PERMEABILITY OF POLYMERIC PACKAGING MATERIALS

Stanislav Zeman[1], Ľubomír Kubík[2]

[1]Department of Animal Husbandry and Food Production Mechanization
[2]Department of Physics
Slovak University of Agriculture in Nitra

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Abstract

The paper deals with study of permeability of polymeric packaging materials. The review of gas diffusion through polymeric membrane is presented. The signification of the quantities attached in corresponding equations is analyzed. Permeability coefficient at thermodynamic equilibrium is equal a product of diffusion and solubility coefficients. It depends on polymeric structure of material and also on the properties of diffusive molecules. The experimental methods of determination of polymer barrier properties suitable of permeability determination are also presented in the paper.

WŁAŚCIWOŚCI MECHANICZNE OPAKOWAŃ I ICH ODPORNOŚĆ NA OBCIĄŻENIA ZEWNĘTRZNE

Stanislav Zeman, Ľubomír Kubík

Słowacki Uniwersytet Rolniczy w Nitrze

Słowa kluczowe: dyfuzja gazów, prawa Ficka, metody wyznaczania przepuszczalności.

Streszczenie

Polimery są materiałem, który często jest stosowany do produkcji opakowań produktów spożywczych. W artykule przedstawiono analizę dyfuzji gazów przez polimerową membranę, podkreślając fizykalne znaczenie poszczególnych wielkości występujących w odpowiednich zależnościach matematycznych. Współczynnik przepuszczalności, który przy termodynamicznej równowadze jest równy dyfuzji i rozpuszczalności, zależy zarówno od struktury polimeru, jak i od właściwości dyfuzyjnych molekuł. W artykule przedstawiono metody eksperymentalnego badania „barierowych" właściwości polimerów zdeterminowanych ich przepuszczalnością.

Introduction

The role of plastic packaging materials, which we apply to packaging of foodstuff, is preservation of original quality of foodstuff from external unfavorable influences. We can achieve it by means of the barrier properties of

packaging material. The required protection of the foodstuff may be achieved with a single layer of polymer or necessitates the use of multilayered films including different polymers, coatings and metal foils. The barrier properties of the packaging material mainly originate from its permeability to gases and vapors that are noxious to the quality of product. For the majority of foods, the gains and loss of moisture leads to the destruction or noxious biological defects (Jase et al. 1994, Ashley 1985, Pye et al. 1976).

The choice of a packaging material should take into account all components of the foods as well as packaging material in consequence its interactions by influence of different storage conditions. The polymeric materials are so varied that we an always find an appropriate film or laminate for a given application. However, the absolute barrier does not exist. It is necessary to adapt barrier properties to the real life. One of the crutial criteria of choice is the knowledge of the permeability of the polymeric packaging to the gases and vapors which are crucial of preservation of food quality. The permeability of gases and vapors depends mainly on the polymer structure.

Basic principles of permeability of packaging materials

Steady state

Transfer of gases and vapors in polymers is realized by mechanisms of diffusion. Diffusion is a flow of matter which originates as consequence of chemical potential difference of migrant material in different location of the system. The amount of substance flow is defined as

$$\lim_{\Delta t \to 0} \frac{dn}{dt} \tag{1}$$

then the density flux J of gases and vapors is given by:

$$J = \frac{Q}{St} \tag{2}$$

where:
Q is the amount of substance of gases or vapors (mol),
S is the surface of packaging material and t is the time.

The First Fick's law is defined:

$$J = \frac{1}{S} \frac{dn}{dt} = -D \frac{\partial c}{\partial x} \tag{3}$$

where:
n is amount of substance,

D is diffusivity coefficient and $\frac{\partial c}{\partial x}$ is concentration gradient in direction of axis x.

