Effect of Sorbed Water and Temperature on the Optical Properties and Density of Thin Glassy Polymer Films on a Silicon Substrate

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ABSTRACT: The effect of relative humidity and temperature on the refractive index and thickness of thin glassy polymer films ($l \sim 500$ nm) supported on silicon substrates was measured using ellipsometry. The polymers considered, polysulfone and a polyimide, exhibited increasing refractive index and film thickness with increasing relative humidity. The effect of exposure to high water activity on dry glassy polymer film properties was studied. The specific refraction, as used in the Lorentz−Lorenz equation, was determined directly for these polymers, and its dependence on temperature and aging history was examined. Water vapor sorption in thick polymer films ($l \sim 100\ \mu$m) was measured using gravimetric techniques and shown to be consistent with the water vapor sorption measured in thin films using ellipsometry. The thin film water vapor sorption data are compared to the extreme possibilities of volume additivity and constant volume as water is sorbed; the results fall in between these limits but closer to the constant volume case.

Introduction

Glassy polymers are nonequilibrium materials that spontaneously, but usually slowly, evolve over time toward an equilibrium state; this evolution is manifested by changes in properties like density, permeability, etc. This process is known as physical aging and has been studied extensively for bulk materials.[1] More recently, thin polymer films ($l < 1\ \mu$m) have been observed to physically age orders of magnitude more rapidly than bulk systems.[2−21] This phenomenon is interesting because of its broad impact in several technologies and the unanswered scientific questions regarding why physical dimensions affect aging rates so drastically. If the mechanisms were fully understood, better performance predictions and perhaps ways to arrest physical aging for systems comprised of thin glassy polymer films, such as gas separation membranes, could be developed.

Variable angle spectroscopic ellipsometry, a sensitive and precise technique for measuring surface and film properties, is a valuable tool for studying physical aging in thin polymer films.[16,19] It has been noted that the ellipsometry results can vary somewhat depending on ambient humidity. Understanding how experimental conditions, e.g., temperature, relative humidity (RH), etc., affect thin polymer film properties is essential for accurate analysis because of the extreme sensitivity of ellipsometry. Despite the potential impact, few studies report the influence of humidity on ellipsometry measurements.[22,23] Kleinfeld and Ferguson studied the effect of humidity on multilayered composite films of poly(diallyldimethylammonium chloride) and a synthetic silicate mineral.[23] Mathe et al. measured the swelling of natural polysaccharides at various humidity levels and reported refractive index values calculated from an additive model.[22] Other methods, such as prism coupling and interferometry, have also been used to measure the effect of humidity on film refractive index.[24−31] The majority of these studies focused on polymer waveguide applications. Scherer and Bailey were among the first to investigate the dependence of water absorption on refractive index using waveguides. Their work on cellulose acetate also included the effect of humidity on film thickness.[31] The literature shows that the effect of humidity on refractive index depends on the nature of the polymer. Ellipsometry has been used more broadly to study thermal properties of polymers (e.g., glass transition, thermal expansion, thermooptic properties, etc.). The influence of temperature on film properties below the glass transition will be briefly discussed in this paper.

The Lorentz−Lorenz equation provides a fundamental relationship between density and refractive index[32]

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{\rho N_{\text{av}} \alpha}{3 M_0 \epsilon_0} \qquad (1)$$

where ρ is the polymer density, N_{av} is Avogadro's number, α is the average polarizability of the polymer repeat unit, M_0 is the polymer repeat unit molecular weight, and ϵ_0 is the permittivity of free space. Only refractive index and density are expected to change with physical aging, simplifying the Lorentz−Lorenz equation to

$$L = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \rho C \qquad (2)$$

where L is defined as the Lorentz−Lorenz parameter. The specific refraction, C, is presumed to be a constant for a given substance, i.e., an additive and constitutive property such that the Lorentz−Lorenz equation can be applied to mixtures. The Lorentz−Lorenz equation has been tested for many systems including gases, liquids, solids, and polymers with remarkable success.[33−37] Recently, Krishnaswamy and Janzen reported using refractive index to determine the density of polyethylene more simply and accurately than standard density gradient techniques.[35]

In previous studies, specific refraction values have been calculated from bulk polymer properties or from group contribu-

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tion methods described by Van Krevelen, which give accurate predictions for many polymers.[38] This study determines C experimentally and tests the assumption that it is constant during physical aging by examining the relationship between refractive index and density in films of the same polymer at various densities. The density of glassy polymers can be controlled to varying degrees by exposure to high-pressure CO_2 and thermal annealing. Exposure to high-pressure CO_2 (tens of atmospheres) is known to decrease the density of glassy polymers by dilation and swelling.[39−50] Conversely, polymer density can be increased by annealing at elevated temperatures below the T_g, where physical aging occurs at measurable rates in bulk specimens.[39,41,51−53] Chan and Paul demonstrated both of these effects in polycarbonate.[39]

This study examines the influence of relative humidity and temperature on thin glassy polymer film properties as measured by ellipsometry. The effect of exposure to high relative humidity on dry film properties is also examined. To relate refractive index changes to density changes through the Lorentz−Lorenz equation, the specific refraction of the polymers studied is determined experimentally. Water vapor sorption in thick polymer films ($l \sim 100$ mm) is presented and compared with ellipsometry results.

