ANALYSIS AND MODELLING OF ACTIVE BARRIER MATERIALS CONTAINING OXYGEN SCAVENGERS

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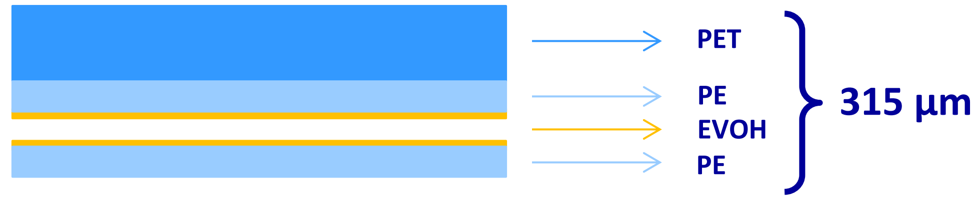
OUTLINE

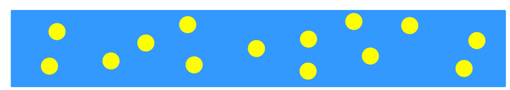
- Aims
  - Testing Oxygen Scavengers (OS) to increase shelf life of meat stuffed “Ravioli”
- Experimental results
  - Oxygen concentration inside the package
- Modelling results
  - Diffusion
  - Reaction
  - OS films Behavior
- Conclusion

