Seminar

ADVANCES IN CELLULOSE-BASED MATERIALS IN FOOD PACKAGING

In collaboration with:

Aarhus University

VTT Technical Research Centre of Finland

Seminar under the scope of COST Action CIRCUL-A-BILITY CA19124, supported by COST (European Cooperation in Science and Technology).

COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.

CATÓLICA ESCOLA SUPERIOR DE BIOTECNOLOGIA PORTO

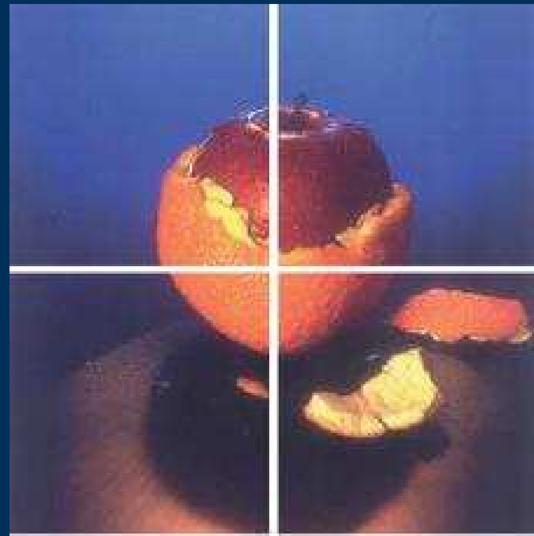
FROM FOSSIL TO FOREST

CIRCUL-A-BILITY

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

Funded by the European Union

CATÓLICA
FACULTY
OF BIOTECHNOLOGY
PORTO



Food protection, shelf-life and barrier properties

Fátima Poças

cost
EUROPEAN COOPERATION
IN SCIENCE & TECHNOLOGY
Funded by the
European Union
FROM
FOSSIL
TO
FOREST

Agenda

- The role of packaging
- Food protection requirements
- Barrier properties
- Specific aspects of barrier in paper and board
- Shelf-life estimation

The role of packaging

- Definition:
  - *Coordinated system of preparing products for transport, distribution, storage, purchasing and final use and …. Disposal !!!*
  - *"Any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties." Regulation (EC) nº 1935/2004*
- Food packaging represents approximately ½ of the total packaging by weight and 2/3 by volume

The role of packaging

- Packaging in an integral part of the product and consumer experience

- Packaging functions

  Protection - Security

  Preservation - Quality and safety

  Information - Traceability

  Service and convenience - Consumer

The role of packaging

- European Parliament resolution of 16 May 2017 on initiative on resource efficiency (2016/2223(INI))
- Food waste reduction target of 30% by 2025 and 50% by 2030 compared to the 2014 baseline, in line with the 2030 Agenda for Sustainable Development of the UN from 25 September 2015 (Goal 12.3)
- "… stresses the positive contribution of food packaging materials and solutions to the prevention of food loss and food waste along the supply chain, for example packaging that reduces food loss in transport, storage and distribution, and that preserves the quality and hygiene of food for longer, or that extends shelf life; … "

Examples

MAP convenience package for cheese.
Retail losses compared to unpacked counter products
5 % → 0.4 %

Source: FITNESS1

Vacuum skin package for roast beef.
Retail losses compared to MAP package 12 % → 3 %

Typical convenience packages for fruit and vegetables.
Retail loss reduction highly variable; it ranges from factor 12 down to factor 2

The role of packaging

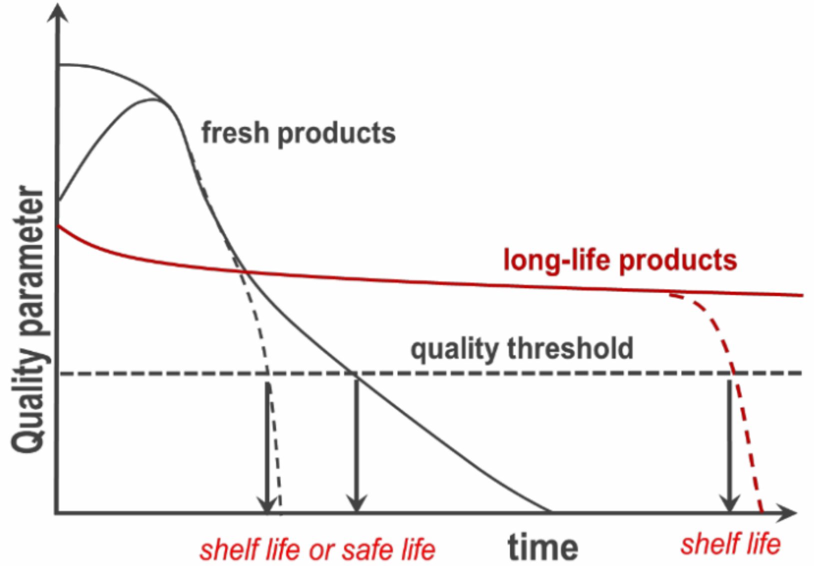
Avoid food losses

Generation of waste and litter

Consumption of limited resources

Food protection requirements

- Food quality over time
  - Long-life products: slow quality decay, continuous or fast after an induction period
  - Fresh products: fast decay due to own metabolism or microbial activity

