MOISTURE TRANSPORT THROUGH NON-POROUS HYDROPHILIC MEMBRANES USED IN PROTECTIVE CLOTHING

by

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Original scientific paper
DOI: 10.2298/TSCI1305293Z

The three-step upright cup method was employed to determine the total moisture transfer resistance and the two air layer resistances on both sides of the membrane. The effective moisture diffusion coefficient in air layer between the membrane and water surface was determined by the regressive method, and the effective moisture diffusion coefficient of membrane was calculated. Experiments were conducted on a non-porous hydrophilic thermoplastic polyester elastomer membrane. The moisture transfer process through the membrane was modeled by using the solution-diffusion model. The effects of membrane microstructure on membrane permeation were analyzed based on the solution-diffusion model and experimental data. The results show that the effective diffusion coefficient can be used to evaluate the mass transfer process through the non-porous hydrophilic thermoplastic polyester elastomer membrane.

Key words: *moisture transport, diffusion coefficient, non-porous hydrophilic membrane, solution-diffusion model*

Introduction

With the development of membrane technology, membranes have shown its potential to be commercialized as waterproof breathable material in textile field. Membrane-laminated fabric is one of the most important applications in protective clothing, such as fire-fighter's personal ensemble. Such membranes are referred to as semi-permeable materials which possesses a rather high permeability towards water vapor while acting as a barrier towards liquid water [1, 2].

Example of the semi-permeable materials is the non-porous, dense thermoplastic polyester elastomer membrane (TPEE). Moisture transfer through TPEE can be described by the solution-diffusion theory. Only lower molecular weight species that are sufficiently soluble in the polymer will permeate through the membrane. TPEE is composed of PBT (polybutylene terephthalate) as the hard segment, and polyether or polyester as the soft segment. The typical structure of TPEE is illustrated in fig. 1 [3]. The moisture transport through the semi-permeable membrane has been a subject of interest in the past few years. Therefore, there are many testing methods which can be used to measure the water vapor transmission rate (WVTR) of the waterproof and breathable membranes including the upright cup method (ASTM E96), the inverted cup method, the sweating hot plate method (ISO 11092), and the dynamic moisture permeation cell (DMPC) method [4]. Due to its simplicity in structure and ease in operation, the upright cup method has been widely used in the laboratory test. Moreover, several fabric samples can be

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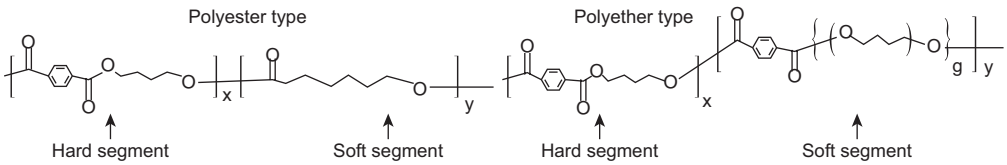

Figure 1. Typical structure of TPEE

tested on the upright cup at the same time. So, it is an efficient method for evaluating WVTR of the membrane sample under the steady environment. In this paper, an improved upright cup method is proposed to measure the moisture diffusivity of the hydrophilic membrane based on three step tests and the improved method is called as the three-step method.

Experimental

Experimental apparatus and method

The water vapor transmission rate was measured by the upright method, which is described in the ASTM E96 Procedure B, Standard Test Methods for Water Vapor Transmission of Materials. As shown in fig. 2, the sample is placed on a cup containing distilled water and housed in an environmental trunk with 23 °C and 50% relative humidity. The air velocity in the trunk is 2.80 ± 25 m/s. The water vapor transmission rate (WVTR) in units of g/m^2·24 h is calculated by the weight change of the assembled specimen cup after 24 hours. The driving force for moisture transfer through the dense membrane is the vapor concentration difference between the two sides of the membrane. A demonstration of the above water vapor transport process is made by considering the 1-D diffusion problem. The purpose of WVTR tests is to determine the intrinsic water vapor diffusion resistance through the membrane sample. The above-mentioned, obtained water vapor resistance is the total moisture resistance, which can be represented by the sum of the moisture resistance R_c [scm^{-1}] caused by the air gap between water surface and specimen inner surface, intrinsic diffusion resistance R_f [scm^{-1}] through specimen and boundary air layer diffusion resistance R_a (scm^{-1}), *i. e.*:

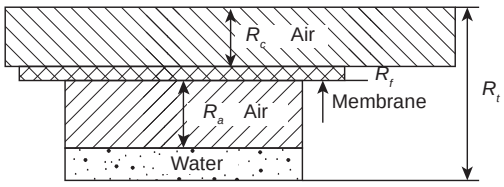

Figure. 2 Arrangement of the testing apparatus

$$R_t = R_c + R_f + R_a \tag{1}$$

The membrane resistance R_f can thus be obtained by subtracting the two air layer resistances from the total resistance [6],

$$R_f = R_t - R_c - R_a = R_t - R_c - \frac{L_a}{D'_{va}} \tag{2}$$

where L_a [m] is the air gap thickness, and D'_{va} [m^{2}s^{-1}] – the equivalent diffusivity of moisture in the air gap, which will be further addressed later.

