

Moisture-Sorption Characteristics of Starch/Low-Density Polyethylene Films

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ABSTRACT: Moisture-sorption characteristics of starch/low-density polyethylene (LDPE) blends were carried out at 27°C for water activity (a_w) from 0.1 to 0.9. The sorption data were used to fit six different sorption isotherm models proposed in the literature. The model constants were determined by linear fitting of the sorption equations. The ranges of applicability of water activity for the isotherm models reported in the article lies between 0.1 and 0.4 (monomolecular layer) for the BET model and between 0.3 and 0.9 (multimolecular and capillary condensation layers) for other models. The value of the coefficient of determination ($R^2 = 0.97 \pm 0.02$) confirms the linear fitting of the equations studied. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1193–1202, 2002; DOI 10.1002/app.10417

Key words: starch; LDPE; sorption isotherm; water activity; polyethylene (PE); blends; hydrophilic polymers; films

INTRODUCTION

One of the challenges faced by food-packaging technologists in their efforts to produce bio-based primary packaging is to match the durability of the packaging materials with respect to the product shelf life. The biologically based packaging material must remain stable without changes in its mechanical and/or barrier properties, must function properly during storage until disposal, and has to undergo degradation on the land.¹ Polymers like low-density polyethylene (LDPE) and poly(vinyl alcohol) (PVA) containing starch have been reported in the literature as suitable packaging materials^{2–4} for intermediate moisture foods. Water activity (a_w) has become the basic

controlling factor in the preservation of moisture-sensitive material for food applications against microbiological, chemical, and physical deterioration.⁵ With starch being hydrophilic in nature, there is a need to address the sorption influence of starch present in LDPE/starch films, to make it suitable for food packaging. However, little research has been done on the sorption characteristics of starch-based film⁶ used for food packaging. Corn starch was used for the present study, since the mechanical properties of films with corn starch are better than are those other type of starches.⁷ The purpose of the present work was to study the moisture-sorption characteristics of starch-filled LDPE films. Equations for modeling water-sorption isotherms are of special interest in many aspects of food preservation by dehydration.⁸ The sorption isotherms obtained from experimental data result in an estimation of the equilibrium moisture content, which is necessary

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to predict the hygroscopic properties of the film. The equilibrium moisture content is an important quantitative measure in the practice of food storage, packaging, and drying.⁹

Many mathematical relations have been proposed in the literature to model hygroscopic equilibrium data in food-application systems.^{10,11} In the present article, we studied the behavior of water activity on LDPE/starch blends, employing six sorption isotherm models proposed by Brunauer–Emmett–Teller,¹² Smith,¹³ Halsey,¹⁴ Caurie,¹⁵ Bradley,¹⁶ and Oswin.¹⁷ Applicable ranges of water activity for the sorption isotherms of LDPE/starch films are reported.

EXPERIMENTAL

Preparation of LDPE/Starch Films

Commercial-grade LDPE (FS040) was procured from M/s IPCL (Vadodara, India), and corn starch, from a local market (Mysore, India). A series of LDPE/starch composites were prepared by varying the starch content from 10 to 50% (w/w) using carbon tetrachloride (CCl₄) as a solvent. LDPE/starch films with more than 50% starch concentration were very brittle in nature. LDPE/starch films of size 12 × 12 cm were cast using a thermopress casting machine at 140–150°C under 150-kg/cm² pressure. The cast films with a thickness of 70–80 μm were collected and stored in polyethylene bags at 4°C. The structure–property relationship of these films was described in our earlier communication.¹⁸

Standards for Water Activity (*a_w*)

Saturated salt solutions of lithium chloride (LiCl), potassium acetate (CH₃COOK), magnesium chloride (MgCl₂), potassium carbonate (K₂CO₃), sodium dichromate (Na₂Cr₂O₇), sodium nitrite (NaNO₂), sodium chloride (NaCl), potassium chromate (K₂CrO₃), and ammonium phosphate (NH₄)₂PO₄ were 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.¹⁹ All chemicals were analytical grade obtained from M/s Reachem Laboratories Chemicals Limited (Chennai, India). The above saturated solutions were put into different desiccators in which the samples were placed.

