Moisture Sorption Studies of PEO/ Starch Blended Films for Food Packaging Applications

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Abstract

A series of polyethylene oxide (PEO) and starch blends were prepared by extrusion and their films prepared by compression molding. Moisture sorption characteristics of PEO-starch blended films were carried out at 27 °C for water activity (a_w) ranged from 0.1 to 0.9. The sorption data at different a_w were used to fit different sorption isotherm models as proposed in the literatures. The model constants were determined by linear fitting of the sorption equations. The high coefficient of determination R^2 (ranged from 0.7 to 1) confirms the applicability of the equations employed. The study on the application of such water activity data of PEO/starch blended films on different model equations will be helpful in prediction of durability and functional behavior of moisture sensitive bio polymeric films for food packaging applications.

Keywords; PEO; Starch; Moisture-Sorption; water activity.

1. Introduction

One of the challenges faced by the food packaging technologists in their efforts to produce bio-based primary packaging is to match the durability of the packaging materials with respect to product shelf life. The biologically based packaging material must remain stable without changes in mechanical and/or barrier properties must function properly during storage until disposal and has to undergo degradation on the land. Polymers like low-density polyethylene (LDPE) and polyvinyl alcohol (PVA) containing starch have been reported in literature as suitable packaging materials (Baldevraj et al, 2002, 2003b, Srinivasa et al, 2007) 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 (Berg and Bruin, 1981). However, since both PEO and starch are hydrophilic in nature it is essential to study their sorption influence to render their suitability for packaging application. An important role of packaging film is to reduce exchange of water between the product and the environment (Coupland et al, 2000). The barrier property of such (packaging) films depends on both molecule diffusion co-efficient and solubility of water in the matrix (McHugh and Krochta, 1994). The moisture sorption isotherm is a means to characterize the water absorption property of the film, which in turn is transmitted to the product inside. Moisture sorption is important for predicting stability and quality changes during packaging and storage of food products. Equations for modeling water sorption isotherms are of special interest in many aspects of food preservation by dehydration. The sorption isotherms obtained from experimental data facilitate estimation of equilibrium moisture content, which is necessary to predict the hydrophilic properties of the film. The equilibrium moisture content is a quantitative measure in the practice of food storage, packaging and drying. Many mathematical relations have been proposed in literature to model hygroscopic equilibrium data related to food systems as well as bio- films. Chirife and Iglesias (Chirif and Iglesias, 1978) reviewed a number of isotherm equations for food and food products. The chung and pfost model described well the adsorption isotherm of mushrooms over 30-70 °C for water activity between 0.2-0.8 by Shivhare et al, 2004. Gennadios and Weller, 1994 reported isotherm for corn zein, wheat gluten and mixed protein films and showed GAB isotherm model to have good description of their data. Chinnan and Park (Chinnan and Park, 1995) reported sorption isotherm for methyl and hydroxyl propylcellulose films. BaldevRaj et al, 2002 studied sorption isotherm of LDPE/Starch and PVA/Starch BaldevRaj et al, 2003 blended films respectively. Sudhamani et al, 2005 studied microbially produced polysaccharide/PVA blended films and reported in literature as suitable packaging materials for intermediate moisture foods. Srinivasa et al, 2003; Srinivasa et al, 2007 have studied the moisture sorption of chitosan/ PVA and the effect of plasticizers and fatty acids on the chitosan blended films. Olivas et al, 2008 revealed alginate –calcium films proved to be very strong at higher relative humidity. The uses of PEO/starch blends as a packaging material have better prospects when compared with LDPE/starch blends since LDPE is non-biodegradable.

The objectives of this study are; (i) to determine the moisture sorption isotherms and (ii) to determine and evaluated the applicability of different sorption models to experimental data over different a_w intervals.

2. Experimental
2.1 Materials
Polyethylene oxide (PEO) of molecular weight (~200 kDa) was procured from Sigma Aldrich, St.Louis, MO, USA and corn starch was obtained from M/S Riddhi Siddhi, Gluco Bio Ltd. Gokak, Karnataka, (India) respectively. All other chemicals were of analytical grade and obtained from M/s SD Fine Chemicals, Bangalore, Karnataka, (India).