So the equivalent diffusivity of moisture in the membrane can be expressed by:

$$D'_{vf} = \frac{\delta}{R_f} \tag{3}$$

where D'_{vf} [m^{2}s^{-1}] is the equivalent diffusivity of moisture in the membrane, and δ [m] – the thickness of membrane.

In actual test, tests were run for different air gap thicknesses L_a to avoid possibility that the membrane adsorbed the liquid water by using the same membrane sample. Thus, the equivalent diffusivity D'_{va} in the air gap can be estimated from the slope of a plot moisture resistance against the air gap thickness by the regression of the experimental data.

The total moisture resistance and the convection resistance can be calculated as [7]:

$$R_t\,(23\ °\mathrm{C}) = 6998.4/WVTR_t \tag{4}$$

The water vapor transmission rate was calculated as:

$$WVTR = \frac{G}{t \cdot A} \tag{5}$$

where $WVTR$ [$\mathrm{gm}^{-2} \cdot 24\mathrm{h}$] is the water vapor transmission rate, G [g] – the weight change, t [h] – the time, and A [m^2] – the test area.

Experimental sample

The sample used in the experiments is dense TPEE membrane provided by FSPG Hi-Tech Co. Ltd., China. The reason for selecting the non-porous membrane is that it is cheap, highly permeable, and has a certain mechanical strength. According to the information offered by the manufacturer, the membrane thickness is 25 μm. The measured density of the membrane is 1008 kg/m^3.

Experimental procedure

In order to extract the membrane resistance from the total resistance, three series of tests were schemed and executed. The first test was to obtain the convective mass transfer resistance in the air layer over the membrane. In this test, no membrane was used and the cup was full of water with the water surface exposed directly to the air stream.

The second test was to investigate the equivalent diffusivity of moisture in the air gap between the membrane and the surface of the water. Then, the moisture resistance in the air gap can be determined. Membrane is used in this test. The water vapor permeability cup high 11.5 cm, diameter 6.4 cm, these cups were poured into 2 cm, 4 cm, 6 cm, and 8 cm high degree of distilled water, respectively. Put the sample on the cup and then fix the sample. Each cup was weighed on balance, put the cup into climatic chamber and then the time and the weight were recorded after 24 hours.

The third test was to obtain the total moisture resistance. The total moisture resistance is determined in the same way as that in the second test. According to ASTM E96, tests were carried out for the membranes with an air gap thickness of 3.5 cm.

Theoretical model

Mass transport through a non-porous hydrophilic membrane can be described by the solution-diffusion model (SDM). The mass transport process can be divided into three steps in terms of the SDM mechanism, which is shown in fig. 3 [8]. The water vapor first is adsorbed in the surface of the membrane with high concentration, and then diffuses through the

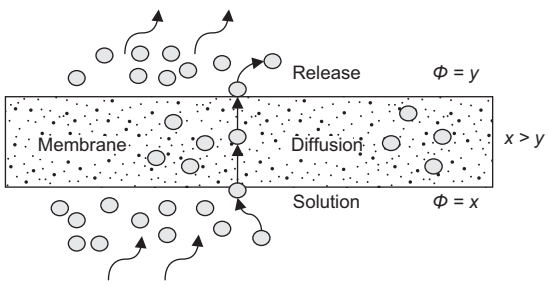

Figure 3. Mass transfer through a membrane

membrane owing to driving force from concentration difference. Finally, the water vapor desorbs from the side of the membrane with low concentration.

In the paper, the governing equations for predicting a χ-parameter reflecting the enthalpic balance between similar (polymer segment/polymer segment and water/water) and dissimilar (polymer segment/water) contacts are developed [8]. Further, the relation between the amount of absorbed water and air humidity can be expressed in terms of Henry's law:

$$\theta = \frac{\phi}{\mathrm{e}^{\chi+1}} \tag{6}$$

where θ is the amount of absorbed water, and ϕ – air relative humidity.