Sorption Experiments

LDPE/starch film specimens of size 1 × 1 cm were conditioned to 65% RH at 27 ± 1°C LDPE/starch

before they were exposed to different water activities (*a_w*) at 27°C. The initial moisture content (IMC) of the LDPE/starch films (in duplicate) were measured on a dry-weight basis by drying in a hot-air oven at 100 ± 5°C until constant weight was obtained. The approximate time taken for drying was 4 h. The sorption isotherm determination was performed²⁰ by exposing 1 g of the film in desiccators having different *a_w* from 0.11 to 0.92 at 27 ± 1°C. The samples were weighed until equilibrium (i.e., ±0.05% change in moisture content) was attained for a period of 25–30 days.

Sorption Isotherm Models

Six sorption isotherm equations of Brunauer–Emmet–Teller, Smith, Halsey, Caurie, Bradley, and Oswin were used to fit the experimental LDPE/starch film sorption isotherm data. A rearrangement of the equations was performed to facilitate the determination of the appropriate coefficients using statistical modeling. Those models are expressed and rearranged as given below:

Brunauer–Emmet–Teller (BET) Isotherm Model

The sorption model that has received the greatest application to sorption studies on food applications is that of BET, the usual mathematical form of which is given as follows:

$$a_w / [(1 - a_w) \times M] = 1 / (M_m \times C) + \{[(C - 1) / a_w] \times [1 / (C \times M_m)]\} \quad (1)$$

where *M_m* is the monolayer moisture content, and *C*, the constant related to the net heat of sorption. 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.²¹

The BET monolayer concept is a reasonable correct guide for two important aspects, namely, (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.²²

Equation (1), rearranged by Caurie,²³ is given below:

$$1 / [(1 - a_w) \times M] = 1 / M_m + \{[1 / (C \times M_m)] \times [(1 - a_w) / a_w]\} \quad (2)$$

From a linear plot of $1/[(1 - a_w) \times M]$ versus $[(1 - a_w)/a_w]$, the BET constants, M_m and C , were computed.

Smith Isotherm Model

Smith suggested that sorption isotherms of biopolymers could be represented by the equation

$$M = M_b - M_a \times [\ln(1 - a_w)] \quad (3)$$

where M_b and M_a are constants. From a linear regression of M versus $\ln(1 - a_w)$, the Smith constants were computed.

Halsey Isotherm Model

An expression for condensation of a multilayer at a relatively large distance from the surface was proposed by Halsey:

$$a_w = \exp(-a/RT^\theta) \quad (4)$$

where a and r are constant parameters, $\theta = M/M_m$, and R is the gas constant at temperature T . The above equation was simplified for the isothermal sorption characteristic²⁴ as

$$\ln(M) = a + b \times \{\ln[-\ln(a_w)]\} \quad (5)$$

where a and b are Halsey constants, which can be estimated from a linear plot of $\ln(M)$ versus $\ln[-\ln(a_w)]$.

Caurie Isotherm Model

Caurie proposed the following equation for the estimation of water activity as

$$\ln(M) = \ln A - r \times a_w \quad (6)$$

where r and A are constants, and M , the moisture concentration. Caurie plotted the above equation for the sorption data of gelatin, but did not report the goodness of fit of the above equation. From the linear plot of $\ln(M)$ versus a_w , the Caurie constants were computed.

Bradley Isotherm Model

The following expression relating water activity and equilibrium moisture content was suggested by Bradley:

$$\ln(1/a_w) = K_2 \times K_1^M \quad (7)$$

where K_2 is a function of the sorptive polar groups, and K_1 , a function of the dipole moment of the sorbed vapor. Bradley assumed that the first layer is sorbed because of strongly induced dipoles and these dipoles, in turn, polarize the subsequent layers.

The above equation can be rearranged to eq. (8) to determine K_1 and K_2 by linear regression of $\ln[\ln(1/a_w)]$ versus M :

$$\ln[\ln(1/a_w)] = \ln(K_2) + M \times \ln(K_1) \quad (8)$$

Oswin Isotherm Model

This model is based on the mathematical series expansion for sigmoid-shaped curves and may be written as follows:

$$M = a\{[a_w/(1 - a_w)]\}^n \quad (9)$$

where a and n are constants. Equation (9) can be rearranged as follows:

$$\ln(M) = \ln(a) + n \ln[a_w/(1 - a_w)] \quad (10)$$

where a and n are determined by the linear regression of $\ln(M)$ versus $\ln[a_w/(1 - a_w)]$.

