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Thermodynamic Properties of Water in Amorphous Carbohydrates: Physical and Chemical Considerations

Johanna Claude

Job Ubbink

Nestlé Research Center – Lausanne - Switzerland

Outline

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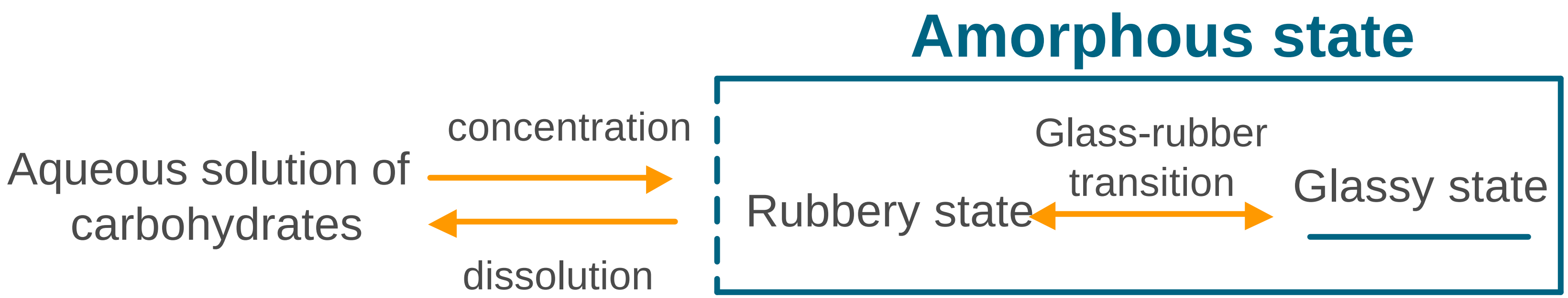
- Amorphous carbohydrates in foods : phase behavior and physical properties
- Polymer physics approach
- Water : a key parameter
- Probing the molecular level
  - Thermodynamic
  - nanostructure
- Chemical stability
  - Heating in sealed cell maltodextrin
  - Color change
- Concluding remarks

Phase Behavior and Physical Properties of Amorphous Carbohydrates Determine Food Quality



Polymer Physics of Amorphous Carbohydrates

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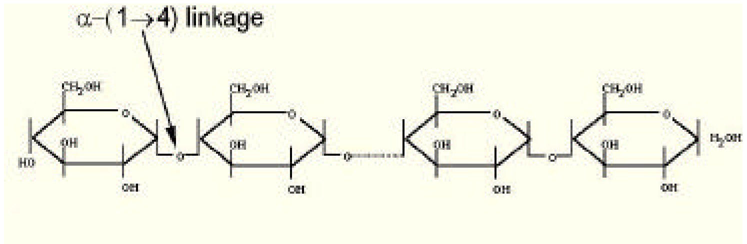
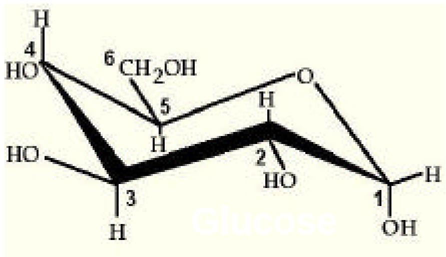
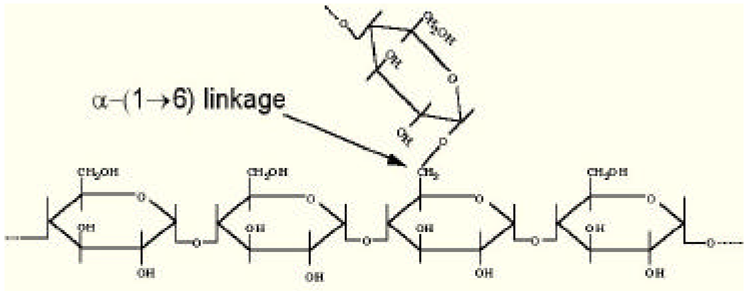
Model food polymer: maltodextrin
- Hydrolysis product of starch
- Mainly α-(1→4) bonded glucose residues
- Some branching because of α-(1→6) linkages
- Amorphous







