

OPTICAL INTERFERENCE METHOD FOR THE STUDY OF MOISTURE SWELLING IN PET FILMS

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ABSTRACT

A method for measuring moisture swelling of amorphous PET films by using Rayleigh interferometer is reported. Plots of the optical path of light transmission in the polymer vs. soaking time were obtained, and from the same curves, the dependence of time on the moisture swelling, saturated water absorption and diffusion coefficient of PET films were estimated. These results are in agreement with those obtained by weighing method. It is shown that optical interference method is a simple but sensitive method for the study of water absorption and swelling in transparent polymer films.

INTRODUCTION

The water absorption of polymers has been studied for years. This is because that water absorption, one of the important parameters of performance, is of great practical significance in the manufacture and processing of polymers used as protective paint, film and fibre, especially for the strong water-absorbing materials.

In general, this parameter can be determined by the direct methods, such as weighing method, capacity method, and floatation method on the basis of the change of polymer weight before and after absorbing water; and the indirect methods through infrared spectrum analysis, dielectric test, NMR and DSC, etc^[1]. Recently, a new method — bending-cantilever method for the study of moisture swelling in polymers, has been developed by Berry and Pritchett^[2].

The present paper shows how moisture swelling in PET films can be studied by a simple yet sensitive optical interference method, by which subtle changes of the optical path less than $0.02\mu\text{m}$ can be detected. Moreover it can be used continuously in real time to observe the dependence of time on absorbed water and to obtain the equilibrium water absorption, swelling factor and the diffusion coefficient of water in the polymer films.

THEORY

The optical path δ of light transmission in the homogeneous transparent polymer film can be expressed as the product of its refractive index n and geometrical length l :

$$\delta = nl. \quad (1)$$

The micro-change of the optical path of film samples caused by water absorption can be detected

very sensitively by the optical interference method.

Differentiating Eq.(1) totally, we may write

$$\frac{d\delta}{\delta} = \frac{dn}{n} + \frac{dl}{l}. \quad (2)$$

It is shown that the rate of change in the optical path $\frac{d\delta}{\delta}$ must necessarily equal the algebraic sum of the relative change in the refractive index $\frac{dn}{n}$ and the linear swelling factor $\frac{dl}{l}$. Moreover, in theory a linear swelling factor is equal to one-third of the volumetric swelling factor. Thus, we have

$$\frac{dw}{w} = \frac{d\rho}{\rho} + 3 \frac{dl}{l} \quad (3)$$

where $\frac{d\rho}{\rho}$ is the rate of density change of the sample caused by absorption of water, and $\frac{dw}{w}$ is the weight water absorption factor.

Let it be supposed that the additive property principle on the density ρ , the specific volume V and the refractive index n is satisfied, i.e.

$$\rho = \left(\frac{l_0}{l}\right)^3 \rho_0 + \left[1 - \left(\frac{l_0}{l}\right)^3\right] \rho_w \quad (4)$$

$$V = \left(\frac{l_0}{l}\right)^3 V_0 + \left[1 - \left(\frac{l_0}{l}\right)^3\right] V_w \quad (5)$$

$$V(n-1) = \left(\frac{l_0}{l}\right)^3 V_0(n_0-1) + \left[1 - \left(\frac{l_0}{l}\right)^3\right] V_w(n_w-1) \quad (6)$$

where some parameters for the drying sample are indicated as the symbols with low-marker 0, and those for water with low-marker w . Differentiating Eqs. (4)—(6) totally and making use of Eqs. (2) and (3), so that, we finally find the following relation:

$$\frac{dn}{n} = \left(\frac{\rho}{\rho_w}\right)^2 \left(\frac{n_w}{n} - 1\right) \frac{dw}{w} \quad (7)$$

$$\frac{dl}{l} = \frac{1}{3} \frac{\rho}{\rho_w} \frac{dw}{w} \quad (8)$$

$$\frac{d\delta}{\delta} = \left\{ \frac{\rho}{\rho_w} \left[\frac{\rho}{\rho_w} \left(\frac{n_w}{n} - 1 \right) + \frac{1}{3} \right] \right\} \frac{dw}{w} \quad (9)$$

In general, absorption of water in polymers is very small, therefore the variables ρ and n in the right side of Eqs. (7)—(9) may be regarded as constants and replaced with ρ_0 and n_0 respectively. As a result, it is concluded that the weight water-absorption factor and the linear swelling factor are proportional to the rate of change in the optical path. So long as plots of the rate of change in the optical path vs. soaked time are given, the time-dependence of the water-absorption and the swelling factor can be obtained.