TESTING "RAVIOLI" SHELF LIFE

- Commercial multilayer system



- Amorphous PET monolayer with Oxygen scavengers

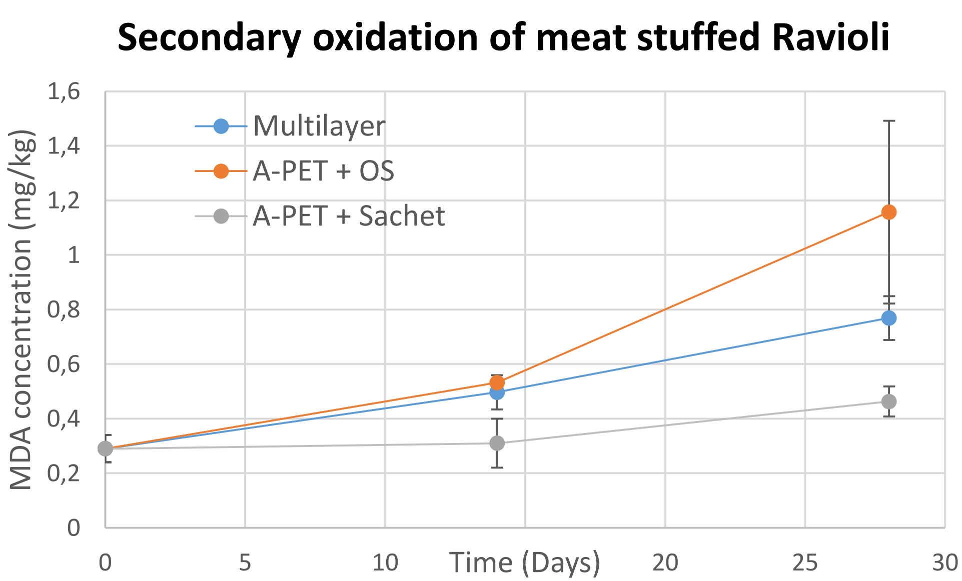


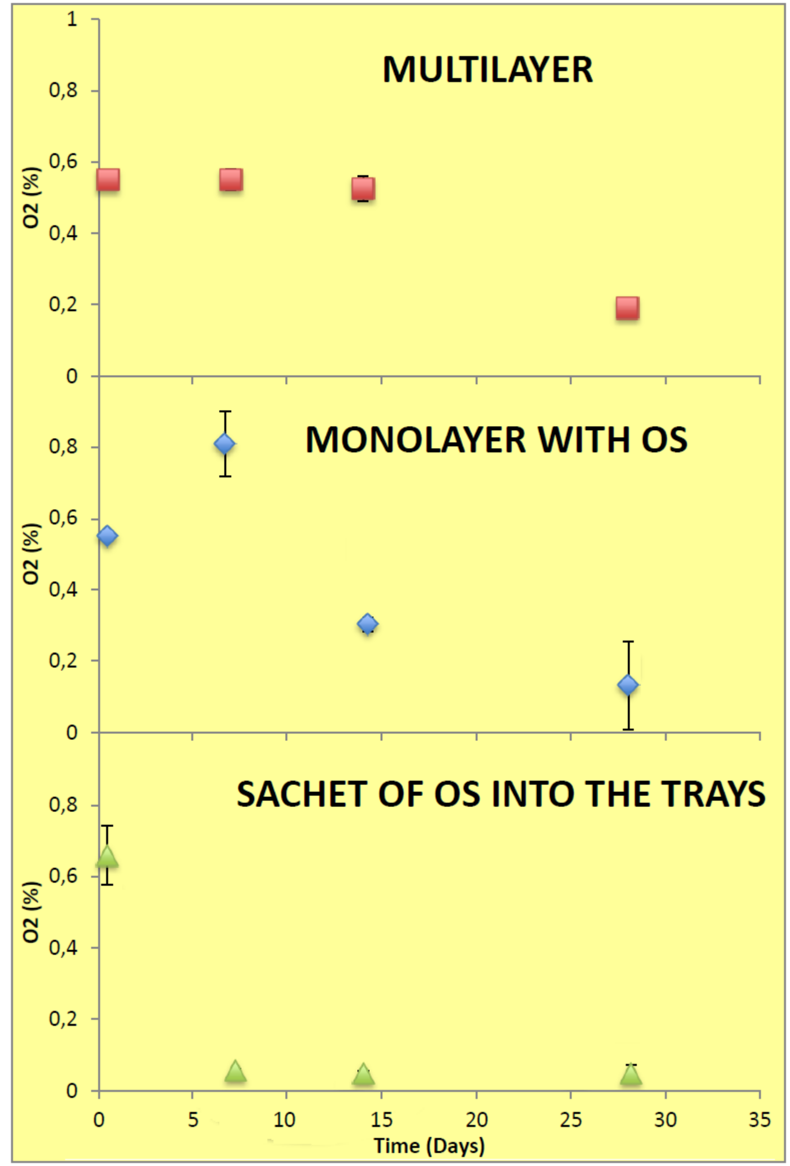
- Amorphous PET + Oxygen scavenger in sachets within the package

TESTING "RAVIOLI" SHELF LIFE

- Sachets show the best properties

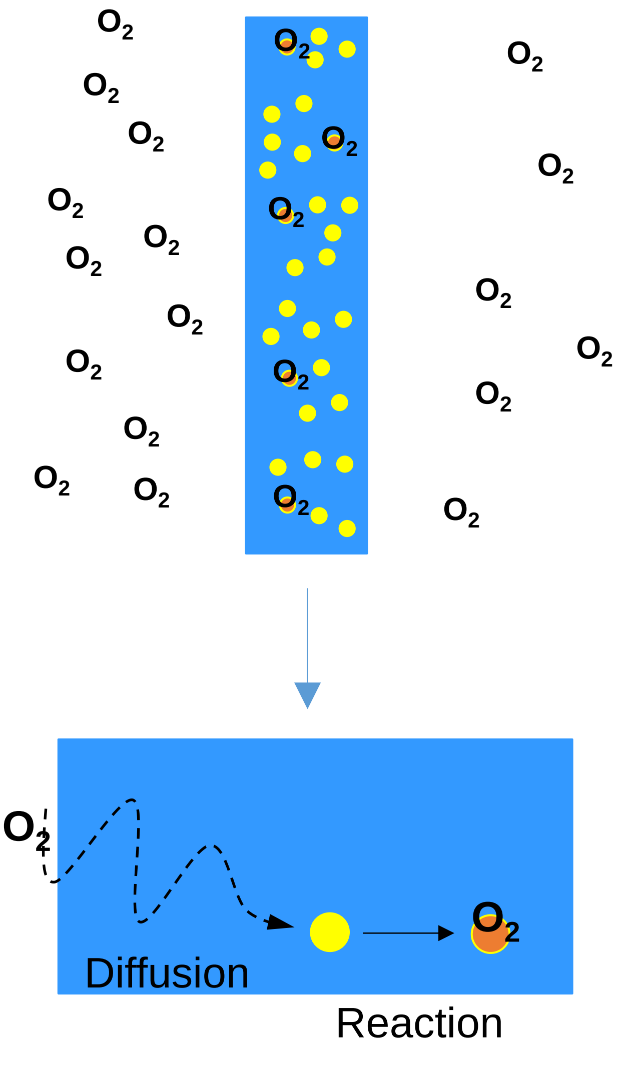
- The monolayer system with oxygen scavengers results very similar, if not worse, than the multilayer barrier materials.





