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Review Article

Food Packaging Permeability Behaviour: A Report

Valentina Siracusa

Department of Industrial and Mechanical Engineering, Engineering Faculty, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

Correspondence should be addressed to Valentina Siracusa, vsiracus@dmfci.unict.it

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The use of polymer materials in food packaging field is one of the largest growing market area. Actually the optimization behaviour of packaging permeability is of crucial importance, in order to extend the food shelf-life and to reach the best engineering solution. Studying the permeability characterization of the different polymer material (homogeneous and heterogeneous polymer system) to the different packaging gases, in different environmental condition, is crucial to understand if the selected material is adapted to the chosen food contact field. Temperature and humidity parameters are of crucial importance for food quality preservation, especially in real life situations, like food market, and house long-life use. The aim of this report was to collect information about the state of the art on the permeability characteristics of the polymer packages used on food field.

1. Introduction

In contrast to glass or metal packaging materials, packages made with plastic are permeable at different degrees to small molecules like gases, water vapour, and organic vapour and to other low molecular weight compounds like aromas, flavour, and additives present into food. As a consequence of the barrier properties of the material, the transfer of this molecules ranges from high to low. The knowledge of the solution/diffusion/permeation behaviours of these molecules through the polymer film has become more and more important in recent years, especially for polymers used in the food packaging field where contamination from external environment has to be avoided and the shelf life of the food controlled by the use of modified atmosphere packaging (MAP) techniques. Many factors that can influence the polymer packages performance must be taken into consideration to design the correct package market solution.

The use of different polymers in food packaging industry depends on the properties of the food product. Also, manufacturing, handling, and packaging engineering procedures can influence the final properties of packaging material, especially in terms of barrier properties which are, further, strictly correlated to the intrinsic structure of the polymer such as degree of crystallinity, crystalline/amorphous phase ratio, nature of polymer, thermal and mechanical treatment before and after food contact, chemical groups present into the polymer (polar or not), degree of cross-linking, and glass transition temperature (T_g) [1, 2]. The selection of the best packaging material is a crucial point for food market, because it needs to be versatile enough to withstand handling process forces maintaining physical and chemical integrity and suitable for barrier properties to several gases used in MAP techniques (e.g., O_2, N_2, CO_2) [3]. Furthermore, the intrinsic composition of the packed food (e.g., pH, fat content, aroma compound) may have an influence on the sorption characteristics of the packaging materials, while environmental factors like temperature and, for some polymers, relative humidity may affect their barrier characteristics [4].

A lot of polymers present on the market are used in the packaging field, in direct contact or not with the food:

(i) polyolefins, which include low-, linear low-, and high-density polyethylene (LDPE, LLDPE, HDPE), polypropylene (PP), and biaxially oriented polypropylene (BOPP);

(ii) copolymers of ethylene, like ethylene-vinyl acetate (EVA), ethylene-vinyl alcohol (EVOH), and ethylene-acrylic acid (EAA);

(iii) substituted olefins, like polystyrene (PS), high-impact polystyrene (HIPS, with 1,3-butadiene isomer added during the polymerization of the PS), oriented polystyrene (OPS), poly(vinyl alcohol) (PVOH), poly(vinyl chloride) (PVC), and poly(vinylidene chloride) (PVdC), and poly(tetrafluoroethylene) (PTFE);

(iv) polyesters, like polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and relative copolymer PET-PEN;

(v) polycarbonates (PC);

(vi) polyamide (PA);

(vii) acrylonitriles, like polyacrylonitrile (PAN) and acrylonitrile/styrene (ANS);

(viii) regenerated cellulose.

(ix) polylactic acid (PLA) as biodegradable polymer for food packaging contact.

These are the most common polymers used in the food packaging industry thanks to their general good performances like chemical and heat resistance, low, medium, and high gas permeability and water vapour transmission rate, good abrasion resistance, good thermal and mechanical behaviour, and so on. All the chemical-physical characteristics of these materials are well described in the literature [5–7].

However, since contact with foods may alter the polymer performances, it is important to study the barrier characteristics of the material under realistic conditions. For example, the absorption of ambient vapour or liquid can cause an increase of polymer plasticization, resulting in a decrease in mechanical properties [8, 9]. The aim of this paper is to give an overview on the state of the art of the permeability behaviour of the polymer packages used for food applications.

2. Permeation Theory

2.1. General Concepts and Equations. Several factors can influence the barrier properties of a packaging material, like food contact and environmental conditions such as temperature and relative humidity. Permeates diffusion across a film is influenced by the film structure, film permeability to specific gases or vapour, thickness, area, temperature, difference in pressure, or concentration gradient across the film.

