Modeling of Moisture Sorption Isotherms of Poly(vinyl alcohol)/Starch Films

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ABSTRACT: Studies on the moisture sorption characteristics of poly(vinyl alcohol)/starch blends for water activity (a_w) values of 0.1–0.9 were performed at 27°C. The equilibrium moisture content at different a_w values was used to fit different sorption isotherm models proposed in the literature. The ranges of a_w applicable for the different sorption isotherms were reported. The model constants of the sorption equations were determined by linear fitting. The value of the coefficient of determination (0.98 ± 0.01) confirmed the goodness of fit of the equations studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3874–3881, 2003

Key words: biodegradable; films; hydrophilic polymers

INTRODUCTION

With growing awareness of the use of bio-based primary packaging materials, plastic films in food packaging are becoming undesirable. Starch has been considered a candidate in certain thermoplastic applications because of its known biodegradability, availability, and low cost. Poly(vinyl alcohol) (PVA) blended with starch can result in films with excellent functional properties suitable for food packaging. The combination of synthetic and bio-based packaging materials has been proposed to increase the efficiency of food quality preservation.[1] The mechanical and barrier properties of bio-based materials must remain stable and function appropriately during storage. They should not pose any environmental hazards when ultimately disposed.[2] The use of PVA/starch blends as packaging materials has better prospects than low-density polyethylene (LDPE)/starch blends because LDPE is nonbiodegradable. However, because both PVA and starch are hydrophilic in nature, it is essential to study their sorption influence to render them suitable for packaging applications. Corn starch was employed in this study because the mechanical properties of films with corn starch were found to be better.[3] The moisture sorption characteristic of starch-filled PVA films were studied in this work. Information on sorption isotherms of PVA/starch films is not available at present. In this communication, studies of the moisture sorption characteristics of PVA/starch films and the applicable ranges of the water activity (a_w) are described.

EXPERIMENTAL

Preparation of the PVA/starch blends

Chemical-grade PVA was procured from Qualigens, Ltd. (Mumbai, India), and corn starch (Riddhi Siddhi) was acquired from a local market in Mysore, India. A series of PVA/starch blends were prepared by variations in the starch content of 10–50% (w/w) with water as a common solvent. The films were cast by the heating of the blends around 80–100°C with constant stirring for 2 h. The solution concentration was optimized at 2.3% (w/v). The solution was poured into a glass plate mold lined with a polyester film through a funnel containing cotton (so that the formation of air bubbles would be avoided). The film was dried at an optimum temperature of 60°C for 8–9 h so that a smooth, flexible, and readily removable film would develop. The cast film was 35 cm × 25 cm with a thickness of 30–40 μm. The dried films were stored at 65% relative humidity (RH) because the initial moisture content (IMC) of the dried film was the same as that of the films stored at 65% RH.

Standards for a_w

Saturated salt solutions of lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, sodium dichromate, sodium nitrite, sodium chloride, potassium chromate, and ammonium phosphate were

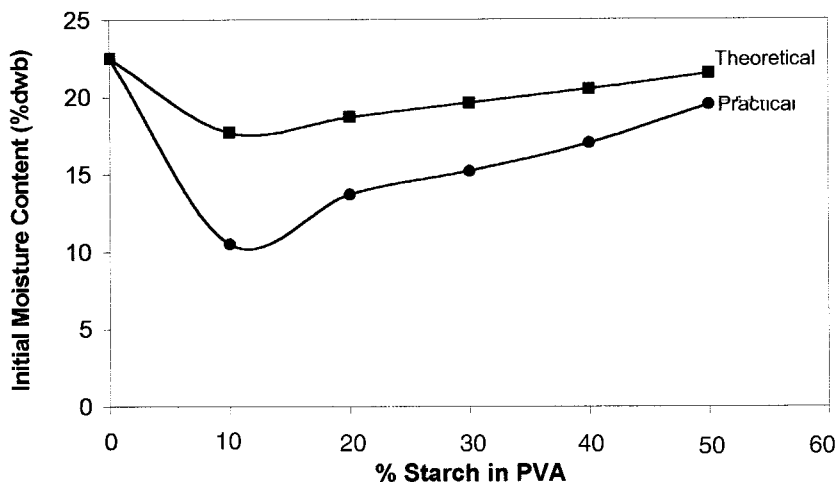*Correspondence to:* B. Raj (baldev1564@yahoo.com).

