

Testing Water Vapour Permeability through Porous Membranes

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Abstract

A fast gravimetric method for determining water vapour permeability through porous membranes is presented. The research was conducted on polyester filter track membranes and polyurethane membranes. Based on the results of continuous measurement of mass changes under isothermal conditions, the water vapour permeability has been determined. The permeability and diffusion coefficients, as well as the tortuosity, factor have been evaluated.

Key words: water vapour permeability, membrane, microporous, gravimetric method.

Introduction

The use of polymer membranes in modern sportswear and protective clothing has become more and more common. Optimal selection of membrane structure and physico-chemical properties is intended to ensure the directional transport of water vapour, without its condensation, at a rate adapted to that of moisture release from the human organism. For that reason, it is important to be familiar with the membrane's structure, porosity, pore size and shape distribution, as well as sorption and diffusion properties. Such characteristics of membranes can be obtained by various methods, more or less close to subsequent conditions of their use with variable temperature, relative humidity and outer air flow rate [1,2]. A method for membrane testing, based on the water vapour transport forced by the relative humidity of air under isothermal conditions, has been developed at the Institute of Textile Materials Engineering [3].

The driving force of water vapour diffusion through a membrane is the difference between the partial pressures of water vapour in air on both its sides. In a stationary state, an equilibrium is established on both membrane sides between the water concentration on the membrane surface and the water vapour concentration in air that is dependent on the temperature of the membrane surface and its surroundings. If the partial water vapour pressures on both membrane sides are different, a gradient of water concentration is established in the membrane. In porous membranes, the water transport consists of three processes: water diffusion in the polymer, water diffusion in air that fills the pores of the membrane, and the sorption/desorption of water on the external membrane surface and internal pore surface. It is the polymer type and structure, i.e. the size, tortuosity and type of pores (closed/open), that is of decisive importance in water transport through membranes. Based on the analysed effect

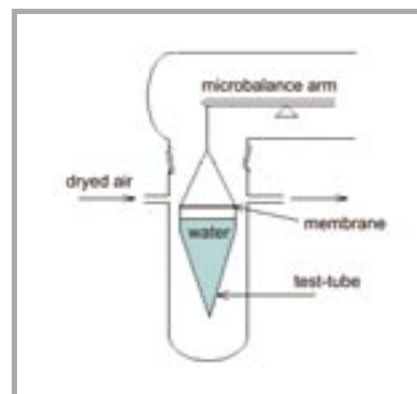


Figure 1. Scheme for testing water vapour permeability through membranes.

of the membrane structure on water vapour permeability, the water permeability through polyurethane and polyester membranes of different structures has been determined.

Experimental

Materials

The following membranes were used in testing: standard filter track membranes (T) made by the Institute of Chemistry and Nuclear Technology (IChiTJ) in Warsaw from a polyester film manufactured in Nitron-Erg (Krupski Młyn), with the characteristics given in Table 1, and hydrophobic polyurethane membranes (U) with the parameters listed in Table 2.

Porosity $\epsilon = 100(\rho_0 - \rho) / \rho_0$, %
 ρ_0 - membrane polymer density, g/cm³
 ρ - apparent membrane density, g/cm³
 calculated from surface weight and thickness.

Assumed polyurethane density:
 $\rho_0 = 0.9$ g/cm³.

Testing the water vapour permeability

The water vapour permeability was determined by the gravimetric method developed at the Institute of Textile Materials Engineering [3], and the scheme

Table 1. Characteristic of track membranes T (according to IChiTJ).

Sample	Thickness, μm	Diameter of pores, μm	Number of pores per cm^2	Porosity ϵ , %	Surface area of pores, cm^2
T-1	10	1.3	7.5×10^6	10	0.995
T-2	10	2.3	1.4×10^6	6	0.582

Table 2. Characteristic of polyurethane membranes U (*thickness was determined on membrane cross-sections under a stereoscopic microscope –at magnification 40 \times).