http://www.poco.phy.cam.ac.uk/research/starch/0

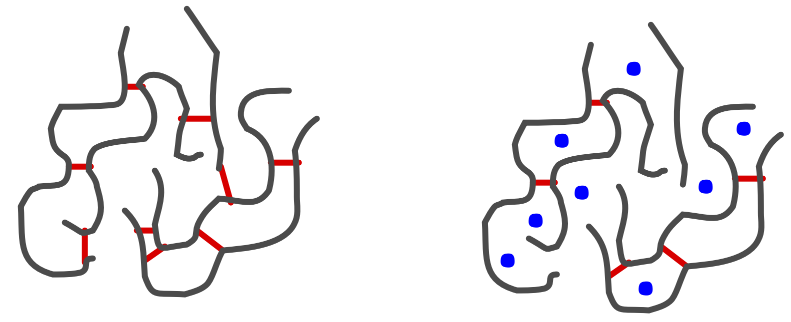
Hydrolysis determines
- Molecular weight (DE1 = starch; DE100 = glucose)
- Polydispersity (often Mw/Mn > 5)

Hydrogen Bonding in Amorphous Carbohydrates and the plasticization by Water

Material	Mw	Tg (dry) [K]
Glucose	180	304
MD DE35	1600	353
MD DE21	7000	388
MD DE6	86000	425
Starch	∞	520

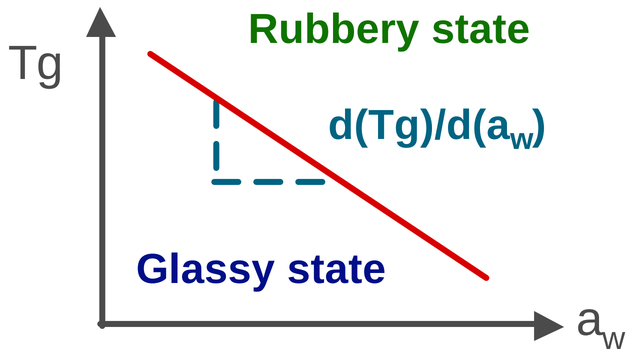
In comparison:

Material	Mw	Tg [K]
Polystyrene	4000	313
Polystyrene	300,000	372
Polyethylene	∞	140
Poly(vinyl)chloride	∞	358



High 'dry' Tg of biopolymers because of extensive hydrogen bonding in dry state

But consequently **water** is a highly efficient plasticizer!



Material	$d(Tg)/d(a_w)$ [K]
MD DE35	-182
MD DE21	-176
MD DE6	-176

Study Combines Thermodynamics With nanostructural Investigations

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Thermodynamics
- Sorption behavior
- PVT properties

Nanostructure
- Defects in molecular packing
- Hydrogen bonding

Annealed polymers

Chemical stability
- Kinetics of caramelization in glassy and rubbery matrices

Annealing of Polymer Matrices

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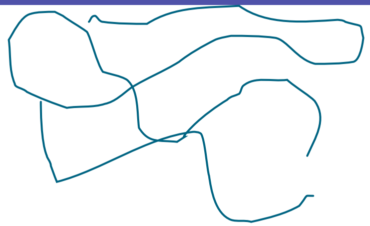
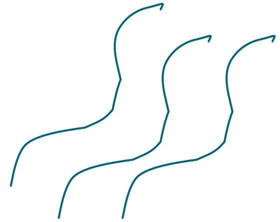
Method 1



DRY POLYMER

Annealing

above Tg
under vacuum

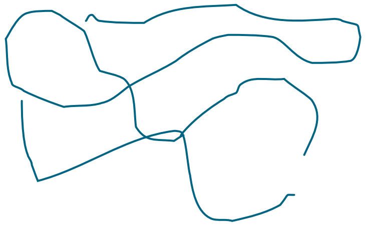


POLYMER ANNEALED

→Potential problems:

• Water is key element in carbohydrates + Chemical degradation

Method 2



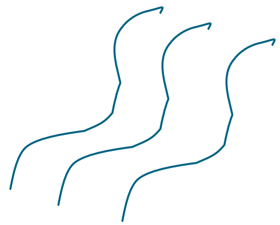
POLYMER + WATER

initial water activity

Annealing of polymers equilibrated

+ WATER

Hermetically sealed sample container



POLYMER + WATER ANNEALED

final water activity

→ Potential problem: Chemical degradation

How to follow degradation ?

