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Calculation of Diffusion Constants in Thin Polymer Films using DVS

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This application note describes the measurement of moisture diffusion coefficients in polymer thin films by measuring adsorption isotherms on the thin films in a DVS instrument.

Introduction

Moisture diffusion in thin polymer films is of interest to a variety of different industrial sectors including packaging materials and membrane technologies.

Method

The method used to calculate the diffusion constants for the thin films utilises diffusion equations first employed by Crank and Park [1]. A thin film sample is suspended in the DVS and the sorption kinetics for a series of steps in humidity are recorded in the usual manner. For a single step in humidity, and a double-sided thin film of thickness d, the initial kinetics of sorption into the bulk may be described by the following equation,

$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}} \qquad (1)$$

where M_t = amount adsorbed at time t,

M_∞ = amount adsorbed at thermodynamic equilibrium,

D = diffusion constant.

This equation is generally valid for values of M_t/M_∞ <0.4, where a plot of M_t/M_∞ against $t^{1/2}/d$

should be linear. The diffusion constant D may then be calculated from the slope of this line.

In the present study, the diffusion of moisture into a 15mg sample of polyimide film 7.5 microns thick was studied in a DVS instrument. The sample was exposed to increasing steps in humidity from 0% RH to the desired humidity and back down to 0% RH, such that both sorption and desorption steps were measured for each discrete humidity. The data acquisition interval was set to 2 seconds as the kinetics were expected to be fast.

Results

Figure 1 shows the sorption and desorption kinetics for the polymer film for steps from 0% RH to 20% RH, 40% RH and 60% RH. The red line shows the change in mass referenced to the mass after drying, and the blue line shows the humidity profile.
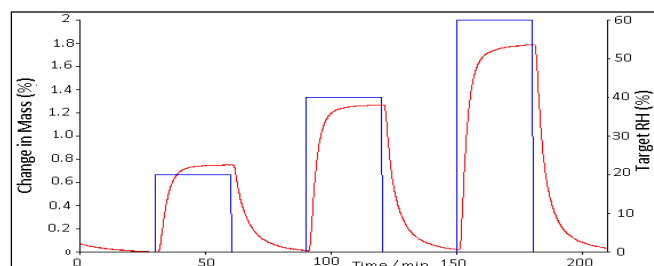

Figure 1. Sorption and Desorption kinetics on a 7.5μm polyimide film.

For each discrete step in humidity M_t/M_∞ is plotted against $t^{1/2}/d$, as shown in Figure 2, and a least squares line of best fit is fitted to the initial slope of this plot for $M_t/M_\infty < 0.4$, shown by the blue line. From this plot, values of the diffusion coefficient are calculated, and shown in Table 1 below.

Table 1. Diffusion coefficients from initial slopes.

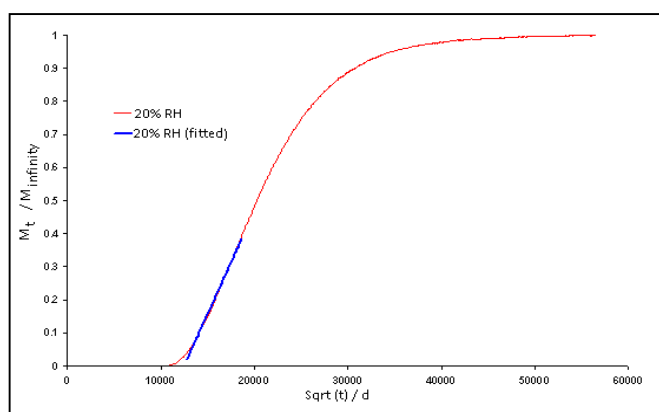| Previous RH (%)	Target RH (%)	Diffusion Coeff. (cm²/s)	R-squared (%)
0.0	20.0	7.63E-10	99.55
20.0	0.0	4.38E-10	99.58
0.0	40.0	9.04E-10	99.52
40.0	0.0	6.05E-10	99.59
0.0	60.0	9.30E-10	99.54
60.0	0.0	6.55E-10	99.57

Figure 2. Diffusion plot for 0% RH to 20% RH step in humidity on a 7.5μm polyimide film.

The tabulated data shows that for steps from 0%RH to the specified RH, the diffusion constant increases slightly with increasing partial vapour pressures of water. However this increase is relatively small and it would appear that the diffusion constant is not strongly dependent upon the concentration of water vapour present.

Conclusion

The above DVS methodology may be used to rapidly assess the diffusion of moisture in thin polymer films such as packaging and membrane materials. The analysis of the experimental data for these experiments may be performed using the Advanced Data Analysis add-in suite, facilitating rapid and reliable evaluation of experimental data.

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References

[1]Crank J. and G.S. Park. *Diffusion in Polymers*, Academic Press New York (1968).