PACKALL

PackAlliance:
European alliance for innovation training
& collaboration towards future packaging

Linking Academy to Industry.

Training program: modules

- New materials and biomaterials
- **Eco-design & novel manufacturing processing**
- Citizen and Consumer Engagement
- Residue management and valorisation

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Course 1 - Novel Manufacturing Processing for Packaging Systems

5. Technological requirements of new sustainable packaging solutions (0.3 ECTS)
    5.1. Analysis of the technological trends for the food packaging in the next future

    5.2. Technological requirements of new sustainable packaging solutions

        Mechanical and barrier properties

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Mechanical Properties

The relationships between the loads applied to a material and the deformations induced by the application of these loads determine the mechanical behavior of a material.

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Mechanical Properties

To describe the behaviour of a solid after the application of a force, it is convenient to classify the type and direction of the force in question:

Static forces: those applied constantly or for discrete times;

Dynamic forces (or impact): those that are exhausted in a short time as a result of an impact or vibration, in order to verify the ability of the material to absorb the energy of the impact;

Cyclic forces: those in which the load values vary between a minimum and a maximum value for a large number of times.

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Mechanical Properties

- Tensile behavior (elasticity and plasticity)
- Compression Behavior
- Toughness and Resilience
- Hardness
- Impact resistance
- Properties of friction

Tensile behaviour

Tensile tests are the most commonly used tests to determine the mechanical properties such as:

- Young’s modulus
- Poisson's ratio
- Yield strength
- Elongation at break
- Toughness.

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Tensile behaviour

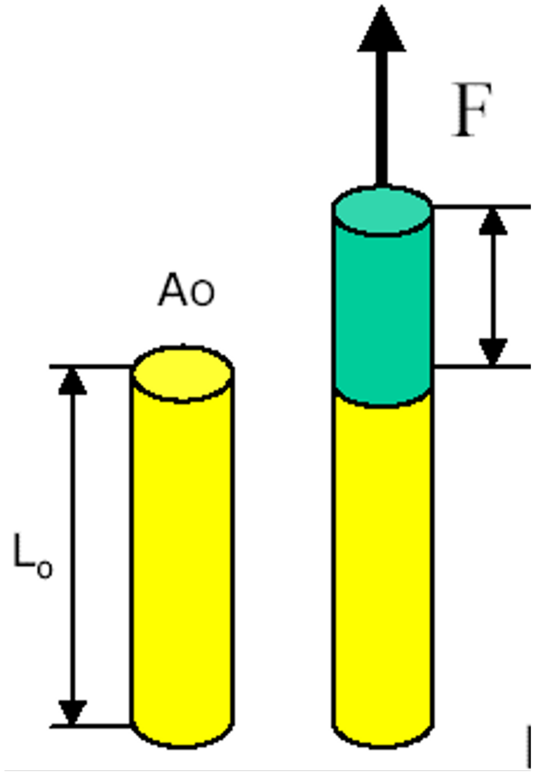
A controlled deformation is applied to a specimen and the response of the sample is measured in terms of strength

