Stresses Associated with Diffusion in Polyimide and Polyacrylics Films

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ABSTRACT: When a constrained polymeric thin film is immersed in a liquid medium, its state of stress changes because the diffusion of the liquid into the film causes it to swell. Polyimide and polyacrylics films are used in the laminated structures of inkjet printheads. Swelling behavior of the films in various ink component solutions are of great interest because they are closely related to the delamination problem. Swelling stress at constant strain was measured using an environmental tensile tester at both ambient and elevated temperatures. Two kinds of information were extracted. One is the extent of stress relaxation, which is the amount of stress decay between initial stress and equilibrium stress. The difference in the extent of stress relaxation could result in delamination if two different materials with different swelling characteristics are bonded together and exposed to a swelling agent. The other piece of information was the diffusion coefficients of the liquid agents into the polymer films. The magnitude of the diffusion coefficient indicates the rate of proceeding by the penetrant, i.e., the rate of swelling of the films. The results show that the extent of stress relaxation and diffusivity are different for two films. In addition, the diffusion in polyimide film is Fickian and the diffusion in polyacrylics film is pseudo-Fickian. The changes in mechanical properties after swelling also differ. Among all the ink solutions tested, one component was identified as the most influential and detrimental agent. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2661–2670, 2006

Key words: swelling; stress; diffusion; polyimide

INTRODUCTION

The multilayer assembly of an HP inkjet printhead contains two polymer films laminated one on another. Top layer, polyimide (Kapton® E) film is an orifice layer. The middle layer polyacrylics film is a negative photoresist. It functions as a barrier layer and adhesive layer. It is also a structure layer that creates channels and wells for ink storage and passage. These two layers of films are laminated onto an inorganic substrate (silicon wafer). For the photoresist coating to function reliably, it must maintain a high level of mechanical integrity during the lifetime of the printhead. One important factor is the ability to withstand the swelling of the ink. Swelling of polymer films may change their state of stress or mechanical properties.

Most researchers[1–8] study this type of diffusion in polymers based on the measurement of the mass uptake by a gravimetric method using a precision Cahn electrobalance (Cahn Instruments, a subsidiary of Thermo Electron Corporation, www.thermo.com). This paper presents a novel experimental technique to study the diffusivity by measuring the swelling stress of the polymers with time when they are immersed in liquid media. It is shown that the swelling stress is proportional to the mass uptake, and the diffusion coefficient can be retrieved if a proper model of mass transport is assumed. This swelling method has the advantage of not only obtaining the diffusivity but also monitoring the swelling stress in situ. Swelling of the polyimide and polyacrylics films are investigated at ambient and elevated temperatures. Diffusion mechanism and kinetics are discussed for these two films. Mechanical properties of the films after swelling are measured and compared for different permeating agents.

EXPERIMENTAL

Liquid media and films

Various liquid media were used in performing the swelling experiments. HP ink solution was provided by Hewlett–Packard and its chemical composition is proprietary and unknown to us. pH buffer solutions were purchased from Aldrich to simulate model inks. Solutions 3, 4, and 5, each contains 68.5% reverse osmosis water, 1.5% Tergitol (surfactant) and 30% 1,2-Hexanediol, 1,5-Pentanediol and Pyrrolidinone, respectively. Polyimide (Kapton type E) and polyacrylics (IJ series) films were supplied by Hewlett–Packard.

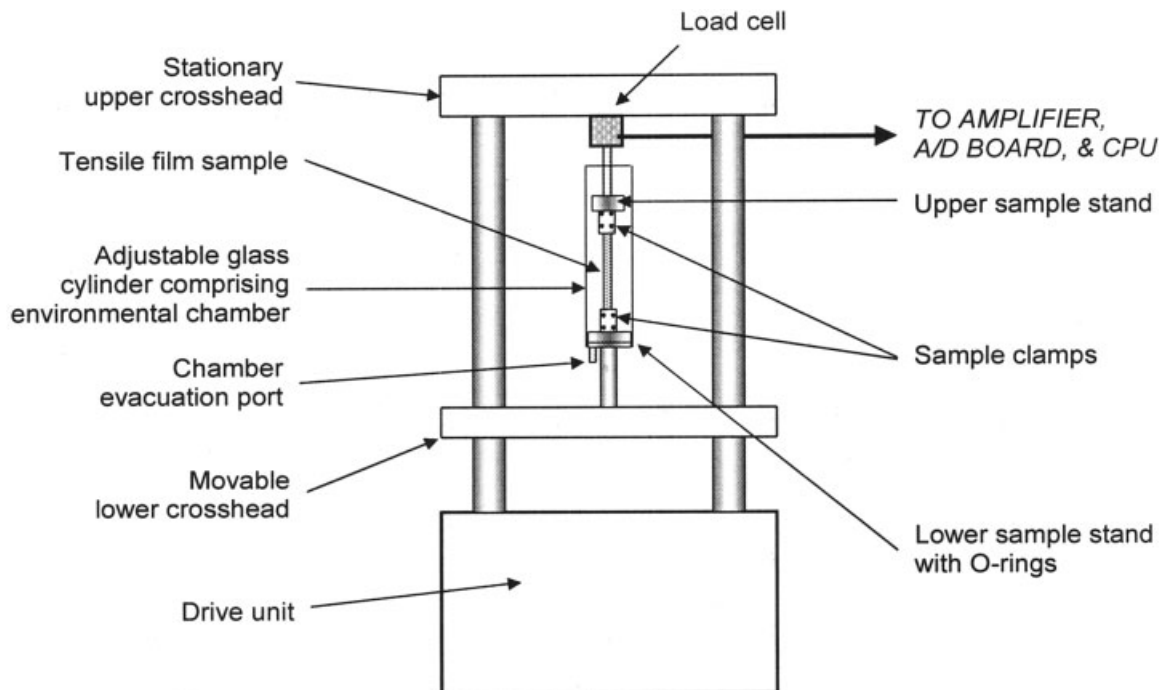*Correspondence to:* R. J. Farris (RJFarris@Polysci.umass.edu).

