

# Concentration dependence of the microscopic mobility of water in polymer membranes

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## Introduction

Gravimetric vapor sorption provides the means for simultaneous determination of the isothermal concentration of water vapor and the chemical diffusion coefficient given a defined sample geometry such as a polymer film.

The present study determines both properties for two polymer packaging films, one of which has undergone treatment to reduce the transmission rate of water. The microscopic (self-) diffusion coefficient is also calculated from these results to show the effect of the treatment on water mobility and to assess how this varies as a function of water content.

Diffusivity calculations [1] are based on transport through a homogeneous plane sheet which is a one-dimensional solution of Fick's law (ignoring edge effect) for a substance diffusing through an infinite plane of a homogeneous medium where, in steady state, the rate of transfer,  $F$ , is given by,

$$F = -D_i \frac{\partial c_i}{\partial x} \quad (1)$$

$D_i$  is the chemical diffusion coefficient,  $c_i$  is the concentration of absorbed species and  $x$  is the film thickness. The diffusion coefficient will be a function of temperature and concentration depending on the sample properties.

Fick's law can be solved for defined boundary conditions to give the time dependence of water content. For example, if the medium is initially in steady state and the concentration at all surfaces is suddenly changed (i.e., by changing relative humidity during a dynamic water sorption experiment) then the mass ( $m$ ) of the diffusing species ( $i$ ) will vary with time according to,

$$m(t) = m_0 + \Delta m \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{k} \exp\left(-D_t \frac{k}{l^2}\right) \right] \quad (2)$$

where  $k = (2n+1)^2\pi^2$ ,  $t$  is elapsed time,  $l$  is the plate half-thickness,  $m_0$  is the initial equilibrium mass and  $\Delta m$  is the mass change when medium is once more in equilibrium. The half-thickness is used above since in a sorption experiment all plate surfaces are exposed and the substance is assumed to diffuse uniformly to the centre plane.

The microscopic diffusion coefficient  $D_i^*$  (self-diffusion in the absence of a chemical potential gradient) is related to the chemical diffusion coefficient by [2],

$$D_i^* = D_i \frac{\partial(\ln c_i)}{\partial \ln a_i} \quad (3)$$

where  $a_i$  is the activity of species  $i$ . Therefore, by combining the measured isotherms and chemical diffusion coefficients we can derive values for the mobility of water equivalent to those directly measured by NMR or Quasi-Elastic Neutron Scattering (QENS). This is particularly useful for assessing relative changes in mobility as a function of concentration since high-resolution data in precisely controlled conditions is provided by gravimetric sorption experiments.



Figure 1: The IGAcorp Gravimetric Vapor Sorption Analyser

## Procedure

All measurements were carried out using a standard Mk IV IGAcorp (see Technical Data Sheet 143) with a 2cm square film of thickness 0.1mm directly suspended into the IGAcorp controlled climate chamber. All reported measurements were performed automatically at controlled relative humidity (+/-0.1% RH).

Sorption isotherms were determined at intervals of 5% RH for both samples and at a temperature regulated to 40+/-0.05 °C by a refrigerated re-circulating water bath. The IGA method of real time analysis was used to fit kinetic parameters of an exponential model and adjust the data collection time accordingly with an end-point criterion that the weight is 95% relaxed.

## Results

An example of the raw data recorded for one of the isothermal measurements is shown in Fig. 2. This data is analysed in real

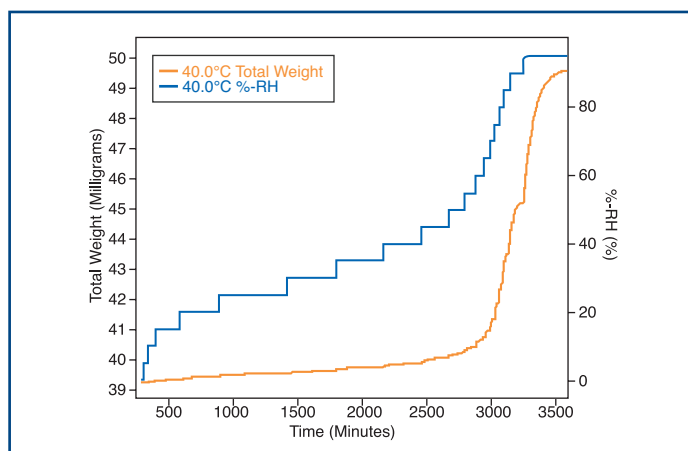


Figure 2: Raw data for the isothermal uptake of water on the treated polymer sample.

