

Prediction of Gas Permeability of Nylon From Glass-Transition Temperature

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SYNOPSIS

A method to predict the permeability coefficients of gases in nylons at different relative humidities was proposed. The model was tested for Nylon 6 and 6,6 with oxygen as a permeant. Very good agreement between the predicted and experimentally determined values was found. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The shelf life of foods is limited due to chemical, physical, and enzymatic reactions that occur during storage. Chemical changes resulting from oxidation reactions are very common in foods as well as in many other products. To diminish such reactions, the access of oxygen to packaged products has to be limited. During the last two decades, plastic packages have been continuously replacing other materials. However, all polymers are permeable to gases, vapours, and aroma compounds. Information on, or the ability to predict gas (and especially oxygen) permeability of plastic packages is therefore of great importance. Some of the hydrophilic polymers (like the nylons) are very good oxygen barriers, in addition to their enhanced mechanical properties. Moisture, however, significantly affects the mechanical as well as barrier properties adversely and as a result their properties depend on the relative humidity of the environment. The determination of gas permeability of plastic films at different relative humidities is difficult and requires special sophisticated and expensive equipment.

Salame¹ suggested a theoretical model to predict the permeability coefficients of gases in polymers. The model takes into account the chemical structure and morphology of the polymer and the nature of the permeating gas. This model however, does not take into consideration the effect of moisture (or

relative humidity, RH) on the permeability of hydrophilic polymers.

The present work is aimed at extending currently available models so that the effect of moisture content (depending on the relative humidity of the environment) in hydrophilic polymers could be taken into consideration.

Theoretical Model

The permeability coefficient, P , is normally described as a product of the diffusion and solubility coefficients, D and S , respectively²:

$$P = DS \quad (1)$$

D and S depend on temperature according to:

$$D = D_0 \exp(-E_d/RT) \quad (2)$$

$$S = S_0 \exp(-\Delta H_s/RT). \quad (3)$$

Therefore:

$$\begin{aligned} P &= D_0 S_0 \exp[-(E_d + \Delta H_s)/RT] \\ &= P_0 \exp(-E_p/RT) \end{aligned} \quad (4)$$

where D_0 , S_0 , and P_0 are preexponential constants; E_d and E_p are the activation energies for diffusion and permeation, respectively; ΔH_s is the enthalpy of dissolution; R is the universal gas constant; and T is the absolute temperature.

The parameters D_0 , S_0 , E_d , and ΔH_s are therefore required in order to predict the permeability coef-

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ficient, P . Salame¹ suggested correlations for the calculation of these parameters. He also suggested that the permeability coefficient of polymers could be predicted (or calculated) from a permachor parameter, π , from the following equation:

$$P = A \exp(-s\pi) \quad (5)$$

where A and s are constants for a specific gas, polymer, and temperature. According to Salame's permachor model, each polymer can be divided into segments of different chemical structures, each of which assumes a permeachor number. The permeachor number of the polymer as a whole is then the sum of the permeachor values of the segments in its repeating unit (monomer).

Equation (5) has been shown¹ to predict the permeability coefficients of different polymers well. As was pointed out earlier, however, this model does not take into account the effect of moisture on the permeability coefficient of some important hydrophilic barrier polymers like the nylons.

Salame³ suggested that the Permeachor number depends on two important parameters of the polymer: the cohesive energy density (CED) and the specific free volume, (FV). He suggested the following correlations between the permeachor number and the two above-mentioned parameters:

$$\pi = 61 \ln(\delta^2/\text{FV}) - 355 \quad (6)$$

for polymers not containing chlorine and fluorine atoms in their structure and:

$$\pi = 32 \ln(\delta^2/\text{FV}) - 140 \quad (7)$$

for polymers containing those halogen atoms. δ in eqs. (5) and (6) is the well-known solubility parameter:

$$\delta = (\text{CED})^{0.5} = \left(\frac{E_v}{V_m} \right)^{0.5} \quad (8)$$

where E_v is the molar heat of vaporization (also known as the cohesive energy) and V_m is the molar volume.