Figure 1 Moisture content of the PVA/starch films at 65% RH and 27°C.

used as a_w standards of 0.11, 0.22, 0.33, 0.44, 0.54, 0.64, 0.75, 0.86, and 0.92, respectively.[3] The saturated solutions were placed in different desiccators so that different RHs would be obtained. The PVA/starch films were exposed to these environments according to a standard procedure reported by Labuza.[4]

Sorption experiments

The film specimens of the PVA/starch blends were cut into 1 cm $\times$ 1 cm pieces. The films were conditioned to 65% RH at 27 $\pm$ 1°C and exposed to different a_w values for sorption isotherm determination, as discussed by Raj et al.[3]

Sorption isotherm models

A number of sorption isotherm models have been reported in the literature. These models—Brunauer–Emmet–Teller (BET), Smith, Guggenheim–Anderson–de Boer (GAB),[5] Harkins–Jura,[6] Bradley, Oswin, Halsey, Caurie, Kuhn,[7] and Henderson[8]—were used to fit the experimental sorption isotherm data of the PVA/starch films. The BET, Smith, Bradley, Oswin, Halsey, and Caurie models were reported by Raj et al.[3] A rearrangement of some of the equations was performed to facilitate the determination of the appropriate coefficients with a linear fitting.

GAB isotherm model

The GAB isotherm model can be represented as follows:

$$1/M = [(1 - C)K/C]a_w + [1/(CK)/a_w + (C - 2)/2]$$

$$\text{(1)}$$

where M is the equilibrium moisture content and C and K are GAB model constants. With $1/M$ as a dependent variable and a_w and $1/a_w$ as independent variables in multiple regression, C was calculated from the intercept of eq. (1). Because the coefficient of $1/a_w$ was nonsignificant and negligible in the model, the second term in the right-hand side (RHS) of eq. (1) was eliminated. From a linear regression of $1/M$ versus a_w, the GAB constants were computed.

Harkins–Jura isotherm model

The Harkins–Jura model equation relating a_w and M is

$$\ln a_w = B - A/M^2 \qquad \text{(2)}$$

where A and B are Harkins–Jura model constants.

Henderson isotherm model

Henderson formulated the following expression relating a_w and M:

$$\ln M = [\ln[\ln(1/(1 - a_w)]]/B - [\ln(A)]/B \qquad \text{(3)}$$

The Henderson model constants, A and B, were calculated from a linear plot of $\ln M$ versus $\ln\{\ln[1/(1 - a_w)]\}$.

RESULTS AND DISCUSSION

IMC and moisture sorption isotherms

The IMC values of pure PVA, PVA/starch films, and starch powder was determined on a dry weight basis, gravimetrically, after they were exposed to 65% RH ($a_w = 0.65$) at 27 $\pm$ 1°C. As can be seen in Figure 1, the pure PVA film and starch film showed IMCs of 22.5
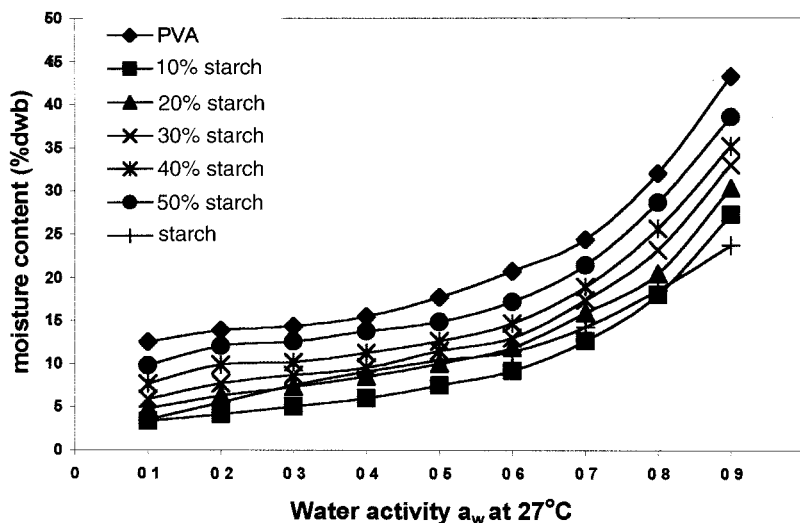
Figure 2 M values of PVA/starch films at different a_w values.

