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

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S *Supporting Information*

ABSTRACT: The conventional method for synthesizing waterborne polymer colloids is emulsion polymerization using surfactants. An emerging method is the use of secondary dispersions (SD) of polymers in water, which avoids the addition of any surfactant. Although there are numerous studies of the water barrier properties (sorption, diffusion, and permeability) of waterborne emulsion (Em) polymer coatings, the properties of SD coatings, in comparison, have not been thoroughly investigated. Here, dynamic water vapor sorption analysis is used to compare the equilibrium sorption isotherms of the two forms of styrene−acrylate copolymers (Em and SD) with the same monomer composition. From an analysis of the kinetics of vapor sorption, the diffusion coefficient of water in the polymer coatings is determined. The combined effects of particle boundaries and surfactant addition were investigated through a comparison of the properties of SD and Em coatings to those of (1) solvent-cast polymer coatings (of the same monomer composition), (2) Em polymers that underwent dialysis to partially remove the water-soluble species, and (3) SD polymers with added surfactants. The results reveal that both the particle boundaries and the surfactants increase vapor sorption. The diffusion coefficients of water are comparable in magnitude in all of the polymer systems but are inversely related to water activity because of molecular clustering. Compared to all of the other waterborne polymer systems, the SD barrier coatings show the lowest equilibrium vapor sorption and permeability coefficients at high relative humidities as well as the lowest water diffusion coefficient at low humidities. These barrier properties make SD coatings an attractive alternative to conventional emulsion polymer coatings.

KEYWORDS: secondary dispersion, surfactant-free, barrier coatings, sorption isotherms, latex films, water diffusion coefficients, emulsion polymers
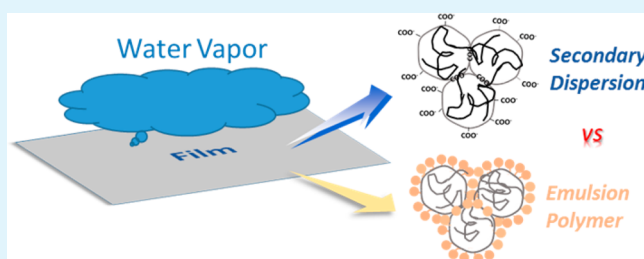
1. INTRODUCTION

Synthetic polymer colloids dispersed in water, known as latex, continue to be of strong practical interest for applications in waterborne coatings and adhesives. Latex films have two distinguishing characteristics. First, they contain emulsifiers, usually ionic surfactants, which are a necessary ingredient in standard methods of emulsion polymerization.[1] Second, because latex films are deposited from colloids, residual boundaries exist between the constituent particles for extended periods of time[2] or even indefinitely in some cases.[3]

The diffusion,[4−8] sorption,[4−6,8−10] and permeability[5,6] of both water vapor and liquid in latex films (and formulated coatings) have been topics of scientific research for the past few decades. The phenomena of water sorption, swelling, and extraction of surfactants from latex coatings are of particular relevance for art conservation.[6] Studies of water vapor and liquid transport have obvious relevance to the improvement of barrier[11] and anticorrosion coatings[12] and also the evaluation of their weathering characteristics[13] and hydroplasticization.[14] The presence of surfactants and the existence of particle boundaries have both been implicated in the sorption and diffusion of

water (from both the liquid and vapor states) in latex films, as is apparent from the brief review that follows.

The sorption of liquid water in latex films was found to be strongly dependent on the surfactant system used in their preparation.[15] The surfactant mobility, crystallinity, and surfactant polarity were each found to affect the water uptake. Highly mobile and crystallizable surfactants yielded high water uptake for films containing ionic surfactants.[15] The polarity of polymeric surfactants also had a large effect, with the more hydrophilic systems yielding greater water uptake.[15]

Roulstone et al.[16] concluded that the water vapor permeability of poly(butyl methacrylate) latex films was significantly increased by the addition of a cationic surfactant, but a small amount of an anionic surfactant lead to a lower permeability because of the formation of denser films with better particle packing. A nonionic surfactant was found to act as a plasticizer to encourage particle coalescence, but it also added hydrophilicity. Aramendia et al.[17] likewise saw large

differences in liquid water uptake when comparing polymers containing nonionic and anionic surfactants. They reported that the removal of surfactants can create defects that enable water permeability.

Whereas polymers are generally nonporous systems, latex polymer films are distinguished by having measurable porosities[18] and void contents,[19] even after particle coalescence has progressed for several days. Moreover, it has been proposed that the boundaries between particles can act as a pathway for the transport of diffusing molecules such as water. For instance, the permeability of water vapor was found to be higher in a latex film compared to that in a solvent-cast film of the same copolymer.[20] Richard[21] concluded that the water vapor permeability in carboxylated latex arises from the sorptive affinity of the hydrophilic species at the particle interfaces that create a cellular membrane structure.

To avoid the use of surfactants in waterborne colloidal coatings, one strategy is to synthesize polymer colloids by the technique of emulsifier-free emulsion polymerization.[22−25] An alternative strategy to produce surfactant-free polymer colloids in water is through the preparation of aqueous secondary dispersions.[26−28] To prepare a secondary dispersion, a polymer is initially synthesized via solution polymerization in a volatile organic solvent, and then the viscous polymer solution is dispersed in an aqueous phase after the neutralization of its acid groups with a base (to provide stabilization). The organic solvent is finally removed by evaporation under vacuum.[19] Although there are several reports on the synthesis of secondary dispersion polymers, there have been no reports of water vapor sorption and diffusion in these types of polymers. Moreover, there have been no reports of comparisons between the barrier properties of second dispersion polymer coatings and conventional emulsion polymer coatings.

A primary aim of this research is to measure (1) the equilibrium water vapor sorption isotherms and (2) the diffusion kinetics of water in emulsion polymer coatings in comparison to those in secondary dispersion polymer coatings. Our underlying hypothesis was that the vapor sorption and the diffusivity of water will be lower in secondary dispersion material because of the absence of surfactant that can adsorb water and resides at particle boundaries, providing a pathway for transport. To explore the effect of particle boundaries, we dried the emulsion polymer and dissolved it in an organic solvent before casting it from the solution. The resulting solution-cast coatings have the same chemical composition as the emulsion polymers, but there are no particle boundaries. To investigate the effect of chemical species in the aqueous phase of the emulsion polymers, we performed dialysis to reduce their concentration. Additionally, surfactant was added to the secondary emulsion polymers by two different methods to provide information on the effect of surfactants on water vapor sorption and diffusion.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Polymer Synthesis and Preparation. *Emulsion Polymerization.* A 2 L three-neck round-bottom glass reactor equipped with a stirrer, N_2 inlet, and thermometer was loaded with demineralized water (543.3 g) and ammonium dodecylbenzenesulfonate (ADBS) (19.0 g of a 10 wt % solution in water) and adjusted to a pH of 7 by the addition of ammonia (25 wt %). An initiator solution was prepared by dissolving ammonium persulfate (APS) (1.54 g) in demineralized water (27.5 g) and ADBS (40.4 g of a 10 wt % solution in water). A monomer feed was prepared by mixing acrylic acid (AA) (38.0 g), styrene (S) (167.5 g), 2-ethylhexyl acrylate (2-EHA) (92.3 g), and *n*-