Van Krevelen⁴ has shown that the cohesive energy of a polymer can be calculated from the cohesive energy of the repeating groups in its structure. He has also shown how FV and V_m of a polymer can be calculated from its structure and degree of crystallinity.

Thus, if E_v , FV, and V_m are known (or can be calculated), one can predict the permeability coef-

ficient of a polymer from eq. 5 together with eqs. (6) [or (7)] and (8).

It is well known that moisture acts as a plasticizer in hydrophilic polymers and therefore affects their glass-transition temperature, T_g . The T_g of these polymers is usually above the temperature of their normal application as a gas barrier material (room temperature and below) and therefore, during their application, they are in their glassy state.

Hayes⁵ suggested that the energy of vaporization of a polymer depends on two parameters: the T_g and the mobility parameter, n , according to:

$$E_v = (0.5RT_g - 25)n. \quad (9)$$

The mobility parameter of a polymer can be calculated from eq. (9) using known values of E_v and T_g .

It is generally assumed⁶ that the free volume of a polymer does not change below its T_g . We suggest that the mobility parameter of the polymer segments also does not change below T_g . Based on this assumption, it is possible to calculate the variation in the cohesive energy, E_v , with the change in T_g as a function of moisture content in the polymer (or RH) from eq. (9). The calculated E_v values from eq. (9) together with the V_m and FV values calculated according to Van Krevelen⁴ can then be used for consecutive calculation of the cohesive energy density δ , eq. (8), permachor value π , eq. (6) and permeability coefficient P , eq. (5), respectively. Using eq. (4) enables one to predict the permeability coefficient at different temperatures.

EXPERIMENTAL

Materials

A 22- μm film of Nylon 6 (Pastopil, Kibbutz Hazorea, Israel) and a 28- μm film of Nylon 6,6 (Du Pont, Canada) were used in the present study. The crystalline fraction, X_c , in these films was 0.40 and 0.57, respectively.

Desicators containing saturated salt solutions and petrie dishes above the solution with a predetermined weight of the film sample were used to obtain sorption isotherms of the films at 25°C.

The following saturated salt solutions were used: lithium chloride, RH = 15%; potassium acetate, RH = 23%; magnesium chloride, RH = 45%; strontium chloride, RH = 71%; sodium chloride, RH = 75%; potassium sulphate, RH = 97%.

Methods

A sample of the saturated film was placed in a small differential scanning calorimeter (DSC) dish and its T_g measured at a heating rate of $5^\circ\text{C}/\text{min}$. A Mettler DSC, Tca10 was used for this purpose. Oxygen permeability measurements of the nylon films was carried out using an OX-TRAN 100 Permeability tester made by Mocon, USA.

RESULTS AND DISCUSSION

In Figure 1 the variation in T_g with RH of Nylon 6 film as measured in the current study by DSC is compared to that given by Kettle⁷ for Nylon 6 pellets determined by dilatometric methods. It can be seen that the variation is similar and the values are comparable except for those at the highest, RH = 0.97, level. In Figure 2 the permeability coefficients calculated from the T_g by the method outlined above is plotted against the relative humidity. The value $n = 44$ was used in these calculations. This value was calculated from eq. (9) using $E_v = 13,690$ cal/mol determined according to Van Krevelen⁴ and $T_g = 336^\circ\text{K}$ at RH = 0.⁸ The values of $A = 0.1126$ and $s = 5639$ [calculated according to Salame¹] were used in eq. (5) for calculating the permeability coefficients from the permachor values. In the same figure the permeability coefficients at 0, 50, and 95% RH, as measured in the present study, are also given. It can be seen that the agreement between the predicted and actually measured values is very good except for the value calculated from the results of Kettle for RH = 0.97.⁷

We had difficulties in measuring the T_g of Nylon 6,6 at different RH levels by DSC as the reproduc-

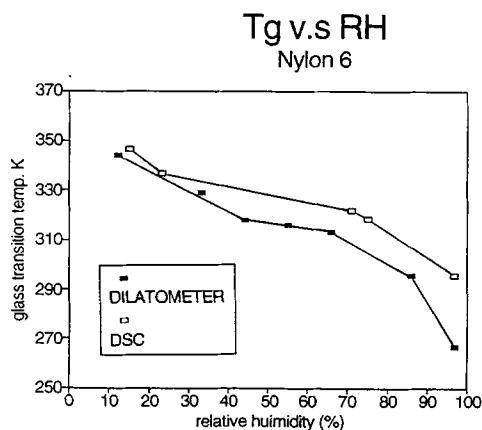


Figure 1 The effect of relative humidity on the glass-transition temperature on Nylon 6.

