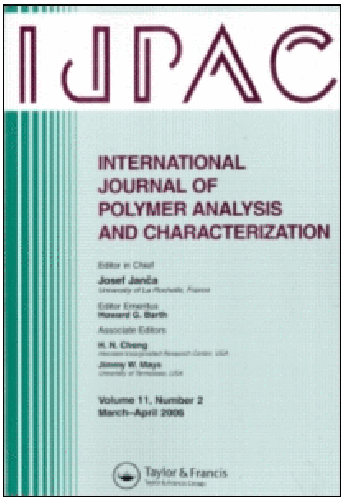

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

A Device for Characterizing Water Vapor Permeability of Polymer Membranes

Jianhua Huang[a]
[a] School of Textile and Material, Wuhan University of Science and Engineering, Wuhan, Hubei, China

To cite this Article Huang, Jianhua(2008) 'A Device for Characterizing Water Vapor Permeability of Polymer Membranes', International Journal of Polymer Analysis and Characterization, 13: 1, 37 — 48

To link to this Article: DOI: 10.1080/10236660701760262

URL: http://dx.doi.org/10.1080/10236660701760262

International Journal of Polymer Anal. Charact., 13: 37–48, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236660701760262

A Device for Characterizing Water Vapor Permeability of Polymer Membranes

Jianhua Huang
School of Textile and Material, Wuhan University of Science
and Engineering, Wuhan, Hubei, China

Abstract: The ability of polymer membranes to transport moisture vapor plays a major role in the applications of waterproof breathable clothing materials. There is a couple of test methods available for measuring water vapor permeability of polymer membranes or laminated fabrics. They are either time-consuming or require large samples. A new test device was developed for determining the water vapor permeability of polymer membranes. It utilizes PTFE film and potassium acetate to generate a moisture permeation cup. Saturated nitrogen gas was used to yield a water vapor source. This test method offers short test time and calls for small sample size. The test results from the new method correlated well with those obtained from the ASTM E96-BW method. The subsequent measurements indicated that the water vapor diffusion resistance of one layer of microporous PTFE membrane was approximately 4.4 s/m and that the moisture vapor transport behavior of the PTFE membrane did not change as a function of water content in the membrane.

Keywords: Measurement; Polymer membrane; PTFE membrane; Water vapor permeability

Received 4 September 2007; accepted 22 October 2007.

The author would like to thank the University Grant Council of Wuhan University of Science and Engineering for funding this project through Grant WUSE-20053116.

Address correspondence to Jianhua Huang, School of Textile and Material, Wuhan University of Science and Engineering, Wuhan, Hubei 430073, China. E-mail: wuseksu@wuse.edu.cn

INTRODUCTION

Polymer membranes laminated to textiles have received broad applications in breathable clothing items.[1–5] The water vapor permeability of polymer membranes is a key property of wear comfort. The polymer membrane serves as a liquid barrier and is vapor-permeable so that the water vapor emanating from the skin can be transported through the clothing system.

There exists a couple of standard test methods for measuring the water vapor permeability of polymer membranes.[6,7] The ASTM E96 method was originally developed for determining the water vapor transmission rate of materials with low vapor permeability and is not suitable for highly permeable film. A shallow cup is filled with distilled water and covered with the sample. The whole assembly is then weighed and reweighed after a certain elapse of time. The water vapor permeability of the fabric is the loss in weight of water in the cup, expressed in $g/m^2/day$.[6] The water vapor permeability is influenced by the still air layer resistance below the fabric, which dominates the total resistance. The intrinsic water vapor resistance of the sample is our present interest. The test method may mask the slight differences in the water vapor transmission rate between relatively permeable fabrics, though corrections can be made due to the still air layer through a complicated formula for highly permeable samples. In addition, several sources of error (edge effect, leakage effect, and effect of film thickness and film area) were identified.[8] The specific water vapor transmission rate of highly permeable film increased dramatically with increasing thickness, and it decreased with increasing film area regardless of thickness. For more permeable film, the water vapor flux across the film becomes high so that the relative humidity at the inner side of the film is less than 100%. This leads to decreasing pressure difference, resulting in low water vapor transmission rate. Increasing the area of a highly permeable film increases the flux enough to affect the relative humidity at the inner side of the film. This has the effect of decreasing the pressure gradient and accordingly decreasing the water vapor transmission rate. Decreasing the thickness of a highly permeable film has the same effect as increasing the area.[8] Finally, the air gap in the cup grows as the water evaporates. As a consequence, this also reduces the relative humidity at the inner surface of a highly permeable film.