Experimental Section

Materials. Two glassy polymers, a polyimide commercially known as Matrimid 5128 and bisphenol A-based polysulfone (PSF), were used as received in this study. The glass transitions of Matrimid and PSF are reported as 310 and 186 °C, respectively.[11] Detailed descriptions of these polymers have been reported previously by Huang and Paul.[11]

Film Preparation. The film preparation procedures described here are given in detail by Huang and Paul.[12] Thin films ($l \sim 500$ nm) were prepared by spin-casting polymer solutions onto silicon wafers at 1000 rpm for 60 s using cyclopentanone as the solvent. The films were removed from the wafer surface using deionized water and placed on thin wire frames. The freestanding films were then dried and heated above their T_g in a N_2-purged oven to remove prior history before gently placing them onto precut silicon wafer squares. Samples were aged at 35 °C and 0% RH for sufficient time (>1000 h) so any property changes that might occur during the experiments reported here due to further physical aging would be negligible.

Thick films ($l \sim 100$ μm) were prepared by solution casting onto silicon wafers using metal casting rings. The casting solvent was methylene chloride, and glass plates were used to slow evaporation. The films were allowed to dry for 1 week at room temperature and then dried at 100 °C in a vacuum oven for 2 days. Densities of the thick films were altered using high-pressure (60 atm) CO_2 or annealing below the glass transition temperature. These treatments were applied for times ranging from 30 min to several weeks, producing polymer films with a range of densities.

Density Measurements. Densities were measured at 23 °C using a density gradient column based on aqueous calcium nitrate solutions by the standard technique (ASTM D 1505). The column was calibrated with glass floats of known density. Three pieces of each sample were placed in the column and allowed to equilibrate for 24 h before measurement. The accuracy was ±0.0003 g/cm^3.

Abbe Refractometer. A Fisher Scientific Abbe-3L refractometer was used to measure the refractive index of thick films. The refractive index was measured at the sodium D line ($\lambda = 589.3$ nm) with an accuracy of ±0.0002 refractive index units. Water from a temperature-controlled bath was circulated through the refractometer to regulate the measurement temperature. 1-Bromonaphthalene was used as a contacting liquid. Measurements were made quickly after removing polymer samples from vacuum to minimize any errors caused by water vapor sorption or contact with 1-bromonaphthalene.

Ellipsometry. A variable angle spectroscopic ellipsometer, model 2000D, manufactured by J.A. Woollam Co. was used to determine the thickness and refractive index of thin films. Measurements were taken at wavelengths from 400 to 1000 nm at three angles of incidence 65°, 70°, and 75°. The program WVASE32 was used to fit the data to a model of the polymer film and substrate system. The polymer refractive index was calculated using the Cauchy equation

$$n = A + B/\lambda^2 + C/\lambda^4 \tag{3}$$

where A, B, and C are constants and λ is the light wavelength. All refractive index values are reported at the sodium D line.

The ellipsometer was placed in an environmental chamber where the relative humidity, as measured by a Tracable Hygrometer from Fischer Scientific, was controlled with dry nitrogen which could also be bubbled through water. The relative humidity was controlled ±0.3%, and the sample temperature was controlled ±0.1 °C using a Melcor thermoelectric heater/cooler and temperature controller.

Two types of experiments were used to examine the influence of humidity on film properties. Real-time experiments began with a dry polymer film in the environmental chamber at a relative humidity of 10% or less, and then the film properties were measured in situ as the relative humidity was slowly raised above 60% and lowered again below 10%. The cycle lasted ~3 h. The humidity range was selected on the basis of ellipsometer operating conditions. Step change experiments were performed as follows: A dry polymer film was measured using ellipsometry at 10% RH for 10 min and then stored at 10% RH as the chamber was humidified to 50% RH. The film was immediately placed in the ellipsometer and measured for another 10 min. With the film stored at 50% RH, the chamber was brought back to 10% RH, and then the film properties were again measured for 10 min.

Kinetic Gravimetric Sorption. Kinetic gravimetric sorption experiments were done using a McBain spring balance system.[54] The system consisted of a water-jacketed glass chamber attached to a vacuum pump for penetrant removal and polymer degassing. A water bath controlled the chamber temperature to ±0.1 °C. The polymer sample (~30 mg) was attached to a quartz spring and placed in the chamber. The spring was purchased from Ruska Instrument Corp., Houston, TX, with a measured spring constant of 0.23 mg/mm.

Previously sorbed air gases and water vapor were removed by exposing the polymer to vacuum for at least 24 h before experiments began. The polymer sample was then exposed to water vapor at fixed pressures. The spring elongation was measured and recorded as a function of time using a charge-coupled device camera interfaced with a computer.[55] The spring constant was used to convert the displacement data to mass uptake. Equilibrium mass uptake and diffusion coefficients were extracted from these kinetic sorption data.