butyl methacrylate (*n*-BMA) (169.6 g). Isooctyl thioglycolate (3.5 g) was included in the monomer feed as a chain transfer agent to reduce the polymer molecular weight. The reaction mixture was heated to 65 °C. When it reached this temperature, 10% of the monomer feed was added to the reactor, after which the reactor contents were heated to 75 °C. A solution of APS (0.81 g) in water (4.0 g) was then added, and the mixture was left to react. The temperature rose to 85 °C during the reaction. After 10 min, the monomer feed and initiator feed were added simultaneously over a period of 90 min. The addition of acidic monomers reduced the pH to <3. When both feeds were completed, demineralized water was added (9.2 g) and followed by the addition of ammonia (7.4 g, 25 wt % (aq)) and demineralized water (7.4 g) to adjust the pH to 6. The temperature was kept constant at 85 °C for another 30 min, after which the reactor contents were cooled to 50 °C. Thereafter, *t*-butyl hydroperoxide (0.14 g, 70 wt % (aq)) in demineralized water (0.79 g) was added, followed by the addition of a solution of isoascorbic acid (0.24 g) in demineralized water (10.84 g) over a period of 30 min. After 10 and 20 min of addition of the isoascorbic acid solution, another shot of *t*-butyl hydroperoxide (0.14 g, 70 wt % (aq)) in demineralized water (0.79 g) was added. After all of the isoascorbic acid solution was added, the temperature was maintained at 50 °C for 30 min, and then the batch was cooled to 35 °C. At this point, the dispersion was neutralized by the addition of sufficient ammonia solution (15.5 g (25 wt %) in 15.5 g water) to adjust the pH to a final value of 7.4. An ammonium surfactant (rather than a cationic form) and neutralization with volatile ammonia (rather than nonvolatile bases) were used to reduce the amount of cations in the emulsion polymer dispersion. The final latex dispersion had a solids content of 40 wt %. This emulsion polymer is referred to hereafter as **Em**.

Solution Polymerization. A 5 L stainless steel high-pressure reactor equipped with a stirrer, N_2 inlet, and thermometer was charged with MEK (1050 g) and heated to 140 °C. A monomer and initiator mixture was prepared by adding the monomers S (873 g), 2-EHA (481 g), AA (196 g), and *n*-BMA (884 g) along with initiators di-*t*-butyl peroxide (8.2 g) and *t*-butyl perbenzoate (6.5 g). After the reactor temperature reached 140 °C, the monomer and initiator mixture was pumped to the reactor over a course of 240 min. After the monomer and initiator were added, the reactor temperature was maintained at 140 °C for another 120 min, after which the contents were cooled to room temperature. The solution polymer had a solids content of 70 wt %. The molecular weight of the polymer was set by the concentration of the initiator; a chain transfer agent was not used. This solution polymer is referred to hereafter as **SL**.

Secondary Dispersion. In a 2 L glass reactor equipped with a stirrer and thermometer, 571 g of the polymer solution (synthesized by the method described above) was added and heated to 60 °C. When the temperature stabilized at 60 °C, 19.8 g of N,N-dimethyl ethanolamine (DMAE) was added over a 5 min period. The mixture was then stirred at 60 °C before demineralized water (631 g) was added over 10 min, during which the temperature dropped to 42 °C. The temperature was set at 40 °C. After 15 min, the MEK was removed by means of vacuum distillation until the residual level of MEK was below 200 ppm, as determined by gas chromatography. The final dispersion had a solids content of 38 wt %, and the pH was 7.4. This secondary dispersion polymer is referred to hereafter as **SD**. A schematic diagram showing the steps in the preparation of the SD polymers is presented in Figure S1 in the Supporting Information.

Dialyzed Emulsion Polymer. To investigate the effects of the presence of surfactants and interparticle boundaries, we prepared dialyzed emulsion polymer (designated as **DEm** hereafter). The emulsion polymer dispersion was filled into a dialysis tubing (obtained from Sigma-Aldrich, D6191) that retained the species with a molecular weight above 12 kDa. The latex in the tubing was then immersed in a glass beaker filled with deionized (DI) water. The dialysis process lasted for a week, and the DI water was changed daily. Some of the excess surfactant and other water-soluble material was thought to be removed according to the surface tension analysis of the dispersions using a Wilhelmy plate (NIMA, Coventry, UK). The initial surface tension of the Em dispersion (30 wt %) was 20.5 mN/m. It increased

Table 1. Comparison of the Main Features of Three Types of Polymers

polymer type	surfactant present	particle size (nm)	particle size dispersity	molecular weight, M_w (kDa)	polydispersity index, M_w/M_n	T_g (°C)
Em	yes	98	0.25	55	4.6	29
SD	no	200	0.24	32	5.3	33
SL	no			32	5.3	35

