

Moisture sorption isotherm and isosteric heat of sorption of edible films made from blends of starch, amylose and methyl cellulose

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Article history

Received: 13 July 2011
Received in revised form:
14 September 2011
Accepted: 14 September 2011

Abstract

Effect of incorporation of amylose, and methylcellulose in glycerol-water as well as glycerol-polyethylene glycol-water plasticized starch films on their moisture sorption characteristic was determined at 25, 35, and 45°C using isopiestic vapor transfer technique. Among the three models like GAB, modified Oswin and Peleg for sorption, modified Oswin was found to be the best describing the behavior. Within the temperature range studied, methylcellulose reduced the moisture content of starch film for both the plasticizer systems. For amylose incorporation, reduction in equilibrium moisture content occurred at all the temperatures for glycerol-water plasticizer, whereas for glycerol-polyethylene glycol-water such effect was evident at 25°C only. Addition of amylose and methylcellulose, respectively, increased and decreased the net isosteric heat of moisture sorption of control starch film; for all the films developed, exponential function fitted the net heat of sorption values at various moisture contents.

Keywords

Moisture sorption,
edible film from starch,
amylose and
methylcellulose,
isosteric heat of sorption of
edible film

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Introduction

Biopolymer based self supporting edible films (SSEF) have enormous applications in food processing for better quality control like retainment of volatile flavors when used for making pouches. When placed inside fabricated foods, such films can be used as barrier of lipid migration in-between different zones, carrier of antimicrobials at specific sensitive sites, etc. (Chowdhury and Das, 2010).

Solution casting is the widely used technique for edible film preparation. This involves thermal-gelatinization/solubilisation of the polymer in presence of plasticizer, spreading the mass in a thin layer followed by drying and peeling. In addition to water, glycerol and/or polyethylene glycol have been widely used as plasticizers in such formulations (Ayranci, 1995; Bertuzzi *et al.*, 2007). Several polysaccharides like amyloses, amylopectins, cellulose derivatives, starches, gums, etc. have been attempted for film casting (Chang *et al.*, 2006; Talja *et al.*, 2007). Among these, amylose and methylcellulose are reported to be promising (Debeaufort *et al.*, 1994; Rindlav-Westling *et al.*, 1998; Turhan and Sahbaz, 2004). Being straight chain carbohydrate, amylose develops close matrix by inter-linkage with adjacent chains during processing and post-processing conditions and thereby results in strong flexible

film (Rankin *et al.*, 1958). For methylcellulose, the chains, which remain as bundle in native state, open up during gelatinization, and ultimately remain associated by both hydrophobic force among the methyl groups and hydrophilic force among the unsubstituted regions (Haque and Morris, 1993). This forms a continuous matrix in the film and produces desirable characteristics. Starch contains both linear amylose and branched amylopectin; presence of side chains of amylopectin affects the matrix development by amylose, which results in high moisture absorbing capacity and poor mechanical properties of starch film. Nevertheless, starch is a preferred raw material for its low cost and renewable nature. Attempts are being taken to improve the properties of SSEF by blending starch with different other biopolymers or their derivatives (Suzuki *et al.*, 2005; Campos *et al.*, 2010). Such composite films uses the advantages associated with different participating components. Arvanitoyannis and Biliaderis (1999) measured the thermal, mechanical and permeability properties of films made from blends of soluble starch and methyl cellulose. Peressini *et al.* (2001) optimized the level of methylcellulose and plasticizer in a blend of starch and methylcellulose. Psomiadou *et al.* (1996) characterized edible film prepared by extrusion technique from blends of starch and methylcellulose. In spite of the presence of amylose in native starch, it

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has been reported by Rindlav-Westling *et al.* (2002) that incorporation of additional amylose improves the crystalline character of starch matrix which ultimately causes an improvement in mechanical properties of film.

Macromolecular network determining the properties of biopolymer based edible films is dependent on moisture content (Stading *et al.*, 2001; Jansson and Thuvander, 2004). Moisture sorption isotherm (MSI) provides information on the moisture holding capacity of the films at variable relative humidity (water activity, a_w) at a particular temperature, and is essential tool for design of drying, packaging and storage systems (Mali *et al.*, 2002; Villalobos *et al.*, 2006). Moisture sorption isotherms can be described by several model equations as moisture content a function of a_w (Chirife and Iglesias, 1978; Rizvi, 1986). Estimation of model constants (i.e., modeling) from the experimental sorption data obtained at minimum three temperatures helps to generate MSI at any unknown temperature within the range studied. A thermodynamic parameter such as net isosteric heat of sorption (q_{st} , defined as the total heat of sorption of water minus the heat of vaporization of water, at the system temperature) is frequently computed from MSI data at different temperatures (Stencl *et al.*, 2010); q_{st} determines the temperature dependence of water activity (a_w) as described by Clausius-Clapyron equation. Knowledge of the q_{st} provides an indication of the binding energy of water molecules on the substrate, and is very important in drying and storing operations (Iglesias and Chirife, 1982).

A few information on MSI of starch, amylose and methylcellulose films are available (Debeaufort and Voilley, 1995; Ayranci, 1996; Cruz *et al.*, 2001; Myllarinen *et al.*, 2002; Turhan and Sahbaz, 2004; Bertuzzi *et al.*, 2007; Talja *et al.*, 2008; Perdomo *et al.*, 2009). However, in mixed polymer system, all the participating components influence the matrix, and limited data are available on their moisture sorption characteristics.

The objectives of this work are to: (i) obtain the effect of incorporation of amylose, and methylcellulose in glycerol-water as well as glycerol-polyethylene glycol-water plasticized starch films on their moisture sorption characteristics at 25, 35, and 45°C; (ii) find out a suitable model describing the sorption isotherms; and (iii) calculate the net isosteric heat of sorption of the films.

