

# TECHNISCH-WETENSCHAPPELIJKE RUBRIEK

onder redactie van het instituut voor voedingsonderzoek TNO, Zeist

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## Gas permeability of hydrophilic films

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### Samenvatting

Er wordt een methode beschreven voor het meten van de gasdoorlatendheid van hydrofiele films (cellulose, enz.) door middel van de vacuümtechniek, waarbij de hele film met behulp van een „zeef-film” is geconditioneerd op een bepaalde relatieve vochtigheid.

Factoren die de gasdoorlatendheid van een hydrofiele film kunnen beïnvloeden worden besproken. Metingen van de zwelgraad aan een cellulose- en een nylon 6-film, welke de eventuele invloed van een voorbehandeling tonen, worden vermeld.

De invloed van de relatieve vochtigheid op de zuurstofdoorlatendheid van een cellulosefilm wordt door meetresultaten geïllustreerd.

### Summary

A method is given to measure the gas permeability of hydrophilic films (cellulose, etc.) under constant relative humidity of the whole film, by using the vacuum technique with a "sieve film".

Factors affecting the gas permeability of hydrophilic films are discussed. Measurements of the degree of swelling on a cellulose and a nylon-6 film are produced which show any possible influence of a pre-treatment of these films. The influence of the relative humidity on the oxygen permeability of a cellulose film is illustrated by measurement.

### Résumé

Il est décrit une méthode pour mesurer la perméabilité au gaz des pellicules hydrophiles (en cellulose, etc.) au moyen de la technique à vide, où, à l'aide d'une "pellicule-tamis" ("pellicule-filtre"), la pellicule entière est conditionnée à une certaine humidité relative.

Des éléments, pouvant influencer la perméabilité au gaz de la pellicule hydrophile, sont discutés. Des mesures du degré de gonflement à une pellicule en cellulose et à une pellicule en nylon-6, montrant l'influence éventuelle d'un traitement préalable sont communiquées.

L'influence de l'humidité relative sur la perméabilité à l'oxygène d'une pellicule en cellulose est illustrée par des résultats de mesures.

### Zusammenfassung

Es wird eine Methode beschrieben zum Messen der Gasdurchlässigkeit hydrophiler Folien (aus Zellulose, u.s.w.) mittels Vakuumtechnik, wobei die ganze Folie mit Hilfe einer Siebfolie auf eine bestimmte relative Feuchtigkeit konditioniert ist.

Faktoren, welche die Gasdurchlässigkeit hydrophiler Folien beeinflussen können, werden besprochen. Messungen des Quellungsgrades bei einer Zellulosefolie und einer nylon-6-Folie, welche den eventuellen Einfluss einer Vorbehandlung zeigen, werden erwähnt.

Der Einfluss der relativen Feuchtigkeit auf die Sauerstoffdurchlässigkeit einer Zellulosefolie wird durch Messresultate verdeutlicht.

### Introduction

It is known from the literature (1, 2, 3, 4, 5, 6) that the presence of water vapour has much influence on the gas permeability of hydrophilic films, e.g. cellulose film and polyamide (nylon). The sorbed water vapour plasticizes the film facilitating the diffusion of gas through the film. Therefore, when measuring the gas permeability of a hydrophilic film, the relative humidity of the gas must be considered. The influence of the relative humidity on the gas permeability of polyamides has been studied by Simril and Hershberger (1), Meyer, Rogers, Stannett and Swarc (2), Müller and Hellmuth (3). They

found that the  $\text{CO}_2$ -permeability of a nylon film at 100% R.H. is increased nearly a threefold over the dry gas value.

The influence of the relative humidity on the gas permeability of cellulose films is much greater. An increase in the oxygen permeability of a cellulose film is said to be 30,000 fold, as the R.H. increases from zero to saturation (6). The influence of the relative humidity on the permeability of cellulose film is great, as the degree of swelling is influenced by the percentage of moisture in the film. This degree of swelling is also dependent on the structure of the material which, in its turn is determined by the way of preparing, the pre-treatment, the solvent in the case of a coating, the adhesion in the case of a laminate, etc..