An assumption in using the diffusion flux definition through the membrane is that the water vapor transmission rate through the membrane satisfy the Fick's law:

$$WVT_{\mathrm{film}} = D'_{vf}\,\frac{\Delta\theta}{\delta} = D'_{vf}\,\frac{\Delta c}{\delta} \tag{7}$$

where Δc is the water vapor concentration difference between the two boundary air layers of membrane.

A relationship between relative humidity ϕ and absolute humidity w, temperature T of air can be acquired as [9]:

$$\frac{\phi}{w} = \frac{\mathrm{e}^{5294/T}}{10^6} - 1.61\,\phi \tag{8}$$

The second term on the right side of the equation will generally have less than a 5% effect, and it can be usually neglected.

A relationship can be found between the water vapor concentration and the absolute humidity:

$$c = \rho_a\, w \tag{9}$$

where ρ_a is the density of air (1.29 kg/m^3).

Substituting eqs. (8) and (9) into eq. (7) and re-arranging it as:

$$WVT_{\mathrm{film}} = 10^6 D'_{vf}\,\frac{\rho_a}{\delta \mathrm{e}^{5294/T}}(\phi_2 - \phi_3) \tag{10}$$

On the other hand, substituting eqs. (8) and (9) into eq. (7), we have:

$$WVT_{\mathrm{film}} = \rho_f\,\frac{D'_{vf}}{\delta}\,\frac{\phi_2 - \phi_3}{\mathrm{e}^{\chi+1}} \tag{11}$$

Combined eq. (10) with eq. (11), the following equation can be described as:

$$\chi = \ln\frac{\mathrm{e}^{5294/T}}{10^6\,\rho_a} - 1 \tag{12}$$

The moisture transfer process can be analyzed based on the experimental data and mentioned theoretical model on molecular structure of the hydrophilic membrane.

Results and discussion

The equivalent diffusivity of moisture in the air gap

The relationship between moisture resistance and the thickness of the air layer is shown in fig. 4. The test results show that there is a rather good linear relationship between the total moisture resistance and the air gap thickness indicated by the regression coefficients R^2. The value of the equivalent diffusivity (D'_{va}) is $2.545 \cdot 10^{-5}$ m^2/s obtained from the fitted data. In general, the value of the moisture diffusivity, at ambient temperature of 23 °C, is $2.538 \cdot 10^{-5}$ m^2/s. Moderate similarity is found between the two values.

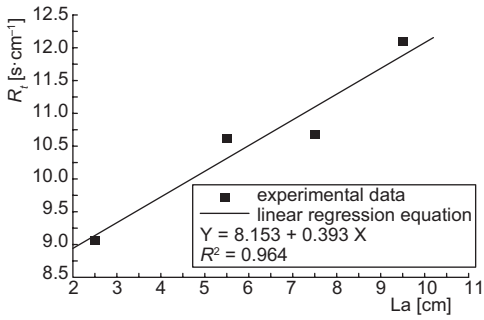

Figure. 4 The relationship between moisture resistance and the thickness of the air layer

The equivalent diffusivity of moisture in the membrane

The convective resistance R_c is 1.103 s/cm, which was calculated according to eq. (4). From eq. (2), the intrinsic moisture resistance of the test membrane R_f can be obtained by subtracting the convective resistance and the air gap resistance from the total resistance. The calculated value of the membrane resistance is 7.382 s/cm and then we can obtain the value of $3.387 \cdot 10^{-8}$ m^2/s for the equivalent moisture diffusivity D'_{va} in the membrane by eq. (3). As we know, the equivalent moisture diffusivity is one of physical properties of the membrane. The WVRT of membrane can be evaluated by the moisture diffusivity. Simultaneously, the microstructure and hydrophilic segment within the membrane will exert a substantial influence on the WVRT of the membrane.

The value 2.805 of the χ-parameter can be extracted from eq. (12). The χ-parameter reflects the interaction between an averaged, imaginary hydrophilic segment and a water molecule. As a consequence, the hydrophilic materials are modeled as homogeneous materials. Next, we will comment on the apparent hydrophilic characteristics of the membrane material according to the value of the χ-parameter. It is clear that more than 2 wt.% of water vapor is solved in the polymer membrane under saturated vapor pressure (100% RH). This reveals the typical hydrophilic characteristics of the polymer materials. TPEE film is composed of a large amount of polyester and polyether with linear molecular chain structure. Higher hydrophilic monomer content will certainly result in a molecular/ether bond ladder for moisture transmission with the shorter steps. Accordingly, the water vapor could transfer more easily through TPEE membrane. Furthermore, the hydrophilic polymer will take on a clear swelling characteristic in water. Spontaneously, moisture will also have expediter diffusing channels in swelled polymer film [10].