The other test method, a sweating guarded hot plate instrument, can be used to evaluate the water vapor permeability of polymer laminated textiles by measuring the heat of evaporation.[7] To measure the evaporative resistance of the sample, distilled water is fed to the surface of the porous plate from a dosing device. A piece of smooth water vapor-permeable, liquid water-impermeable cellophane membrane is fitted over the plate. The test fabric is placed above the membrane. The heating power to maintain the plate at a constant temperature of 35°C is an indicator of water evaporation rate. Air temperature is set at 35°C and relative humidity is controlled at 40%. After steady state is reached, the evaporative resistance of the fabric is determined based on the heating power, the water vapor pressure gradient between the plate surface and the air, and the area of the test section. By using the latent heat of vaporization of water, the evaporative resistance value can be easily converted to water vapor permeability ($g/m^2 \cdot h \cdot Pa$). The sweating guarded hot plate method best simulates the heat and/or moisture transfer from the body surface through the clothing system to the environment. It can offer reproducible and repeatable results.[9–11] The main disadvantage of this method, however, is that a sweating guarded hot plate, climate-controlled chamber, and data acquisition system are expensive and complicated to use and that the length of the test period is not less than 60 min due to high thermal inertia.

The purpose of this article is to introduce a new test apparatus for measuring the water vapor permeability of polymer membranes accurately in a short period of time.

METHODS

The new test apparatus is schematically shown in Figure 1. It consists of a desiccator cup and a flow cell. Potassium acetate is employed as the desiccant. The saturated potassium acetate solution is prepared by mixing 100 g of dry potassium acetate with 30 g of distilled water. The mixture is equilibrated at 23°C for a period of at least 12 h so as to be homogeneous. The desiccator cup, made from transparent plastic, has an

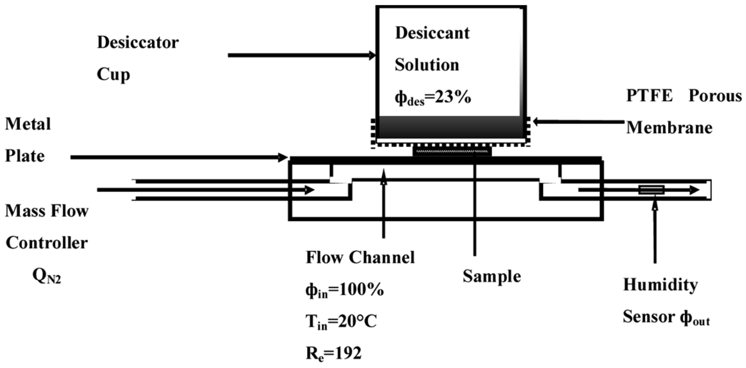

Figure 1. Internal view of new test apparatus.

internal diameter of 85 mm. The saturated potassium acetate solution is poured into the desiccator cup. A circular piece of waterproof and vapor-permeable polytetrafluoroethylene (PTFE, Teflon) membrane is adopted to cover the desiccator cup by using a rubber band to maintain the membrane taut. The edge of the cup assembly is then rolled against a hot iron. The cup seal is checked for leaks by inverting the cup over absorbent paper for 3 min.

The duct in the middle of the flow cell has ports for flow inlet and outlet in either side. A saturated nitrogen stream can pass through the duct. A piece of stainless steel metal plate of a thickness of 0.5 mm is employed to provide the test area. The hole in the center of the plate that determines the test area of the specimen is 60 mm × 20 mm. The specimen should be big enough to cover the hole. The metal plate is positioned above the flow cell. The specimen is mounted on the plate to cover the hole. The desiccator cup is inverted and positioned above the sample. This arrangement guarantees that the sample is in direct contact with the PTFE film.