Permeability, as reported in the literature, is defined as the quantification of permeate transmission, gas or vapour, through a resisting material [2, 10]. So, the concept of permeability is normally associated with the quantitative evaluation of the barrier properties of a plastic material. In a material without defects like pinholes or cracks, the primary mechanism for gas and water vapour flow through a film or coating is an activated diffusion. This means that the permeate dissolves in the film matrix at the higher concentration side, diffuses through the film, driven by a concentration gradient, and evaporates from the other surface. Differences in the solubility of specific gases may influence the diffusivity of gases across the film. The second step of the permeability phenomenon, the diffusion, depends on the size, shape, and polarity of the penetrating molecule of the permeant and on the crystallinity, degree of cross-linking and polymer chain segmental motion of the polymer matrix. As reported from Kofinas et al. [11], gas molecules are unable to permeate through the polymer crystallites, because they are insoluble into the material. Thus, the gas permeation into semicrystalline polymers is then confined into the amorphous regions. The reduction of crystallite permeability reduction is due to the decrease in available volume of polymer for gas penetration and to a large tortuous path between the crystallites. The reduction in permeability value is proportional to the volume fraction of the crystalline phase.

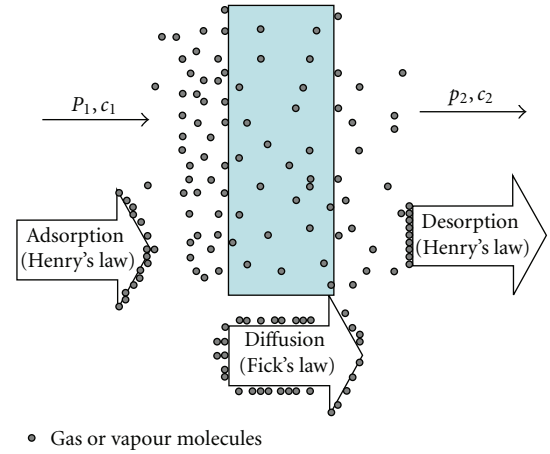


Figure 1: General mechanism of gas or vapour permeation through a plastic film.

Concerning the theory, the permeation of gas through a polymer is described by a diffusion model, using Henry and Fick's laws to obtain the expression that relates the permeation rate with the area and thickness of the film [7]. The mechanism can be described in a very simple way like in Figure 1, for an homogeneous polymer film with thickness of l and p as the permeant pressure (with $p_1 > p_2$) and c as the different permeant concentration through the film (with $c_1 > c_2$).

The permeate (gas or vapour) flux, indicated by J, is described by Fick's First Law:

$$J = -D \cdot \Delta c, \tag{1}$$

which, for one-dimensional diffusion through a polymer membrane and in stationary conditions, can be written as $J = -D(\Delta c/l)$, where J is the diffusion flux (expressed in mol cm^{-2} s^{-1}), D the diffusion coefficient or diffusivity (expressed in cm^2/s), and Δc the concentration difference (expressed in mol/cm^3) across the membrane thickness l (expressed in cm). D reflects the speed at which the permeant diffuses through the polymer. When the diffusion mechanism is in its steady state, the equilibrium of the gas concentration c at the surface and the gas partial pressure p obey to Henry's law. When the permeant is a gas, it is more

convenient to measure the vapour pressure p (expressed in atm), so Δc can be replaced by $S\Delta p$, where S (expressed in mol/cm^3 atm) is the solubility coefficient which reflects the amount of permeant in the polymer and Δp is the pressure difference across the film. Equation (1) becomes

$$J = -D\left(\frac{S\Delta p}{l}\right). \tag{2}$$

The product DS is indicated as permeability coefficient (or constant) or permeation coefficient or simply as permeability (P).

If S is independent of the concentration, that means a linear relationship between concentration-distance through the polymer, the permeability coefficient P can be defined as

$$P = -\frac{(J \cdot l)}{\Delta p} = DS. \tag{3}$$

The ratio P/l, indicated by q, is named permeance.

The diffusion takes place only in one direction only, through the film and not along or across it; moreover D and S coefficients are independent from the permeate concentration. This behaviour of molecular diffusion in polymer is indicated as Fickian behaviour. Obviously, as also reported by Robertson [12], there are a lot of realistic cases where these hypotheses are not valid as, for example, when the steady state takes long time to be reached (like glassy polymer) or when the D and S coefficients are correlated to the interaction between permeate and polymers, like the interaction between water and hydrophilic film or like solvent vapour which diffuses through polymer films. These cases are indicated as non-Fickian behaviour.

There are a lot of data in literature [5, 7, 12] which gives a good and complete mathematical description of the permeation mechanism theory.

Permeation through a series of different defect-free polymeric layers (laminate) is described by the Ideal Laminate Theory (ILT), as reported by Grüniger and Von Rohr [13]. The overall permeability of the laminate, P_L, is a function of the thickness l_i and of the permeabilities P_i of the single layer L:

$$\frac{P_L}{\Sigma l_i} = \frac{1}{\Sigma(l_i/P_i)} = \frac{TR_L}{\Delta p}. \tag{4}$$

Further, especially for laminates, it is often more convenient to use instead of P the transmission rate TR, which is described as the quantity of permeant passing through a film, per unit of area, per unit of time, at steady state.