O_2 SCAVENGING PROCESS

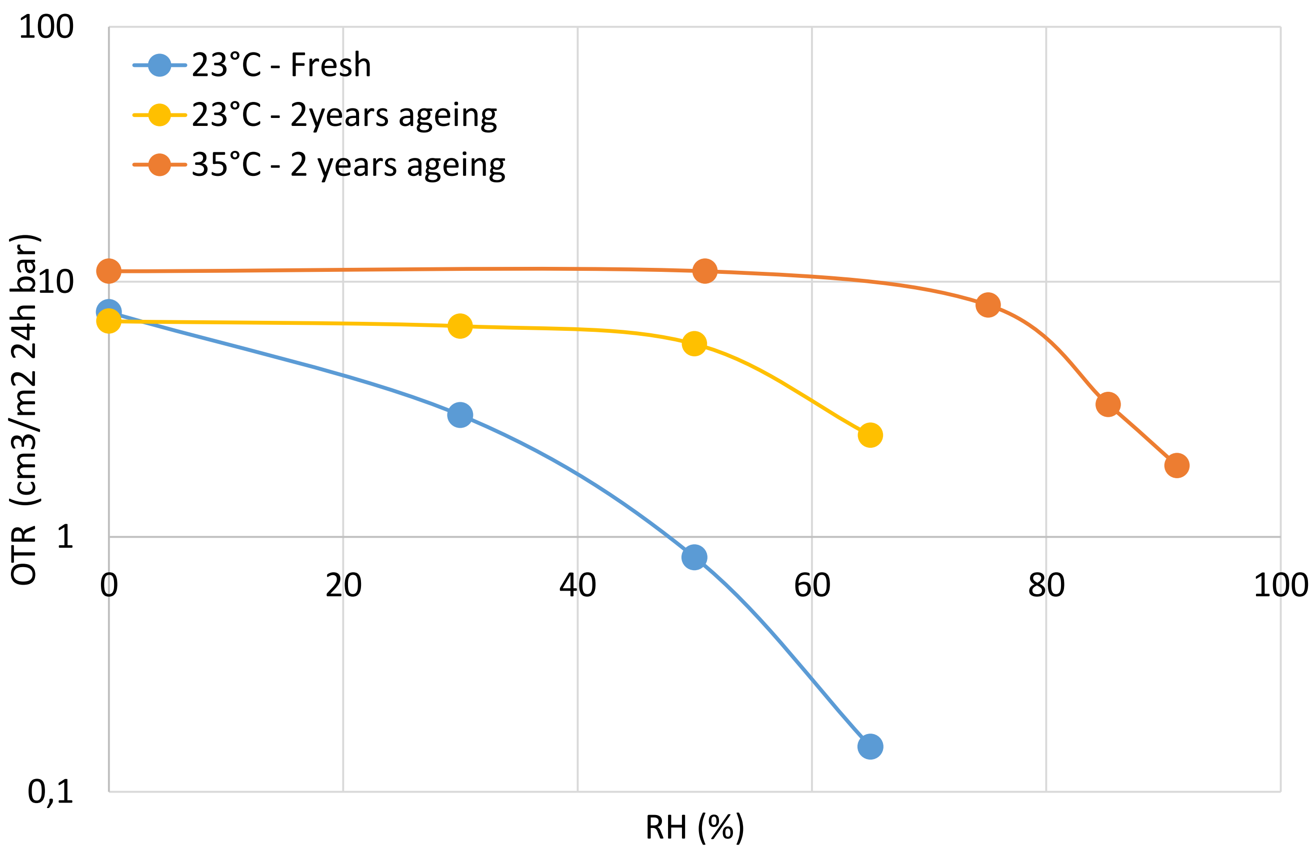
- Oxygen scavengers based composite films follows a complex mechanisms: oxygen have to diffuse into the materials in order to reach, and react with, the scavenger.
- Deeper understanding of the different process involved in the overall mechanism is needed to understand the observed behavior:
    - Is mass transport a limiting factor?
    - What is the reaction rate of the scavengers with Oxygen?
    - Are there other parameters to be considered (RH, temperature… etc.. etc…) ?