and 13%, respectively, when equilibrated to 65% RH. The IMC values of PVA/starch films with different starch contents (10–50%) lay in the range of 10.5–19.5%. The corresponding theoretical IMC values of PVA/starch were 17.75–21.55%. This uncharacteristic change in the experimental IMC value might have been due to the formation of hydrogen bonds between PVA and starch at the 10% starch level, which might have reduced its capacity to absorb high moisture contents. With a further increase in the starch content from 10 to 50%, the starch partially gelatinized. The gelatinization of starch in the PVA/starch films might have enabled the films to pick up moisture in increasing order from 13.75 to 19.5% at $a_w = 0.65$.

The sorption isotherm curves were drawn from the moisture content and a_w, as shown in Figure 2. The association between a_w and the moisture content (at a constant temperature) can practically be described by a moisture sorption isotherm.[9] The moisture sorption isotherm curves of the PVA/starch blends, as shown in Figure 2, were typically sigmoidal. Primarily, the sorption isotherms showed a sorption behavior consisting of a monomolecular layer, an active molecular layer, and a multimolecular layer. The pure PVA exhibited higher sorption behavior than the pure starch. The slope of the isotherm curves (Fig. 2) decreased tremendously with increasing a_w in the PVA/starch films with the incorporation of a 10% (w/w) starch content, and the slope of the sorption isotherm curves further increased with an increase in the starch content in the PVA/starch films. The slope order was highest in pure PVA and was followed by 50, 40, 30, 20, and 10% starch in the PVA/starch films. The slope for the pure starch film was between the sorption isotherms of the PVA films with 10 and 20% starch contents. This uncharacteristic pattern of sorption isotherms was expected because of the formation of hydrogen bonds

between the PVA and starch polymer network. This resulted in the gelatinization of starch in the PVA matrix with increasing starch content. An increase in the gelatinization of starch increased the moisture-retention capacity of the PVA/starch films.

The M values of the PVA/starch films with 10, 20, 30, 40, and 50% (w/w) starch at extrapolated a_w values of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 at 27°C were measured from Figure 2 for an analysis of the applicability of a_w for all the sorption isotherm models. For starch contents greater than 50%, the PVA/starch films could be cast by a solution method. One of the important observations made during the experimentation was that no visual microbial growth was observed even at 92% RH in any of the samples until the end of the experiment for 25–30 days when the samples attained equilibrium with respect to moisture pickup.

Sorption model analysis

The sorption isotherm constants computed from the isotherm graphs with the M–a_w data for different sorption models are reported in Table I.

BET

It is well recognized that the BET monolayer equation is an effective method for estimating the amount of water bound to specific polar sites in dehydrated systems used for food applications.[10] The BET monolayer concept is a reasonably correct guide for two important reasons: (1) the mobility of small molecules in several food systems becomes apparent at the BET monolayer and (2) the BET monolayer correlates well with the total number of polar groups binding water. From a linear plot of $1/[(1 - a_w)M]$ versus $(1 - a_w)/a_w$,