Figure 1 Schematic of the ETT.

Swelling stress

Stress relaxation was measured using an environmental tensile tester (ETT). A schematic of the ETT is shown in Figure 1. The ETT is a small one-dimensional tensile testing device (very similar to an Instron tensile tester) that has been modified to carry out tensile experiments on samples submerged in a liquid environment. An adjustable glass cylinder rests on the lower sample stand with rubber O-rings in place to prevent leakage and cylinder slippage. The glass cylinder serves to "cup" the tensile sample so that a liquid may be poured from the top to completely submerge the sample. The lower sample stand/grip is firmly attached to a movable crosshead, which moves down at controlled speeds and to controlled lengths to pull the sample under tension. The length of the glass cylinder allows the sample to be pulled in tension while still in complete submersion in the liquid environment. An evacuation port for the environmental chamber is also located in the lower sample stand, so that the liquid may be drained from the chamber without disturbing any other part of the set-up.

The experimental procedure for stress relaxation behavior is similar to that of measuring mechanical properties. The sheets of Kapton E films were cut into rectangular strips of about 5 mm in width and 65 mm in length and then glued with an instant adhesive to thick paper tabs that ensured a specimen length of exactly 50 mm. At least five samples were tested for each set of experiments. Each sample was tested in the ETT at a constant deformation of 2 mm or 4% strain.

This deformation was small enough so that the material demonstrated linear elastic behavior, critical in subsequent diffusion analyses. In ambient air, the samples were pulled in tension at a speed of 5 mm/min. to the appropriate deformation length of 2 mm and then were allowed to stress-relax for ~24 h. After a sufficiently long period, the samples reach an equilibrium or "plateau" stress, and it is in this relaxed stress-state that the sample experiences before exposure to the liquid environment. A liquid medium (~150 mL) was then introduced into the environmental chamber, completely submerging the sample. Swelling stress relaxation ensued and was recorded in the function of time for ~15 h.

Gravimetric measurement

Diffusion coefficients can also be retrieved from a gravimetric method, which monitors the mass uptake by the sample with the exposing time. A film sample was soaked in a liquid agent for certain length of time, and then taken out and tested the weight loss at a high temperature in a thermogravimetric analyzer (TGA). It was confirmed that all the penetrants diffused into the films will evaporate out once the temperature reaches 200°C at a heating rate of 10°C/min. So, the weight loss is proportional to mass uptake. By varying the soaking time and using a blank sample as calibration, a sorption curve (normalized mass uptake with respect to equilibrium mass uptake *versus* square root of time) can be constructed. Diffusion coefficients can then be calculated.
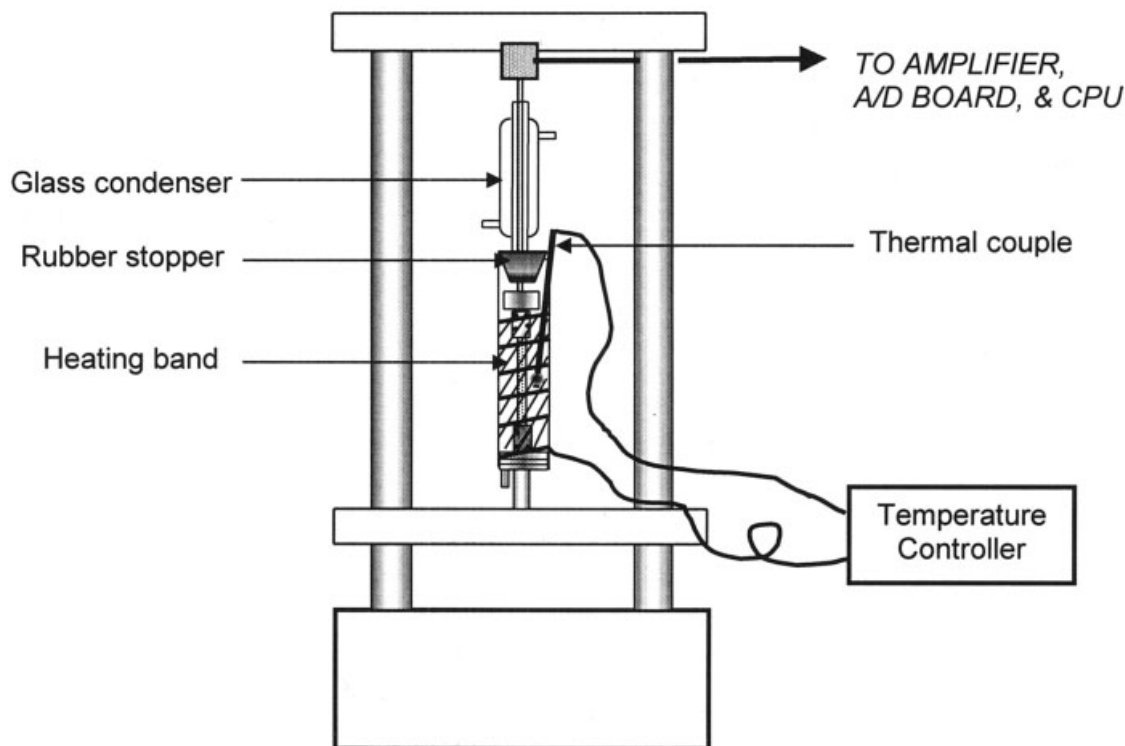
Figure 2 Schematic of the modified ETT.