Nominal stress

$$\sigma = \frac{F}{A_o}$$

Nominal deformation

$$\varepsilon = \frac{\Delta L_o}{L_o}$$



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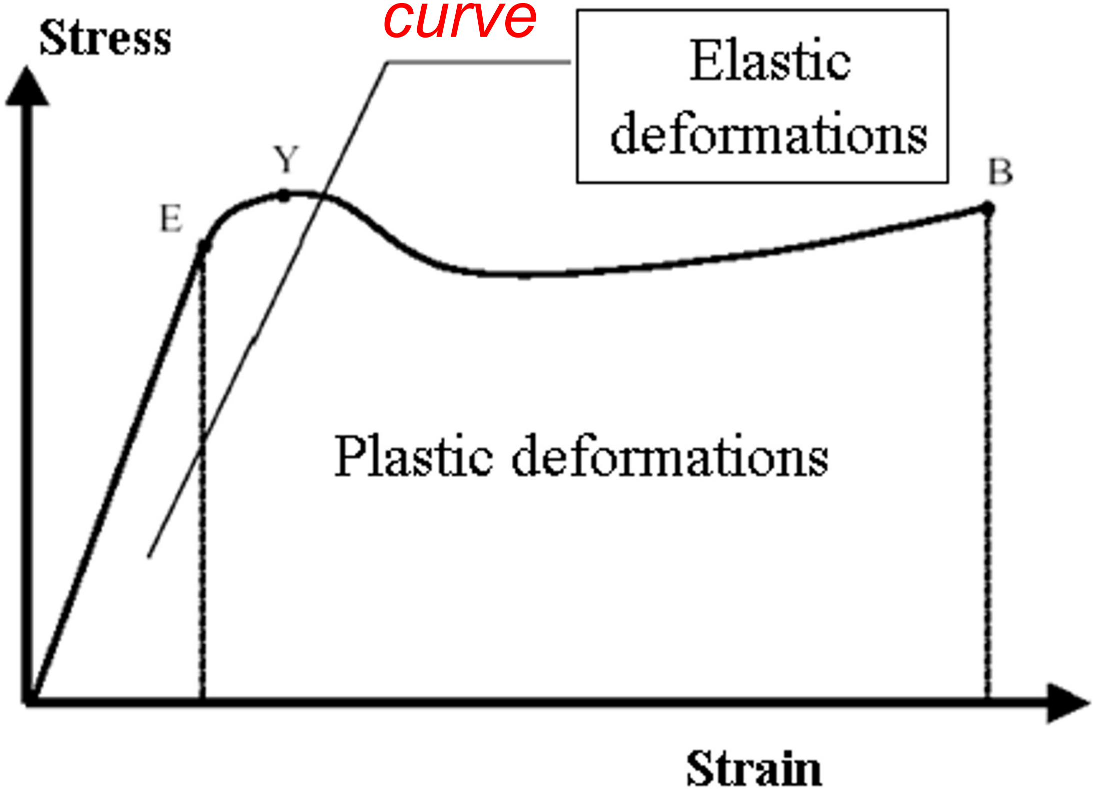
Tensile behaviour

Stress-strain curve



E = elasticity limit;

Y = yield limit;

B = break limit

Elastic deformation: When the stress is removed, the material returns to the dimension it had before the load was applied. Deformation is *reversible*, non permanent.

Plastic deformation. When the stress is removed, the material does not return to its previous dimension but there is a *permanent*, irreversible deformation.

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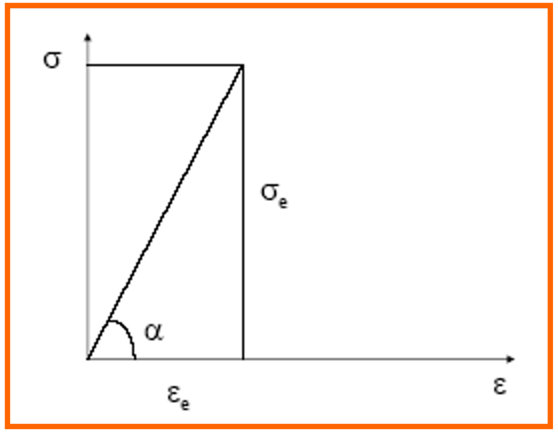
Elastic behaviour

In the initial part of the stress-strain curve (elastic region) there **is proportionality between σ and ε** (Hooke's law, Young's modulus, E).

$$\sigma = E\varepsilon$$

Young's modulus E depends on the ability of atomic bonds to deform □ The higher the bond strength, the greater the **stiffness** of the material.



$$\mathrm{E} = \frac{\sigma_e}{\varepsilon_e} = \frac{A\sin(\alpha)}{A\cos(\alpha)} = tg(\alpha)$$