Materials and Methods

Materials

The biopolymers used in film casting included corn-starch (amylose content 21 %, procured from local market), potato amylose (AM) (obtained as a gift from Sigma Chemical Company, USA), methylcellulose (MC) (28-32 % methoxy content, Loba Chemie., Pvt. Ltd., India), and gelatin (Loba Chemie., Pvt. Ltd., India). Water used in the blend was glass distilled. Besides water, two other plasticizers used included glycerol (Gly, 87 %, analar, Merck Specialities Pvt. Ltd., India) and polyethylene glycol (PEG, molecular weight 400, Merck Specialities Pvt. Ltd., India).

Methods

Preparation of blends and casting of film

Blends were prepared using 6g biopolymer containing cornstarch as the main component along with MC, AM and gelatin, in definite combinations. Plasticizers added were categorized in two groups like binary system containing Gly (2 ml) plus water (78 ml), and ternary system containing Gly (1.46 ml), PEG (1 ml) and water (77.54 ml), total amount being 80 ml in each blend. Table 1 shows the detail composition of blends and the acronyms assigned for the films prepared. For blends containing AM, 1g AM was dissolved in 30 ml portion of water (out of total water) taken in a 250 ml conical flask by swirling. Cornstarch (5 g) plus remaining plasticizers for the respective system were added to the preformed amylose solution and mixed well manually with spatula. For MC incorporated films, 0.15 g MC was soaked in 30 ml portion of water in a 250 ml conical flask for overnight. The mixture was heated in boiling water bath for 10 min in order to obtain clear solution that was naturally cooled to attain room temperature. As the MC containing film also contained gelatin, 1g gelatin was dissolved separately in another 30 ml portion of water taken in a 250 ml conical flask by stirring with a spatula. Cornstarch (4.85 g) was added in the gelatin solution. The content was transferred quantitatively by washing with water to the MC solution; the remaining plasticizers were added and mixed well. Preparation of respective control blend as indicated in Table 1 was similar excepting the prior dissolution of AM and MC as mentioned above.

The blend was gelatinized by heating in a boiling water bath for 10-12 min with continuous manual stirring with a spatula. The hot gelatinized starch gel was spread maintaining the thickness of 2 mm on polypropylene plate with the help of Thin Layer Chromatography (TLC) applicator. The cast film was

Table 1. Composition of blends and acronyms of developed self supporting edible film

Blend type	Blend composition							Acronym of developed SSEF
	Polymer, g (% w/w of blend) ^a				Plasticizers, ml (% w/w of blend) ^a			
	Starch	MC	AM	Gelatin	Gly	PEG	Water	
Binary Amylose Control	6 (6.94)	0	0	0	2 (2.85)	0	78 (90.21)	B-AM-C
Binary Amylose	5 (5.78)	0	1 (1.16)	0	2 (2.85)	0	78 (90.21)	B-AM
Binary Methylcellulose Control	5 (5.78)	0	0	1 (1.16)	2 (2.85)	0	78 (90.21)	B-MC-C
Binary Methylcellulose	4.85 (5.61)	0.15 (0.17)	0	1 (1.16)	2 (2.85)	0	78 (90.21)	B-MC
Ternary Amylose Control	6 (6.94)	0	0	0	1.46 (2.08)	1 (1.31)	77.54 (89.67)	T-AM-C
Ternary Amylose	5 (5.78)	0	1 (1.16)	0	1.46 (2.08)	1 (1.31)	77.54 (89.67)	T-AM
Ternary Methylcellulose Control	5 (5.78)	0	0	1 (1.16)	1.46 (2.08)	1 (1.31)	77.54 (89.67)	T-MC-C
Ternary Methylcellulose	4.85 (5.61)	0.15 (0.17)	0	1 (1.16)	1.46 (2.08)	1 (1.31)	77.54 (89.67)	T-MC

^a Values in parenthesis represents the amount of ingredients in %, w/w of blend

Table 2. Models fitted to the experimental data

Model	Equation
GAB	$M = \frac{M_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$
Peleg	$M = K_1 a_w^{n_1} + K_2 a_w^{n_2}$
Modified Oswin	$a_w = \frac{1}{\{(A + BT)M^{-1}\}^x + 1}$

a_w , equilibrium relative humidity in decimal; M, equilibrium moisture content in % (db); M_0 , monolayer moisture content in % (db); T, temperature in °C; A, B, C, K, K_1 , K_2 , n_1 , n_2 and x, sorption isotherm constants as applicable in respective equation.

dried in an incubator at 40°C for 24 h. The dried film was peeled off from the plate and stored in between two ordinary writing paper sheets for about three months to facilitate structural reorganization of interactive ingredients in the film matrix (Das, 2008; Chowdhury and Das, 2010).

Determination of equilibrium moisture content (EMC)

Equilibrium moisture content was determined using isopiestic vapor transfer technique at three different temperatures (25°C, 35°C and 45°C), in three replications. Effect of AM and MC i.e. treatment effect on the EMC following F-test (analysis of variance) and t-test (for pair comparison between control and treatment) at 1 or 5% level of significance (Gomez and Gomez, 1984). All these calculations including the evaluation of standard deviation (SD) were done using Microsoft Excel 2007 (Microsoft Corp., USA). Details of methodology and statistical calculations are described elsewhere (Chowdhury and Das, 2010).

Fitting of EMC data to various isotherm models

Three MSI models, such as Guggenheim-Anderson-De Boer (GAB), Peleg and modified Oswin, as described in Table 2, were tried to fit the experimental data. Non-linear regression analysis

was used to calculate the respective constants using the softwares like, Microsoft excel 2007 (Microsoft Corp., USA), Systat 8.0 (SPSS, Inc., 1998), and Origin 6.0 (Microcal Software, Inc., 1998) (Chowdhury and Das, 2010).

