Determination Of Moisture Content And Drying Rates Of Thin Films And Coatings With The Quartz Crystal Microbalance/Heat Conduction Calorimeter

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The behavior of both inorganic and organic thin films and coatings in the electronics and pharmaceutical industries is influenced by the presence of moisture retained from the original drying and curing process or moisture absorbed from the surroundings while the product is stored or in use. By combining a quartz crystal microbalance/heat conduction calorimeter[2] with a relative humidity generator based on mass flow controllers, we have measured both the equilibrium water content, the heat of sorption, and the water vapor diffusion coefficient in thin films of two polymer systems: (a) Eudragit RS and Eudragit NE, acrylate copolymers used in enteric coatings in pharmaceutical products; and (b) composite polyethylene oxide/polyacrylic acid coatings prepared layer-by-layer and being studied for use in membranes.
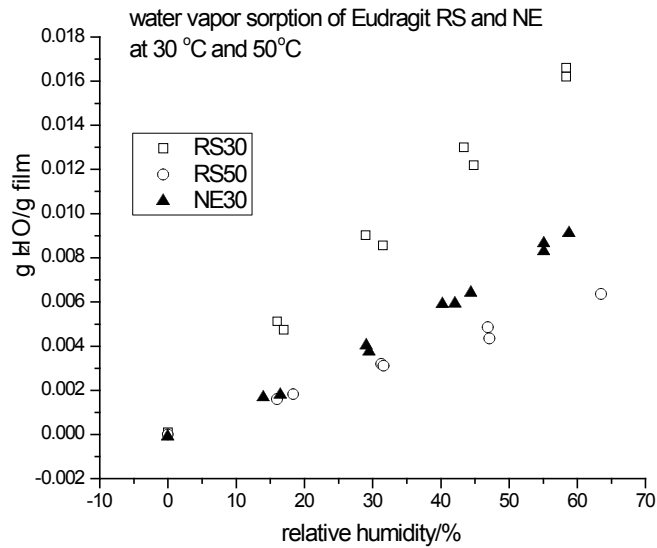
Moisture Sorption in Pharmaceutical Coatings

The Eudragits are copolymers of partial esters of acrylic and methacrylic acids with alcohols containing a low amount of quaternary ammonium groups. The Masscal G1 was used to collect gravimetric and calorimetric data on moisture sorption by thin films (3. 9 mg, 6 μm) of Eudragit NE and Eudragit RS at 30˚C and 50˚C and relative humidity from 0 to 60%. Water vapor sorption enthalpies and sorption isotherms were calculated, and they show that the two films interact differently with water vapor. Figure 1 shows the water vapor sorption isotherms.

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[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.
[2] See www.Masscal.com

water vapor sorption of Eudragit RS and NE at 30 °C and 50°C

y-axis: g H2O/g film (values: -0.002, 0.000, 0.002, 0.004, 0.006, 0.008, 0.010, 0.012, 0.014, 0.016, 0.018)

Legend:
□ RS30
○ RS50
▲ NE30

x-axis: relative humidity/% (values: -10, 0, 10, 20, 30, 40, 50, 60, 70)

Figure 1. Water Vapor Sorption Isotherms in Eudragit RS and Eudragit NE

The water vapor sorption isotherms are linear with relative humidity over the measured range of 0 to 60%.

Simultaneous measurements of heat flow and mass change enable us to calculate the calorimetric enthalpy of water vapor sorption in Eudragit RS; we obtain -43±3 kJ/mole of H_2O. The calorimetric water vapor sorption enthalpy in Eudragit NE is -31±3 kJ/mole of H_2O.

The van't Hoff relationship for the chemical process

Eudragit RS + H_2O(v) ⇔ Eudragit RS•H_2O(adsorbed)

can be expressed as

$$\ln(K_2/K_1)/\{1/T_2 - 1/T_1\} = -\Delta H_{sorption}/R$$

Using the data of Figure 1 we compute the van't Hoff enthalpy of water sorption in Eudragit RS to be -43 kJ/mole of H_2O. This agrees well with the calorimetrically determined enthalpy of water sorption determined on the same film. Both films show

increasing motional resistance with relative humidity, indicating a softening consistent with the role of water as a plasticizer. The Eudragit NE film at 50˚C also shows a slow loss with time of another volatile component, producing a slight stiffening of the film.