TEMPERATURE RH AND TIME

- Oxygen permeation experiments at different humidity and temperatures

$$OTR = \frac{J}{p_{out} - p_{in}}$$



- Water is needed for the oxygen scavenger to be active.
- The material is subject to ageing and loses its activity with time
- Temperature increases the overall oxygen permeability

DIFFUSION

- Oxygen and water diffusivity and solubility in amorphous PET have been measured.
- Fick's Law has been used to solve mass balance with different boundary conditions and to evaluate penetrant diffusion coefficients

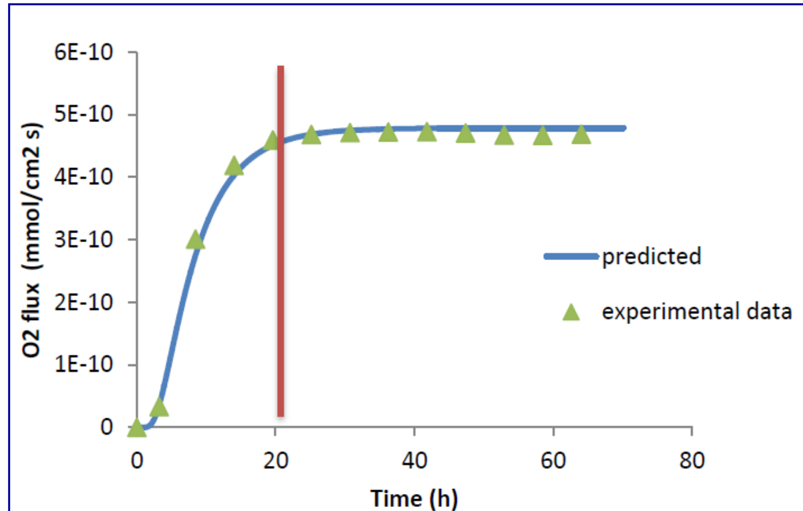
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

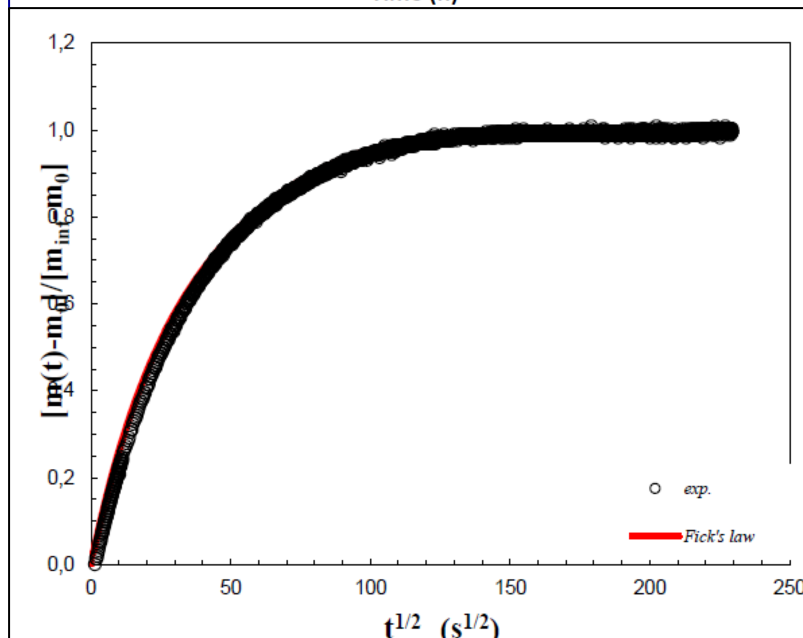
For Oxygen:

