

The Study of Moisture Sorption into Polymer Films using the Response Test Method

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Abstract

A fully automated climate controlled gravimetric analyser the IGAsorp has been utilized to study the moisture sorption into polymer films using the response test method. Fits were performed on the measured data in order to determine equilibrium uptakes as a function of relative humidity and chemical diffusion coefficients as a function of concentration more accurately and in shorter times than when using traditional test methods.

Introduction

Polymer films are extensively used as packaging/coating materials in the food and pharmaceutical industries. Many are used for cosmetic reasons but an increasing proportion provide a functional benefit such as controlled release or protection from moisture.

Drugs and foods are often sensitive to moisture and therefore careful attention must be paid to the properties of the packaging/coating materials in the presence of moisture.

The present study demonstrates how the IGAsorp can be utilized to determine both equilibrium moisture contents and diffusion coefficients to allow quality and reliability to be assessed.

Moisture Diffusion Theory

Moisture diffusion in polymers is a complicated process with many influencing factors. The moisture sorption may cause the material to expand and water molecules may also bond with the polymer chains present and become immobilized.

Despite the complex nature of moisture sorption, using the response test is still a powerful method for quickly assessing the moisture sorption properties such as diffusion coefficients and equilibrium moisture contents of the material.

In this study the samples are relatively thin. Therefore diffusion into the edges of the sample may be neglected and the diffusion can be modeled based on a one-dimensional Fickian model.

Fick's second law for one-dimensional diffusion is of the form:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{Eq 1.1}$$

where C is the concentration of the diffusing substance, t is time, D is the diffusion coefficient and x is the length parallel to the concentration gradient.

Thin film samples can be considered to be flat plates of thickness l . Both surfaces (top and bottom) are assumed to be at a constant concentration C_1 with an initial concentration of C_0 within the film. For example, if the medium is initially in steady state and the concentration at all surfaces is suddenly changed (i.e. by changing the pressure or humidity in a sorption experiment).

The boundary conditions stated mathematically are:

$$C=C_1 \quad x=-l/2, x=l/2 \quad t \geq 0$$

$$C= C_0 \quad -l/2 < x < l/2 \quad t=0$$

$$\frac{\partial C}{\partial x} = 0 \quad x=0 \quad t \geq 0$$

Using the above boundary conditions Fick's Law can be solved to give the time dependence of concentration as shown below:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{-D(2n+1)^2 \pi^2 t / l^2\right\} \quad \text{Eq 1.2}$$

t is the time measured from when the concentration is changed, l is the plate thickness, m_0 is the initial equilibrium mass and Δm is the change in the mass from m_0 to the new equilibrium mass.

The above equation describes the change in mass $m(t)$ due to the movement of the diffusing species responding to the sudden change in pressure/humidity around the sample.

The half thickness ($l/2$) is used as the diffusion length above since in a typical sorption experiment the entire plate is measured and the substance is assumed to diffuse uniformly to the central plane.

The IGA response method is ideally suited to directly determine all the fundamental physical properties referred to above for some known plate thickness since the diffusion coefficient can either be estimated from the equilibration time or from a curve fit (albeit that the summation 1.2 has to be truncated).

However, expression 1.2 must be applied with caution for a number of reasons all of which change the solution to the diffusion equation either in terms of the boundary conditions or the fundamental differential equation (non-Fickian behaviour):-

- i) Edge effects cannot be ignored except for thin films or where the edges can be de-activated.
- ii) Many real-world media are not homogeneous (e.g. laminates)
- iii) The diffusing substance may interact more strongly at different sites (locations) in the medium (e.g. hydrogen bonding may effect moisture diffusion) and diffusion rate is therefore not independent of concentration.
- iv) The medium may swell (e.g. during absorption) and/or generate internal stress due to the interaction which can lead to non-Fickian behavior depending on the rate of mechanical relaxation compared to the rate of diffusion.
- v) If the interaction is exothermic or endothermic then the sorption-time curve will include a contribution from thermal diffusion depending on the rate of heat transport compared to the rate of molecular diffusion.

Generally, expression 1.2 is valid if the rate of molecular diffusion is low (e.g. vapour diffusion) and if the concentration change is small: The diffusion coefficient determined will be an average value for a given concentration change if diffusion is concentration dependent. The validity of the Fickian model can also be readily assessed from the curve fit, notably that when uptake is plotted against time^{1/2} the initial trend is linear to at least 50% of the equilibrium uptake.

Apparatus

The uptake of moisture was studied using an IGA-sorp gravimetric analyser. The IGA-sorp is a fully automated and computer controlled instrument which continuously monitors the moisture content of the sample whilst accurately controlling both the temperature and relative humidity. A schematic of the IGA-sorp is presented in figure 1. A sensitive microbalance (resolution of 0.1µg) is utilized to measure changes in the moisture content of the sample. The microbalance is mounted in a thermostated enclosure to remove thermal coefficients of the weighing system and thus provide higher stability. The sample temperature is regulated to $\pm 0.05^{\circ}\text{C}$ by a water bath which pumps water through a network of channels in the sample block. The temperature can be varied between 5 and 80°C. An additional internal heater is situated in the sample chamber for rapid drying, temperatures up to 250°C. The relative humidity is controlled in the sample chamber dynamically by combining different flow rates of wet and dry gas streams prior to injection. The reservoir in the sample block is utilized to humidify a gas stream and thus produces the wet stream. The RH sensor is used to measure and control the relative humidity in the sample chamber. The RH can be varied between 0 and 95%.