Goodness of fit to the models

The goodness of fit of the models were compared using coefficient of determination (r^2), mean relative deviation error (MRE %), root mean square error (RMSE) and residual plots. MRE and RMSE were calculated using equations (1) and (2) (Kaleemullah and Kailappan, 2004; Aviara, *et al.*, 2006).

$$MRE (\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{M_{ei} - M_{pi}}{M_{ei}} \right| \dots (1)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (M_{ei} - M_{pi})^2 \right]^{1/2} \dots (2)$$

Where M_{ei} is the *i*th experimental EMC value, M_{pi} is the *i*th predicted EMC value using the particular model, and N is the number of experimental data. The residual plot is a plot of ($M_{ei} - M_{pi}$) versus M_{ei} .

Though the value of r^2 , RMSE and MRE close to 1, 0 and <10 %, in that order are the requisite criteria for acceptance of a model (Lomauro *et al.*, 1985), a model is accepted when its residual plot shows random nature i.e., distribution of the ($M_{ei} - M_{pi}$) values lie in a horizontal band around zero and maintains no clear pattern.

Net isosteric heat of sorption

Equation (3) was used to calculate the net isosteric heat of sorption (q_{st})

$$\ln a_w = -\frac{q_{st}}{RT} + z \dots (3)$$

where R is the universal gas constant, z is the integration constant and T is absolute temperature. Details of calculation is discussed elsewhere (Kaymak-Ertekin and Gedik, 2004; Chowdhury and Das, 2010).

Results and Discussion

Equilibrium moisture contents (EMC)

The average of experimental EMC data of triplicate samples for the SSEF prepared from blends of starch containing AM and MC, with binary and ternary systems of plasticizers are presented in Tables 3 and 4, respectively, along with their standard

Table 3. Equilibrium moisture content of binary mixture plasticized films at different temperature and relative humidity

Temperature (°C)	Water activity	*EMC (% db) ± SD			
		B-AM-C	B-AM	B-MC-C	B-MC
25	0.113	5.721±0.005	4.626±0.006	5.660±0.047	4.530±0.005
	0.237	6.981±0.006	6.378±0.006	8.425±0.009	6.553±0.008
	0.327	10.371±0.008	8.168±0.004	11.381±0.010	7.103±0.005
	0.443	13.312±0.007	10.557±0.006	13.542±0.003	10.900±0.003
	0.528	15.713±0.006	13.013±0.007	17.493±0.020	14.132±0.007
	0.742	25.523±0.006	21.875±0.037	24.965±0.005	20.642±0.005
	0.752	29.891±0.005	23.534±0.017	27.447±0.005	24.704±0.011
	0.843	32.419±0.008	29.350±0.045	35.952±0.067	32.153±0.167
	35	0.112	4.133±0.006	3.517±0.014	4.700±0.011
0.215		5.991±0.007	4.463±0.018	5.316±0.013	5.683±0.051
0.320		8.534±0.008	6.690±0.018	9.592±0.012	6.528±0.012
0.436		10.012±0.015	7.953±0.017	11.171±0.016	8.571±0.014
0.499		13.776±0.005	8.518±0.006	12.921±0.020	10.925±0.010
0.720		22.967±0.009	16.342±0.011	21.703±0.007	18.012±0.010
0.748		24.448±0.007	19.897±0.011	25.615±0.003	22.860±0.003
0.829		29.735±0.007	27.323±0.010	32.438±0.030	28.122±0.004
45		0.111	3.534±0.006	2.889±0.017	*3.367±0.021
	0.197	4.971±0.005	3.902±0.011	5.485±0.024	4.650±0.038
	0.311	6.843±0.006	4.690±0.008	7.938±0.005	6.060±0.003
	0.429	9.737±0.006	5.774±0.008	8.695±0.013	7.833±0.004
	0.469	11.524±0.005	6.001±0.012	10.263±0.005	8.624±0.008
	0.699	18.728±0.006	13.753±0.007	18.900±0.013	15.481±0.009
	0.745	21.489±0.004	16.832±0.006	21.664±0.009	20.449±0.008
	0.817	25.442±0.007	20.991±0.004	27.915±0.008	27.361±0.021

*Average of three replications ± SD. For each temperature, F test was positive ($p < 0.01$) for variation of EMC with water activity.

*EMC of the film containing FP is not significantly different (t-test, $p > 0.05$) from corresponding control.

Table 4. Equilibrium moisture content of ternary mixture plasticized films at different temperature and relative humidity

Temperature (°C)	Water activity	*EMC (% db) ± SD			
		T-AM-C	T-AM	T-MC-C	T-MC
25	0.113	6.340±0.106	3.844±0.007	4.441±0.003	3.431±0.009
	0.237	7.115±0.011	5.168±0.013	5.115±0.011	4.596±0.007
	0.327	8.428±0.006	7.412±0.004	6.912±0.005	5.990±0.006
	0.443	12.304±0.010	8.431±0.006	8.526±0.006	9.879±0.015
	0.528	14.231±0.009	9.833±0.005	11.625±0.009	9.917±0.004
	0.742	21.764±0.010	19.821±0.007	18.664±0.007	15.047±0.007
	0.752	26.619±0.007	20.845±0.004	21.965±0.008	17.850±0.006
	0.843	*32.586±0.003	*32.591±0.007	30.492±0.008	30.347±0.005
	35	0.112	4.588±0.007	4.303±0.002	4.813±0.003
0.215		7.247±0.005	5.715±0.006	5.500±0.004	5.198±0.007
0.320		7.941±0.006	9.199±0.006	7.335±0.001	6.192±0.005
0.436		9.097±0.004	10.714±0.003	9.827±0.004	9.896±0.003
0.499		12.560±0.005	12.224±0.003	13.891±0.002	11.988±0.003
0.720		19.744±0.002	20.324±0.002	19.916±0.005	16.331±0.005
0.748		23.336±0.005	23.612±0.004	25.119±0.005	19.572±0.006
0.829		28.940±0.004	33.707±0.004	31.881±0.004	32.169±0.002
45		0.111	3.549±0.003	5.000±0.003	5.012±0.005
	0.197	4.229±0.003	7.100±0.003	6.324±0.004	5.594±0.003
	0.311	6.667±0.004	10.566±0.005	8.932±0.008	7.296±0.006
	0.429	9.245±0.005	12.703±0.004	11.476±0.007	10.776±0.008
	0.469	9.598±0.007	14.962±0.005	15.478±0.004	12.936±0.005
	0.699	18.455±0.003	21.499±0.008	22.225±0.007	17.921±0.009
	0.745	21.757±0.004	25.997±0.006	27.992±0.010	25.065±0.008
	0.817	26.262±0.006	33.856±0.005	33.012±0.014	32.733±0.005