TABLE I
Values of Sorption Isotherm Model Constants and R^2 Determined from the Linear Fitting of Sorption Equations for PVA/Starch Films

| Isotherm model	Starch content in PVA/starch film	Constants by linear fitting of sorption isotherms		R^2	Range of a_w
	% (w/w)	M_m	C		
BET	10	3.08	−115.79	0.94	0.1–0.4
	20	3.95	−105.46	0.90	
	30	5.68	−45.13	0.98	
	40	6.44	−31.69	0.96	
	50	7.88	−23.94	0.99	
	% (w/w)	M_b	M_a		
Smith	10	7.05	13.13	0.98	0.2–0.9
	20	4.98	12.59	0.99	
	30	3.46	12.31	0.98	
	40	2.57	11.51	0.98	
	50	0.49	11.07	0.99	
	% (w/w)	K	C		
GAB	10	0.51	2.61	0.97	0.1–0.9
	20	0.35	2.41	0.97	
	30	0.28	2.34	0.98	
	40	0.21	2.27	0.98	
	50	0.16	2.21	0.98	
	% (w/w)	B	A		
Harkins–Jura	10	−0.12	31.45	0.96	0.4–0.9
	20	−0.07	62.50	0.99	
	30	−0.06	80.00	0.99	
	40	−0.03	109.89	0.99	
	50	0.01	166.67	0.98	
	% (w/w)	K_1	K_2		
Bradley	10	0.07	0.77	0.98	0.4–0.9
	20	0.19	0.85	0.98	
	30	0.21	0.87	0.98	
	40	0.26	0.89	0.98	
	50	0.31	0.94	0.99	
	% (w/w)	a	n		
Oswin	10	7.72	0.58	0.99	0.5–0.9
	20	9.96	0.51	0.99	
	30	11.23	0.50	0.99	
	40	12.51	0.48	0.99	
	50	14.72	0.45	0.99	
	% (w/w)	a	B		
Halsey	10	1.78	−0.70	0.99	0.4–0.9
	20	2.10	−0.60	0.99	
	30	2.22	−0.58	0.99	
	40	2.36	−0.55	0.99	
	50	2.54	−0.50	0.99	
	% (w/w)	A	r		
Caurie	10	1.74	−2.95	0.98	0.4–0.9
	20	2.87	−2.51	0.98	
	30	3.32	−2.45	0.97	
	40	4.05	−2.30	0.97	
	50	5.34	−2.10	0.96	
	% (w/w)	a	b		
Kuhn	10	1.94	3.85	0.98	0.2–0.6
	20	3.86	4.15	0.99	
	30	5.23	4.08	0.99	
	40	7.30	3.72	0.99	
	50	9.51	3.85	0.99	
	% (w/w)	K	n		
Henderson	10	2.60	0.48	0.97	0.1–0.6
	20	2.90	0.41	0.99	
	30	3.03	0.36	0.98	
	40	3.17	0.28	0.96	
	50	3.39	0.24	0.96	
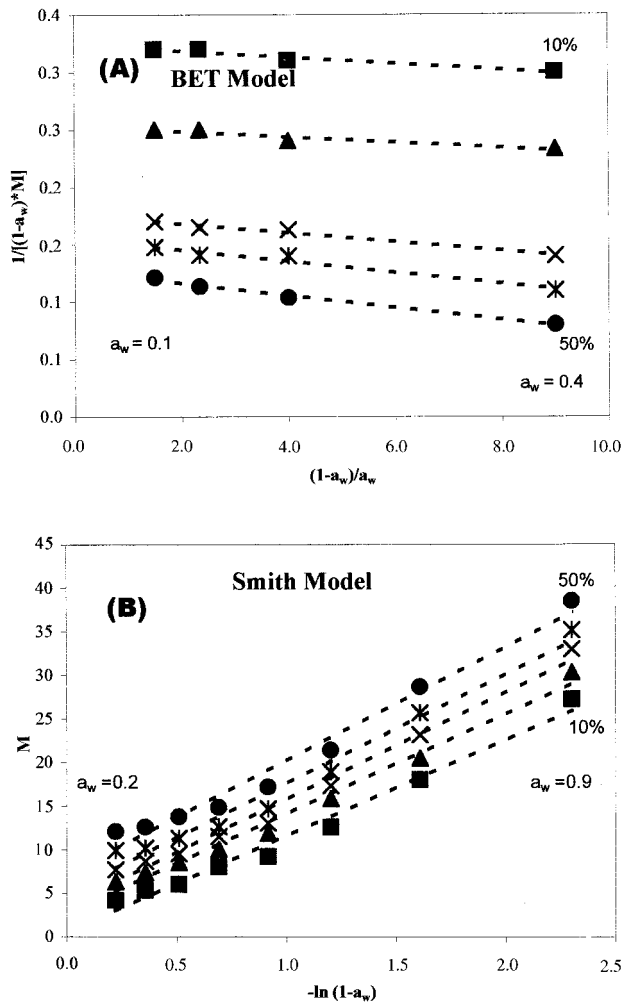
Figure 3 Data for the experimental sorption models (symbols) and fitted models (broken lines): (■) 10, (▲) 20, (×) 30, (+) 40, and (●) 50% PVA.