Any sample will come to an equilibrium moisture uptake capacity at a defined humidity and temperature. If either of these conditions are altered the sample will either release or take up moisture to maintain energetic equilibrium. The IGA-sorp software exploits this phenomena. From an equilibrium state, the relative humidity is rapidly changed to a new set-point and then regulated at this new value. The sample will react by altering its adsorbed capacity. The trend of the data (mass versus time) is analysed in real-time as the sample capacity approaches the new equilibrium condition. This relaxation is used to determine when the new equilibrium condition has been achieved. Once attained the equilibrium uptake values can be recorded. The method provides a consistent analysis from sample to sample thus removing human subjectivity. The kinetic data usually discarded or not measured with other techniques is accessible and can prove to be just as valuable as the equilibrium data. The analysis package of the IGA-sorp software allows the kinetic data to be fitted using equation 1.2 with a 100 term summation to realize chemical diffusion coefficients.

Method

The sample was loaded into the IGA-sorp where its initial mass was determined. The sample was then dried in flowing nitrogen at 25°C. Once dry the sample mass was recorded in order to determine the mass loss due to drying and the dry mass of the sample. The RH was varied from 0-90%RH in steps of 10%RH and the resulting relaxation of mass due to water sorption was monitored.

Results

The measured uptake and calculated diffusion coefficients (using expression 1.2) are presented in figure 2. Uptake is expressed in terms of the percentage of the dry weight of the sample and is plotted as a function of the square root of time. The plotted fit is based on a least squares analysis using equation 1.2 with 100 terms in the summation. It can be observed that the fit is in good agreement with the experimental data. As described in the theory section the first 50% of the uptake is linear as a function of $t^{1/2}$ and thus indicates that the water diffusion process in this material is Fickian.

Conclusions

The equilibrium uptake of the sample at 25°C and 85%RH was found to be 1.6% dry weight and the chemical diffusion coefficient associated with a change in concentration from 0-1.6% at 25°C was found to be Fickian with a value of $1.52\text{E-}8\text{ cm}^2/\text{s}$. The response method using the IGAsorp was found to be a valuable source of important physical parameters required when assessing the quality of polymer materials used in the food and pharmaceutical industries.

¹J.Crank ‘The Mathematics of Diffusion’ 2nd Edition, Clarendon Press, 1975

²P.R.Stonadge, M.J.Benham and D.K.Ross ‘The Measurement of Concentration Dependent Hydrogen Diffusion Coefficients in the Solid-Solution Alloy Pd-Y’, Separation Technology, 1994

³Investigation into the Moisture Barrier Properties of Polyvinyl Alcohol Film Coatings, Glatt 6th Int Symp on Solid Drug Dosage Forms, Oct 1996, Basel, Switzerland.

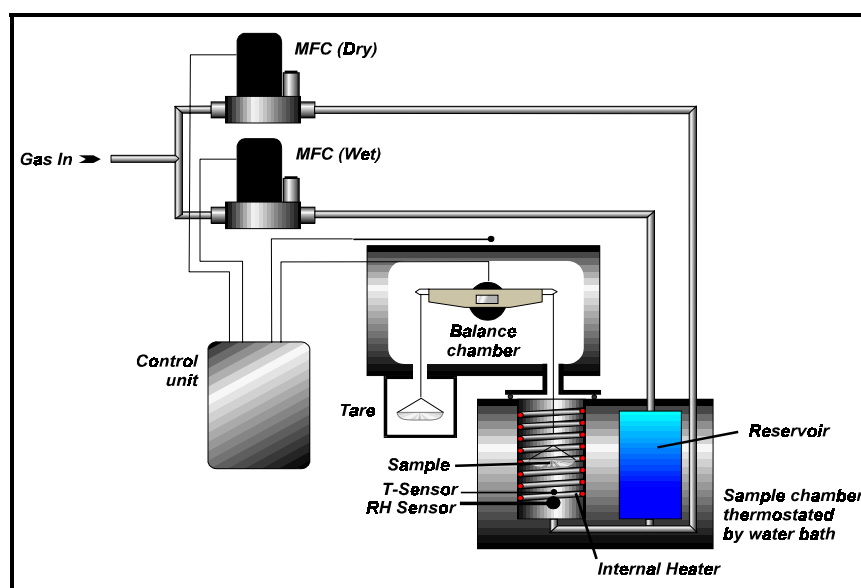


Figure 1, A Schematic representation of the IGAsorp.

Figure 2, A climatic response test on a polymer component showing the excellent agreement between the measured and fitted data.

