MOISTURE/SORPTION CHARACTERISTICS OF STARCH-FILLED POLY (STYRENE-CO-BUTYL ACRYLATE) LATEX BASED COMPOSITES REINFORCED WITH POLYESTER NONWOVEN FABRIC

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Abstract:

Poly (styrene-co-butyl acrylate) latex was prepared with a 70:30 weight ratio of styrene to butyl acrylate. The prepared latex was incorporated with various weight percentages of cornstarch. The cornstarch-filled copolymer latex was used as a matrix to fabricate the polyester nonwoven fabric reinforced composites. The pickup ratio of latex to fabric was maintained at 3.2:1. The moisture sorption characteristics of composites were examined at 27^0C for water activity (a_w) from 0.1 to 0.9. The sorption data was 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 Braunauer-Emmet-Teller (BET) model, and between 0.3 and 0.9 (multimolecular and capillary condensation layers) for other models. The value of the coefficient of determination (R2 = 0.97±0.02) confirms the linear fitting of the equations studied.

Key words:

polyester nonwoven fabric, styrene-co-butyl acrylate latex, starch, composites, water activity and sorption isotherm

Introduction

The sorption properties of any material are very important for the design and optimisation of many processes such as drying, packaging and storage. The sorptive uptake of composites by saturated solutions of different compounds having different water activities at a constant temperature yields sorption isotherms. One of the major challenges today is to maintain the mechanical and/or barrier properties during storage until disposal [1]. Water activity (a_w) has become the basic controlling factor in the preservation of moisture-sensitive material for packaging applications against microbiological, chemical and physical deterioration [2]. Because of the hydrophilic nature of starch, there is a need to address the sorption influence of starch present in the composites to make it suitable for barrier application. Corn starch was used for the present study, since the mechanical properties of composites with corn starch are better than those of the other types of starches [3]. The purpose of the present work is to study the moisture-sorption characteristics of starch-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites. Equations for modelling water absorption isotherms are of special interest in many aspects of preserving food by dehydration [4]. The sorption isotherms obtained from the experimental data result in an estimation of the equilibrium moisture content, which is necessary to predict the hygroscopic properties of the composites. The equilibrium moisture content is an important quantitative measure in the practice of food storage, packaging and drying [5].

Many mathematical models have been proposed in the literature for modelling hygroscopic equilibrium data in material preservation [6-8]. In an earlier communication [9], the authors have studied the physico-mechanical and water absorption behaviour of the composites. The present article deals with the behaviour of water activity on starch-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites, employing six sorption isotherm models proposed by Brunauer, Emmett & Teller [10], Smith [11], Halsey [12], Caurie [13] and Oswin [14]. Applicable ranges of water activity for the sorption isotherms of composites are reported.

Experimental

Materials

Styrene (St) and butyl acrylate (BA) monomers of pure reagent grade were obtained from Aldrich chemical, USA and used directly after removing the inhibitor. Linear alkyl benzene sulphonate (LABS), potassium persulphate (PPS), sodium hydroxide, tapioca starch (used as protective colloid) and corn starch (used as filler) were obtained from SD Fine Chem., India.

Uniaxially-oriented, polyester-based, needle-punched nonwoven (150 g/m^2) fabric with a density of 0.2 g/cc, an air permeability of 27-mt^3/m^2/min at 20 WG and a burst strength of 8 kg/cm^2 was procured from the local supplier. The fibre used to make the fabric has a 3 denier × 64 mm length.

Standards for water activity (a_w)

Saturated salt solutions of lithium chloride ($LiCl_2$), potassium acetate (CH_3COOK), magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), sodium dichromate ($Na_2Cr_2O_7$), sodium chloride (NaCl), potassium chromate ($K_2Cr_2O_3$) and ammonium phosphate [$(NH_4)_2$ PO_4] were used as a_w standard of 0.11, 0.22, 0.33, 0.44, 0.54, 0.64, 0.75, 0.86 and 0.92 respectively. All chemicals were of analytical grade obtained from M/s from the Ranbaxy Chemicals Company. The saturated solutions of these chemicals were put into different desiccators in which the samples were placed.

Preparation of starch filled poly(styrene-co-butyl acrylate) latex

The copolymerisation of styrene and butyl acrylate monomer was carried out using conventional emulsion polymerisation [15]. The weight ratio of styrene to butyl acrylate was maintained at 70:30. Aqueous cornstarch of 50 %, was prepared and a calculated amount of cornstarch dispersion was added to the copolymer latex. The ratio of copolymer latex to cornstarch was varied over a range of 100:0 to 50:50 on a dry-to-dry weight basis.