- Detection of degradation products
- Changes in molecular weight profile
- Color changes

Caramelization Reactions Generally Studied in Dilute Solutions

'Caramelization' comprises a whole range of (complex) chemical reactions:

Initial step:

Loss of water; formation of the anhydro form of the sugar

Second step

Further loss of water; formation of water-soluble caramelan (color); some formation of flavor compounds

Subsequent steps

Formation of very dark, insoluble pigments; formation of flavor compounds arising from sugar fragmentation and dehydration

Hermetically-sealed Stainless Steel Cell

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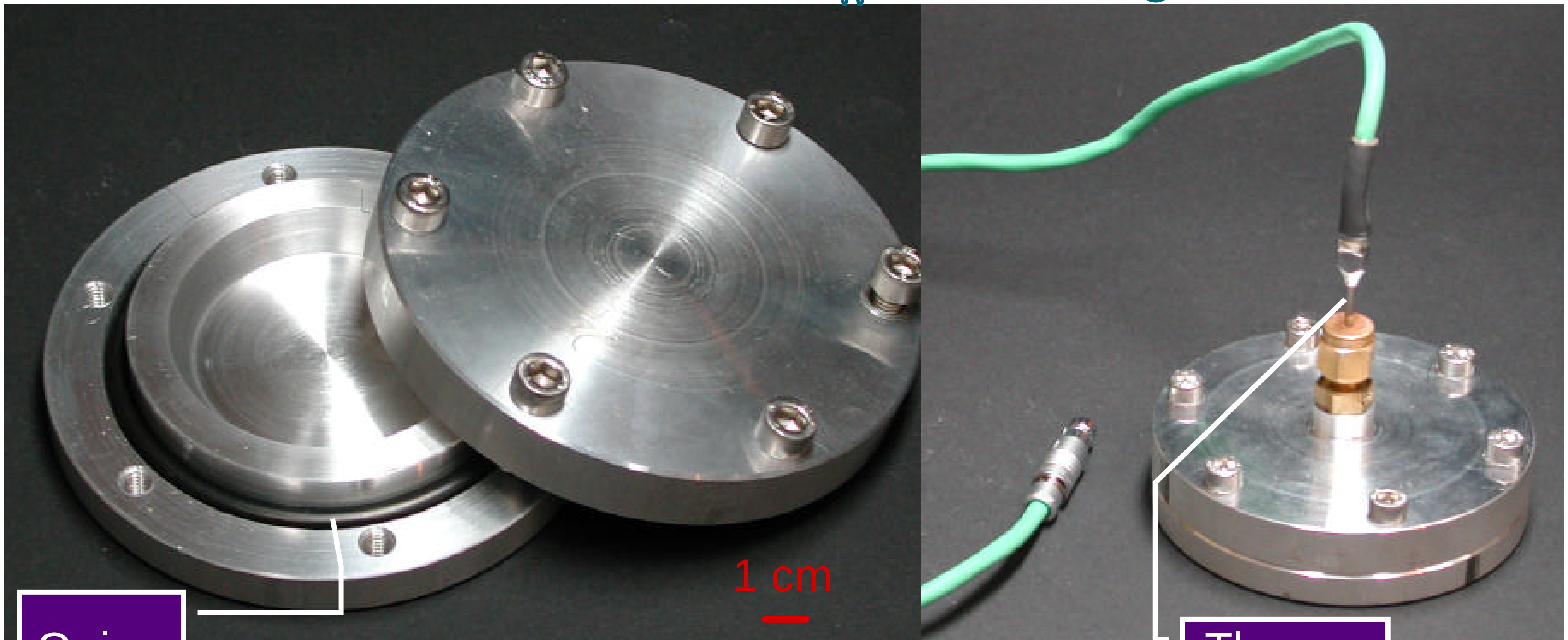
Maltodextrin IT-12 , a_w 0.15 , Tg = 88°C



Temperatures tested in an oven:

58°C – 88°C – 118°C – 188°C

Color Measurements

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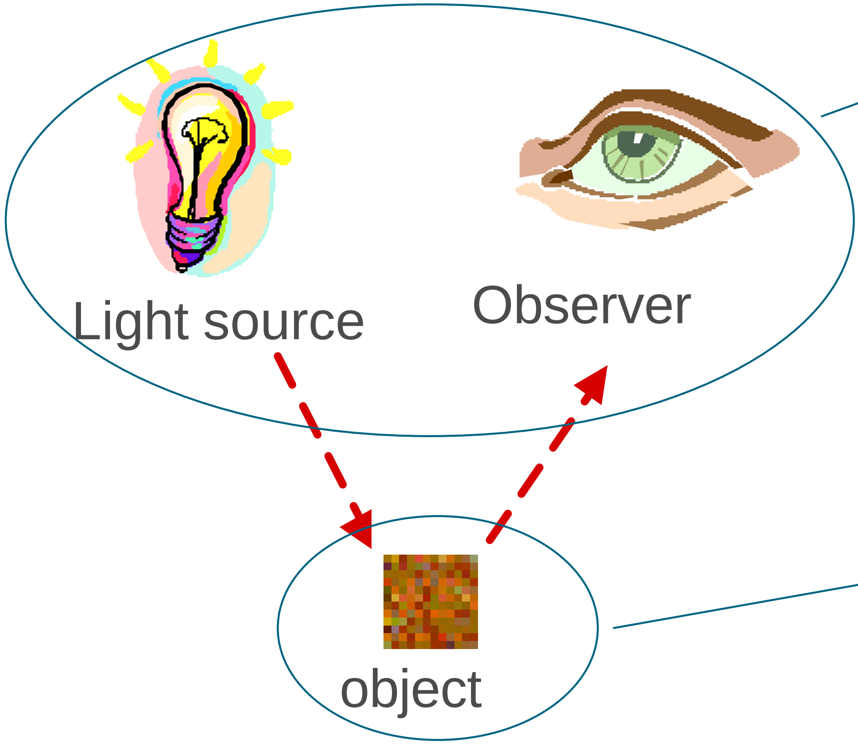
- Macbeth Color-Eye XTH
  - Spectrophotometer
  - CIE standard daylight illumination source D_{65}
  - Standard observer 10°