2.2 Extrusion Process for PEO/Starch Films

A series of PEO/starch blends, namely 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 were extruded, using mixing extruder (LE-075, Custom scientific instrument). Rotor and header temperature were maintained at 80 °C and 100 °C, respectively. The screw rotation was set at 60 rpm. Once, the set temperatures of rotor and header were attained, then several compositions of physically blended PEO/starch samples were fed separately through the feed hopper into the feed section of the barrel. As a result, continuous strands of PEO/starch blends emerged through the die. These strands were then passed through the pelletizer in order to obtain pellets. The prepared pellets of different compositions of PEO/starch blends were used for processing films by thermo-press technique at 80-90 °C at 100 Kg/cm^2 pressure and were cooled slowly. The processed films were collected and then stored in sealed aluminum foil based pouches at 4 °C to prevent any interaction with atmospheric moisture.

2.3 Sorption Studies

Saturated salt solutions of lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, sodium dichromate, sodium nitrite, sodium chloride, potassium chromate and potassium nitrate 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. The above-saturated solutions were placed in different desiccators to obtain different relative humidities (RH) for the exposure of PEO/starch blended films. PEO/starch blended films were conditioned to 65% RH at 27 ± 1°C before they were exposed to different water activities (a_w). The initial moisture content (IMC) of the PEO/starch films (in duplicate) were measured on dry weight basis by drying in vacuum oven at 60 ± 2 °C at 550 mm Hg pressure till a constant weight was obtained. The approximate time allowed for drying the specimens was 6 - 8 h. The sorption isotherm determination was performed by exposing 1 g (approximately) of the film specimen, 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.

2.4 Sorption Isotherm models

Various sorption isotherm model equations such as Brumauer–Emmet–Teller (BET), Smith, Halsey, Oswin, Henderson, Kuhn, Iglesias and Chirife, and Freundlich were used to fit the experimental data of PEO/starch film sorption isotherm. Rearrangements of the equations were performed to linear form to determine the appropriate constants (Table.1) by regression analysis using MS-Excel software. The sorption data were analyzed according to the models and corresponding constants were determined.

3. Results and Discussion

3.1. Moisture Sorption Studies

The IMC values of pure PEO, PEO/starch blended films in different ratios and starch powder was determined gravimetrically on dry weight basis, after equilibrated to 65% RH (a_w= 0.65) at 27 ± 1° C. The sorption isotherm curves were drawn from the moisture content and a_w, as shown in Fig 1. As can be seen in Fig 1, the pure PEO film and starch showed IMCs of 1.1 and 10.16 respectively, when equilibrated to 65% RH.

The IMC values of PEO/starch blended films with different starch contents (10 to 50%) lay in the range of 2.49–7. The association between a_w and the moisture content (at a constant temperature) can practically be described by a moisture sorption isotherm. The moisture sorption isotherm curves of the PEO/starch blends, as shown in Fig 1, were typically sigmoidal. Primarily, the sorption isotherms showed a sorption behavior consisting of a monomolecular layer phase below 0.2 a_w, a multimolecular layer phase ranging from 0.2 to 0.7 a_w and a capillary condensation phase from 0.7 a_w and above.
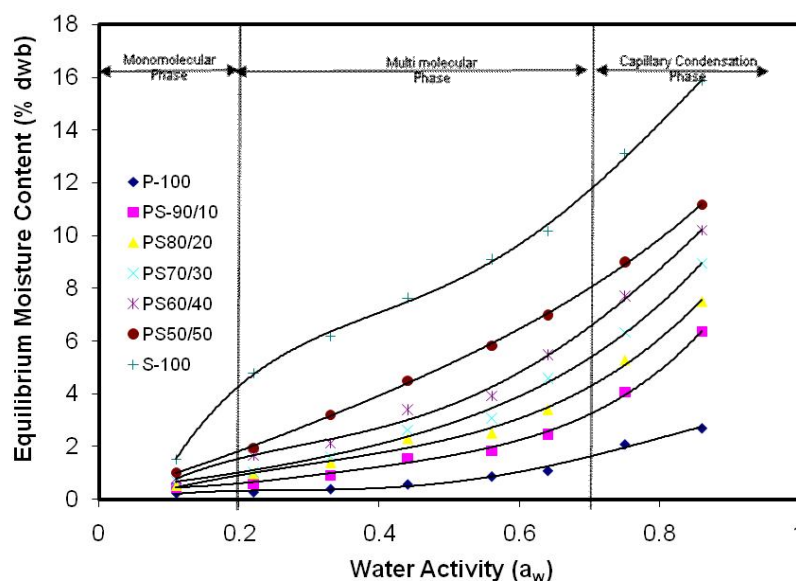

Figure 1: Equilibrium moisture content of PEO/starch blended films at different water activities.