The problem inherent in measuring the gas permeability of hydrophilic films under constant relative humidity is that the film has to be conditioned on both sides (entry- and exit side) at the same relative humidity, and that the water content of the film during the measurement should be in equilibrium with the partial water vapour pressure on both sides. This problem can easily be solved by the TNO method of placing a "sieve" film under the hydrophilic specimen to be tested, as will be described hereafter.

**Method of operation** for the measurement of the gas permeability of hydrophilic films under constant relative humidity. A usual technique for measuring the flow of a test gas through a membrane involves the placing of a film between an evacuated chamber of known constant volume (measuring chamber) and a reservoir containing the test gas at a known pressure (test gas supply system). One then measures the amount of gas penetrating through the film per unit of time by determining the increase of pressure in the initially evacuated chamber, using a suitable manometric device (e.g. McLeod manometer).

Such an apparatus was for instance used by Barrer (7, 8) and has been developed further by Stannett et al (2). The high-vacuum technique applied by these research workers was the starting point in developing the TNO gas permeability apparatus (see Fig. 1). A description of this apparatus and the working method is given in "Plastica" (9).

Buchner (4, 10), Pilar (5) and Fricke (11) assert that measurements of the gas permeability of hydrophilic films under constant relative humidity, are impossible with the high-vacuum technique in that the exit side is at 0% relative humidity (vacuum). The problem can be solved, however, by placing a "sieve" film under the hydrophilic specimen to be tested. This is a film with a high gas permeability but a low water vapour permeability (polyethylene is found suitable for this purpose).

In this case the relative humidity in the interface can be calculated as follows (see Fig. 2).

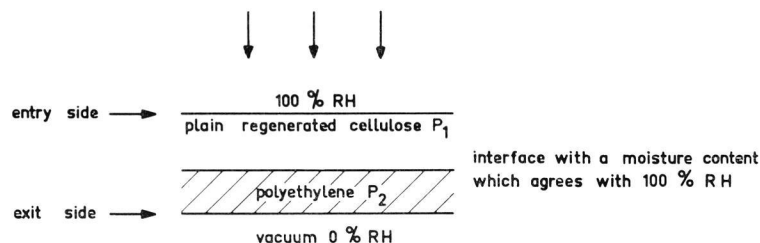
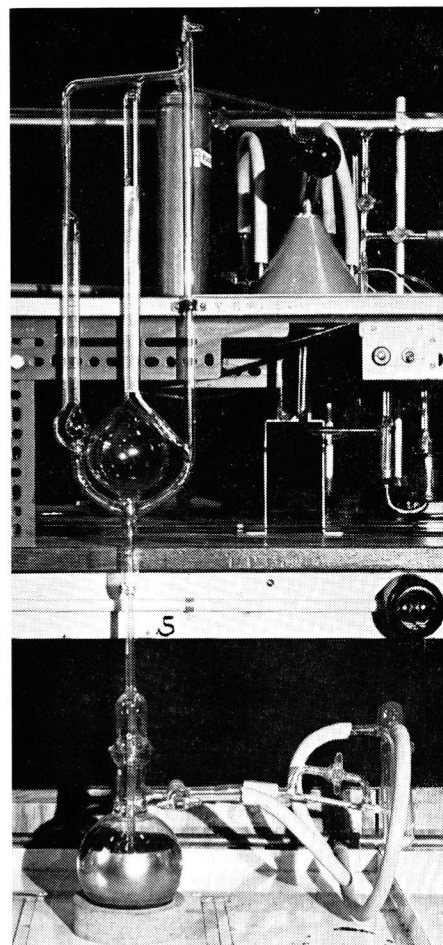


Fig. 2. Relative humidity of a plain regenerated cellulose film determined by using polyethylene as a "sieve" film.