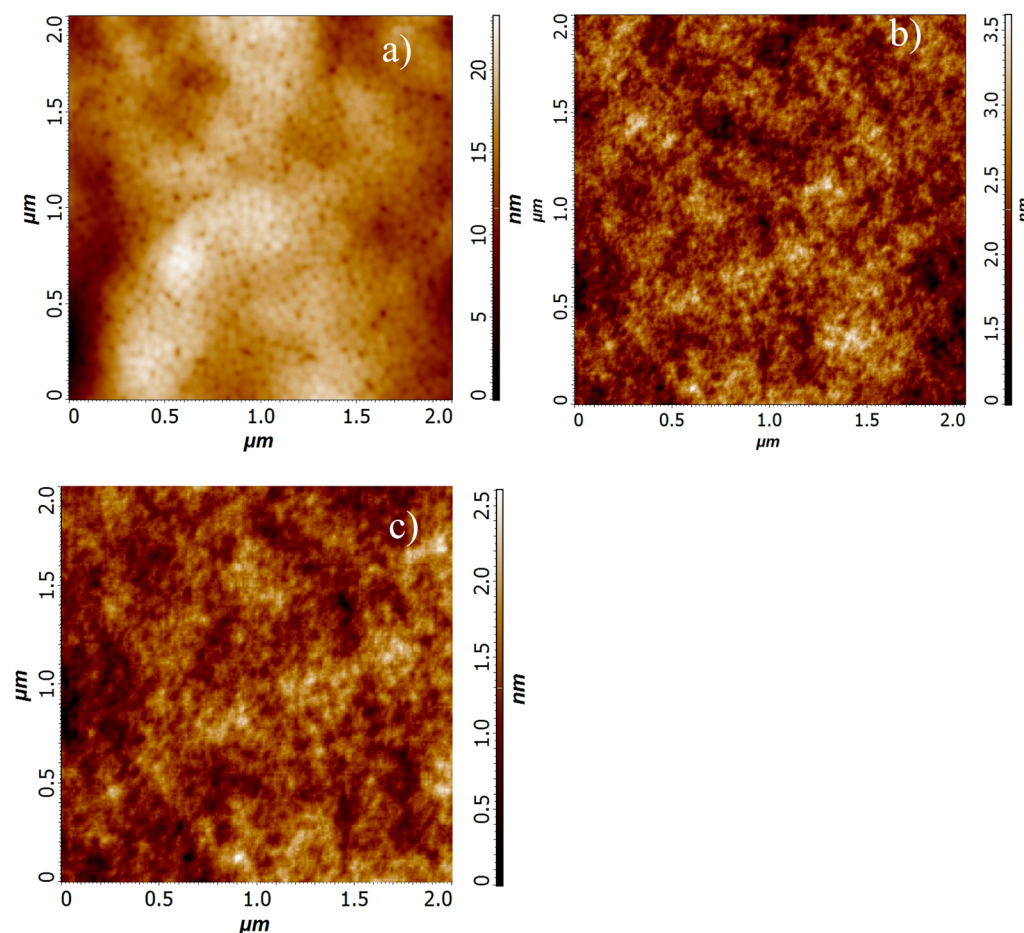**Figure 1.** AFM height images (2 μm × 2 μm) of the surfaces of three types of coating: (a) emulsion polymer (Em), rms roughness S_q = 14.3 nm; (b) secondary dispersion (SD), S_q = 1.8 nm; and (c) solution (SL), S_q = 1.0 nm.

to 39.8 mN/m (30 wt %) after being dialyzed, which indicates the removal of some surface-active species.

Solution Polymer from the Emulsion Polymer. The emulsion polymer was cast on a poly(tetrafluoroethylene) (PTFE) substrate, dried thoroughly at 50 °C for 1 day, and then dissolved in methyl ethyl ketone (MEK) solvent to make a polymer solution (designated hereafter as **Em-MEK**). The solids concentration in the solution in MEK was 40 wt %.

Secondary Dispersions with Pre- or Post-added Surfactant. The secondary dispersion with pre-added surfactant (designated as **SD-pre**) was made by the addition of 3 wt % of ADBS (measured on the polymer weight) during the secondary dispersion process of the solution polymer. The surface tension decreased significantly from 34.9 to 6.2 mN/m after being emulsified. The secondary dispersion polymer with post-added surfactant (designated as **SD-post**) was obtained by the addition of the same concentration of surfactant after the completion of the secondary dispersion process. The surface tension was 30.5 mN/m. It appeared that the surfactant was not absorbed, probably because of charge repulsion between the anionic surfactant and the COO^- groups on the particles. The surfactant solution was added using a micropipette into the secondary dispersion while agitating using a magnetic stirring bar at 60 rpm. After the

completion, the resultant dispersion was continuously stirred for several hours.

2.2. Characterization. *Atomic Force Microscopy.* Atomic force microscopy (AFM) was carried out on the specimens on a commercial microscope (NT-MDT, Moscow) in semicontact mode using a Nanosensors PPP-NCH-W cantilever with a nominal resonant frequency in the range of 204 to 497 Hz and a force constant between 10 and 130 N m^{-1}. A set point ratio (ratio of the landed magnitude to the free oscillation magnitude) of 0.75 was used. Films for AFM were cast onto PET sheets using a 60 μm spiral bar coater. They were then allowed to dry in air for 24 h before additional drying in an oven at 50 °C for another 24 h. Samples were kept in air at room temperature and were rinsed with deionized water to remove surfactant prior to analysis. The root-mean-square (rms) roughness (S_q) of the surfaces was measured from the images using Nova software (NT-MDT).

Moisture Sorption. Sorption isotherms were obtained using a benchtop dynamic vapor sorption analyzer (IGAsorp, Hiden Isochema, Warrington, UK). It uses an ultrasensitive microbalance to measure the mass of the sample as a function of time and relative humidity (RH) at a fixed temperature. The inlet pressure had a constant value of 4.0 bar. The capacity of the balance is 100 mg, and its resolution is 0.1 μg. Controlled humidity was maintained using a

laminar flow with wet–dry vapor mixing at a constant mass flow rate (500 mL/min) with feedback control. This flow rate avoided mass transfer limitations.

In an adsorption experiment, the sample was initially held at an RH of 0% at a temperature of 25 °C until the mass was stable over time, indicating equilibrium. This mass was used as a reference mass for the mass uptake calculations. The RH was increased to 90% in steps of 10%. At each RH, the mass was recorded as a function of time until it reached equilibrium, which was designated to be when the mass increase fell below 0.01% over an interval of 1 min. The water activity, a_w, is defined as RH/100.

Samples for moisture sorption experiments were prepared by casting the polymer dispersions and solutions onto a PTFE block with an average wet thickness of 300 μm. The coatings were then dried at room temperature for 1 d and then peeled off the substrate. The sample size was 1 × 1 cm. Specimens were stored in an airtight desiccator with silica gel away from direct sunlight. Before the sample was placed on the hanging pan of the humidity chamber, its thickness was measured using a digital caliper. The pans were cleaned using acetone prior to use.

Differential Scanning Calorimetry. Small pelletlike samples were prepared for differential scanning calorimetry by drying 1 mL droplets of the waterborne or solventborne polymers in air for 24 h before drying in an oven at 50 °C in air for 24 h. The glass transition temperature (T_g) of the polymers was measured with a commercial differential scanning calorimeter (TA Instruments DSC-Q1000, UK) at a heating rate of 10 °C/min in nitrogen. The samples were heated from −60 to 60 °C and then cooled to −60 °C, followed by a second heating from −60 to 60 °C. The T_g was found using TA Instruments Universal Analyzer software, taking the midpoint of the transition in the second heating as the value for T_g

3. RESULTS

3.1. Structure and Properties of Polymer Coatings.

The monomer composition in the emulsion (Em), secondary dispersion (SD), and solution (SL) polymers was nominally the same. The characteristics of these three main polymers are presented in Table 1. The mean particle size of the Em polymer is lower, and its molecular weight is higher, in comparison to the values in SD polymer. The T_g of the Em polymer is 4 °C lower than that of the SD polymer, which can be attributed to the plasticizing effect of the surfactant. In all of the aqueous dispersions, the pH was adjusted to 7 prior to use. According to the literature value[29] of pK_a = 6.5 for poly(acrylic acid), the carboxylic acid groups in the waterborne colloids will be fully ionized to COO⁻ when the coatings are cast.