D = 4.6 E^{-9} cm^2/s
S = 0.00312 $mmol/cm^3$

For water:

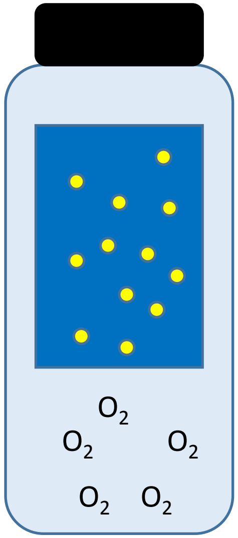
D = 7.5 E^{-9} cm^2/s
S = 0.2015 $mmol/cm^3$





REACTION

- Analysis of film response in a closed system allowed to model the reaction rate.



T = 23° C ; RH = 100% ; O_2 concentration = 6; 10; 20 $\%_{vol}$

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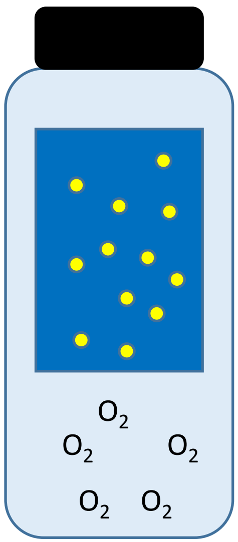
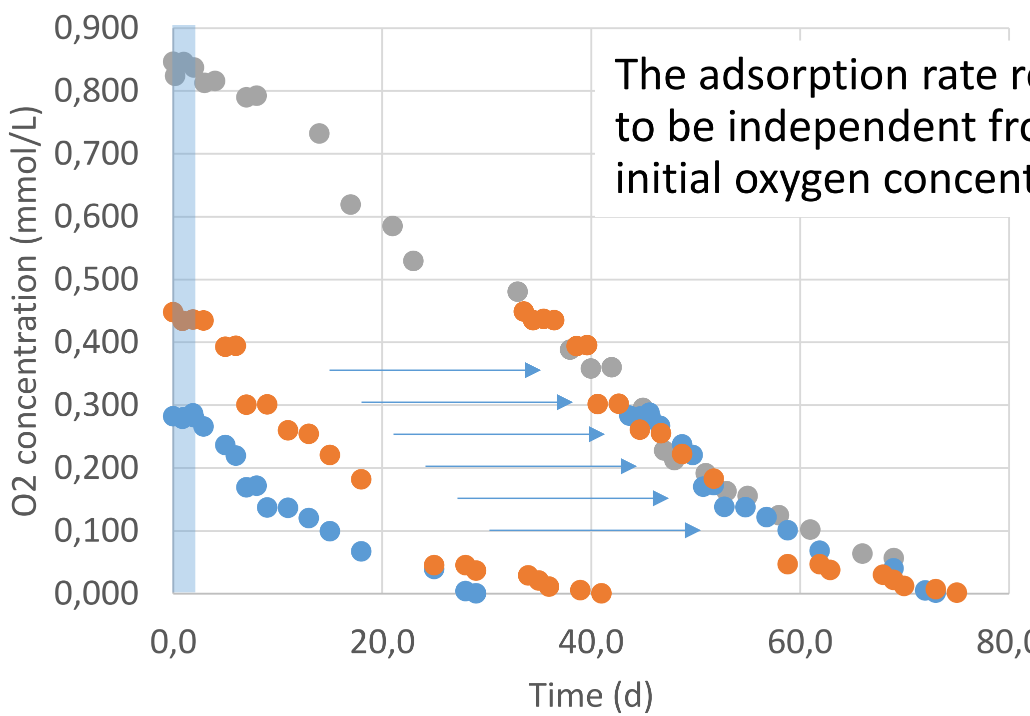


