A NMR approach to understand water behaviour on chitosan/ glycerol films

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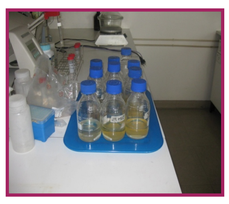
INTRODUCTION

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 investigate the effect of polysaccharide/ plasticizer concentrations on the molecular mobility of chitosan/ glycerol films.** The primary role of plasticizers is to improve the flexibility and processability of polymers. Plasticizers, by reducing the intermolecular forces soften the rigidity of the film structure and increase the mobility of the biopolymer chain units. These additives reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time as increasing its chain flexibility, resistance and dielectric constant. However, due to some relationship between polymer/ plasticizer concentrations, an antiplasticization phenomenon may occur. A stronger interaction might be occurring between the polymer and the plasticizer, which decreases the free volume and the molecular mobility of the polymer. Water, itself, also should be considered as a plasticizer. Most food polymers are thermoplastic and subject to water plasticization. It is known that a range of hydrophilic biological systems, such as chitosan films, can absorb water molecules creating hydrogen bonds, thus influencing the relaxation properties of biopolymers. All these effects, contribute to changes on the polymer free volume and thus on the molecular mobility of the polymeric matrix.

MATERIALS & METHODS

Film forming solutions (FFS) preparation

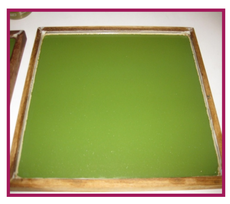


chitosan (1%, 2% and 3% w/v)

in 1% lactic acid

10%, 50% and 90% w/v of glycerol

Film preparation



300ml FFS was casted in 32X40 cm plates,

dried at 40ºC and stored at 22ºC/53%RH

NMR measurements

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)

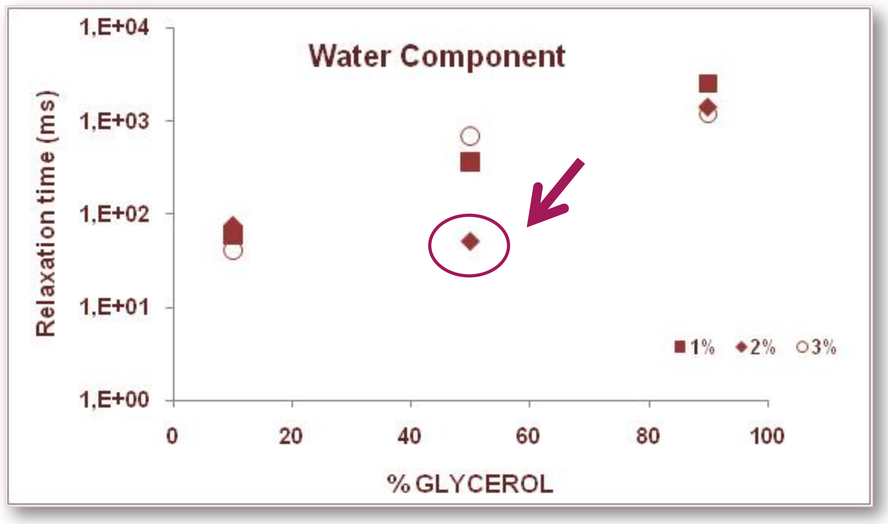
X – relaxation time (ms)

A1 and A2 – pre-exponential factors

RESULTS & DISCUSSION

relaxation time (T2) varied exponentially with glycerol concentration increasing

Relaxation time T2 or the proton from water component



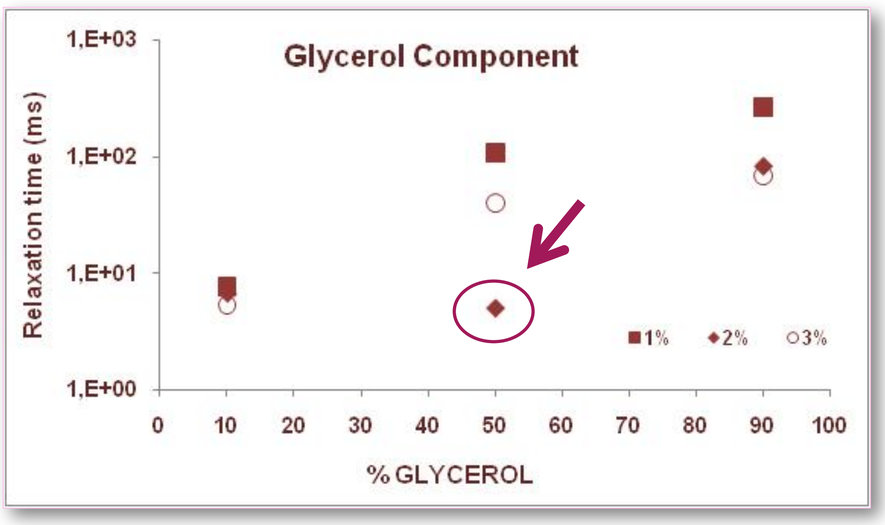
no effect of chitosan concentration was observed

water presented is "free" from the polymeric chain

exception was 2% chitosan +50% glycerol

ANTIPLASTICIZATION PHENOMENON

Relaxation time T2 for the proton from glycerol component



exception was 2% chitosan +50% glycerol

glycerol may be "entrapped" in chitosan chain network

relaxation time (T2) decreased with chitosan concentration increasing

CONCLUSIONS

- Glycerol may be entrapped in the chitosan chain network, while the water present in the system contributing to the film plasticization is free from the polymeric chain.
- The use of new tools for research in food systems may provide important knowledge on structure-function properties with wide applications in the industry.

ACKNOWLEDGEMENTS

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