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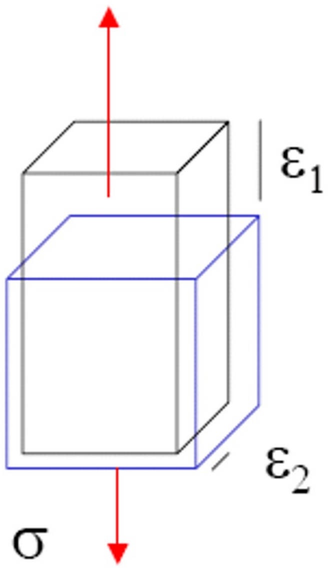
Elastic behaviour

Poisson's ratio

In the elastic region, applying a uniaxial tension, there is a transverse contraction proportional to the applied longitudinal strain. This transverse deformation is measurable by the change of the specimen diameter.

The constant of proportionality between the deformations is the Poisson's ratio (positive value) that can be assessed by measuring the transverse strains.

If the behavior is isotropic the Poisson's ratio is defined:



$$\nu = -\frac{\varepsilon_{transverse}}{\varepsilon_{longitudinal}} = -\frac{\varepsilon_2}{\varepsilon_1}$$

- For an ideal material should be v=0.5 (It corresponds to a zero variation of the volume)
- In the most commonly used materials 0.25< v<0.4 (increase in volume)

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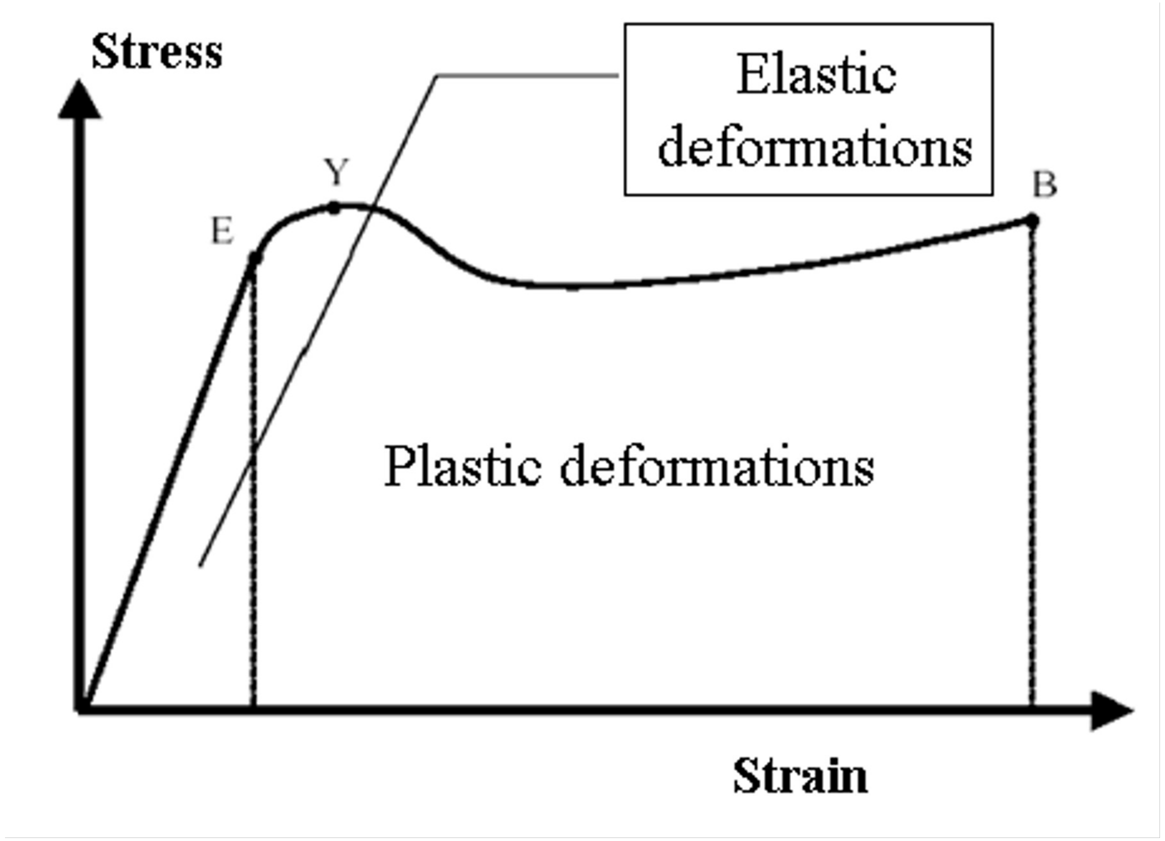
Elastic behaviour