RESULTS AND DISCUSSION

The relationship between a_w and the moisture content (at constant temperature) is described practically by a moisture sorption isotherm.²⁵ The effect of the starch content on the moisture-sorption characteristic of LDPE/starch blends is shown in Figure 1. Plain LDPE film did not exhibit any moisture sorption. All the moisture-sorption isotherm curves were typically of sigmoid shape as exhibited by pure starch, which is given for comparison. As evident in the Figure 1, the sorption isotherms had three phases of sorption behavior, namely, the monomolecular layer phase below 0.2 a_w , the multimolecular layer phase from 0.2 to 0.7 a_w , and the capillary condensation phase from 0.7 and above a_w . With increasing starch content and increasing a_w , the slope of the isotherms increased, solely due to higher sorption of water molecules by starch²⁶ and higher equilibrium moisture content or more

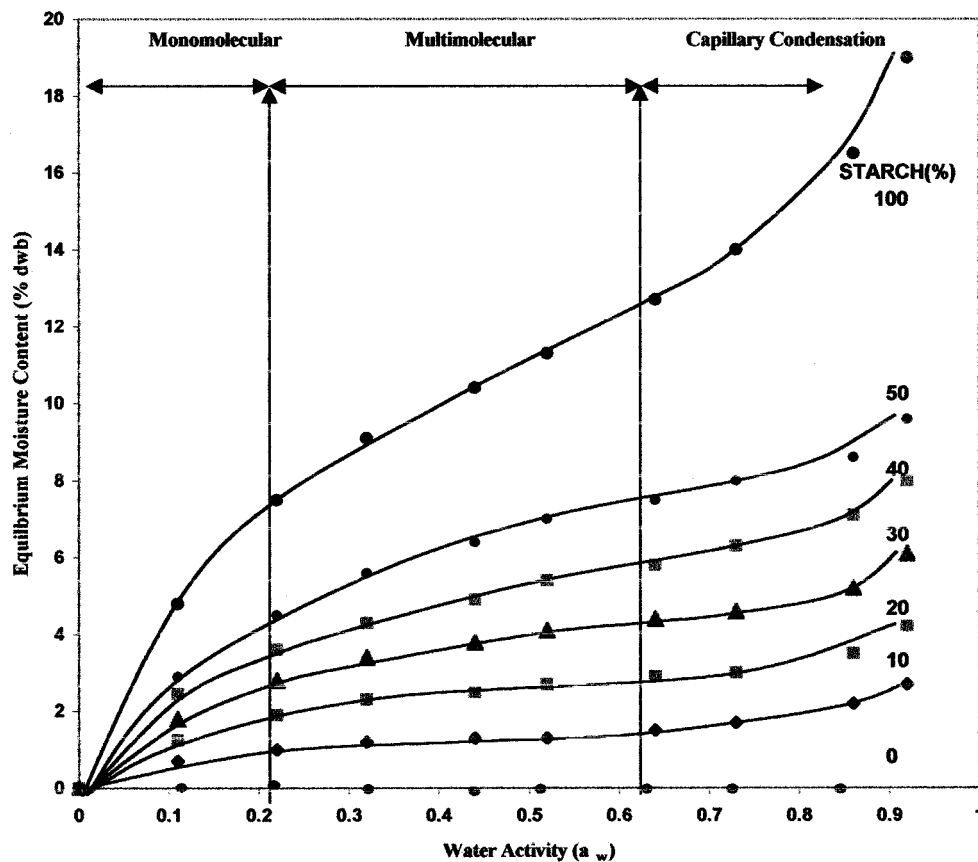


Figure 1 Moisture-sorption isotherm of starch-filled LDPE/starch films.

sorption capacity of starch. The initial moisture content (IMC) values of LDPE/starch blends with varying starch content from 10 to 50% and their corresponding water activity is shown in Table I. It was observed that the a_w values increased with increasing starch content to 30%. Beyond 30% of starch in LDPE films, the a_w value was almost constant. This may be due to that (i) 30% starch is the optimized concentration which was on the surface of the LDPE matrix and (ii) a further

increase in the starch content that remained embedded in the core layer of films rendered it unavailable for evaporation. Hence, the water activity remained the same. The equilibrium moisture-content values for 10, 20, 30, 40, and 50% (w/w) starch in LDPE/starch films at a_w values of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 were taken from Figure 1 for analyzing the applicability of water activity for the six sorption models. LDPE/starch films with greater than 50% starch could not be extruded to study the sorption behavior, due to the brittleness of the films.

