

Mass Diffusion Coefficients of Polymer Films Using Real-Time Holographic Interferometry

J. K. VRTIS* and R. J. FARRIS

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

SYNOPSIS

The mass diffusion coefficient is obtained using real-time holographic interferometry. The stresses induced during desorption and absorption of moisture are monitored as a function of time at various relative humidities. A mathematical relationship is applied to relate these stresses to the moisture diffusion through the thickness of the films. The advantage of the holographic interferometry technique is that both the swelling stress as a function of time and the mass diffusion coefficient can be quantified simultaneously during the same experiment. Several films and coatings were investigated: polyimides (PMDA-ODA and BPDA-PAA), photographic gelatin, and cellulose acetate. Each exhibited characteristic Fickian diffusion behavior. A gravimetric technique was employed to validate the holographic interferometry results. The moisture diffusion coefficients determined by holographic interferometry agreed well with reported literature values. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The mass diffusion coefficient is often determined using one of several techniques. The most common are gravimetric techniques.¹ Other techniques have been designed which are simpler than the conventional gravimetric methods.^{2,3} In these techniques, the property measured as a function of time at specific relative humidities is correlated to the mass uptake. The mathematical relationship was developed elsewhere⁴ and was outlined by Jou.³ For example, the swelling strain or swelling stress can be monitored as a function of time. These properties are then related to mass uptake through application of linear elasticity theory.

Recall the stress-strain relationship for a one-dimensional, homogeneous, linear elastic, isotropic material subjected to isothermal conditions:

$$E[\epsilon_{xx} - \beta' \Delta c(x, y, z, t)] = \sigma_{xx} \quad (1)$$

where E is the tensile modulus; ϵ_{xx} , the strain; β' , the swelling coefficient; c , the concentration; and σ_{xx} ,

the stress. A relationship³ for the average property through the volume can be established by

$$\bar{\Gamma} = \frac{1}{V} \int \Gamma(x, y, z, t) dV \quad (2)$$

where Γ is either ϵ_{xx} , σ_{xx} , or Δc and V represents the volume of the sample. The average mass uptake per unit volume is expressed by eq. (3):

$$\Delta \bar{c}(t) = \frac{1}{V} \int \Delta c(x, y, z, t) dV \quad (3)$$

The total amount of moisture absorbed by the film is written as

$$M_t(t) = \int \Delta c(x, y, z, t) dV = V \Delta \bar{c}(t) \quad (4)$$

Equation (1) is integrated through the volume to yield eq. (5):

$$\bar{\sigma}_{xx}(t) = E[\epsilon_{xx} - \beta' \Delta \bar{c}(t)] \quad (5)$$

For a constrained sample, $\epsilon_{xx} = 0$; therefore, eq. (5) reduces to

* To whom correspondence should be addressed at Intel Corp., M/S CH5-147, 5000 W. Chandler Blvd., Chandler, AZ 85226.

$$\Delta\bar{\sigma}_{xx}(t) = -E\beta'\Delta\bar{c}(t) \quad (6)$$

where $\Delta\bar{\sigma}_{xx}(t) = \bar{\sigma}_{xx}(t) - \bar{\sigma}_{xx}(0)$. Analogously for a material under constant stress, $\sigma_{xx} = 0$, eq. (5) yields

$$\Delta\bar{\epsilon}_{xx}(t) = \beta'\Delta\bar{c}(t) \quad (7)$$

where $\Delta\bar{\epsilon}_{xx}(t) = \bar{\epsilon}_{xx}(t) - \bar{\epsilon}_{xx}(0)$.