Yield strenght

The yield strength **separates** the region of **elastic behavior** to the **plastic behavior** region.
Sometimes this value is not easily detectable.
The apparent limit of elasticity is defined at 0.2% of permanent deformation



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Ductility and brittleness

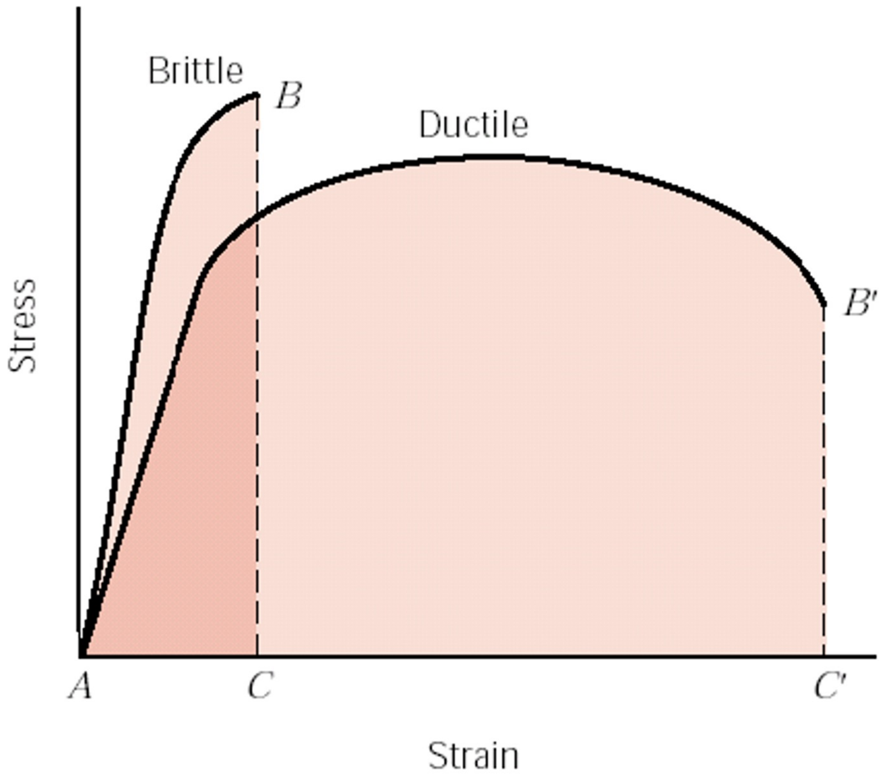
Once reached the limit of elastic deformation, there are two possible material behaviors:

- the sample **breaks** □ **BRITTLE MATERIAL**
- the sample **continues to deform**, and the deformation remains even after the applied force is cancelled □ **DUCTILE MATERIAL**

Brittleness and ductility depend on temperature.

The measure of the **ductility** of a material is the percentage **elongation at break**:

$$\text{Elongation at break} = \frac{L - L_0}{L_0} * 100$$



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Toughness

It is the energy required to fracture a material under a static load. It is represented by **the area under the real curve σ-ε of the tensile test**.