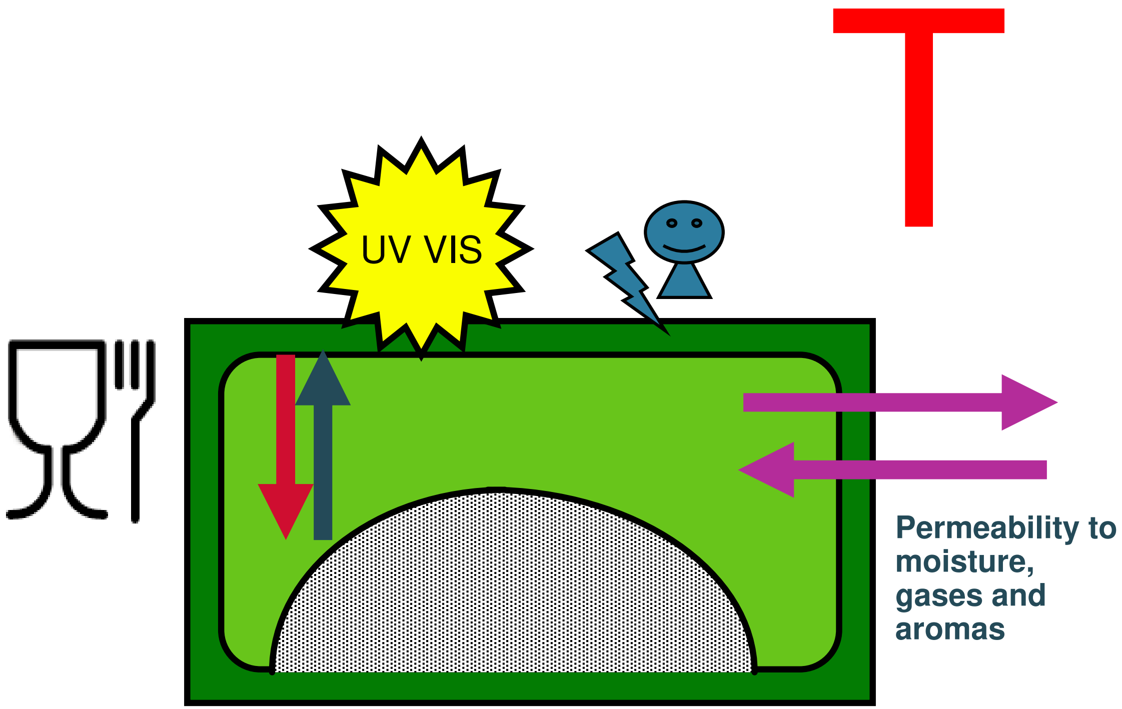


Food protection requirements

DECAY MECHANISMS FOR DIFFERENT FOOD GROUPS	
Dry fatty (Snacks, dry soups, cereals)	Fat oxidation
Dry low fat (Bakery products)	Water uptake
Compact fatty (Vegetable oils, butter)	Fat oxidation, water loss or uptake at slow rate
Dairy (Cheese, yogurt, milk)	Microbial growth, water loss, off-flavours
Convenience (sandwiches, RTE)	Microbial growth, water loss, fat oxidation
Fresh produce	Microbial growth water loss, textural changes
Fresh meat (Poultry, beef)	Colour changes, microbial growth
Prepared meat	Microbial growth, water loss, fat oxidation, colour changes
Frozen	Water loss, freezer burn, fat oxidation
Beverages (juices, soft drinks, beer)	Flavour and vitamins loss, colour changes,

Factors for quality lost

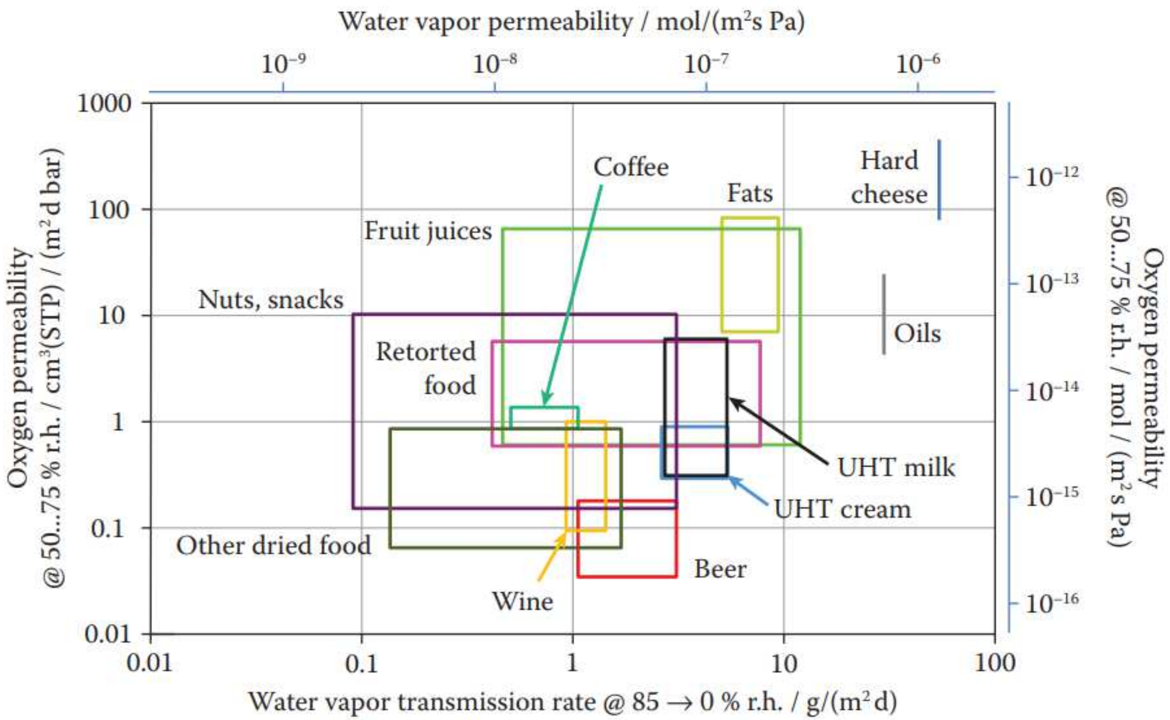
- Water balance
- Oxygen balance
- Impact of light
- Transport of other substances
- Loss of flavours
- Uptake of contaminants



How does packaging protect the food

- Moisture uptake or loss
  - Provides a barrier
- Oxygen effect
  - Provides a barrier
  - Modified atmosphere to reduce the O_2 in head space
- Effect of light
  - Different degrees of barrier and wavelengths
- Microbial degradation
  - Integrity (tightness)
  - MAP, active packaging