The surface morphologies of the three types of polymer coatings are shown in the AFM height images in Figure 1. Individual particles are apparent at the surface of the Em film, whereas in the SD and SL films, there are no obvious particle boundaries. The Em film has the greatest surface roughness as a result of the particle structure, whereas the SL film, cast from solution, has the lowest roughness. Individual particles cannot be observed at the surface of the SD films, indicating that the particles have coalesced, which is not the case for the Em films.

3.2. Water Vapor Sorption Isotherms.

Dynamic water vapor sorption analysis was performed on all seven types of polymer coating. The results from a typical experiment are shown in Figure 2 for an SL coating. The water vapor activity (a_w) is varied from 0, indicating the dry state, to 0.90 with steps of 0.1. It can be seen that successive sorption mass uptake curves appear in response to the steps in the external water activity. At each step, the sorbed water vapor approaches equilibrium as time increases and the saturated state is reached. The equilibrium sorbed amount is obtained as a function of water activity to provide a sorption isotherm. In section 3.4,
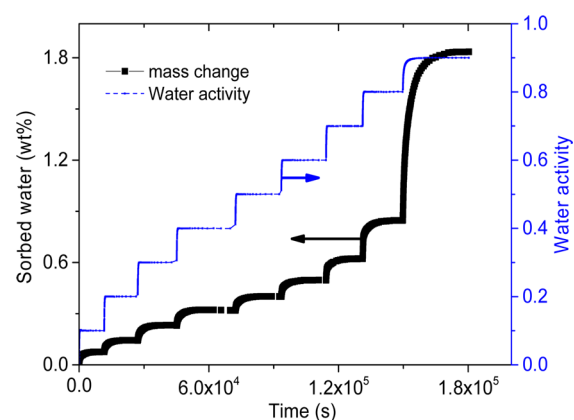

Figure 2. Water vapor sorption kinetics in an SL coating as the water vapor activity, a_w, increases over a range of 0 to 0.9 with increments of 0.1. The black line is the water vapor uptake curve. The blue line is the water activity curve.

studies of the dynamics of vapor sorption will be presented, in which measurements of the sorbed water amount as a function of time are used to calculate the diffusion coefficients of each water activity.

3.3. Comparison of Sorption Isotherms for Water-borne and Solvent-Cast Polymers.

Figure 3 presents the water vapor sorption isotherms for the seven types of polymer. The total mass uptake is the sum of water *adsorbed* on internal surfaces (such as the walls of pores) and water *absorbed* in the polymer phase. Because it is not possible to conclusively distinguish adsorption and absorption using gravimetry, the process is referred to simply as sorption. Attempts were made to fit the data to three different sorption models: (1) the Brunauer–Emmett–Teller (BET) model,[30,31] (2) the ENSIC model,[30,32,33] and (3) the Guggenheim–Anderson–De Boer (GAB) model.[31,34−37] A comparison of the fitting to the data using these three models is presented in Figure S2 in the Supporting Information.

The GAB model is a modified form of the well-known BET model, which is used to describe mathematically the mass fraction m_t (expressed on the dry sample mass) sorbed at equilibrium as a function of the water activity a_w. The GAB model is expressed as[35]

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

where m_m is the monolayer moisture content (in units of g H₂O/100 g), K is the ratio of the heat of adsorption to the heat of liquefaction, and C_{GAB} is a material constant.[30] Although C_{GAB} is essentially used as a fitting parameter, in the model it is physically related to the heat required for the sorption of the first layer and multilayers of water vapor at a given temperature.[38] Whereas the BET model has been applied successfully to describe the water sorption by hydrophilic glassy polymers only at low activities ($a_w < 0.5$), the GAB model has been applied successfully in fitting data across the entire range of activity from 0 to 0.95 in such systems where Type II and III BET isotherms are found.[35] The GAB model has been applied previously to the sorption of water vapor in nonporous hydrophilic polymers, e.g., poly(acrylic acid)[38] and carbohydrate polymers,[39] and poly(hydroxybutyrate).[40] The GAB model assumes that vapor adsorbs on inner surfaces in multilayers; however, it is able to describe adequately the

isotherms found for nonporous polymers.[41] Because latex films are known to have porosity, the model is particularly suitable for this system. According to the GAB model and other localized sorption theories, the penetrating molecule is assumed to bind at specific sites, including the boundaries between particles, in pores, in micro- and nanocavities, and at polar centers.[30]

On the basis of the correlation coefficient (R^2), the GAB model was determined to provide the best fit to the experimental data of the three models. Hence, the values of the three parameters of the GAB model will be employed here in a quantitative comparison of the sorption isotherms. The solid lines in Figure 3 show the fits to the GAB model for each
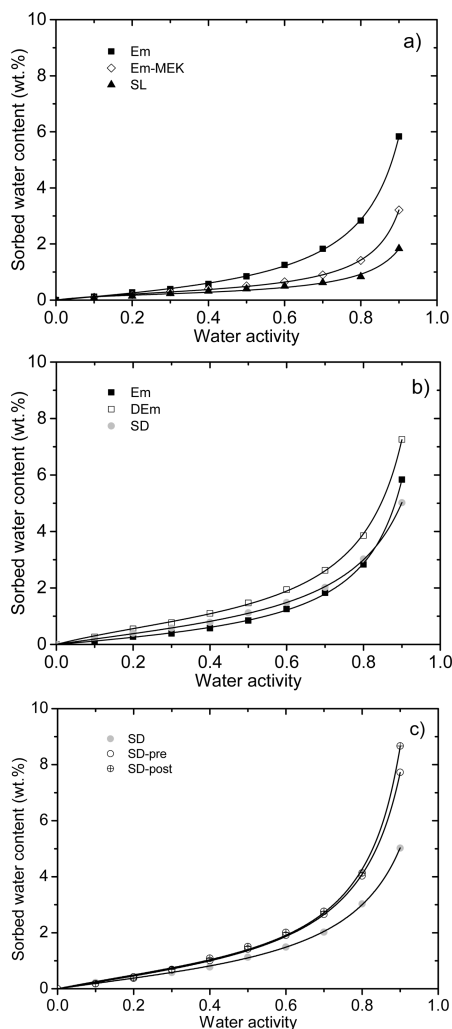
Table 2. Best-Fit Parameters of the GAB Models for Water Vapor Sorption in the Seven Different Types of Polymer Coating

type of film	fitting parameters in the GAB model			
	m_m (g/100 g)	C_{GAB}	K (J/J)	R^2
SL	0.19	10.33	0.99	0.9917
Em	0.73	1.83	0.98	0.9979
DEm	0.93	3.88	0.97	0.9996
Em-MEK	0.28	6.00	1.02	0.9997
SD	0.72	4.01	0.96	0.9981
SD-pre	0.92	3.25	0.98	0.9992
SD-post	0.95	2.87	0.99	0.9986