McLeod Manometer

Fig. 1. Gas permeability apparatus developed at the Central Laboratory TNO.

The rate of permeation,  $q$ , through each layer must be constant under steady state conditions, and if we assume that the permeability constants ( $P_1, P_2$ ) are independent of pressure:

$$q = P_1 \frac{p_1 - p_2}{x_1} = P_2 \frac{p_2 - p_3}{x_2}$$

Where:  $p_1, p_2, p_3$  = pressures of the gas on the surface in equilibrium with the film.  
 $x_1, x_2$  = thickness of the film layers.

In the case of two layers (1 = cellulose film, 2 = polyethylene) of the same thickness ( $x_1 = x_2$ ) when at the entry side of layer 1 there is 100 % relative humidity and at the exit side of layer 2 there is 0 % relative humidity, the relative humidity in interface ( $RH_2$ ) can be calculated as follows:

$$RH_2 = 100 \% \frac{1}{\frac{P_2}{1} + \frac{1}{P_1}} \approx 100 \%,$$

where  $P_1$  = Water vapour permeability of cellulose film =  $5000 \times 10^{-9} \text{ cm}^3/\text{cm}^2/\text{sec}/\text{mm}/\text{cm Hg}$ .  
 $P_2$  = Water vapour permeability of polyethylene =  $90 \times 10^{-9} \text{ cm}^3/\text{cm}^2/\text{sec}/\text{mm}/\text{cm Hg}$ .

Thus we can determine the gas permeability of a hydrophilic film, while the whole film is conditioned at a constant relative humidity. Although this theory employs "ideal" laws of permeability for water vapour, it should lend a fair approximation to the "sieve" film system.

The influence of the relative humidity on the oxygen permeability of a plain regenerated cellulose film is illustrated in Fig. 3. The test gas is at a constant R.H. controlled by an appropriate saturated salt solution. A 100 % relative humidity is realized by flushing the test gas through a washing bottle filled with water, or a layer of water on top of the specimen.

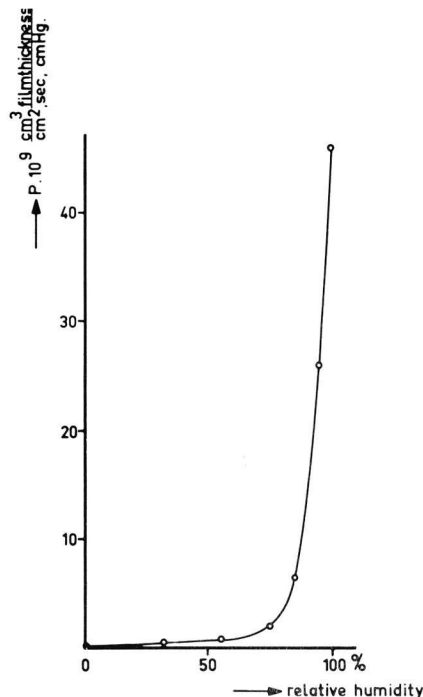


Fig. 3. Influence of the relative humidity on the oxygen permeability of a plain regenerated cellulose film.

It is interesting to note that the greatest effect of the relative humidity on the gas permeability begins to occur at 70 - 80 % R.H. This has also been found by Pilar (5).

We can use the "sieve" film in the case of a laminate, but mostly the hydrophilic film is laminated with a hydrophobic material in order to decrease the water vapour permeability. In this case the film is measured with the hydrophobic (polyethylene, saran, etc.) side immediately to the high vacuum, influence of the relative humidity on the gas permeability of e.g. polyethylene or saran has never been found.

When the hydrophilic material is coated on both sides with a hydrophobic film it is necessary to precondition the film in the atmosphere of interest, because it is too time-consuming to do this on the gas permeability apparatus.

