

Humidity Sensitivity of the Media: A Study of Water Vapor Diffusion in Polymer Film

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Abstract

The transport of water vapor molecules through the imaging media exposed to different humidity conditions is formulated using diffusion as well as sorption model. The "effective diffusivity" (D_{eff}), which includes diffusivity (D) and sorption constant (R) is the key parameter for controlling the transport rate of the diffusants. A microwave frequency resonant apparatus capable of measuring the amount of moisture in a sample with high resolution and fast response time was employed in this study. This technique provides a non-invasive means of monitoring water content in a coated polymeric film as a function of time. A good correlation between model calculations and experimental data is observed for several samples. In all cases, the effective diffusivities of water obtained from the histogram matching technique are lower than the literature values. These results indicate a comparatively strong interaction between the water molecules and the polymer matrix through the sorption mechanism.

Introduction

Water vapor molecules transport through a thin film of coating is a subject of great interest in many areas, such as photographic films, adhesives, sealants, and electronics. Water is capable of forming hydrogen bonds which makes its interaction with polymeric molecules, and consequently its diffusion and sorption phenomena different from other diffusants. A major concern for imaging products is the effect of humidity on product performance under various environmental conditions. Since polymeric materials tend to be "brittle" when dry and "elastic" in the wet state, the functional properties of the coated films which are also related to the adsorption and desorption of the water molecules within polymer matrix.

Among the many techniques that have been used for measuring water content in a thin film coating, microwave interferometry and infrared absorption are the choices for their sensitivity and fast response time. Moreover, they can be used as on-line detectors due to their non-invasive nature. In this study, we employed the microwave frequency resonate technique to monitor the free and bound water

present in thin polymeric films coated on polyester substrates.

Water molecules, either in a free or bound state are highly polar and have a dielectric constant of approximately 78. The dielectric constants of typical coating substrates, such as paper or plastic materials are much lower and range from 2.3 to 3.5. Due to this large difference the "signal to noise" ratio for the dielectric constant change due to moisture variation in coatings is very high. The energy storage value of a capacitor is critically affected by the dielectric constant and a cavity resonator can be used to measure this value directly, which is a measure of the change in water content of a substrate over a period of time.

So far, the attention has been concentrated on the impact of humidity on the image performance, but there is very little understanding of how water vapor molecules transport in the media from a mechanistic point of view. In this paper, we have used a well known theoretical model to delineate the diffusion and sorption processes of water vapor through a thin film coating. Based on this model, the effective diffusivities of different samples were obtained by matching theoretical curves with experimental data.

Diffusion Model

A diffusion model is used to describe the penetration of water vapor molecules in a polymer film.¹ The fundamental differential equation of diffusion in an isotropic medium can be represented by Fick's law. In our case we consider one-dimensional diffusion in a medium bounded by two parallel planes, e.g. the planes at $x = 0$ and $x = l$. These will apply in practice to diffusion into a thin plane sheet that effectively all diffusing molecules enter through the plane surface and a negligible amount through edges. Here, we set aside the issue of the multi layer structure of coatings because the results from this model can be extended to a more complicated system. The final solution can be represented by

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{1/2} \left(\frac{1}{\pi^{1/2}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{2(Dt)^{1/2}} \right) \quad (1)$$

Where D is the diffusion coefficient, t the time, l the thickness of coatings, M_t the total amount of vapor adsorbed

by the film at time t , M_∞ the equilibrium sorption attained theoretically after infinite time, and $ierfc$ the integral of the error function. The equation (1) is formulated in such a way that a simple experiment can be performed by measuring the amount of water adsorbed in a polymer sheet as a function of time, then the diffusivity can be computed with known physical thickness of the sample. On the other hand, if we know the diffusivity we should be able to predict the rate of water diffusion.

Experimental

A microwave frequency resonant cavity detector has been of invaluable service in measuring small changes in coated polyester photographic and commercial imaging media. Resolution to $\pm 10 \text{ mg/m}^2$ is possible with ambient temperature control to 0.5°C . The response speed of this technique is limited only by the ability of the hardware used to measure the transducer operating frequency and rates of 0.05 seconds per update are easily accomplished. Rates greatly in excess of this are possible but for work on moisture equilibration in coated materials are not required.