Fabrication of composite

Polyester nonwoven fabric of 150 g/m^2 was impregnated into a bath containing corn starch-filled poly(styrene-co-butyl acrylate) latex-based matrix. The dipped fabric is squeezed in a two-roll squeezer to adjust the desired optimised pickup of latex to fabric (3.2:1). After the desired latex pickup was adjusted, the impregnated fabric was dried in a hot air oven at 150^{0}C for 20min. The composites were fabricated with a latex-based matrix filled with different weight ratios of corn starch, viz. 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 on a dry-to-dry weight basis.

Sorption experiments

Composite specimens of size 1×1 cm^2 were conditioned at 65% RH and 27 ± 1^{0}C before being exposed to different water activities (a_w) at 27^{0}C. The initial moisture content (IMC) of the composite specimens of different compositions were measured on a dry-weight basis by drying in a hot-air oven at 100 ± 5^{0}C until constant weight was obtained. The approximate time taken for drying was 6 h. Exposing the specimens in desiccators with different a_w from 0.11 to 0.92 at 27 ± 1^{0}C performed the sorption isotherm determination. The composite specimens were weighed until equilibrium (i.e. ±0.05 % change in moisture content) was attained for a period of 50 to 60 days.

Sorption isotherm models

Five sorption-isotherm equations by Braunauer-Emmet-Teller (BET), Smith, Halsey, Caurie and Oswin were used to fit the experimental cornstarch-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites' sorption isotherm data. A re-arrangement of the equations was performed to facilitate the determination of the appropriate coefficients using statistical modelling. Those models are expressed and rearranged, and are discussed below.

The Braunauer-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 moisture content and C is the constant related to the net heat of sorption. It is well recognised that the BET equation is an effective method for estimating the amount of water bound to specific polar sites.

The BET concept is a reasonably correct guide for two important reasons; namely, (i) the mobility of small molecules in several food systems becomes apparent on the BET monolayer and (ii) the BET monolayer correlates well with the total number of polar groups binding with water.

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

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

The 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.

The Halsey isotherm model

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

$$a_w= e^{(-Ea/RT\theta)} \quad (4)$$

where $\theta = M/M_m$ and R is the gas constant at temperature T. The above equation was simplified for the isothermal sorption characteristic as follows:

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

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

The Caurie isotherm model

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

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

where r and A are constants and M is the equilibrium moisture content. From the linear plot of $\ln (M)$ versus a_w, the Caurie constants were computed.

The Oswin isotherm model

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

$$M = a \{[a_w/(1-a_w)]\}^{n} \quad (7)$$

where a and n are constants. Equation (7) can be rearranged as follows;

$$\ln (M) = \ln (a) + n \ln [a_w/(1-a_w)] \quad (8)$$

'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. The effect of cornstarch content on the moisture-sorption characteristic of composites are shown in Figure 1. All the moisture-sorption isotherm curves typically displayed a sigmoid shape. Baldevraj et al. [9] made a similar observation with respect to pure starch and LDPE/starch blends. As is evident from Figure 1, the sorption isotherms had three phases of sorption behaviour, namely the monomolecular layer phase from 0.2 a_w, the multi-molecular layer phase from 0.2 to 0.7 a_w and the capillary condensation phase from 0.7 and above a_w. With the increase in the starch content and the increase in a_w, the slope of the isotherms increased, due to the higher sorption of water molecules by starch and/or more sorption capacity of starch. The initial moisture content (IMC) values of poly(styrene-co-butyl acrylate)/polyester nonwoven composites with varying starch content from 0 to 50%, and their corresponding water activities are shown in Table 1. It was observed that the a_w values increased with the increase in the starch content up to 30%. Beyond 30% of starch in the composite, the a_w value was almost constant. This may be due to the optimised concentration of starch content at 30%. The equilibrium moisture content values for 0, 10, 20, 30, 40 and 50% (w/w) starch in poly(styrene-co-butyl acrylate)/polyester nonwoven composites 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 obtained from Figure 1.

Table 1. Variation of IMC with water activity (aw) for poly (styrene-co-butyl acrylate) – polyester nonwoven fabric composites.

