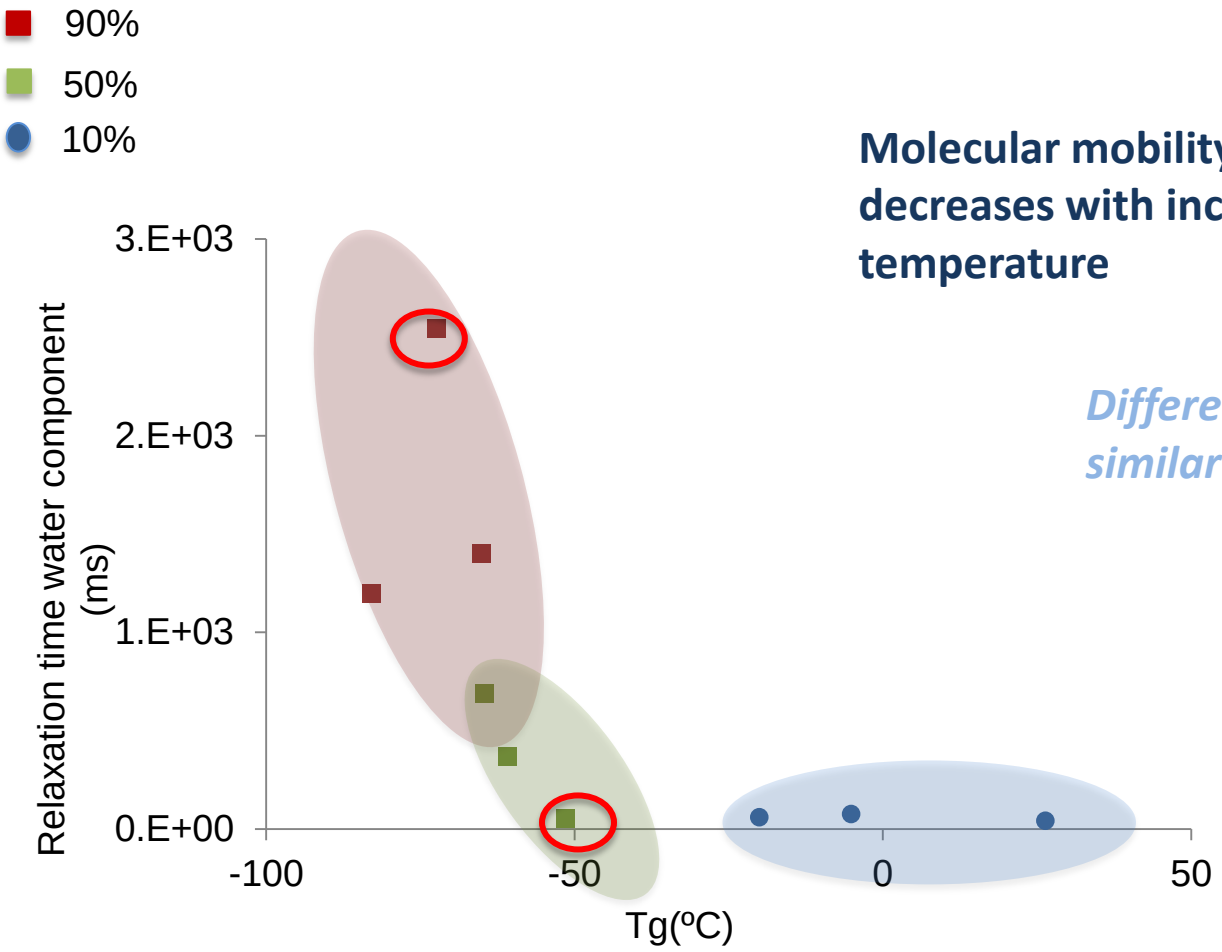
3%
2%
1%

Results – *characterization of films*

Thermal properties – *glass transition temperature*



Results – *Mobility vs Glass Transition*



Molecular mobility at room temperature decreases with increasing glass transition temperature