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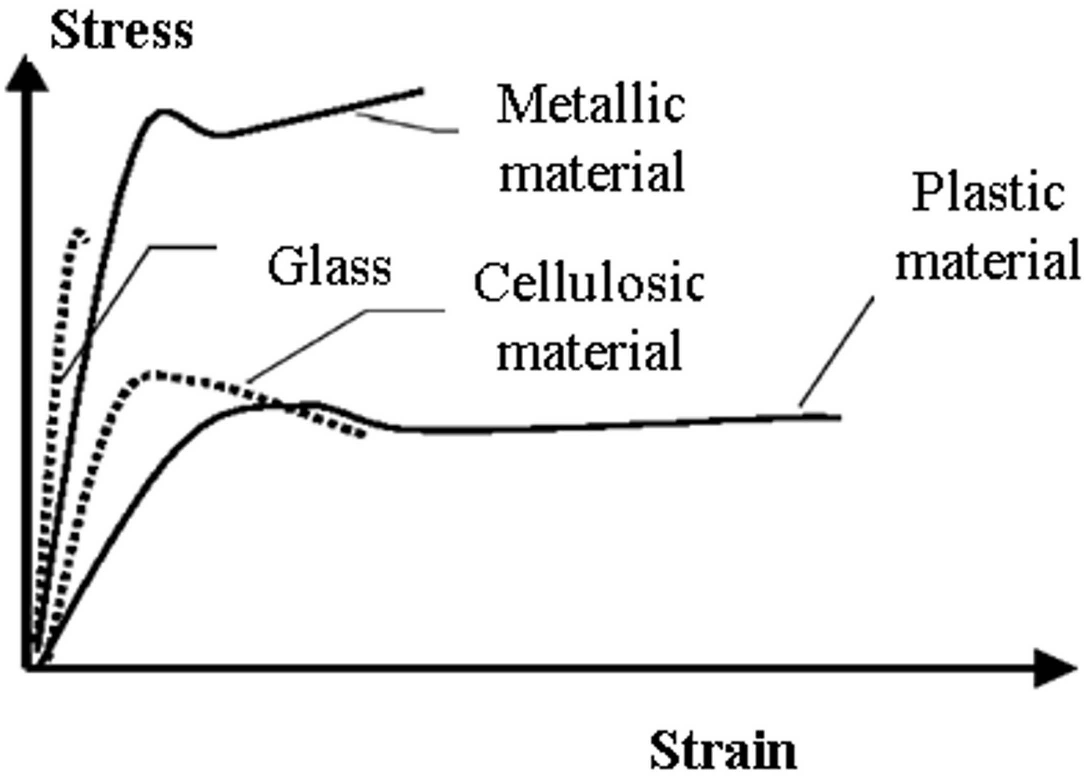
Stress-strain curves for different materials



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Mechanical properties of some packaging materials

MATERIAL	Young’s modulus (Mpa)	Strain at break (%)	Stress at break (Mpa)
Polyester	4000-5000	50-120	170-270
Polypropilene	2000-3500	600-800	35-50
Aluminum	70000	-	70-210
Tin plate	1800000	-	33-740
Glass	70000	-	70

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Interaction package/food

Interaction package/food is the result of a transfer of matter between the container, food and external environment, capable of modifying the properties of the food and/or packaging.

Depending on the type of molecule involved in the transfer of matter and how this interaction discloses, we talk about:

- **gas permeation**
- **absorption of organic molecules**
- **migration**

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Permeability

In contrast to packaging materials made from glass or metals, packages made from **polymers** are **permeable to small molecules** such as gases, water vapour, organic vapour and other low molecular weight compounds.

