# Molecular mobility, crystallinity and barrier properties of chitosan films

Joana F. Fundo[1], Cristina L.M. Silva[1], Mafalda A.C. Quintas[1,2]

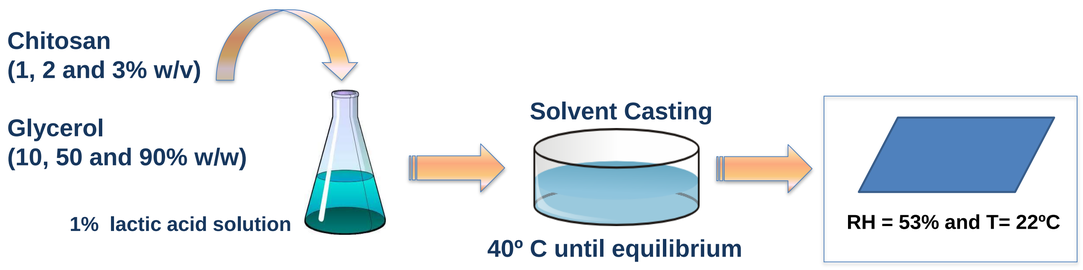
**1.** CBQF, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Porto, Portugal

**2 -** IBB, Centre of Biological Engineering, Universidade do Minho, Braga, Portugal

## Introduction

Solid-state wideline NMR spectroscopy is a powerful technique which provides information on the molecular dynamics in dense complex systems. **The objective of this work was to describe the link between water and the plasticizant mobility in the partially polymeric structure of chitosan films and the measured barrier properties.** Chitosan is a biocompatible, biodegradable, with antimicrobial activity and filmogenic biopolymer. As such, chitosan edible films attract interest in the food preservation and packaging technology fields, were the barrier properties are crucial parameters for the success of these applications.

## Material and Methods




**FILMS Characterization**

- **Films chitosan, glycerol and water content**
  - Spectrophotometric method for chitosan
  - Quantitative enzymatic determination for glycerol
- **Films thickness determinations**
- **Thermal analysis**
  - Scan from -150 to 200ºC; 20ºC/min
  - Crystallinity (melting ∆h)
- **Water vapor permeability determination – ASTM E 96-92 Method**
- **NMR determination**

***Free Induction Decay and Spin Spin Relaxation***

Bruker AVANCE III 300 MHz

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

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

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

**Y** – intensity (Hz)
**X** – relaxation time (ms)
**A1 and A2** – pre-exponential factors

## Conclusions

- Glycerol is inserted between the chitosan chains, decreasing intermolecular attractions and increasing free volume, thus facilitating molecular migration.
- The usefulness of NMR and molecular mobility studies in the matrix characterization and development of edible films with improved functionality.

### Acknowledgements

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## Results and Discussion

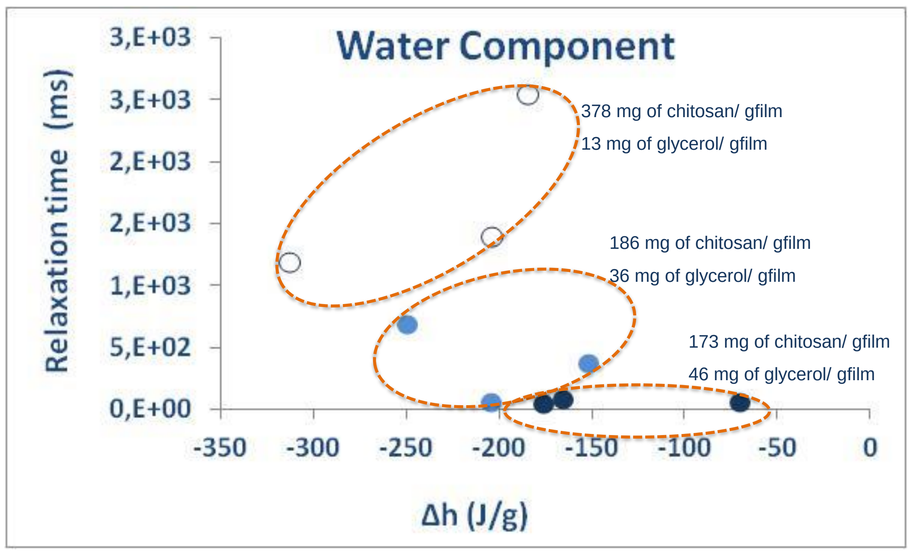
**Films thickness and composition characterization**

