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Properties and sorption studies of chitosan–polyvinyl alcohol blend films

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Abstract

Chitosan–polyvinyl alcohol (PVA) blend films were prepared and characterized for mechanical and optical properties. Intermolecular interaction between chitosan–PVA blend was investigated using FTIR. Moisture sorption characteristics of chitosan–PVA blend at 25 °C were studied for water activities ranging from 0.11 to 0.92. The moisture content increased with increase in PVA concentration. The moisture sorption data were used to fit eight sorption models and constants were determined by linear fitting. The co-efficient of linear regression (0.98–0.99) and root mean square error values (1.08–15.32) confirmed the best fit for all the models. GAB model was applicable for a wide range of water activity.

Keywords: Chitosan–polyvinyl alcohol blend; Optical properties; Water activity

1. Introduction

Approximately 40,000,000 tons of plastic packaging is used annually world wide, and a majority of this is put to one time use and is discarded later. This contributes to an appreciable amount of total waste stream (around 20 vol% world wide) (Hally et al., 2001) and in India its contribution is approximately 3 million tons (Modi, 2000). Plastic materials are non-degradable in nature and result in continuous accumulation in the environment and causes severe pollution. As a result interest exists on developing biodegradable plastic materials from natural sources such as starch, cellulose, chitosan, etc. Chitosan is a deacetylated form of chitin, the second most abundant natural polymer obtained from shells of crab, shrimp and krill. Chitosan is non-toxic, biodegradable and has film forming properties, which find applications in various fields.

Polyvinyl alcohol (PVA) is a synthetic water soluble polymer with good film forming property, which offers good tensile strength (TS), flexibility and barrier properties to oxygen and aroma (Schellekens & Bastiansen, 1991).

Polymer blending is one of the effective methods for providing new desirable polymeric materials for a variety of applications. Improvement of the selectivity of chitosan membrane by manipulating its chain flexibility is a promising approach for producing polymeric packaging films for specific purposes (Arvanitoyannis, Kolokuris, Nakayama, Yamamoto, & Aiba, 1997). PVA blended with starch and LDPE as packaging materials for intermediate moisture foods have been reported (Holton, Asp, & Zottola, 1994). Studies on chitosan–PVA blend films for medical devices and controlled delivery of drugs (Miya, Yoshikawa, Iwamoto, & Mima, 1983) are reported.

An important role of packaging material as a packaging film or an edible film is to reduce exchange of water between product and environment (Coupland, Shaw, Monahan, Oriordan, & Osullivan, 2000). The barrier property of film depends on both molecular diffusion co-efficient and its diffusion into the matrix (McHugh & Krochta, 1994). The moisture sorption isotherm is a means to characterize the water absorption of the film, which in turn is transmitted to the product

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inside. Knowledge of sorption isotherm is also important for predicting stability and quality changes during packaging and storage of food product. Chirife and Iglesias (1978) reviewed a number of isotherm equations for food and food products and relatively only a few isotherms are reported for packaging film materials. 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 (1995) reported sorption isotherm for methyl and hydroxypropyl cellulose films. Wiles, Vergano, Barron, Bunn, and Testin (2000) reported sorption behaviour of chitosan films. Mechanical properties of chitosan–PVA films were studied by Blair, Guthrie, Law, and Turkington (1987) and Park, Jun, and Marsh (2001), but no work has been reported on sorption isotherm studies of such blend films. The objective of this work was to produce chitosan–PVA blend films and to study their optical, mechanical and FTIR properties, and to develop suitable sorption isotherm models.

2. Experimental

2.1. Materials

Chitosan sample (Degree of Deacetylation DD, 78% and molecular weight 100,000 Da), obtained from CFTRI Resource centre at Mangalore was prepared from shrimp chitin by *N*-deacetylation with 40% sodium hydroxide solution at 100 °C for 60 min. PVA chemical grade was obtained from Loba Chemi Pvt Ltd, Mumbai. (Dp 1700–1800).

2.2. Preparation of chitosan–PVA blend films

A series of chitosan–PVA blends were prepared from varying concentration of chitosan using dilute acetic acid as a solvent. The PVA was dissolved in hot water with constant stirring. After complete solubilization the PVA solution was cooled, and 1% acetic acid and chitosan were added. After complete dissolution the blend was passed through 80 No. sieve followed by degassing and films were prepared by wet casting method (Srinivasa, Ramesh, & Tharanathan, 2002). The chitosan (2%, w/v) and PVA (2.3%, w/v) concentrations were optimized for preparation of pure and blend chitosan–PVA films.