Results and Discussion

Effect of Relative Humidity on Thin Film Properties. Figure 1 shows the effect of relative humidity on the refractive index of a thin Matrimid film at room temperature as measured by ellipsometry. The refractive index increases linearly with humidity, changing by $\Delta n = 0.005$ when relative humidity was changed from 10% to 60%. From simple additivity concepts, the refractive index would decrease since the value for water is 1.333; thus, further analysis is needed to understand the increase in n with increasing humidity. Over the same relative humidity range, the Matrimid film thickness increased by 1.5 nm (i.e., 0.31%), as shown in Figure 2. A control experiment showed the substrate thickness did not depend on humidity, so any thickness changes were of the polymer film. Figures 3 and 4 show the effect of relative humidity on the refractive index and film thickness for PSF, respectively. The same qualitative trends were seen for PSF as Matrimid; however, the magnitudes are

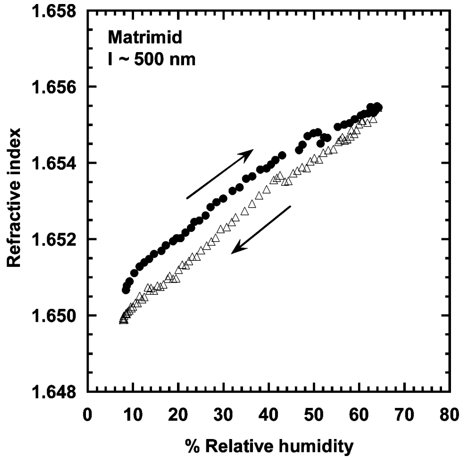

Figure 1. Effect of relative humidity on refractive index of a thin Matrimid film at 25 °C while humidifying (●) and drying (△).

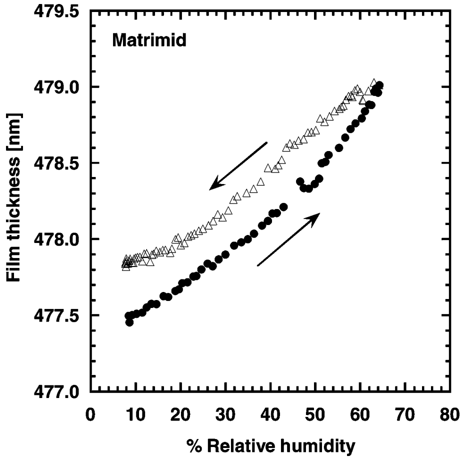

Figure 2. Effect of relative humidity on film thickness of a Matrimid film at 25 °C while humidifying (●) and drying (△).

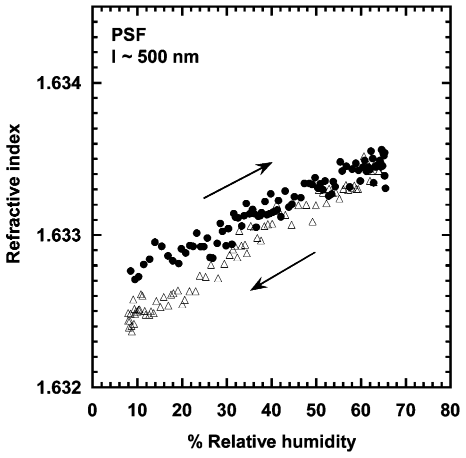

Figure 3. Effect of relative humidity on refractive index of a thin PSF film at 25 °C while humidifying (●) and drying (△).

significantly less. PSF exhibited a Δn increase of 0.001 and a thickness increase of 0.7 nm (i.e., 0.16%) when RH was raised from 10% to 60%. While these property changes are small, they are significant when studying small changes like those accompanying physical aging.

Exposure to increased water activity can result in semipermanent property changes, as seen by the different starting and ending points in Figures 1−4. Semipermanent indicates that although these changes may be reversed after sufficient aging, they remain during the time scale of the experiments. This conditioning phenomenon is known to occur in other polymer/penetrant systems but is rarely reported for water vapor.[46] Hennig et al. reported contact angle hysteresis in polyimide films exposed to liquid water.[56] Several issues were examined to confirm that film history was the cause for these changes. First, the time required for thin films to sorb an equilibrium amount of water vapor by diffusion is orders of magnitude shorter than the time required for each measurement, discounting diffusion kinetics as a cause for the observed hysteresis in thickness and refractive index; this calculation will be described later. Next, relative humidity step change experiments were performed. The results of these experiments for Matrimid are shown in Figures 5 and 6. The dry film (i.e., the film exposed to 10% RH) refractive index was lower after exposure to the 50% RH environment, and the dry film thickness increased. These changes are consistent with polymer dilation occurring as a result of water sorption. Although the changes were smaller in PSF, similar qualitative results were seen but are not shown for brevity. While the magnitude of the changes measured in the step change experiments roughly matched those of the real-time experiments, there are many factors which influence these changes (such as sample history, time of exposure, and RH), and investigating all of these factors is beyond the aims of this study. Last, real-time experiments were performed on polymers that had been aged in a humid environment. Because these polymers had always been exposed to high humidity, one would expect no hysteresis effects, and none was found.