Protection requirements

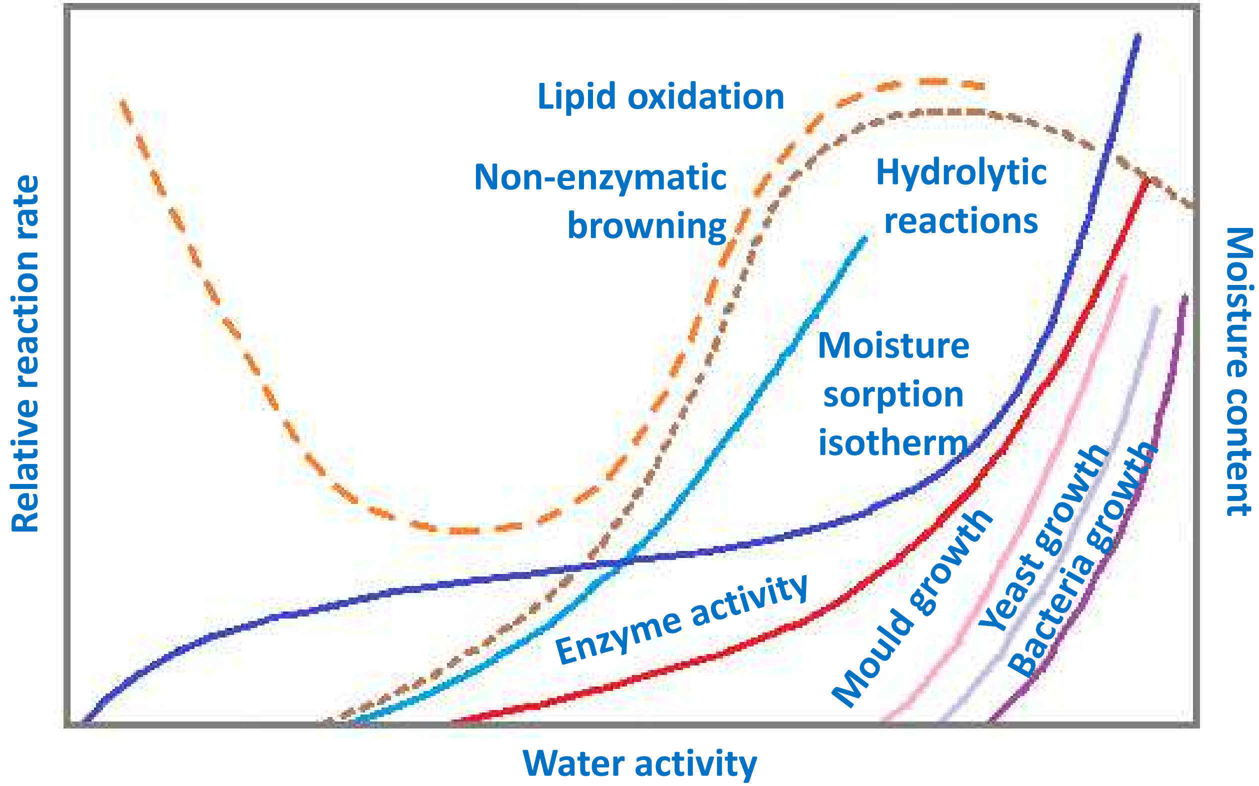


Source: Preeti Singh, Ali Abas Wani, Horst-Christian Langowski, 2017

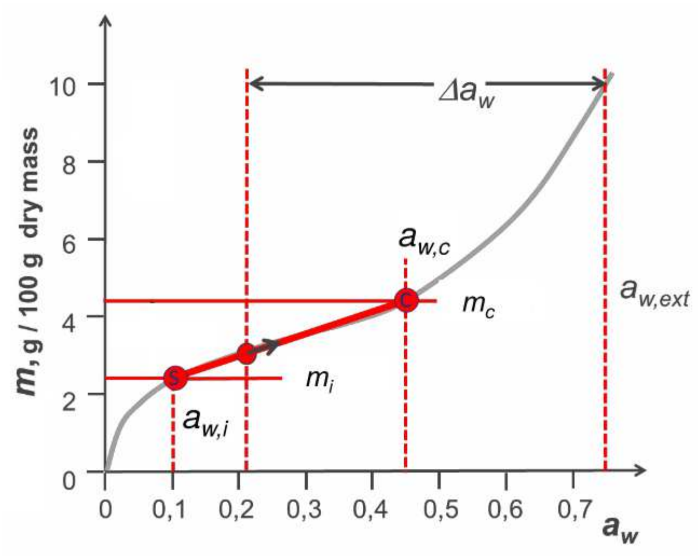
Definitions - moisture in food

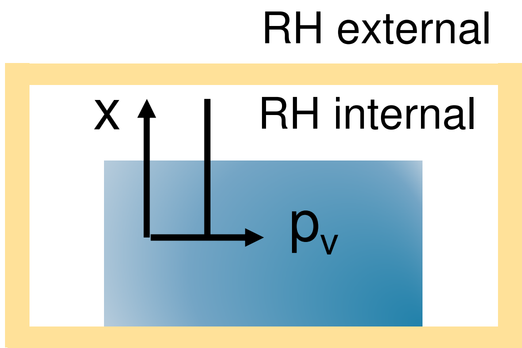
- Water activity (aw)
  - Indication of the free water (bonding strength of water in the product)
  - Is the ratio between the vapor pressure in the food and the vapor pressure of pure water under identical conditions (saturation vapor pressure)
  - Corresponds to the relative humidity of the air just above the product in equilibrium at a given temperature
- Water content or moisture
  - Percentage of water in the product
  - Dry or wet basis

The importance of moisture

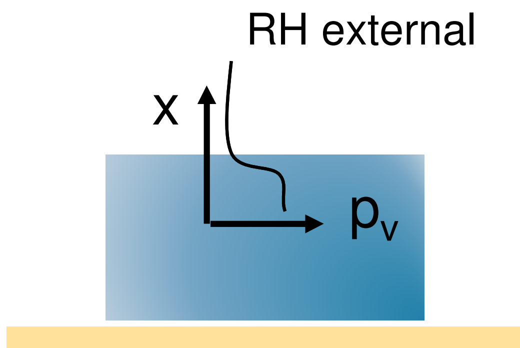


The importance of moisture





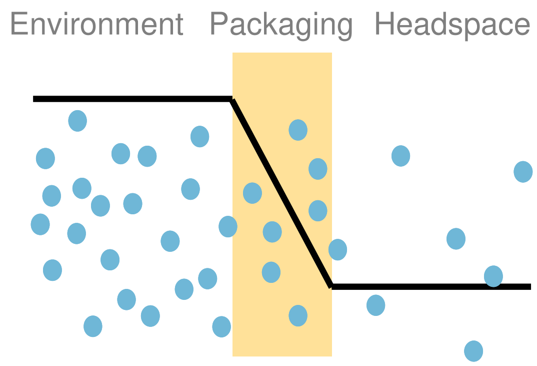
Equilibrium



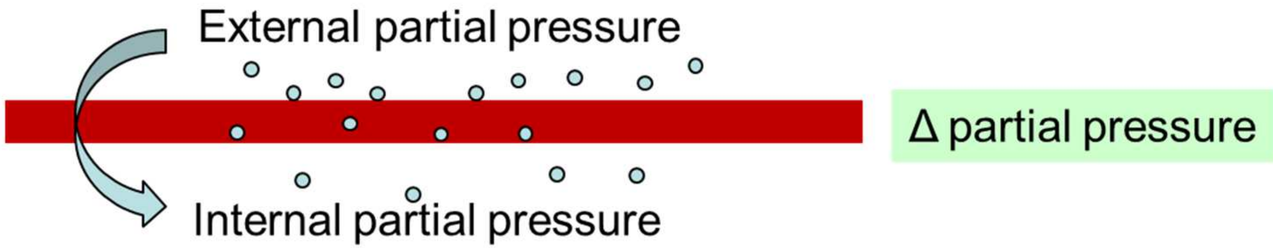
Desiccation

Permeation – physical principles

1. Permeant dissolves in the material: Henry´s law
   - The solubility of a gas in polymers follows Henry´s law (concentration in the material is proportional to the partial pressure of the permeant in the gas phase)
   - Some substances may plasticise or swell the polymer, in which case Henry´s law is not valid
   - In semi-crystalline polymers, dissolution occurs only in the amorphous phase
2. Permeant diffusion through the polymer: Fick´s laws of diffusion
   - When there is a concentration gradient between each side of the material, the molecules diffuse from the high concentration side to the low concentration
3. Permeability is the product of diffusion and solubility



