

Accurate and stable equal-pressure measurements of water vapor transmission rate of organic electronics packages reaching the $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ range

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Abstract

The water vapor transmission rate (WVTR) of a gas barrier coating is a critically important parameter for flexible organic device packaging, but its accurate measurement without mechanical stress to ultrathin films has been a significant challenge in instrumental analysis. At the current stage, no reliable results have been reported in the range of $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ that is required for organic light emitting diodes (OLEDs). In this article, we describe a solution for this difficult, but important measurement, involving enhanced sensitivity by a cold trap, stabilized temperature system, pumped sealing and calibration by a standard conductance element.

1. Introduction

The water vapor transmission rate (WVTR) of a gas barrier coating is a critically important parameter for flexible organic electronic device packaging, but its accurate measurement without mechanical stress to ultrathin films has been a significant challenge in instrumental analysis. At the current stage, no reliable results have been reported in the range of $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ that is required for organic light emitting diodes (OLEDs).

As for the major reasons of difficulties, we point out that the amount of water on the surface with a monolayer absorption is 10^3 - 10^4 times greater than the amount transmitted from the $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ sample (60 cm^2) per hour. The amount of the adsorbed water must be stable at the steady state within the inverse of this ratio (10^{-3} - 10^{-4}). If this value deviates, the obtained WVTR value fluctuates and the measurement will be impossible. The adsorption enthalpy of H_2O molecules on electropolished stainless steel is $\Delta H \sim 0.10 \text{ eV}$. The allowance of the temperature deviation ΔT is estimated from $f(T + \Delta T)/f(T) = 1 \times 10^{-3} \sim 1 \times 10^{-4}$ where $f(T) = \exp(-\Delta H/kBT)$, which results in a $\Delta T \sim 20 \text{ mK}$ when $T = 300 \text{ K}$. Deviation in the room temperature and other environments (e.g., sunshine, wind from air conditioner) will easily exceed this limit.

Another problem is calibration of the detector. The detectors sensitive enough for the measurement of the 10^{-6} WVTR range require calibration. We have noticed that the pumping speed is also a variable, if a vacuum pump is used in the instrument. It is less recognized that the sensitivity of electron multiplier used in the mass spectrometer fluctuates by more than 200%.

In this presentation, we describe a solution for this dif-

ficult, but important measurement, involving enhanced sensitivity by a cold trap, stabilized temperature system, pumped sealing and calibration by a standard conductance element. We demonstrate the actual measurement of barrier samples having a $1.7 \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$ WVTR. The standard deviation was $7 \times 10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ over repeated measurements for one year.

2. Experimental

a cold trap, and a measuring chamber, which is equipped with a quadruple mass spectrometer (QMS).

A film sample with a $\Phi 60 \text{ mm}$ circle permeated area, was placed in the sample chamber, then held down by a fluoropolymer o-ring from both sides. The sample chamber has a outer hull to pump out. This is necessary to prevent the water vapor from the wet side or in the atmosphere to diffuse into the dry side through the o-ring. An ordinary elastomer o-ring is highly permeable to H_2O compared to the barrier sample. By pumping the outer hull, the H_2O molecules diffused from the wet side will be pumped out and does not permeate through the o-ring seal of the dry side. The whole system, inside and outside of the sample chamber was pumped out and heated (80 – 130°C) to remove the water molecules in the sample and on the chamber wall. After 24 hours, the chamber containing the sample was cooled to the measurement temperature (40°C).

The carrier gas with an H_2O concentration less than 1 ppb, produced by passing through an alkali getter (GP-10, Pureron Japan, Inc.), was supplied to the wet and dry sides of the system until it reached atmospheric pressure. The o-ring seal was mechanically pressed from the both sides and water vapor container was connected to the wet side. In order to keep a specific humidity in the upper side, the temperatures of liquid water in the water container and carrier gas were separately controlled (two-temperature method).

The H_2O vapor permeated through the sample was quantified by amplification using a cold trap. After the accumulation time (3 hours), the dry side of the sample space was disconnected from the downstream to prevent a pressure deviation and connected to the cold trap. The pressures of the wet and dry sides are regulated by two independent pressure gauges (0.1% accuracy of 10^5 Pa) on the both sides and automatic carrier gas supply to the dry side. The temperature of the cold trap was decreased to 77 K to trap the H_2O molecules. During this operation, the H_2O vapor keeps permeating through the sample and is accumulated in the sample space.

When the condensation time (within 15 minutes) passes, the remaining carrier gas in the cold trap was pumped out to a high vacuum in order to enable the accurate measurement by a quadrupole mass spectrometer.