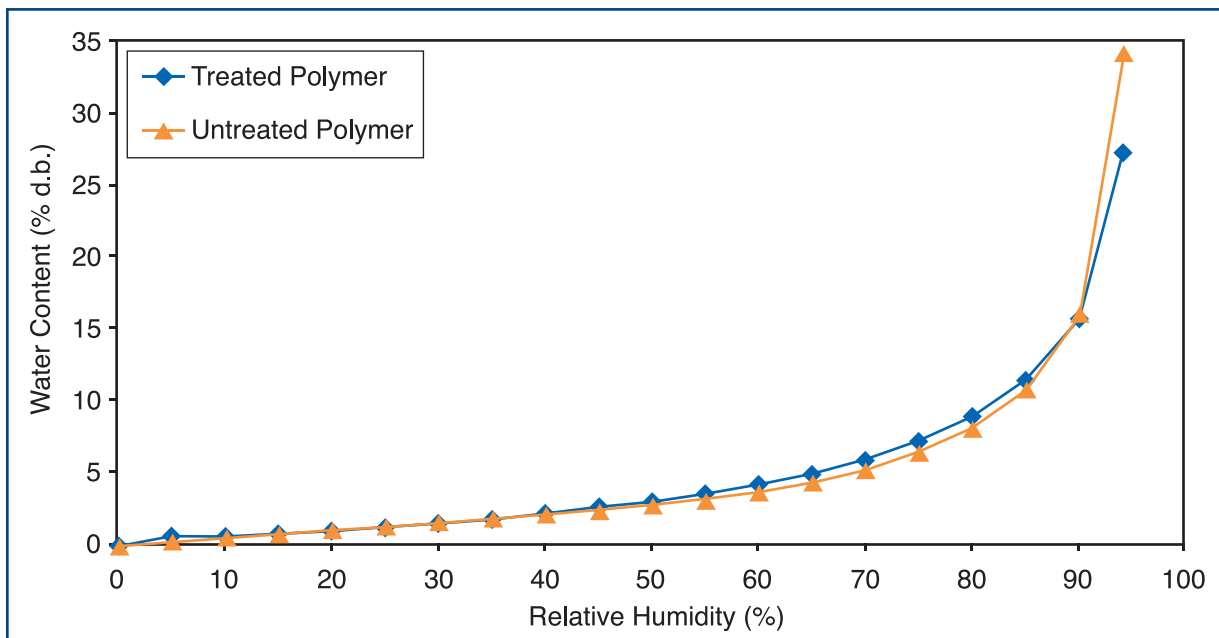


Figure 3: Comparison of the isothermal uptake of water vapor on treated and untreated polymer samples.

time to derive the asymptotic uptake isotherms (Fig. 3) by trend analysis in the long time limit and a detail of the analysed kinetic responses presented in IGA<sub>so</sub>rp software chart recorder format is also shown in Fig. 4.

The kinetic data is reanalysed using equation 2 with the summation truncated to 1000 terms. This method enables comparison of the model with the data as shown in Fig. 5. The data is near linear to a fractional uptake of around 0.5, when plotted against the square root of time, which is characteristic of a Fickian process. The data is near linear to a fractional uptake of around 0.5, when plotted against the square root of time, which is characteristic of a Fickian process. These calculations are also corrected for swelling due to water absorption by assuming a linear dependence on water content.

The variation of chemical diffusion coefficient calculated for each isothermal point with relative humidity is shown in Fig. 6.