the BET constants M_m (the monolayer moisture constant) and C were computed. The experimental sorption data applied to the BET model for various starch contents of the PVA/starch films, as shown in Figure 3(A), were found to fit well for $a_w = 0.1–0.4$. Chirife and Iglesias[11] and Raj et al.[3] demonstrated that the BET equation was good for the aforementioned range of a_w. The BET constants were determined from a linear fitting of the BET equation,[3] and the corresponding values are given in Table I. The values of M_m varied from 3.08 to 7.88, indicating that different PVA/starch blends had different capacities for moisture sorption and also for the availability of free water. The monomolecular moisture parameter of the BET equation is important for shelf-life studies.

Smith

From a linear regression of M versus $\ln(1 - a_w)$, Smith[3] constants such as M_b and M_a were computed from the

intercept and slope of the line. The Smith model was good for $a_w = 0.2–0.9$ and is depicted in Figure 3(B). This agreed with the results of Sudhamani et al.,[12] who reported that the Smith equation fit well for $a_w = 0.2–0.9$. The Smith constants were evaluated in a way similar to that used for the BET constants.

GAB

This model has been applied a great deal in the sorption studies of foods. Because the coefficient of $1/a_w$ was nonsignificant and negligible in the model, the second term (RHS) in eq. (1) was eliminated. With $1/M$ as a dependent variable and a_w and $1/a_w$ as independent variables in multiple regression, the GAB constants C and K were computed from a linear regression of $1/M$ versus a_w. From Figure 4(A), it can be observed that the experimental sorption data of the PVA/starch films obtained from the GAB model fit very well for $a_w = 0.1–0.9$. The constants for the GAB model, K and C, are given in Table I. They agreed with the results of Iglesias and Chirife,[13] who reported the sorption behavior of food products.
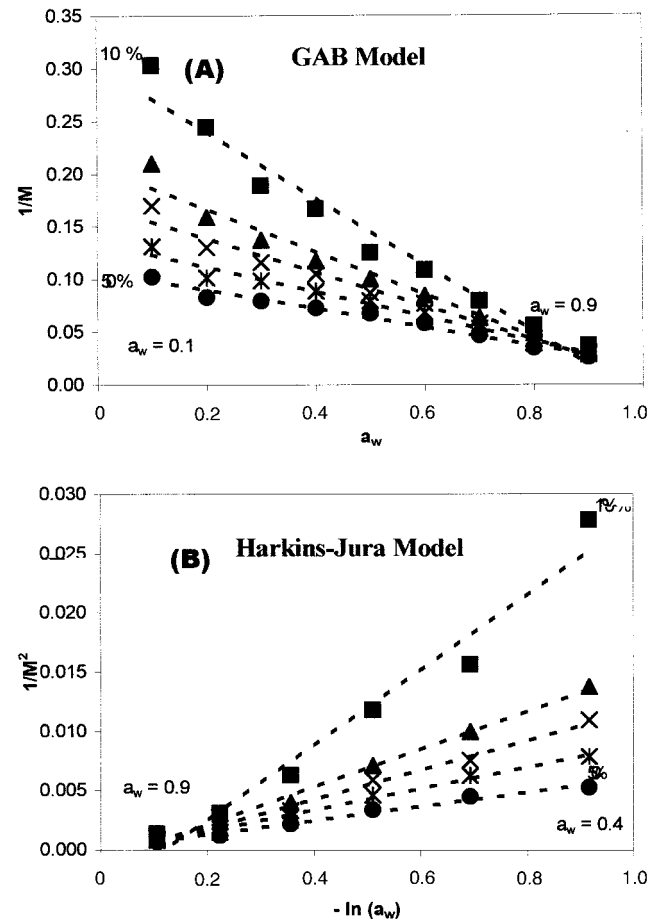

