As. J. Food Ag-Ind. **2009**, 2(04), 478-488

OPEN ACCESS

Asian Journal of Food and Agro-Industry
ISSN 1906-3040
Available online at www.ajofai.info

Research Article

Effect of glycerol concentration on sorption isotherms and water vapour permeability of carboxymethyl cellulose films from waste of mulberry paper

Pornchai Rachtanapun[1]* and Wirongrong Tongdeesoontorn[2]

[1]Department of Packaging Technology, Faculty of Agro-Industry, Chiang Mai University, Chiang Mai 50100 Thailand.

[2]School of Agro-Industry, Mae Fah Luang University, Chiang Rai 57100 Thailand.

*Author to whom correspondence should be addressed, email: p.rachta@chiangmai.ac.th

This paper was originally presented at Food Innovation Asia 2009, Bangkok, Thailand.
Received 21 June 2009, Revised 2 November 2009, Accepted 8 December 2009.

Abstract

The effect of glycerol concentration on the sorption isotherms and water vapour permeability (WVP) of carboxymethyl-cellulose (CMC) films from waste mulberry paper (CMCm) was investigated. The knowledge of sorption isotherms is also important for predicting moisture sorption properties of films *via* moisture sorption empirical models. The moisture sorption isotherms of CMCm films plasticized with glycerol (0, 0.1, 0.2, 0.3 and 0.4 %v/v) were studied at various relative humidities (13.5, 36.5, 46.5, 66.8, 77.3 and 93.8 %RH), at 25 ± 1°C. The equilibrium moisture content of the films increased dramatically above a_w = 0.6. Guggenheim-Anderson-de Boer (GAB), Brunauer-Emmett-Teller (BET) and Oswin sorption models were fitted to the experimental data. The results showed that increasing glycerol concentration caused an increase in the monolayer water content (M0) of films. The GAB model was found to be the best-fit model for CMCm films at a_w 0.1-0.8), 25 ± 1°C. WVP of CMCm film was higher than WVP of commercial CMC film, and WVP of CMCm film increased from 10.383×10^{-5} to 10.826×10^{-5} $g.m/m^2.mmHg.day$ with increasing glycerol concentration.

Keywords: Carboxymethyl cellulose, CMCm, GAB, BET, Oswin, WVP, WVTR, Thailand

Introduction

Cellulose is a main component of plants and wood and may be converted to useful derivatives by etherification [1]. Carboxy methyl cellulose (CMC) is the most important water-soluble cellulose derivative, with many applications in food, cosmetics, pharmaceuticals and detergents [2]. Production of CMC is carried out by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt [3]. The substitution of the hydroxyl groups by the carboxy methyl group is slightly preponderant at C-2 of the glucose [4]. Cellulose, which is modified to be CMC, can be extracted from many sources such as banana pseudo stems [5], sticky rice husk and cotton [6], sugar beet pulp [7], orange peel [8], papaya peel [9, 10, 11] and waste of mulberry paper [12].

In the northern part of Thailand, there are many industries, which use natural materials as raw materials in their production process. After the production process, the natural materials such as mulberry paper, corncob and bamboo are discarded as waste. These wastes of natural materials have cellulose as a component. Especially, waste of mulberry paper has a lot of cellulose due to the production process, which extracts cellulose from mulberry bark to make paper [13]. Extracting cellulose from the waste of mulberry paper and modifying it to CMC for biodegradable film production is potentially a good way to utilize and reduce the waste. Also, it can provide a value for the waste and waste recovery is beneficial to the environment.

Most biodegradable films, except lipid-based, are sensitive to moisture and their properties change with changes in relative humidity. The water transmission of hydrophilic films varies nonlinearly with water vapour pressure. If the films are cationic and strongly hydrophilic, water will interact with the polymer matrix, increasing the permeation for water vapour [14]. The water sorption isotherm of a material represents the equilibrium relationship between their moisture content and the water activity (a_w) at constant temperature and pressure. The sorption isotherms obtained from experimental data result in an estimation of equilibrium moisture content, which is necessary to predict the properties of films in different environments pertinent to their applications [15]. Some authors have studied the WVP and sorption isotherms of biodegradable films. Li *et al*. [16] studied WVP of rice starch/CMC blended film. Suppakul [17] reported the sorption characteristics of cassava flour film plasticized with sorbitol.

The object of this research was to study the effects of the amount of glycerol concentration as a plasticizer in CMC films on water vapour transmission rate (WVTR), permeability coefficient (P) and moisture sorption isotherms of carboxy methyl cellulose films.