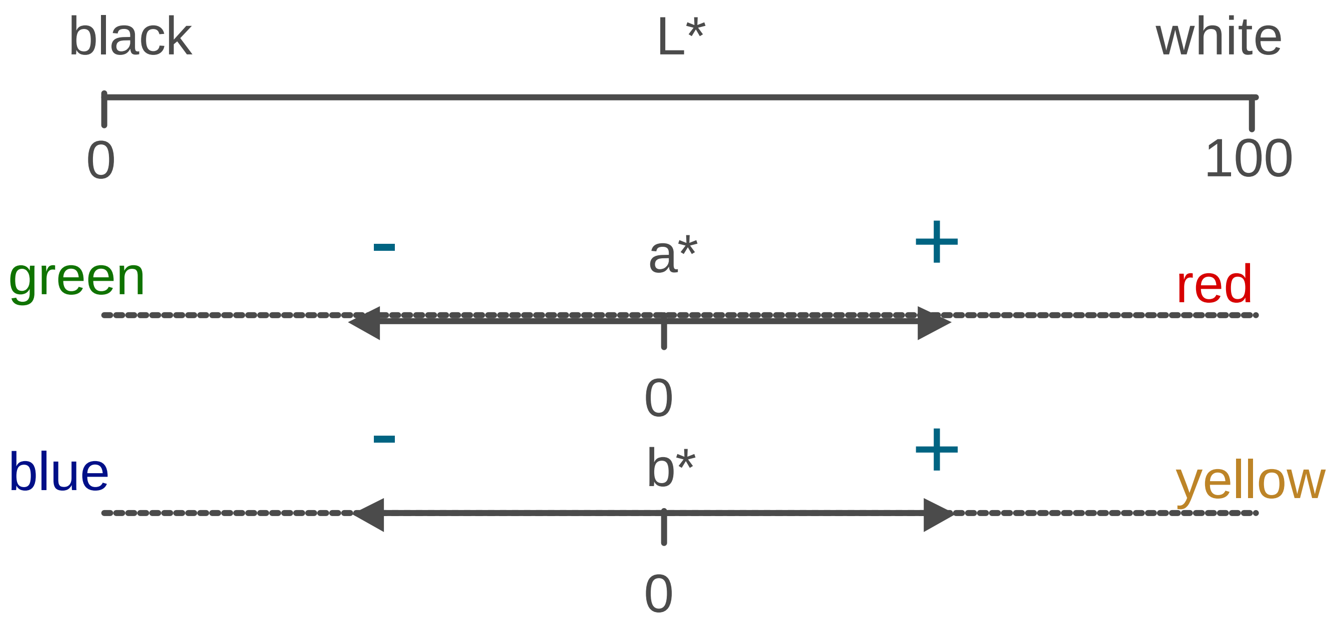
Maltodextrin IT-12 188°C

30 min 60 min 120 min

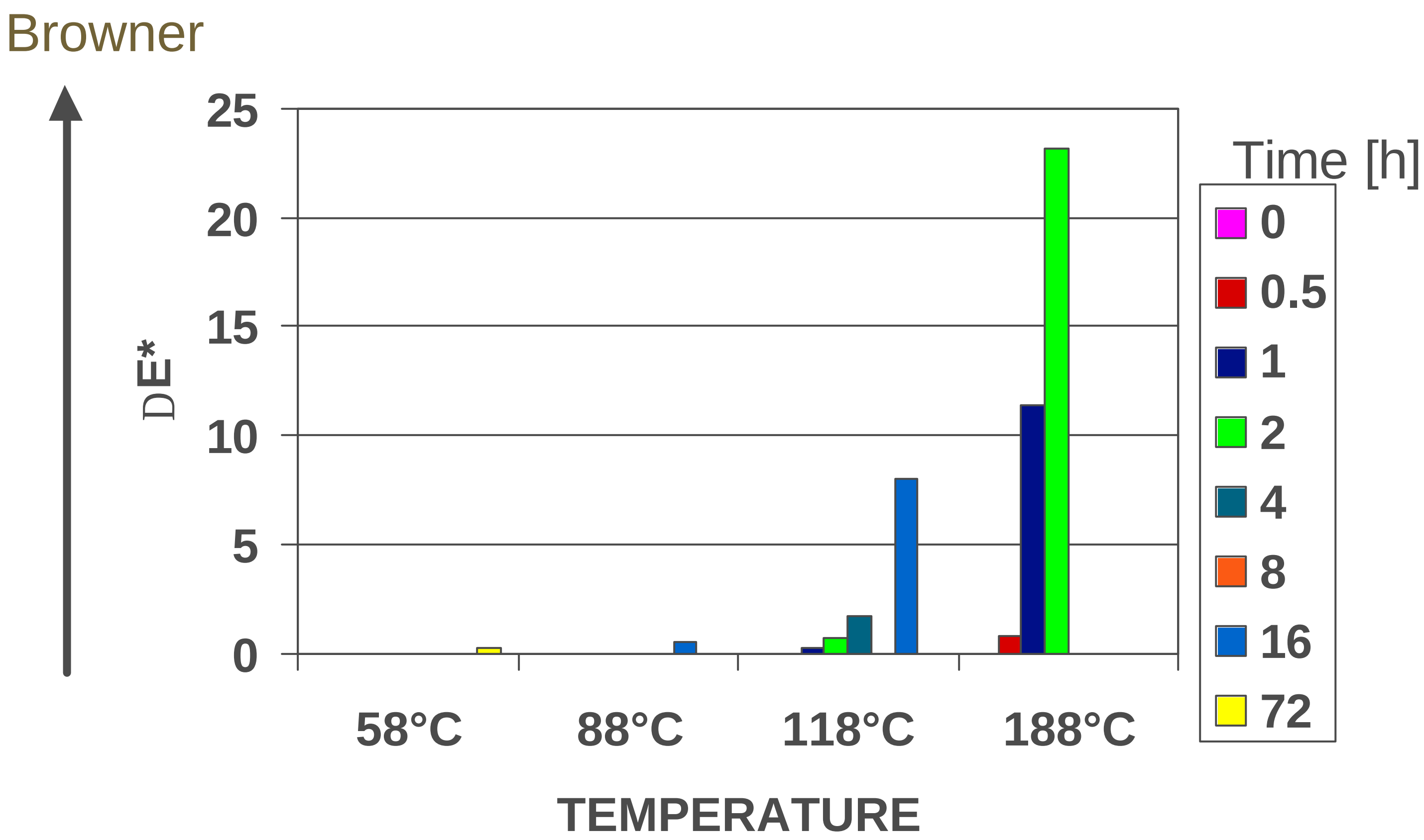
Color Measurements L*a*b*

Hunter-Scotfield equation

$$\Delta E^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2}$$



Color Evolution at Four Temperatures



$$\Delta E^{*} = \sqrt{(\Delta a^{*})^{2} + (\Delta b^{*})^{2} + (\Delta L^{*})^{2}}$$