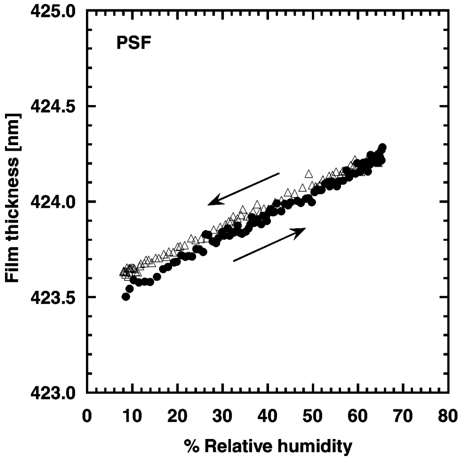

Figure 4. Effect of relative humidity on film thickness of a PSF film at 25 °C while humidifying (●) and drying (△).

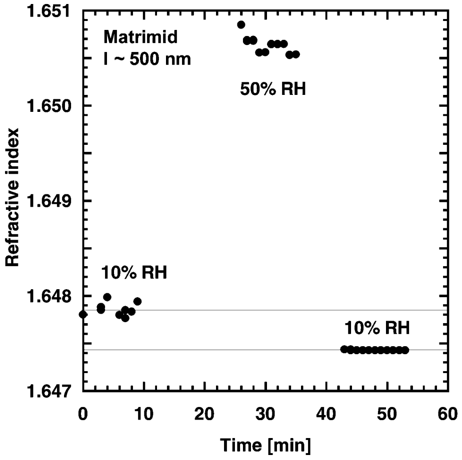

Figure 5. Refractive index of an initially dry thin Matrimid film exposed to step changes of relative humidity.

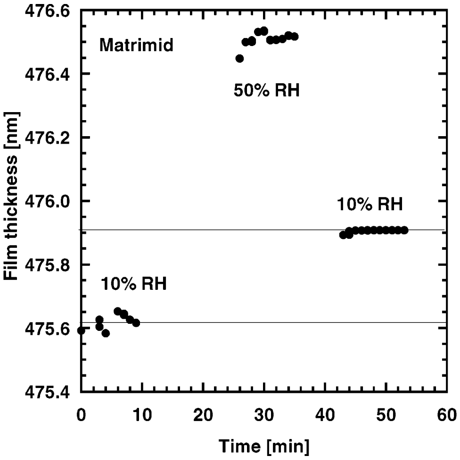

Figure 6. Film thickness of an initially dry Matrimid film exposed to step changes of relative humidity.

Table 1. Effect of Prior Treatment on Density and Refractive Index

material	treatment	time (h)	ρ_{wet} (g/cm^3)	ρ_{dry} (g/cm^3)	refractive index
Matrimid	CO$_2$ (60 atm)	2	1.2493	1.2138	1.6357
		4	1.2505	1.2141	1.6342
		15	1.2505	1.2136	1.6333
		24	1.2481	1.2098	1.6308
	none	0	1.2527	1.2185	1.6382
	anneal at 280 °C	2	1.2537	1.2217	1.6420
		9	1.2582	1.2275	1.6444
		15	1.2670	1.2379	1.6477
		20	1.2698	1.2410	1.6483
PSF	CO2 (60 atm)	2	1.2377	1.2299	1.6295
		5	1.2376	1.2300	1.6290
		24	1.2360	1.2281	1.6287
	none	0	1.2378	1.2302	1.6300
	anneal at 165 °C	1	1.2397	1.2326	1.6328
		6	1.2401	1.2332	1.6332
		30	1.2409	1.2340	1.6334
		384	1.2419	1.2350	1.6340

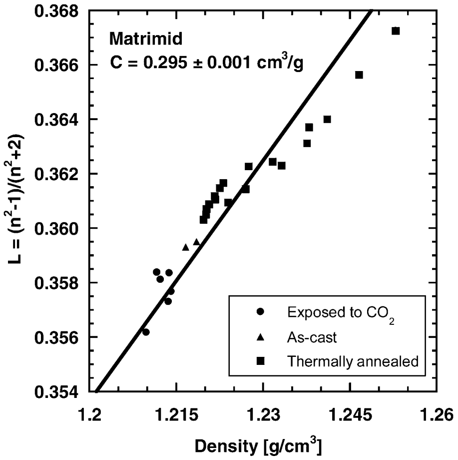

Figure 7. Lorentz−Lorenz parameter, *L*, of Matrimid films exposed to CO$_2$ (●), as-cast films (▲), and annealed films (■) as a function of density. The line represents a least-squares fit of the data to eq 2.

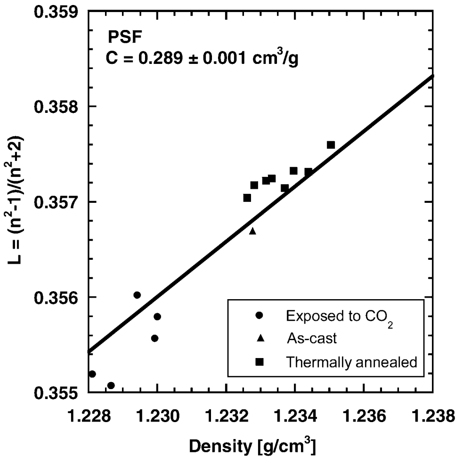

Figure 8. Lorentz−Lorenz parameter, *L*, of PSF films exposed to CO$_2$ (●), as-cast films (▲), and annealed films (■) as a function of density. The line represents a least-squares fit of the data to eq 2.