Materials and Methods

Materials

Waste of mulberry paper was purchased from Bankradassa (Chiang Mai, Thailand). NaOH, isopropyl alcohol (IPA), chloro acetic acid, methanol, ethanol, acetic acid, glycerol, carboxy methyl cellulose (CMCc), distilled water were purchased from Northern Chemical Co., Ltd. (Chiang Mai, Thailand).

CMCm film preparation

CMCm films were prepared as described in a previous study [12]. Glycerol (0, 0.1, 0.2, 0.3 and 0.4 %v/v) was added as plasticizer.

Water vapour transmission rate (WVTR) and permeability coefficient (P)

Water vapour transmission of films was measured using the ASTM E96-93 [18]. Aluminum cups with a diameter of 8 cm and depth 2 cm were employed. After placing 10 g of dried silica gel in each cup, they were covered with film samples prepared in our experiment, cut circularly (ϕ=7 cm) and sealed using melted paraffin. The cups were weighed along with their content and placed in desiccators kept at 25 ± 1°C. The relative humidity was maintained by saturated solutions of NaCl in the bottom of the desiccator to provide 75% RH at 25 ± 1°C. Cups were weighed every 24 hours for 2 weeks. WVTR (g/day.m^2) was calculated from slope of weight gain and time per area of film sample as follows [19, 20, 21]:

$$WVTR = \frac{weight\ gain\ (g)}{time\ (day) \times area\ of\ \ film\ sample\ (m^2)} \tag{1}$$

Permeability coefficient (P) (g.m/m^2.mmHg.day) was calculated from [15, 16]:

$$P = \frac{WVTR \times L}{\Delta p} \tag{2}$$

$WVTR$ is the measured water vapour transmission rate (g/day.m^2) through the film specimen, L is the mean film thickness (m), and Δp is the partial water vapour pressure difference (mmHg) across two sides of the film specimen.

The partial water vapour pressure difference (Δp) across two sides of the film specimen was calculated by using the following equation [19, 20, 21]:

$$\Delta p = Ps\frac{(RH_{out} - RH_{in})}{100} \tag{3}$$

Ps is saturated water vapour pressure, RH_{out} is relative humidity outside the cup, RH_{in} is relative humidity inside the aluminum cup.

Moisture sorption isotherms

Various film specimens were pre-dried in a hot air oven for 3 hours and placed in a desiccator for 2 days. Next, films were placed in the desiccator over saturated solution having desired relative humidity (13.50, 36.50, 46.50, 66.80, 77.30 and 93.80 %RH). The film specimens were weighed every 24 hours. When the two consecutive weights were equal, it was assumed that an equilibrium condition was reached. Under the above conditions, and equilibrium period of 7 days was sufficient to establish moisture equilibrium. Percent equilibrium moisture content (%EMC) was calculated by equation 4 [21, 22]:

$$Me = \frac{We}{Wi}\left(Mi + 1\right) - 1 \quad (g/g\ dry\ product) \tag{4}$$

Where; *We* is the equilibrium weight of carboxymethyl cellulose films from waste of mulberry paper (g), *Wi* is the initial weight of carboxymethyl cellulose films from waste of mulberry paper (g), and *Mi* is the initial moisture content of carboxymethyl cellulose films from waste of mulberry paper (g/g).

Moisture sorption isotherm curve fitting

Isotherm models from the literature [17, 22] were selected for fitting the experimental data of sorption isotherms of cassava flour film and instant noodles with rice flour, respectively. Those models are expressed and rearranged as given below.

GAB (Guggenheim-Anderson-de Boer) model:

$$M = \frac{M_0\, C\, k\, a_w}{(1 - a_w)[1 + (C - 1)k\, a_w]} \tag{5}$$

Where M = equilibrium moisture content on a dry basis, M_0= GAB monolayer moisture content, C = Guggenheim constant, k = factor correcting properties of the multiplayer molecules corresponding to the bulk liquid and a_w = water activity. The three parameters of GAB model were obtained from its second-order polynomial form ($y = \alpha x^2 + \beta x + \gamma$), as follows:

$$\alpha = {}^{k}\!\big/_{M_0[1/c - 1]},\quad \beta = {}^{1}\!\big/_{M_0[1 - 2/C]},\quad \gamma = {}^{1}\!\big/_{M_0\, kC} \tag{6}$$

This model was solved using linear regression analysis with the least sum of squares method to obtain α, β and γ and subsequently the parameter values M_0, C and k.