Sample formulation poly (styrene-co-butyl acrylate / strarch	IMC	Water activity (a_w)
90/10	0.89	0.22
80/20	2.10	0.33
70/30	4.18	0.54
60/40	6.05	0.64
50/50	9.12	0.64

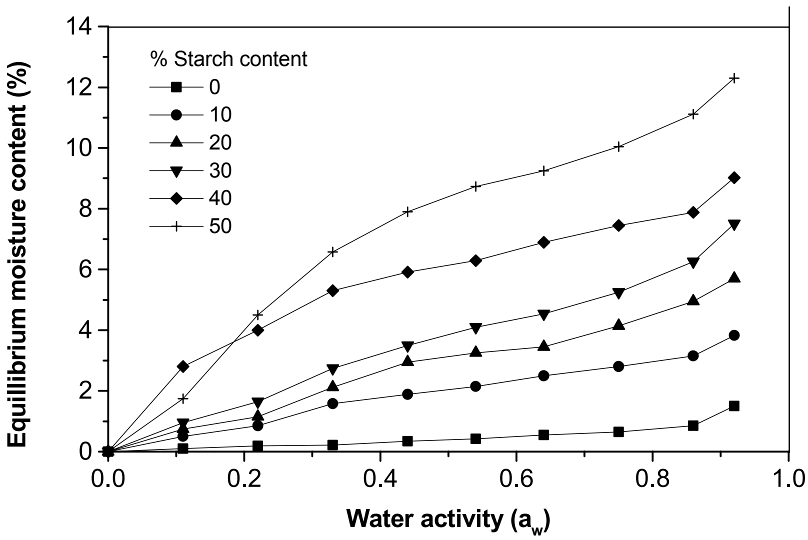

Figure 1. Moisture-sorption isotherm of starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

Sorption model analysis

From the IMC-a_w data, BET isotherm graphs were drawn, and the results are presented in Table 2. The applicability of BET over the entire region of 0.1-0.9 a_w was studied. The experimental sorption data applied to the BET model for the varying starch content in poly(styrene-co-butyl acrylate)/polyester nonwoven composites as shown in Figure 2 was found to fit for a_w in the range 0.1-0.4. Iglesias & Chirife [15], Kumar & Balasubramanyam [16] and Baldevraj & Siddaramaiah [9] showed that the BET equation holds only between water activities from 0.05 to 0.45, confirming the above finding. To evaluate the BET constants, a linear fitting of Equation (2) was done. M_m varied between 0.63 and 4.92 for composites with a starch content from 10 to 50% respectively, indicating that composites with different amount of starch content 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 composites could be construed as practically homogeneous up to this maximum, and that water fills the active sites in multilayer. This is in consonance with the results computed by Iglesias & Chirife [17]. The monolayer moisture parameter of the BET equation is important for commercial shelf-life studies.

Table 2. Sorption isotherm model constants and coefficient of determination (R2) from linear-fitting equations for poly (styrene-co-butyl acrylate) – polyester nonwoven fabric composites.

Isoterm model	Equation No.	Starch content in composite sample	Constants by linear fitting of sorption isotherms		R^2	Range of a_w
BET	2		M_m	C		0.1-0.4
		10	0.63	54.13	0.95	
		20	0.94	46.14	0.98	
		30	1.21	47.44	0.99	
		40	1.61	41.29	0.95	
		50	4.92	59.25	0.97	
Smith	3		M_b	M_a		0.3-0.9
		10	0.89	1.24	0.99	
		20	1.23	1.93	0.97	
		30	1.53	2.51	0.98	
		40	2.47	2.93	0.99	
		50	4.40	3.60	0.98	
Hasley	5		a	b		0.4-0.9
		10	0.25	-0.54	0.99	
		20	0.62	-0.57	0.97	
		30	0.87	-0.56	0.98	
		40	1.21	-0.52	0.99	
		50	1.66	-0.46	0.99	
Caurie	6		A	r		0.3-0.9
		10	0.57	-2.12	0.99	
		20	0.78	-2.27	0.99	
		30	1.04	-2.24	0.99	
		40	1.53	-2.10	0.98	
		50	2.60	-1.88	0.97	
Oswin	8		a	n		0.5-0.9
		10	1.68	0.43	1.00	
		20	2.45	0.44	0.99	
		30	3.16	0.44	0.98	
		40	4.32	0.41	0.98	
		50	6.59	0.37	0.97	

The Smith model represented by Equation (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 [18], 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 as the BET constants. The Smith constants M_b and M_a lie in the ranges 0.89 to 4.40 and 1.24 to 3.60 for composites with starch content varying from 10 to 50% respectively. From Figure 4, it is observed that the experimental sorption data of starch-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites applied to the Halsey model, as given in Equation (4) fitted for a_w in the range 0.4-0.9. The range of applicability for a_w was within the limits for sorption behaviour reported in the range of a_w from 0.1 to 0.8 by the Halsey model [19]. The Halsey constants a and b varied from 0.25 to 1.66 and –0.54 to –0.46 for composites with varying starch content from 10 to 50% respectively.