Specific Refraction. In this study, the specific refraction, *C*, was calculated by directly measuring the refractive index and density of a thick polymer film. To accurately determine the specific refraction, it is necessary to measure the refractive index and density of the polymer in the same state. While both refractive index and density measurements were performed at 23 °C, the refractive index was measured using dry films, but the density was measured using films in a water solution. To correct for the density change due to water sorption, the activity of water in the density gradient column was required; it was determined to be 0.85.[57−59] Using the water activity in the column and the known effect of water on film properties, the density was corrected to the dry state.[60] The effect of prior treatment on the apparent density as measured in the gradient column, ρ_{wet}, corrected density, ρ_{dry}, and refractive index is recorded in Table 1. Figure 7 presents the Lorentz−Lorenz parameter, *L*, for Matrimid films at a range of densities achieved by exposure to 60 atm of CO$_2$ at 25 °C or annealing at 280 °C for times ranging from 30 min to several weeks. A fit of the data to eq 2 gives a specific refraction of 0.295 ± 0.001 cm^3/g for Matrimid. It is important to note that the specific refractions given here are for the wavelength of 589.3 nm. An estimate for the Matrimid specific refraction using a group contribution method to calculate *n* was previously reported to be 0.305 cm^3/g.[16] Figure 8 shows the Lorentz−Lorenz parameter for PSF films over a smaller range of densities achieved using the methods described earlier. In this case, the annealing temperature was 160 °C. The specific refraction of PSF was determined to be 0.289 ± 0.001 cm^3/g. Previously, an estimate from reported bulk properties was given as 0.288 cm^3/g.[16]

Effect of Temperature on Thin Film Properties. The specific refraction is expected to be independent of temperature as defined in the Lorentz−Lorenz equation. To test this hypothesis, polymer refractive index and film thickness were measured at temperatures ranging from 20 to 75 °C. If polarizability is not a function of temperature, the specific refraction will remain constant, and the change in refractive index is due simply to film expansion or contraction. Analysis of the simplified Lorentz−Lorenz equation as a function of temperature gives

$$\frac{\mathrm{d}\ln C}{\mathrm{d}T} = \frac{\mathrm{d}\ln L}{\mathrm{d}T} + \frac{\mathrm{d}\ln l}{\mathrm{d}T} \tag{4}$$

where *l* is film thickness. Equation 4 assumes that the polymer film expands only in the direction normal to the substrate; evidence supporting this assumption is given later. Figures 9 and 10 show the refractive index and film thickness as a function of temperature for a PSF film as measured by ellipsometry. Analysis of the data for PSF shows $\mathrm{d}\ln L/\mathrm{d}T = -(29.3 \pm 0.1) \times 10^{-5}$ °C^{-1}, $\mathrm{d}\ln l/\mathrm{d}T = (27.4 \pm 0.1) \times 10^{-5}$ °C^{-1}, and, from eq 4, $\mathrm{d}\ln C/\mathrm{d}T = -(1.9 \pm 0.1) \times 10^{-5}$ °C^{-1}. If these values are used to estimate film properties as a function of temperature, the specific refraction changes would be less than 2% of the

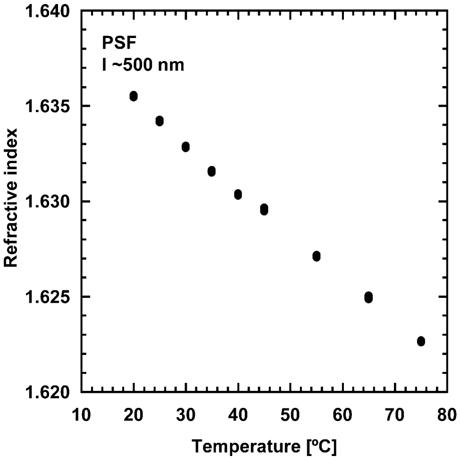

Figure 9. Effect of temperature on the refractive index of a thin PSF film.

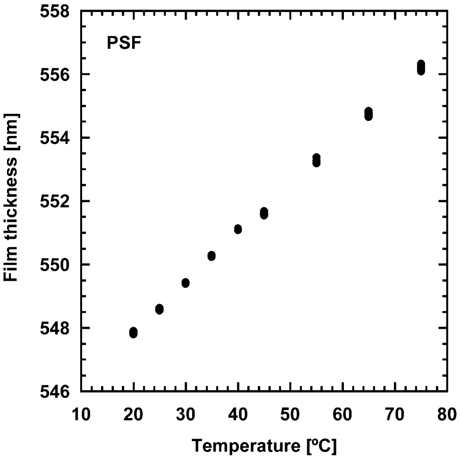

Figure 10. Effect of temperature on film thickness of a PSF film.

associated density changes. This small change in specific refraction is negligible compared to other property changes. Similar results were found for Matrimid: d ln L/d$T = -(30.0 \pm 0.3) \times 10^{-5}$ °C^{-1}, d ln l/d$T = (24.4 \pm 0.2) \times 10^{-5}$ °C^{-1}, and, from eq 4, d ln C/d$T = -(5.7 \pm 0.4) \times 10^{-5}$ °C^{-1}. Using these values to estimate Matrimid film properties as a function of temperature gives specific refraction changes which are 5% of the related density changes. The small change in C with temperature deduced from these observations further supports the application of the Lorentz–Lorenz equation to Matrimid and PSF.