In the ILT model, the layer order is not relevant. However, if the layer presents defects, it is not able to hold. Because of the lateral spreading of the concentration profile near the defects, the transport is no longer just a one-dimensional problem. The diffusion equation (4) has to be solved in three dimensions to derive the concentration profile:

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right\}. \tag{5}$$

The gas flux J is calculated from (1) and the gas flow rate J through the defect area A_d is derived by integration of J. In the steady state, (5) reduces to the Laplace equation and the concentration profile becomes independent of D. Thus, J is directly proportional to D. In order to present the calculations for J in a general way, independent of the diffusion coefficient or permeability of the polymer, J was related to J_{1D} that represents the gas flow rate through the defect in the one-dimensional case, that is, the flow rate through the area A_d if the barrier layer was absent. If the gas flow ratio J/J_{1D} is known for a given defect geometry, the transmission rate of the barrier/polymer composite TR_c can be calculated from the transmission rate TR_p of the polymer and the number density n of defects (number/area), where θ is the defect area fraction. The relative equation will be

$$\mathrm{TR}_c = n \cdot A_d \cdot \mathrm{TR}_p \cdot \left(\frac{J}{J_{1D}}\right) = \theta \cdot \mathrm{TR}_p \cdot \left(\frac{J}{J_{1D}}\right). \tag{6}$$

This model is valid under the assumption that the defects are uniform and distributed each other at a constant distance [13].

The manometric method used to determine the gas permeability parameters is one of the most common, simple, and economic method. For an homogeneous polymer material, (7) to (13) are taken into consideration to provide determination of the permeability, diffusion, and solubility constants of a gas through a film.

Gas transmission rate or permeance (q) is expressed as the volume of permeant passing through a film, per unit area and time, at steady state of the sample, as reported on (7) [1]:

$$\mathrm{GTR\ (or\ } q) = k_1\left[\frac{V}{T(29N - t_L)}\right], \tag{7}$$

where $k_1 = 9.89 \cdot 10^8$, GTR (or q) is the permeance (expressed in cm^3/m^2 day bar), V is the measured volume (expressed in mL), N is the slope of the measured curve (expressed in sec), T is the temperature (expressed in K), and t_L is the time-lag value (expressed in sec).

The common unit used is cm^3(STP)/(m^2 day), at 1 atmosphere pressure difference. If the permeates are O_2, CO_2, N_2, or other gases, the initials will be O_2TR, CO_2TR, N_2TR, and others.

For an homogeneous plastic film the P, D, and S coefficients of the dry gas test in the film are calculated according to the following equations [1, 14].

Permeability constant:

$$P = k_2 q l \tag{8}$$

with $k_2 = 1.16 \cdot 10^{-9}$ and l = polymer thickness (expressed in cm).

Diffusion constant:

$$D = \frac{l^2}{6t_L}. \tag{9}$$

Solubility constant:

$$S = k_3\left[\frac{qt_L}{l}\right) \tag{10}$$

with $k_3 = 6.94 \cdot 10^{-9}$.

Using the Arrhenius equation and the Van't Hoff relationship, it is possible to describe, respectively, the dependence between the temperature and the permeability P (expressed in $cm^3/cm\,s\,bar$), solubility S (expressed in $cm^3/cm^2\,bar$), and diffusion D (expressed in cm^2/s), as shown in the following equations [1].

Activation energy for permeation:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right). \tag{11}$$

Activation energy for diffusion:

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right). \tag{12}$$

Heat of sorption:

$$S = S_0 \exp\left(-\frac{H_s}{RT}\right). \tag{13}$$

P_0, D_0, and S_0 are preexponential factors; E_p and E_d are the activation energies for permeation and diffusion respectively (expressed in J/mol); H_s is the heat of sorption (expressed in J/mol); R is the gas constant (of 8.314 J/mol K); T is the temperature (expressed in K). Generally these equations could accurately characterize a gas diffusivity/temperature behaviour of a polymer except where there is a strong interaction between the polymer and the gas molecules (e.g., water vapour and hydrophilic polymers). In addition, the previous equations could only predict the effect of temperature above the glass transition temperature (T_g). At or below T_g the polymer conformation is set and the rotational movements, responsible for diffusional properties, are blocked [15].

In order to calculate the activation energy for diffusion (E_d) and heat of sorption (H_s), a linear approximation between $\ln D$ (and $\ln S$) and the reciprocal of absolute temperature is performed. Combination of (11) to (13) shows that the apparent activation energy for permeation, E_p, is a sum of a thermodynamic (H_s) and a kinetic (E_d) parameters for a particular permeate:

$$E_p = E_d + H_s. \tag{14}$$

The heat of sorption, H_s, defines the effect of temperature on gas solubility coefficient in a given polymer. This value is governed primarily by the negative enthalpy change associated with the gaseous permeates, being sorbed into the polymer matrix, and by the positive enthalpy required to create a site into which a permeate can sorb [2].

The calculation of permeability constant for multilayered films is performed using the following relation [1]:

$$PT = \frac{l_T}{[(l_1/P_1) + (l_2/P_2)]}, \tag{15}$$

where P_T is the total permeability, l_T is total thickness, l_{1-n} is thickness of individual layer, and P_{1-n} is permeability of individual layer.