Applying the general relationship of eq. (2) and normalizing the stress and strain of eqs. (6) and (7), the transient swelling stress and strains can be expressed as

$$\frac{\Delta\bar{c}(t)}{\Delta\bar{c}(\infty)} = \frac{\Delta\bar{\sigma}(t)}{\Delta\bar{\sigma}(\infty)} = \frac{\Delta\bar{\epsilon}(t)}{\Delta\bar{\epsilon}(\infty)} = \frac{M(t)}{M(\infty)} \quad (8)$$

Through the relationship of eq. (8), the change in stress or strain with time can be correlated to the mass uptake with time relationship. Therefore, experiments designed to measure stress or strain as a function of time can be used to determine D_{eff} . This relationship was the premise for applying holographic interferometry to the determination of the mass diffusion coefficients of the materials used in this research.

Holographic interferometry has recently been used to determine the mass diffusion coefficients of polymers.³ This technique used a one-dimensional beam sample of a polymer coated on a substrate. A hologram was made of the beam sample prior to moisture diffusion. The beam was then subjected to a specific humidity and the number of interference fringes as a function of time were counted. From these measurements, the mass diffusion coefficient was determined. This method focused solely on the determination of the mass diffusion coefficient. A new adaptation, presented in this text, simultaneously measures the stress as a function time at various humidities in addition to determining the mass diffusion coefficient.

In this work, holographic interferometry is applied to a two-dimensional membrane sample. The stress is measured as function of time at various relative humidities. A plot of the normalized stress vs. $\text{time}^{1/2}$ correlates well with analogous mass uptake experiments. A comparison of this technique to a gravimetric technique and a comparison to literature values are presented.

EXPERIMENTAL

Sample Preparation

Four materials were used in these experiments: alkaline-processed bone gelatin, cellulose acetate, and

polyimides PMDA-ODA and BPDA-PPA. The thickness of the gelatin, cellulose acetate, and polyimides averaged 20, 128, and 25.6 μm , respectively. Uniaxial samples with dimensions 5 mm wide and 100 mm long were used for the gravimetric technique employing a Cahn 2000 microbalance.

The gelatin membrane was prepared from a bilayer gelatin on a substrate. The cellulose acetate and polyimide samples were made from films. Details are discussed elsewhere.⁵

A steel washer was adhered to cellulose acetate using a diglycyl ether bisphenol A-type epoxy. The assembly was placed in a 135°C oven for 2 h. At 135°C, the cellulose acetate was above its glass transition temperature and the manufacturing stress stored in the material was released. Upon cooling, the stresses were reintroduced and stored in tension in the membrane.

A similar procedure was applied to make the PMDA-ODA polyimide membrane sample. This polyimide membrane was used as a control. PMDA-ODA has been widely studied and its mass diffusion coefficient is well documented.⁶⁻⁸ Therefore, the holographic technique applied to diffusion using membrane geometries can be validated using the polyimide sample and comparing the results to the literature value. The BPDA-PAA polyimide membrane was fabricated similarly except that a quartz washer was required and the polyimide precursor was employed as the adhesive.

Holographic Interferometry

The experimental setup was equivalent to that described by Vrtis and Farris.⁵ Figure 1 illustrates the equipment layout. The biaxial stress as a function of time at various humidities was determined. The frequency of the 2,1 mode was monitored as a function of time. Initially, the membrane was brought to its zero-stress state and then dried at 0% RH. From the zero-stress state to 0% RH, the stress and time were monitored. After equilibrium was reached, the membrane was then subjected to a higher relative humidity and, again, the stress and time were monitored. A normalized stress vs. $\text{time}^{1/2}$ was plotted and the mass diffusion coefficients were calculated using the initial slope and half-time methods.^{9,10}

Gravimetric Technique

The most common method for determining the mass diffusion coefficient is by a gravimetric technique. A Cahn 2000 microbalance was employed to determine the mass uptake and the mass diffusion coef-