Table I Variation of IMC with water activity (a_w) for LDPE/Starch Films

Sample Formulation LDPE/Starch (w/w)	IMC	Water Activity (a_w)
90/10	1.5	0.56
80/20	2.9	0.64
70/30	4.5	0.68
60/40	6.0	0.68
50/50	7.7	0.68

Sorption Model Analysis

From the IMC- a_w data, BET isotherm graphs were drawn and the results are presented in Table II. The applicability of the BET equation over the entire region of 0.1-0.9 a_w was studied. The range of applicability of the equation from 0.1 a_w to the actual inflexion point is also reported in Table II. The experimental sorption data applied

Table II Sorption Isotherm Model Constants and Coefficient of Determination (R^2) from Linear-fitting Equations for LDPE/Starch Films

Isotherm Model	Equation No.	Starch Content in LDPE/Starch Film % (w/w)	Constants by Linear Fitting of Sorption Isotherms		R^2	Range of a_w
			M_m	C		
BET	2		M_m	C		0.1–0.4
		50	4.54	12.51	0.96	
		40	3.35	16.87	0.96	
		30	2.52	16.23	0.99	
		20	1.70	18.30	0.95	
		10	0.62	28.85	0.97	
Smith	3		M_b	M_a		0.3–0.9
		50	5.41	1.96	0.96	
		40	3.96	1.84	0.98	
		30	3.00	1.37	0.97	
		20	1.95	0.97	0.99	
		10	0.95	0.76	0.99	
Halsey	5		a	b		0.4–0.9
		50	1.87	-0.19	0.98	
		40	1.60	-0.23	0.99	
		30	1.32	-0.22	1.00	
		20	0.90	-0.24	0.99	
		10	0.29	-0.31	0.99	
Caurie	6		A	r		0.3–0.9
		50	4.47	-0.85	0.99	
		40	3.25	-0.98	0.99	
		30	2.48	-0.95	0.97	
		20	1.64	-0.97	0.96	
		10	0.81	-1.26	0.96	
Bradley	8		K_1	K_2		0.4–0.9
		50	1.97	0.01	0.99	
		40	2.01	0.04	0.99	
		30	2.60	0.03	0.99	
		20	3.64	0.05	0.98	
		10	5.03	0.13	0.98	
Oswin	10		a	n		0.5–0.9
		50	7.04	0.15	1.00	
		40	5.39	0.18	0.99	
		30	4.06	0.18	0.99	
		20	2.65	0.20	0.98	
		10	1.46	0.28	0.99	

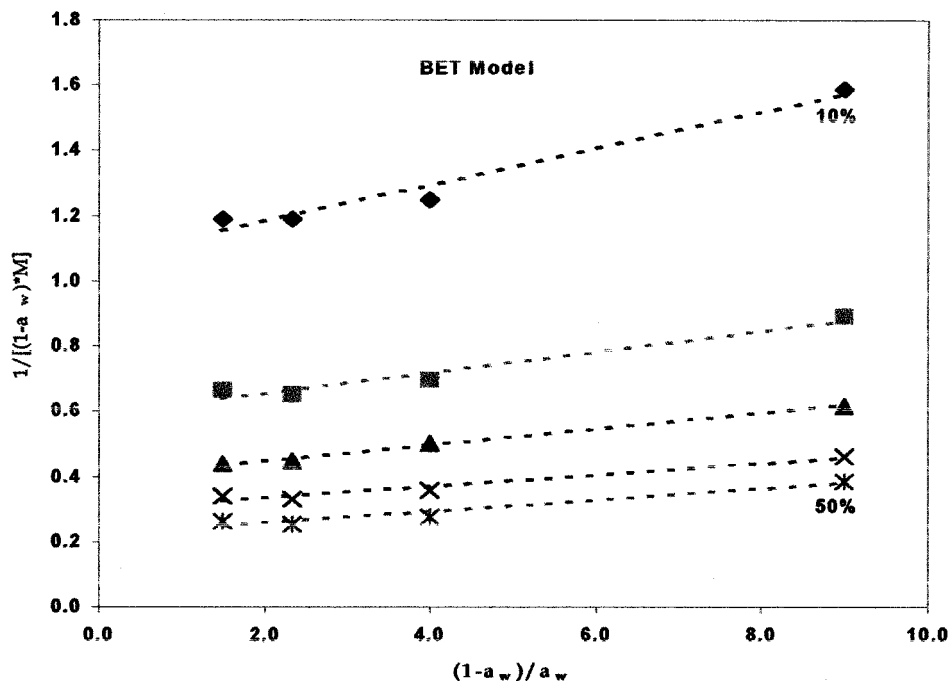


Figure 2 BET sorption isotherm model of LDPE/starch.

