Supporting Information

Water Vapor Sorption and Diffusion in Secondary Dispersion Barrier Coatings: A Critical Comparison with Emulsion Polymers

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Figure S1. Schematic representation of the stages in the preparation of secondary dispersions of polymers. (Re-drawn from *Prog. Organ. Coatings*, 26, B. Schlarb, M.G. Rau, and S. Haremza, “Hydroresin dispersions: new emulsifier free binders for aqueous coatings,” pp 207-215 Copyright (1995), with permission from Elsevier (reference 1). After solution polymerization, the polymer is neutralized with N,N-dimethyl ethanolamine (DMAE) and dispersed in water. The solvent is removed under vacuum to leave a dispersion of polymer in water.

BET and ENSIC Sorption Isotherm Models

The classical BET model is usually used in a linearized form with two parameters. It can be expressed by^{2, 3}

$$m_t = \frac{m_m C_{BET} a_w}{(1 - a_w)(1 + (C_{BET} - 1)a_w)} \quad (\text{Eq. 1})$$

where m_t is the mass fraction of water vapour on the dry basis of sample, m_m is the monolayer capacity (g H₂O/m³), a_w is the water activity and C_{BET} is a BET constant, taking into account the adsorption heat of the first monolayer and indicating the segmentation of high sorption layers. It can be roughly estimated by:

$$C_{BET} = e^{(H_1 - H_L)/RT} \quad (\text{Eq. 2})$$

where H_1 is the heat required for the adsorption of first layer of water moisture, H_L is the heat of liquefaction, R is the ideal gas constant, and T is the temperature. In this work, m_m and C_{BET} were varied to fit the data for the various polymers. The BET model is commonly considered to have a good

agreement with the experimental data of the water vapour sorption in hydrophilic polymers at relatively low activity.⁴

The GAB model is slightly different from the form of the BET model. It can be expressed by⁴

$$m_t = \frac{m_m C_{GAB} K a_w}{(1 - K a_w)(1 + (C_{GAB} - 1) K a_w)} \quad (\text{Eq. 3})$$

where two parameters a_w and m_m are used from the BET model. C_{GAB} is a GAB constant, indicating the heat required for the condensation of water vapour at a given temperature. $K (J \cdot J^{-1})$ is the ratio of heats of adsorption and that of liquefaction. It is a factor for multilayer molecules compared to bulk liquid.³

Perrin⁵ and Favre⁶ developed a modified equation, in which a parameter to characterize the penetrant-penetrant interactions k_s (mutual penetrant interaction parameter) is introduced. The interactions between the polymer and penetrant are taken into account by using a parameter k_p , which is comparable to the Flory-Huggins interaction parameter. Their equation can be expressed by

$$m_t = \frac{e^{(k_s - k_p) a_w} - 1}{(k_s - k_p) / k_p} \quad (\text{Eq. 4})$$

This model is called the ENSIC model. Altinkaya *et al.*⁷ studied the water isotherms in waterborne acrylic films and found that the ENSIC model fit the sorption isotherms well over the whole range of water activities.

Figure S2. Water sorption isotherms (experimental data) for seven types of polymer film (identified in the legend) compared to the GAB, BET and ENSIC models. The red line shows the BET model fit, the green line shows the GAB model fit, and the blue line represents the ENSIC model fit.

Table S1. Molar water content sorbed by structural groups of amorphous polymers at different relative humidities at 25 °C. Data from ref.⁸

Group	Relative humidity				
	0.3	0.5	0.7	0.9	1
-CH ₃					
-CH ₂	1.5×10 ⁻⁵	2.5×10 ⁻⁵	3.3×10 ⁻⁵	4.5×10 ⁻⁵	5.0×10 ⁻⁵
-CH					
-C=O	0.025	0.055	0.11	0.20	0.3
0.001	0.002	0.003	0.004	0.005
-COO-	0.025	0.05	0.075	0.14	0.2
-COOH	0.2	0.3	0.6	1.0	1.3
-COO ⁻	1.1	2.1	4.2

Figure S3. Comparison of calculated sorbed water content at equilibrium with the experimental data. The calculation method used the data from ref.⁸ that is listed in Table S1.

Figure S4. Correlation of the sorption isotherm parameters in the GAB model for the two solvent-cast and five waterborne polymers.

Figure S5. The plots of M_t/M_{inf} against the diffusion time in SL films at 26 °C corresponding to various water vapour activities, a_w , over a range from 0 to 0.9, as indicated on the plots. The red line represents the best fit to Eq. 5.1 by a regression of the experimental data, where the diffusion coefficient, D , is the only adjustable parameter. The black squares in the curves represent the experimental data. The best-fit values of D are shown on each graph. The graph in the top row, on the right, shows a plot of M_t/M_{inf} as a function of $\sqrt{t}$. At early times, it shows a linear correlation, indicating a Fickian diffusion.

Figure S6. Water diffusion coefficients as a function of the sorbed water content (wt.%) for various films at a water activity of (a) $a_w = 0.3$; (b) $a_w = 0.7$; and (c) $a_w = 0.9$.

Figure S7. Permeability of various polymer films as a function of the water activity.

a) Em (■), Em-MEK (◇), and SL (▲); b) Em (■), DEm (□), and SD (●); c) SD (●), SD-pre (○), and SD-post (⊕).

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