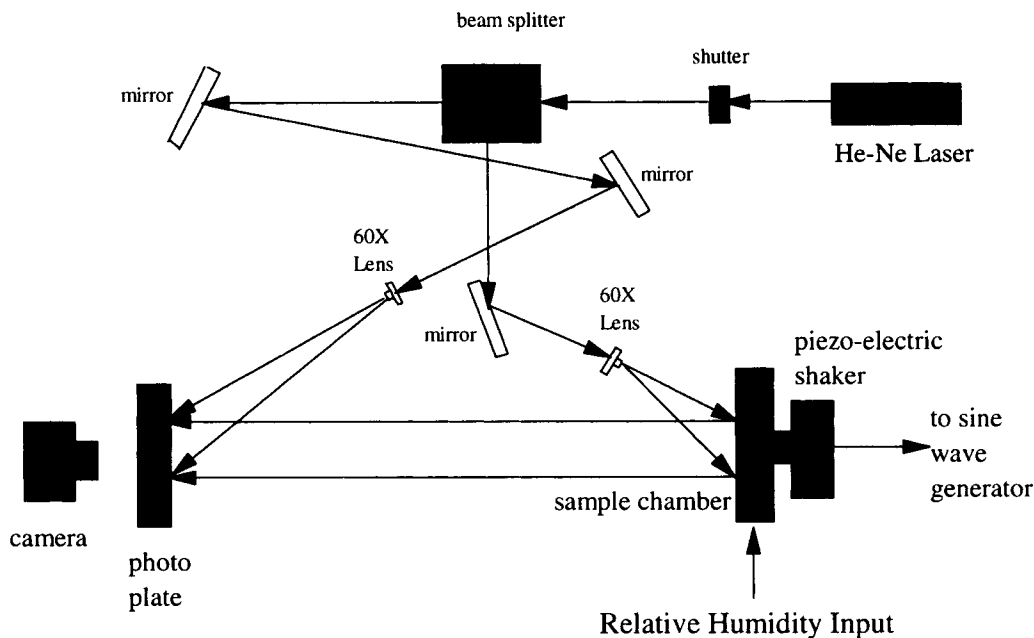


Figure 1 Holographic interferometry setup for relative humidity introduction.

ficient of a material.¹¹ A uniaxial sample was hung from the microbalance and the mass uptake as a function of time at various humidities was recorded. Figure 2 depicts the microbalance setup. A 5 mg weight was hung from the bottom of the sample to avoid adherence to the chamber walls due to the flow of the moisture-saturated gas. The sample was initially dried at 0% RH for 24 h. Relative humidity was introduced and the weight increase as a function of time monitored until equilibrium was reached. The sample was once again exposed to 0% RH and the weight loss monitored.

The % weight gain (loss) was recorded as a function of time and a normalized mass uptake, M_t/M_∞ , vs. $time^{1/2}$ plotted. The initial slope and half-time methods were employed to calculate the effective mass diffusion coefficient, D_{eff} .

RESULTS

Transient swelling stress as a function of time was monitored to ensure that equilibrium stress was reached. Each material was subject to a specific sorption cycle. The gelatin and cellulose acetate membranes were initially dried at 0% RH using dry compressed helium gas as the transport medium. Each was exposed to 54% RH for a defined period of time and then again subjected to 0% RH.

The validity of the holographic interferometry method to determine the mass diffusion coefficient

was investigated using a polyimide (PMDA-ODA) membrane. In addition, the technique was used to quantify the mass diffusion coefficient of BPDA-