Mechanical properties

Since the ETT is adapted from a tensile tester, it is capable of measuring the force-displacement and determining the tensile properties of the film samples. Tensile tests were run on the ETT setup at a cross head speed of 10 mm/min. immediately after the liquid agents were drained after the swelling stress relaxation experiments. As a comparison, the tensile properties of the as-received films were also measured on the ETT.

Elevated temperature experiment

Since the working temperature for an inkjet printhead ranges from room temperature to about 70°C, swelling and diffusion behavior at 70°C were studied in addition to the ambient temperature experiments. To do this, the ETT needed to be modified. A heating device and a temperature control mechanism were required. Also, precautions were taken to prevent the environmental liquid agent from evaporating and escaping from the environmental chamber. Since all of the solutions are mixtures with water being the major component, evaporation can be selective depending on the volatility of the components. Evaporation will condense the solution and change the concentration profile. A crude evaporation test was performed for HP ink vehicle. An amount of solution similar to that used in the actual experiment was placed in a glass cylinder

with a cross-sectional area similar to the cylindrical environmental chamber. Then the glass cylinder was put into a silicon oil bath without covering the opening while the solution temperature was kept at 70°C. Since the typical time required for swelling stress relaxation experiment is about 15 h at ambient temperature, the evaporation test was set to last 16 h. It was found that both weight loss and volume loss for the HP ink vehicle were about 17%. The outcome convinced us that a condenser was necessary to be assembled on top of the environmental chamber to minimize the evaporation. Figure 2 shows the schematic of the modified ETT. Here, a rubber heating band wrapped tightly around the glass cylinder acts as the heating device. A thermocouple is used to monitor the temperature. Both are connected to a temperature/heating control unit.

THEORY

One-dimensional hygrothermal elasticity

The one-dimensional stress and strain relationship for a linear and isotropic material can be described by the eq. (1) of one-dimensional hygrothermal elasticity.[9]

$$\sigma_{xx} = E[\varepsilon_{xx} - \alpha \Delta T(x,y,z,t) - \beta \Delta c(x,y,z,t)] \qquad (1)$$

where, σ, stress components; ε, strain components; E, Young's modulus; α, coefficient of thermal expansion

(cm/cm°C); β, swelling coefficient (cm/cm per unit wt % mass uptake); ΔT, temperature change; and Δc, concentration change.

If an average property throughout the volume is defined as follows:

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

where, V, sample volume; and Γ can be σ_{xx}, ε_{xx}, ΔT, or Δc.

Then, the integration of eq. (1) over volume yields:

$$\bar{\sigma}_{xx}(t) = E[\bar{\varepsilon}_{xx}(t) - \alpha\Delta\bar{T}(t) - \beta\Delta\bar{c}(t)] \qquad (3)$$

If the material is maintained at an isothermal condition ($\Delta T = 0$), eq. (3) can be reduced to

$$\bar{\sigma}_{xx}(t) = E[\bar{\varepsilon}_{xx}(t) - \beta\Delta\bar{c}(t)] \qquad (4)$$

In a stress relaxation measurement, the sample is kept at constant length ($\Delta\varepsilon = 0$), and the swelling stress can be obtained from eq. (4) as follows:

$$\Delta\bar{\sigma}_{xx}(t) = -\beta E\Delta\bar{c}(t) \qquad (5)$$

where, $\Delta\bar{\sigma}_{xx}(t) = \bar{\sigma}_{xx}(t) - \bar{\sigma}_{xx}(0)$

Note that the total mass uptake of the film caused by solvent penetration is given by,

$$M_t(t) = \int \Delta c(x,y,z,t)dV = V\Delta\bar{c} \qquad (6)$$

It can be seen from eqs. (5) and (6) that the normalized transient swelling stress with respect to the equilibrium swelling stress is in direct proportion to the normalized mass uptake with respect to the mass uptake at the equilibrium:[10]

$$\frac{M_t(t)}{M_\infty(\infty)} = \frac{\Delta\bar{c}(t)}{\Delta\bar{c}(\infty)} = \frac{\Delta\bar{\sigma}_{xx}(t)}{\Delta\bar{\sigma}_{xx}(\infty)} \qquad (7)$$

Therefore, the swelling information is linked to the mass uptake by the transport phenomenon. With an appropriate model for mass transport, the diffusion coefficients can be retrieved from the information of swelling stress.