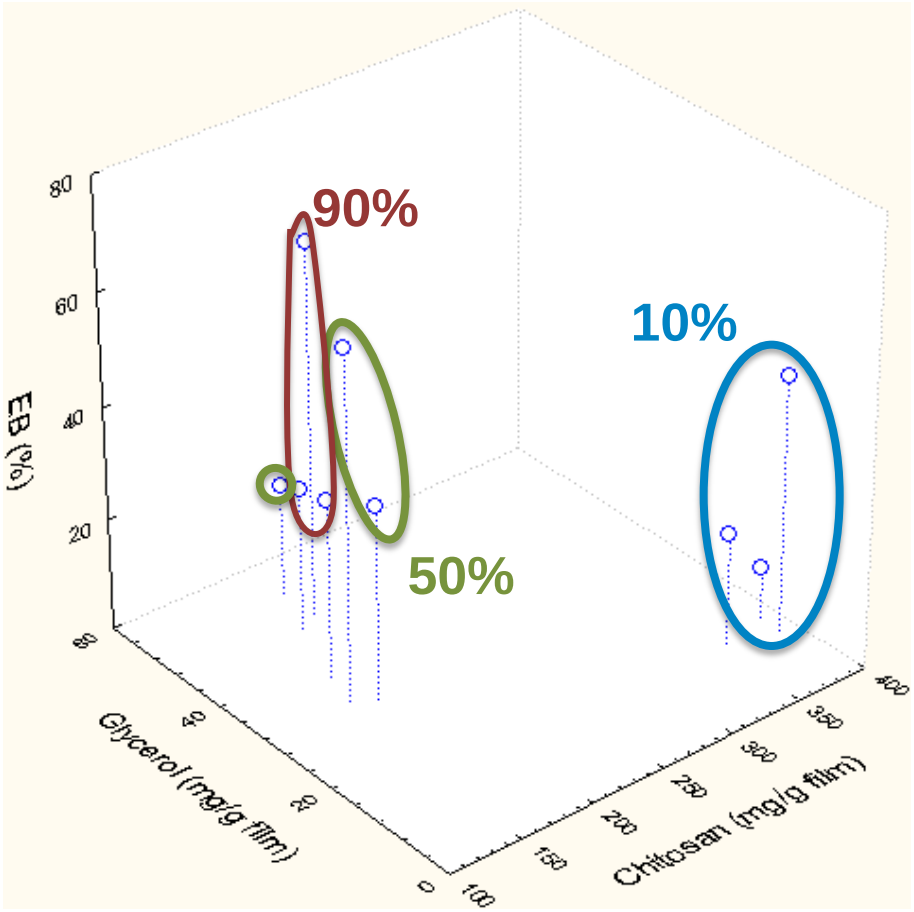
Differences in structure for films with similar composition