to the BET model for the varying starch content of LDPE/starch films, as shown in Figure 2, was found to fit well for a_w in the range of 0.1–0.4. Iglesias and Chirife²⁷ and Kumar and Balasubramanyam²⁸ showed that the BET equation holds

well only between water activities from 0.05 to 0.45, confirming the above finding. To evaluate the BET constants, a linear fitting of eq. (2) was done. M_m varied between 0.62 and 4.54 for films with a starch content from 10 to 50%, respec-

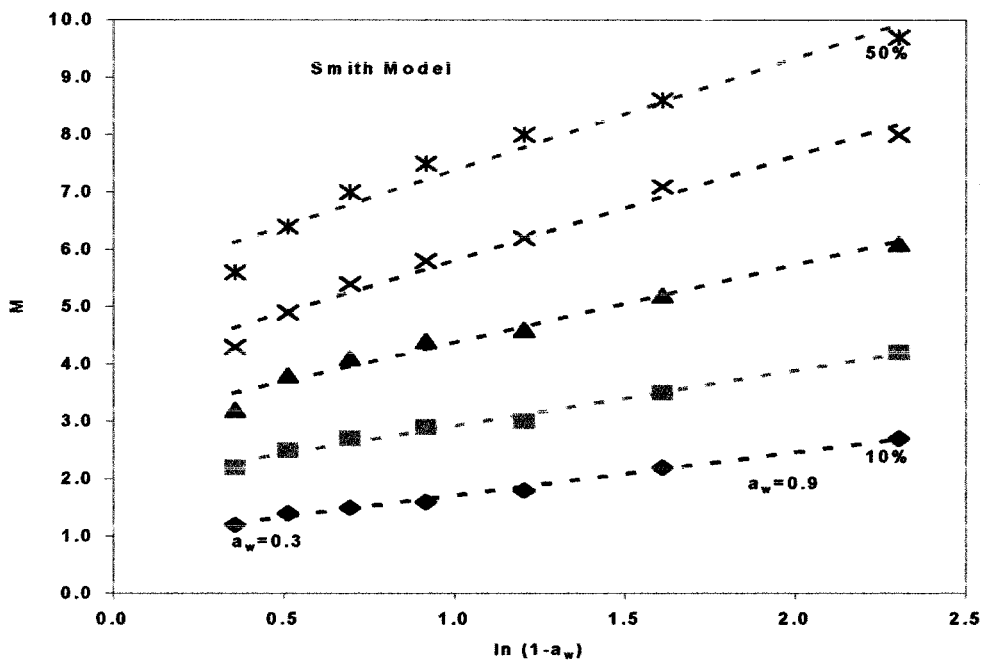


Figure 3 Smith sorption isotherm model of LDPE/starch.