Permeability Coeff. V.S RH Nylon 6

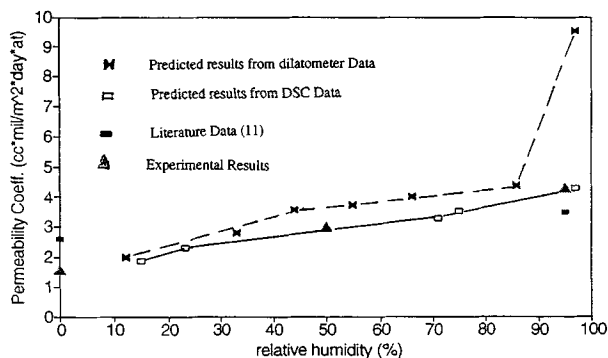


Figure 2 Effect of relative humidity on the permeability coefficient of Nylon 6.

ibility of the results was not satisfactory. In order to test the validity of the currently suggested method also for Nylon 6,6, we used data from literature. Reimschuessel⁹ reported graphically the variation in the ratio T_g/T_{g0} (where T_{g0} is the glass-transition temperature at zero water uptake) of Nylon 6,6 as a function of water uptake. These results were obtained by nuclear magnetic resonance (NMR). We have extracted these results and by using the sorption isotherm for Nylon 6,6 published by Starkweather¹⁰ and the value of $T_{g0} = 323^\circ\text{K}$,⁸ we have plotted the relation between T_g and RH in Figure 3. In Figure 4 the variation in the permeability coefficients of Nylon 6,6 calculated from the T_g is plotted as a function of the RH. The value of $n = 91.9$ was used in these calculations. This value was also calculated from eq. (9) using $E_v = 27,390$ cal/mol determined according to Van Krevelen⁴ and $T_g = 323^\circ\text{K}$ at RH = 0.⁸ Shown in the same figure are

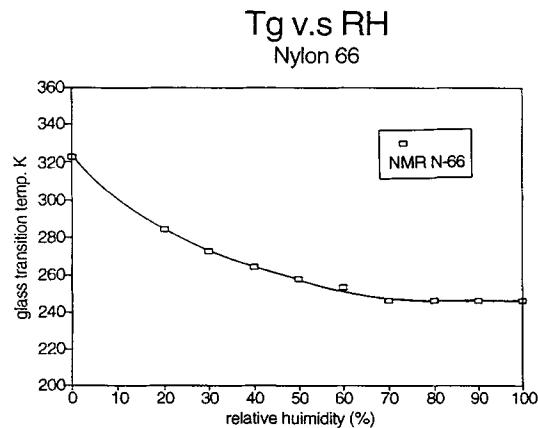


Figure 3 Effect of relative humidity on the glass-transition temperature of Nylon 6,6.

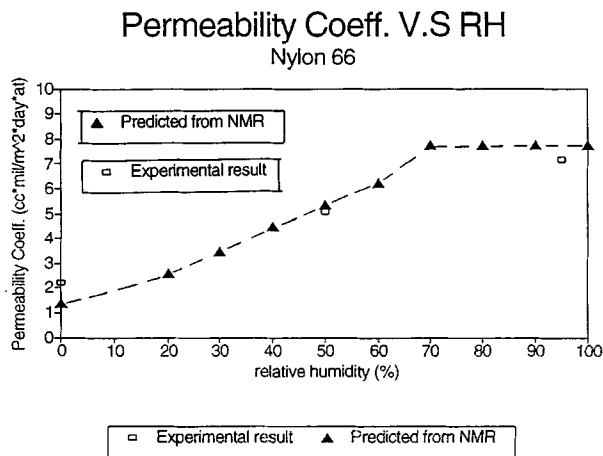


Figure 4 Effect of relative humidity on the permeability coefficient of Nylon 6,6.