The saturated nitrogen stream is generated by passing a dry nitrogen stream through three bubblers filled with distilled water. The pure nitrogen stream comes from a nitrogen gas tank with a technical grade of 99.99%. The water vapor concentration gradient on the both sides of the sample drives the water vapor from the bottom side of the sample to the upper side. At the outlet of the flow cell, a probe is utilized to measure the relative humidity of the outgoing nitrogen stream. The signal is processed by humidity transmitter HMT 333, manufactured by Vaisala Inc. Meanwhile, the air temperature is recorded. The accuracy of the humidity sensor is ± 1% from 0 to 90%. The accuracy of the temperature sensor is ± 0.2°C. The nitrogen gas flow is controlled by the mass flow controller GFC 17 (Aalborg Instruments, Inc.). The accuracy of this mass flow controller is ± 1.5% of full scale (2 L/min). The repeatability is ± 0.5% of full scale and the response time is 1 s.

The mass flow rate is controlled to approximately 2000 cm^3/min. For many mass flow rate controllers, the indicated volumetric flow rate on the digital readout is not the actual volumetric flow rate at the test conditions, but is referenced to standard conditions. These reference conditions may vary for different mass flow controllers, and the manufacturer's specifications should be consulted for the reference conditions used for different flow controllers. For the GFC 17 flow controller, the standard conditions of 70°F (21.1°C) and atmospheric pressure (101325 Pa) are specified by the manufacturer. The actual volumetric flow rate varies with the temperature and pressure of the actual flow. The pressure correction is negligible. Thus, only the temperature correction is necessary. Consequently, the actual flow rate is given by:

$$Q = Q_s \times \frac{T_a}{T_s} \tag{1}$$

where Q = actual volumetric flow rate (cm^3/min), Q_s = indicated volumetric flow rate from the mass flow controller (cm^3/min), T_a = ambient ambient temperature (K), and T_s = reference temperature used by the mass flow meter (294.25 K).

The size of the duct of the flow cell is 0.02 m wide, 0.100 m long, and 0.004 m high. The speed of the nitrogen gas stream depends on the volumetric flow rate and the size of the duct. As a result, the speed of the gas flow is calculated from:

$$V = \frac{Q_s \times T_a}{H \times W \times T_s} \times \frac{10^{-6}}{60} \tag{2}$$

where V = speed of the gas flow (m/s), Q_s = indicated volumetric flow rate from the mass flow controller (cm^3/min), H = height of the duct (0.004 m), and W = width of the duct (0.02 m).

The indicated volumetric flow rate is set to approximately 2000 cm^3/min. The air temperature is controlled at 20°C. The speed of the gas flow is found to be 0.41 m/s. Therefore, the dimension of the duct is designed to minimize the contribution of the boundary air layer resistance to the measurement.

In addition, the Reynolds number (Re) of the gas flow can be estimated by:

$$Re = \frac{D_e \times V \times \rho}{\mu} \tag{3}$$

where D_e = equivalent diameter of the duct (m), ρ = density of nitrogen stream (g/m^3), and μ = viscosity of nitrogen gas (g/m/s).

The equivalent diameter of the duct is 0.0067 m according to the size of the duct. The density of nitrogen gas is 1.25 kg/m^3. The viscosity of nitrogen gas is 0.00001785 kg/m/s. Therefore the Reynolds number (Re) of the gas flow is 192, which is far smaller than 2000. Consequently, the flow is highly laminar. The entry angles and end-effects on the flow would be negligible. The entrance length of the nitrogen gas is long enough to get a stable, fully developed flow.

Water vapor transmission through the sample is driven by the vapor concentration difference. The water vapor flux across the sample is calculated from the water balance in the nitrogen gas stream as the difference between the water content in the incoming wet (saturated) nitrogen gas stream and that in the outgoing wet nitrogen stream:

$$m = \frac{Q_{N_2+H_2Oin} \times C_{in} - Q_{N_2+H_2Oout} \times C_{out}}{A} \times \frac{10^{-6}}{60} \cong \frac{Q_{N_2} \times (C_{in} - C_{out})}{A} \times \frac{10^{-6}}{60} \tag{4}$$

where m = water vapor flux across the sample ($kg/m^2/s$), $Q_{N_2+H_2Oin}$ = actual volumetric flow rate of the incoming wet (saturated) nitrogen gas stream (cm^3/min), $Q_{N_2\ +\ H2Oout}$ = actual volumetric flow rate of the outgoing wet nitrogen gas stream (cm^3/min), Q_{N_2} = actual volumetric flow rate of dry nitrogen gas stream (cm^3/min), A = test area (m^2), Q = actual actual volumetric flow rate (cm^3/min), C_{in} = water vapor concentration of incoming wet (saturated) nitrogen gas stream (kg/m^3), and C_{out} = water vapor concentration of outgoing wet nitrogen gas stream (kg/m^3).