Figure 4 Data for the experimental sorption models (symbols) and fitted models (broken lines): (■) 10, (▲) 20, (×) 30, (+) 40, and (●) 50% PVA.
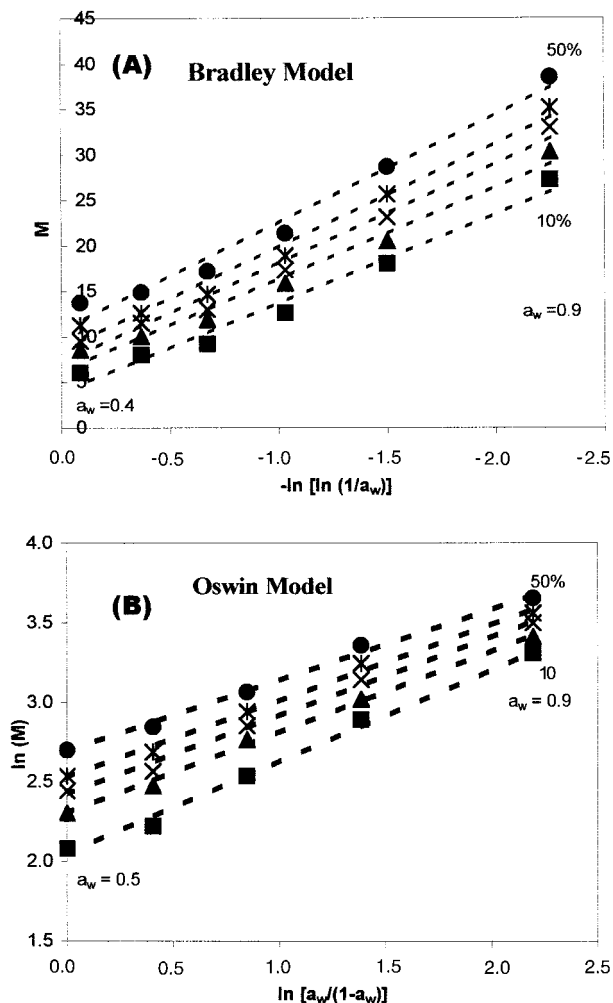
Figure 5 Data for the experimental sorption models (symbols) and fitted models (broken lines): (■) 10, (▲) 20, (×) 30, (+) 40, and (●) 50% PVA.

Harkins–Jura

The Harkins–Jura model equation was good for a_w = 0.4–0.9, as shown in Figure 4(B). The Harkins–Jura model constants (Table I) were determined by the linear fitting of eq. (2).

Bradley

The relevance of the Bradley equation is a function of the sorptive polar groups and dipole moment of the sorbed vapor. Bradley assumed that the first layer was sorbed because of strongly induced dipoles and that these dipoles in turn polarized the subsequent layers. The Bradley model was applied to experimental sorption data for the different contents of PVA in the PVA/starch films, as shown in Figure 5(A). The model was in good agreement for a_w = 0.4–0.9. This range agreed with the goodness of fit of the Bradley equation from 0.3 to 0.9 reported in the literature[14] because of the sorption of water by the proteins.

Oswin

This model is based on a mathematical series expansion for sigmoidal curves, a and n being determined by the linear regression of ln M versus $\ln[a_w/(1 - a_w)]$. The use of the Oswin model for the experimental sorption data of the PVA/starch films was studied. From Figure 5(B), it can be observed that the experimental sorption data of the PVA/starch films applied to the Oswin model, as given by the Oswin equation,[3] fit very well for a_w = 0.5–0.9.