also the permeability coefficients experimentally determined in the present study. It can be seen that the agreement between the predicted and experimentally determined values is good. The plateau in the calculated permeability coefficient curve results from the plateau in the T_g/T_{g0} as a function of water content curve reported by Reimschuessel.⁹ In Figures 5 and 6 the solubility parameter and the permachor values, as calculated from eqs. (6) and (8), respectively, are given for the two nylons as a function of the relative humidity. As expected, the solubility parameter and the permachor number decrease (the permeability coefficient increases) with the increase in RH because water acts as a plasticizer in hydrophilic polymers, causing a loosening in their structure.

As the currently suggested model is not confined to any specific permeating gas, the hereby proposed

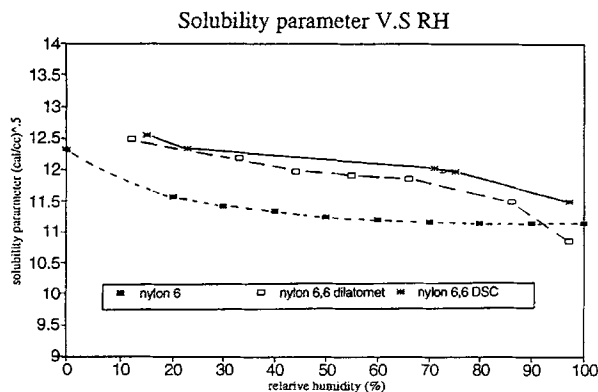


Figure 5 Effect of relative humidity on the solubility parameter of Nylon 6 and Nylon 6,6.

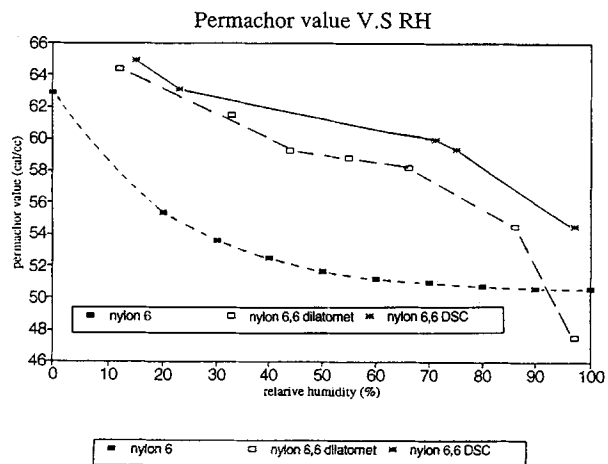


Figure 6 Effect of relative humidity on the permachor number of Nylon 6 and Nylon 6,6.

method could be used for the prediction of permeability coefficients of different gases and aroma in nylons at different RH levels. However, it should be stressed that the method may not be accurate for hydrophilic gases that could interact with the varying amount of water absorbed in the nylon at different relative humidities.

REFERENCES

1. M. Salame, *Polym. Eng. Sci.*, **26**, 1543 (1986).
2. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975.
3. M. Salame, private communication (1990).
4. D. W. Van Krevelen, *Properties of Polymers*, Chap. 7, Elsevier, Amsterdam, 1990.
5. R. A. Hayes, *J. App. Polym. Sci.*, **5**, 318 (1961).
6. F. Rodriguez, *Principles of Polymer Systems*, McGraw-Hill, New York, 1970.
7. G. J. Kettle, *Polymer*, **18**, 742 (1977).
8. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975.
9. H. Reimschuessel, in *Handbook of Fiber Science and Technology*, Vol. 4, Chap 2, M. Levin and E. M. Pearce, eds., Marcel Dekker, New York, 1985.
10. H. W. Starkweather, *Water in Polymers*, ACS Symposium, Series 127, American Chemical Society, Washington, D.C., 1980, p. 433.
11. M. Bakker and D. Eckroth, *The Wiley Encyclopedia of Packaging Technology*, John Wiley & Sons, Inc., New York, 1986.

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