BET model:

$$M = \frac{(M_0 + T)\, C\, a_w}{(1 - a_w)[(1 - a_w) + C\, a_w]} \tag{7}$$

Where M_0 and C = constants. Both constants were obtained from the slope and intercept of the linear plots of $a_w/[(1-a_w).M]$ vs. a_w. M_0 = 1/ (intercept + slope) and C = 1/ (intercept. M_0)

Oswin model:

$$M = k[a_w/(1 - a_w)]^C \tag{8}$$

Where k and C = constants. Both constants were obtained from the slope and intercept of the linear plots of log M vs. log $[a_w/(1-a_w)]$.

Results and Discussion

Effect of amount of glycerol in CMC$_m$ films on water vapor transmission rate (WVTR) and permeability coefficient (P)

Effect of amount of glycerol in CMCm films on water vapour transmission rate (WVTR) and permeability coefficient (P) was studied. WVTR could be calculated from the slope of weight gain and time per area of film samples.

WVTR and P increased with increasing amount of glycerol (Table 1) because addition of glycerol as a plasticizer in film could increase free volume between polymer chains, reduce cohesive energy and lower Tg [23]. Therefore, water vapour could easily pass through the film [24].

Table 1: Water vapour transmission rate (WVTR) and permeability coefficient (P) of films.

Films	WVTR (g/day.m^2)	P (g.m/m^2.mmHg.day)
CMC_c	61.34	9.733 x 10^{-5}
CMC_m non glycerol	65.44	10.383 x 10^{-5}
CMC_m + 0.1 ml glycerol	66.36	10.529 x 10^{-5}
CMC_m + 0.2 ml glycerol	67.32	10.682 x 10^{-5}
CMC_m+ 0.3 ml glycerol	67.49	10.709 x 10^{-5}
CMC_m + 0.4 ml glycerol	68.23	10.826 x 10^{-5}

Moisture sorption isotherms

Plotting between %EMC and time at different relative humidity provides the sorption isotherm curve as shown in Figure 1. The sorption isotherms gave the characteristic sigmoid-shaped type II isotherm curve of normal moisture adsorption isotherm [25] similar to those observed for salted crackers [21], potato flakes [26] and starches [27, 28]. Glycerol concentration affected the %EMC of films. Films with a higher concentration of glycerol absorbed more moisture at a given A_w due to glycerol being a hydrophilic plasticizer that loosened the structure of films [29]. The addition of plasticizer increased hydrophilicity of films by exposing their hydroxyl groups. Similarly, Mahmoud and Savello [30] reported increase of moisture content in whey protein films as the glycerol concentration in the film formulation increased.

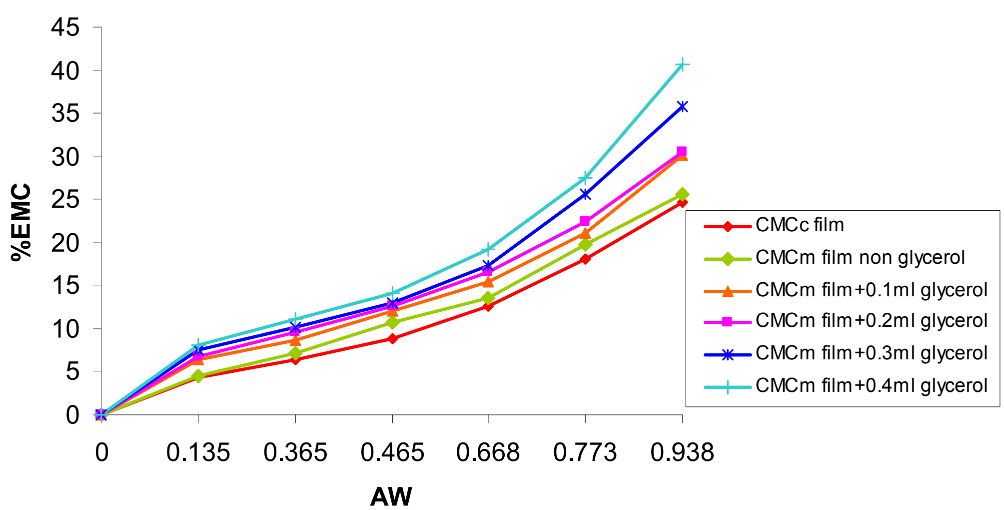

Figure 1. Sorption isotherm of CMC_m film with different glycerol content.

Fitting of sorption isotherm models to experimental data

Measured sorption isotherm data were fitted to GAB, BET and Oswin's equations. The constants are shown in Table 2.