Effect of Particle Boundaries. We first consider the coatings that are deposited from colloidal polymers. Figure 3a compares the water sorption isotherms for Em coatings (which are cast from particles) with those in Em-MEK and SL coatings, which are cast from a solution in organic solvent. The isotherm of the SL film is linear at lower activities ($a_w < 0.8$), which is consistent with Henry's Law, in which the mass sorbed is directly proportional to a_w. All of the other polymers studied here display a Type III BET sorption isotherm. This type of isotherm is characteristic of hydrophobic polymers containing some polar groups,[42] such as −COOH in the polymers studied here. It is explained by the clustering of the penetrating water molecules, which are nonsolvent but can swell the polymer. The formation of water clusters at increasing activities can influence the kinetics of the sorption process,[8,43] and this influence will be reported for these systems in section 3.4.

AFM surface analysis and cross-sectional analysis using scanning electron microscopy (not shown here) found that there are no pores visible in the SL film (within the resolution of the techniques). Assuming that the SL film is fully nonporous, the sorbed water must be dissolved within the polymer phase. The chemical composition of the SL film is known, and there are reported values of the molar water sorption per structural group of the monomer compositions (see the data from van Krevelen et al.[42] in Table S1 in the Supporting Information). Therefore, the experimental equilibrium sorption isotherm can be compared to what is predicted when assuming additivity of the sorption of independent structural groups.[14] The dependence of the mass uptake on water activity for the SL film is broadly consistent with the predictions, but the experimental values are lower (see the comparison in Figure S3 in the Supporting Information). The greatest contribution to the water sorption is from the carboxylic acid (−COOH) group in the acrylic acid comonomer. In the polymeric state, sorption can be reduced by the rigidity of the molecules and molecular entanglements, which are not considered when summing the sorption of the constituent chemical groups. Hence, the predictions are not expected to agree perfectly in the case of a polymer. Furthermore, it was assumed in the calculation that there is no ionization of −COOH to form −COO⁻ as the SL film was cast from the organic solvent, but the presence of −COO⁻ would increase the water sorption according to the data in Table S1 in the Supporting Information.

The sorption of water vapor by the SL coating provides a baseline for comparison because it is nonporous and surfactant-free. As a general trend, it can be seen that the solvent-cast films (SL and Em-MEK) sorb a lower amount of water vapor compared to that in the waterborne Em film, especially at

Figure 3. Water sorption isotherms for the seven types of polymer coating (identified in the legends). The data points present the experimental data. The solid line shows the best fit to the GAB model using the parameters listed in Table 2. (a) Em (□), Em-MEK (◇), and SL (▲); (b) Em (■), DEm (□), and SD (●); c) SD (●), SD-pre (○), and SD-post (⊕).

of the data sets using the values of the fitting parameters listed in Table 2. Linear regression was performed using a Levenberg−Marquardt algorithm with Origin software (version 8.5). To reduce the effects of correlation between the parameters, we initially set K to 1.0 while C_{GAB} and m_m were fit. After the initial values of C_{GAB} and m_m were obtained, all three parameters were then varied to find the best fit.

higher water activities. The equilibrium moisture content of the Em film is 5.8 wt % at $a_w = 0.9$; the value for the Em-MEK film is lower at 3.2 wt % at the same activity, and the SL film is only 1.8 wt %. The additional water uptake in the Em film compared to that in the Em-MEK film is attributed to the presence of particle boundaries and nanopores between particles, which provide adsorption sites. There are differences in the chemical composition of the Em-MEK and SL polymers that can explain their differences in water sorption, as will be discussed next.

Effect of Surfactant. In the waterborne systems, there are some differences in chemical composition that can potentially change the hydrophilicity and hence the moisture sorption. The Em polymer contains 3 wt % anionic surfactant (ADBS), whereas the SD polymer is free of surfactant. The water phase of Em polymers contains nonadsorbed surfactant and residual species from the initiator, whereas the water phase of the SD polymer contains only the ions used to adjust the pH. The monomer compositions of Em and SD polymers are nominally the same, but the distribution of monomer units along the molecules and within the particles could differ between the two. In particular, the monomer distribution in the emulsion polymer is expected to be less random in distribution along the molecule. Thus, there are several differences between the Em and SD polymers. Figure 3b compares the vapor sorption isotherms of Em, DEm, and SD polymers. Some of the surfactant has been removed from the DEm film by dialysis, yet it sorbs 7.3 wt % water at $a_w = 0.9$, which is more than what was found for the original Em film. This result can be explained by the heterogeneities in the distribution of the hydrophilic species in the DEm polymer, which form randomly distributed water pockets and increase the water content in the aggregates of surfactants. A second factor is that the water-soluble species in the original Em polymer (such as polyacrylate oligomers, which have been studied elsewhere)[44] could increase the rate of particle coalescence by plasticizing the polymer near the particle interfaces.[14,45] When the Em polymer is dialyzed, there would be little or no interfacial plasticization, and water could be adsorbed along the noncoalesced particle boundaries.

The equilibrium sorption of the SD polymer at $a_w = 0.9$ is 5.0 wt %, which is slightly lower than what was found in the Em polymer. The differences in the chemical compositions of the SD and Em polymers have only a minor effect on the equilibrium vapor sorption. In Figure 3a, the greater water sorption in the Em-MEK polymer compared to that in the SL polymer is explained by the presence of the surfactant in the former and possibly some differences in the randomness of the monomer distribution.

The SD-pre and SD-post coatings contain the same amount of surfactant, but it could be distributed differently within them depending on the method by which it is added to the SD polymer dispersions. In the SD-pre polymers, the surfactant is used in the emulsification process, during which it will adsorb at the polymer–water interfaces in a monolayer. In the SD-post polymers, however, monolayer adsorption might not be achieved. Comparing their sorption isotherms provides insight into the effects of surfactant on the water vapor sorption. In Figure 3c it is seen that, in comparison to the SD polymers, the SD-pre and SD-post polymers sorb more (7.7 and 8.7 wt %, respectively). The additional amount of sorbed water is attributed to water adsorption by the added surfactant. We propose that in the SD-post film, the surfactant is heterogeneously distributed and exists in clusters or agglomerates. Thus, it is more accessible and has a higher probability

for water encounters with the surfactant molecules, and its equilibrium water sorption is higher than that found in the SD-pre film.