Packaging material barrier - definitions



Material

Package:
Surface area
Thickness

Conditions:
Temperature
Relative humidity
Time

Packaging barrier – definitions and units

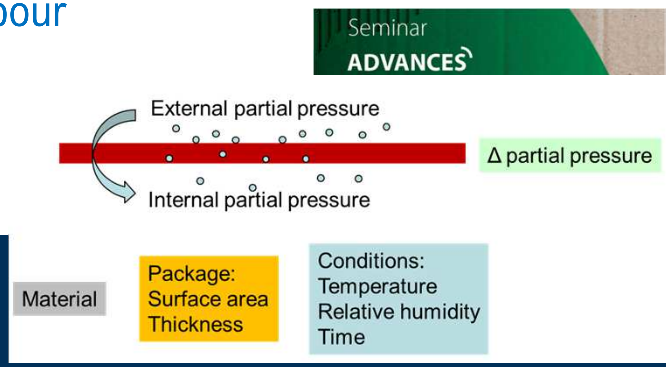
- Permeation occurs when there is a difference in concentration or partial pressure of gas/vapour between inside and outside the package
- Permeability = Amount of gas/vapour that crosses the packaging wall, per unit area, per unit of time and per unit of differential pressure of gas/vapour, normalized per thickness

  g μm/m^2/day/bar or cc μm/m^2/day/bar

  in SI units: mol/m/s/Pa
- Permeance = Amount of gas/vapour that crosses the packaging wall, per unit area, per unit of time and per unit of differential pressure of gas/vapour

  g /m^2/day/bar or cc μ/m^2/day/bar
- Transmission rate – Amount of gas/vapour that crosses the packaging wall of certain thickness, per unit area, per unit of time under certain conditions of differential pressure of gas/vapour

  g/m^2/day or cc/m^2/day it depends on the testing conditions

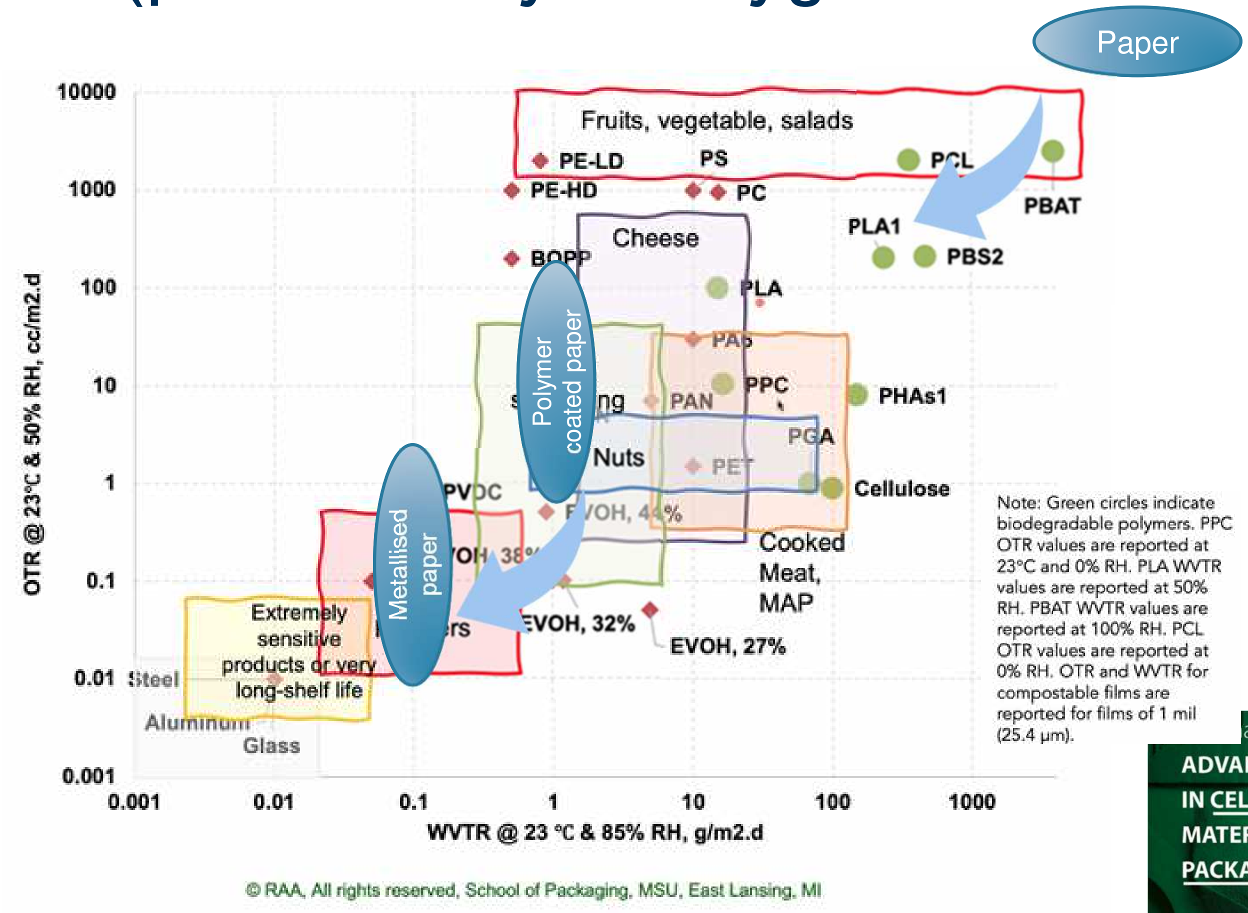


Permeability of polymers

- Polarity – interaction between the material and the permeant
    - A polar permeant will dissolve more readily in a polar material
- Crystallinity
    - Permeants will not dissolve in the crystalline fraction of a material
    - The apparent diffusion rate is reduced in semi-crystalline polyemers as compared to amorphous
- Density
    - Denser materials have lower permeation rates
- Glass transition temperature
    - The higher the difference between the Tg and the testing temperature, the slower the diffusion

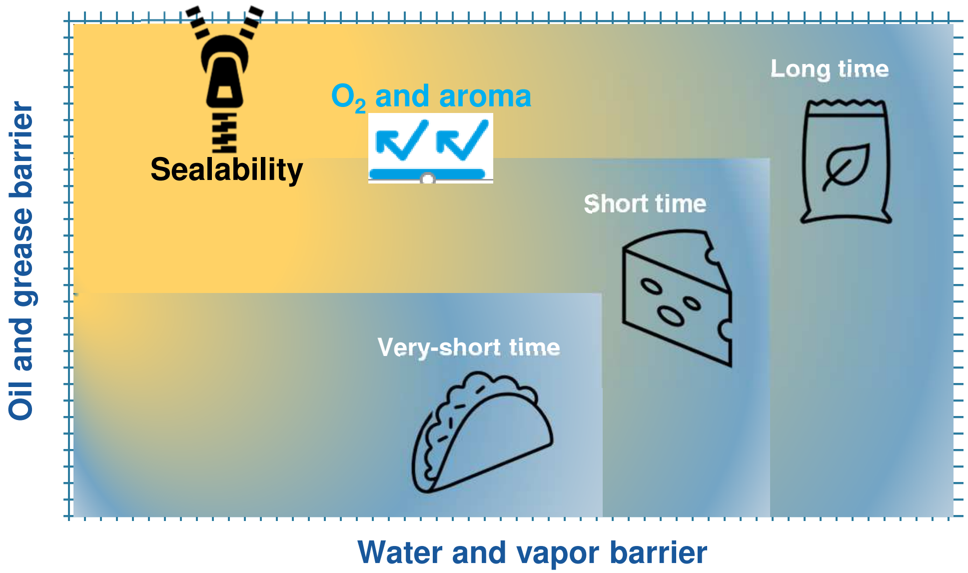
Barrier requirements (permeability to oxygen and moisture)