Water Sorption in Thick Films. Sorption of vapors and gases is history dependent in glassy polymers.[61] An example of this phenomenon is *n*-hexane sorption in glassy polystyrene microspheres, studied by Enscore et al.[51] These history effects require thick and thin films to have equivalent thermal history when their behaviors are compared. To achieve the equivalent thermal history of the aged thin films studied by ellipsometry, thick Matrimid films were annealed at 280 °C for 10 h. Afterward, the thick film had the same refractive index, and thus density, as the thin film. This treatment allows for the meaningful comparison of water vapor sorption in thin and thick films. Figure 11 shows the water vapor sorption isotherms for as-cast and thermally annealed Matrimid films ($l \sim 100$ μm). At an activity of 1.0, an as-cast film sorbed 4.5 wt % water, and the annealed film sorbed 2.9 wt %. The as-cast sorption data were fit to the Flory–Huggins theory, with a χ of 2.2, using a partial molar volume of 18.1 cm^3/mol for water. A linear isotherm (i.e., Henry's law) matched the annealed sorption data well. Interestingly, these isotherms do not show any evidence of concave activity dependence at low RH as might be expected from the dual mode sorption model.[62] These data are consistent with considerable literature results for water sorption in other glassy polymers including several polyimides.[63−68] The water vapor sorption isotherms for as-cast and annealed PSF films are shown in Figure 12. The annealed sample was heated at 150 °C for 24 h to match the state of the aged PSF thin films. PSF sorbs 1.1 wt % water in the as-cast film and 0.8 wt % in the annealed film. These values match data in the literature and are significantly less than those in Matrimid.[69,70] The as-cast sorption data were fit to the Flory–Huggins theory with a χ of 3.4, while the annealed sorption data obey Henry's law. For both Matrimid and PSF, the water vapor sorption was reduced by ~30% in the annealed films as compared to the as-cast films.

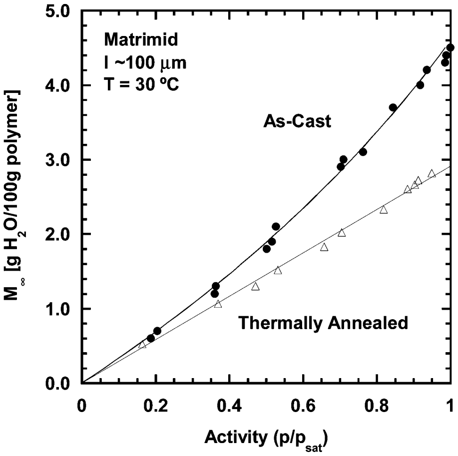

Figure 11. Sorption isotherms for water in as-cast (●) and annealed (△) Matrimid films. As-cast film data fitted to Flory–Huggins theory with a χ value of 2.2. Annealed film data follow linear fit.

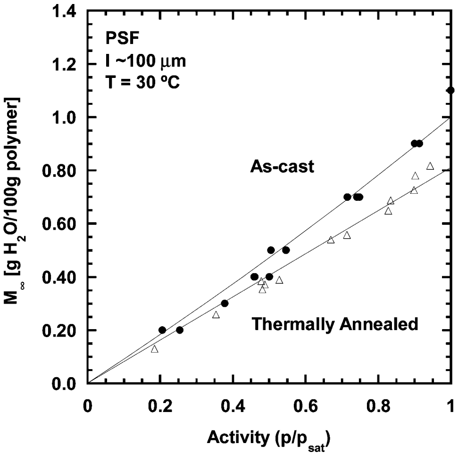

Figure 12. Sorption isotherms for water in as-cast (●) and annealed (△) PSF films. As-cast film data fitted to Flory–Huggins theory with a χ value of 3.4. Annealed film data follow a linear fit.

The uptake of liquid water by Matrimid and PSF films was also measured by a pat and dry technique. The weight of thick films was measured after drying for 48 h in vacuum, and the wet film weights were measured after patting off excess water from films soaked in water for 48 h. The weight of water sorbed in as-cast and annealed films of Matrimid was 4.1% and 2.9% and 0.8% and 0.6% in PSF, respectively. These values closely match the results from spring balance experiments when the vapor sorption results are extrapolated to 100% RH.