When vapour of water or organic molecules is used in the permeability measurements, the transmission rate is reported as Vapour Transmission Rate (VTR), expressed as the mass of water, per unit area, per unit time. The common unit is $g/(m^2\,day)$, specifying the test conditions like temperature and relative humidity on both sides of the film.

2.2. Units and Barrier Properties. A lot of different units for the permeability appear in the scientific literature. An attempt to rationalize these units from a practical point of view was made on 1983 from Huglin and Zakaria [16]. For the permeability they proposed 10^{-10} (cm^3 (STP) cm)/cm sec (cm Hg). This unit has been adopted by ASTM, giving the name barrer in honour of the New Zealander Richard Barrer who first introduced the permeability constant P as a product of D and S. The most used SI unit is cm^3 (at 273.15 K and 1 atm) cm/cm^2 sec (cm Hg). When the permeability coefficient is measured with the manometric method, using the Brugger Instrument GDP-C model, the following unit cm^3/m^2 day bar (where day means 24 hrs) is used to express the permeability value. In the literature [7, 10, 17] are reported several tables containing the converting factors for permeability, permeance, and gas transmission rate from one system of units to another.

Difficulty and uncertainty are sometimes experienced in interpreting the permeability coefficients from tables and converting them into different units.

The determination of the barrier properties of a polymer is crucial to estimate and predict the product-package shelf-life. The specific barrier requirement of a package system depends upon the food characteristics and the intended end-use applications. Generally plastics are relatively permeable to small molecules such as gases, water vapour, organic vapours, and liquids, and they provide a broad range of mass transfer characteristics, ranging from excellent to low barrier values, which are important in the case of food products. Water vapour and oxygen are two of the main permeants studied in packaging applications, because they may move from the internal or external environment through the polymer package wall, resulting in possible negative changes in product quality and shelf-life [18]. For example, the improving of the oxygen barrier performances of a film is of great importance because oxygen promotes a lot of degradation mechanisms of a food, such as corrosive phenomena, oxidations, and great modification of organoleptic properties [19].

To avoid food degradation, carbon dioxide becomes more and more important for MAP technology because it can potentially reduce the degradation phenomena associated with processed fresh vegetable products, leading to a significantly longer shelf-life. For example, for fresh products like fresh cut fruits, potatoes, and vegetable (ready to eat), respiration rate is of a great importance in the MAP design, in which the identification of the best packaging solution technology is a crucial factor.

The most important barrier properties of polymer films used in food packaging applications are following reported [20].

Oxygen Transmission Rate (OTR). The oxygen barrier property of a food packaging container for fresh product

(e.g., fruits, salad, ready-to-eat meals) plays an important role on its preservation. The oxygen barrier is quantified by the oxygen permeability coefficients (OPCs) which indicates the amount of oxygen that permeates per unit of area and time in a packaging materials (kg·m/(m^2·s·Pa)). So, when a polymer film packaging has low oxygen permeability coefficients, the oxygen pressure inside the container drops to the point where the oxidation is retarded, extending the shelf-life of the product. Generally the biodegradable polymers like polylactic acid (PLA), which is one of the most diffused polymer in food packaging field, present OTR values of one or more order of magnitude below to those of the synthetic polymer used in the same field like PET and OPS.

Together with the permeability coefficient the *oxygen transmission rate* (OTR), expressed in cc/m^2 s, is given. The OPC is correlated to the OTR by the following:

$$\text{OPC} = \frac{\text{OTR} \cdot l}{\Delta P}, \tag{16}$$

where l is the thickness of the film, and ΔP is the difference between oxygen partial pressure across the film [Pa]. $\Delta P = p_1 - p_2$, where p_1 is the oxygen partial pressure at the temperature test on the test side, and p_2 is equal to zero on the detector side.

Water Vapour Transmission Rate (WVTR). The water vapour barrier properties for the packaged food product, whose physical and chemical deteriorations are related to its equilibrium moisture content, are of great importance for maintaining or extending its shelf-life. The water vapour barrier is quantified by the water vapour permeability coefficients (WVPC) which indicates the amount of water vapour that permeates per unit of area and time in a packaging material (kg·m/(m^2·s·Pa)). For fresh food it is important to avoid dehydration while for bakery or delicatessen it is important to avoid water permeation. The water vapour transmission rate (WVTR) is expressed in cc/m^2·s (or g·/m^2·day). The WVPC is correlated to the WVTR as described in (15) for the oxygen parameter.

Carbon Dioxide Transmission Rate (CO_2TR). As the oxygen and water vapour barrier properties, the carbon dioxide barrier property is of particular importance on food packaging applications. The carbon dioxide barrier is quantified by the carbon dioxide permeability coefficient (CO_2PC) which indicates the amount of carbon dioxide that permeates per unit of area and time in a packaging material (kg·m/(m^2·s·Pa)). Together with the permeability coefficient is given the carbon dioxide transmission rate (CO_2TR), expressed in cc/m^2·s (or g/·m^2·day). The CO_2PC is correlated to the CO_2TR as described above in (15).