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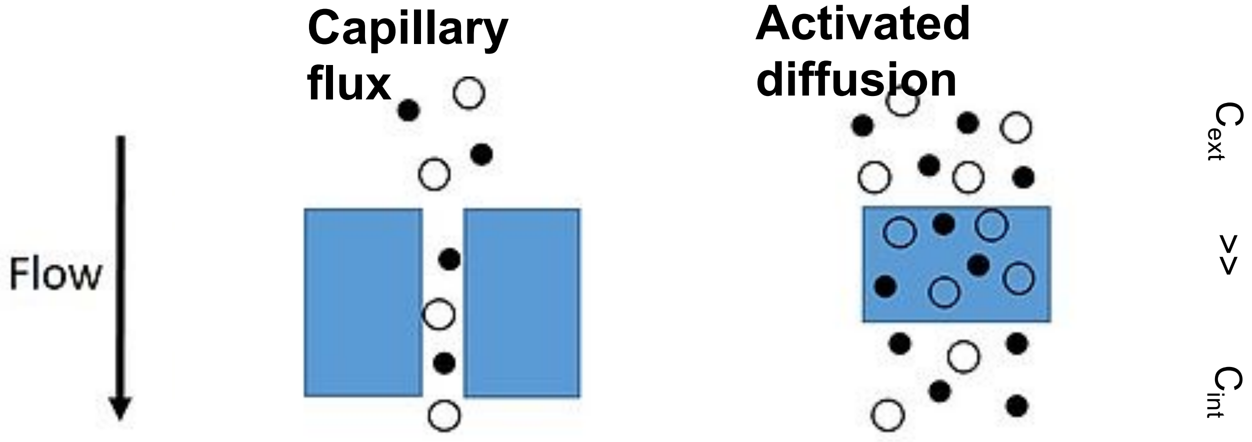
Permeability

There are 2 processes by which gases and vapours may pass through polymeric materials:

- The gases and vapours flow through microscopic pores, pinholes and cracks in the material (**Capillary flux**)
- The gases and vapours dissolve in the polymer at one surface, diffuse through the polymer trough inter and/or intra molecular vacancies by virtue of a concentration gradient, and evaporate at the other surface of the polymer. This “solution-diffusion” process (also known as “**Activated diffusion**”) is described as **true permeability**.



Capillary flux

Activated diffusion

Source: https://en.wikipedia.org/wiki/Membrane_gas_separation

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Permeability

Cracks and/or micro and macroscopic breaks: these flaws are accidental and therefore unpredictable, a consequence of mechanical stress (abrasion) and physical damage (cracks);

Micro or macroscopic pores and capillaries: they vary in size and are the result of punctures or non-uniform distribution of the material components (fillers, pigments or other ingredients) or defects in welds;

Inter and/or intra molecular vacancies: they represent the spaces between molecules or within the same molecule that allow the passage of gases. Their dimensions are small and variable as a consequence of thermal motions since they are subject to molecular motions. They depend on the nature and the morphology of the polymer.

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Permeability

Permeability is defined as *the quantification of permeate transmission, gas or vapour, through a resisting material.*

The concept of permeability is normally associated with the quantitative evaluation of the **barrier properties** of a material. A material with good barrier properties has a low permeability, whereas materials with low barrier properties have high permeability.

The analysis and evaluation of the permeability of packaging are of fundamental importance for the **quality of a packaged food** because the exchange of O_2, CO_2 and H_2O(g) between the inside and outside of the box might cause alterations of the food.