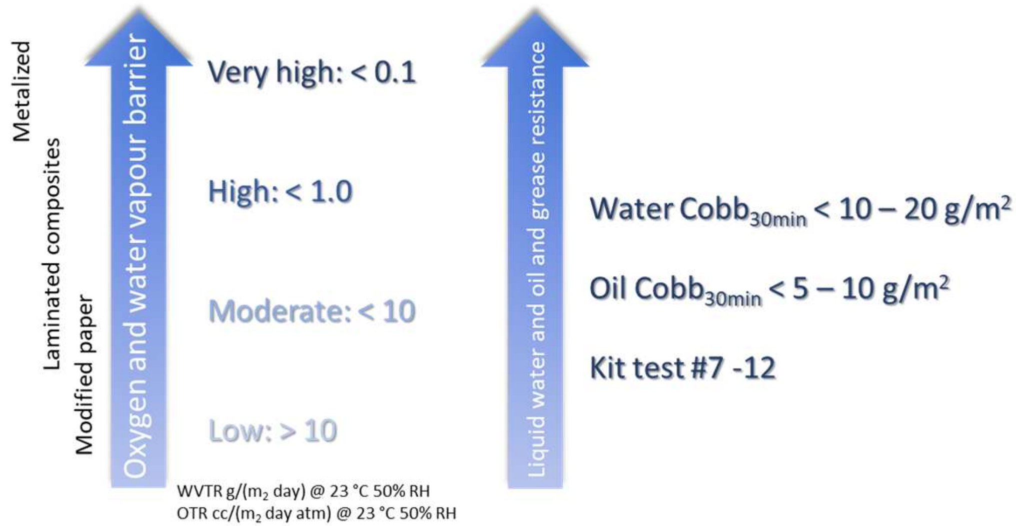
- Specific for food types
- Impact in shelf-life



Packaging requirements for paper and board

- Barrier to grease, oxygen, water vapour, water



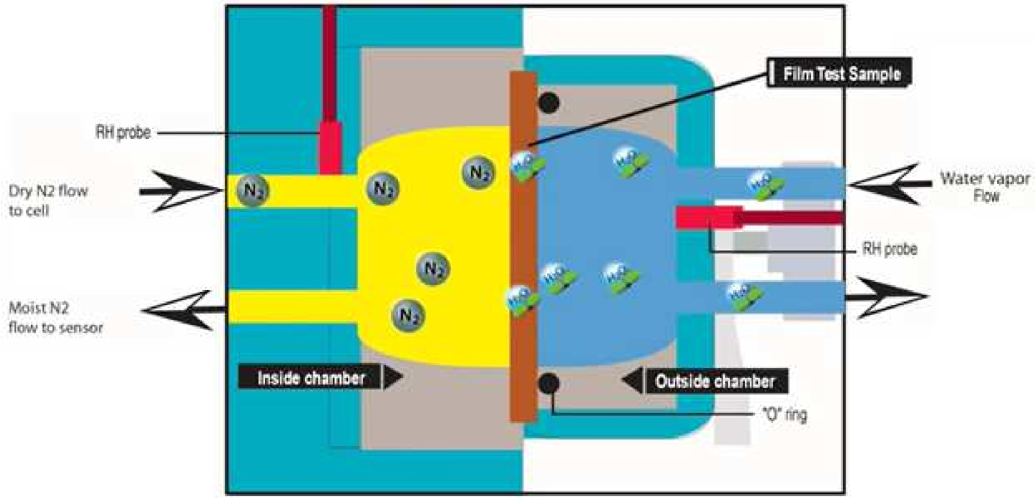


Measuring permeability

- Different methods and standards
- Principle: permeant at high concentration is applied in one side of the material; the amount of permeant on the other side (lower concentration) is measured, over time, for a certain surface area
- Standard conditions for measurement:
  - T: 23 ºC, 38 ºC
  - HR: 0, 50 or 90%
  - O_2: 100% or 21% (air)

Isostatic method

- A testing chamber is separated in two parts by the sample
- A constant partial pressure gradient of the permeant is applied in each side by a continuous flow of the permeant in one side and an inert gas on the other side
- The permeant molecules cross the material and are carried by the gas to the sensor:
  - Infra red for moisture and CO_2
  - Coulometric for moisture and oxygen
- Main standards: ASTM D3985; ASTM F1249



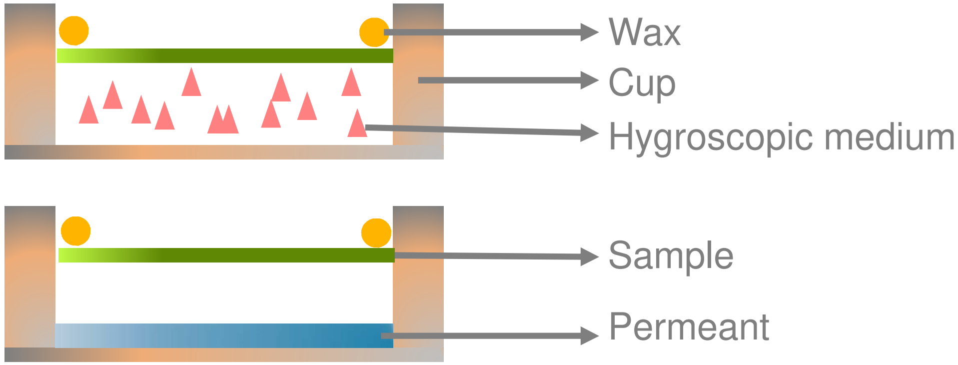
WVTR infrared sensor

Seminar
ADVANCES
IN CELLULOSE-BASED
MATERIALS IN FOOD
PACKAGING
22 to 23 May 2023

Oxygen – coulometric sensor

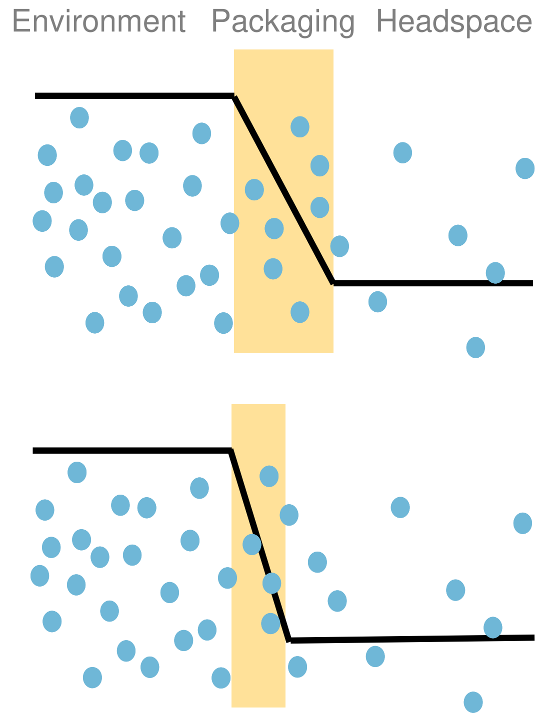
Moisture, solvents – gravimetric method

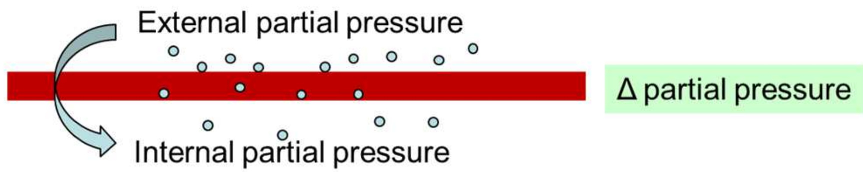
- Cup is sealed by the sample, containing either a desiccant or the permeant
- External temperature and relative humidity are set to constant
- Weight loss or gain is measured
- The slope of the weigh gain/loss curve is used to calculate the rate
- ASTM E96; ISO 2528