The kinetics of water vapor sorption in an annealed Matrimid film subjected to a step change in gas-phase humidity from 0

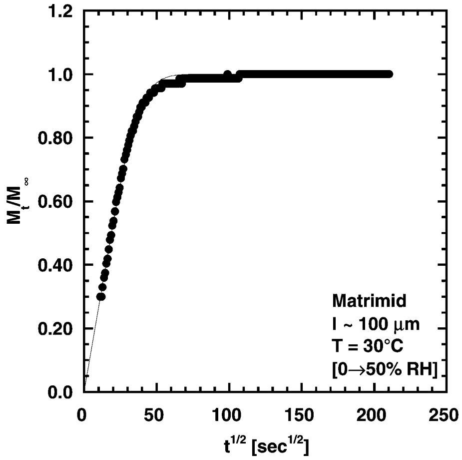

Figure 13. Kinetics of water vapor sorption in Matrimid at 30 °C. The curve represents a best fit to the Fickian sorption model (eq 5) to the data.

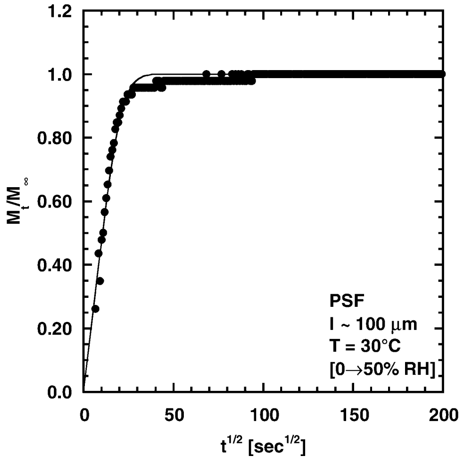

Figure 14. Kinetics of water vapor sorption in PSF at 30 °C. The curve represents a best fit to the Fickian sorption model (eq 5) to the data.

to 50% are presented in Figure 13. The mass uptake at time t, M_t, normalized by the equilibrium mass uptake, M_∞, is plotted against the square root of time since the experiment began. The kinetic sorption data were modeled by Fickian penetrant diffusion into a semiinfinite plane sheet[71]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-\bar{D}(2n+1)^2\pi^2 t}{l^2}\right) \quad (5)$$

where $\bar{D}$ is the average diffusivity, which for Matrimid was $(1.5 \pm 0.4) \times 10^{-8}$ cm^2/s.

Figure 14 shows the kinetics of water vapor sorption in an annealed PSF film as a result of a step increase in gas-phase humidity from 0 to 50%. Analysis of the data yields a diffusivity of $(2.9 \pm 0.8) \times 10^{-8}$ cm^2/s for water in PSF. Within experimental error, the water diffusion coefficients found here are essentially independent of RH, which agrees with literature results for PSF and several polyimides.[63,64,69]

Using the diffusion coefficients from the kinetic sorption data, the longest time for the thin films to reach equilibrium, as estimated by $4l^2/\bar{D}$ (the factor of 4 accounts for one-way transport in the supported films), is less than a second, significantly less than the time scale of the ellipsometry measurements (~60 s), verifying the earlier assumption that the time for thin film samples to reach equilibrium with the water vapor was short compared to the experimental time scale.

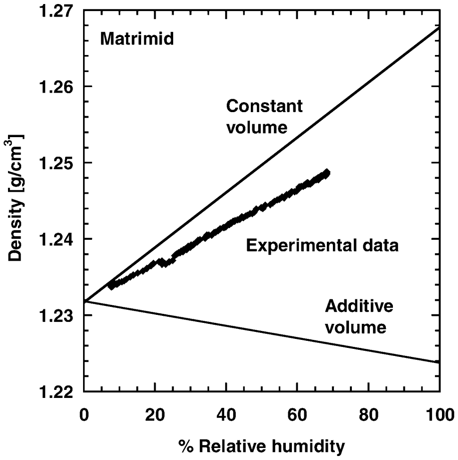

Figure 15. Relationship between density and relative humidity for Matrimid. Lines represent limiting cases for comparison.

Effect of Water Sorption on Thin Film Density. The Lorentz−Lorenz equation for mixed systems is[32]

$$L = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \rho\sum_{i=1}^{k} w_i C_i \quad (6)$$

where w_i and C_i are the mass fraction and specific refraction of component i, respectively, and k is the number of components. For the case of polymers containing sorbed water, eq 6 can be used to calculate the density of the mixture from its refractive index as follows

$$\rho = \left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right)\frac{1}{(w_{\text{water}}C_{\text{water}} + (1 - w_{\text{water}})C_{\text{polymer}})} \quad (7)$$

where w_{water} is the water mass fraction in the polymer at a given relative humidity, measured from sorption experiments, C_{water} is the specific refraction of pure water, 0.206 cm^3/g, and C_{polymer} is the polymer specific refraction. This approach assumes, of course, that the equilibrium sorption in thick and thin films is the same when compared in the same state, i.e., at the same n or ρ. There are two limiting cases for how density changes due to water sorption in a glassy polymer: one assumes the sample volume does not change upon sorption of water, while the other assumes the mixture to obey volume additivity. In the constant volume case, water sorption results in no dimensional changes in the sample, and the density is given by

$$\rho = \frac{\rho_{\text{polymer}}}{1 - w_{\text{water}}} \quad (8)$$

In the additive volume limit, the sample volume increases by the volume of water sorbed, and the density is given by

$$\rho = \left(\frac{w_{\text{water}}}{\rho_{\text{water}}} + \frac{1 - w_{\text{water}}}{\rho_{\text{polymer}}}\right)^{-1} \quad (9)$$

The results from application of the Lorentz−Lorenz equation for mixtures, eq 7, to the Matrimid and PSF data are shown by the points in Figures 15 and 16. The limiting cases of volume additivity and constant volume are shown for comparison; the experimental data lie between these limiting cases. The relative amount of water that occupies void volume or swells the polymer film is dependent on the nature of the system being studied. This fact helps explain why relative humidity has varying effects on film properties for different polymer systems.