Permeability of gases and vapors in the steady state, assuming that J=const. and $D \neq f(c)$, by integration trough of thickness of film from x_1 to x_2 and from c_1 to c_2 we obtain:

$$J\,x = -D(c_2 - c_1) \tag{4}$$

and

$$J = D\frac{c_1 - c_2}{x} \tag{5}$$

Substituting instead of J From relation (2) we obtain:

$$\frac{Q}{S\,t} = \frac{D(c_1 - c_2)}{x} \tag{6}$$

and

$$Q = \frac{D(c_1 - c_2)}{x}S\,t \tag{7}$$

In the case the concentration is sufficiently low the Henry's law is valid:

$$c = \sigma\,p \tag{8}$$

where:

p is the pressure of the diffused gas

σ is a gas solubility coefficient (Henry's constant).

By substituting instead of c in relation (7) form relation (8) we obtain:

$$Q = \frac{D\sigma(p_1 - p_2)S\,t}{x} \tag{9}$$

At thermodynamic equilibrium the gas permeability coefficient P is given by relation:

$$P = D\sigma \tag{10}$$

Permeability is depended on solubility and diffusivity. These quantities are functions of optional volume, cohesive energy and polymer morphology (McBride et al. 1979). Than permeability is defined:

$$P = \frac{Q\,x}{S(p_1 - p_2)\,t} \tag{11}$$

Permeability of unit thickness of the film is:

$$P_x = \frac{P}{x}, \text{ then from relation (11)} \quad P_x = \frac{Q}{S\,\Delta p\,t} \tag{12}$$

and diffusion is realized only one direction.

Non-steady state

Speed of diffusion in the polymer is limited. Density flux of gases and vapors is given by Second Fick's law. We define the amount of substance of gases and vapors as

$$Q = \frac{D c_1}{x}\left(t - \frac{x^2}{6D}\right) = \frac{D c_1 t}{x} - \frac{c_1 x}{6} \tag{13}$$

where Q is linear function of t.

When we assuming that $Q=0$ and $t=L$, from the Figure 1 results after extrapolation

$$\frac{D c_1 L}{x} = \frac{c_1 x}{6} \tag{14}$$

and than

$$D = \frac{x^2}{6L} \quad \text{and} \quad L = \frac{x^2}{6D} \tag{15}, \tag{16}$$

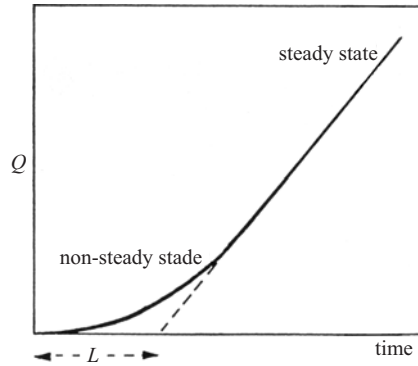where x is thickness of the foil.

Fig. 1. Typical permeation and time lag curve by JASSE et al. (1994)

In the case the polymers include dispersed porous particles with vast surface and the solubility of gases don't agree with Henry's law the sorption (or penetrant concentration) c_H is calculated according to Langmuir isotherm (SOHAIL et al. 1997, JASSE et al. 1994, KOROS et al.1992, HACE et al. 2004):

$$c_H = \frac{c_H' b p}{1 + b p} \tag{17}$$

Here c_H is the penetrant concentration in microcavities or holes in the polymer matrix, $c_{H'}$ is saturation concentration of the penetrant species in the microvoids, p is the equilibrium pressure and b is Langmuir's hole-capacity constant.

The coefficients permeability P and P_x are function of temperature and may be expressed by Arrhenius relation (JASSE et al 1994):

$$P_x = P_0 \exp\left(-\frac{E_d}{RT}\right) \tag{18}$$

where:
P_0 is permeability at infinity temperature,
E_d activation energy for permeation,
R is universal gas constant and
T is absolute temperature.