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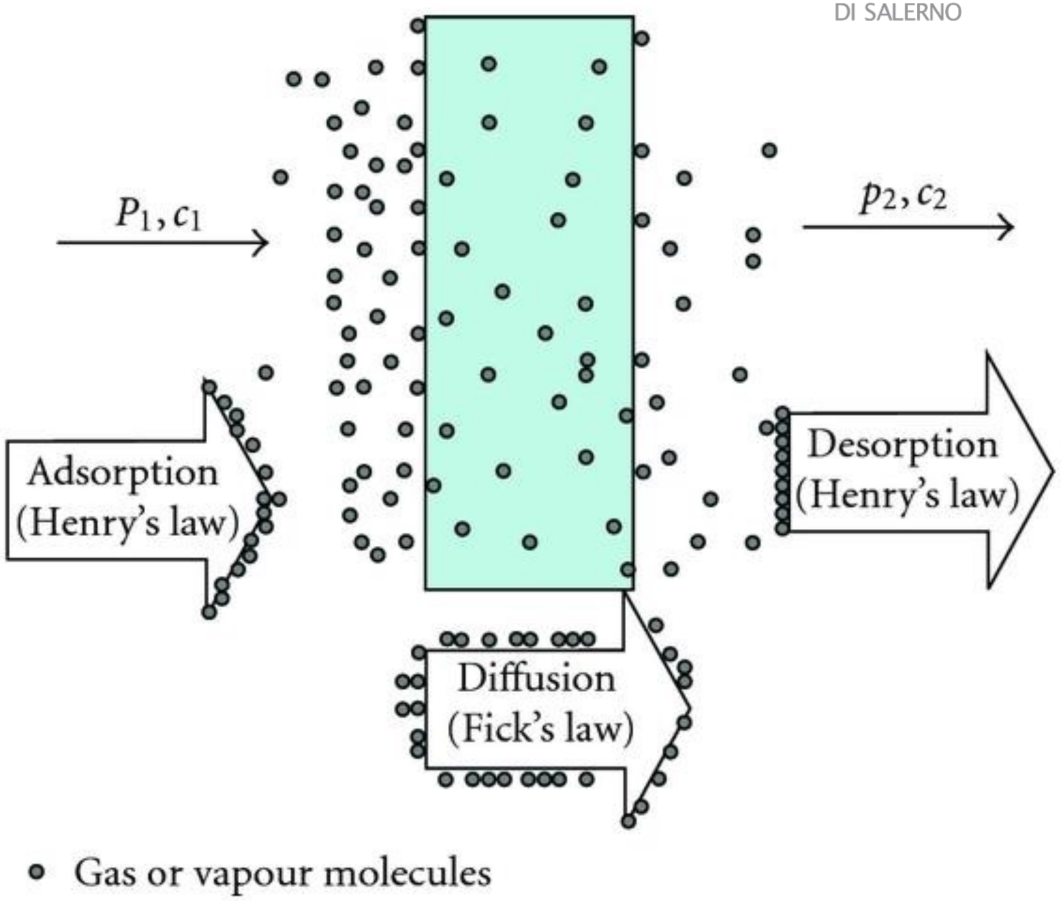
Permeation Mechanism

The transport of a gas molecule through a homogeneous, non-porous polymer membrane can be described as the following process:

- **(i)** **ADSORPTION:** condensation and solution of the penetrant at one surface of the membrane (*favoured by temperature decreases and pressure increases*)
- **(ii)** **DIFFUSION:** in a form of a liquid, through it under the influence of a concentration gradient (*favoured by increase in temperature*)
- **(iii)** **DESORPTION:** **evaporation** at the other surface to the gaseous state.



Source: Siracusa (2012). International Journal of Polymer Science.

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Diffusive Flux

Consider a polymer membrane of thickness **l**, of surface **A** submitted to a fluid and **Q** the total amount of penetrant which has passed through this membrane during the time **t**

DIFFUSIVE FLUX:

$$J = Q/At$$

J *= The quantity of penetrant, which crosses the polymer membrane during one unit of time and by unit of area.*

The diffusive flow of matter can be described quantitatively by

FICK'S TWO LAWS

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Diffusive Flux

FICK'S FIRST LAW: used to calculate the flow of permeant in the STEADY STATE, i.e. in the condition that the concentration profile doesn't change with time and the flux is constant.

$$J = -D\frac{dc}{dx}$$

FICK'S SECOND LAW: allows to evaluate the change in concentration of permeant inside the package with variable speed, that is in the TRANSIENT STATE (the concentration profile varies over time) therefore during the so-called delay time (Lag Time).

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

D = Diffusion coefficient *square of the length per unit time* (**$cm^2 s^{-1}$**);

C = concentration of permeant *mass or volume of permeant per unit volume of material* (**$mol\ cm^{-3}$**)*;*

X = length in flow direction (cm).

t = time (s)

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Diffusion in polymers

DIFFUSION FASTER for…

- amorphous structure
- lower melting T materials
- higher molecular mobility
- presence of secondary bonding
- lower density materials
- smaller diffusing atoms
- higher affinity with the permeant

DIFFUSION SLOWER for…

- crystalline structures
- higher melting T materials
- lower molecular mobility
- presence of covalent bonding
- higher density materials
- larger diffusing atoms
- lower affinity with the permeant

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Sorption in polymers

The term sorption is generally used to describe the initial penetration and dispersal of permeant molecules into the polymer matrix, and includes both absorption and adsorption, as well as the trapping in microvoids or the clustering of aggregates.