*Average of three replications ± SD. For each temperature, F test was positive ($p < 0.01$) for variation of EMC with water activity.

*EMC of the film containing FP is not significantly different (t-test, $p > 0.05$) from corresponding control.

deviation. From the analysis of variance and t-test, it is evident from the tables that, unless otherwise indicated, the EMC of the films containing AM and MC are different at 1 % level of significance from their respective controls at 25, 35, and 45 °C. Thus, for both the binary and ternary plasticizer systems, AM and MC at the incorporated levels modify the

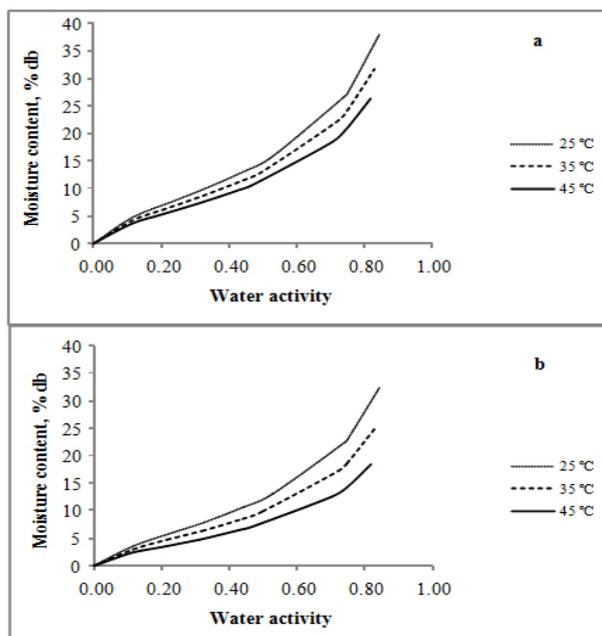


Figure 1. Effect of temperature on moisture sorption isotherm of glycerol-water plasticized starch film containing amylose (a) B-AM-C and (b) B-AM.

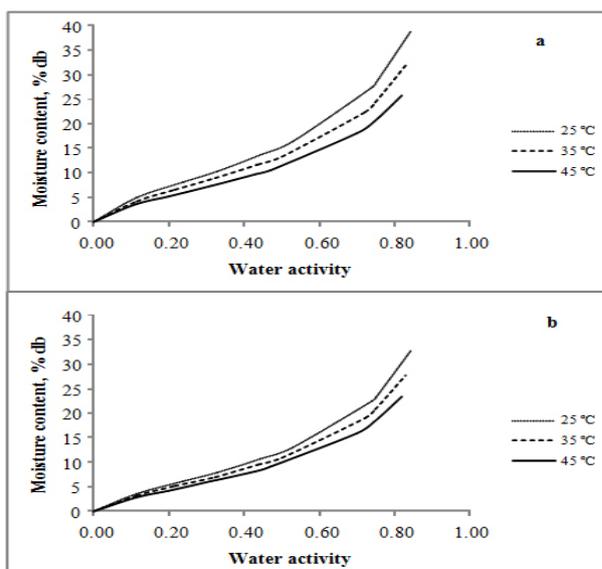


Figure 2. Effect of temperature on moisture sorption isotherm of glycerol-water plasticized starch film containing methylcellulose (a) B-MC-C and (b) B-MC

EMC of starch film.

Fitting of sorption models

The estimated values of the coefficients for different MSI models and the respective error terms are presented in Tables 5-7 for films from binary and ternary plasticizers. It is evident from the tables that r^2 s, MREs and RMSEs are comparable for all the three models for all the SSEF developed. However, for binary system SSEF, 66 %, and 58 % of the residual plots (calculated out of total plots for 25, 35, and 45 °C) indicated pattern behavior using GAB and Peleg models, respectively. On the other hand,

Table 5. Estimated parameters and comparison criteria for different films using GAB model