There are several methods to measure the gas permeability of the food polymer packaging, well described in literature [5, 7].

3. Relationships between Polymer and Permeant Properties

Van Krevelen [21] claims that the permeability ratio between two gases through a series of thin polymeric film is constant, reporting that, taking nitrogen as the standard gas, it is possible to calculate the permeabilities of the other gases by simple factors. These factors are reported in Table 1, for a range of different gases [7]. In Table 2 are reported the relative values of permeability for the most commercial polymers, as reported by Guisheng et al. [22]. They demonstrated with experimental data that the relative values of permeability represent in some cases a very variable property depending on several factors like properties of the materials under study, gases analysed, temperature and relative humidity of the environment (external and in food contact), thermal and mechanical treatments, and so on. They suggested that, to estimate the permeabilities of a polymer for different gases, much care must be used to the proposed relative value and that the literature data must be confirmed by experimental ones. They found big differences especially for the relative value associated to the CO_2, while for the O_2 gas good agreement exists between the literature and experimental data.

Table 1: Relative value of permeability parameters (no-dimensional value).

Gas	P	D	S	E_p	E_d
N_2 (= 1)	1	1	1	1	1
CO	1.2	1.1	1.1	1	1
CH_4	3.4	0.7	4.9	(1)	(1)
O_2	3.8	1.7	2.2	0.86	0.90
He	15	60	0.25	0.62	0.45
H_2	22.5	30	0.75	0.70	0.65
CO_2	24	1	24	0.75	1.03
H_2O	—	5	—	0.75	0.75

Table 2: Relative value of permeabilities for the most commercial polymer (no-dimensional value).

Polymer	N_2	O_2	CO_2
Polystyrene sheet	1	2.6	10.4
LLDPE	1	3.1	11.1
LDPE	1	3.1	10.7
HDPE film	1	3.2	11.9
PP film	1	4.3	13.6
Nylon 6 film	1	3.4	18.4
PET film	1	3.6	17.8

The gases normally used in the modified atmosphere packaging are nitrogen, carbon dioxide, and oxygen (N_2, O_2, CO_2), whose properties are reported in Table 3 [1, 14, 23]. Other gases like Ar, CO, and N_2O are also under study in the food packaging field [24, 25] but until now few studies were made on the polymer film gas permeability for food packaging application. Kofinas et al. [11] studied the gas permeability coefficient of gases like He and CH_4, other than the usual gas, but without food simulants or real food contact.

Table 3: The most important properties of gases used in the permeability experiments.

Properties	N_2	CO_2	O_2
Molecular diameter/cm·10^{-8}	3.15	3.34	2.98
Mean free path/cm·10^{-6}	9.29	6.15	9.93
Average velocity/cm s^{-1}·10^{-2}	471	376	440
Van der Waals constant a/bar L^2 mol^{-2}	1.39	3.59	1.36
Van der Waals constant b/L mol·10^{-2}	3.91	4.27	3.18
Molar mass/kg $kmol^{-1}$	28.013	44.01	31.999
Critical volume/cm^3 mol^{-1}	90.1	94	78
Viscosity/μP	176	147	204
Gas density/kg m^{-3}	1.25	1.98	1.43
Molecular volume/cm^3 mol^{-1}	31.2	30.7	25.6
Solubilities of gases in water at different temperatures/cm^3 dm^{-3}	16.0 (20°C) 12.5 (40°C) 10.2 (60°C)	878 (20°C) 530 (40°C) 360 (60°C)	31 (20°C) 23 (40°C) 19 (60°C)
Diffusion coefficients of gases in water at 20°C/cm^2 s^{-1}·10^5	1.64	1.77	1.8
Kinetic diameter/cm 10^{-8}	3.64	3.30	3.46
Critical temperature/K	126.2	304.2	154.8
Critical pressure/MPa	3.39	7.39	5.08
Gas constant/kJ kg^{-1} K^{-1}	0.2968	0.1889	0.2598
Effective diameter/cm 10^{-8}	3.66	3.63	3.44
Collision diameter/cm 10^{-8}	3.68	4.00	3.43
Lennard-Jones force constant	91.5	190	113

4. Barrier Properties, Morphology, Thermal Treatment, and Mechanical Behaviour

Galić et al. [2] analysed the thermal behaviour of PE and PP material and their gas permeability parameters, using oxygen and nitrogen as permeating gases, at different temperatures (20, 40, and 60°C). By differential scanning calorimetry (DSC) they found that the tested polymers showed great structural stability also after sterilization process and after materials exposition to electromagnetic radiation (microwave oven) but, effectively, they did not make a correlation between the structural characteristics (crystalline/amorphous ratio) and the gas barrier properties. Many researchers [5, 7] report that there is a direct correlation between chemical structure and morphological properties, like density, crystallinity, and orientation with the permeability behaviour for a given polymer, but until now few studies describe this correlation. For example, Pauly [10] studied the effect of crystallinity on the permeability coefficient of HDPE when O_2 is used as permeant. He found a decrease in permeability of 38 and 19.3%, respectively, with crystallinity increasing of 60%, 69%, and 81% (P·10^{-11} of 54.9, 20.9, and 10.6 cm^3(STP) cm/cm^2 s (cm Hg)). Also Kofinas et al. [11] describe the permeability behaviour for polyethylene/poly(ethylene-propylene) semicrystalline diblock copolymers to several gases, showing a decrease in permeability with the increase of crystallinity and not a dependence of the permeability from the molecular weight of the polymer. It would be very interesting, to better understand this phenomena, to find a very good correlation between permeability measurements and polymer morphology, for each kind of materials, also after food contact which may alter the film characteristics.