From the water vapor isotherms of the different polymer coatings, it is concluded that the amount of water vapor uptake in an equilibrium state at an RH of 90% follows the order: SD-post > DEm > SD-pre > Em > SD > Em-MEK > SL. The two solvent-cast polymers (Em-MEK and SL) display isotherms that are flatter (shallower slope) and have less curvature with increasing activity in comparison to those of the five colloidal waterborne polymers. Analysis of the isotherms also reveals a trend in the GAB parameters: generally, the two solvent-cast polymers (SL and Em-MEK) have lower m_m values and higher C_{GAB} values in comparison to those of the five waterborne polymers (see Figure S4 in the Supporting Information).

It is instructive to examine the monolayer moisture content, m_m, which is a measure of the sorptive capacity. The Em and SD films have higher values of m_m (0.73 and 0.72 g/100 g, respectively) in comparison to those in the SL and Em-MEK films (0.19 and 0.28 g/100 g, respectively), which can be explained by a higher internal surface area in the former resulting from their constituent particles. Hence, the mass of a monolayer of water in the Em and SD films is higher. The effects of surfactant leading to a higher water monolayer sorption can be observed in the values of mm for SD-pre and SD-post (0.92 and 0.95 g/100 g, respectively) compared to the value in SD (0.72 g/100 g). The results indicate that the monolayer sorption is increased only with the addition of surfactant to the SD polymer. In a study of blends of surfactant with hydrophilic hydrocolloids, Villalobos et al.[46] found that m_m increased slightly as the hydrocolloid was increased in proportion to the surfactant. They explained the results by an increased number of available hydrophilic adsorption sites.

It is somewhat surprising that m_m for Em and SD polymers are essentially the same, despite the presence of surfactant in the Em polymer and their differences in particle sizes. The particle size of the SD polymer is twice that of the Em polymer, which means that the particle surface area per unit volume of Em coating (before particle coalescence) is twice that of the SD coating. However, according to standard models of polymer sintering during film formation,[47] the rate of particle deformation driven by the reduction of surface energy varies inversely with the particle size. Thus, although the Em coating initially has a larger interfacial area per unit volume, the smaller Em particles are expected to be deformed to a greater extent at a particular time in comparison to the larger SD particles. The results indicate that these two competing effects lead to similarities in the water sorption of the Em and SD polymers.

3.4. Water Vapor Diffusion. Next, we consider the rates of water vapor sorption in polymer coatings, as are characterized by the diffusion coefficients obtained from the standard model of Fickian diffusion. Figure 4 presents representative dynamic data for an SL film with an external water activity of $a_w = 0.5$. M_t, which is the mass of the sorbed water in the polymer at a time of t, and which is normalized by the total mass of sorbed water in the equilibrium state, M_∞. If the water has a single diffusion coefficient, D, in the polymer, the normalized mass sorption of water is given by the equation[48]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{l^2}\right]$$
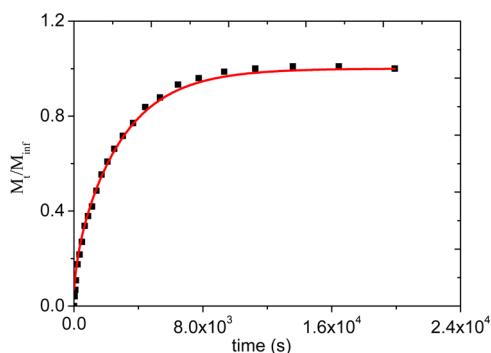
$$(2)$$

Figure 4. An example of the kinetics of water sorption in an SL polymer, in which the normalized water mass uptake (M_t/M_∞) is shown as a function of time with $a_w = 0.5$. The data are well fit by the Fickian diffusion equation (eq 2) with $D = 2.0 \times 10^{-8}$ cm^2/s, shown as the solid red line.
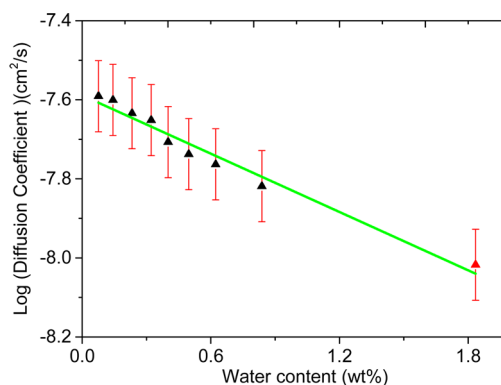

Figure 5. A plot of the logarithm of the water diffusion coefficient against the sorbed water content in an SL coating. The green line shows the fit to eq 3.

where l is the thickness of the dry film. Figure 4 demonstrates that the data can be fit to eq 2 by regression with D as the only adjustable parameter. In most cases, an adequate fit, determined by a low χ^2, was obtained when using only two terms in the summation ($n = 0$ and $n = 1$). The model was found to be in good agreement with the experimental data for the SL film at this water activity and others in the range from 0 to 0.9 (Figure S5 in Supporting Information). For the particular example in Figure 4, D was found to be 2.0×10^{-8} cm^2/s, which is slightly lower than the value of 5×10^{-8} cm^2/s that was reported elsewhere for an acrylic latex film containing anionic surfactant.[9] It is inexplicably higher than the value of $D = 4 \times 10^{-9}$ cm^2/s that was reported for a carboxylated poly-(styrene−butadiene) latex containing sodium lauryl sulfate surfactant.[7]

In hydrophobic polymers, in which the solubility of water is very low, the water diffusivity is independent of the water content. However, when there is some hydrophilic character, water molecules form clusters at polar centers that reduce the molecular mobility. In such instances, van Krevelen and te Nijenhuis[42] proposed that D depends on the water sorption w (expressed as weight percent) as

$$\log D = \log D_{w=0} - s \cdot w \qquad (3)$$

where $D_{w=0}$ represents the diffusion coefficient in the initial dry polymer, and s is a constant (given as 0.08 by van Krevelen and te Nijenhuis).[42] For the SL polymer, D was measured over a range of a_w from 0 to 0.9. At each a_w, the sorbed amount w is obtained from the sorption isotherm. Figure 5 presents the data to test the predictions of eq 3 and obtains the expected linear relationship with $D_{w=0} = 10^{-7.6}$ cm^2/s and $s = 0.25$.