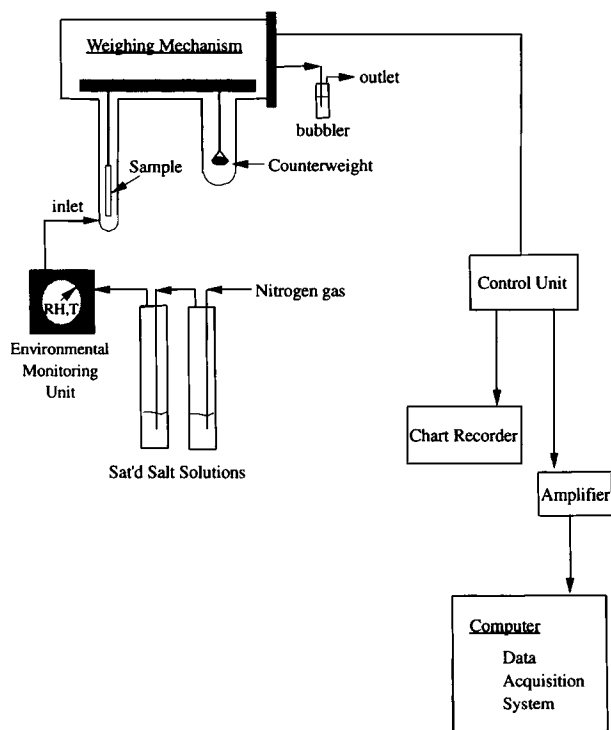


Figure 2 Schematic of Cahn 2000 microbalance used to determine mass uptake as a function of time at various relative humidities.

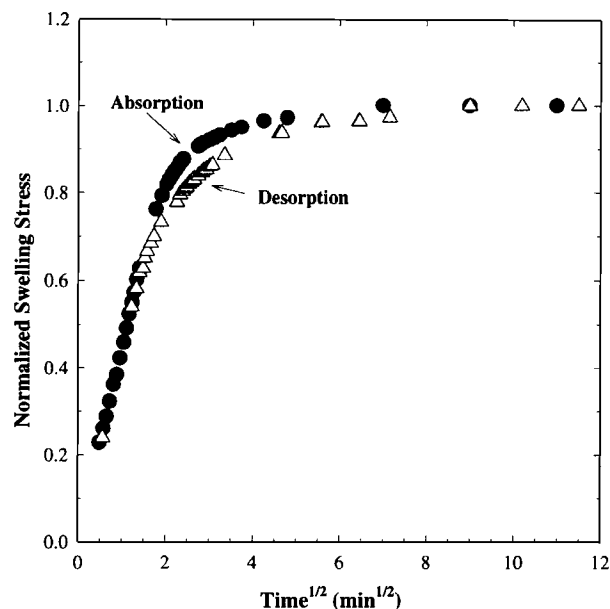


Figure 3 Normalized biaxial swelling stress vs. $\text{time}^{1/2}$ for gelatin as measured using holographic interferometry method.

PAA polyimide. The polyimides were exposed to similar sorption cycles as the preceding materials. The samples were initially dried at 0% RH. This was followed by exposure to 100% RH using helium as the transport gas which was bubbled through room-temperature water. The 2,1 resonant frequency mode was monitored as a function of time.

Cellulose acetate is a biaxially oriented material. Normally, to resolve the stresses in a biaxially oriented material, a square membrane is used and the stresses along the two principal directions are determined.¹² The determination of the diffusion coefficient requires the normalization of the swelling stresses. Therefore, by monitoring only the frequency change of a single mode (in this case, the 2,1 resonant frequency mode) as a function of time, the average swelling stress was used to determine the mass diffusion coefficient.

Figures 3–5 depict the normalized swelling stress vs. $\text{time}^{1/2}$ characteristics for gelatin, cellulose acetate, and PMDA–ODA, respectively. Similar behavior was observed for the BPDA–PAA polyimide. Analogous curves, via the gravimetric method, are depicted in Figures 6 and 7 for gelatin and cellulose acetate, respectively. The polyimide showed similar results and are illustrated elsewhere.³ The plots of the normalized stress and normalized mass uptake vs. $\text{time}^{1/2}$ indicate that the diffusion characteristics for these materials are Fickian.