2.3. Optical properties

Colour, opacity and Haziness of the films were measured using colour measuring instrument D-3500d Minolta (Minolta, Japan).

2.4. Mechanical properties

A LLOYD universal testing machine (LLOYDS, UK) was used to measure TS and percent elongation (%E) at break. The samples (100 × 15 mm) were cut and film thickness was measured. The jaw separation was 50 mm and the rate of loading was 50 mm/min. TS was calculated by dividing the maximum (peak) load by original cross-sectional area. The average TS, %E and modulus of elasticity values were measured for five replicates.

2.5. Infrared spectroscopy

IR spectra in the range 3200–1000 cm^{-1} of chitosan–PVA blends were scanned in a FTIR spectrometer (Perkin–Elmer spectrum 2000, USA) under dry air at room temperature. Absorbed solvents were removed from blend films by keeping in 0% RH desiccators.

2.6. Sorption studies

Saturated salt solutions of lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, magnesium nitrate, sodium nitrite, sodium chloride, potassium chromate and ammonium phosphate were used to obtain different RH combinations having a_w values of 0.11, 0.22, 0.33, 0.44, 0.54, 0.64, 0.72, 0.86 and 0.92, respectively. These saturated solutions were taken in different desiccators. Prior to keeping the film, specimens were conditioned to 65% RH at 27 °C. The initial moisture content of the blend films was measured in duplicate on dry basis (db in %) by drying in hot air oven at 100 ± 2 °C to constant weight (AOAC, 1990). The sorption experiments were carried out by keeping approximately 500 mg of blend films (1 cm × 1 cm) in desiccators, removing at frequent intervals and weighing until they reach constant weight (within ±5%). All chemicals were of analytical grade.

2.7. Sorption models

A number of sorption isotherm models has been reported in the literature. In the present study BET (Labuza, 1968), GAB (Bizot, 1983), Caurie (1970), Halsey, Smith, Oswin, Bradley (Chirife & Iglesias, 1978) and Harkins and Jura (Labuza, 1968) models were used for fitting the sorption data. The equations were rearranged to linear form to determine the appropriate constants (Table 1) by regression analysis using MS-Excel Software (Microsoft Inc. 2000).

The sorption data were analysed according to the models and the corresponding constants were determined. The goodness of fit of each model was computed in terms of coefficient of determination (R^2) from the plot of experimental (M_{exp}) and predicted (M_{pre}) sorption moisture and root mean square error (RMSE) values, as

Table 1
Moisture sorption models used

Sl no.	Model	Equation	Linearized equation	Constants	Reference
1	BET	$M = \frac{M_m C a_w}{(1-a_w)[(1+(C-1)a_w]}$	$\frac{aw}{(1-a_w)M} = \frac{(C-1)}{M_m C} + \frac{1}{M_m C}$	M_m, C	Bizot (1983), Caurie et al. (1976), and Labuza (1968)
2	GAB	$\frac{M}{M_0} = \frac{GKa_w}{(1-Ka_w)[1-Ka_w+GKa_w]}$	$M = \frac{a_w}{(Aa_w^2)+Ba_w+C]}$, where $A = \frac{K}{M_0[(1/G)-1]}$, $B = \frac{1}{M_0[1-(2/G)]}$, $C = \frac{1}{M_0 GK}$	M_0, G, K	Bizot (1983)
3	Caurie	$\ln M = a + ba_w$	$\ln M = a + ba_w$	a, b	Caurie (1970)
4	Halsey	$\ln = \exp[\frac{-a}{RT\theta^r}]$	$\ln(\theta) = a + r[\ln - (\ln a_w)]$	a, r	Chirife and Iglesias (1978)
5	Smith	$M = M_b - M_a \ln(a_w)$	$M = M_b - M_a \ln(1-a_w)$	M_a, M_b	Chirife and Iglesias (1978)
6	Oswin	$M = [\frac{a_w}{(1-a_w)}]^n$	$\ln M = \ln a + n \ln[\frac{a_w}{(1-a_w)}]$	a, n	Chirife and Iglesias (1978)
7	Bradley	$\ln[\frac{1}{a_w}] = K_1 \times K_2^M$	$\ln[\frac{1}{a_w}] = \ln K_1 + M \ln(K_2)$	K_1, K_2	Chirife and Iglesias (1978)
8	Harkins–Jura	$\ln(a_w) = B - [\frac{A}{M^2}]$	$\ln(\ln a_w) = \ln A + B \ln(M^2)$	A, B	Labuza (1968)

follows

$$\mathrm{RMSE} = \{[(M_{exp} - M_{pre})/M_{exp}]^2/N\}^{0.5} \times 100 \qquad (1)$$