Mrkić et al. [26] studied the influence of the temperature, from 10 to 60°C, and of the mechanical stress on the barrier properties of commercial polymers based on PE, biaxially oriented polypropylene (BOPP), and PA, using carbon dioxide, oxygen, nitrogen, and air as gases test. As it is well known, the gas transport coefficients like permeability to gases or water vapour, diffusion, and solubility change generally not only with the physicochemical characteristics of the polymer but also with the temperature associated with a mechanical stress. They found that crease mechanical stress causes changes on the barrier properties but it does not change in the thermal behaviour of the polymer matrix, both monofilm and laminate. Generally the highest change in gas permeance with increased stress cycle was observed with film having a metallized layer in the structure. This is because, although the barrier properties of metallized polymer are improved, they are susceptible to roughening of the surface during growth, and to the incorporation of voids and pinholes during the deposition of the film. The lowest effect of mechanical stress on gas permeance was observed for PE.

The effect on the permeability of the temperature increment was reported: until 40°C the permeability is almost the same, while at 50 and then 60°C a permeability

increase is registered, mostly due to enhanced motion of the polymer segments and increased energy level of permeating molecules. Furthermore, high temperatures increase the free volume in the polymer matrix. As described by Mrkić et al. [1], the highest effect of temperature was observed on PE film, compared with the other polymers studied (PA, PA/PE, BOPP, and BOPP/PE) attributed to the decreasing in crystallinity as analysed by DSC. As reported previously by other authors [27, 28], the sorption and the diffusion phenomena took place exclusively in the amorphous phase of a semicrystalline polymer and not in its crystalline zones. The crystalline portion increases the effective path length of gas diffusion and it seems to reduce the polymer chains mobility in the amorphous phase because chain-ends are blocked in the crystalline phase lamellae.

Cocca et al. [29] report also the influence of crystal polymorphism (α and α' form) on the barrier properties and mechanical performance poly(L-lactic acid) (PLA), a biodegradable polymer actually taken into consideration for the food packaging field. They found that the polymorphic structure significantly affects the Water Vapour Permeability, decreasing for the film containing a large fraction of α crystals related to the tighter molecular packing chain segments, together with the strong coupling with the amorphous portions of the macromolecules, which reduce the diffusion of the adsorbed water vapour.

Mrkić et al. [1] reported the E_P, E_D, and H_S parameters of the polymers PE, PA, PA/PE, BOPP, and BOPP/PE under study, making also a correlation with the gas properties, showing the Arrhenius behaviour in the temperature range under study. They found an excellent correlation between experimental and calculated values.

Kanehashi et al. [30], in a very interesting manuscript, dealing with the dependence for 300 crystalline and liquid crystalline polymers to permeability and diffusivity behaviour, pointed out how the value decreases with increasing the crystallinity for higher crystallinity range. On the contrary, at lower crystallinity range the value is almost constant or shows a slightly increase.

5. Simulating Conditions and Food Packaging Simulant Interaction

Some of the most common polymers used in food packaging field were tested simulating food preparation treatments such as microwave, pasteurization, and freezing, which are the treatments for food preservation that may be used also in a household. These kinds of researches are particularly important because the storage of packaged foods under irregular conditions can cause undesirable side effect (like oxidation, colour and aroma modification, changes in organoleptic properties, etc.) that could influence in a negative way the food quality. Moreover, the study of the polymer material stability by thermal experiments is a crucial factor to well understand if the package is adequate or not to protect the food. Kljusurić [31] made a thermal study, by differential scanning calorimetry (DSC), on several commercial polymer films like PP, PE, PHB, PP/PE, and PP with PP/PVDC. Authors found a correlation between the barrier properties and the physical data of the tested film, like crystallinity. The results showed that simulated processes have a larger influence on polymer stability, evaluated by measuring the enthalpy value changes. Anyway DSC techniques alone cannot prove the suitability of the packaging in fact migration data of the material from the food and vice versa are also of crucial importance to evaluate the suitability of polymer for food. For the hydrophilic polymer, the protective capacity of the packaging material depends on the relative humidity of the environment and on the water activity of food, so it is of great importance to determine its behaviour regarding the water sorption and its influence on permeability characteristics.