The calculated diffusion coefficient for PMDA–ODA polyimide using this holographic interferom-

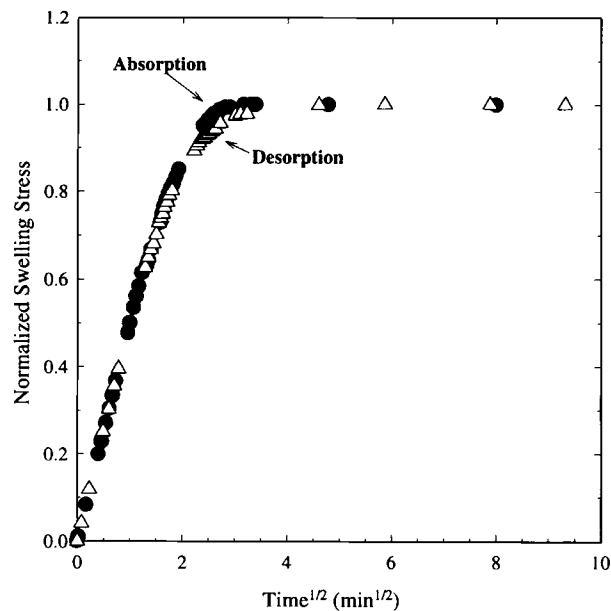


Figure 4 Normalized biaxial swelling stress vs. $\text{time}^{1/2}$ for cellulose acetate determined by holographic interferometry.

etry method was $2.08 \text{ E-}09 \text{ cm}^2/\text{s}$ (absorption, initial slope method). This result agrees with the reported literature value of $2.00 \text{ E-}09 \text{ cm}^2/\text{s}$.³

The BPDA–PAA polyimide exhibited a lower diffusion coefficient ($5.82 \text{ E-}10 \text{ cm}^2/\text{s}$, absorption, initial slope method) than did the PMDA–ODA. This

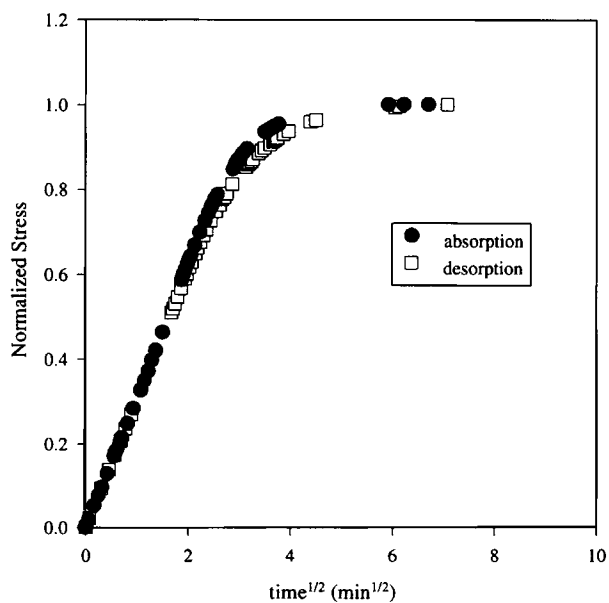


Figure 5 Normalized swelling stress vs. $\text{time}^{1/2}$ for polyimide (PMDA–ODA) using holographic interferometry.

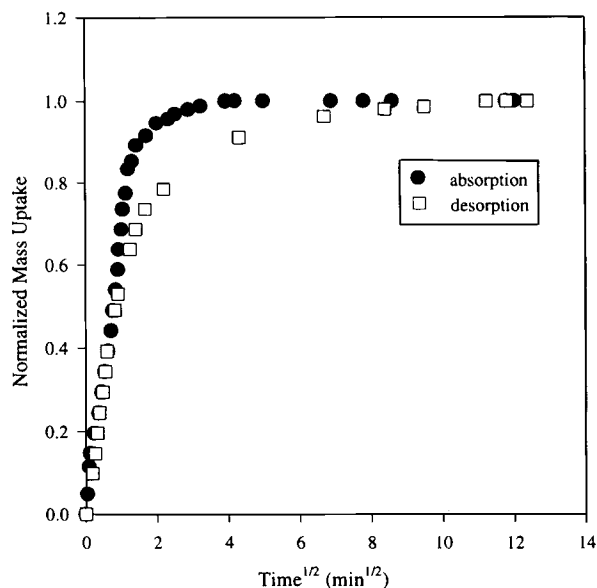


Figure 6 Normalized mass uptake vs. $\text{time}^{1/2}$ for gelatin using the gravimetric technique.

lower value is due to the molecular rigidity of the BPDA-PAA which inhibits the moisture diffusion process.