PEO/starch blends had a tendency to lose moisture up to 0.24 in pure PEO and 1.52 in pure starch at 0.11 a_w respectively. Similarly, the values of PEO/starch blended films with different starch ratios (10 - 50%) lay in the range of 0.46 – 1.02. In multi-molecular layer phase, there has been a slow pick up in the moisture uptake in all combinations from 0.64 a_w to 0.7 a_w. In PEO it was from 1.1 at 0.64 a_w to 1.6 at 0.7 a_w where as, for starch, it was from 10.16 at 0.64 a_w to 11.62 at 0.7 a_w. In the capillary condensation phase, all combinations including plain PEO, plain starch and PEO/starch blends have shown a tendency to increase in moisture picks up to 2.71 for plain PEO and 15.85 for starch. Similar trends have also observed in blends of LDPE/starch (BaldevRaj et al, 2002), PVA/starch BaldevRaj et al, 2003b, polysaccharides / PVA (Sudhamani et al, 2005) and in chitosan /PVA (Srinivasa et al, 2003) with different ranges of moisture–sorption. The pure PEO exhibited lowest sorption isotherm behavior and the pure starch showed highest. The slope of the isotherm curves (Fig 1) was found to increase with an increase in starch content in the PEO/starch blended films. This was due to the higher moisture absorption capacity of starch. The slope order was highest in pure starch and was followed by 50, 40, 30, 20, 10 and 0 % (% w/w) starch in the PEO /starch films. The equilibrium moisture content

values for 0, 10, 20, 30, 40, 50 and 100% (%w/w) starch in PEO/starch blends at 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 taken from experimental data for analyzing the applicability of the eight sorption isotherm models. One of the important observations made during the study was that no visual microbial growth was observed up to 86% 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. However, microbial growth was observed at 92% RH and the PEO and starch blended films were too sticky to handle at this condition with EMC greater than 60 for films with a starch content ranging from 0 to 50%.

3.2. Sorption Model Analysis

Table 1: Linearized form of sorption models.

Sl No	Name of the Model	Equation	Linear Equation	Constants
1.	BET	$\dfrac{a_w}{(1-a_w)M} = \dfrac{1}{M_m C} + \dfrac{1}{CM_m}\left[\dfrac{(C-1)}{a_w}\right]$	$\dfrac{1}{(1-a_w)M} = \dfrac{1}{M_m} + \dfrac{1}{CM_m}\left[\dfrac{(1-a_w)}{a_w}\right]$	M_m, C
2.	Smith	$M = M_b - M_a \ln(1-a_w)$	$M = M_b - M_a \ln(1-a_w)$	M_b, M_a
3.	Halsey	$\ln(a_w) = \dfrac{-a}{RT\theta_r}$	$\ln(M) = a + r(\ln\{-\ln(a_w)\})$	a, r
4.	Oswin	$M = a\left(\dfrac{a_w}{1-a_w}\right)^n$	$\ln M = \ln a + n\ln\left(\dfrac{a_w}{1-a_w}\right)$	n, a
5.	Henderson	$\ln M = \dfrac{\ln\left[\ln\left\{\dfrac{1}{1-a_w}\right\}\right]}{B} - \dfrac{\{n A\}}{B}$	$\ln M = \dfrac{\ln\left[\ln\left\{\dfrac{1}{1-a_w}\right\}\right]}{3} - \dfrac{\{n A\}}{B}$	B, A
6.	Kuhn	$M = \dfrac{a}{\ln a_w} + b$	$M = \dfrac{a}{\ln a_w} + b$	a, b
7.	Iglesias and Chirife	$M = A + B\left\{\dfrac{a_w}{1-a_w}\right\}$	$M = A + B\left\{\dfrac{a_w}{1-a_w}\right\}$	B, A
8.	Freundlich	$M = A(a_w)^{1/b}$	$\ln M = \ln A + \dfrac{1}{b}\ln a_w$	A, b

Table 2: Sorption isotherm model constants and coefficient of determination (R^2) from linear fitting equations for PEO/starch blended films.