Halsey

This model proposes an expression for the condensation of multilayers at relatively large distances from the surface. The Halsey constants were estimated from a linear plot of ln M versus $\ln[-\ln a_w]$. In Figure 6(A), the range of applicability for a_w is shown to be within the limits of the sorption behavior reported for a_w = 0.4–0.9 by Halsey.[15]
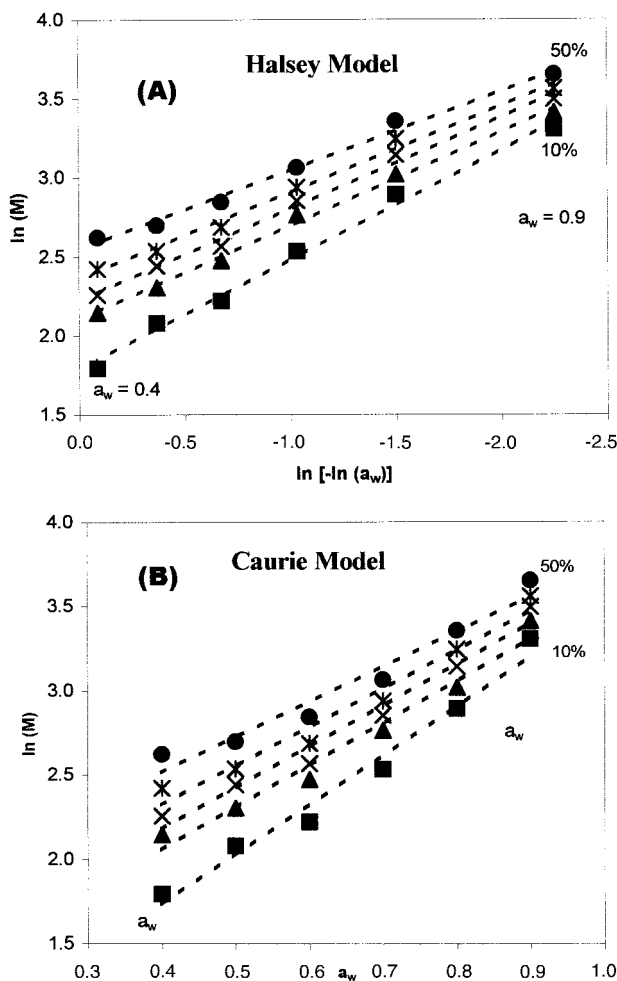

Figure 6 Data for the experimental sorption models (symbols) and fitted models (broken lines): (■) 10, (▲) 20, (×) 30, (+) 40, and (●) 50% PVA.
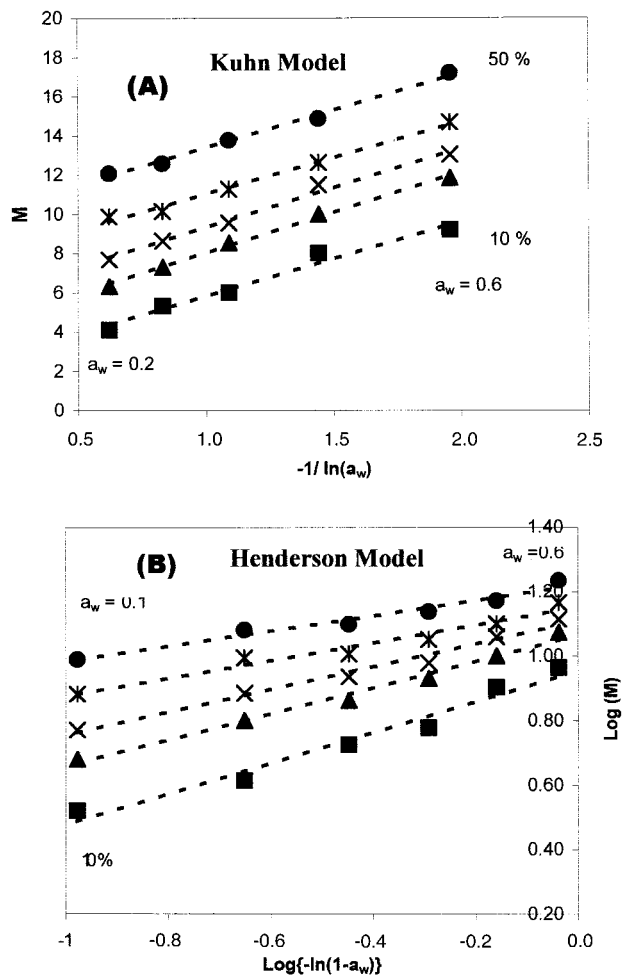
Figure 7 Data for the experimental sorption models (symbols) and fitted models (broken lines): (■) 10, (▲) 20, (×) 30, (+) 40, and (●) 50% PVA.