Diffusion coefficients

Fickian diffusion was assumed in these experiments, since it has been proved that moisture absorption by polyimide films agrees fairly well with the Fick's law.[2,5,7,11,12] The Fickian equation for mass transfer through a film is as follows:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial y^2} \qquad (8)$$

Initial condition $c = c_i = 0 \quad -h/2 < y < h/2$

Boundary condition $c = c_\infty \quad y = \pm h/2$

where, c_i and c_∞, initial and equilibrium concentration, respectively; h, film thickness; y, the coordinate through thickness; and D, diffusion coefficient.

The solution is documented as:[13]

$$\frac{c - c_i}{c_\infty - c_i} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}$$

$$\times \cos\left[\frac{(2n+1)\pi y}{h}\right]\exp\left[\frac{-D(2n+1)^2\pi^2 t}{h^2}\right] \qquad (9)$$

Diffusion coefficients can be calculated using various techniques. In this work, three methods, initial slope method, half-time method, and moment analysis method, are adopted as follows.

Initial slope method[13]

$$D = \pi\left(\frac{\text{slope } h}{4}\right)^2 \qquad (10)$$

Half-time method[13]

$$D = \frac{0.0492\ h^2}{t_{1/2}} \qquad (11)$$

Moment analysis method[14]

$$D = \frac{h^2}{12\int_0^{\infty}\left(1 - \frac{M_t}{M_\infty}\right)dt} \qquad (12)$$

where, slope, the initial slope of the sorption curve (M_t/M_∞ versus $t^{1/2}$); h, film thickness; $t_{1/2}$, time when mass uptake by the film is half of the amount at equilibrium; M_t, mass uptake at time t; and M_∞, mass uptake at equilibrium.

RESULTS AND DISCUSSION

Swelling stress and diffusion coefficients

The swelling behaviors of Kapton E film and the IJ series film in various liquid agents are of great interest because it is closely related to the delamination problem. How much stress develops during swelling and how fast the ink solutions diffuse are among the important factors that determine the life of an inkjet printhead. A typical time profile of the swelling stress
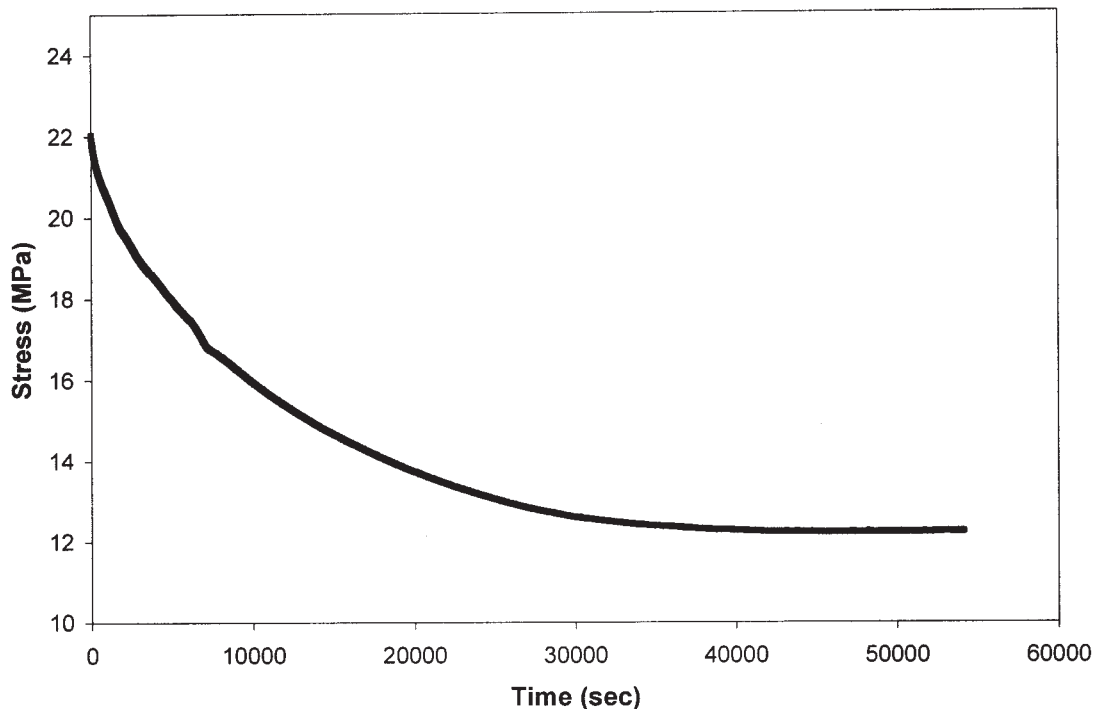
Figure 3 A typical graph of swelling stress in function of time obtained on the ETT.

recorded from an ETT experiment is shown in Figure 3. Note that the initial stress value is the same equilibrium or "plateau" stress of the material when stress relaxed in ambient air. Hence, it can be seen that the liquids promote further stress relaxation as they slowly diffuse into and swell the material. Based on eq. (7), a sorption curve can be constructed as shown in Figure 4. Hence, the diffusion coefficients from three methods can be calculated.