Sorption Model	Range of water activity	PEO /starch films(%wt)	Constants by linear fitting of sorption isotherms		R^2
BET	0.11-0.44		Mm	C	
		P-100	5.59	0.06	0.65
		PS-90/10	6.18	0.13	0.79
		PS80/20	4.98	0.34	0.99

		PS70/30	8.21	0.19	0.91
		PS60/40	8.21	0.31	0.98
		PS50/50	9.63	0.39	1.00
		S-100	12.8	0.98	0.94
Smith	0.11-0.86		Mb	Ma	
		P-100	-0.12	1.42	0.96
		PS-90/10	-0.30	3.18	0.97
		PS80/20	-0.10	3.78	0.99
		PS70/30	-0.08	4.54	0.99
		PS60/40	0.23	5.12	0.99
		PS50/50	0.91	5.55	0.98
		S-100	2.67	7.17	0.96
Halsey	0.44-0.86		a	r	
		P-100	-0.64	-0.93	0.95
		PS-90/10	0.23	-0.87	0.98
		PS80/20	0.62	-0.75	0.97
		PS70/30	0.82	-0.75	0.97
		PS60/40	1.09	-0.68	0.96
		PS50/50	1.46	-0.53	0.97
		S-100	1.96	-0.44	0.98
Oswin	0.11-0.86		n	a	
		P-100	1.6	47.88	0.99
		PS-90/10	1.42	2.15	0.98
		PS80/20	1.44	3.31	0.99
		PS70/30	1.46	4.55	0.98
		PS60/40	1.54	7.01	0.98
		PS50/50	1.60	11.13	0.97
		S-100	1.83	39.24	0.89

The sorption isotherm constants computed from the isotherm graphs using the EMC-a_w data for different sorption models were reported in Table 2. It is well recognized that the BET mono-layer equation is an effective method for estimating the amount of water bound to specific polar sites in dehydrated systems used for food applications (Labuza, 1968).

Sorption Model	Range of water activity	PEO /starch films(%wt)	Constants by linear fitting of sorption isotherms		R^2
	0.33-0.86		B	A	
		P-100	0.80	0.14	0.98
		PS-90/10	0.84	0.83	0.98
Henderson		PS80/20	0.96	1.22	0.97
		PS70/30	0.94	1.39	0.98
		PS60/40	1.02	1.71	0.98
		PS50/50	1.26	2.42	0.99

		S-100	1.68	3.95	0.99
Kuhn	0.11-0.65		A	B	
		P-100	-0.61	-0.12	0.98
		PS-90/10	-1.18	-0.09	0.99
		PS80/20	-1.53	-0.01	0.98
		PS70/30	-1.89	-0.01	0.98
		PS60/40	-2.23	0.19	0.98
		PS50/50	-2.60	0.66	0.94
		S-100	-3.36	2.36	0.88
Iglesias & Chirife	0.11-0.65		B	A	
		P-100	0.54	0.16	0.99
		PS-90/10	1.23	0.35	0.97
		PS80/20	1.66	0.53	0.95
		PS70/30	2.27	0.50	0.98
		PS60/40	2.65	0.82	0.97
		PS50/50	3.55	1.11	0.96
		S-100	4.58	2.95	0.85
Freundlich	0.33-0.86		A	B	
		P-100	3.28	0.49	0.95
		PS-90/10	6.89	0.52	0.94
		PS80/20	8.25	0.59	0.94
		PS70/30	10.26	0.58	0.96
		PS60/40	11.77	0.63	0.96
		PS50/50	12.93	0.77	0.99
		S-100	16.92	1.04	0.96

The BET mono-layer concept is a reasonable correct guide for two important aspects, namely; (i) mobility of small molecules in several food systems becomes apparent at BET mono-layer and (ii) the BET mono-layer correlates well with the total number of polar groups binding water. From a linear plot of $1/[(1-a_w)*M]$ versus $[(1-a_w)/a_w]$, the B.E.T constants, Mm and C were computed. The experimental sorption data applied to BET model for the varying starch content of PEO/starch films were found to fit well for a_w in the range 0.1 - 0.4. Chirife et al, 1978, BaldevRaj et al, 2002; 2003b; Sudhamani et al, 2005; Srinivasa et al, 2003; 2007b have demonstrated that the BET equation holds well between water activities for 0.05 - 0.45, which confirms the above findings. The BET constants were determined from a linear fitting of BET equation (Table 1) and the corresponding values are given in Table 2. The values of monomolecular moisture content (Mm) varied from 5.59 to 12.80 indicating that different PEO/starch blends had varying capacities for moisture sorption and also for availability of free water. The monomolecular moisture parameter of BET equation is important for shelf life studies.