Model Parameters	Nature of film	25°C	35°C	45°C	Nature of film	25 °C	35 °C	45 °C		
M ₀	B-AM-C	13.001	11.024	9.728	T-AM-C	7.984	7.109	8.187		
C		4.630	3.741	3.894		12.876	11.522	3.914		
K		0.773	0.814	0.812		0.905	0.921	0.881		
r ²		0.986	0.995	0.998		0.986	0.992	0.997		
RMSE		1.328	0.960	1.294		1.238	0.805	0.479		
MRE (%)		6.938	7.303	10.290		7.931	5.779	5.307		
Residual Plot		Pattern	Pattern	Pattern		Pattern	Random	Pattern		
M ₀		B-AM	8.618	5.060		4.572	T-AM	5.248	6.601	8.726
C			6.102	11.133		6.549		13.394	12.821	11.164
K			0.862	0.988		0.973		0.998	0.972	0.912
r ²	0.997		0.996	0.990	0.998	0.996		0.994		
RMSE	0.534		1.302	1.731	0.361	0.609		0.789		
MRE (%)	4.684		8.506	14.641	3.636	5.184		5.622		
Residual Plot	Pattern		Pattern	Pattern	Random	Pattern		Random		
M ₀	B-MC-C		9.919	8.339	6.899	T-MC-C		5.861	7.583	10.142
C			9.754	6.890	7.304			10.810	7.194	5.742
K			0.867	0.911	0.935			0.963	0.931	0.875
r ²		0.996	0.995	0.997	0.993		0.988	0.991		
RMSE		0.712	0.750	0.425	0.798		1.140	1.041		
MRE (%)		3.284	6.972	3.993	7.192		9.576	7.331		
Residual Plot		Random	Pattern	Random	Pattern		Pattern	Pattern		
M ₀		B-MC	7.767	6.639	4.984		T-MC	4.221	4.864	6.708
C			7.312	7.097	12.273			34.7999	25.660	10.679
K			0.910	0.936	1.006			1.019	1.021	0.978
r ²	0.990		0.990	0.997	0.982	0.983		0.987		
RMSE	1.049		0.897	0.473	1.233	1.279		1.182		
MRE (%)	6.875		6.838	2.380	9.487	9.966		6.672		
Residual Plot	Random		Random	Pattern	Pattern	Pattern		Pattern		

Table 6. Estimated parameters and comparison criteria for different films using Modified Oswin model

Model Parameters	Nature of film	Values	Nature of film	Values		
A	B-AM-C	19.212	T-AM-C	17.202		
B		-0.174		-0.142		
x		1.791		1.816		
r ²		0.998		0.996		
RMSE		1.424		1.186		
MRE %		5.166		7.718		
Residual Plot		Random		Random		
A		B-AM		17.733	T-AM	4.375
B				-0.225		0.238
x				1.707		1.806
r ²	0.996		0.998			
RMSE	1.287		1.729			
MRE %	9.058		6.994			
Residual Plot	Random		Random			
A	B-MC-C		20.761	T-MC-C		5.812
B			-0.209			0.193
x			1.829			1.719
r ²		0.998	0.997			
RMSE		1.187	1.156			
MRE %		6.785	8.073			
Residual Plot		Random	Random			
A		B-MC	15.370		T-MC	5.785
B			-0.124			0.151
x			1.714			1.720
r ²	0.997		0.996			
RMSE	1.255		1.879			
MRE %	2.257		9.000			
Residual Plot	Random		Random			

for ternary systems out of total plots, 75 % of the residual plots using GAB and 66 % by Peleg showed pattern behavior. Interestingly, using modified Oswin, irrespective of plasticizers and biopolymer compositions all the residual plots indicated random behavior.

Thus, from the present study, modified Oswin model is the best model to fit and predict the MSI of starch-based films within the temperature range studied. Chen (2002) and Chowdhury and Das (2010) also reported the suitability of modified Oswin model for sorption behavior of high starch products.

Table 7. Estimated parameters and comparison criteria for different films using Peleg model

Model Parameters	Nature of film	25°C	35°C	45°C	Nature of film	25°C	35°C	45°C		
K ₁	B-AM-C	36.294	32.439	24.414	T-AM-C	38.193	37.505	32.157		
n ₁		2.142	2.675	3.097		3.598	4.208	3.482		
K ₂		8.146	10.968	14.010		12.360	13.042	11.714		
n ₂		0.182	0.451	0.650		0.342	0.449	0.578		
r ²		0.991	0.997	0.998		0.987	0.994	0.998		
RMSE		1.061	0.747	1.176		1.180	0.721	0.301		
MRE (%)		3.391	4.579	8.034		6.720	5.688	3.821		
Residual Plot		Pattern	Pattern	Pattern		Pattern	Pattern	Random		
K ₁		B-AM	31.871	51.871		34.519	T-AM	64.974	76.043	77.862
n ₁			3.315	6.032		3.776		6.688	8.138	9.046
K ₂	12.138		11.936	5.395	13.111	19.755		24.933		
n ₂	0.453		0.574	0.252	0.579	0.729		0.747		
r ²	0.999		0.997	0.998	0.999	0.998		0.998		
RMSE	0.280		1.169	1.328	0.271	0.423		0.463		
MRE (%)	1.477		7.545	8.891	2.878	4.076		3.000		
Residual Plot	Pattern		Random	Pattern	Pattern	Random		Random		
K ₁	B-MC-C		45.683	43.380	40.563	T-MC-C		13.705	18.166	21.881
n ₁			7.330	5.514	5.046			0.593	0.708	0.728
K ₂		25.969	19.598	15.161	48.336		45.383	37.371		
n ₂		0.743	0.714	0.642	5.775		5.563	4.764		
r ²		0.996	0.995	0.998	0.992		0.987	0.991		
RMSE		2.452	0.728	0.366	0.828		1.161	1.037		
MRE (%)		15.718	6.744	3.787	7.375		9.678	7.000		
Residual Plot		Pattern	Random	Random	Pattern		Pattern	Pattern		
K ₁		B-MC	19.632	11.840	12.085		T-MC	17.354	20.589	21.114
n ₁			0.757	0.510	0.572			0.842	0.890	0.796
K ₂	41.586		39.380	58.399	161.256	256.012		87.461		
n ₂	6.038		4.323	6.179	13.774	15.208		8.712		
r ²	0.989		0.992	0.997	0.992	0.994		0.989		
RMSE	1.084		0.796	0.403	0.787	0.704		1.064		
MRE (%)	7.530		4.335	2.761	6.612	7.290		7.319		
Residual Plot	Pattern		Random	Random	Pattern	Random		Pattern		

Moisture sorption isotherms (MSI)

Figures 1- 6 in different combinations show the best-fit computation of the MSIs from modified Oswin model for different films. All isotherms irrespective of temperature and composition show a similar sigmoidal shape (Type II according to BET classification) which is common for many hygroscopic products. A very clear as well as definite trend of increase in moisture content with increase of the water activity is observed that ensures multilayer sorption characteristics of the films (Coupland *et al.*, 2000; Erbas *et al.*, 2005; Chowdhury and Das, 2010).