The oscillator used in our experiments has an active measurement area of 16 cm^2 (approximately 4 cm on edge). The sample is placed coated side of substrate up on the flat platten of the test bed which is essentially a parallel plate capacitor, with the edges of the plates brought to the surface of the cavity containing the capacitor. The substrate has a fixed mass and a fixed value of dielectric material. The substrate may contain absorbed moisture as do the coatings on it. As the sample system adjusts its moisture load to reach equilibrium with the air space above it, the quantity of water in close proximity to the capacitor plates changes. This is the only variable which changes and impacts the capacitor value. For a simple parallel plate capacitor:

$$C = \kappa \epsilon A/d \quad (2)$$

where C = Capacitance in farads
 ϵ = Permittivity constant
 κ = Dielectric constant (air = 1.00054, water = 78)
 A = Area of each plate
 d = Distance between the plate surfaces

In our apparatus all mechanical parameters are held constant, so the only variable is the quantity of dielectric material in the system. The capacitor is oriented in a parallel plate configuration component of a high frequency oscillator. The resonant frequency of the oscillator decreases in direct linear proportion to the change in dielectric value of the capacitor.

Results and Discussion

Generally imaging media are stored and used in a wide range of environmental conditions. It has been recognized that there is a strong correlation between imaging quality and ambient humidity for photographic films as well as non-photographic media. Therefore, one major requirement for an optimum performance of the media is to contain the rate and

amount of moisture uptake or loss under various surroundings. The measurement and analysis of transport process of water vapor molecules in polymer films have proven to be valuable in the understanding of the humidity sensitivity of these systems.

The physics of diffusion in polymers is exceedingly complicated. Important variables include the chemical nature of polymer, its molecular weight distribution, the degree of cross-linking, and the nature of plasticizer used. The properties of the diffusing solute or penetrant are evidently relevant not only to the molecular weight but also to the chemical properties. The greatest importance is perhaps the interaction of the solute and polymer molecules. Since polyvinyl alcohol cross linked by boric acid was used in this study, we know that a strong interaction between water vapor and coated polymer must exist due to hydrophilic nature of the materials. In order to accommodate this effect, a modified diffusion model with sorption phenomenon is needed.

Diffusion Accompanied by Sorption Model

In most cases, the transport rates through films are governed both by the basic rate constant for diffusion, the diffusion coefficient, and by the extent of equilibrium sorption which is an equilibrium thermodynamic quantity. If the adsorption by which the immobilized water is formed proceeds very rapidly compared with the diffusion process, local equilibrium can be assumed to exist between the free and immobilized components of the diffusing substance. Usually, a suitable type of adsorption isotherm is used for this kind of application. Here, we adopt the simplest case analogous to Henry's law, the concentration of immobilized substance is directly proportional to the concentration of substance free to diffuse. The sorption constant R which relates to the interactions between solute molecules and polymer matrix was chosen in our case. When substituting into the diffusion model, it is shown to be the usual form of equation for diffusion governed by an effective diffusion coefficient, D_{eff} , which is given by $D/(R + 1)$. Clearly the effect of the adsorption is to slow down the diffusion process.

Two samples of 50 micron thickness of PVA coatings were used in this study. Sample 1 was stored in the oven at 160°F and 20% relative humidity (RH) and sample 2 at 100°F and 80% RH for 6 hours of equilibration. Both samples were taken out from the oven and put on the sample holder kept at 72°F and 45% RH monitored by microwave frequency resonant cavity detector continuously. The data are reported as the fraction mass uptake or loss (with respect to the equilibrium value) as a function of time.