### Degree of swelling

As has already been noted, the degree of swelling of a hydrophilic film influences the gas permeability. The swelling properties can be determined by measuring the amount of liquid absorbed by the film. This can be done by weighing the film after the swelling has reached its equilibrium value. The difference between this weight ( $w$ ) and the dry weight ( $w_0$ ) is the weight of the liquid absorbed.

The degree of swelling is defined as  $\frac{w - w_0}{w_0}$  g solvent/g polymer.

We have measured the swelling properties of a plain regenerated cellulose film and a nylon 6 film in ethanol at 20 °C. The film had been preconditioned in order to remove plasticizers etc., 24 hrs in water and 60 hrs in ethanol. After swelling the films were deswelled partly in benzene. Swelling in ethanol and deswelling in benzene were repeated 4 times. Finally the dry weight ( $w_0$ ) was determined. The results are shown in Table 1.

**Table 1.** Degree of swelling of a cellulose film and a nylon 6 film in ethanol at 20 °C.

	degree of swelling ( $I$ )	
	cellulose film	nylon 6.
first measurement . . . . .	0.62	0.11
second measurement . . . . .	0.45	0.11
third measurement . . . . .	0.31	0.11
fourth measurement . . . . .	0.28	0.11

From this table it is seen that the degree of swelling of the cellulose film does not reach an equilibrium value, but that the degree of swelling is dependent on each pre-treatment of the film.

This may be due to the remarkable structure of the cellulose skeleton, that might in its turn be caused by the presence of polar hydroxyl groups, which may form many hydrogen bonds. These bonds are obviously rather stable unless other compounds (water, urea, formalin, alkali, etc.) are present which are able to break them.

The effect of deswelling is also known in osmometry. The semipermeable cellulose membranes used in osmometry are not stable; the permeability through the pores decreases in the course of time, as a consequence of the deswelling due to which the pores are becoming smaller.

Accordingly, the gas permeability of a cellulose film at a constant relative humidity is not a constant, but it depends on the pre-treatment of the film. Although the degree of swelling of the nylon 6 film in our experiments has a constant value, it is known from the literature (3) that the pre-treatment of a nylon 6 film can influence the degree of swelling too.

**Conclusions**

- 1) The gas permeability of a hydrophilic film depends on the degree of swelling of the film, caused by water absorbed.
- 2) The relation between relative humidity of the gas and the degree of swelling of a plain regenerated cellulose film is not univocal, but depends on the pre-treatment of the film.
- 3) For the measurement of the gas permeability of a hydrophilic film it is necessary to condition the whole film on both sides at the same relative humidity.
- 4) By using a "sieve" film it is possible, using the vacuum-technique, to measure the gas permeability of hydrophilic films with the relative humidity as a parameter.
- 5) The greatest effect of the relative humidity on the gas permeability of plain regenerated cellulose film begins to occur at 70 - 80 % R.H..

**References**

(1) Simril, V. L. and Hershberger, A. Mod. Plastics 27, no 11, 95 (1950).	(5) Pilar, F. L. J. Pol. Sci., 45, 205 (1960).
(2) Meyer, J. A., Rogers, C. E., Stannett, V. and Swarc, M. Tappi Monograph Series no 23 (1962).	(6) Notley, N. T. J. Appl. Chem., 13, 107 (1963).
(3) Müller, R. H. and Hellmuth, E. Kolloid Zeitschrift 177, 1 (1961).	(7) Barrer, R. M. Trans. Farad. Soc., 35, 628 (1939).
(4) Buchner, N. and Schricker, G. Kunststoffe 50, 156 (1960).	(8) Barrer, R. M. and Skirrow, G. J. Pol. Sci., 3, 549 (1948).
	(9) Huldy, H. J. Plastica 15, 146 (1962); 15, 210 (1962).
	(10) Buchner, N. Kunststoffe, 49, 401 (1959).
	(11) Fricke, H. L. Package Engineering, 51 (Dec. 1962).