Testing parameter - thickness

- The lower the thickness
  - higher the concentration gradient
  - higher diffusion rate and transmission rate
- Permeability is independent of thickness
- Permeance is inversely proportional to the thickness
- Permeability values can only be applied to homogenous material





Material

Package:
Surface area
Thickness

Conditions:
Temperature
Relative humidity
Time

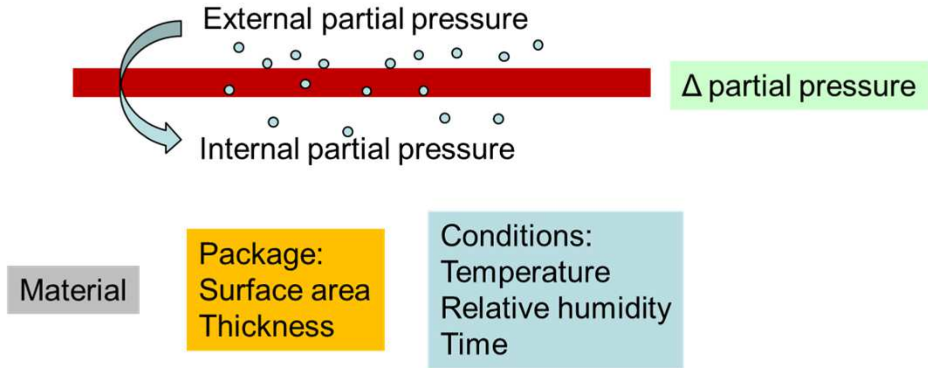
Testing parameter - temperature

- Temperature affects both solubility and diffusion rate
- Permeation rate is affected by temperature
- Many cases the Arrhenius 'law can be applied
- Increasing 10 ºC leads to double the transmission rate

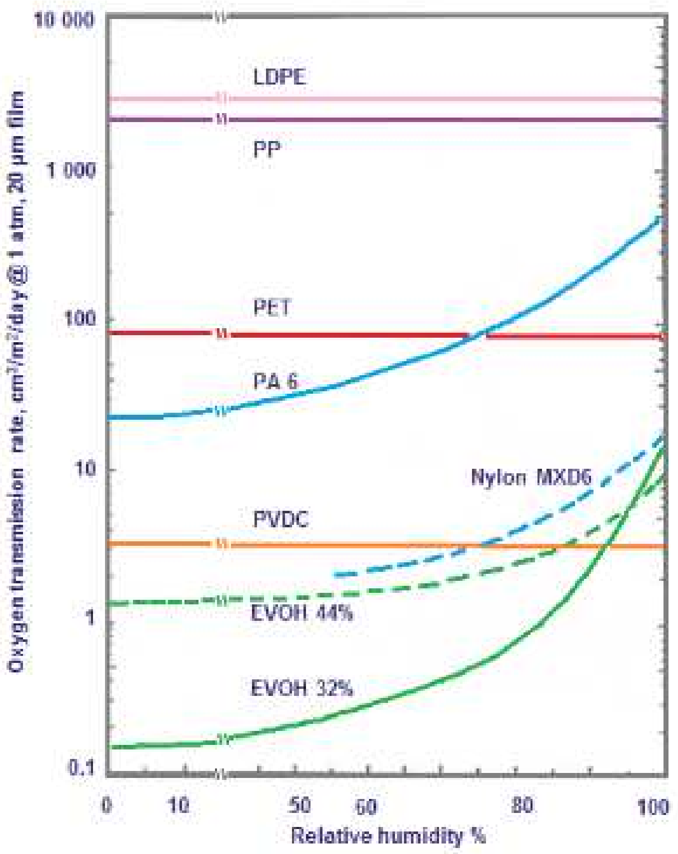
$$k = k_o e^{-\frac{E_a}{RT}}$$

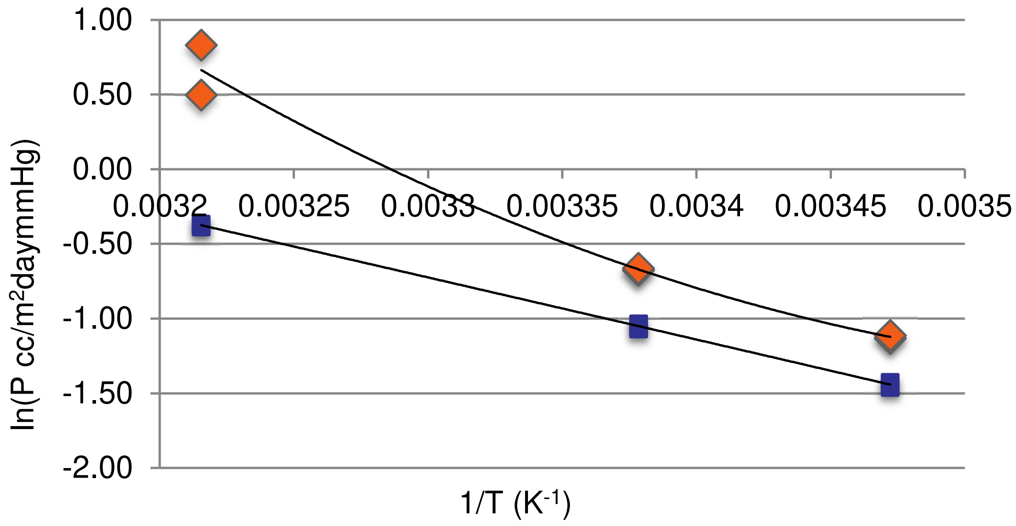
Testing parameter – partial pressure gradient

- For materials for which Henry’s law is applicable, measuring with higher concentration of permeant will proportionally increase the solubility and hence the permeation rate
- This is not applicable to moisture sensitive materials
- Example: testing OTR with 100% oxygen yields a permeation rate ~ 5 times higher than with 21% oxygen