Arrhenius Plot Indicates Absence of Tg Effects

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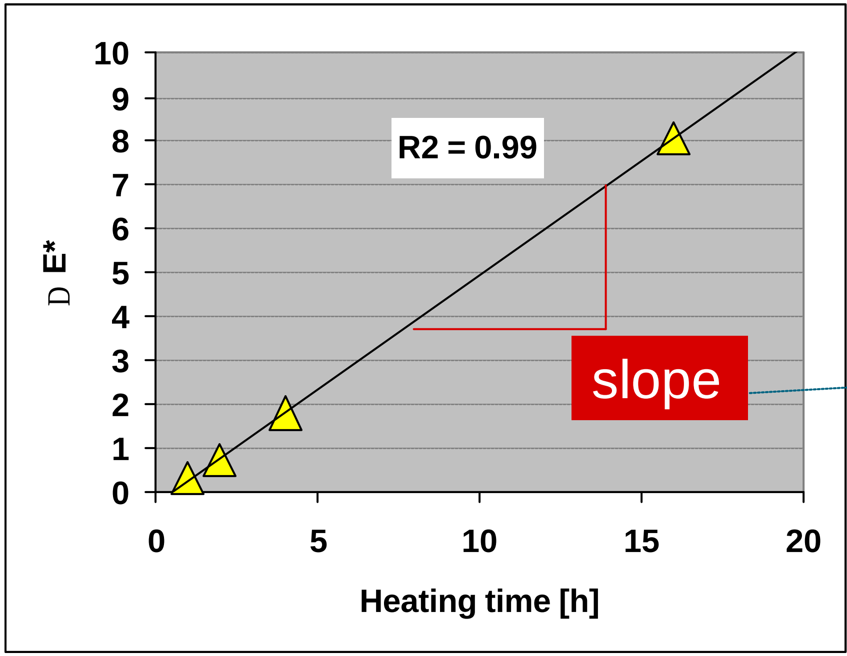
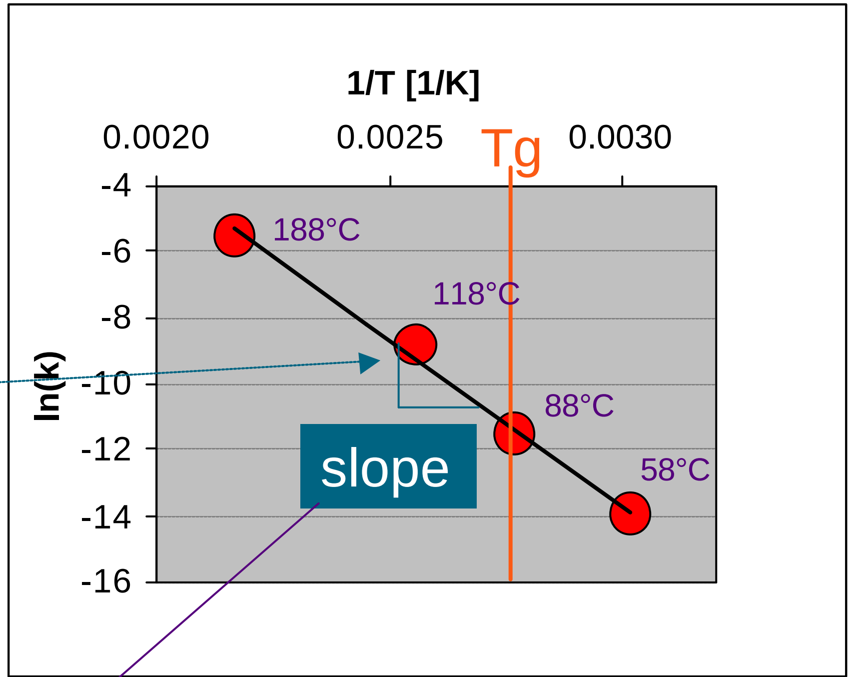
Color evolution at 118°C → Arrhenius plot