The polyimide diffusion coefficient results from the holographic interferometry correlated well with the published value. Therefore, holographic interferometry using the membrane geometry was a valid method for determining the mass diffusion coefficient. The holographic interferometry and gravimetric results are compared in Table I.

It was earlier postulated that the gelatin should have a greater mass diffusion coefficient than that of cellulose acetate due to its quick response to humidity variations. Further investigation indicated that the amount of moisture uptake was greater for gelatin than for the cellulose acetate within the same time interval. Figure 8 depicts this comparison.

To better understand this phenomenon, recall that the diffusion coefficient is a measure of the movement of a penetrant through a film or sheet. Its units of measure are cm^2/s . Therefore, the diffusion coefficient does not express the amount of penetrant entering the film, but, instead, indicates the rate at which it enters through the thickness.

Referencing Figure 8, it was apparent that the amount of moisture absorbed by gelatin in the first 5 min is ~ 13 times greater than the amount absorbed by cellulose acetate in the same time interval. It is the amount of moisture that affects the material properties of gelatin and cellulose acetate. Therefore, the humidity swelling coefficient combined with the diffusion coefficient are required to understand the

transient dimensional instability behavior of the bi-layer system.

A comparison of the mass diffusion coefficients for the four materials investigated is presented in Table I. Overall, the mass diffusion coefficients were the same whether holographic interferometry or the gravimetric method was used. There was a discrepancy in the diffusion coefficients for gelatin between the two methods. Several possible explanations can be argued: First, the volume of the Cahn 2000 chamber was greater than that of the holographic chamber. It is possible that the sample in the gravimetric chamber was not completely dry for the same drying interval as for the holographic interferometry chamber. This could lead to inflated diffusion coefficient results. Second, recall that a small weight was hung from the bottom of the gravimetric sample. This was necessary due to the adverse affect of the sample clinging to the walls of the chamber as a result of the moisture/compressed gas flowrate. Although the weight was small, gelatin creeps at higher humidities and this phenomenon could contribute to erroneous diffusion coefficient results.

CONCLUSIONS

A new technique for determining the mass diffusion coefficient was introduced. Holographic interferometry has the flexibility of measuring the stress as a function of time at various humidities in parallel to

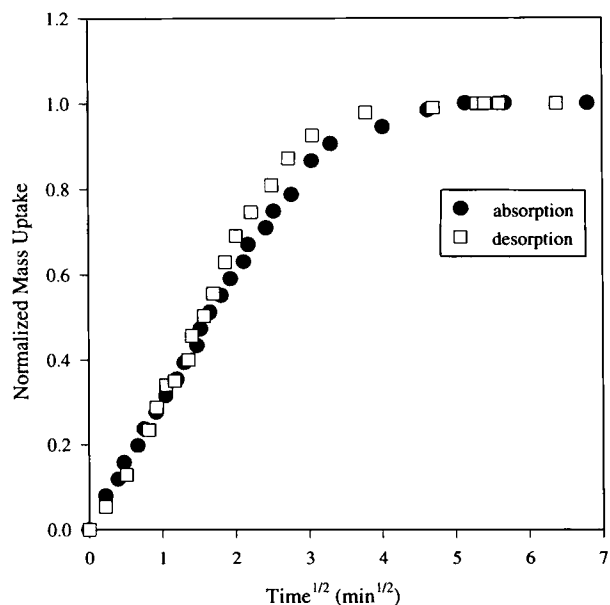


Figure 7 Normalized mass uptake vs. $\text{time}^{1/2}$ for cellulose acetate using the gravimetric technique.