At ambient temperature

Two kinds of information can be extracted from the investigation of stress relaxation upon exposure to various liquid agents. One is the extent of stress relaxation, which is the amount of stress decay between initial stress and equilibrium stress. The difference in the extent of stress relaxation could result in delamination if two different materials with different swelling capabilities were bonded together and exposed to a swelling agent. The extent of relaxation in various liquid agents for Kapton E and IJ series films at room temperature are listed in the Tables I and II. For Kapton E films exposed to the various solutions, the extent of relaxation in HP ink solution is the smallest. The stress decays in other liquid agents are of the same magnitude. For IJ series films, the stress relaxes the least in HP ink solution and the most in solution 3. The extents of relaxation are similar in other liquid agents. The largest swelling stress relaxation appears in the case of IJ series film in solution 3 (1,2-Hexanediol/

water). IJ series film is completely relaxed and free of stress in solution 3. In fact, the samples were swelled and expanded in width and thickness, while the gauge length was held constant; as a consequence, the samples buckled between the sample grips.

Overall, IJ series films have a little larger stress relaxation than Kapton E films in all swelling agents except in pH 10 buffer and reverse osmosis (R/O) water. This is most likely because IJ series film is far less stiff than Kapton E film according to their Young's moduli (Kapton E ~5 GPa, IJ series ~1.5 GPa). Another possible reason is the solubility difference of liquid agents in both films. The liquid agents are more readily dissolved in IJ series film, and therefore IJ film swells more. There are some differences between the relaxation of Kapton E and IJ series films in various liquid agents. Those swelling-induced stress mismatches could cause problems, especially in a geometrically constrained structure. Moreover, a printhead assembly is a three-layer laminated structure with a stiff substrate that has zero swelling capability. The stress mismatch between the hard substrate and the soft films upon swelling is another factor causing possible debonding. If the stress relaxation in R/O water is considered to be the standard, it seems that certain substance(s) in the HP ink solution suppress the stress relaxation. Such substance(s) are definitely in none of the other solutions because they all promote stress relaxation. The extent of relaxation for Kapton E and IJ series films is almost the same in pH buffer solutions and R/O water.
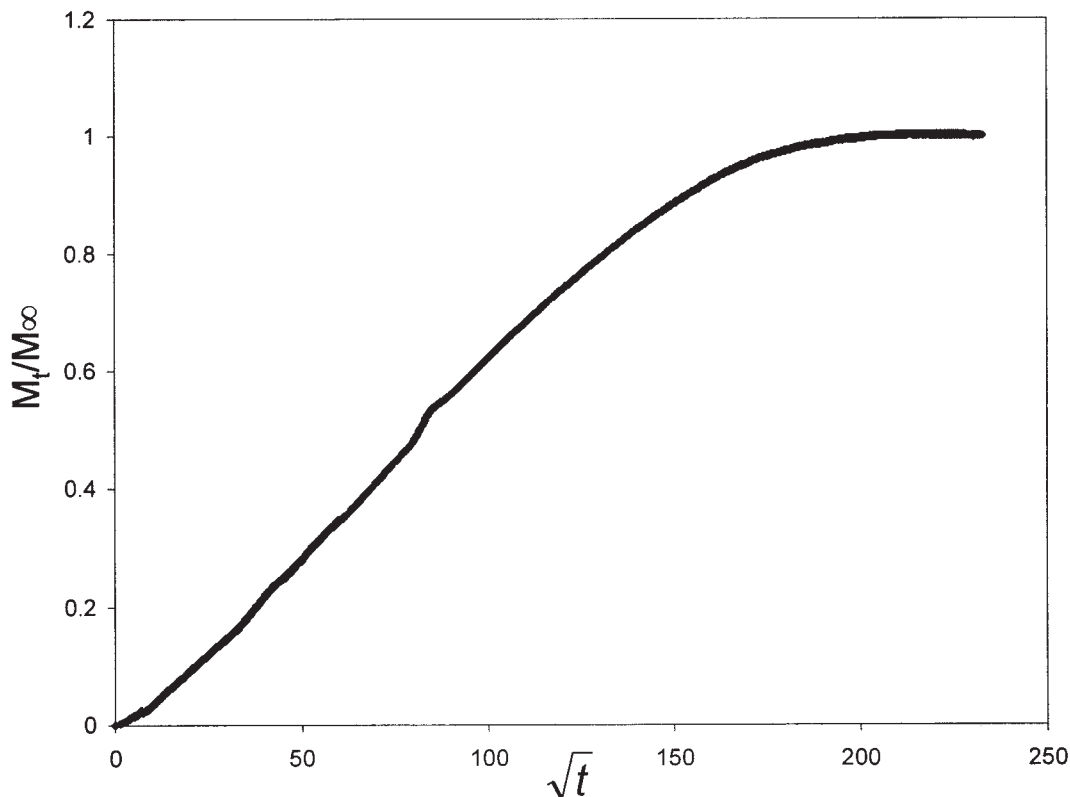
Figure 4 A typical sorption curve.

Another piece of information is the diffusion coefficient of the liquid agents into the polymer films. The magnitude of the diffusion coefficient indicates the rate of proceeding by the penetrants. Diffusion coefficients can be calculated from the three aforementioned methods by manipulating the stress relaxation data. Diffusion coefficients of various liquid agents in Kapton E and IJ series films are listed in the Tables III and IV.