The Smith model has also shown to fit water sorption isotherms of various biopolymers (Labuza, 1968). Protein films showed goodness of fit in the range of 0.33

to 0.84 a_w as reported by Gennadios et al, 1994. A good fit was documented for adsorption and desorption isotherms of Virgina-type peanuts above a_w of 0.3 (Young, 1976). Smith model gave a satisfactory fit for water sorption curves of several food commodities including dried peas, dried figs, etc., (Pixton and Howe, 1983). In the present study, from a linear regression of M versus ln (1-a_w), the Smith constants like Mb and Ma were computed from intercept and slope of the line. The Smith model holds well for a_w in the range of 0.1 - 0.86. This was in conformity with the result of reported literatures (Sudhamani et al, 2005; Srinivasa et al, 2003; 2007b). The Smith constants were evaluated in a similar way compared to the BET constants. The smith constants **Mb** and **Ma** ranged from -0.12 to 2.67 and 1.42 to 7.17 for films with a starch content ranging from 0 to 100%.

Use of Halsey model is recommended for meat, milk products and vegetables (Boquet et al, 1978). This model was successfully applied for water sorption data of several nuts and oil seeds Lomauro et al, 1985°; 1985b; Iglesias et al, 1975 and Chirif et al, 1978 found that, Halsey model useful to explain reasonably well the sorption of dried figs, apricots. Halsey model was proposed an expression for condensation of multilayer's at relatively large distance from the surface. In this investigation the Halsey model was found good for a_w in the range of 0.4 – 0.86. Halsey constants were estimated from a linear plot of ln(M) versus [ln {-ln(a_w)}] and constants **a** and **r** varied from -0.64 to 1.96 and -0.93 to -0.44, respectively. This was in conformity with the result of reported literatures (Sudhamani et al, 2005; Srinivasa et al, 2003; 2007b).

Oswin model was found very suitable to describe sorption isotherms of proteins and starchy foods. Boquet, et al, 1978 and Lomauro et al, 1985a; 1985b concluded that this model fitted sorption data for a considerable number of nuts, spices, coffee, etc. This model is based on the mathematical series expansion for sigmoid shaped curves, n and a are determined by linear regression of ln (M) versus ln(a_w / (1- a_w)). The use of oswin model for the experimental sorption data of PEO/starch films was studied. It was observed that the experimental sorption data of PEO/starch films applied to Oswin model as given in Oswin equation (Table 1) fitted very well for a_w in the range of 0.1 - 0.86. The oswin constants n and a varied from 1.6 to 1.83 and 47.88 to 39.24 for films with different starch concentrations are shown in Table 2.

The Henderson constants **B** and **A** were calculated from a linear plot of ln (M) versus [ln(-ln(1/(1-a_w)))].These constants varied from 0.80 to 1.68 and 0.14 to 3.95 respectively. This model was good for a_w ranged from 0.33 to 0.86.

The constants **a** and **b** of the Kuhn model varied from -0.61 to -3.36 and -0.12 to 2.36, respectively is given in Table.2 for films with a starch content ranging from 0 to 100%. It was observed that experimental sorption data of PEO/starch films applied to the Kuhn model, fit very well for a_w ranged from 0.11 to 0.65.The results were in accordance with literature reports (BaldevRaj et al, 2003).

Iglesias et al, 1975 described the lower portion of air dried beef isotherm between 0.1 to 0.45 a_w. This model holds good for a_w ranging from 0.11 to 0.65. The constants **B** and **A** varied from 0.54 to 4.58 and 0.16 to 2.95, respectively for the films with PEO concentration ranging from 0 to 100% are shown in Table 2.

Freundlich model is useful in the analysis of sorption phenomena in high sugar foods like most fruits. The Freundlich constants A and b estimated from the linear plot

of (ln M) versus (-ln(a_w)) in the a_w range of 0.33 to 0.86, varied from 3.28 to 16.92 and 0.49 to 1.04 (Table 2) as starch concentration increased. The constants derived from different sorption models were useful in the evaluation of the stability of PEO/starch based packaging films. Linear models with high R^2 are considered to be statistically acceptable.

4. Conclusion

In summary, the PEO/starch blended films showed several interesting characteristics. The moisture sorption characteristics of PEO/starch in PEO/starch blends are significant for ascertaining its use as a bio-packaging material. The data confirms the applicability of these models for different ranges of water activity varying from a range of 0.1 to 0.4 for BET, 0.11 to 0.86 for Smith, Oswin, 0.44 to 0.86 for Halsey, 0.33 to 0.86 for Henderson, Freundlich and 0.11 to 0.65 for Kuhn, Iglesias & Chirife isotherm models. Smith model found to be the best model as its applicability ranges from 0.11 to 0.86. Overall, the sorption analysis of different models showed extremely good to very good fit as determined by R^2 values will provide insight into the prediction of the durability under the specified range and functional behaviour of biopolymer based packaging materials.

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