For BET and GAB models, the most accepted model for food or edible materials [17], monolayer water content (M_0) of CMCm films with and without glycerol were presented in a range of 5.99-8.25 and 2.45-3.76 g water/ g dry film, respectively. This value indicated the maximum amount of water that could be adsorbed in a single layer per gram of dry film and it is a measure of the number of sorption sites [31]. The results showed that GAB gave higher M_0 than the BET model. These results agreed with Timmermann *et al.* [32]. For the GAB model, the C parameter in the GAB model is related to the difference of the magnitude in the upper layers and in the monolayer [33]. M_{0GAB} and M_{0BET} of CMCm films increased with increasing glycerol content. These results may be related to higher hygroscopicity of glycerol which agreed with the M_0 of cassava starch films plasticized with glycerol [34].

Oswin model provided good descriptions of the moisture isotherms throughout the entire range of water activity [35]. However, in this case, maximum %RMS value was obtained for the Oswin model. Thus, the GAB model was found to be the better estimator for predicting the equilibrium moisture content of CMCm films with and without glycerol than BET and Oswin models. This result agreed with cassava flour film plasticized with sorbitol which was best fitted with the GAB model [17].

Figure 2 shows experimental versus predicted moisture content by GAB, BET and Oswin's models of the CMCp film with and without cornflour which obtained the diagonal lines for low and intermediate a_w levels (0.1-0.8), indicating low interaction between components in accordance with their separation in independent phases as observed during the film drying [36]. At more than 0.8, it can also be observed that the point rapidly increased on the diagonal, as a result of the interaction between the water molecules and the polar groups of the film [17]. These results indicated that all models can be used to predict moisture content of CMCp film with and without cornflour at a_w 0.1-0.8.

Table 2. Sorption isotherm model constants of cassava starch based film with gelatin and CMC plasticized with 30% (w/w) glycerol at 22 ± 1°C.

Films	GAB				BET			Oswin		
	Mo	C	Km	%RMS	M0	C	%RMS	k	C	%RMS
CMC_m films treated without glycerol	5.9889	37.2034	0.8468	26.58	2.4588	-5.9372	58.09	0.3998	1.0015	93.76
CMC_m films treated with 0.1 ml glycerol	6.8648	86.4404	0.8426	28.54	2.8369	-5.7882	59.95	0.3557	1.0833	93.89
CMC_m films treated with 0.2 ml glycerol	7.5156	76.9754	0.8231	21.87	2.9172	-5.5559	56.88	0.3450	1.1101	93.96
CMC_m films treated with 0.3 ml glycerol	7.6394	109.0560	0.8574	21.00	3.3456	-5.9900	55.23	0.3633	1.1447	94.60
CMC_m films treated with 0.4 ml glycerol	8.2542	107.6564	0.8657	10.54	3.7594	-6.2005	57.62	0.3374	1.1830	92.90