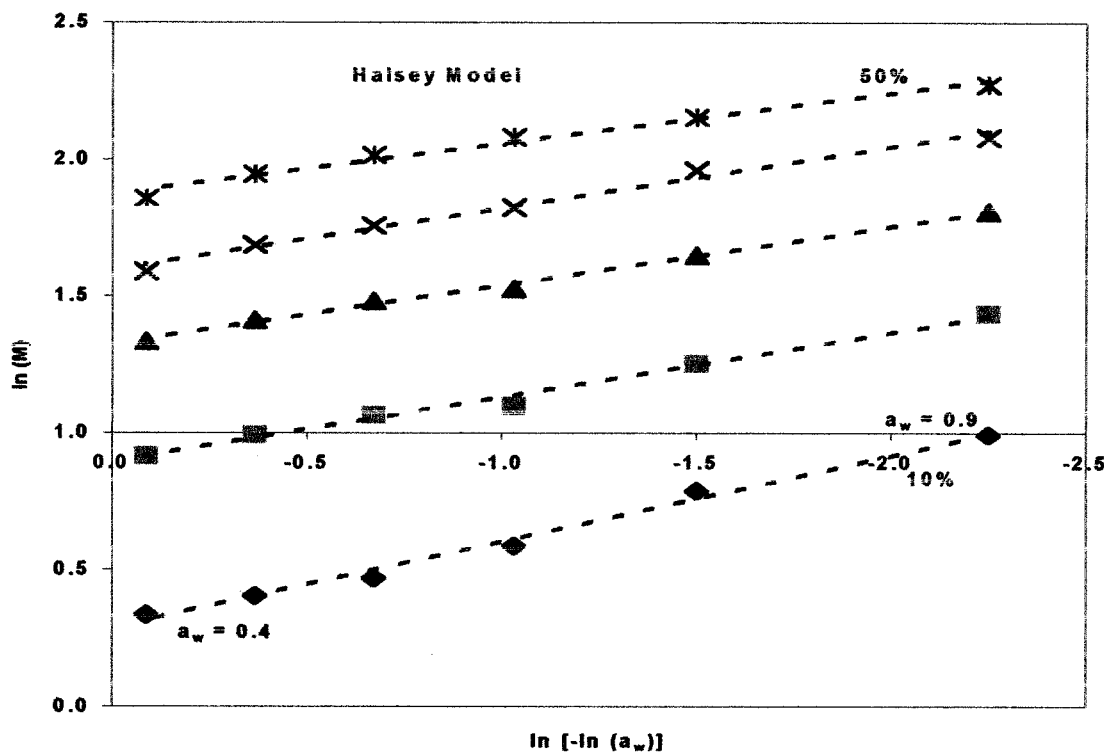


Figure 4 Halsey sorption isotherm model of LDPE/starch.

tively, indicating that different LDPE/starch blends have varying capacities for water binding and availability of free water. The applicability of the BET equation, in general, is restricted to water activities below $0.4 a_w$, which shows that the adsorbent surfaces of the LDPE/starch blends could be construed as practically homogeneous up to this maximum and that water fills the active sites in multilayers. This is in consonance with the results computed by Iglesias and Chirife.²⁹ The monolayer moisture parameter of the BET equation is important for commercial shelf-life studies.

The Smith model represented by eq. (3) holds good for a_w in the range 0.3–0.9, as shown in Figure 3. This was in conformity with the result of Young,³⁰ who reported that the Smith equation fits well for a_w in the range 0.4–0.9. The Smith constants were evaluated in a similar way compared to the BET constants. The Smith constants M_b and M_a ranged from 0.95 to 5.41 and 0.76 to 1.96 for films with a starch content ranging from 10 to 50%, respectively. From Figure 4, it is observed that the experimental sorption data of LDPE/starch films applied to the Halsey model, as given in eq. (4), fitted very well for a_w in the range 0.4–0.9. The range of applicability for a_w

was within the limits for sorption behavior reported in the range of a_w from 0.1 to 0.8 by Halsey.³¹ Halsey constants a and b varied from 0.29 to 1.87 and -0.31 to -0.19 for films with a starch content ranging from 10 to 50%, respectively.

In Figure 5, the Caurie model given by eq. (5) for the experimental sorption results was in good agreement for a_w in the range 0.3–0.9. The hypothesis by Caurie that a_w is valid from 0 to 0.85 for most foods merely supports the above range of determination for a_w obtained by linear fitting. Caurie constants A and r ranged from 0.81 to 4.47 and -1.26 to -0.85 for different starch concentration films, respectively. The relevance of the Bradley model applied to the experimental sorption data for different contents of starch in the LDPE/starch films, as shown in Figure 6, was found to be in good agreement for a_w in the range of 0.4–0.9. This range was in conformity with the goodness of fit of the Bradley equation from 0.3 to 0.9 reported in the literature³² due to the sorption of water by peanut protein films. The Bradley constants, K_1 and K_2 , varied from 5.03 to 1.97 and 0.13 to 0.01 for the films, respectively. The use of the Oswin model given by eq. (10) for the experimental sorption data of LDPE/starch films fitted