A lag time of about 2 days is observed before oxygen scavenger becomes active



The adsorption rate results to be independent from the initial oxygen concentration

REACTION

- The analysis of the kinetic behavior can be made by considering mass balance equation in a closed systems (neglecting mass transport resistance):

$$\frac{dC_{O_2}}{dt} = -R \qquad t = 0 \Rightarrow C = C_0$$

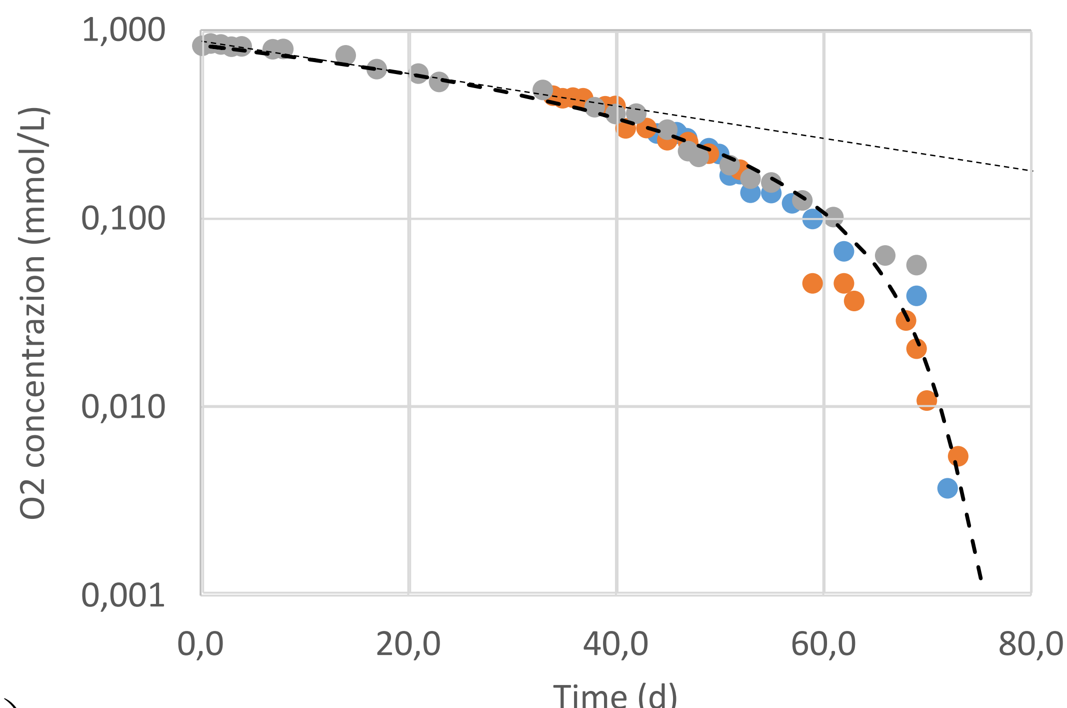
- If $R = k\,C$ (1st order system)

$$\Rightarrow \quad C_{O_2} = C_0 \exp(-kt)$$

- If R follows Michaelis Menten equation:

$$\frac{dC_{O_2}}{dt} = -\frac{v_{Max} C_{O_2}}{K_M + C_{O_2}}$$

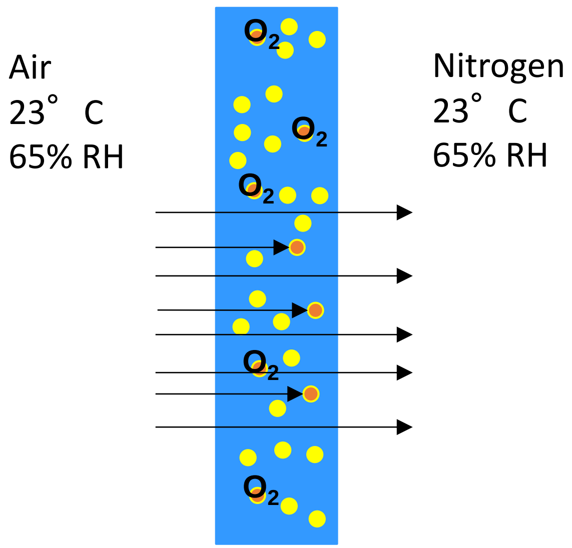
$$\Rightarrow \quad t = \frac{K_M}{v_{Max}} \ln\left(\frac{C_0}{C_{O_2}}\right) + \left(\frac{C_0 - C_{O_2}}{v_{Max}}\right)$$

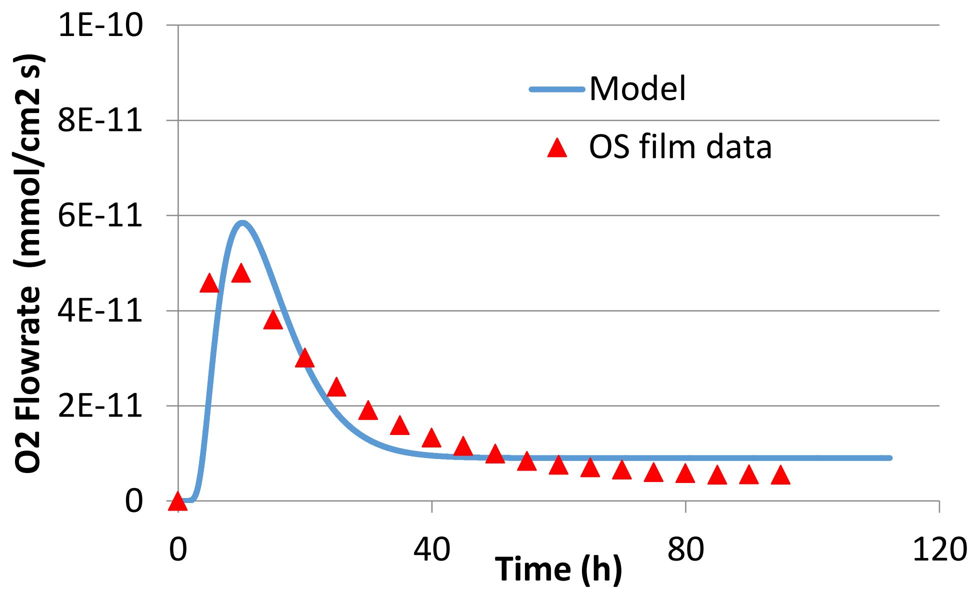


Vmax (mmol/cm^3/s)	1,50E-10
K_M(mmol/cm^3)	2 E-05

DIFFUSION + REACTION

- Analysis of film response in a controlled permeation experiments confirmed the presence of a lag time for scavenger activation.





$$\frac{dC_{O_2}}{dt} = D\frac{\partial^2 C_{O_2}}{\partial x^2} - R(t-\tau)$$

Vmax ($mmol/cm^3/s$)	3.41E-8
K_M($mmol/cm^3$)	2 E-07
τ (h)	4.8

The model gives a good qualitative description of experimental data, but more information are needed to explain the observed delay in scavenger activation.

CONCLUSION

- Different active packaging have been considered for fresh ravioli preservation
  - OS films showed poor properties if compared with sachets
- Experimental tests and modelling were conducted to better understand the oxygen permeability in the PET+OS films
  - Results showed that Michaelis Menten type kinetics can be used to describe reaction between OS and oxygen
  - Complex interaction between diffusion need to be considered to properly analyze the material permeation behavior
  - A delay in the activation of OS is evidenced which is the main cause of the poor results obtained by this type of packaging.

THANK YOU

QUESTION?