The study of the permeability characteristics of polymer material with food simulants, which normally contain water, is an important key to well understand its suitability as food packaging. The change in the permeability data after the contact with food simulants is principally due to the swelling effect of the water molecules. Normally, the simulants permitted from the law [32] are aqueous solutions of ethanol (15% v/v) or acetic acid (3% w/v) and distilled water. Of course the experiments are made also taking into consideration the temperature increments, generally from 20 to 60°C.

Galić and Ciković [23] reported the experimental study on the gas permeability of commercial polymer like PE, PP, Cellophane PVDC coated (commercial name XSAT), Paper/PE, and PA/PE determined before and after being exposed to food simulant (permitted from the EEC Directives) with N_2, CO_2, and O_2 gases. They found that the permeability to these gases of all investigated samples increased significantly after being exposed to food simulants showing that, according to the literature [33], under the action of water the polymer swells and changes its structure, making the diffusion of gases or vapour through it easier. It is obvious that it is important to take into consideration the chemical structure of the polymer like its hydrophobic or hydrophilic nature. So, the permeability of a hydrophilic polymer, such as PA in PA/PE copolymer and XSAT, depends largely on its water content, and an exposition to a liquid aqueous media, like a food solution simulant, strongly reduces its barrier properties, promoting an extremely high increase of permeability. Regarding PE and PP, which are hydrophobic films, the gas permeability values (for N_2, CO_2, and O_2) are strongly affected after the contact with the food simulants. The reason may be a consequence of a difference in crystallinity and morphology of films as well as the presence of additives, residual monomers, or oligomers.

Anyway, the effect of the different used food simulants is almost the same for all the studied polymers except for the Paper/PE, which showed a difference regarding the type of food simulant used, with the highest value in permeability changes when exposed to acetic acid solution, probably due to a minor stability of the monomer to acetic acid instead of ethanol solution.

Moreover, the experiments showed that the effect of the aqueous solutions on polymer permeability is similar to that produced by the temperature increments: the increase

permeability with the temperature is mostly due to the enhanced motion of the polymer chain and to an increased energy level of permeating molecules [34]. The E_a value of the permeation process decreases for all polymers after being exposed to food simulants.

In a very old publication, Woodward et al. [35] reported that the introduction of water in a semicrystalline polymer affects principally the amorphous region, breaking-up the hydrogen bonds between the polymer chain and giving, as a consequence, a reduction in the barrier properties of the material.

6. Gas Permeability of Silicon-Oxide-Coated Polymer Film and Plasma Pretreatment

In packaging industry, the deposition of amorphous silicon oxide (SiO_x) and other ceramics on polymer films is of increasing engineering interest to prevent the permeation through the material of gases like oxygen, carbon dioxide, or water vapour. The barrier films, 10–100 nm thick, are produced by sputtering, electron beam evaporation, or plasma enhanced chemical vapour deposition (PECDV), which is a relatively low-price technique. Normally a thin SiO_x layer is put between or on polymeric films, with a technology still in development. SiO_x is an inert oxide accepted from the EU Directive on migration [36]. The x-value, the oxygen quantity present in the oxide network, ranges from 1.5 to 1.8, where the high x-value gives not only the best oxygen barrier effect but also the highest tendency toward yellowing [14]. In the literature [13] it was reported that with this coating the gas transmission rate can be reduced substantially, with a degree of reduction dependent on polymer film thickness, on permeating gas, and on barrier film quality. But, when ceramics are used to improve the gas barrier properties, there is another factor that greatly influences and dominate the gas permeability parameter, which is the presence and the amount of defects in the coating oxide, like pinholes, grain boundaries, and microcracks. Roberts et al. [37] have shown that for inert gases, normally used on food packaging field, the contribution of defects to permeation increases with increasing atomic/molecular radius ($He < Ne < Ar = O_2$), with oxygen permeation completely defect-dominated. Grüniger and Von Rohr [13] applied a numerical calculation to predict the influence of defects on barrier properties of polymer materials. The presented results can be applied to a barrier/polymer configuration where the permeability of the barrier material itself and its thickness can be neglected. They found that the best solution for good permeability behaviour is to protect the ceramic barrier film by placing it between two polymeric layers, making a sandwich structure, with a polymer layer of low permeability adjacent to the barrier.

Hedenqvist and Johansson [38] studied the oxygen transport properties of the SiO_x coating on PET, LDPE, HDPE, and PP films, obtained using cold plasma technology, making a comparison between the data obtained experimentally with those obtained using a computer model. Moreover, for the first time, they obtained the oxygen diffusivity and solubility of an SiO_x coating in a polymer layer. They found that the oxygen diffusivity of the coated film was about four order of magnitude lower than that of the polymer substrate, while the oxygen solubility was higher than that of PP film. These results were explained by the presence of not continuous voids through the coating. In addition, SiO_x coatings on packaging film are sensitive to mechanical impact during handling, like package converting, bending/folding operation, shipping, and so forth. Of course the oxygen permeability increases monotonically with increasing the roughness of the surface substrate, because gas molecules can move between a more flexible path.