We obtained the diffusion coefficients for water at multiple water activities in the various other polymer types. However, in these other systems in which there are heterogeneities, the linear dependence predicted in eq 3 was not found. Instead, D showed a better inverse correlation with a_w, which determines w through the sorption isotherms (Figure 3). Hence, the data will be presented as a function of a_w. Extending the equation of van Krevelen and te Nijenhuis, we propose an exponential equation to describe the dependence:

$$D = D_{a_w=0} \cdot e^{(-a_w/c)} + D_{a_w \approx 1} \qquad (4)$$

where c is a dimensionless parameter to describe the exponential dependence. A lower value of c indicates that D

depends more strongly on the water concentration. The subscripts on D designate the values at the lowest a_w of 0 and the highest a_w of 1.

A comparison of results from the Em, Em-MEK, and SL films (Figure 6a) shows the effects of particle boundaries on the diffusion dynamics and will be considered first. D for water molecules in the Em and Em-MEK films decreases strongly with increasing external water activity (a_w) and hence also with the sorbed water content, as shown by the fits to eq 4. For the Em and Em-MEK films, there are particularly high values of D (8.9×10^{-8} and 8.1×10^{-8} cm^2/s, respectively) observed at $a_w < 0.3$. The fast diffusion cannot be explained by the presence of particle boundaries in the solvent-cast Em-MEK film. Instead, we attribute the faster diffusion to the presence of the polar sulfonate groups in the surfactant and other polar species in the latex serum. In the initial dry state at $a_w = 0$, the polar groups are not hydrated. Because the activity is raised, the attraction of water to the polar groups provides a driving force for transport. Water molecules that are weakly bound to the hydrophilic polar groups are able to move along pathways of surfactant and thereby result in a much higher rate of diffusion in comparison to that of the SL films that do not contain surfactants.

At higher activities ($a_w > 0.6$), water in the Em-MEK and Em films diffuses at the same slower rate as in the SL film (within the errors of the measurement). The presence of surfactant and particle boundaries does not have an obvious effect on diffusivity at high sorbed water contents. When larger amounts of water are absorbed in the Em and Em-MEK films, water molecules can become bound in clusters that develop at polar centers within the film. Clustering of water molecules is known to reduce molecular mobility and cause the diffusion rate to slow at higher water activities.[42] In colloidal films, water clusters can form at particle boundaries as illustrated in Figure 7.

It is noteworthy that water diffuses at the same rate in the Em films as in the Em-MEK films that have no particle−particle interfaces nor voids at plateau borders. Only at $a_w = 0.2$ is there any apparent effect of the presence of the boundaries when diffusion is slower in the Em-MEK film. This result points to the conclusion that chemical effects have a greater influence than structural effects on water diffusivity.

The influence of the chemical nature of the particle interfaces on water diffusivity is explored by comparing the results from Em, DEm, and SD films (Figure 6b). At low water activities, D is significantly higher for the Em film. In the other two films, which have fewer polar groups at the particle boundaries, there
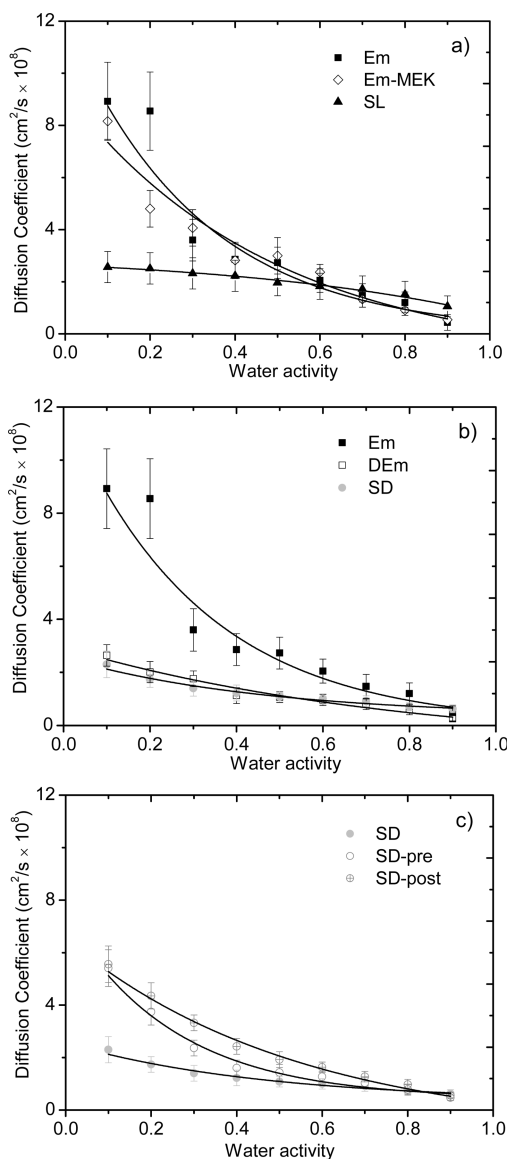
Figure 6. Diffusion coefficient of water in the various polymer coatings as a function of the water activity, a_w. The solid line represents the fit using eq 4. The samples and symbols are the same as used in Figure 3. (a) Em (■), Em-MEK (◇), and SL (▲); (b) Em (■), DEm (□), and SD (●); (c) SD (●), SD-pre (○), and SD-post (⊕).
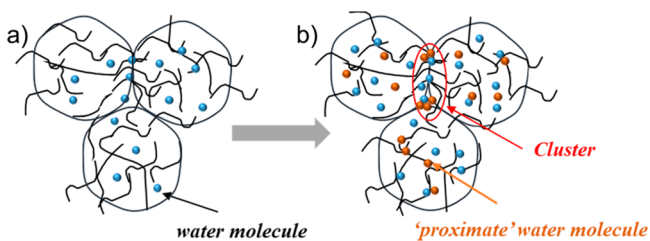

Figure 7. Illustration of the sorbed water molecules in an Em coating with boundaries between particles (a) when the sorbed water content is low (at low a_w) and (b) at high a_w when the water molecules at the particle boundaries (blue spheres) sorb other penetrant water molecules (orange spheres) in the proximity to form clusters. Redrawn from ref 49.

is no driving force from the hydration of the particle boundaries, which can explain the lower D. Figure 6c presents

the diffusion coefficients of water vapor in SD, SD-pre, and SD-post films and reveals the effects of surfactant addition. At $a_w = 0.1$, the diffusion coefficient is 5.6×10^{-8} cm^2/s for the SD-post film, which is close to the value of 5.4×10^{-8} cm^2/s for the SD-pre film. A lower diffusion coefficient ($D = 2.3 \times 10^{-8}$ cm^2/s) is found for the SD film without surfactants. Water vapor diffuses faster in the SD-pre and SD-post films than in the SD film across the whole range of water activities, which indicates that the surfactant at particle boundaries assists the water transport. Diffusivity is strongly dependent on activity in the SD-pre and SD-post films, dropping an order of magnitude from $a_w = 0.1$ to $a_w = 0.9$, whereas there is a weaker dependence in the SD film. At higher activities, the diffusion coefficient of water in all three types of film are low, which points to the effects of water clustering at higher concentrations, regardless of the local chemistry. The Zimm−Lundberg model[43] allows the calculation of the size of water clusters, using appropriate assumptions, but such calculations are beyond the scope of this work.