M_{exp} moisture content experimental (% db)
M_{pre} moisture content predicted (% db)
N number of observations

3. Results and discussion

3.1. Optical property

Colour of the packaging is an important factor in terms of general appearance and consumer acceptance. The Hunter L, a, b values for the different blends of chitosan–PVA are reported in Table 2. The main difference observed was that films with higher concentration of PVA had lighter colour as indicated in L values. The measure of hunter b (yellowness) values showed an increase from -0.31 for PVA to 8.26 for chitosan films. Similar changes were also observed in Hunter a values. The colour measurement may be affected by film thickness. The opacity of the film indicates the degree of transparency of films. The chitosan film showed a higher value (8.11%) and as chitosan concentration decreased the value also decreased and lowest value was observed in PVA film (7.03%). A similar trend was also observed in haze value where chitosan film had highest value (3.45%) and PVA films had the lowest value (1.30%).

3.2. Mechanical properties

Mechanical properties of chitosan–PVA blend films cast in different proportions are shown in Table 3. Chitosan films (100%) showed higher TS (55.46 MPa) whereas pure

Table 2
Optical properties of chitosan–PVA blend films

Chitosan–PVA (%ratio, w/v)	Hunter colour values			Opacity (%)	Haze (%)
	L	a	b		
100–0	96.48	−1.20	8.26	8.11	3.45
80–20	97.05	−1.09	6.60	7.98	2.53
60–40	96.90	−0.82	3.96	7.80	2.12
40–60	96.93	−0.65	1.31	7.83	1.96
20–80	96.93	−0.54	1.27	7.61	1.84
0–100	98.21	−0.39	−0.31	7.03	1.30

Table 3
Mechanical properties of chitosan–PVA blend films

Chitosan–PVA (%ratio, w/v)	Tensile strength (MPa)	%Elongation	Modulus of elasticity (MPa)
100–0	55.56(4.65)[a]	8(2.56)	1874(342)
80–20	46.99(3.85)	26.84(7.87)	1527.84(248)
60–40	31.95(6.20)	28.9(11.7)	539.22(98.71)
40–60	37.23(3.82)	60.58(9.01)	345(105)
20–80	32.0(5.65)	70.55(6.91)	231(72.43)
0–100	25.64(3.86)	105.47(6.87)	120(56)

[a] Indicates standard error of mean.

PVA films had lower values (25.24 MPa). The TS of blend films showed a decreasing trend with increase in PVA concentration. At 60–40 concentration of chitosan–PVA the TS was higher as compared to those of 80–20 and 40–60 blend films. Blair et al. (1987) have observed a similar trend with chitosan–PVA blends of different proportions. TS was reduced in the presence of PVA, probably due to reduced crystallinity of chitosan in the blend. Miya et al. (1983) also studied similar blends and observed that PVA molecule in the blend tend to disrupt crystallinity of chitosan. On the contrary, an increase in TS of blend films has been reported (Park et al., 2001). The 80–20 blend is having better property than 60–40 blends, since there is a sudden decrease in the modulus of elasticity and no significant changes were observed in TS. The lower strength of PVA may also be due to its low degree of polymerization.

The results of %E at break showed that the chitosan films had lower strength compared to PVA films. In blended films %E decreased with increase in chitosan concentration.