For Kapton E films, diffusion coefficients are on the order of 10^{-10} cm^2/s. They all have similar values regardless of different liquid agents. Moreover, three

methods yield consistent results indicating the diffusions in Kapton E films are fairly Fickian. For IJ series films, diffusion coefficients are on the order of 10^{-11} cm^2/s. They all have similar values except for Solution 3. Diffusion coefficients of Solution 3 are almost twice the magnitude of other liquid agents, and Solution 3 also produces the largest stress relaxation as mentioned before. There might exist some favorable physical or chemical interaction between Solution 3 and IJ series films that enhance the diffusion. Three methods show nonconsistency, and half-time method gives considerably large results. This is due to the non-

TABLE I
Extent of Relaxation (MPa) in Various Liquid Agents for Kapton® E Film at Ambient Temperature

	Kapton® E film		
	Initial stress	Equilibrium stress	Stress difference
HP ink solution	23.6	16.2	7.4 ± 0.9
pH 4 buffer	23.5	13.3	10.2 ± 1.2
pH 7 buffer	24.8	14.0	10.8 ± 0.6
pH 10 buffer	23.7	13.5	10.2 ± 0.8
Solution 3	22.2	11.2	11.0 ± 0.5
Solution 4	22.9	12.6	10.3 ± 1.2
Solution 5	22.6	11.8	10.8 ± 0.2
R/O water	22.0	12.1	9.9 ± 0.3

TABLE II
Extent of Relaxation (MPa) in Various Liquid Agents for IJ Series Film at Ambient Temperature

	IJ series film		
	Initial stress	Equilibrium stress	Stress difference
HP ink solution	9.9	1.6	8.3 ± 1.2
pH 4 buffer	12.1	1.0	11.1 ± 0.6
pH 7 buffer	12.5	1.4	11.1 ± 0.8
pH 10 buffer	11.9	1.7	10.2 ± 0.5
Solution 3	13.0	0	13.0 ± 0.9
Solution 4	13.4	1.1	12.3 ± 1.1
Solution 5	12.8	1.5	11.3 ± 0.8
R/O water	11.1	1.5	9.6 ± 0.2

TABLE III
Diffusion Coefficients (10^{-10} cm²/s) of Various Liquid
Agents in Kapton® E Film at Room Temperature

	Kapton® E film		
	Initial slope	Half time	Moment analysis
HP ink solution	3.00 ± 0.40	2.67 ± 0.42	2.49 ± 0.22
pH 4 buffer	3.13 ± 0.63	2.81 ± 0.51	2.66 ± 0.35
pH 7 buffer	3.13 ± 0.13	2.71 ± 0.34	2.61 ± 0.25
pH 10 buffer	3.25 ± 0.37	2.68 ± 0.19	2.68 ± 0.32
Solution 3	2.97 ± 0.27	2.51 ± 0.35	2.55 ± 0.23
Solution 4	3.09 ± 0.27	2.83 ± 0.19	2.69 ± 0.21
Solution 5	2.91 ± 0.37	2.94 ± 0.44	2.87 ± 0.39
R/O water	3.17 ± 0.09	2.58 ± 0.25	2.49 ± 0.20

Fickian, anomalous nature of the diffusion in IJ series films. Non-Fickian behavior will be discussed in detail in a later section of this paper.

Generally, diffusion coefficients in IJ series films are almost one order of magnitude smaller than in Kapton E films. In other words, diffusion into Kapton E films is faster than into IJ series films. This might have a profound influence in terms of stress buildup during swelling. For example, although the final stress decays for Kapton E and IJ series films differ by only 1 MPa in HP ink solution, the stress mismatch could be much larger during the swelling process before equilibrium is reached because the two materials have different swelling rates and one is covering the other.

Apparently, diffusion coefficients are not pH-dependent for both films. Furthermore, similar diffusivities of various liquid agents in both films suggests that there is little difference in diffusion rates between water and other components in the solutions, except 1,2-Hexanediol.

At elevated temperature

The extent of stress relaxation for Kapton E film at 70°C in various liquid agents is shown in Table V.

TABLE IV
Diffusion Coefficients (10^{-11} cm²/s) of Various Liquid
Agents in IJ Series Film at Room Temperature

	IJ series film		
	Initial slope	Half time	Moment analysis
HP ink solution	5.34 ± 0.70	16.6 ± 4.6	8.48 ± 0.47
pH 4 buffer	5.88 ± 0.91	26.9 ± 3.5	9.67 ± 1.42
pH 7 buffer	5.76 ± 0.97	25.4 ± 1.7	9.11 ± 1.07
pH 10 buffer	5.93 ± 0.57	23.4 ± 2.5	9.28 ± 1.03
Solution 3	9.43 ± 1.12	47.4 ± 5.8	17.4 ± 3.8
Solution 4	6.80 ± 0.69	26.6 ± 1.3	10.4 ± 0.8
Solution 5	5.52 ± 0.68	22.0 ± 4.2	8.74 ± 0.78
R/O water	5.99 ± 0.30	18.7 ± 1.3	9.03 ± 0.44

TABLE V
Extent of Stress Relaxation (MPa) for Kapton® E Film in
Various Liquid Agents at 70°C

	Kapton® E film		
	Initial stress	Equilibrium stress	Stress difference
HP ink solution	19.0	9.6	9.4 ± 0.7
Solution 3	18.9	8.5	10.4 ± 0.3
Solution 4	18.3	8.8	9.5 ± 0.7
Solution 5	18.9	9.4	9.5 ± 0.6
R/O water	18.4	8.3	10.1 ± 0.4

Stress decays are of similar magnitude in all liquid agents. Compared to the results from the room temperature experiments, the stress relaxations are comparable, except that stress relaxation in HP ink solution rises to the same level as other liquid agents. It appears that high temperature promotes the stress relaxation in HP ink solution. In addition, the time needed for reaching the equilibrium final stress is much shorter at 70°C. It takes only 3 h instead of 15 h at ambient temperature.