Caurie

The model given by Caurie plotted the aforementioned equation for the sorption data of gelatin, but it did not report the goodness of fit of the equation. From a linear plot of ln M versus a_w, the Caurie constants were computed. The Caurie model given by the Caurie equation[3] for the experimental sorption results was in good agreement for $a_w = 0.4$–0.9. From Figure 6(B), the hypothesis by Caurie that a_w is valid from 0 to 0.85 for most foods merely supports the aforementioned range of determination for a_w.

Kuhn

The model constants were determined from a linear regression of M versus $\ln(1/a_w)$. From Figure 7(A), it can be observed that the experimental sorption data of the PVA/starch films applied to the Kuhn model, as given by the equation,[3] fit very well for $a_w = 0.2$–0.6. The constants for the Kuhn model, a and b, are given

in Table I. They agreed with the results of Cherife et al.[16]

Henderson

The Henderson model constants, A and B, were calculated from a linear plot of ln M versus $\ln\{\ln[1/(1 - a_w)]\}$. The Henderson model represented by eq. (3) was good for $a_w = 0.1$–0.6, as shown in Figure 7(B). The Henderson equation fit well for $a_w = 0.1$–0.6. The Henderson model constants (Table I) were determined by the linear fitting of sorption isotherms.

As evident from Figures 3–7, the linear fitting of the sorption equation (denoted by broken lines) was employed for the determination of the appropriate model constants. The 10 sorption models were used to evaluate the model constants for different ranges of a_w to determine the shelf life of packages and the applicability of the models discussed. The values of the coefficient of determination (R^2) for the models are given in Table I. The applicable a_w values were estimated for the Smith model (0.2–0.9), GAB model (0.1–0.9), Harkins–Jura model (0.4–0.9), Bradley model (0.4–0.9), Oswin model (0.5–0.9), Halsey model (0.4–0.9), and Caurie model (0.4–0.9). It can be inferred that although the approaches of the different models are different, they can still be used for the listed ranges of a_w. However, a very short range of $a_w = 0.1$–0.4 was observed for the BET relation because the BET constants are applicable only for monomolecular layer systems. The reliable values of R^2 (0.98 ± 0.02) obtained from all the models indicated that the linear fitting approach used to evaluate all the models was adequate.

CONCLUSIONS

The moisture sorption isotherms of PVA/starch films are essential for determining the sorption influence of PVA and starch in these films. The sorption data are very useful in choosing suitable blends for packaging by the judicious selection of water-vapor-barrier packaging materials. The water activity is one of the single most important factors affecting the shelf life of intermediate moisture food. The sorption constants (slopes) of different model equations are significant in the evaluation of the stability and package life of biofilms. The moisture sorption characteristics of PVA and starch in PVA/starch blends are critical for ascertaining their use as biopackaging materials. As far as their use is concerned, they can be used under any humid conditions up to 92% RH, as the films are not affected by microbial contamination even under these conditions. However, their barrier properties have to be considered for the required use. With growing awareness of the use of moisture-sensitive films for food packaging, this study on the applicability of the

water activity provides insight into the prediction of the durability of packaging materials.

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