Figure 1 shows the moisture uptake curve for sample 1 and Figure 2 shows the loss of moisture for sample 2. It can be seen that both theoretical curves correlates well with the experimental data. Based on psychrometric chart, the moisture contents in the ambient at $160^\circ \text{F} / 20\% \text{RH}$, $100^\circ \text{F} / 80\% \text{RH}$, $72^\circ \text{F} / 45\% \text{RH}$ are 0.045, 0.035, 0.0075 pound water per pound dry air, respectively. Evidently, the moisture retention is more or less dependent on the RH instead of absolute water content in the air. In the literature, the diffusivity is frequently calculated from the initial slope

or the half-life.² The drawback of these kinds of approximation is that errors can be very high due to the uncertainty of initial and final data points. The diffusivity obtained from equation (1) by the history matching method is 2×10^{-10} cm²/sec. This indicates that a strong sorption is involved in the diffusion process because the diffusivity reported in the literature is orders of magnitude higher than the values in this study. The important observation to make here is that as long as the diffusion is Fickian, an effective diffusivity can be used to simulate the diffusion accompanied by sorption process. It is shown that this holds for moisture uptake as well as loss condition.

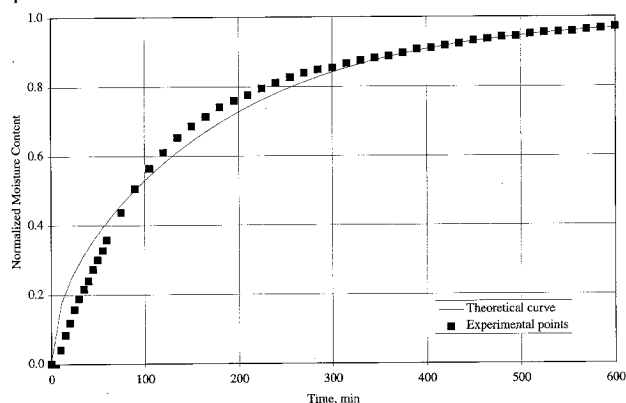


Figure 1. Moisture Uptake as a Function of Time.

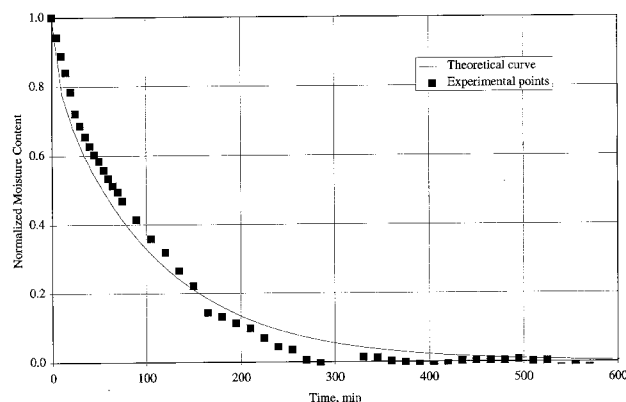


Figure 2. Moisture Loss as a Function of Time.

As indicated, the water molecule is relatively small and in the liquid state it is strongly associated through hydrogen bonding. The combination of these features distinguishes it from the majority of organic penetrants. Strong localized interactions may develop between the water molecule and suitable polar groups of the polymer; while in relatively non-polar systems, clustering or association of the sorbed water is possible. In addition, the polymer medium has a considerable effect on diffusion. Basically, diffusion is controlled by the ease of forming enough free space to enable the unit diffusion step to occur. In the free volume theory of diffusion, this is discussed in terms of the probability of finding enough local free volume which form the activation energy viewpoint, the process is discussed in terms of the energy needed to create the free space. In both theories the flexibility of the polymer chain and the cohesive energy of the polymer are important. Both decreasing chain flexibility and increasing cohesive energy lead to the regular decrease in diffusivity D . Therefore, polymer systems with high cross linked densities will decrease the chain flexibility and this usually been found to increase the activation energy and to decrease the diffusion coefficient. In general, the more polar groups present in the polymer matrix such as PVA, the higher will be its sorptive affinity towards water. However, the accessibility of these groups, the degree of crystallinity of the matrix and the relative strengths of water-water and water-polymer bonds are important factors in deciding the total regain and tend to rule out any simple correlation between the number of polar groups and the solubility.

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References

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