The water vapor concentration of the nitrogen stream is governed by the perfect gas law:

$$C_1 = \frac{\phi_1\ P_{sat}\ M_w}{100 \times R\ T_{in}} \tag{5}$$

$$C_2 = \frac{\phi_2\ P_{sat}\ M_w}{100 \times R\ T_{in}} \tag{6}$$

where Φ_1 = relative humidity of the incoming wet (saturated) nitrogen gas stream (%), Φ_2 = relative humidity of the outgoing wet nitrogen gas stream (%), P_{sat} = water vapor saturated pressure at the test temperature (Pa), M_w = molecular weight of water vapor (0.018015 kg/mol), mol), R = universal gas constant (8.315 J/mol/K), and T_{in} = temperatemperature of the incoming wet (saturated) nitrogen gas stream inflow cell (K).

The water vapor transmission rate of the sample is then determined by:

$$WVT = m \times 1000 \times 3600 \times 24 \tag{7}$$

where WVT = water vapor transmission rate of the sample ($g/(m^2 \cdot day)$).

The water vapor diffusion resistance is the reciprocal quantity of water vapor transmission. The relationship between the water vapor transmission across the sample gas gap and the water vapor concentration gradient in this gap is governed by Fick's law:

$$m = D_{H_2O-N_2} \times \frac{\Delta C}{L} = \frac{\Delta C}{R} \tag{8}$$

where $D_{H_2O-N_2}$ = diffusion coefficient of water vapor in the gas phase (m^2/s), $\Delta C/L$ = water vapor concentration gradient in the gas phase in the gap (kg/m^4), ΔC = water vapor concentration difference in the gas phase across the gap (kg/m^3), L = thickness of the gap (m), and R = water vapor diffusion resistance of the gap (s/m).

The total water vapor diffusion resistance R_t of the sample plus the boundary air layers (series of the resistances) is determined by

$$R_t = \frac{\Delta C}{m} \tag{9}$$

where R_t = total water vapor diffusion resistance (s/m).

Since the relative humidity of the incoming stream is declining down the length of the sample, the water vapor concentration difference between the two sides of the sample is getting smaller at the downstream end of the sample. The water vapor concentration difference across the sample is calculated as the log mean difference:[12]

$$\Delta C_{\log} = \frac{\Delta C_{in} - \Delta C_{out}}{\ln(\Delta C_{in}/\Delta C_{out})} \tag{10}$$

where: $\Delta C_{in} = C_{in} - C_{des}$ = water vapor concentration difference across the sample at the incoming end of the flow cell (kg/m^3),

$$C_{des} = \frac{\phi_{des}\ P_{sat}\ M_w}{100 \times R\ T_{in}} \tag{11}$$

C_{des} = water vapor concentration over the saturated potassium acetate solution in the desiccator cup (kg/m^3), Φ_{des} = relative humidity in equilibrium with saturated potassium acetate solution in the desiccator cup (%), and $\Delta C_{out} = C_{out} - C_{des}$ = water vapor concentration difference across the sample at the outgoing end of the flow cell (kg/m^3).

Since the saturated nitrogen gas stream is entering the flow cell, ΔC_{in} is the concentration difference between the water vapor concentration in the incoming wet (saturated) nitrogen gas stream and the water vapor concentration over the saturated potassium acetate solution in the desiccator cup. The latter, ΔC_{out}, is the concentration difference between the outgoing wet nitrogen gas stream and the water vapor concentration over the saturated potassium acetate solution in the desiccator cup.

The relative humidity in equilibrium with saturated potassium acetate solution in the desiccator cup at the temperature T_{in} (°C) can be expressed as:[13]

$$RH = \phi_{des} = 22.4388 + 0.156288 \times T_{in} - 0.00612868 \times T_{in}^2 \tag{12}$$

The temperature of the desiccant solution is set at 20°C. The relative humidity over the saturated potassium acetate solution turned out to be approximately 23%.