Diffusion coefficients of various liquid agents in Kapton E film at 70°C are shown in Table VI. Again, they are of the same magnitude regardless of solution compositions. Compared to the results from the room temperature experiments, diffusion coefficients at 70°C are 20~30 times larger. Diffusion and swelling are much faster at 70°C, which explained the short time to reach equilibrium stress. It was noticed that the three methods no longer yielded similar results as at room temperature. Again, it may be due to the increasing tendency towards non-Fickian diffusion as temperature is raised. Temperature seems to change the kinetics of diffusion.

Gravimetric measurement that leads to diffusion coefficient was performed to confirm the reliability of the ETT results. Diffusion coefficients were obtained by manipulating the weight loss data from TGA (shown in Table VII) for ambient temperature and 70°C. The results agree fairly well with the ones from the ETT. Therefore, the ETT is a trustworthy method

TABLE VI
Diffusion Coefficients (10^{-9} cm²/s) of Various Liquid
Agents in Kapton® E Film at 70°C

	Kapton® E film		
	Initial slope	Half time	Moment analysis
HP ink solution	5.88 ± 0.59	9.04 ± 0.84	5.15 ± 0.88
Solution 3	5.57 ± 0.21	7.61 ± 1.23	3.88 ± 0.40
Solution 4	5.35 ± 0.23	6.83 ± 0.88	3.86 ± 0.51
Solution 5	5.44 ± 0.16	7.73 ± 1.04	3.97 ± 0.53
R/O water	5.29 ± 0.41	7.74 ± 0.56	3.99 ± 0.29

TABLE VII
Diffusion Coefficient (cm²/s) Obtained from Gravimetric Measurement

	Kapton® E film in HP ink solution	
	Ambient	70 (°C)
Initial slope	2.14×10^{-10}	5.06×10^{-9}
Half time	1.72×10^{-10}	8.75×10^{-9}
Moment analysis	2.51×10^{-10}	4.24×10^{-9}

to obtain the diffusion coefficients. It is also a better method in a sense that the ETT can monitor the swelling stress in situ.

Arrhenius analysis

Assuming the diffusion coefficient obeys simple Arrhenius relation, i.e., $D = A \exp(-E/RT)$, then $\ln D = -E/RT + \ln A$, where D is diffusion coefficient, E is activation energy, R is universal gas constant, T is absolute temperature (Kelvin), and A is certain constant. If we plot $\ln D$ versus $1/T$ using data at two temperatures (ambient and 70°C), the apparent activation energies obtained from the slopes are shown in Table VIII. They are all comparable, indicating that the energy barriers are similar in magnitude.

Non-Fickian behavior

There is abnormal behavior associated with film thickness in the ETT measurement. Namely, diffusion coefficients change with film thickness (Table IX). Two kinds of Kapton E films (55 and 28 μm) and two kinds of IJ series films (28 and 14μm) with different thickness were tested on the ETT under the same conditions. For Kapton E films, the diffusion coefficients of thin film are almost one half of those of thick film. Interestingly, the thin films have one half of the thickness as the thick films. But this linear relationship between thickness and diffusion coefficients does not hold for the IJ series films. The thin IJ film exhibits much smaller diffusion coefficients.

The time dependent swelling of a polymer can be generally described by the following eq. (13). It is called the power law model, with n being the diffusional exponent. In this equation M_t/M_∞ represents

TABLE VIII
Activation Energy (KJ/mol) for Diffusion

	Activation energy
HP ink	8.46
Solution 3	8.07
Solution 4	7.73
Solution 5	7.86
R/O water	8.00

TABLE IX
Diffusion Coefficients (10^{-10} cm²/s) for Kapton® E and IJ Series Films of Different Thickness

	Kapton® E		IJ series	
	55 (μm)	28 (μm)	28 (μm)	14 (μm)
HP ink				
Initial slope	2.81	1.45	0.562	0.285
Half time	2.78	1.66	2.557	0.725
Moment	3.13	1.03	0.879	0.340
pH 4 buffer				
Initial slope	2.95	1.42	0.588	0.148
Half time	2.77	1.64	2.687	0.527
Moment	2.81	1.01	0.967	0.251
pH 7 buffer				
Initial slope	3.03	1.44	0.576	0.143
Half time	2.68	2.69	2.537	0.784
Moment	2.60	1.38	0.911	0.252
pH 10 buffer				
Initial slope	3.25	1.37	0.593	0.216
Half time	2.68	1.89	2.341	1.35
Moment	2.71	1.13	0.928	0.451

the fractional uptake of solvent (or release of a solute) normalized with respect to the equilibrium conditions. The variables k and n are constants which can be related to diffusion coefficients and the specific transport mechanism. This equation is used to account for the coupled effects of Fickian diffusion and viscoelastic relaxation in polymer systems.

$$\frac{M_t}{M_\infty} = kt^n \tag{13}$$

$$
\begin{aligned}
&n > 1 \quad \text{supercase II} \\
&n = 1 \quad \text{case II} \\
&1/2 < n < 1 \quad \text{anomalous} \\
&n = 1/2 \quad \text{classical/Fickian} \\
&n < 1/2 \quad \text{pseudo-Fickian}
\end{aligned}
$$

where, M_t, mass uptake at time t; M_∞, equilibrium mass uptake; t, time; and k, constant.