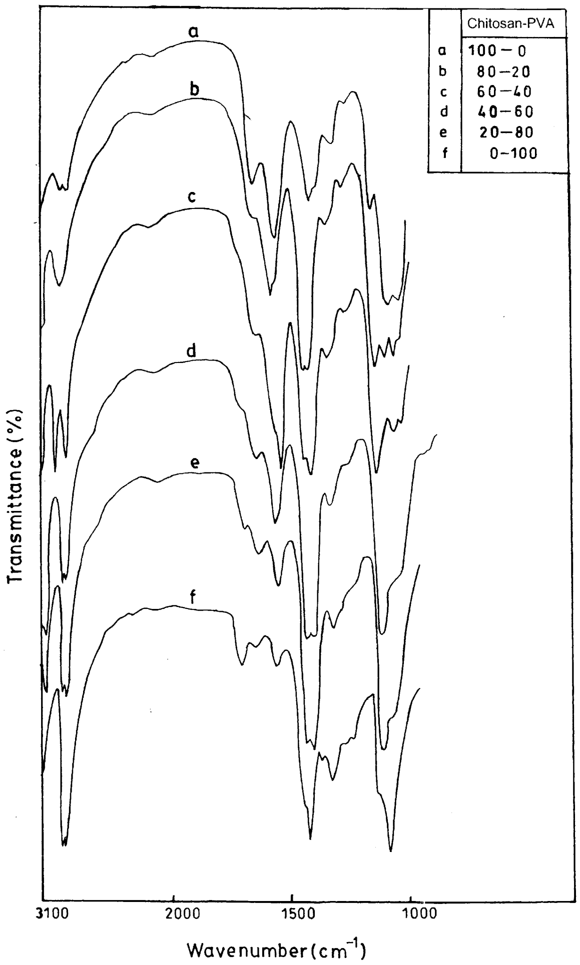

Fig. 1. FTIR spectra of chitosan–PVA blend films.

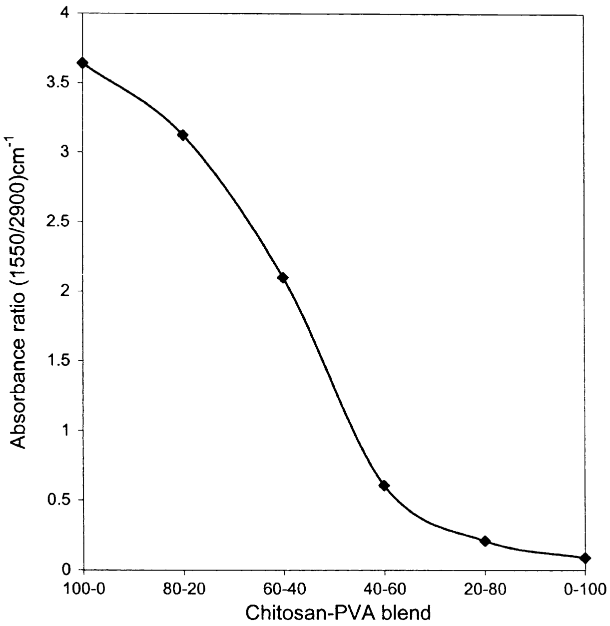

Fig. 2. Ratio of absorbance at (1550/2900) cm^{-1} of blend films.

3.3. FTIR characterization

FTIR spectra of chitosan, PVA and their blends are shown in Fig. 1. The absorption peaks around 1640 and 1560 cm^{-1} are attributed to asymmetric stretching and bending of acetamido groups, respectively. The change in the characteristic shape of the chitosan spectra as well as shifting of peak to a lower frequency range due to hydrogen bonding between –OH of PVA and –OH or NH_2 of chitosan were observed in the blend films. To determine the blending ratio, a base line was drawn with reference to –CH stretching (by PVA) around 2900 cm^{-1} and the ratio of absorption was made with respect to 1550 cm^{-1}. A graph was plotted between chitosan–PVA concentration versus 1550/2900 cm^{-1} ratios (Fig. 2), whose regression coefficient was found to be 0.94.

3.4. Sorption models

The relationship between a_w and moisture content (at constant temperature) is described by moisture isotherm. The time to reach equilibrium was about 25–30 days for different films and at 92% RH, some mould was detected by visual inspection at edges and on the surface at the end of 25th day. The sorption isotherm curves for equilibrium moisture content (db) obtained form different concentrations of chitosan–PVA blends, shown in Fig. 3, had three phases, viz. (I) region A—corresponding to <0.2 of a_w which relates to adsorption of monomolecular film of water, (ii) region B—corresponding to adsorption of additional layers over this monolayer at a_w 0.2–0.7 and (iii) region C—for $a_w > 0.7$, corresponding to condensation of water in the pores of the material followed by dissolution of soluble material. At lower a_w the slope of the curve was