Absorption and Permeability of Water in a Multilayer PEO/PAA Polymer Film

The measurement and control of water permeability in polymer films and membranes is important in many industrial applications, such as membranes for fuel cells and gas separation, high performance electronic coatings, packaging, drug delivery systems, and contact lenses. The most common property used to quantify moisture sorption is permeability, P, defined as the product of the solubility S and the diffusion coefficient D. The solubility of gases in polymers is an equilibrium thermodynamic property – the slope of the sorption isotherm (mass fraction or volume fraction of vapor sorbed *vs* partial pressure) and is normally measured with a gravimetric technique. The diffusion coefficient is a dynamic property, the proportionality constant relating flux and concentration gradient, and it is measured with both steady state and time-dependent techniques that differ from those used for solubility. We show here that it is possible to measure *both* the solubility and the diffusion coefficient, and thus the permeability, of water in a thin polymer film applied to the surface of a quartz crystal microbalance.

The multilayer films were prepared for us by graduate student Nathan Ashcraft of Professor Paula Hammonds's research group in the chemical engineering department at MIT. Ashcraft used the method of layer-by-layer dip-coating at a controlled pH of 2.5 to deposit 90 bilayers of polyethylene oxide/polyacrylic acid. The film thickness was 11μm. After overnight drying at 0% RH, the relative humidity above the film was then increased stepwise by 5% in one-hour intervals. Figure 2 shows the response of the film to these humidity changes. Notice that all three signals take several hours to equilibrate. If the mass m(t) of a polymer film is measured continuously as the partial pressure of an absorbing species in contact with that film is varied in a stepwise manner, then the diffusion coefficient of the species can be calculated from

$$\frac{-1}{\pi^2} \ln\left(\frac{(m_p^\infty - m_p^t)\pi^2}{8(m_p^\infty - m_p^i)} \right) = \frac{D}{l^2} t$$
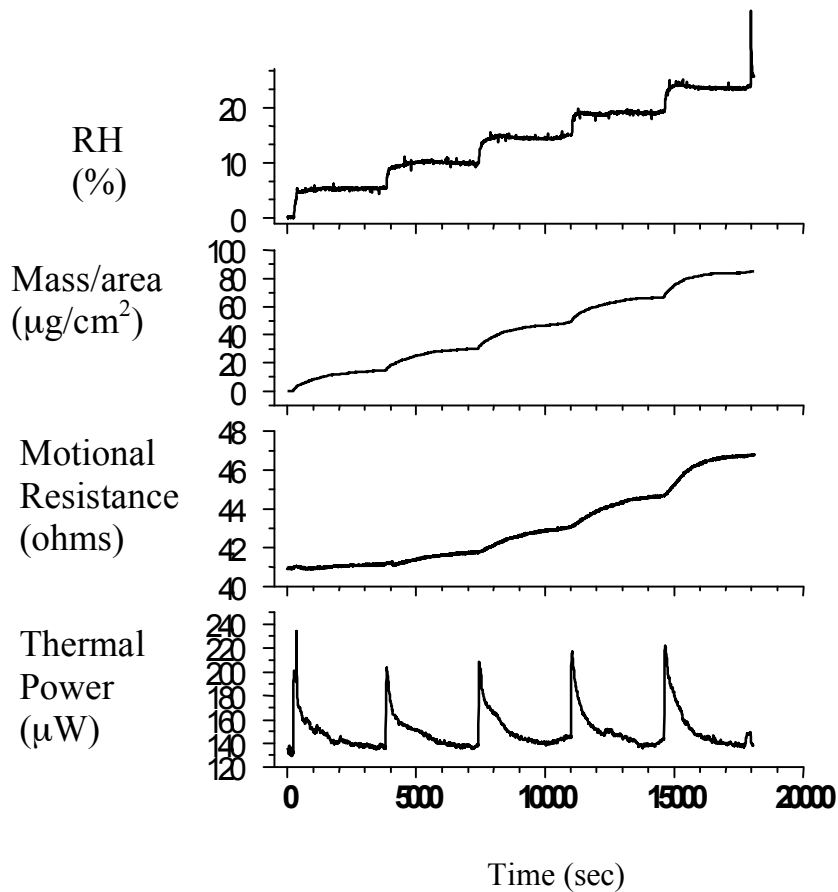
Figure 2. QCM/HCC collected when the PEO/PAA film is exposed to one-hour step-wise changes in relative humidity at 30˚C.

Here m_p^t is the mass of the film plus sorbate taken up at any time t, D is the diffusion coefficient, l is the film thickness, and t is the time. Using this equation and the data from Figure 2 and from two other runs at 30˚C, we find that water diffusion coefficients in the PEO/PAA film range from 1×10^{-10} cm^2/s at 0-10% relative humidity and increase to 4×10^{-10} cm^2/s at 50-60% relative humidity.