Galić and Ciković [14] studied the gas barrier properties of triplex film coated with silicon oxide (PET/PET + SiO_x/PE) before and after the exposure to food simulants, at different temperatures ranging from 20 to 60°C. They found that the exposure to aqueous solution does not affect the permeability characteristics of the coated films which are still able to maintain the original barrier properties to protect the product against gases during processing and handling and during the contact with liquid media. Unfortunately, to our knowledge, there are not studies on the solvent absorption mechanisms aimed to well explain how the Si-O network can influence the barrier effect of a film.

In a very recent work Plog et al. [39] deal with how plasma technology can be used to insert nanoscale SiO_x layers into PET foils to enhance the barrier properties to water vapour, reducing the permeation by more than 2 factors in comparison with the uncoated PET foil. Plasma pretreatment of polymer films can be a useful key to improve the barrier properties of food packaging systems [40].

7. Permeability Behaviour of Nanocomposites Polymers Food Packaging

The possibility to improve the barrier performance of food polymer packaging by the application of nanocomposites is a very attractive field because it is a very low-cost procedure. To well understand the permeability behaviour and the role of the chemical structure of the polymer matrix, there must be taken into consideration the principal factors affecting the permeability related to both polymer and nanocomposites, such as degree of crystallinity and crystal phases of the polymer, mobility of the amorphous phase, level of the dispersion, and orientation of the nanocomposites into the polymer matrix.

Russo et al. [19] studied new copolyamide-based nanocomposite films, using a statistical copolymer of the nylon-6 with a partially aromatic structure randomly inserted in the polymer chain and commercial organomodified montmorillonite as nanocomposite. They found a correlation between the oxygen barrier properties and the mechanical performances. The permeability data were interpolated using different theoretical approaches and not directly on the experimental film with or without contact with food or simulant solutions. So, it would be interesting to test these new materials in real life conditions. However they found that the nanocomposite film with the highest molecular weight copolyamide determines the

most significant oxygen barrier improvements, showing how the molecular weight of the polymer matrix is a crucial factor for the barrier properties. Obviously the O_2 barrier increases as the weight percent of nanocomposites contents increases, as it is demonstrated from the calculation of the O_2 diffusion coefficient D, which decreases in value as the nanocomposite weight percentage increases. As it is well known, gas permeation is greatly dependent on the diffusion process of the gas through the polymer and, with the presence of the nanocomposites, which make more the diffusive path for the permeant gas during its transport through the polymer difficult, the diffusion coefficients D can be strongly influenced by the nanomorphology achieved in the polymer sample film. The enhancement in the O_2 barrier seemed to be unrelated to the crystallinity degree or to the crystal phase of the material but it was related to the dispersion and orientation of the nanoparticles into the matrix.

Recently a review appeared on the polymer permeability with clay nanocomposites which deals with how nanoparticle can improve the barrier properties of polymers due to a lengthening of the diffusion of the permeants through a tortuous path. More measurements are required to well understand the effect of nanoparticles on the permeation process for different matrix or for the same matrix but different inorganic particles and/or different concentrations [41]. Also Azeredo [42] writes an interesting review dealing with how nanocomposites can be used to improve the performance of polymer materials used not only in food packaging field for gas barrier but also in other fields such as antimicrobial activity, enzyme immobilization, oxygen scavenging ability, and biosensing. So, nanocomposites cannot only passively protect the food against environmental factors but also incorporate properties to the packaging materials enhancing stability of foods [41, 43, 44].

Nanotechnology was also used to improve performance of biodegradable films like starch/clay nanocomposite films, obtained by polymer melt processing techniques [45], testing the conformity of these materials for food packaging field, in conformity with the actual regulations and European directive. Also, polylactide (PLA) [46] and poly(ε-caprolactone) [47] were reinforced with nanoparticles and mechanical, thermal, and barrier properties of the resulting materials were analysed in order to study the performance.

Also edible films with nanoparticles into the structure have appeared on literature, confirming that this field is increasing in interest from researcher. Barrier and mechanical properties of the obtained films (hydroxypropyl methylcellulose with chitosa/tripolyphosphate nanoparticles) show good value, according to the requirement in the edible food contact polymer pointed out as the nanotechnology can improve the functionality of the edible films [48].

8. Conclusions

To our knowledge, there are no data on the behaviour of the material in contact with food in real conditions, during processing and distribution. Most of the studies in this direction have been performed with stimulant solutions.

Moreover the experiments are generally performed from 20 to 60°C and it is necessary to take into consideration the permeability data also under these temperatures value, at which normally the fresh food could be subjected. The permeability data at storage food temperature are totally different from those registered at ambient temperature (23°C), especially when the packaging material is in contact with food and enclosed in a humid ambient.

It is important to know if there is interaction between food and packaging and consequently to well understand the factors that can influence the transport mechanism through the material. In this field temperature and relative humidity play a key role. As for the most common commercial polymer like polyolefin, the relative humidity has a considerable effect on permeability and sorption characteristics.

New polymers nanocomposite-based films are of highly attractive in the field of food polymer packaging because they present improvements in gas barrier properties. Actually they can be employed as an innovative solution to satisfy the most important package requirements such as protection, mechanical and thermal resistance, low cost and recycling.

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