$$\ln(k) = \ln(k_o) - \frac{E_a}{R} \cdot \frac{1}{T}$$

E_a = 80 KJ/mol

Annealing leads to water release and change of physical state of matrix

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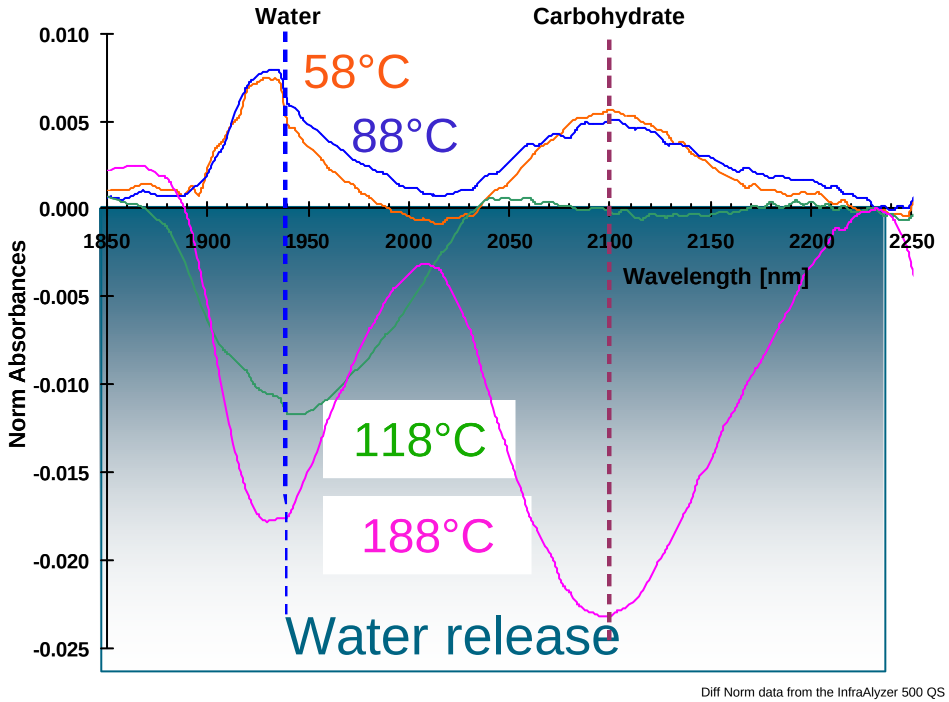
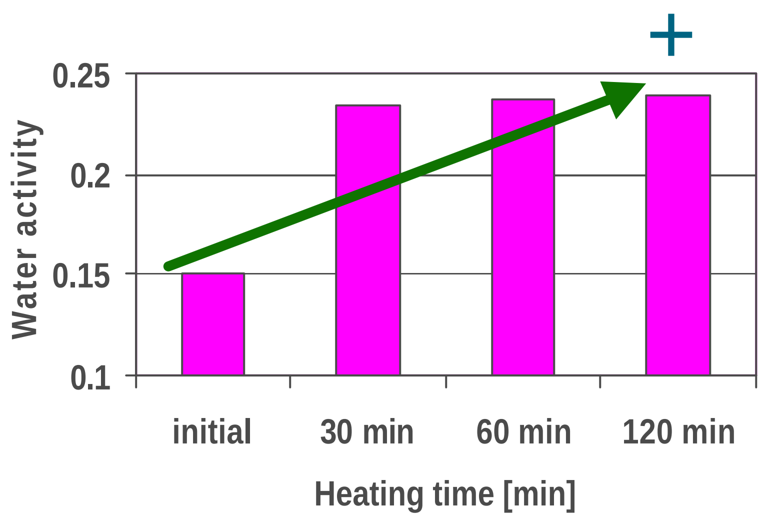
NIR spectra



Normalized Differences absorbance with initial maltodextrin IT-12

Water activity

Rotronic sensor



Concluding remarks

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- Annealing behavior has to be clear before thermodynamic and nanostructural studies

- Annealing via heat induces degradation / caramelization in carbohydrates

- Color and water measurements as proof of thermal degradation
  - Color formation already happens below glass transition and is Tg independent.
  - Increase of a_w by water release

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