Table I Comparison of the Mass Diffusion Coefficients for Gelatin, Cellulose Acetate, and Polyimides PMDA-ODA and BPDA-PAA Using Holographic Interferometry and Gravimetric Techniques

Material	Technique	Analysis Method	Diffusion Coefficient, D_{eff} (cm ² /s)	
			Absorption	Desorption
Gelatin	Gravimetric	Initial slope	4.61 E-09	5.51 E-09
	Gravimetric	Half-time	4.62 E-09	5.53 E-09
	Holographic	Initial slope	2.17 E-09	2.11 E-09
	Holographic	Half-time	2.18 E-09	2.09 E-09
Cellulose acetate	Gravimetric	Initial slope	5.00 E-08	4.86 E-08
	Gravimetric	Half-time	5.02 E-08	4.87 E-08
	Holographic	Initial slope	5.02 E-08	4.87 E-08
	Holographic	Half-time	5.00 E-08	4.88 E-08
Polyimide PMDA-ODA	Holographic	Initial slope	2.08 E-09	1.98 E-09
	Holographic	Half-time	2.04 E-09	1.97 E-09
Polyimide BPDA-PAA	Holographic	Initial slope	5.82 E-10	5.79 E-10
	Holographic	Half-time	5.90 E-10	5.90 E-10

determining mass transport properties. Its validity was experimentally verified using PMDA-ODA polyimide, which has been well documented in the literature. This technique employed holographic interferometry and used a circular membrane sample geometry to study the mass transport

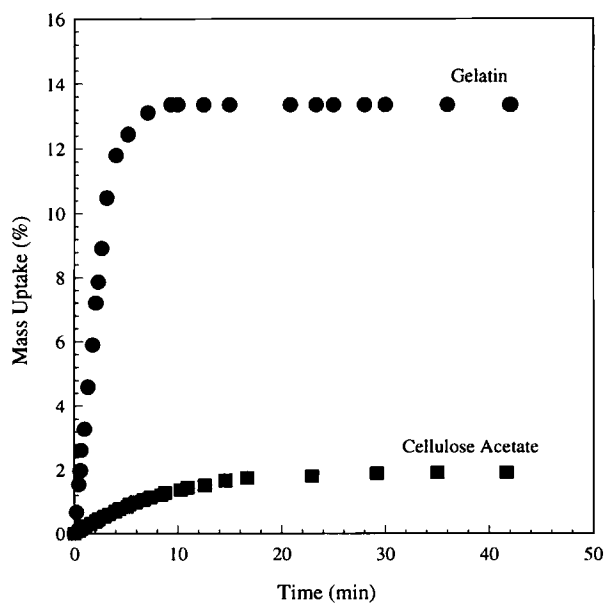


Figure 8 Comparison of the mass uptake of alkaline processed bone gelatin and cellulose acetate at 54% RH as a function of time.

properties of coating and films. The BPDA-PAA polyimide exhibited a lower diffusion coefficient than did the PMDA-ODA due to the rigid molecular backbone, unlike the flexible backbone of the PMDA-ODA. This rigidity inhibits the diffusion of the moisture.

The gelatin and cellulose acetate diffusion coefficients varied by an order of magnitude, with cellulose acetate exhibiting a higher diffusion coefficient. The diffusion coefficients determined by holographic interferometry for gelatin and cellulose acetate were 2.11 E-09 and 5.00 E-08 cm²/s, respectively. This variation was intuitively thought to be incorrect due to the quick response of gelatin-coated bilayer systems to humidity changes. Visual observations indicated that gelatin reacted very quickly to moisture changes. The reason for the quick response was due to the amount of moisture the gelatin picked up in the same interval compared to that of cellulose acetate or polyimide. This response is not solely related to the rate at which the moisture penetrated through the film thickness. This phenomenon was illustrated in a comparison of the percentage of moisture taken up by gelatin with that of cellulose acetate over the same time interval.

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