Effect of temperature on MSI of the films

Figures 1(a, b) and 2(a, b) represent the effect of temperature on MSI of binary system plasticized SSEF representing for AM and MC incorporation as well as their controls, respectively. The curves in both the figures clearly indicate that at any particular water activity EMC of the films decrease with increasing temperature - an expected behavior for MSI except for high sugar foods (Labuza, 1984; Ayranci, 1995; Ayranci and Cetin, 1995). This may be due to reduction in total number of binding sites for water arose from some temperature induced changes in the microstructure of glycerol-water plasticized film matrix. According to Menkov and Durakov (2007) at increased temperatures water molecules get activated to higher energy levels, causing them to become less stable and break away from the water binding sites of the material, thus decreasing the EMC.

Figures 3 (a, b) and 4 (a, b) give the effect of temperature on ternary mixture plasticized films. For T-AM-C (Figure 3a), increase of temperature from 25 to 45 °C decreases the EMC at all a_w values, as observed

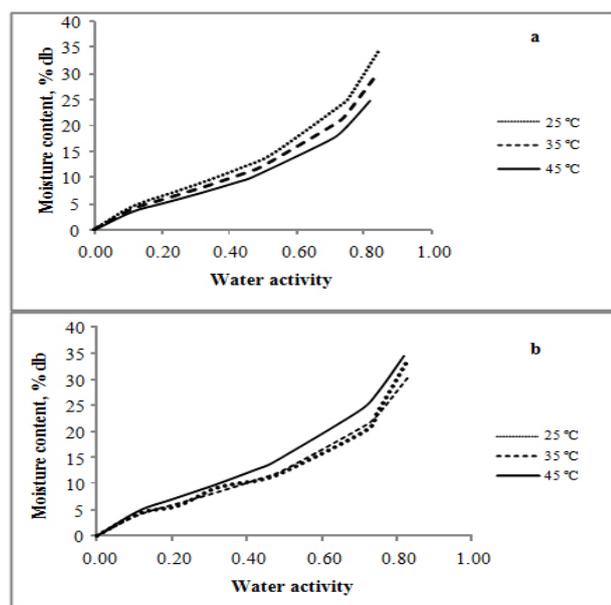


Figure 3. Effect of temperature on moisture sorption isotherm of glycerol-water plasticized starch film containing amylose (a) T-AM-C and (b) T-AM.

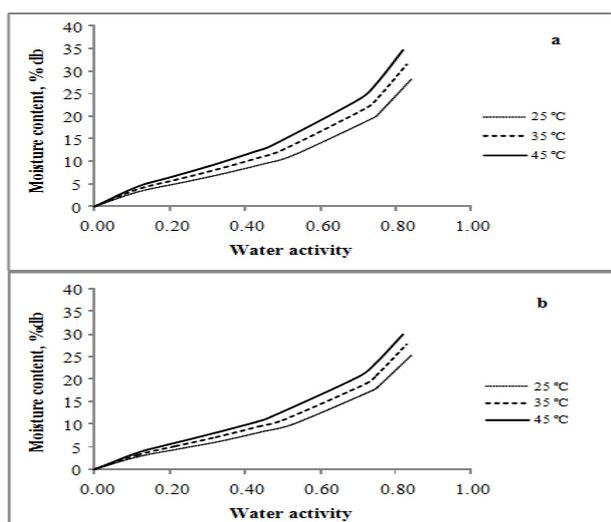


Figure 4. Effect of temperature on moisture sorption isotherm of glycerol-water plasticized starch film containing methylcellulose (a) T-MC-C and (b) T-MC

in Figure 1a for B-AM-C. However, in Figures 3b, 4a, and 4b, some opposite behavior is observed. For T-AM (Figure 3b), though MSI corresponding to 25 and 35 °C are mostly overlapping (upto $\approx 0.7 a_w$), rise of temperature from 35 to 45 °C distinctly increases the EMC of the film. In case of Figures 4a and 4b also, it is observed that the film gradually adsorbs more moisture as the temperature increases. In other words, at any particular moisture content, increase in temperature causes decrease in water activity of the films, suggesting opening up more new binding sites for water, and thus reducing the free energy/water activity of bound water. Probably more water binding sites in the matrix are exposed due to thermal effect

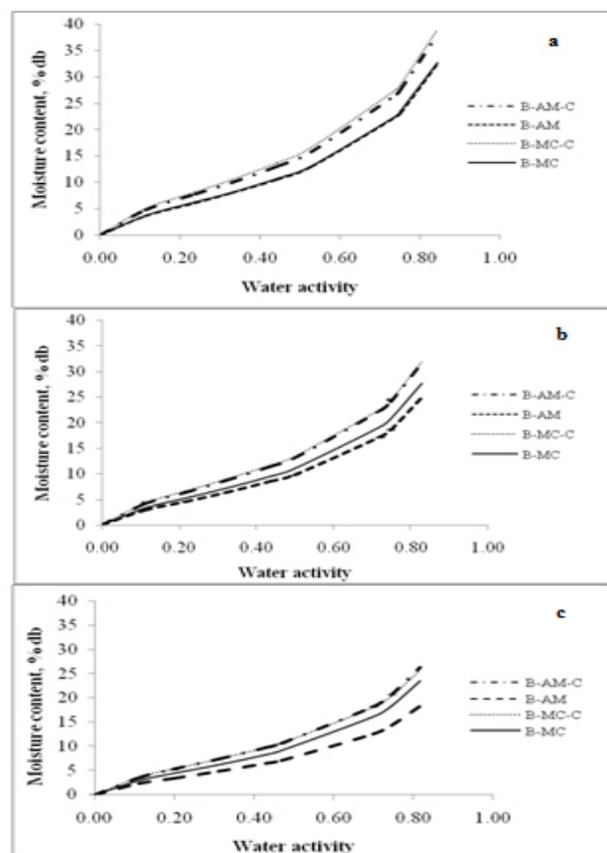


Figure 5. Effect of amylose and methylcellulose on moisture sorption isotherm of glycerol-water plasticized starch film at (a) 25°C, (b) 35°C and (c) 45°C