Sample	Mass per unit area, g/m ²	Thickness* 1, μm	Apparent density ρ , g/cm ³	Porosity ϵ , %
U-1	41.0	69	0.586	31.33
U-2	36.3	60	0.605	29.11
U-3	42.0	51	0.700	30.00
U-4	36.8	99	0.368	57.78
U-5	42.2	60	0.703	22.45
U-6	37.8	50	0.756	15.67
U-7	34.5	62	0.524	41.76
U-8	39.7	62	0.640	28.89
U-9	40.9	60	0.684	23.98
U-10	30.6	38	0.798	11.30

of the testing system is illustrated in Figure 1.

Using the MK2-G5 microbalance (CI Electronics Ltd.), the weight of water vapour passing through the membrane was determined as a function of time. A polyethylene test-tube containing 0.5 ml of water was tightly covered with the membrane under testing with a diameter of 0.9 cm, and was then hung on the microbalance arm. Air dried over a layer of calcium chloride and a layer of silica gel was passed over the membrane. This system simulated the high humidity at the human skin and the low humidity on the outside of clothing. It was assumed in calculations that the humidity at skin is 100% and that of the air passing over the membrane is 0%. At this stage, the temperature gradient was omitted and the tests were carried out under isothermal conditions. In reality, as a rule, the outside temperature is lower than that at the user's skin. The weight of the test-tube with water was recorded at a rate of 10 measurements per minute. Based on the test results of at least three samples, the slope of the straight line W , of the rectilinear dependencies of water weight loss in the test-tube on time (as shown in Figure 2), were determined. They were then used to calculate the membrane's permeability to water vapour P . Examples of these dependencies for T and U membranes are shown in Figure 2.

Results and Discussion

The term 'molecular diffusion' refers to the tumbling of molecules through a medium, and its rate is proportional to the driving force (to the concentration gradi-

ent) and inversely proportional to the resistance of the medium, and by extension to distance also. If the molecules collide frequently, as takes place in diffusion under pressure which is not too low, and the diameter of membrane pores is relatively large in comparison to the mean free path of molecules λ , one can assume that the diffusion takes place according to Fick's law. In the case of the membranes under testing, these conditions are satisfied.

The flow of water molecules through the surface unit J_p , assuming the conditions of ideal gas, can be described by the following equation:

$$J_p = D_p \Delta p / RTl \quad (1)$$

where:

- D_p – the diffusion constant of water vapour through air,
- Δp – the drop in the partial pressure of water in the membrane,
- R – gas constant,
- T – absolute temperature,
- l – membrane thickness.

As the polymer itself of the porous membrane is a partial hindrance to water vapour diffusion, and water molecules have to overcome a tortuous path through the network of linked pores in order to render the real diffusion through the membrane, a corrective coefficient ε/τ was added to this equation, where ε is the membrane porosity and τ is the path tortuosity factor:

$$P = \varepsilon/\tau D_m \Delta p / RTl \quad (2)$$

In equation (2), D_m is an experimental factor of water vapour diffusion through the membrane, and P is the membrane permeability coefficient. The coefficient of water vapour diffusion through air, $D_p=0.2 \text{ cm}^2/\text{s}$ (at a temperature of

295 K), was calculated from Gilliland's semi-empirical equation [4]:

$$D_{AB} = 0.0043 \frac{T^{1.75}}{p(\nu_A^{1/3} + \nu_B^{1/3})^2} \sqrt{1/M_A + 1/M_B} \quad (3)$$

where:

- D_{AB} – the diffusion coefficient of component A through component B, cm^2/s
- T – the temperature, K
- p – the total pressure, atm
- M_A, M_B – the molar weights of components A and B, kg/mol
- ν_A, ν_B – the molar volumes of components A and B in the state of boiling liquid at 1 atm, cm^3/mol .