At intermediate water activities, D is slightly higher in the SD-post film than in the SD-pre film. This difference can be explained by a greater heterogeneity in the distribution of surfactant in the SD-post film. A surfactant monolayer at the polymer−water interface in the SD-pre film might enable the water transport. However, in contrast, the SD-post films might have a less uniformly distributed surfactant, which forms aggregates in some sites.

At the highest water activity, $a_w = 0.9$, water diffuses fastest in the solvent-cast SL polymer, which has the lowest water uptake compared to that of the waterborne polymers. However, in general, at a particular water activity, there is no correlation between the D for the seven types of polymer and their equilibrium water sorption, w. This lack of correlation is apparent (Figure S6 in the Supporting Information). Considering the many differences between the seven types of polymers, it is rather surprising that D differs relatively little (less than 1 order of magnitude in all cases).

3.5. Permeability of Water in Waterborne Polymer Coatings. For many practical applications, water sorption and diffusivity on their own are not of greatest interest. Instead, there is an interest in reducing (or raising) the total amount of water transported through a film per unit of time. The permeability coefficient, P, characterizes the water transport. It is defined as the product of the solubility coefficient, S, and the diffusion coefficient, D:

$$P = S \times D \tag{5}$$

Generally, water permeates in hydrophilic polymers to a greater extent than do permanent gases because of a higher solubility of water compared to that of inert gas molecules. S can be simply obtained from the water vapor isotherms from

$$S = \frac{M_\infty - M_o}{M_o} \tag{6}$$

where M_o is the initial mass at an RH = 0. From the results already reported here, P was calculated for each type of polymer over the range of activities. Figure 8 shows P for water vapor in the films with an external water activity of $a_w = 0.9$. The two solvent-cast polymers (SL and Em-MEK) have the lowest permeabilities. Similarly, Roulstone et al.[20] found that permeability coefficients for latex films were slightly higher than for solvent-cast films. Out of all of the waterborne polymers, the SD polymer has the lowest value of P. The
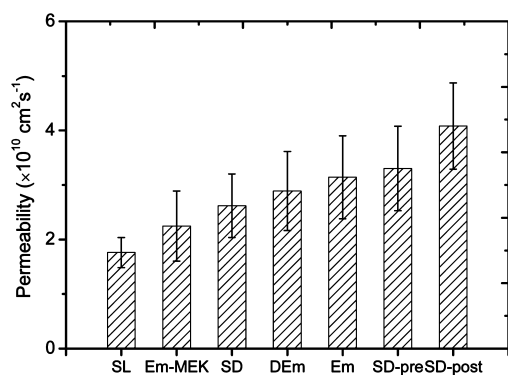
Figure 8. Permeability coefficient of the sorbed water vapor with an external water activity of $a_w = 0.9$ for the seven types of polymer coating.

postaddition of surfactant to the SD polymer films raises P to a value that is approximately double what is found for the SL film. The water permeability coefficients are presented against water activity in Figure S7 in the Supporting Information for all seven types of film. There is a weak positive correlation for each film.

Our calculated values of P for a styrene–acrylic copolymer are higher than the literature values for polystyrene ($P = 1.35 \times 10^{-11}$ cm^2/s) not in the form of latex film.[50] This higher permeability can be attributed to the monomer composition, which includes more hydrophilic acrylic monomers that increases the water sorption. Our P values for the waterborne polymers are slightly higher than what was reported by Kim et al.[9] for the permeability of water vapor in 2-ethylhexyl acrylate copolymer latex films but of the same order of magnitude (equivalent to 1×10^{-10} cm^2/s).

4. CONCLUSIONS

These experiments provide insight into the combined effects of particle boundaries and surfactants on water vapor equilibrium sorption and diffusivity in polymer films. In both waterborne and solvent-cast coatings of a styrene–acrylate copolymer, the water vapor sorption isotherms were classed as Type III, which are typical for hydrophobic polymers containing some polar groups in which the penetrating nonsolvent water molecules form clusters. Fickian diffusion of water was found in all seven types of polymer coating.

Films deposited from secondary dispersions have properties that are attractive for waterborne barrier coatings. Compared to the other waterborne polymer systems, the SD films show the lowest equilibrium vapor sorption at high water activities ($a_w = 0.9$) and the lowest diffusion coefficient at low activities ($a_w = 0.3$). In a comparison of the waterborne polymers, the SD films have the lowest permeability coefficient at high water activities ($a_w = 0.9$), which are of greatest interest in applications. When particle boundaries are removed from the emulsion polymer by dissolving it in organic solvent, the permeability to water vapor is reduced, but it is still higher than the permeability of the corresponding copolymer. These results reveal that the surfactant-free secondary dispersion of polymers in water offers better barrier properties than emulsions polymers with the same copolymer composition. Some of the differences in barrier properties when comparing Em and SD coatings are small in absolute terms, but even marginal differences can be amplified to become significant when a coating is in service for many years. Although our focus here is on applications as

barrier coatings, the results are also highly relevant to waterborne soft adhesives, in which water vapor sorption at relative humidity has been shown to have a detrimental effect on adhesion.[51]

The combination of *added* surfactant and the presence of particle interfaces in the case of secondary dispersions resulted in the highest equilibrium water vapor sorption (and hence the highest permeability to water vapor) at high external water activities. However, the water diffusivity at high activity was similar in value for all of the waterborne systems. In all seven polymer systems, D was described by an exponential dependence on the water activity. Diffusion is slowed by water clustering with increasing amounts of sorbed water at high activity regardless of the structure and any differences in chemical composition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic of the secondary dispersion process; graphs showing BET and ENSIC sorption isotherm models, water sorption isotherms for seven types of film compared to values in models, comparison of calculated sorbed water content with experimental data, correlation of C_{GAB} and m_m for seven types of film, plots of M_t/M_∞ against the diffusion time in SL films corresponding to water vapor activities, water diffusion coefficients as a function of sorbed water content for films at various water activities, and permeability of various polymer films as a function of water activity; and a table showing molar water content sorbed by structural groups of amorphous polymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02446.

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