| Film Forming Solutions | Films Thickness (mm) | | Films Composition (mg/g film) | | | |
|---|---|---|---|---|---|---|
| | | | Chitosan | | Glycerol | |
| | Average value | Range | Average value | Range | Average value | Range |
| 1%chit + 10% gly | 0,055 | [0,05-0,06] | 378 | [357-388] | 13 | [12-15] |
| 2%chit + 10% gly | 0,14 | [0,13-0,15] | 378 | [357-388] | 13 | [12-15] |
| 3%chit + 10% gly | 0,26 | [0,24-0,28] | 378 | [357-388] | 13 | [12-15] |
| 1%chit + 50% gly | 0,055 | [0,05-0,06] | 183 | [172-196] | 36 | [30-46] |
| 2%chit + 50% gly | 0,14 | [0,13-0,15] | 183 | [172-196] | 36 | [30-46] |
| 3%chit + 50% gly | 0,26 | [0,24-0,28] | 183 | [172-196] | 36 | [30-46] |
| 1%chit + 90% gly | 0,055 | [0,05-0,06] | 173 | [158-195] | 46 | [37-53] |
| 2%chit + 90% gly | 0,14 | [0,13-0,15] | 173 | [158-195] | 46 | [37-53] |
| 3%chit + 90% gly | 0,26 | [0,24-0,28] | 173 | [158-195] | 46 | [37-53] |

**Films produced with the same polymer percentage have similar thickness**

**Films produced with the same glycerol percentage have similar composition**

**Relaxation time T2, for the proton from water in function of melting point**



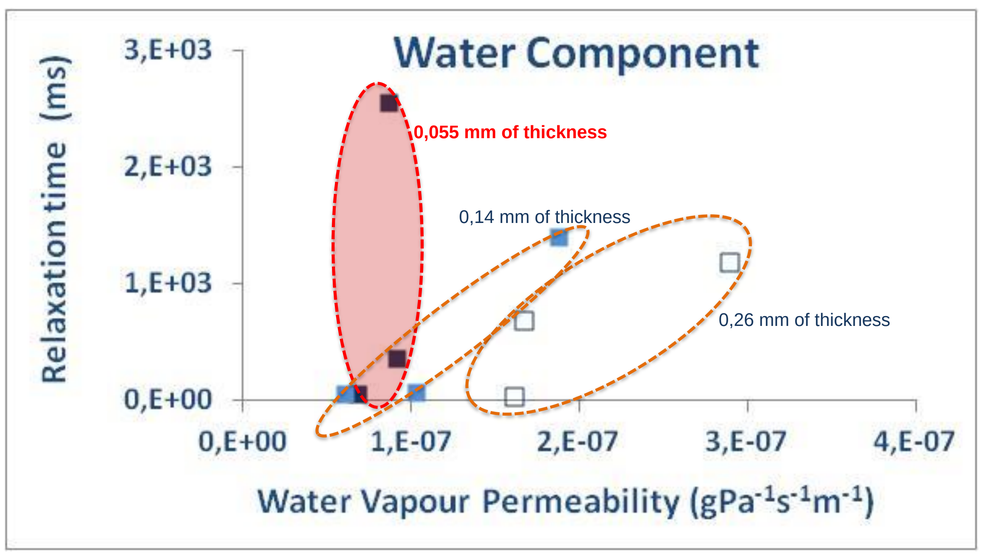

**Films grouped by the same composition**

**Crystallinity increases with increasing water and glycerol mobility** ⟷ **Crystallinity increases in films with lower chitosan concentration and higher plasticizant quantity**

**once polymeric chains are organized in the crystalline form, the interaction polymer/ plasticizant is minimized**

**glycerol increase molecular mobility, facilitating the ordering of polymer chains**

**Relaxation time T2, for the proton from water in function of WVP**




**Films grouped by the same thickness**

**For films with the same thickness**

**Exception** → **0,055 mm**

**Water vapor permeability increases with mobility**

**WVP for thin films is independent of the mobility**