The coefficient of water vapour permeability P was calculated from the following equation:

$$P = \frac{-W}{\pi \phi^2} V_w \frac{l}{p} \cdot \frac{\text{g}}{\text{s} \cdot \text{cm}^2} \cdot \frac{\text{cm}^3}{\text{g}} \cdot \frac{\text{cm}}{\text{Pa}} \quad (4)$$

where:

- ϕ – the sample diameter = 0.9 cm
- V_w – the specific volume of water vapour (STP) $2.063 \times 10^5 \text{ cm}^3/\text{g}$
- l – membrane thickness, cm
- p – the water vapour pressure at the measurement temperature t , Pa
- W – slope of the straight line as in Figure 2, g/s.

The experimental diffusion coefficients, D_m , were calculated from the following equation

$$P = D_m \cdot c/l \quad (5)$$

where c is the concentration of water vapour under the membrane corresponding to the vapour pressure at the measurement temperature in cm^3/cm^3 of water vapour per volume unit.

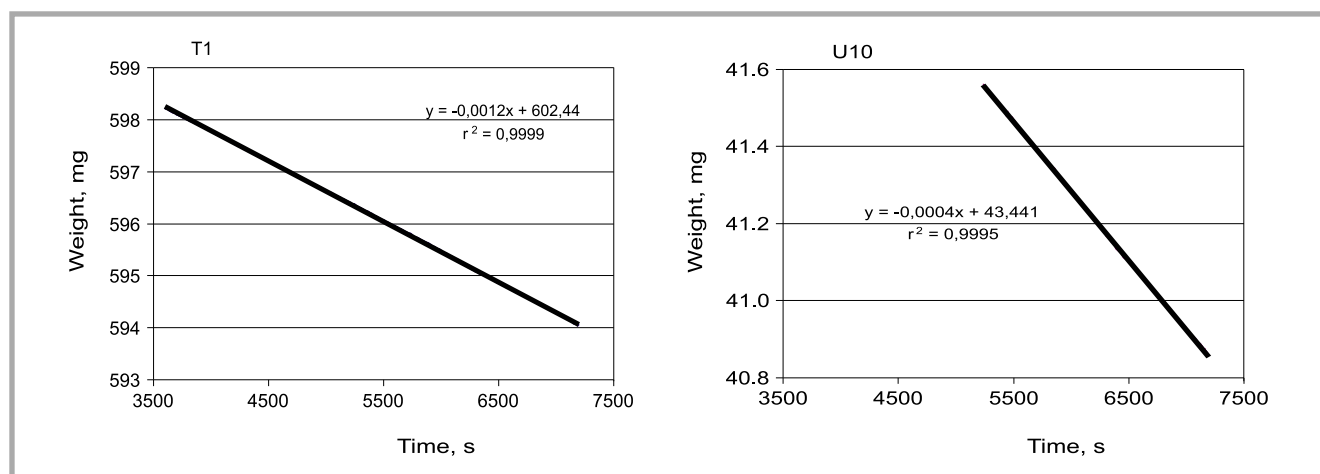


Figure 2. Dependence of the amount of water vapour passing through membranes T-1 and U-10 on time.

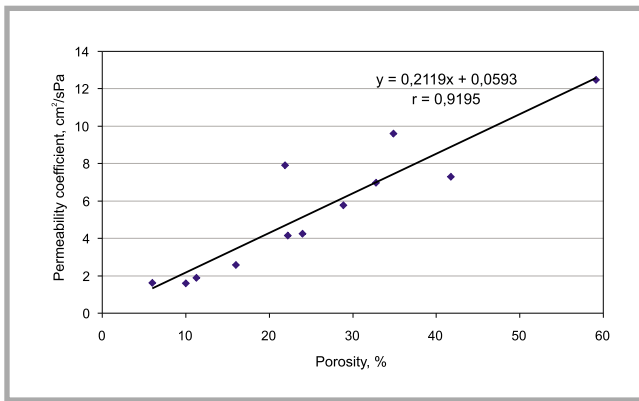


Figure 3. Relationship between the permeability coefficient and porosity.

