



**Sustainpack**

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**"REPORT RESULTING OF MAPPING OUT EXISTING MASS TRANSPORT  
PROPERTIES MEASUREMENTS METHODS"**

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The broad use of polymeric materials in the packaging industry, especially in the food and drug manufacturing, is due to properties such as transparency, chemical stability, low cost, thermoplasticity. The use of composite materials allows one to combine the different physic, chemical, optical, mechanical and thermal properties of different components and functional groups, in order to reduce the amount of material needed, lowering costs and environmental impact. Polymers obtained from renewable resources, or that are easily biodegradable, are under development for the further reduction of environmental waste.

In the food industry, the barrier properties are among the most important parameters characterizing the materials for packaging, due to the importance of the shelf life of packed foods. It is well known that most materials, in particular polymers, are permeable to light components such as liquids and gases, and that variable amounts of these components can pass through the package due to different fugacity of the light component between the sides of the package. To avoid the biodegradation of foods, one must choose materials that can provide a suitable barrier to gases such as oxygen and water vapour, but also to nitrogen and carbon dioxide in those cases in which a controlled atmosphere has to be maintained; the migration of heavier compounds such as aromas must also be avoided in order to keep the organoleptic parameters of foods constant and to avoid contamination or degradation of the packaging.

Important physic and chemical parameters in the description of the barrier properties of a material are gas permeability and diffusivity. The transport of gases through polymers generally is driven by pure molecular diffusion, due to high dilution of the gas in the solid, so that the mass flux obeys Fick's law. Gas diffusivity can be then calculated as the number of gas moles permeated, under steady state conditions, through a solid sheet in unit time, per unit area, under a unit molar concentration gradient. Gas permeability results from the number of gas moles permeated, under steady state conditions, through a solid sheet in unit time, per unit area, under a unit pressure gradient. If the dissolution of the gas or liquid in the solid follows the Henry's Law, the ratio between P and D is also a material property, corresponding to the solubility coefficient of gas component in the solid polymer, expressed in terms of gas molar concentration per unit gas pressure.

The permeability and diffusivity of liquids and gases in solid materials increase with temperature, and can be strongly enhanced by the presence of third components: for example, the permeability of humid oxygen in hydrophilic materials is much larger than the permeability of dry oxygen under the same conditions. It is thus important that the characterization of the mass transport properties of packaging materials is carried out under the most severe conditions of humidity, temperature and concentration gradients, and in perfectly isolated chambers in order to avoid the contamination with atmospheric gases.

The addition of nano fibres or of other fillers to polymers generally enhances the barrier properties if the fibres are impermeable to gases or if they permanently adsorb penetrant molecules on their surface, because the fibres depress the permeability and increase the length of the diffusive path of the molecule in the film. It is important, however, that the characteristic dimensions of the fibres are small, and that they are well dispersed in the matrix, so to avoid the formation of micro voids through which the penetrant molecules

permeate preferentially. The addition of fillers can also stabilize the polymeric structures, making them more resistant to the plasticization induced by swelling penetrants such as water for hydrophilic materials, that makes the polymer more permeable to gases.

The existing studies on the mass transport in ultrabARRIER materials are rare, due to the extreme sensitivity required for the instrumental equipment, which must detect the very low permeation rates typical of such materials, and to the large experimental time required. The characteristic time for permeation, i.e. time needed by the gas for reaching a stable, steady state value of mass flux through the sheet, is directly proportional to the square of the sheet thickness and inversely proportional to the diffusivity.

The measure of gas permeability is typically carried out in a permeation experiment, where a fugacity difference of a certain gas is applied at the sides of a solid sheet of the material under study; in the case of pure gases, a simple gas pressure difference is applied. Due to low permeation rates of barrier materials, it is generally difficult to measure it with commercial flow meters and the most common technique for the characterization of the permeation rate of a single gas through the membrane is a closed-volume manometric technique. In this method, downstream of the membrane, the permeate gas is collected in a closed volume of known dimensions, at fixed temperature. The pressure variation in this volume is thus related, through an appropriate equation of state, to the mass variation due to permeation. The sensitivity of this technique is directly related to the sensitivity of the manometer used for the measurement of downstream pressure: the resolution of commercial absolute manometers is proportional to their full scale value, therefore a small full scale value must be chosen (generally 10 mbar or less) for better sensitivity. For this reason, the initial pressure in the downstream volume must be reduced to the minimum, by using a high-vacuum pump: the maintenance of an hermetic environment in this case is essential for the measurement of the pressure variation due only to permeation through the membrane and not to infiltration from the environment. Therefore, particular care must be taken in the choice of the fittings, which must be totally inert with respect to the gases used, generally made of steel, and leak-proof.