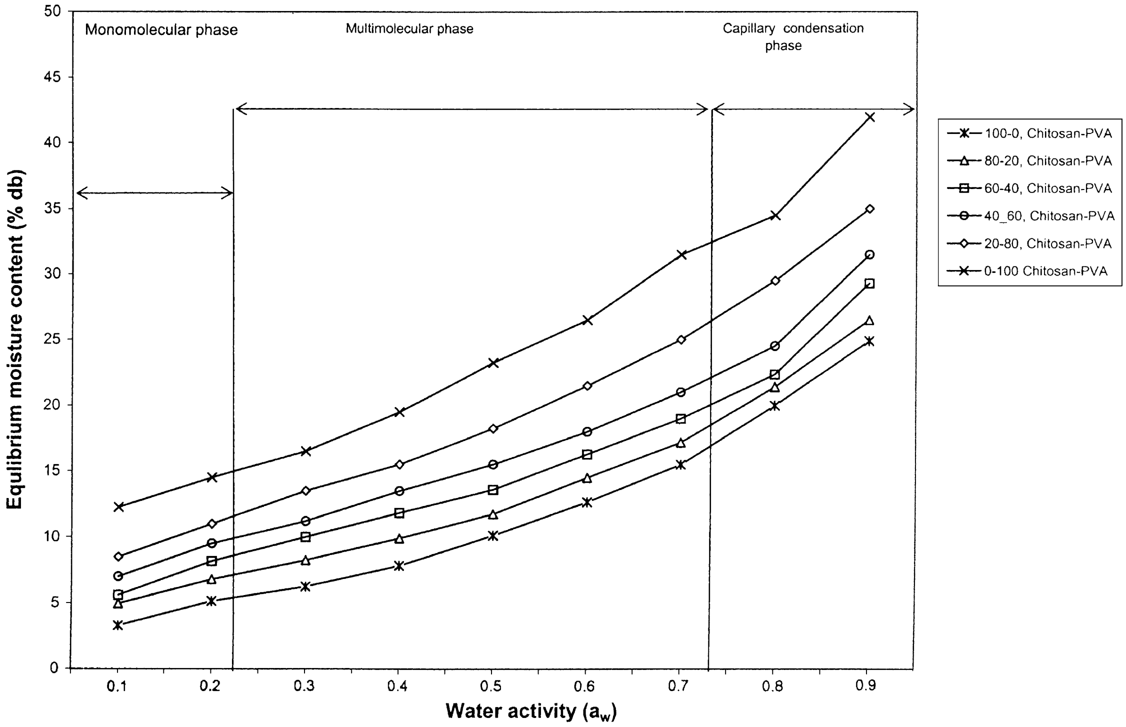

Fig. 3. Sorption isotherm of chitosan–PVA blend films.

less, with increase in a_w the slope increased rapidly. The moisture content in blend films increased with increase in the PVA concentration.

3.5. Sorption model analysis

Although BET model holds only for a limited range of (a_w) two familiar constants—monolayer constant (M_m) and energy constants were obtained, which decreased with increase in PVA concentration. This may be due to reduction in the total active water binding sites. Halsey's model is applicable to a higher range of a_w and is more suitable than BET model. The constant a increased from 2.14 to 3.01, whereas b decreased from 0.52 to 0.34 (Table 4).

The GAB model has received great application in sorption studies of food. The GAB constants M_0, G and K were computed from linear regression of $1/M$ versus a_w. The M_0 values of blend films increased with decrease in PVA concentration, due to increase in total number of available active sites for water binding (Iglesias and chirife, 1976).

The Caurie model holds good for a_w ranging from 0.1 to 0.9. This range was in conformity with the goodness of fit. Caurie constants r and A varied from 2.41 to 1.52 and 2.92 to 10.61, respectively, for the films with chitosan concentration ranging from 0 to 100%. The Halsey constants a and r, estimated from the linear plot of $\ln[M]$ versus $[\ln - \{\ln(a_w)\}]$ in the a_w range 0.1–0.9, varied from 1.43 to 2.84 and 1.45 to 2.32 as the PVA concentration increased. The Smith model is represented by equation, which holds good for a_w range from 0.1 to 0.9 and the constants M_a ranged from -10.02 to -13.34 and M_b ranged from 2.91 to 12.41 for films with chitosan varying from 100 to 0%. This can be attributed to structural differences in the multilayer and capillary condensation zone. The linear form of the Oswin model was applied to experimental data by linear regression analysis. Although the equation gives an acceptable correlation it showed considerable deviation at higher PVA concentration. The constants a varied from 9.84 to 22.13 and n varied from 0.50 to 0.286 (Table 4).