Testing parameter – relative humidity



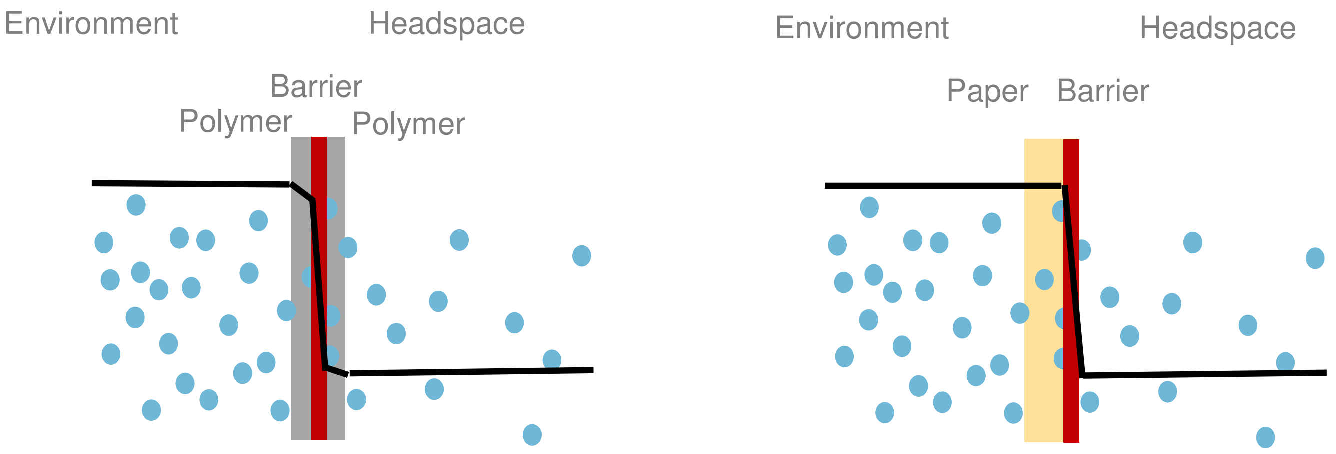


Effect of the temperature and relative humidity in the permeability to oxygen, of PE/PA film:
■ Experimental data at 0% relative humidity
♦ Experimental data at 100% relative humidity

Reporting materials barrier

- Permeability values apply to homogeneous structures following Henry´s law
  - SI = mol/m/s/Pa
  - Always report testing temperature and relative humidity
- Permeance is reported for a certain thickness
  - SI = mol/m^2/s/Pa
  - Always report testing temperature and relative humidity and thickness
- Transmission rate is reported for a given structure
  - Common units:
    - Oxygen: cc/m^2/day
    - Moisture: g/m^2/day
  - Always report testing temperature and relative humidity, thickness and driving force

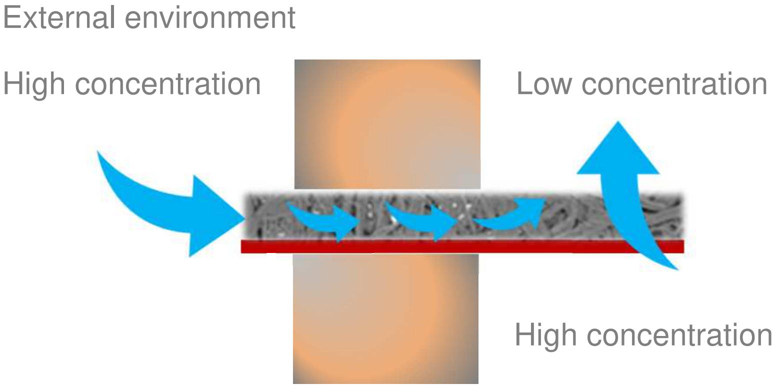
Permeability of multilayer structures



$$TR_M = \frac{1}{\sum \frac{1}{TR_i}} = \frac{1}{\sum \frac{t_i}{P_i}}$$

Specific aspects for coated paper testing – edge effect

- Paper barrier provided by thin coatings on one of the surface
- Paper is hygroscopic and swells when exposed to high humidity
- Permeant can bypass the barrier by entering through the edges of the sample
- Edge effect affects significantly the result
- Orientation of sample is important
- Testing should be performed with the barrier facing the sensor side or by protecting the edges with a high barrier material
- Important to consider when comparing testing of films with performance of packages



Specific aspects for coated paper testing – moisture effect

- Paper is hygroscopic and absorbs water under humid conditions
- Paper expands when absorbs water
- Strain-induced cracking of coatings (ex: metalized paper)

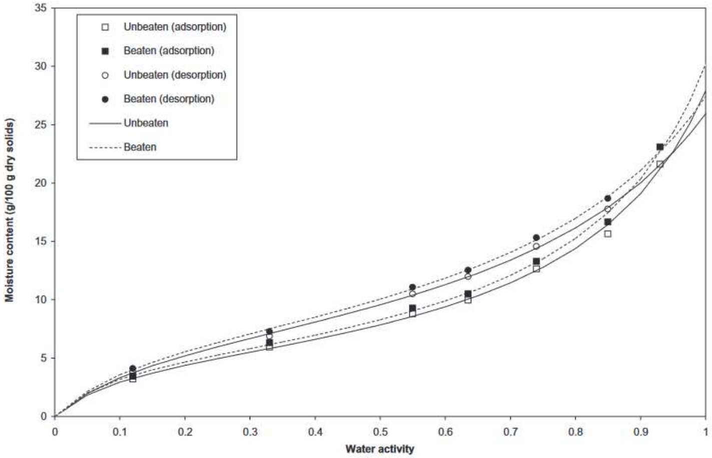


Figure 2. The effect of beating on moisture sorption isotherms of pulp.[8]

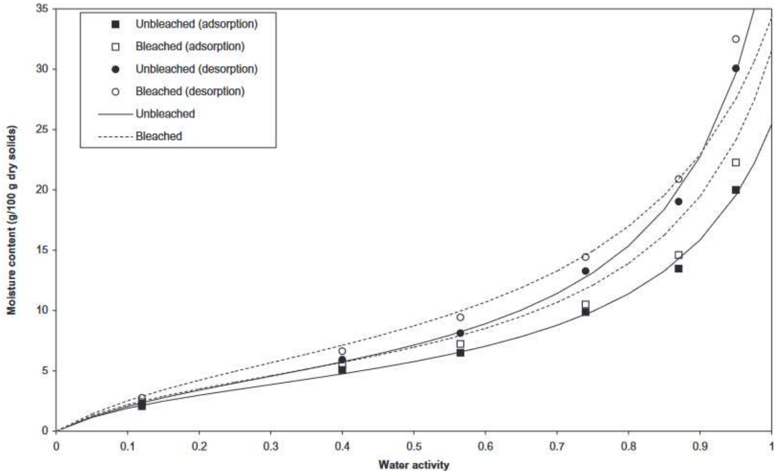


Figure 3. The effect of bleaching on moisture sorption isotherms of pulp.[8]

Using barrier properties to estimate shelf-life

- Product degradation mechanisms and kinetics
  - Moisture uptake
    - Sorption isotherm
    - Critical moisture content (texture, chemical reactions, microbial growth)
  - Oxygen consumption
    - Critical oxygen consumption level (sensory properties, oxidation, vitamin content, etc.)