Permeability of multilayer packaging material

Provided that total thickness of foil is

$$h_c = h_1 + h_2 + h_3 + \cdots + h_n \tag{19}$$

steady flow of gases is constant

$$Q_c = Q_1 = Q_2 = Q_3 = \cdots = Q_n \tag{20}$$

and surface of all layers is the same

$$S_c = S_1 = S_2 = S_3 = \cdots = S_n \tag{21}$$

Than we substitute in relation

$$\frac{Q}{t} = \frac{P}{x} S (p_1 - p_2) \tag{22}$$

and we obtain:

$$\frac{Q_T}{t} = \frac{P_1}{h_1} S_1 (p_1 - p_2) = \frac{P_2}{h_2} S_2 (p_2 - p_3) = \frac{P_3}{h_3} S_3 (p_3 - p_4) \tag{23}$$

For multilayer foil we can obtain:

$$\frac{Q_T h_c}{t S_c P_c} = p_1 - p_4 = \Delta p_i \tag{24}$$

where:

$$\Delta p_i = (p_1 - p_4) = (p_1 - p_2) = (p_2 - p_3) = (p_3 - p_4) \tag{25}$$

than

$$\frac{Q_T h_c}{t S_c P_c} = \Delta p_i = \frac{Q_T}{t S_c}\left(\frac{h_1}{P_1} + \frac{h_2}{P_2} + \frac{h_3}{P_3}\right) \tag{26}$$

and if

$$\frac{h_c}{P_c} = \left(\frac{h_1}{P_1} + \frac{h_2}{P_2} + \frac{h_3}{P_3}\right) \tag{27}$$

than

$$P_c = \frac{h_c}{\dfrac{h_1}{P_1} + \dfrac{h_2}{P_2} + \dfrac{h_3}{P_3}} \tag{28}$$

Methods of determination of permeability packaging materials

Variable pressure method

Jasse et all (1994) present the equipment consisting of testing chamber divided by testing foil on two parts. Testing gas is transported at specific pressure p_1 in the first part of the chamber. The second part is evacuated on the pressure p_2. The experimental conditions are such that $p_1p_2\sim0$ so that $\Delta Q/\Delta t$ can be calculated from $\Delta p_2/\Delta t$. The permeability is given by relation:

$$P = \frac{\Delta Q\, x}{S\, \Delta t\, p} \tag{29}$$

where:
ΔQ is amount of gas penetrated in the time interval Δt in the steady flow,
S is effective area of the and
x is the thickness of the packaging.

The spectrometer may be used on the measurement. The time lag L we can obtain from the samples. This quantity is related to the diffusivity coefficient D by $D=h^2/6L$. From the values of P and D we may calculate the solubility coefficient $\sigma=P/D$.

Differential methods

In these methods the gas streams on one side of the polymer film. The gas crossing the film being carried out towards a detector by helium to produce a signal proportional to the diffusion rate. The analysis may be realized using different techniques such as thermic conductivity detector, flame ionic detection, a gas chromatograph or mass spectrometer. Absorption and desorption runs can be done as illustrated in Figure 2 in the case of a thermic conductivity detector. In this case the permeability is given by:

$$P = \frac{f\, \sigma\, k\, \alpha\, S_\infty\, h}{S\, p} \tag{30}$$

where:
f is gas flow rate,
σ detector sensitivity,
k a molecular factor,
α the detector attenuation,
S_∞ the steady state signal intensity,
h the film thickness.
S is the pressure area and
p is pressure of the gas.

The diffusion constant D is given by:

$$D = \frac{h^2}{7.2 \cdot t_{1/2}} \tag{31}$$

where $t_{1/2}$ is half time necessary to obtain the steady state.

The use of a gas chromatograph as well a mass spectrometer allows us to determine the individual diffusion characteristics of each gas present in the mixture.
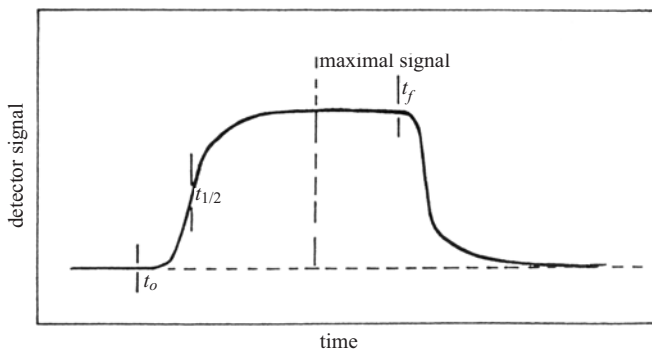

Fig. 2. Thermal conductivity detector output as function of time by PYE et al. (1976)

Parameters affecting packaging permeability

Polymeric materials present a wide range of structures and properties depending on their chemical structure, method of preparation and processing conditions. The presence of additives or use of polymer blends affect barrier properties towards carbon dioxide, oxygen, nitrogen or water vapor. Some permeability data for various polymers are given in Table 1.