The TPEE membrane is widely used in waterproof and breathable fabrics. The water vapor transmission rate through the waterproof and breathable fabrics is considerably high owing to its membrane penetrative characteristics. Solubility and diffusivity are the reflections of water vapor permeability for the membrane. The process involves the diffusion of molecules in the non-porous or dense polymer. The hydrophilic soft segments (fig. 1) within the polymer membrane result in the relatively high water permeability. The high value of intrinsic water vapor diffusivity again reflects the fact the hydrophilic segments increased the increases the amount of adsorbed water on the membrane surface.

In the paper, the requirements in the experiments were taken as similar with that in clothed human body with insensible perspiration or a little sweat. Under this condition, sweat will diffuse through the membrane fabric in the form of water vapor. The relative humidity is 100% within the microenvironment close to the skin. Thus, the vapor is thought to be saturated, and the pressure of that vapor is saturation vapor pressure. However, the vapor is unsaturated outside of the clothing. This will result in water vapor concentration difference between the two sides of the clothing. It is assumed that the mass transfer through the membrane is one-dimensional process.

Conclusions

Moisture transport tests have been conducted on the non-porous hydrophilic TPEE membrane by using three-step method. The effective moisture diffusion coefficient of membrane is obtained under the condition where air layer exists. The test results show that the effective moisture diffusion coefficient of membrane is $3.387 \cdot 10^{-8}$ m^2/s. A characteristic parameter which can reflect the hydrophilic character of the polymer materials is extracted in this paper. The effects of membrane microstructures on the membrane permeation are investigated by using the based-model method integrated with the test data. It is reasonable that the effective diffusion coefficient can be used as the index to evaluate the membrane transfer process.

Acknowledgments

Research work was supported financially by China Postdoctoral Science Foundation under Grant No. 2100470665, National Natural Science Foundation of China (No. 51203196) and the United Foundation from National Natural Science Foundation of China and the People's Government of Henan Province for Cultivating Talents (No. U1204510).

Reference

[1] Stroeks, A., The Moisture Vapour Transmission Rate of Block Co-poly(ether-ester) Based Breathable Films. 2. Influence of the Thickness of the Air Layer Adjacent to the Film, *Polymer, 42* (2001), 25, pp. 9903-9908
[2] Yang, W., A New Method for Fiber Orientation Distribution in a Planar Coneracting Turbulent Flow, *Thermal Science, 16* (2012), 5, pp. 1367-1371
[3] Mayumi, J. J., *et al.,* Material Design and Manufacture of a New Thermoplastic Polyester Elastomer, *Polymer, 40* (2008), 1, pp. 1-9
[4] Huang, J.-H., Qian, X. M., Comparison of Test Methods for Measuring Water Vapor Permeability of Fabrics, *Textile Research Journal, 78* (2008), 4, pp. 342-352
[5] Fan, J., He, J.-H., Biomimic Design of Multi-Scale Fabric with Efficient Heat Transfer Property, *Thermal Science, 16* (2012), 5, pp. 1349-1352
[6] Min, J. C., Hu, T., Moisture Permeation through Porous Membranes, *Journal of Membrane Science, 379* (2011), 6, pp. 496-503
[7] Woo, S. S., *et al*., Heat and Moisture Transfer Through Nonwoven Fabrics, Part II: Moisture Diffusivity, *Textile Research Journal, 63* (1993), 4, pp. 190-197
[8] Stroeks, A., Dijkstra, K., Modelling the Moisture Vapour Transmission Rate through Segmented Block Co-poly(ether-ester) Based Breathable Films, *Polymer, 42* (2001), 1. pp. 117-127
[9] Zhang, L.-Z., Investigation of Moisture Transfer Effectiveness through a Hydrophilic Polymer Membrane with a Field and Laboratory Emission Cell, *International Journal of Heat and Mass Transfer, 49* (2006), 5-6, pp. 1176-1184
[10] Dolmaire, N., *et al.,* Water Transport Properties of Thermoplastic Polyurethane Films, *Journal of Polymer Science, 42* (2004), 3, pp. 473-492

Paper submitted: January 18, 2013
Paper revised: April 26, 2013
Paper accepted: May 14, 2013