Using barrier properties to estimate shelf-life

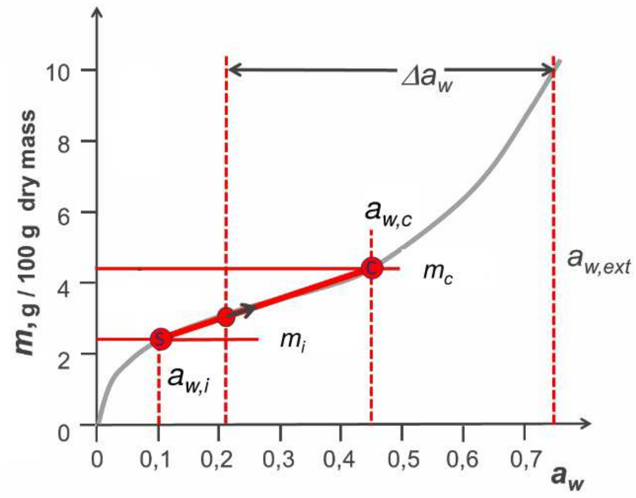
- Moisture uptake

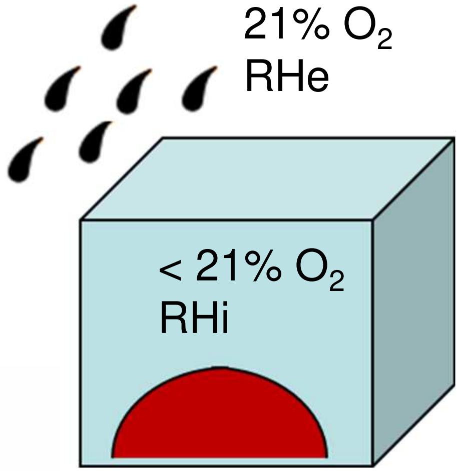
$$Ms\frac{dW}{dt} = \frac{P}{l}A(p_e - p_i)$$

$$p_e = p_s \times HR_e/100$$

$p_i = f(W)$ moisture sorption isotherm

$$\int_{Wo}^{W}\frac{dW}{(p_e - f(W))} = \frac{P}{lMs}At$$





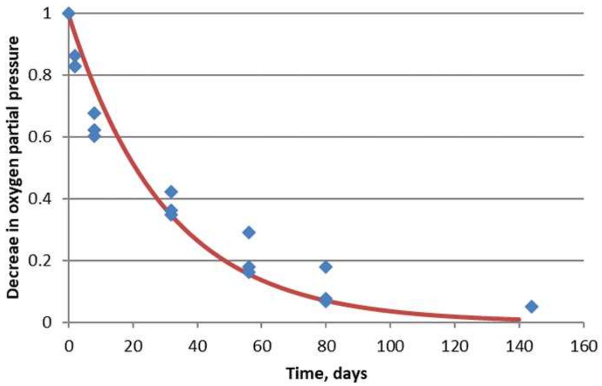
Ms - mass of product dry basis weight, g
W – moisture content g water/g dry product
t – time, days
P – permeability gμ/m2 day mmHg
L – thickness, μm
A – area, m2
p_e p_i – partial pressure water vapor
Ps – saturation pressure water vapor, mmHg
Wo – initial moisture content
Weq – equilibrium moisture content

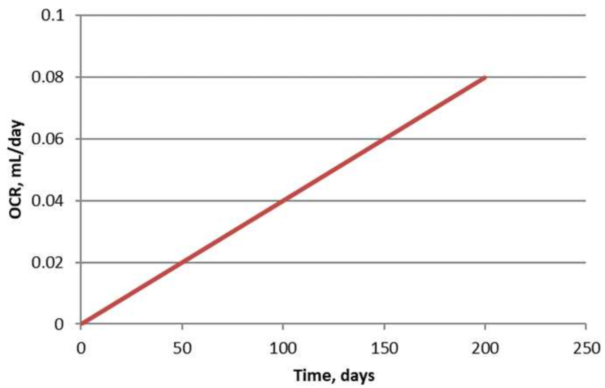
Using barrier properties to estimate shelf-life

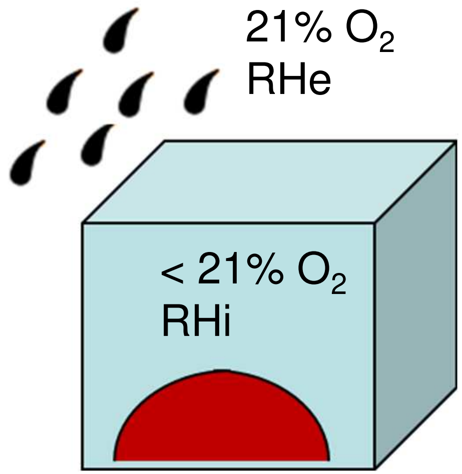
- Oxygen uptake

$$\frac{P}{l}A(p_e - p_i)dt = OCR(p_i)M_s dt + \frac{VH_s}{P_e}dp_i$$

OCR – oxygen consumption rate, function of p_i
In cc/day/g

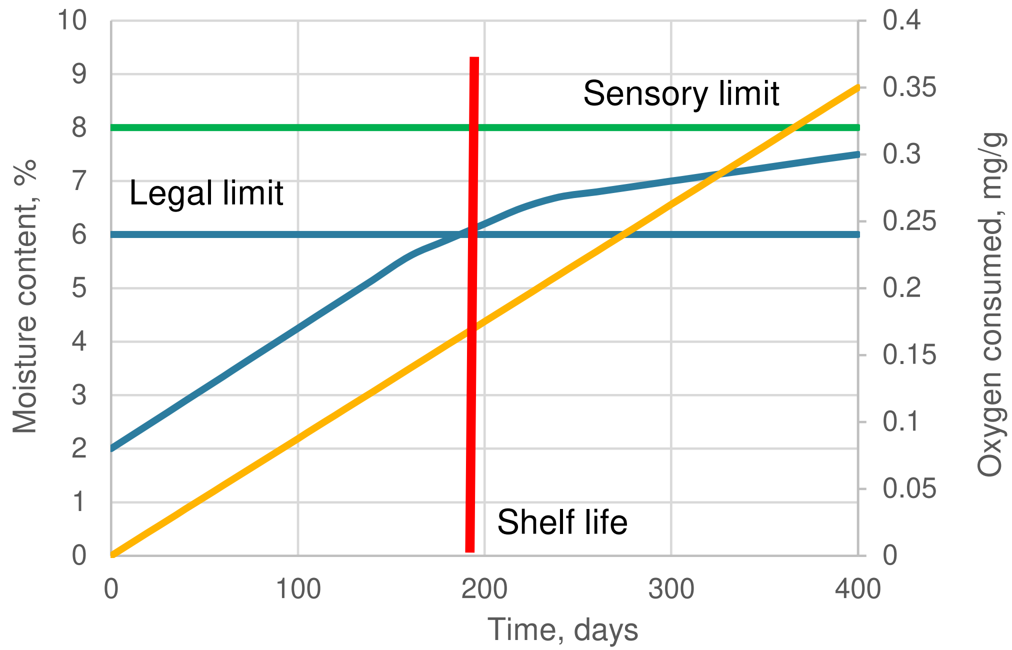






Ms - mass of product dry basis weight, g
W – moisture content g water/g dry product
t – time, days
P – permeability gμ/m2 day mmHg
L – thickness, μm
A – area, m2
p_{ext}, p_{int} – partial pressure water vapor
Ps – saturation pressure water vapor, mmHg
Wo – initial moisture content
Weq – equilibrium moisture content

Simulation of shelf life of a dry product



Conclusions

- Oxygen and water vapour barrier are key properties for the role of packaging
- Different measures and reporting ways of barrier properties of materials
- Testing barrier of paper is not straightforward
- Edge effect and hygroexpansion should be taken into consideration
- Use of models to estimate shelf life

Thank you for your attention

fpocas@ucp.pt

CINATE - Laboratório de Análises e Ensaios a Alimentos e Embalagens

cinate@porto.ucp.pt