EXPERIMENTAL RESULTS

The experimental arrangement is the Rayleigh interferometer system as described in reference [3]. It is based on the principle of the Young's two-beam interference and suited for making a measurement of micro-optical path difference. Test sample and reference one are immersed in two water chambers respectively. The direction of incident light is perpendicular to the surface of the film samples. PET was obtained from the Beijing Yan Shan Petrochemical Corporation as amorphous nuggets, whose limiting viscosity number $\eta = 0.656$, the melting point $T_m = 262^\circ\text{C}$ and the glass temperature $T_g = 70^\circ\text{C}$. Sample I is the sheet whose thickness $l_0 = 720\mu\text{m}$, the refractive index $n_0 = 1.5965$, the density $\rho_0 = 1.338\text{g}/\text{cm}^3$, and whose degree of crystallinity is less than 5%. This sample is regarded approximately as isotropic amorphous and prepared with unidirectional clipping calender method. Sample II is the uniaxially stretching film whose thickness $l_0 = 150\mu\text{m}$. Before testing, samples were heated to $50 \pm 2^\circ\text{C}$ for dry-treatment. After being held at this constant temperature for 24 ± 1 hours, they were cooled to 20°C in the silica-gel exsiccator.

The experimental curve between water-absorption factor and the square root of water-soaked time for two kinds of PET samples are observed from Figure 1. The solid line is obtained by the

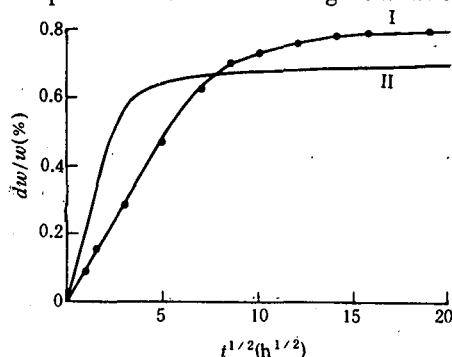


Fig.1 Water-absorption factor of PET as a function of $\sqrt{t}$

I, for $720\mu\text{m}$ thickness calender sheets

II, for $150\mu\text{m}$ thickness stretching films

The data points are measured by weight method.

optical interference method, and the data points represent the values measured with weight method where samples are sheets cut into approximately $720\mu\text{m}$ thickness, 5.0 cm long and 5.0 cm wide. In the present experiments from two different methods the satisfactory agreement is obtained. However, optical interference method is preferred to weight method because of greater accuracy and reliability for film samples. From the solid lines of Fig. 1, it is shown that absorption of water in PET films occurs under the Fickian conditions approximately, i.e., in initial stage, water-absorption factor is proportional to the square root of water-soaked time, and the part of straight line is given by^[4]

$$\frac{W(t)}{W(\infty)} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{l^2} \right)^{\frac{1}{2}} \quad (10)$$

where $W(t)$ is water-absorption factor for t hours, $W(\infty)$ is the equilibrium water-absorption

factor, and D is the diffusion coefficient. These measured data for the equilibrium moisture swelling parameters and the diffusion coefficient are shown in Table 1. Standard errors of the last significant figure are in parentheses. Consistency error of the equilibrium water absorption factor tested many times is less than 3%.

Table 1 Equilibrium water-absorption factor, equilibrium swelling factor and diffusion coefficient for water in the PET films

Samples	Thickness (μm)	Equilibrium water absorption factor (%)	Equilibrium swelling factor (%)	Diffusion coefficient ($10^{-14} \text{ m}^2/\text{s}$)
I. Calender				
Sheets	720(5)	0.80(1)	0.36(1)	42(2)
II. Stretching				
films	150(3)	0.70(2)	0.32(1)	8.6(9)

The diffusion coefficient for water and the equilibrium water-absorption factor are less in the uniaxially stretching film than in the calender sheets. As the polymer chains, assume that a preferred orientation in the stretch direction^[5] and along with the film is stretched, the crystalline region is developed, and the molecular gap thus decreases to that diffusion of water in the film becomes difficult. This is an expected result. On the other hand, for the above discussions it is obvious that the behavior of the polymers under water-absorption is similar in principle to that of the polymers under heating. Either by water-absorbing or by heating, the polymer will expand in volume, and decrease in density and refractive index owing to the additive property^[3]. Therefore it is believed that moisture swelling in polymers is in close relationship with glass transition in polymers. Glass transition temperature drops down with water absorption^[6]. All these results indicate that optical interference method is a simple but sensitive method for the study of water absorption and swelling in the transparent polymer films.

Keywords:

Moisture swelling; optical interference; PET (polyethylene terephthalate)

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