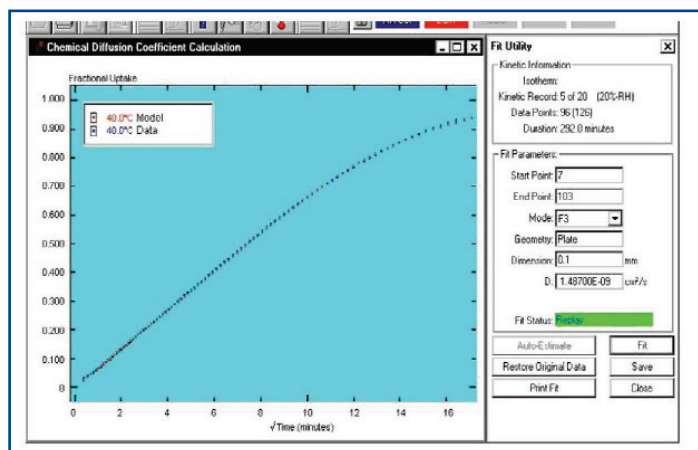


Figure 5: Example of IGA<sub>so</sub>rp diffusion coefficient calculation for an isothermal point of the untreated polymer.

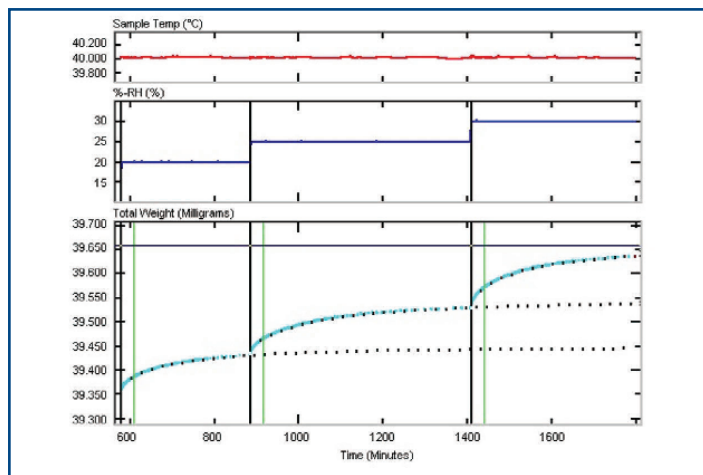


Figure 4: Detail from Fig. 2 in chart recorder format showing analysed trajectories of weight uptake.

The values for  $D_i$ , together with the equilibrium moisture contents, are then used to calculate the microscopic diffusion coefficients  $D_i^*$  using equation 3 (see Fig. 7).

### Discussion

The uptake isotherms for both materials compared on a dry weight basis are quite similar. The untreated material achieves a higher water content (nearly 35% d.b.) compared with the treated polymer and there are other differences in the isotherm shape. The untreated sample is Type III according to the IUPAC classification whereas the treated material has a subtle deviation at low relative humidity and a slight enhancement of uptake which is the Type II characteristic though not strongly developed. There are also deviations in the mid range of humidity but, broadly speaking, the differences are not dramatic.