in presence of PEG, indicating some different type of plasticization in the ternary system than that of binary system (Laohakunjit and Noomhorm, 2004). Increased water binding at higher temperature has been reported elsewhere for food particularly rich in soluble solids and susceptible to structural orientation (Rizvi, 1986; Das and Das, 2002).

Effect of incorporation of AM and MC on the MSI of the films

Figures 5a, 5b, and 5c present the MSIs of glycerol plus water plasticized SSEF viz., B-AM-C, B-AM, B-MC-C, and B-MC at 25, 35 and 45 °C, respectively. In all the figures, isotherms of the control films (B-AM-C and B-MC-C) are not found to be well separated from each other indicating their comparable moisture sorption capacity at the three temperatures; however, there is lowering in the EMC of these films over the entire range of a_w values due to incorporation of either of AM or MC in starch. This may be due to development of compact structure of glycerol-water plasticized film assisted by intermolecular forces of straight chains of amylose or association of methyl groups forming hydrophobic pockets (Haque and Morris, 1993; Rindlav-Westling, 2002). Since high

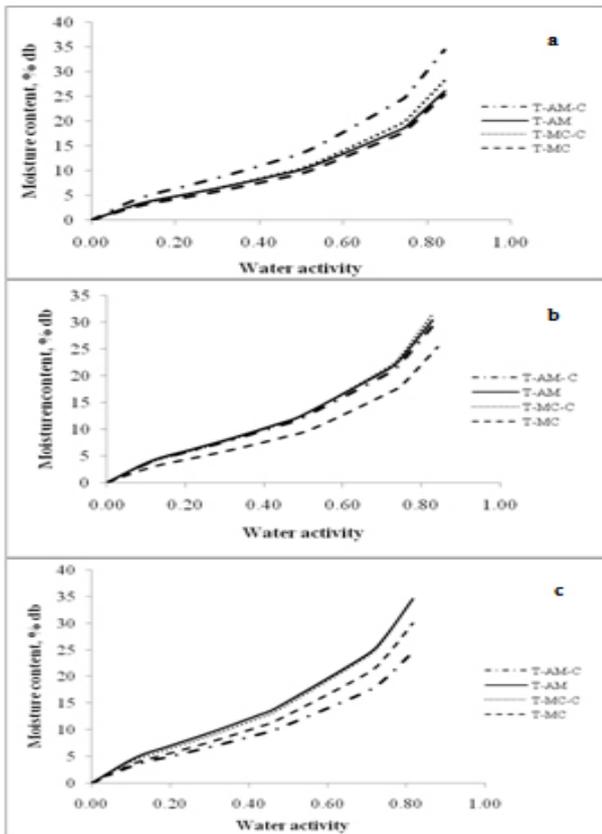


Figure 6. Effect of amylose and methylcellulose on moisture sorption isotherm of glycerol-polyethylene glycol-water plasticized starch film at (a) 25°C, (b) 35°C and (c) 45°C

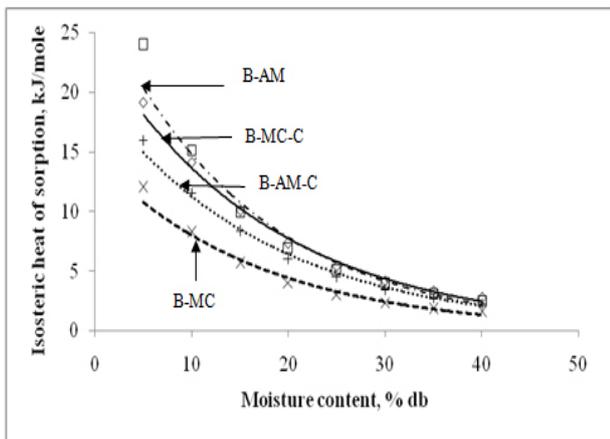


Figure 7. Isosteric heat of sorption of glycerol-water plasticized films

moisture sorption property is the main hindrance of utilization of starch based film, addition of these functional biopolymers may be a beneficial option when the film is plasticized with glycerol and water as used in the present work.

Referring to Figure 5a (25°C), it is found that AM and MC possess comparable capacity to reduce the moisture sorption capacity of control films as the MSIs for B-AM and B-MC appear to be overlapping. Moreover, compared to MC the reduction by AM gradually increases with increase of temperature from 25°C to 35°C (Figure 5b) and 45°C (Figure 5c).