The Bradley model holds good for a_w in the range 0.1–0.9. The constant K_1 was 0.88 ± 0.01, whereas K_2 ranged from 3.0 to 6.78 for 100% chitosan to 100% PVA. Harkins–Jura model was applicable for a_w range between 0.1 and 0.6. The results showed that regression coefficient was very well fitted to blend films, except for 60:40 blend film, whose regression value was 0.91 and RMSE value was 13.25. Sorption analysis of different models showed extremely good to very good fit as determined by RMSE and R^2 values. The constants derived from different sorption models are useful in the evaluation of the stability of chitosan-based packaging films. The applicability of water activity values will throw valuable information on the durability of packaging material for specific purpose. The constants derived from the respective models could be utilized to predict the equilibrium moisture content (EMC) values, in comparison with the experimental values. It can be

Table 4
Sorption isotherm model constants and coefficient of regression (R^2) values for chitosan–PVA blend films

Model isotherm	Range of water activity (a_w)	Chitosan–PVA (%ratio, w/v)	Constants of linear fitting			R^2	RMSE
			M_m	C			
BET	0.1–0.5	100–0	5.45	10.72		0.99	2.15
		80–20	6.18	27.44		0.99	2.31
		60–40	7.16	29.72		0.99	8.50
		40–60	7.89	52.79		0.99	3.99
		20–80	9.46	52.85		0.99	3.23
		0–100	11.74	213.0		0.99	1.08
			M_0	G	K		
GAB	0.1–0.9	100–0	6.82	8.0	0.835	0.99	4.09
		80–20	7.86	14.32	0.80	0.99	2.46
		60–40	9.69	13.13	0.749	0.99	3.12
		40–60	10.13	20.69	0.756	0.99	2.51
		20–80	12.76	18.32	0.725	0.99	2.25
		0–100	15.76	25.59	0.708	0.99	4.14
			a	B			
Caurie	0.1–0.9	100–0	2.92	2.41		0.99	5.65
		80–20	4.36	2.00		0.98	4.32
		60–40	5.12	1.92		0.99	8.61
		40–60	6.34	1.74		0.99	4.42
		20–80	7.71	1.70		0.99	3.26
		0–100	10.61	1.52		0.99	1.82
			a	R			
Halsey	0.1–0.9	100–0	1.43	1.45		0.99	9.93
		80–20	1.93	1.77		0.99	6.83
		60–40	1.89	1.80		0.96	10.86
		40–60	2.29	2.03		0.97	6.65
		20–80	2.32	2.07		0.98	6.59
		0–100	2.84	2.32		0.97	5.47
			M_b	M_a			
Smith	0.1–0.9	100–0	2.91	−10.02		0.99	7.77
		80–20	4.77	−9.87		0.98	6.41
		60–40	5.91	−10.45		0.99	12.21
		40–60	7.18	−10.80		0.98	6.98
		20–80	9.08	−12.12		0.98	8.55
		0–100	12.41	−13.74		0.99	6.62
			a	N			
Oswin	0.1–0.9	100–0	9.84	0.50		0.99	6.64
		80–20	11.63	0.39		0.99	3.78
		60–40	13.95	0.425		0.99	9.16
		40–60	15.04	0.346		0.98	2.80
		20–80	18.04	0.347		0.98	3.90
		0–100	22.13	0.286		0.99	5.19
			K_1	K_2			
Bradley	0.1–0.9	100–0	0.87	3.0		0.99	15.32
		80–20	0.87	3.91		0.99	8.59
		60–40	0.88	4.35		0.99	4.46
		40–60	0.88	5.00		0.99	5.61
		20–80	0.89	5.56		0.99	5.25
		0–100	0.89	6.78		0.99	6.23
			A	B			
Harkins–Jura	0.1–0.6	100–0	23.31	−0.37		0.95	13.25
		80–20	55.43	−0.23		0.99	7.11
		60–40	60.20	−0.32		0.91	13.05
		40–60	114.61	−0.14		0.99	5.52
		20–80	167.73	−0.13		0.99	5.14
		0–100	347.98	−0.03		0.99	2.87