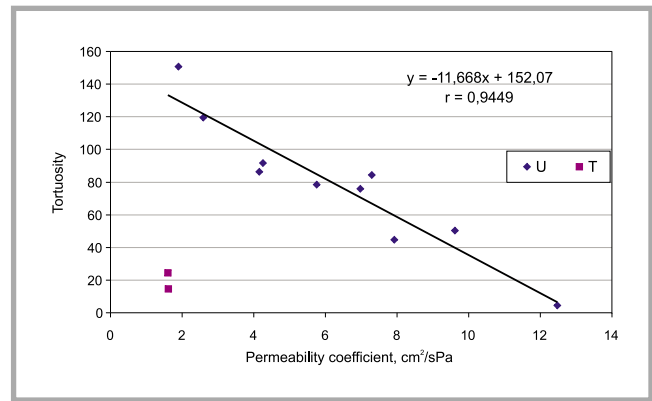


Figure 4. Relationship between tortuosity and the permeability coefficient.

Comparing equations (1) and (2) and substituting the values of ϵ , and D_m and $D_{AB}=D_p$, the tortuosity factor was calculated. The values of P , D_m , ϵ/τ and τ are given in Table 3. Figure 3 shows the dependence of water vapour permeability on the porosity of the membrane. The permeability coefficient and diffusion coefficient increase with the increase in porosity. The approximately rectilinear dependence indicates a similar permeability mechanism in all the membranes, mainly through relatively large open pores. The comparison of membrane diffusion coefficients of about 10^{-3} cm²/s with the free diffusion coefficient of water vapour in air amounting to 0.2 cm²/s, as well as those of polyurethane and polyester equal to 10^{-6} cm²/s [5] and 4×10^{-8} cm²/s [6] respectively, indicates that the pores in both types of membranes are open. As expected, the correlation of permeability coefficient and tortuosity factor is negative (Figure 4).

Hence one may conclude that the increase in porosity in the polyurethane mem-

branes under testing is due to the increase in pore volume and not in the number of pores. In similar studies on porous polyethylene membranes [7], a positive correlation of these coefficients was found; it was also shown that the permeability increases with a simultaneous increase in the number of pores and a decrease in their diameter. In the case of track membranes, the tortuosity is clearly connected with the diameter of pores in the membrane; it assumes low values due to the relative straight direction of the pores and that they go right through the material. The tortuosity of the diffusion path in the T-1 membrane with smaller pores is at the level of the most permeable U-1 and U-4 membranes, even though their porosity is several times lower. This also indicates that polyurethane membranes have large through-pores.

Summary

A fast method for determining water vapour permeability through porous

membranes has been developed. Based on the test results obtained, the character of porosity and the pore size have been assessed. The principle of the determination does not confine the use of this method to testing water vapour permeability, but it permits the method's use for testing the permeability of other volatile liquids through membranes designed for various applications.

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Table 3. The calculated values of P , ϵ/τ , τ , D_m .

Sample	Slope of the straight line W, 10 ⁻⁴ mg/s	Test temperature t, °C	Permeability coefficient P, 10 ⁻⁷ cm ² (STP)/sPa	ϵ/τ 10 ⁻³	τ	D_m , 10 ⁻³ cm ² /s
U-1	12.4	23.7	9.61	7.50	46.55	1.37
U-2	10.5	23.7	6.98	4.32	75.88	0.86
U-3	6.5	24.4	4.15	2.57	86.46	0.44
U-4	11.2	23.6	12.48	12.85	45.93	2.55
U-5	11.3	24.1	7.92	4.90	44.67	0.98
U-6	4.8	24.1	2.59	1.34	119.85	0.27
U-7	9.5	22.8	7.30	4.95	84.36	0.93
U-8	8.0	22.9	5.76	3.69	78.40	0.74
U-9	6.2	23.0	4.25	2.62	91.53	0.53
U-10	4.2	22.4	1.90	0.75	150.67	0.15
T-1	9.9	22.3	1.60	2.21	45.25	0.03
T-2	9.3	21.4	1.62	2.32	25.86	0.03

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