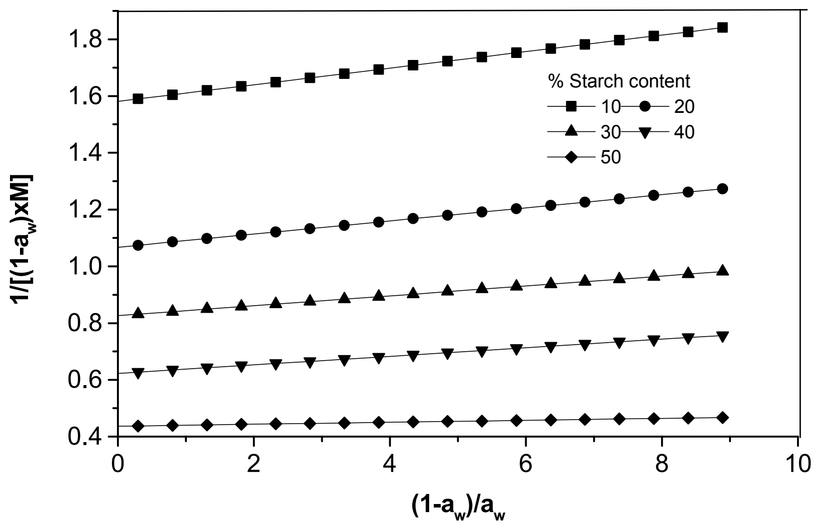

Figure 2. BET sorption isotherm model for starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

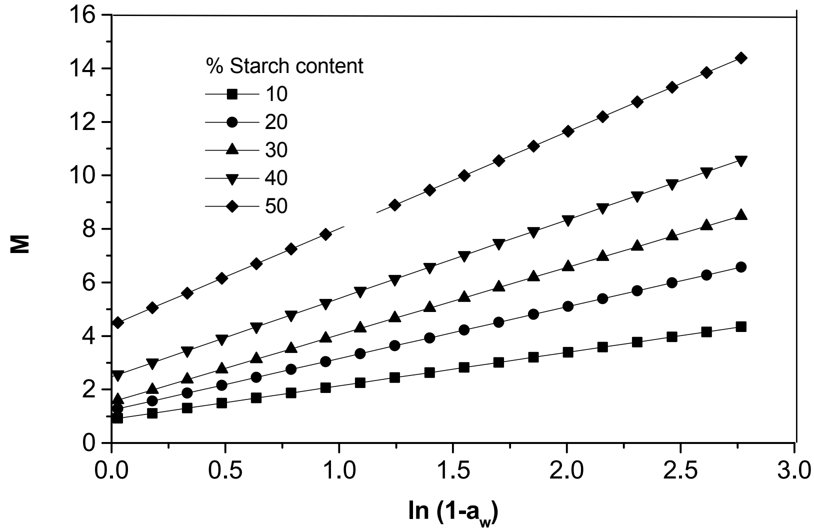

Figure 3. Smith sorption isotherm model for starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

The Caurie model represented by Equation (5) was shown in Figure 5. According to this model, the experimental sorption results were in good agreement for a_w in the range 0.3 to 0.9. The Caurie constants A and r lie in the range 0.57 to 2.60 and –2.12 to –1.88 for different starch contents in poly(styrene-co-butyl acrylate)/polyester nonwoven composites respectively. The Oswin model given by Equation (8) for the experimental sorption data of cornstarch-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites fitted for a_w in the range 0.5-0.9 as shown in Figure 6. The Oswin constants a and n fall within the ranges 1.68 to 6.59 and 0.43 to 0.37 for composites with varying amount of starch from 10 to 50% respectively.

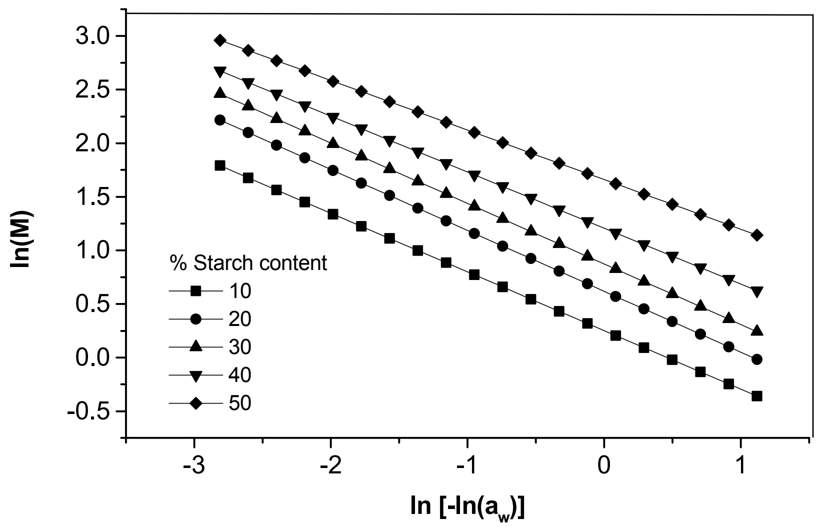

Figure 4. Halsey sorption isotherm model for starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