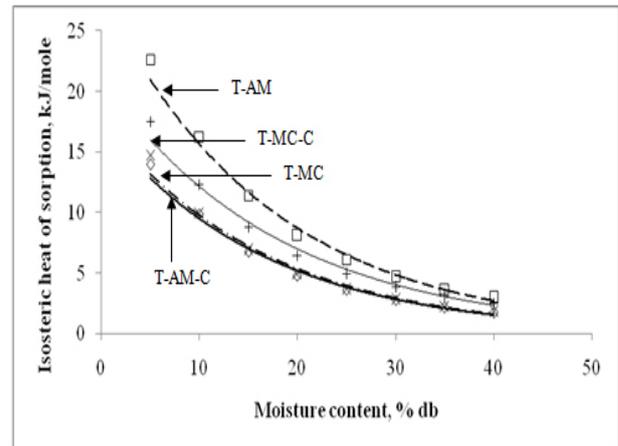


Figure 8. Isosteric heat of sorption of glycerol-polyethylene glycol-water plasticized films

Observation with ternary mixture plasticized films is presented in Figures 6a, 6b, and 6c for 25, 35 and 45°C, respectively. Since MSI corresponding to T-MC in all the figures runs below the MSI corresponding to T-MC-C, it may be accepted that MC lowers the moisture sorption capacity of the respective control film. Moreover, such lowering is more pronounced at 35 and 45°C than that at 25°C. In case of amylose incorporation, the effect is variable. At 25°C, EMC of amylose containing film T-AM is much lower than that of control film T-AM-C. At 35°C both are almost equal, while at 45°C values for T-AM are in fact much higher than that of T-AM-C. At higher temperature, development of compact structure by amylose as mentioned above for the binary plasticizer system is perhaps affected due to presence of PEG in ternary system (Laohakunjit and Noomhorm, 2004). Thus, in mixed polymer based SSEF containing starch and plasticized with glycerol-polyethylene glycol-water, the contribution of MC and AM towards moisture sorption capacity are highly dependent on temperature.

Referring to Figure 6a, as the MSIs for T-AM-C and T-AM are more widely different compared to the MSIs for T-MC-C and T-MC, it can be stated that at 25°C, AM is more efficient in reducing moisture sorption capacity of starch film compared to that of MC. On the contrary at 35°C (Figure 6b), AM is not very effective (MSIs of T-AM-C and T-AM are almost overlapping), whereas the difference between MSIs of T-MC-C and T-MC is higher indicating higher reduction capacity of MC. At 45°C (Figure 6c), AM rather increases the EMCs of their control films; EMCs of T-MC are still lower than that of T-MC-C. Thus, for all the three temperatures for the entire range of a_w , the moisture contents of T-MC films are lower than the T-MC-C films, whereas contribution of AM is temperature dependent.

Net isosteric heat of sorption

Figures 7 and 8 represent the absolute value of net isosteric heat of sorption of binary and ternary mixture plasticized films, respectively, as a function of moisture content (5-40%, db). Irrespective of the film composition, q_{st} decreases exponentially (eq. 4-11) with the increase in moisture content of films (M).

i) q_{st} for binary mixture plasticized films

$$q_{st} = 19.82e^{-0.05M} \dots \dots \dots (4) \text{ for B-AM-C, } r^2=0.993$$

$$q_{st} = 28.04e^{-0.06M} \dots \dots \dots (5) \text{ for B-AM, } r^2=0.981$$

$$q_{st} = 24.03e^{-0.06M} \dots \dots \dots (6) \text{ for B-MC-C, } r^2=0.993$$

$$q_{st} = 14.44e^{-0.05M} \dots \dots \dots (7) \text{ for B-MC, } r^2=0.986$$

ii) q_{st} for ternary mixture plasticized films

$$q_{st} = 17.30e^{-0.06M} \dots \dots \dots (8) \text{ for T-AM-C, } r^2=0.991$$

$$q_{st} = 28.13e^{-0.05M} \dots \dots \dots (9) \text{ for T-AM, } r^2=0.991$$

$$q_{st} = 21.05e^{-0.05M} \dots \dots \dots (10) \text{ for T-MC-C, } r^2=0.990$$

$$q_{st} = 17.78e^{-0.06M} \dots \dots \dots (11) \text{ for T-MC, } r^2=0.988$$

Higher the absolute value of q_{st} , higher is the degree of bonding (Chowdhury and Das, 2010). Thus with increasing moisture content as shown in Figures 7 and 8, higher q_{st} refers to initial occupation of polar sites with high interaction energy on the surface, followed by the gradual filling of the sites involved with less energies (Tsami, 1991; Mc. Minn and Magee, 2003). For binary plasticizer (Figure 7), it is clear that for up to $\approx 40\%$ moisture content, incorporation of amylose in starch increases the q_{st} , whereas MC decreases the same. With ternary mixture of plasticizers also (Figure 8), addition of MC lowers the q_{st} for binding up to $\approx 40\%$ water, while AM shows increasing effect. Such capacity of lowering q_{st} by MC may be due to its methyl content imparting some hydrophobicity in the starch matrix that helps to reduce the binding energy between water and the hydrophilic sites (Haque and Morris, 1993). Increase of q_{st} by AM occurs probably due to its strong hydrophilic character that enhances the attraction for water. However, the difference in the q_{st} among different films narrows down as the moisture content increases above 40 % which may correspond to loosely bound or entrapped water in the matrix due to extensive plasticization (Gabas *et*

al., 2007).

Conclusions

Moisture sorption isotherms of self supporting edible films developed from mixed biopolymer system containing starch plus amylose or methylcellulose, and plasticized with glycerol-water or glycerol-polyethylene glycol-water can be described by modified Oswin model. Irrespective of plasticizer and temperature within 25 to 45°C, methylcellulose reduces the moisture content of starch film. For amylose incorporation, reduction in equilibrium moisture content is observed at all the temperatures for glycerol-water plasticizer, whereas for glycerol-polyethylene glycol-water such effect is evident at 25°C only. Incorporation of amylose increases whereas methylcellulose decreases the net isosteric heat of moisture sorption of starch film, which decreases exponentially with moisture content of the films.

Acknowledgement

Financial assistance from the Ministry of Environment and Forest, New Delhi, India to the first author is acknowledged with thanks.

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