TEST PROCEDURES

The microporous polytetrafluoroethylene membrane was invented in 1970s, offering both waterproofness and high water vapor permeability. It has been widely used in premium outdoor clothing and equipment, diminishing personal discomfort and reducing the temperature drop in the human body. For this reason, PTFE membranes were selected for the tests. The test specimen of PTFE membrane had a thickness of 40 μm, a weight of 0.018 kg/m^2, and a porosity of 70%.

The test apparatus was housed in a test chamber. The air temperature of the chamber was controlled at 20° ± 1°C. It did not fluctuate more than ± 0.1°C during one test run. A rectangular specimen 100 mm × 40 mm in size was carefully mounted on the plate to completely cover the hole (60 mm × 20 mm). The desiccator cup was then positioned above the flow cell. The inlet port of the flow cell was connected to the gas tube. The humidity sensor was inserted into the outlet port of the flow cell. The nitrogen gas tank was opened, and the pressure regulator was adjusted so that a pressure of approximately 138 kPa was applied to the mass flow controller. The nitrogen flow rate was set to approximately 2000 cm^3/min. The analog voltage signal from the mass flow controller and humidity transmitter were input to the Data Acquisition/Switch unit 34970 A, made by Agilent Technologies, Inc. The data were sent to a computer through an RS-232 interface serial port. The mass flow rate, air temperature, and relative humidity of the outgoing stream were collected by the computer every 10 s. Normally the system reached the steady state within about 5 min. The last 10 data points were then used for computing the water vapor transmission rate, plus water vapor diffusion resistance, of the specimen. One to five layers of PTFE membranes were tested.

In order to test the new measuring apparatus, comparison measurements were carried out between the ASTM E96 method and the new method. The inverted cup test method (ASTM E96 Procedure BW) was adopted because it eliminates the air space between the sample and the water surface. This test also reduces the possibility of air penetrating the fabric, which may cause misleading results. In conformity with ASTM E96 Procedure BW, the inverted cup test was conducted at an air temperature of 23°C and 50% relative humidity in a test chamber. The air velocity in the wind tunnel was controlled at 2.8 m/s. The sample was sealed over the mouth of the cup. The cup assembly was placed in an inverted position on the upper deck. The cup assembly was weighed periodically. The water vapor transmission rate of the sample was determined. The PTFE membranes were successively tested in one to five layers using this method.

It would be interesting to investigate the effect of water vapor concentration on the total diffusion resistance of the microporous PTFE membrane. The relative humidity of the nitrogen stream was varied by merging dry and saturated streams, which were from two separate mass flow controllers. The ratio of dry and saturated stream governed the relative humidity of mixed stream in the duct of the flow cell. The water vapor diffusion resistance of the PTFE membrane was determined at a variety of relative humidity levels. The mean relative humidity in the membrane was just the arithmetic average of humidity on both sides of the sample.

RESULTS AND DISCUSSIONS

The total water vapor diffusion resistances obtained from the new test apparatus are plotted against the number of PTFE layers in Figure 2. The water vapor diffusion resistance increased almost linearly with the number of layers. The water vapor diffusion resistance of a single layer of PTFE layer can be determined by:

$$R_m = \frac{dR_t}{dx} \tag{13}$$

where R_m = water vapor diffusion resistance of a single layer of PTFE (s/m), R_t = total water vapor diffusion resistance of a series of PTFE membranes plus the boundary air layer (s/m), and x = number of PTFE layers.

The water vapor diffusion resistance of a single layer of PTFE layer was 4.4 s/m.

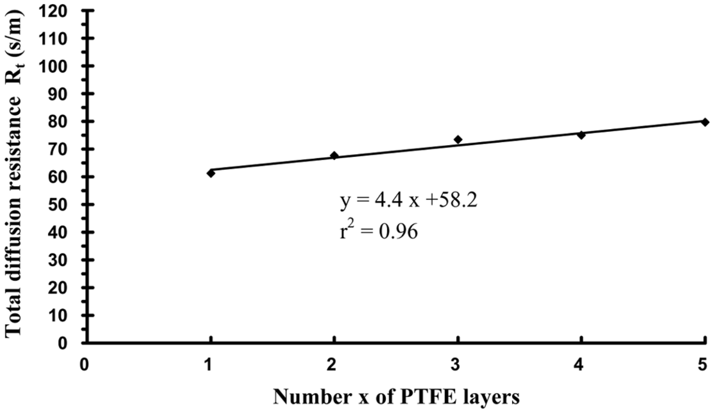

Figure 2. Total water vapor diffusion resistance R_t of the system (20°C, N_2, Reynolds number = 192, series of the resistances).