LEE (1980), MOJUN (2003), PAUL et al. (1973) described the permeation of a gas trough different polymer using the expression:

$$P = A e^{-B(V - V_0)} \tag{32}$$

where:
 A and B are constants characteristics of the gas,
V is the specific volume measured experimentally and
V_0 is an estimation of the specific volume at absolute zero.

BARBARI (1993), KOROS et al. (1980) using sorption and expansion data determined the molar volumes of CO_2 and CH_4 in silicon rubber and calculated the mobile gas concentration for CO_2 and CH_4. The influence of free volume on diffusivity coefficient D and permeability P was described by a study of (MAEDA, PAUL 1987).

During the last period, an increasing interest in polymer blends arose to improve mechanical and barrier properties of packaging materials. Usually polymers are incompatible and only few systems can be considered as compa-

Table 1

Cofficientts of permeability for various polymers by Ashley (1985)

Polymer	P(ml mm cm^{-2} s^{-1} cm Hg^{-1})				$\dfrac{PO_2}{PN_2}$	$\dfrac{PCO_2}{PO_2}$	$\dfrac{PCO_2}{PN_2}$	Structure of polymer
	N$_2$ 30ºC	O$_2$ 30ºC	CO$_2$ 30ºC	H$_2$O, 90% RH 25ºC				
Low density polyethylene	19	55	352	800	2.9	6.4	18.5	Some crystallinity
High density polyethylene	2.7	10.6	35	130	3.9	3.3	13	Crystalline
Polypropylene	–	23	92	680	–	4.0	–	Crystalline
Unplasticized PVC	0.4	1.2	10	1 560	3.0	8.3	25	Slightly crystaline
Cellulose acetate	2.8	7.8	68	75 000	2.8	8.7	24	Glassy amorphous
Polystyrene	2.9	11	88	12 000	3.8	8.0	30	Glassy
Nylon 6	0.1	0.38	1.6	7 000	3.8	4.2	16	Crystalline
Polyethylene terephthalate	0.05	0.22	1.53	1 300	4.4	7.0	31	Crystalline
Plyvinylidene chloride	0.0094	0.053	0.29	14	5.6	5.5	31	Crystalline

tible either completely or in narrow range of concentration. LEE (1980) assuming the free volume of the blend equal to the sum of the free volumes of the components obtained, in incompatible blends, the following expression:

$$\ln \frac{P}{S} = \left[\frac{\Phi_1}{\ln \dfrac{P_1}{S}} + \frac{\Phi_2}{\ln \dfrac{P_2}{S}} \right]^{-1}$$

(33)

where:
S is a constant characteristic of the gas and
Φ_1, Φ_2 are the volume fractions of components 1 and 2.

The thickness of the film also affected on the permeability. The increased thickness reduces gas flow. One of the goals in film manufacture is to obtain as thin a film as possible with good mechanical and transport properties. In practice a thickness of 25 μm is common. Critical value the thickness of the film is 10 μm.

Conclusion

As a permeability of polymeric packaging materials depends on the sorption and diffusion of gases and vapors, it is of relevance to recall the models that apply for prediction of these parameters in the polymers. The

experimental techniques used to measure permeability are based on volumetric, gravimetric or differential methods. These permeability coefficients are influenced by the chemical structure as well as by method of preparation and processing conditions. Some of the structural parameters play a major role in their effect on permeability. The gases and vapors particularly important in food packaging and preservation are O_2 and CO_2 and water vapor. The effect of their shape and size, interaction with the polymer and the influence of temperature and pressure on their sorption and diffusion behaviour may be helpful in the understanding of the variation of their permeation through polymeric packages.

Acknowledgement

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