At a given temperature, the local concentration **C** of the gas dissolved in the polymer can be related to the pressure **P** by the following relation:

$$C = S(C)p$$

- **the concentration C** is expressed in **cm^3 (STP)/cm^3** polymer. In a more explicit way, it is the concentration of the sorbed gas (calculated in the Standard Conditions of Temperature and Pressure, i.e. 273°K and 1atm) by the polymer which is subjected to a pressure p of the penetrant;
- **the solubility coefficient S** is given in **cm^3(STP)/cm^3·MPa**

S(C) is the **SOLUBILITY COEFFICIENT** and is a **measure of affinity polymer-penetrant**

Henry's Law → C= S·P

Applicable for low pressures and ideal gas

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Permeability coefficient

Integrating Fick's first law for the thickness and concentration and assuming Henry's law applies, it is possible to define the amount of gas (**Q**) through the material:

$$Q = \frac{A \cdot t \cdot D \cdot S \cdot (p_1 - p_2)}{l}$$

The product **D·S** is referred to as the "**permeability coefficient"** and is represented by the symbol **Pe**:

$$P_e = D \cdot S$$

$$P_e = \frac{l \cdot Q}{A \cdot t \cdot (p_1 - p_2)}$$

P_e *is "the amount of permeant passing through a surface of unit area and thickness during unit time and due to a unit partial pressure difference"*

Pe is commonly expressed as **cm^3 µm m^{-2} $24h^{-1}$ bar^{-1}**

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Permeability

From the expression of $\mathbf{P_e}$, it is clear that the transmission of gas is inversely proportional to the thickness of the material. The inverse proportionality is not always respected: sometimes, in fact, considering the constant of permeability through different thicknesses of the same material do not get the same value.

PERMEANCE (or permeability):
the amount of gas which passes through a unit surface area, of given thickness, per unit time under a partial unitary ΔP

$$P = \frac{P_e}{l}$$

It is denoted by the letter P and expressed as $cm^3 m^{-2} 24h^{-1} bar^{-1}$

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Gas Transmission Rate GTR

From the expression of Pe, it is also obvious that the transmission of gas is directly proportional to the pressure difference. However, the direct proportionality with ΔP is not always respected. For this reason, ΔP is usually considered as a condition of the measure and another quantity is defined:

GAS TRANSMISSION RATE:
amount of gas passing through a unit surface area of given thickness and under a given partial pressure difference during unit time

$$GTR = P(p_1 - p_2) = \frac{P_e}{l}(p_1 - p_2)$$

It is measured in $cm^3 m^{-2} 24h^{-1}$ and it is denoted as **GTR** that, depending on the permeating species, can take many forms: O_2TR, N_2TR, CO_2TR, WVTR .

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Barrier Properties

proplast
PLASTICS INNOVATION POLE

UNIVERSITÀ DEGLI STUDI
DI SALERNO

(UNI 10534 12/94)

BARRIER	P/WVTR
Very high	< 0.5
High	0.5 - 3.0
Medium	3.1 - 30
Low	31 - 150
Very Low	> 150

cm^{3}m^{-2}24h^{-1}bar^{-1}d at 23°C and 0% UR (gases)

g m^{-2}24h^{-1}bar^{-1}d at 38°C and 90% UR (water vapour)

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Barrier Properties

Polymeric material	Oxygen permeability of a film 25 µm thick (cm^3/m^2 24h bar)
Low density polyethylene(LDPE)	7000-8000
High density polyethylene (HDPE)	2800-3000
Polypropylene (PP)	2300-3700
Plasticized poly(vynil chloride) (PVC)	6000-9000
Polystyrene (PS)	3800-5400
Poly(ethylene terephalate)(PET)	45-90
Polyamide 6 (PA6)	20-40
Polyamide 11 (PA11)	500-1500
Poly(vinylidiene chloride) (PVDC)	12-100
Poly(ethylene vynil alchol) (EVOH)	1-

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