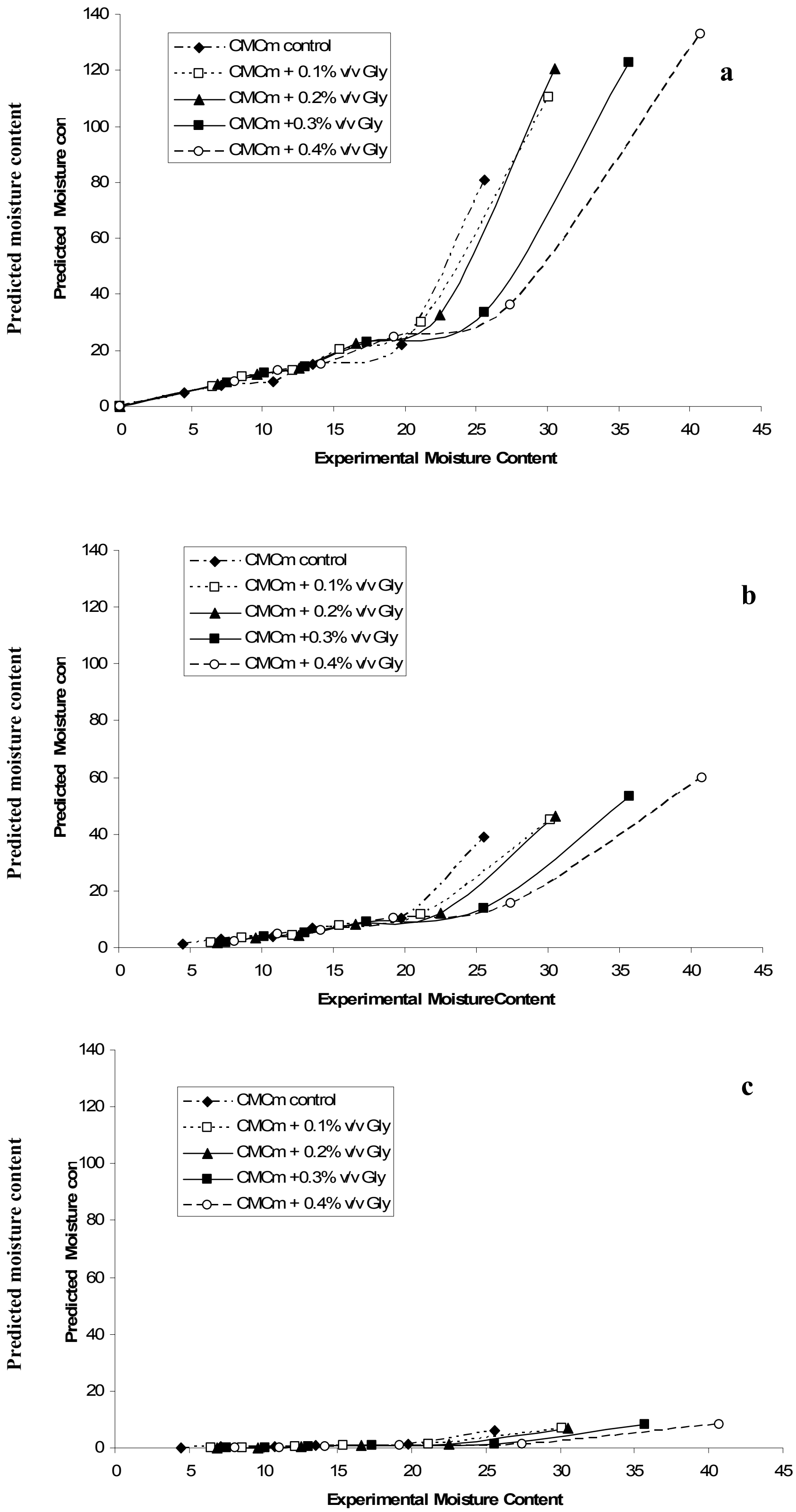

Figure 2. Comparison between experimental moisture content and those predicted by (a) GAB model, (b) BET model and (c) Oswin model of CMC_m films with various glycerol concentrations.

Conclusions

In this research, the production of carboxy methyl cellulose from waste of mulberry paper was studied and the effects of the amount of glycerol concentration as plasticizer in CMC films on water vapour transmission rate and sorption isotherms were investigated. Water vapour transmission rate (WVTR) and permeability coefficient (P) increased with increasing glycerol concentration in film solution. The percent of equilibrium moisture content (%EMC) also increased with increasing glycerol. The GAB model was found to be the best-fit model for CMCm films at a_w 0.1-0.8.

Acknowledgement

The authors are grateful for financial support provided for this research by the Higher Education Commission of Thailand.

References

1. Kirk, R.E. and Othmer, D.F. (1967). Cellulose. **Encyc. Chem. Technol.**, 4, 593–683.

2. Olaru, N., Olaru, L., Stoleriu, A. and Timpu, D. (1998). Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone. **Journal of Applied Polymer Science**, 67, 481–486.

3. Heinze, T. and Pfeiffer, K. (1999). Studies on the synthesis and characterization of carboxymethylcellulose. **Die Angewandte Makromolekulare Chemie**, 266, 37–45.

4. Charpentier, D., Mocanu, G., Carpov, A., Chapelle, S., Merle, L. and Muller, G. (1997). New hydrophobically modified carboxymethyl cellulose derivatives. **Carbohydrate Polymers**, 33, 177–186.

5. Hattori, K., Abe, E., Yoshida, T. and Cuculo, J.A. (2004). New solvents for cellulose II ethylenediamine/thiocyanate salt system. **Polymer Journal**, 36(2), 123–130.

6. Poomsaad, S. (1980). Isolation of cellulose from some plants and synthesis of its derivatives. M.S. Thesis, Chiang Mai University, Chiang Mai, Thailand.

7. Togrul, H. and Arslan, N. (2003). Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. **Carbohydrate Polymers**, 54, 73-82.

8. Yasar, F., Togrul, H., and Arslan, N. (2007). Flow properties of cellulose and carboxymethyl cellulose from orange peel. **Journal of Food Engineering**, 81, 187-199.