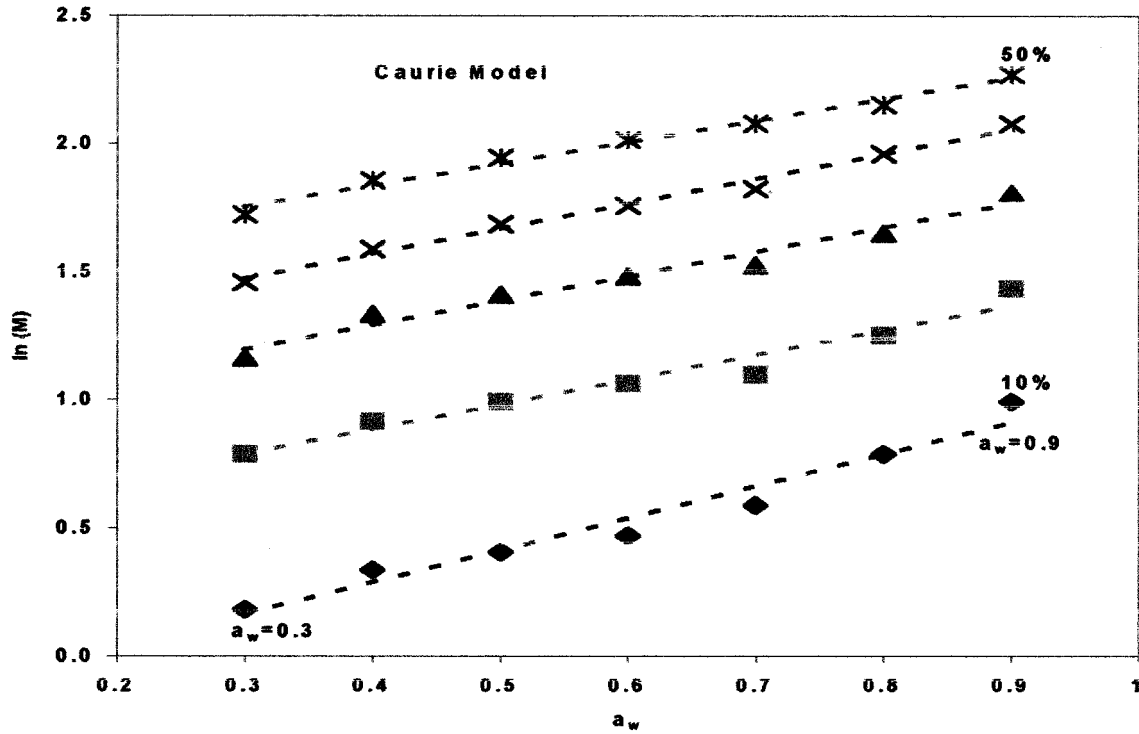


Figure 5 Caurie sorption isotherm model of LDPE/starch.

very well for a_w in the range 0.5–0.9, as shown in Figure 7. The Oswin constants a and n varied from 1.46 to 7.04 and 0.28 to 0.15 for films with a starch concentration from 10 to 50%, respectively.

As evident from Figures 2–7, the linear fitting of the sorption equation, denoted by broken lines, was done using MS Excel software for the determination of the appropriate model constants. The