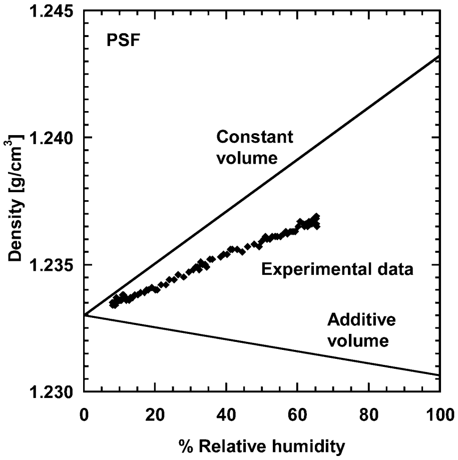

Figure 16. Relationship between density and relative humidity for PSF. Lines represent limiting cases for comparison.

Table 2. Comparison of Equilibrium Water Uptake (in wt %) at 100% RH

	Matrimid	PSF
sorption data (as cast)	4.5	1.1
"pat and dry" data (as cast)	4.1	0.8
sorption data (annealed)	2.9	0.8
"pat and dry" data (annealed)	2.9	0.6
ellipsometry data	2.7	0.7

Comparison of Water Vapor Sorption in Thin and Thick Films. The water vapor mass uptake in thin films can be calculated at any humidity by

$$\%\ \text{mass uptake(RH)} = 100 \times \left[\left(\frac{\rho_{\text{RH}}}{\rho_{\text{RH}=0\%}}\right)\left(\frac{l_{\text{RH}}}{l_{\text{RH}=0\%}}\right) - 1\right] \tag{10}$$

This calculation assumes the film does not expand laterally on the silicon substrate; evidence supporting this assumption will be given. Film thickness and density are nearly linear with RH for the polymers studied here, as seen in Figures 2, 4, 15, and 16. The linear dependence allows the mass uptake at 100% RH to be calculated by extrapolation to compare with results from sorption experiments on thick films. Using the density and film thickness changes extrapolated to 100% RH, the water uptake of thin Matrimid and PSF films was 2.7 and 0.7 wt %, respectively. These data deviate by 0.2 wt % or less from the annealed thick film equilibrium sorption results in Table 2, which compares the equilibrium water mass uptake at 100% RH as measured by the methods used in this study. This excellent agreement suggests water sorption behavior is similar in thick and thin films when they are compared in the same state, and it also supports the accuracy of the Lorentz−Lorenz equation predictions.

Effect of Humidity and Temperature on Thin Film Dimensions. The expansion of supported thin films is often assumed to occur only in the direction normal to the substrate, but this assumption is rarely tested. To test this assumption, the lateral extension of a thin film was measured under various humidity environments using an optical microscope. The distance between the edge of the film and a stationary reference point on the SiO_2 substrate was measured for films exposed to air having 0%, 50%, and 100% relative humidity. No change in lateral dimensions was measured within the $<2\ \mu$m resolution. If the film expanded isotropically, the lateral expansion would have been at least an order of magnitude greater than the experimental resolution. These measurements were also made at temperatures from 30 to 70 °C, which again resulted in no measurable change in the lateral dimensions.

Conclusions

The effect of relative humidity on thin film thickness and refractive index has been determined for two glassy polymers, Matrimid and PSF, by ellipsometry. Both polymers exhibited increasing refractive index and film thickness with increasing RH, with greater changes occurring in the Matrimid film. Further analysis showed that sorbed water expanded the polymer volume but considerably less than expected by volume additivity, i.e., to some extent, water molecules occupy existing free volume in the glassy polymer. Exposure to high activities of water altered the state of the glassy polymer thin films as seen by hysteresis in the ellipsometry measurements. After removal of sorbed water, the glassy polymer is left in a state of lower density than before exposure to water vapor. By direct measurement, specific refraction was determined to be 0.295 cm^3/g for Matrimid and 0.289 cm^3/g for PSF. Specific refraction has also been shown to be independent of density and temperature for the polymers studied, supporting the Lorentz−Lorenz equation. Water vapor sorption was measured in thick polymer films using gravimetric techniques, and the results were shown to match those of films 200 times thinner. The common assumption of uniaxial expansion of thin polymer films on a silicon substrate owing to changes in humidity or temperature was confirmed for these polymer substrate pairs by direct observation. The demonstrated effect of experimental conditions on film properties proves the importance of controlling these conditions when making sensitive measurements with ellipsometry or other methods.

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