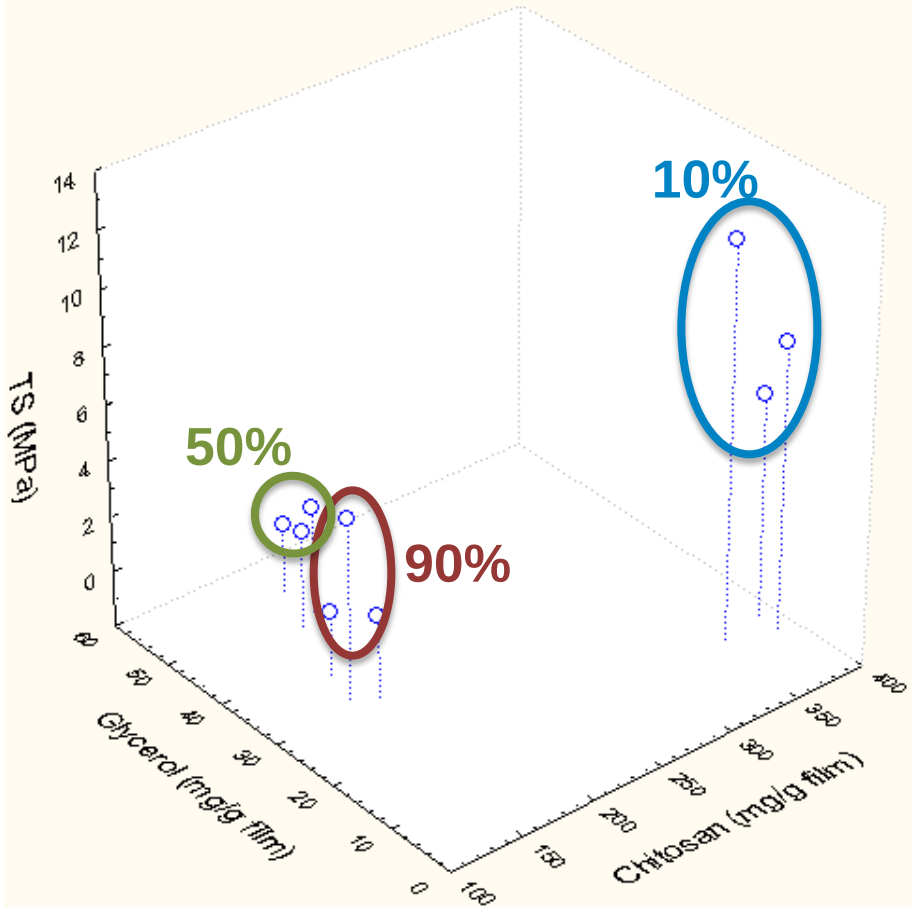
Same behaviour for films with similar thickness