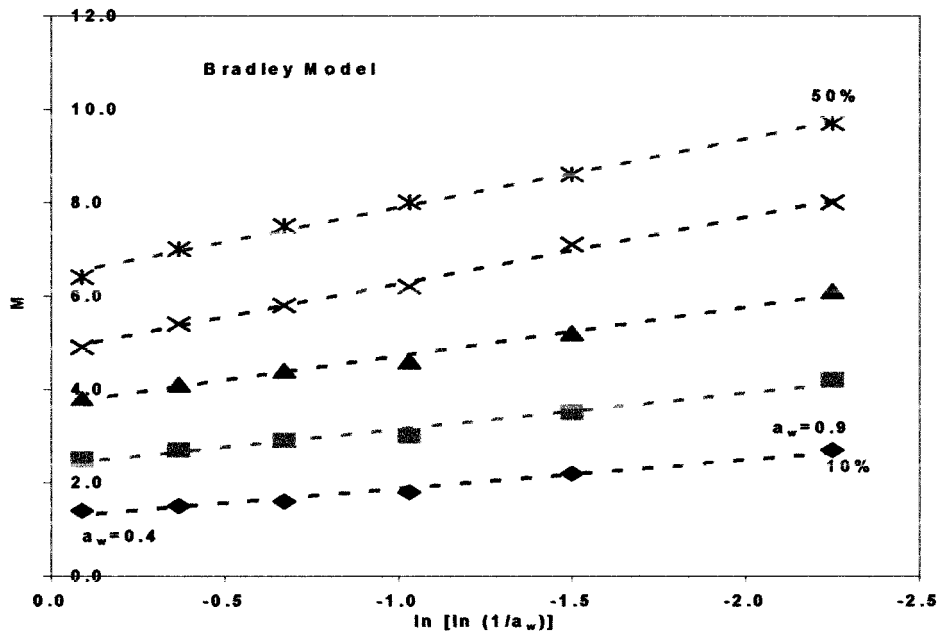


Figure 6 Bradley sorption isotherm model of LDPE/starch.

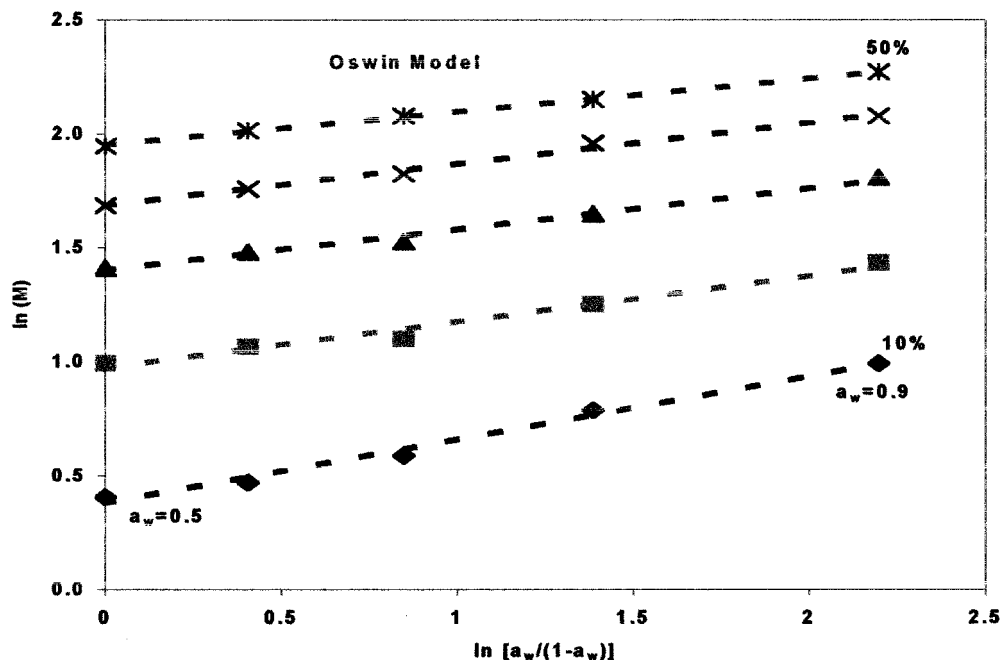


Figure 7 Oswin sorption isotherm model of LDPE/starch.

six sorption models discussed above are used to evaluate the model constants for different ranges of a_w to determine the film durability and the applicability of the models. The values of the coefficient of determination (R^2) for the models are given in Table II. From the table, it is observed that the a_w values estimated by the Smith, Halsey, Caurie, Bradley, and Oswin models are applicable in the range 0.3–0.9. It can be inferred that, although the approach of the above models is different, it can still be used for the above range of a_w . But a very short range of 0.1–0.4 a_w was observed for the BET relation, since the BET constants are applicable only for monomolecular layer systems. The reliable values of the coefficient of determination, $R^2 = 0.97 \pm 0.02$, obtained from all the models indicate that the linear-fitting approach used to evaluate all the models is adequate.

CONCLUSIONS

Moisture-sorption isotherms on starch/LDPE films are essential to determine the sorption influence of starch in the films due to the hydrophilic nature of starch. Water activity is the most important factor, affecting the durability of

the packaging material. The sorptive capacity of the polyethylene-containing films were less due to the presence of hydrophobic polyethylene fractions. The constants (slope) of different sorption model equations are significant in the evaluation of the stability of starch-based biofilms. With the growing awareness on the use of starch-based films for food packaging, the present study on the applicability of water activity will give insight into the prediction of the durability of packaging material.

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