WATER BINDING IN STARCH FILMS

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PLAN

Properties of Plasticized Starch Films:
- Plasticization and Plasticizers
- Glass transition
- Effect of the glycerol content in plasticized starch films

Water-Glycerol–Starch Interactions:
- Water Vapor Adsorption isotherm
- Schematic representation of Water–glycerol-starch interactions
- Phase Diagram from Water vapor adsorption isotherm

Water-plasticizer-Starch Interactions:
- Diethylene Glycol
- Diethylene Glycol monomethyl ether

Conclusion
Properties of Plasticized Starch Films
Plasticization:

**Aim**: To change a rigid material at a certain temperature into a malleable material easier to shape and process

**Method**: To add a small molecule (plasticizer) compatible with the polymer in order to modify its properties

- Decrease of Glass transition temperature
- Increase of deformation rupture for a lower stress
Plasticizers used

Water  H-O-H

Glycerol  CH$_2$OH
           CHOH
           CH$_2$OH

Diethylene glycol

HO-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-OH

Diethylene glycol monomethyl ether

CH$_3$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-OH
GLASS TRANSITION AND OTHER RELAXATION
TRANSITIONS IN POLYMERS

- DMTA and DEA more sensitive to relaxation
  Transitions in Plymers than DSC

- Transitions observed:
  - $\alpha$: Glass transition, Relaxation of skeleton
  - $\beta$: Mobility of small groups of atoms
  - $\gamma$: Mobility of segments of the polymer chain
Glass Transition and Mechanical Properties

![Diagram showing glass transition and mechanical properties. The graph plots log modulus against temperature or log frequency, with key regions marked as Glass, Leathery Region, Rubber Plateau, Elastic or Rubbery Flow, and Liquid Flow.]
Glass transition Temperature and Water activity
Evolution of Glass transition temperature of starch films plasticized with different proportions of glycerol
Plasticized Starch

Tg (°C) vs Water content (%)

- Good mechanical properties

Glycerol content:
- 0%
- 4.82%
- 8.26%
- 12.38%
- 14.79%
- 20.64%
- 28.55%
Evolution of $\beta$ Transition as a function of glycerol Content at different ERH
EFFECT OF POLYOLS IN PLASTICIZED FILMS

- Glass transition depends on polyol concentration
- Effect of polyol is the higher the greater the number of OHs
- Starch molecules are more tightly bound through intermolecular H-bonds in presence of polyols
- Depending on concentration, polyol may bind to water which decreases the amount of water available to starch
- Flexibility of starch chains is reduced in starch-water-polyol system as the thermal motion of water is stabilized
- The antiplasticizing effect of glycerol is influenced by H-bonding between water, starch and glycerol: less free volume is available to starch in presence of glycerol
Water- Glycerol – Starch Interactions
« Properties are drastically changed after plasticizer phase separation »

What is the role of water in this phenomenon ?
Water

Starch

Water

Glycerol

Specific sorption

Multilayer water

Free water
Water vapor adsorption of Plasticized Starch depends on relative humidity.

In the range of specific water adsorption, plasticizer is in competition with water.

Above 50% RH, plasticizer intrinsic hydrophilicity increases the adsorption of water.

What is the effect of plasticizer content (before and after phase separation) on this phenomenon?
Another presentation of water vapor adsorption in plasticized films
Glycerol phase separation

No phase separation
0.5 water / 1 Gluc.

0.5 glycerol / 1 Gluc.
Water content (% w/w)

Glycerol content (% w/w)

1 water / 1 Gluc.

1 glycerol / 3 Gluc.
2 phases
Water mainly in free glycerol
How many free glycerol?
Added glycerol after phase separation

Water uptake (supposed to be mainly in free glycerol)
Free glycerol quantity can be *overestimated* by the ratio:

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\frac{\text{Water uptake for 100 g glycerol added after phase separation}}{\text{Water uptake of pure glycerol at the same RH (%)}}
\]
Overestimation of free glycerol (for 100 g added after phase separation)

Relative humidity (%)
Water (on free glycerol) shifts glycerol on starch (multilayer form)

Water (on starch) shifts glycerol on free glycerol

AND / OR Retrogradation

Water content (% w/w)

Glycerol content (% w/w)
Conclusion

- Water vapor adsorption isotherms of plasticized starch films with glycerol allow understanding of phase hydration properties

- Glycerol phase separation depends on water content

- Considering stoechiometries in water / glycerol / starch systems allows proposition of different types of H-bonding in the different regions of phase diagram

- Considering that all water molecules are adsorbed by glycerol after phase separation and neglecting crystallinity in starch allows (over)estimation of free and multilayer glycerol
Water-plasticizer-starch interactions
Hydration of Starch film plasticized with Diethylene Glycol

% water

% Plasticizer
Hydration of Starch film plasticized with Diethylene Glycol monomethylether
Conclusion

- Effect of Diethylene Glycol (2 OHs) comparable to that of Glycerol as concerns the separation of regions of preponderance of water or of the plasticizer.

- Diethylene Glycol monomethyl ether (only 1 OH) much less hydrophilic does not show a possible separation of phase as for Glycerol or DEG.

- $\beta$ Relaxations transitions show the same trends as Phase diagrams derived from water vapor sorption isotherms.
GENERAL CONCLUSION

- Water Vapor Sorption isotherm of plasticized films allows obtaining of phase diagrams and describing the different hydration mechanisms.

- Glass Transition temperature generally used to describe these systems seems insufficient.

- $\beta$ Transition Relaxation seems more sensitive to peripheral structural phenomena such as phase separation in plasticized films.