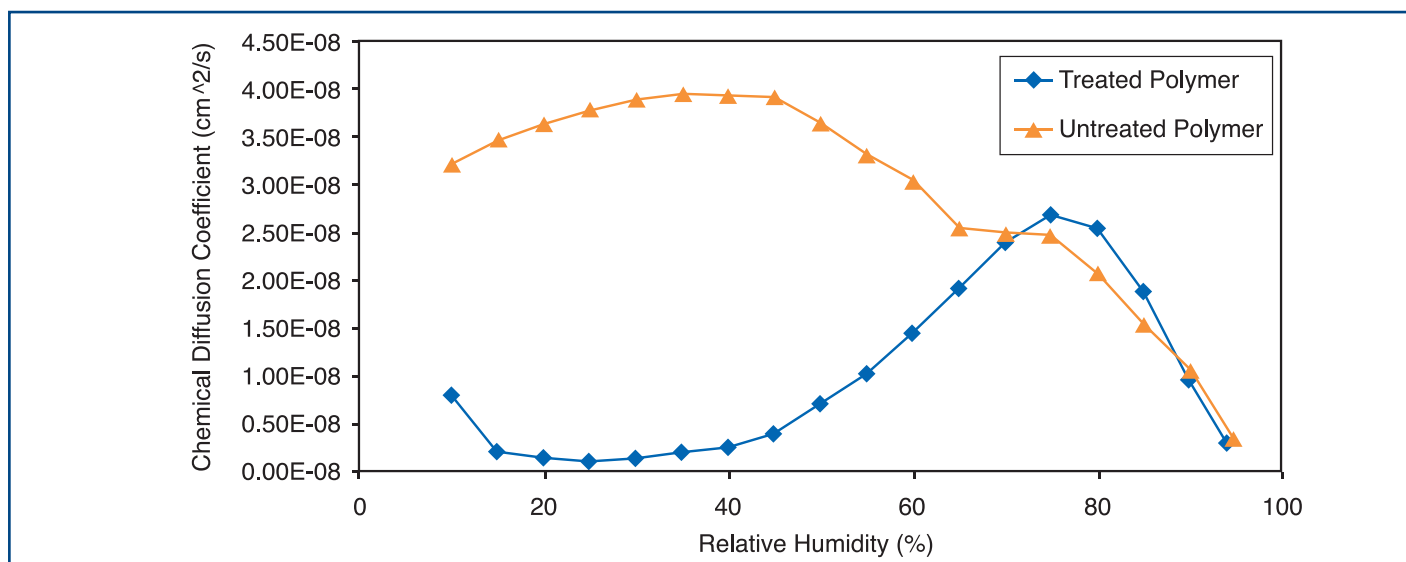


Figure 6: Variation of the chemical diffusion coefficient with relative humidity.

On the other hand significant differences are clearly evident in the diffusive behaviour. Both polymers show smooth variation of the chemical diffusion coefficient but with completely different trends and significantly different values below 70% RH. However, at higher humidity (and water content) the trends and magnitudes are quite similar.

Calculation of the microscopic diffusion coefficient can elucidate this behaviour: The chemical diffusion coefficient governs the flux for Fickian diffusion according to equation 1 and is therefore useful in its own right but microscopic diffusion is the more fundamental property for true comparison.

The calculated values plotted in Fig. 7 show that both materials actually have the same trends in behaviour, i.e., that mobility rises to a peak at 80% RH and then falls above this value. The reduction in mobility at high water content is expected given hindrance which occurs as the water content rises towards saturation. Generally there may also be contributions in this region from stress or water induced structural changes to consider as well.

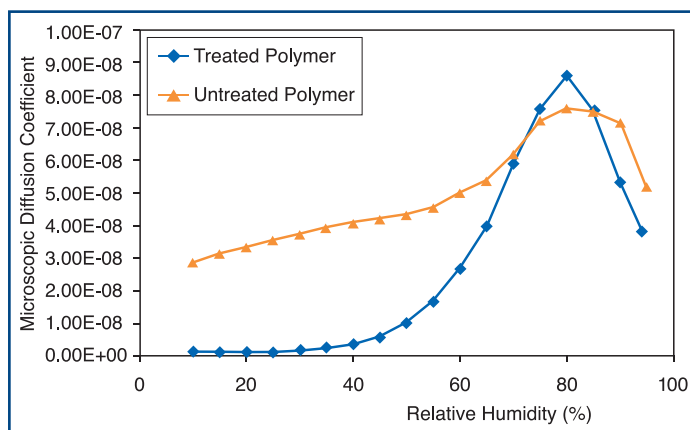


Figure 7: Variation of the microscopic diffusion coefficient with relative humidity.

However, the most significant difference between samples is the magnitude of this variation. The untreated polymer varies by a factor of about three but the variation is nearly two orders of magnitude for the treated polymer. In other words the most important effect of the treatment is to reduce the water mobility at low water content. This is consistent with the addition of active water trapping sites in the treated material that reduce mobility up to a threshold of water content at which they become saturated and water moves more freely again.

## Conclusions

Combined measurements of water content isotherms and water diffusion provide a clear picture of the overall behaviour, and the change in behaviour, of modified polymers particularly given that the water mobility can be calculated directly from the results. Typical characterisation is by MVTR (see IGAsorp Application Note 117) but this cannot independently assess the separate contributions of equilibrium water content and mobility and these are the fundamental physical properties governing transmission.

In the present study the treated material will exhibit comparatively low transmission at low water content (i.e. a significant difference in behaviour when exposed below ~50% RH) but rising significantly as water content increases.

Further study is in progress to assess the temperature dependence of these systems in order to investigate the concentration dependence of activation energy and the heat of sorption.

## References

- [1] J.Crank 'The Mathematics of Diffusion' 2nd Edition, Clarendon Press (1975)
- [2] IUPAC Compendium of Chemical Technology 2nd Edition (1977)