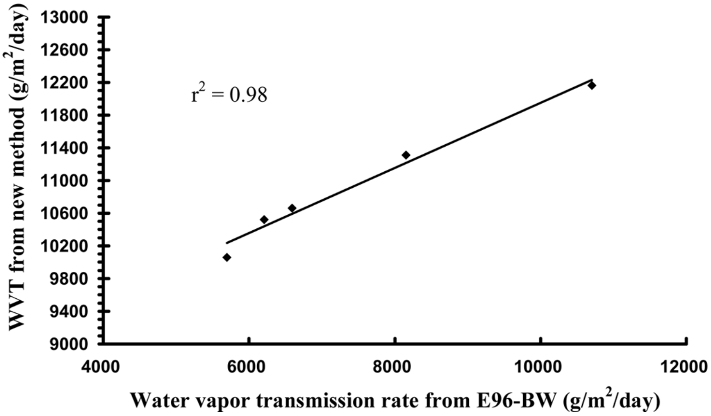

Figure 3. Correlation between water vapor transmission rate from the new method and water vapor transmission rate from inverted cup test.

The test results can be used to estimate the water vapor diffusion resistance of the gaps in the test chamber. It is assumed that the mass transfer resistance is additive; the water vapor diffusion resistance of the gaps in the test chamber can be estimated by:

$$R_0 = R_t - xR_m \tag{14}$$

where R_0 = water vapor diffusion resistance of the gaps in the test chamber (s/m).

From the relation given above, the water vapor diffusion resistance of the gaps in the test chamber is approximately equal to 58.2 s/m.

The water vapor transmission rate data from the new method were plotted versus the WVT data generated with the inverted cup test. As shown in Figure 3, the coefficient of determination was 0.98. The new test method correlated well with the inverted cup test method. Although the cup test is a gravimetric method and the new apparatus directly measures the concentration difference, the correlation between the two is excellent.

The water vapor permeability of a single layer of PTFE membrane exposed to a variety of relative humidity levels was measured by means of the new test apparatus. The water vapor flux values versus the concentration difference across the sample are plotted in Figure 4. It is noteworthy that the water vapor flux across the sample was linearly proportional to the concentration difference. This is ascribable to the fact that the PTFE membrane is hydrophobic and microporous and the water vapor diffusion takes place only through the pore spaces of the membranes.

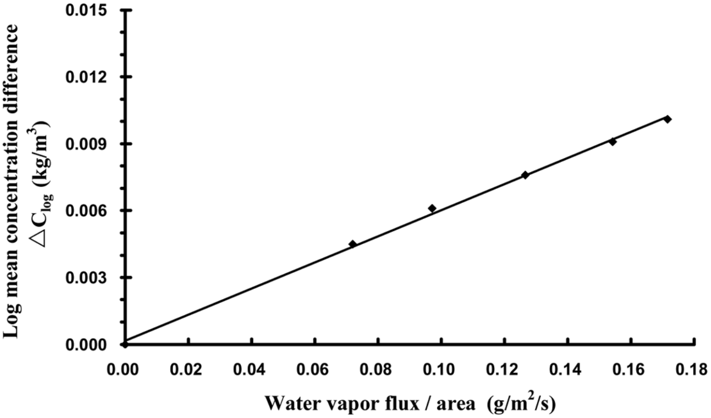

Figure 4. Water vapor flux versus concentration difference across one layer of PTFE membrane and air gaps.

The total diffusion resistance of one layer of PTFE membrane is presented in terms of mean relative humidity in Figure 5. The mean relative humidity in the membrane was defined as the average of the relative humidity of the incoming gas stream and the saturated potassium acetate solution. This definition neglects the variation in vapor concentration along the sample, but it is sufficient to illustrate the general trend of material behavior. As can be seen in Figure 5, the total diffusion resistance of the PTFE membrane remained invariable at various relative humidity levels. As a result, PTFE membrane does not change its water vapor transport property as a function of water content.