This technique is versatile, since it can be applied to all gases, independent of their nature; the interpretation of experimental data is also straight forward, because, due to the low pressure, the ideal gas equation of state can be used for describing the behaviour of the gaseous phase in the downstream volume.

While the permeability is determined under steady state conditions, the diffusivity can be calculated based on transient state data, from the characteristic time of permeation, i.e. the time needed to reach a constant flux through the membrane.

An analogous method can be applied also to study the permeation rate of liquids: in this case, the liquid dissolves into the polymeric matrix and evaporates at the downstream side of the membrane where vacuum conditions are maintained. One can measure the pressure increase or operate in dynamic vacuum conditions, at open volume, by collecting the permeate mass in a cold trap and finally weighing the permeate amount. The mass flux through the membrane can be enhanced by varying dimensional parameters, i.e. by increasing the membrane area and lowering the sheet thickness (in doing this, one must be sure that the physico chemical

properties do not change with thickness, as it sometimes happens for composite structures or due to different preparation methods of the samples of different thickness).

For mixed gases/vapors, the system can be modified by adding a gas-chromatograph or mass spectrometer, for the characterization of permeate gas composition, at the downstream side of the system, and sampling the permeate gas at fixed time intervals. Care must be taken that a sufficient amount of gas is fed into the analytic detector and that there is no contamination with atmospheric gases. For the case of mixed liquids, the permeate composition can be analysed with liquid chromatography or, in particular cases, with refractometry or, for ions and acids, with electrical conductivity measurements, or pH meters.

Other techniques have been developed and patented, aimed to the measurement of permeability of specific gases, such as the coulometric technique for the determination of oxygen concentration. The ASTM standard F1927-98 refers to this technique for the determination of oxygen permeability through barrier materials at controlled relative humidity. This method allows to measure the concentration of oxygen in the downstream side of the membrane; the specimen is mounted as a sealed semi barrier between two chambers at ambient atmospheric pressure. One chamber is slowly purged by a stream of nitrogen at a given temperature and %RH and the other chamber is purged by a stream of oxygen at the same temperature as the N<sub>2</sub> stream but may have a different %RH than the N<sub>2</sub> stream. In this case the environment more closely simulates actual shelf conditions. As oxygen gas permeates through the film into the nitrogen carrier gas, it is transported to the coulometric detector where it produces an electrical current, the magnitude of which is proportional to the amount of oxygen flowing into the detector per unit time.

A method for the determination of water vapour transmission is described in the standard E398-03. It covers dynamic evaluation of the rate of transfer of water vapour through a flexible barrier material. The method is limited to materials composed of either completely hydrophobic materials, or combinations of hydrophobic and hydrophilic materials having at least one surface that is hydrophobic, and the minimum test value is limited by the leakage of water vapour past the clamping seals of the test instrument.

The permeability and diffusivity are essential parameters required for the material choice and design, but also for comparison with the modelling results; therefore, their exact determination is essential for the simulation of the behaviour of materials.

In order to understand the nature of interactions between the penetrant molecule and the solid material, a crucial parameter is the solubility, whose value can be determined from the values of  $P$  and  $D$  obtained from permeation measurements, as discussed above. This indirect calculation procedure can offer just a mean value of the solubility coefficient, however, for the case in which the sorption isotherm does not follow closely the Henry's Law.

In this case, the solubility can also be determined directly, and more accurately, from sorption measurements, where the material sheet is surrounded by a gaseous phase of fixed activity and the mass uptake in the solid is monitored as a function of time. In this kind of experiments, equilibrium is gained when the mass uptake reaches a plateau value, that defines the equilibrium solubility of the gas in the solid at that activity value.

The determination of mass uptake, which is generally rather low, also requires extreme sensitivity of the instrument. Different approaches can be used in this respect. The most common technique is gravimetric, in which the mass increase of the sample is determined through a measure of the weight force exercised on the sample, that increases (decreases) due to gas sorption (desorption). In the quartz spring balance, the elongation of a spring on to which the polymer sample is suspended is monitored and change in sample weight is evaluated through Hooke's law. The sensitivity of this balance can be varied by using springs of different constants. In electronic microbalances (Cahn and similar) the sample is hanged at one arm, while an inert tare is suspended at the opposite arm. The latter apparatus can measure differences between sample weights with the sensitivity of  $10^{-6}$  times their absolute value. All these instruments allow one to monitor also the transient stages of sorption, from which the diffusivity can be estimated. The diffusivity calculated from sorption experiments can be compared to that obtained with permeation experiments in order to detect any anomalous behaviour.