Fickian diffusion is assumed throughout the diffusion calculation for mathematical simplicity. If the diffusion is truly Fickian, results from the three methods should be the same. However, diffusion in polymers is often not Fickian. In our case, for Kapton E films, this assumption is quite adequate because there is an obvious linear portion in the sorption curve (M_t/M_∞ versus $t^{1/2}$). But for IJ series films, such linear correlation could hardly be found. If we take the natural logarithm of both sides of eq. (13), then plot $\ln M_t/M_\infty$ versus $\ln t$, the slope should correspond to the diffusional exponent (n).

$$\ln \frac{M_t}{M_\infty} = \ln k + n \ln t \tag{14}$$

The slope for the curve of Kapton E films is 0.55, which is close to ½, the characteristic n for Fickian diffusion. But the plot for IJ series films shows a slope of 0.28, which indicates the diffusion is pseudo-Fickian type. Therefore, diffusion in IJ series films deviates much more from Fickian behavior than Kapton E films. Because of the non-Fickian behavior, diffusion coefficients calculated from the half-time method for IJ series films shows a discrepancy compared to the other two methods. Also because of that, diffusion coefficients change with film thickness. For the origin of the non-Fickian behavior, two explanations are proposed.

The first is the inhomogeneity of the films. It is not uncommon that the skin and the center of a film are different. They could differ in morphology and composition, etc. Those differences could manifest themselves in the material properties, such as resistance to solvent diffusion. The same solvent may have a smaller diffusion coefficient in the skin and a bigger one in the center, or vice versa. The measured apparent diffusion coefficient is some sort of combination of those two. Individually, either diffusion process, in the skin or in the center, could be Fickian, but the combination might not be. The skin takes a larger proportion of the entire material in a thin film than in a thick film. That explains why diffusion into thin film severely deviates from Fickian behavior. It also explains why diffusion coefficients depend on film thickness.

The second is the morphological difference between thick films and thin films. Polymer chains in thin films are aligned in a much ordered and oriented fashion. Thin films have higher surface-induced in-plane orientation. During manufacturing, microvoids are inevitable and more likely to be trapped in thick films. Although thick films have higher crystallinity, crystal orientation is relatively poor. All these factors contribute to the larger value of diffusivity in thick films.

Mechanical properties

Mechanical properties of Kapton E and IJ series films were investigated before and after the swelling experiments. For Kapton E film, the samples did not break

TABLE X
Mechanical Properties of Kapton® E Films

	Modulus (GPa)
As received	4.94
HP ink solution	4.78
R/O water	4.65
Solution 3	4.66
Solution 4	4.87
Solution 5	4.62

TABLE XI
Mechanical Properties of IJ Series Films

	Modulus (GPa)	Breaking strength (MPa)	Breaking elongation (%)
As received	1.63	34.8	8.72
HP ink solution	1.02	23.0	4.56
R/O water	1.22	26.4	5.00
Solution 3	0.49	10.3	11.7
Solution 4	1.27	26.3	3.67
Solution 5	1.14	26.9	3.75

within the limit of the load cell; therefore, only Young's modulus is reported while breaking strength and elongation are not available (Table X). For IJ series film, Young's modulus, breaking strength, and breaking elongation are shown in Table XI.

Mechanical properties of Kapton E films do not change much after swelling compared to the original material. One possible reason is that Kapton E is a high T_g material, and a small amount of liquid pickup (below 1 wt %) does not change its T_g very much. Kapton E is still in the glassy state despite the plasticization by solvent penetration. Unlike Kapton E films, the mechanical properties of IJ series films after swelling decrease. Especially after exposure to solution 3, Young's modulus and breaking strength of IJ series films drops markedly. Accordingly, breaking elongation increases. Recalling that the largest stress decay and fastest diffusion rate occurred in solution 3, this result is not surprising. The phenomena seem to be related. It may have something to do with the chemical nature of the solution 3. Perhaps the solubility parameters play an important role. IJ series films become much softer and tougher after swelling in solution 3. This is likely due to the suppression of T_g. The solution that is absorbed acts effectively as a plasticizing agent and therefore lowers the T_g of the IJ series films. In conclusion, solution 3, i.e., 1,2-Hexanediol has the most detrimental effect on IJ series films.

CONCLUSIONS

The swelling experiments are able to characterize the swelling stress and mass transport behaviors of polyimide and polyacrylics films exposed to liquid media. This technique is simple and easy to carry out, and the results are reliable and agree with the gravimetric measurement. Swelling stress relaxation in Kapton and polyacrylics films are different, which will create stress mismatch in a laminated structure as in an inkjet printhead. Diffusion in Kapton films is faster than in polyacrylics films as indicated by the calculated diffusion coefficients. Diffusion in Kapton films is Fickian and in polyacrylics films pseudo-Fickian, which indicates different diffusion mechanisms. It is found that

Solution 3 contains a chemical that has the most deteriorating effect on the mechanical properties of the polyacrylics film.

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