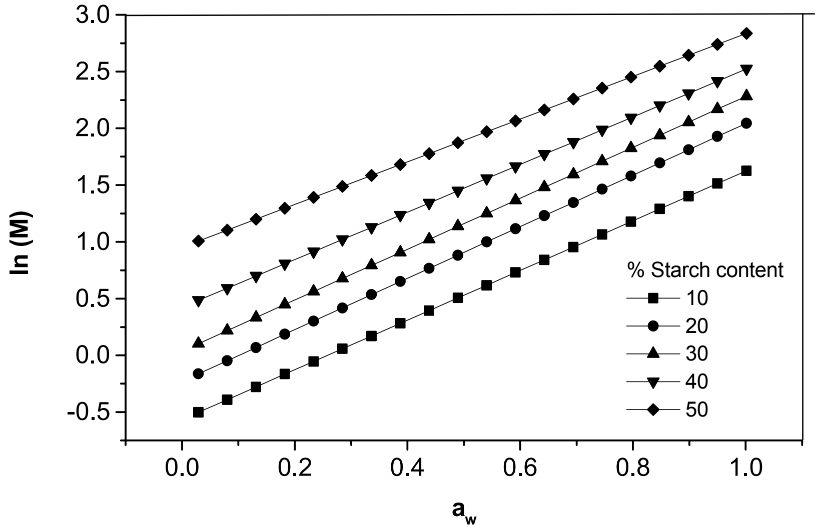

Figure 5. Caurie sorption isotherm model for starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

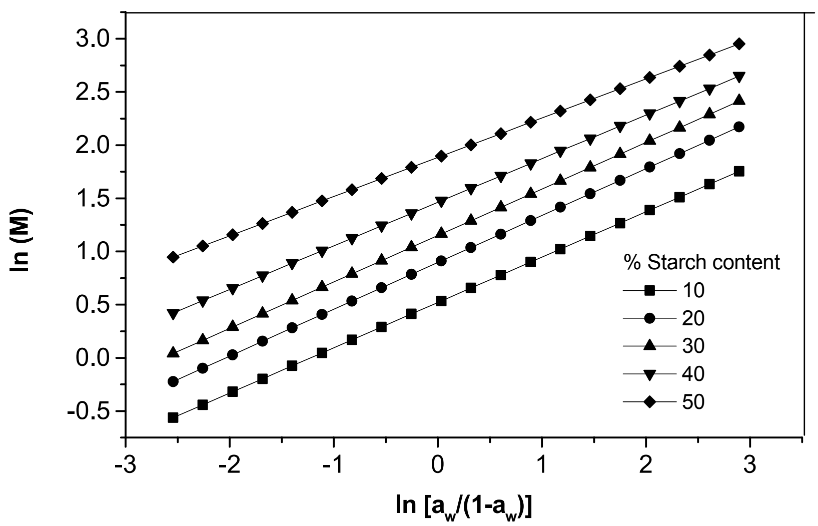

Figure 6. Oswin sorption isotherm model for starch filled poly (styrene-co-butyl acrylate) – polyester nonwoven composites

As is evident from Figures 2-6, the linear fitting of the sorption equation was done using Micorcal Origin 5.0 Professional software to determine the model constants. The five-sorption models discussed above are used to evaluate the model constants for different ranges of a_w to determine the composite durability and the applicability of the models. The values of the coefficient of determination (R^2) for the models are given in Table 2. From the table, it is observed that the a_w values estimated by the Smith, Halsey, Caurie, Bradley and Oswin models are applicable within the range 0.3-0.9. It can be inferred that, although the approach of the above models is different, it can be still be used for the above range of a_w. However, 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-filled poly(styrene-co-butyl acrylate)/polyester nonwoven composites are essential to determine the sorption influence of starch in the composites due to the hydrophilic nature of starch. Water activity is the most important factor affecting the durability of the packaging material. The relative sorptive capacity of the unfilled composites are less connected to the presence of hydrophobic groups. The constants (slope) of different sorption model equations are significant in the evaluation of the stability of starch-filled composites. With the growing awareness of the use of starch-filled composites in various applications, 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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