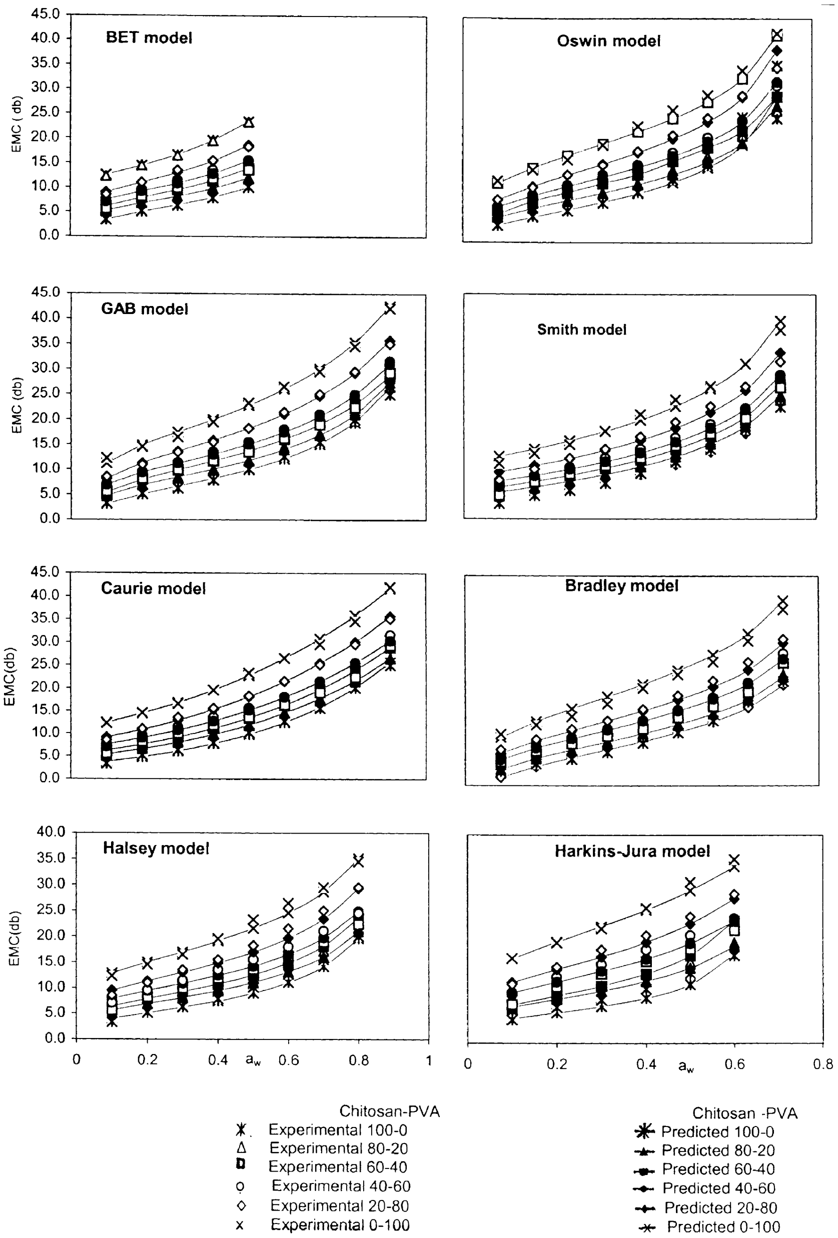

Fig. 4. Sorption isotherm of chitosan–PVA blend films with various sorption models obtained through experiment (with lines) and predicted (symbols).

observed from Fig. 4 that all the models could successfully predict the EMC values at all combinations of chitosan–PVA. However, the GAB model had the lowest RMSE and highest R^2 values, indicating it to be the best model. Linear models with high R^2 and low RMSE are considered to be statistically acceptable.

4. Conclusions

The optical properties and TS of the chitosan–PVA blend films increased while %E decreased with increase in chitosan concentration and a blend ratio of 80–20 was found to be the best. Moisture sorption isotherms showed sigmoid pattern, indicating the influence of PVA concentration. Sorption data were useful in choosing suitable packaging material having a desirable water vapour barrier property. The GAB model showed a better fit compared to other models and is applicable to a wide range of water activity values.

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