Behaviour suggests the increase of mobility with increase of free volume

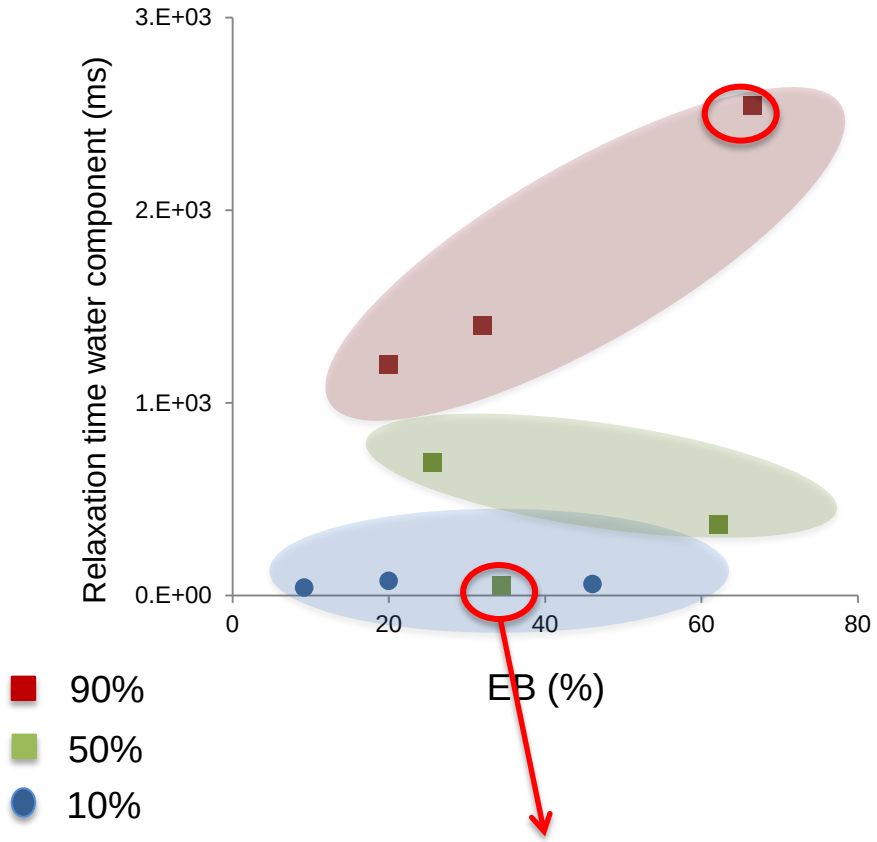
Results – *characterization of films*

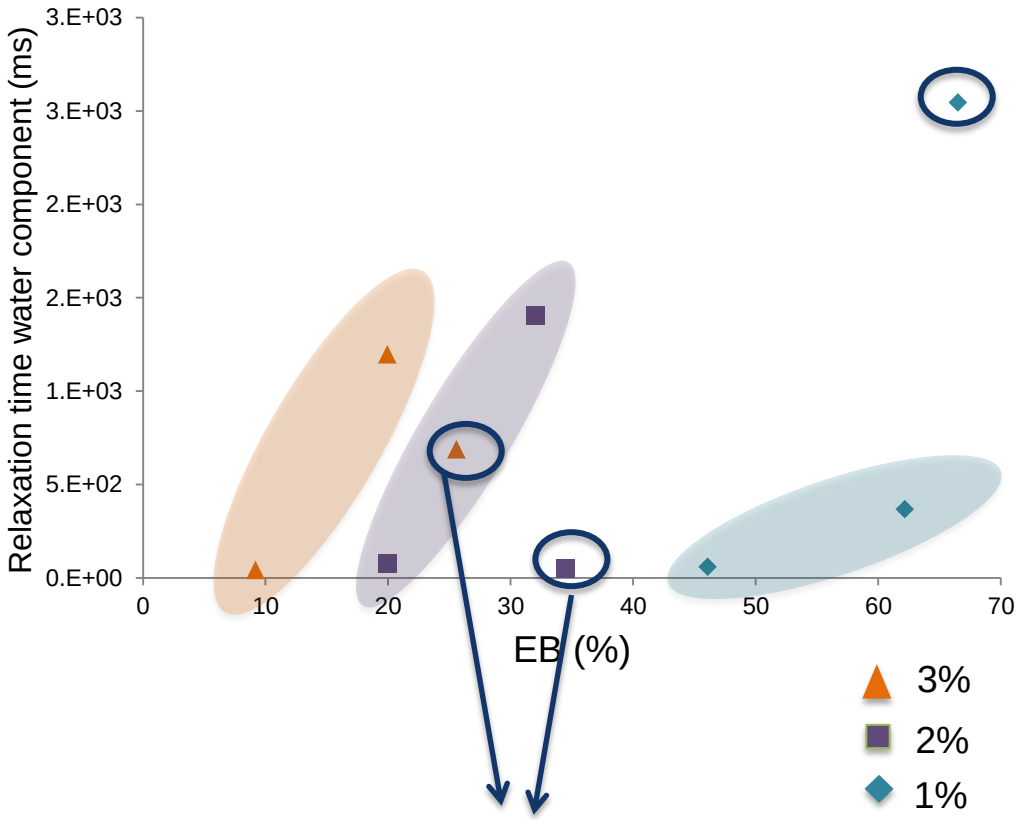
Mechanical properties





Results – *Mobility vs Elongation at Break*





EB much lower than films with similar composition:

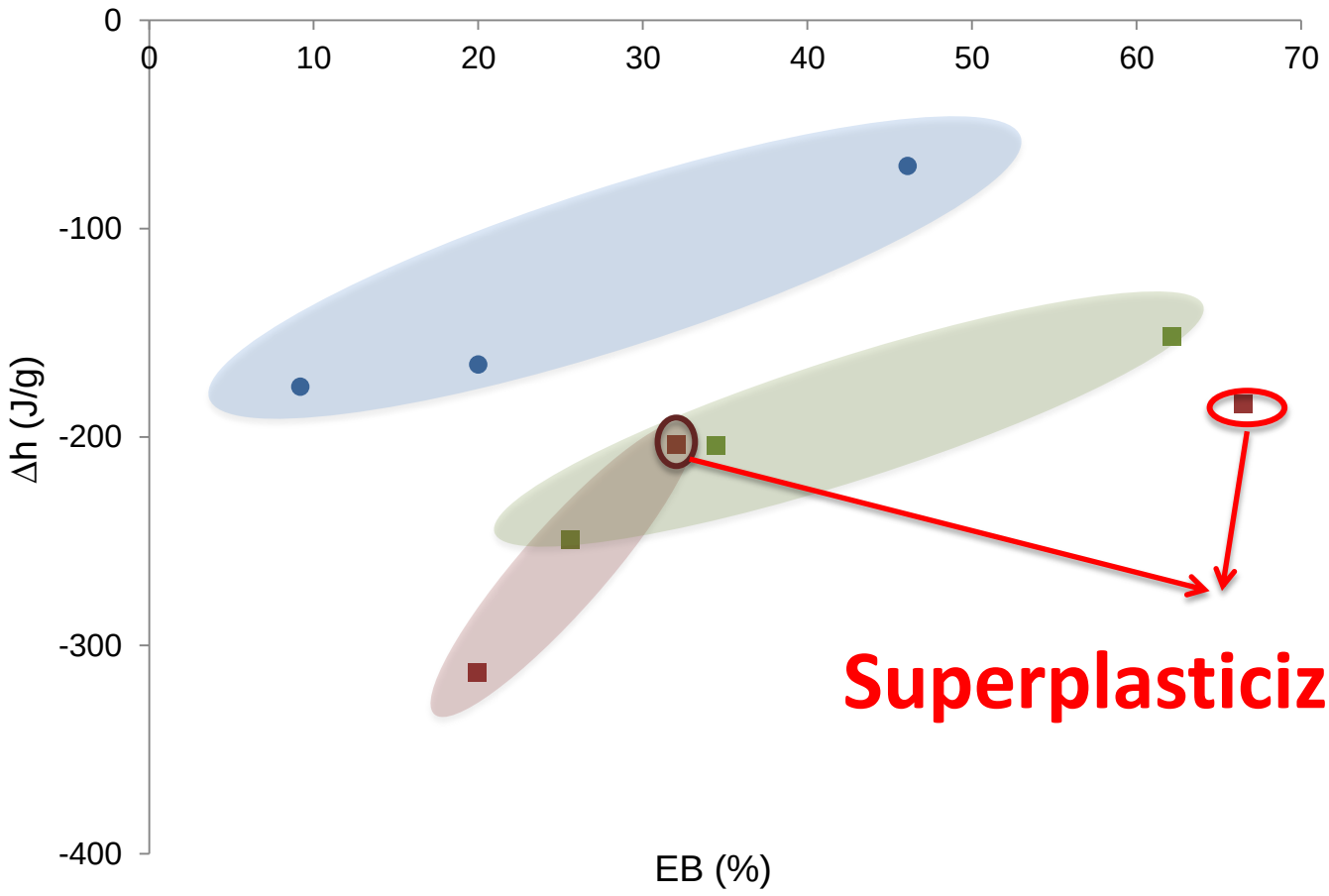
Antiplasticization phenomenon

Increasing Thickness

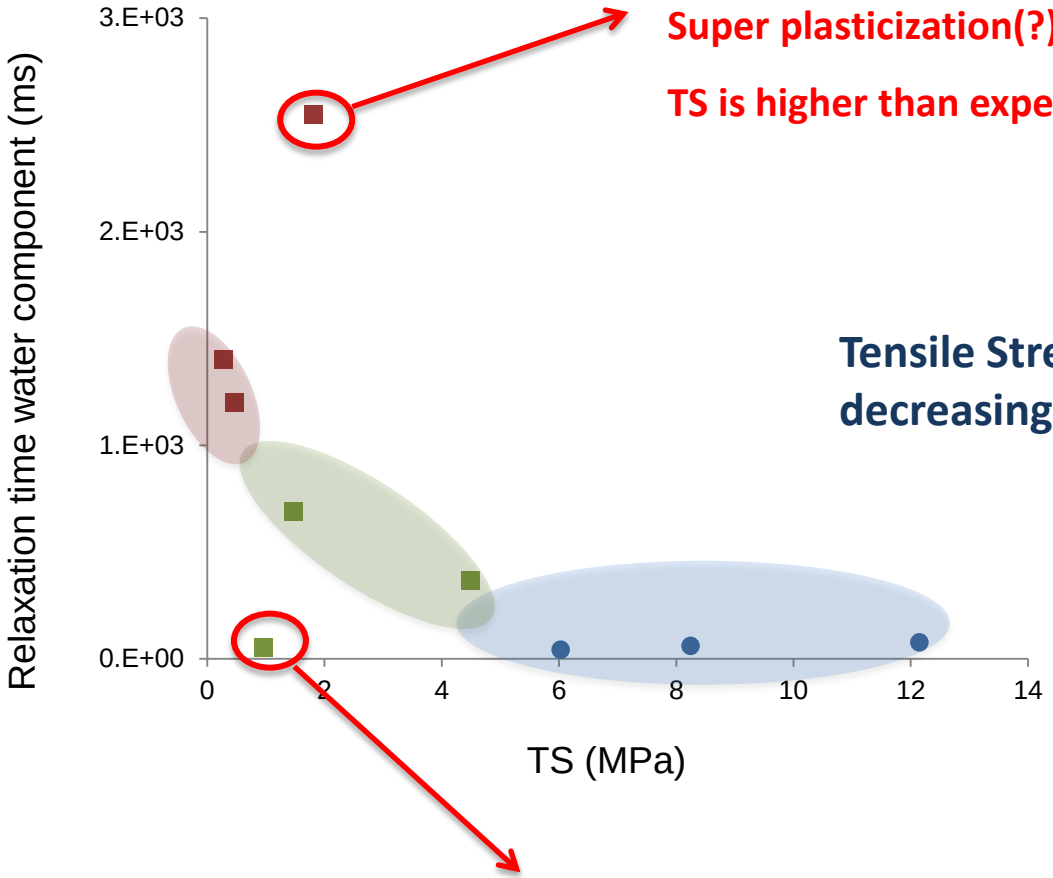
Films with similar thickness ALSO do not present a clear tendency.

Increasing Glycerol

Results – *EB vs Crystalinity*



Results – *Mobility vs Tensile Strenght*



Super plasticization(?):

TS is higher than expected

Tensile Strength increases with decreasing molecular mobility

Stronger molecular interactions make the film "harder to break"

Same behaviour for films with similar thickness

90%
50%
10%

Antiplasticization BUT:

TS does not increase

(crystallinity was of the same level)

Behaviour suggests the increase of mobility with increase of free volume

Conclusions

- **Films composition is governed by the amount of plasticizer in the FFS**
- **Film Thickness**
  - **Is governed by the chitosan content in the FFS**
  - **Correlates with Moisture Content ; Crystallinity and Elongation at Break**

    (affected also by the film composition)
- **Water and Glycerol Mobility is the result of the combined effect of composition and structure of the film**
- **Water molecular mobility correlates differently with MC, Δh and EB**
  - **Depending on the film composition different tendencies are observed**

Conclusions

- **Films composition**
  - Governed by the amount of plasticizer in the FFS
- **Film Thickness**
  - Governed by the chitosan content in the FFS
- **Water and Glycerol Mobility**
  - Result of the combined effect of composition and structure of the film
- **Water Molecular Mobility**
  - Increases with MC of films with the same thickness
  - Decreases with crystallinity of films with the same thickness
    - EB correlates with crystallinity of films with the same composition
  - Glass Transition and Tensile Strength increase with decreasing mobility (free volume)

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Thank you for your attention!

Questions?

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