3. Results

Figure 1 shows an example of the QMS signals during the release of captured water from the cold trap. The difference between QMS ion current I and its background I_0 was initially integrated. Since the background slowly fluctuates during the measurement, spline fitting is used for estimating the background I_0 . This removal of the slow fluctuation is another merit of using this intermittent measurement scheme, which makes the measurement less sensitive to slow temperature fluctuations of the environment.

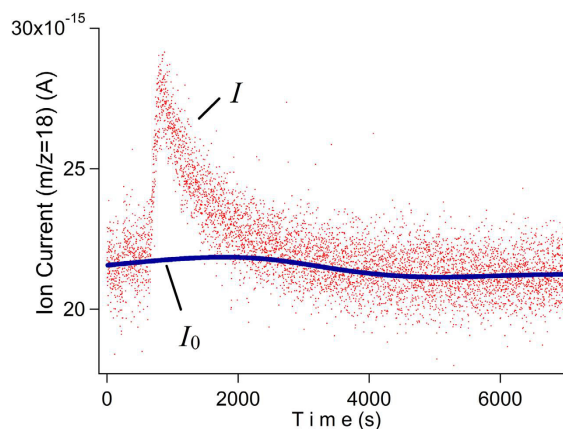
To obtain the amount of water m [g], the integration was divided by the flow rate sensitivity SF , which was obtained by using controlled leak.

$$m = (I - I_0)dt/SF$$

Finally, WVTR [$\text{g m}^{-2} \text{day}^{-1}$] was obtained as follows

$$\text{WVTR} = m/A_{\text{sample}}/t$$

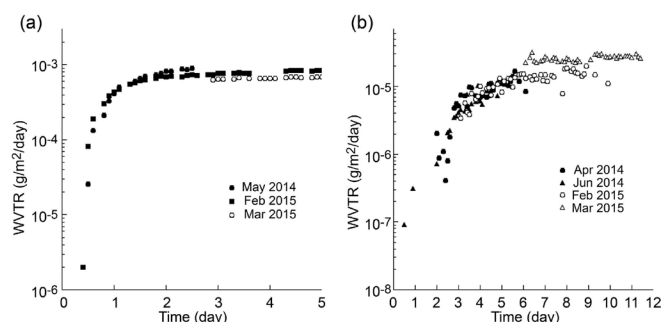
where A_{sample} [m^2] is the sample area, and t [day] is the accumulation time. All the data below are shown after this procedure.



We present measurement of two examples. One was a low-barrier coated polymer film which showed a barrier property of $9 \times 10^{-4} \text{ g m}^{-2} \text{day}^{-1}$ when evaluated by commercially available instrumentation (Technolox). The other was a high-barrier coated one that could not be evaluated by the other setup. The measurements were carried out at 3-hours intervals at 40 °C and 90% RH.

Figure 2(a) shows the results of the low-barrier coated films. It is clearly seen that WVTR reached a stable value within 3 days. A total of 4 days, including a day for conditioning the sample and the apparatus, were required to obtain the result. The average value of the four separate measurements was $8.3 \times 10^{-4} \text{ g m}^{-2} \text{day}^{-1}$, which is close to the value evaluated by the other setup. The standard deviation of our measurements was $8.1 \times 10^{-5} \text{ g m}^{-2} \text{day}^{-1}$.

Figure 2(b) shows the results of the high-barrier coated films. It took 6 days to reach a rough steady state. A total 7 days are necessary to evaluate these films. The average WVTR value of the four separate measurements was $1.7 \times 10^{-5} \text{ g m}^{-2} \text{day}^{-1}$. The standard deviation of the values after “steady state” was $7.1 \times 10^{-6} \text{ g m}^{-2} \text{day}^{-1}$, which was larger than the standard deviation of repeated measurements over one year. We now describe two examples. One was a low-barrier coated polymer film which showed a barrier property of $9 \times 10^{-4} \text{ g m}^{-2} \text{day}^{-1}$ when evaluated by commercially available instrumentation. The other was a high-barrier coated one that could not be evaluated by the other setup. The measurements were carried out at 3-hours intervals at 40 °C and 90% RH.



4. Conclusions

We evaluated the source of errors in WVTR measurement. We demonstrated the measurement of WVTR of $10^{-6} \text{ g m}^{-2} \text{day}^{-1}$ is possible.

References

- [1] Y.Nakano, T.Yanase, T.Nagahama, H.Yoshida, T.Shimada, Scientific Reports 6: 35408 (2016).