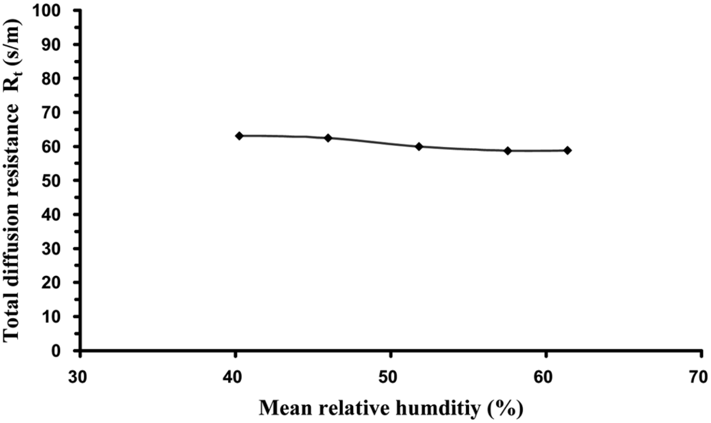

Figure 5. Water vapor transport behavior of the total diffusion resistance R_t at various humidity levels for one layer of PTFE membrane and air gap.

CONCLUSIONS

A new measuring apparatus was developed for measuring the water vapor permeability of polymer membranes. It allows us to determine this critical characteristic of a polymer within a short period of time by using a small sample size. Good correlation was observed between the new test method and ASTM E96. The test results show that the water vapor diffusion resistance of a single layer of PTFE polymer membrane was approximately 4.4 s/m and the water vapor transport property of PTFE membrane was not dependent on the amount of water present in the polymer.

REFERENCES

[1] Van Roey, M. (1991). Water-resistant breathable fabrics. *J. Coated Fabrics* **21**, 20–31.

[2] Kannekens, A. (1994). Breathable coatings and laminates. *J. Coated Fabrics* **24**, 51–59.

[3] Hayashi, S., N. Ishikawa, and C. Giordano. (1993). High moisture permeability polyurethane for textile application. *J. Coated Fabrics* **23**, 74–83.

[4] Painter, C. J. (1996). Waterproof, breathable fabric laminates: A perspective from film to market place. *J. Coated Fabrics* **26**, 107–130.

[5] Gibson, P. W. (2000). Effect of temperature on water vapor transport through polymer membrane laminates. *Polym. Test* **19**, 673–691.

[6] ASTM. (2005). *ASTM E96/E96M: Standard test methods for water vapor transmission of materials*. West Conshohocken, Penn.: ASTM International.

[7] ISO. (1993). ISO 11092: 1993. *Textiles—Physiological effects—measurement of thermal and water vapour resistance under steady-state conditions (sweating guarded hotplate test)*. Geneva: ISO.

[8] Hu, Y., V. Topolkaraev, A. Hiltner, and E. Baer. (2001). Measurement of water vapor transmission rate in highly permeable films. *J. Appl. Polym. Sci.* **81**, 1624–1633.

[9] Gibson, P. W. (1993). Factors influencing steady-state heat and water vapor transfer measurements for clothing materials. *Text. Res. J.* **63**, 749–764.

[10] Gibson, P. W., M. Auerbach, J. Giblo, W. Teal, and T. Endrusick. (1994). Interlaboratory evaluation of a new sweating guarded hot plate test method (ISO 11092). *J. Therm. Insul. Build. Envel.* **18**, 182–200.

[11] McCullough, E. A., J. Huang, and C. S. Kim. (2004). An explanation and discussion of sweating hot plate standards. *J. ASTM Int.* **1**, 1–7.

[12] Islam, M. R., N. E. Wijeysundera, and J. C. Ho. (2003). Evaluation of heat and mass transfer coefficients for falling-films on tubular absorbers. *Int. J. Refrig.* **26**, 197–204.

[13] Greenspan, L. (1977). Humidity fixed points of binary saturated aqueous solutions. *J. Res. Natl. Inst. Stand. Technol.* **81A**, 89–96.