9. Rachtanapun, P., Kumthai, S., Yagi, N. and Uthaiyod, N. (2007). Production of carboxymethylcellulose (CMC) films from papaya peel and their mechanical properties. Proceedings of 45th Kasetsart University Annual Conference. 4: 790-799.

10. Rachtanapun, P., Tiwaratreewit, T. and Khumthai, S. (2007). Effect of bleaching process on mechanical properties of carboxymethyl cellulose from papaya peel. CMU Research Abstract, November 23-25, 2007, Chiang Mai, Thailand.

11. Rachtanapun, P. (2009). Carboxymethyl Cellulose from Papaya Peel/Corn Starch Film Blends, **Kasetsart Journal (Natural Science)** (suppl.), (*In Press*, 2009).

12. Rachtanapun, P., Mulkarat, N. and Pintajam, N. (2007). Effect of sodium hydroxide concentration on mechanical properties of carboxymethylcellulose films from waste of mulberry paper. *The 5th International Packaging Congress and Exhibition*, November 22-24, 2007, Ege, Turkey.

13. Pansuwan, V. and Wansanook, K. (2007). Bark and Core Compostion of Paper Mulberry. The Research Project for Higher Utilization of Forestry and Agricultural Plant Materials in Thailand (HUFA).

14. Gennadios, A., Weller, C.L. and Testin, R.F. (1993). Modification of physical and barrier properties of edible wheat gluten-based films. **Cereal Chemistry**, 70, 426-429.

15. Pascat, B. (1986). Study of some factors affecting permeability, In: Food Packaging and Preservation: Theory and Practice (Mathlouthi, M. (ed.)), Elsevier, London.

16. Li, Y., Shoemaker, C.F., Ma, J., Shen, X. and Zhong, F. (2008). Paste viscosity of rice starches of different amylose content and carboxymethylcellulose formed by dry heating and the physical properties of their films. **Food Chemistry**, 109(3), 616-623.

17. Suppakul P. (2006). Moisture sorption characteristics of cassava flour film. Proceedings of 15th IAPRI World Conference on Packaging. October 2-5, 2006. Tokyo, Japan. pp. 113-117.

18. ASTM (1993). Standard test method for water vapor transmission of materials. Designation ASTM: E96-93, pp. 701-708.

19. Giacin, J.R. and Hernandez, R.J. (1997). Permeability of aromas and solvents in polymeric packaging materials" edited by Brody, A. L. and Marsh K.S., The Wiley Encyclopedia of Packaging Technology, second edition, John Wiley & Sons, Inc., New York.

20. Selke, S.E.M., Culter, J.D. and Hernandex, R.J. (2004). "Plastics Packaging", 2nd edition, Hanser Publishers, Cincinnati.

21. Rachtanapun, P. (2007). Shelf Life Study of salted crackers in pouch by using computer simulation models, **Chiang Mai University Journal of Science**, 34(2), 1-10.

22. Rachtanapun, P., Kumsuk, N., Thipo, K. and Lorwatcharasupaporn, P. (2009). Prediction Models for Shelf Life of Pumpkin Crackers in Different Packages Based on Its Moisture Content, **Chiang Mai University Journal of Science**, (*In Press*, 2009).

22. Suriya, M., Sutmak, T., Nakprasert, K., Chalermchart, Y. and Moungrat, R., (Online) Effect of temperature on the moisture sorption isotherm of instant noodles with rice flour. Available: www.irpus.org/project_file/2549_2007-06-05_R14913007.pdf (August 1, 2007).

23. Giacin, J.R. (1999). Course Pack PKG 825 Polymer packaging, Spring 1999.

24. Gorntard, N., Gullbert, S. and Cuq, J.L. (1993). Water and Glycerol as Plasticizers Affect Mechanical and Water Vapor Barrier Properties of an Edible Wheat Gluten Film. **Journal of Food Science**, 58, 206-211.

25. Labuza, T.P. and Altunakar, B. (2007). Water activity prediction and moisture sorption isotherms. In: Water activity in foods fundamentals and applications (Barbosa-Canovas G. V., Fontana, Jr. A. J., Schmidt, S.J. and Labuza, T.P. eds.), Blackwell Publishing, Iowa, pp. 121-123.

26. Liendo-cardenas, M., Zapata-nornena, C.P., and Brandelli, A., (2003). Sorption isotherm equations of potato flakes and sweet potato flake, **Brazilian Journal of Food Technology**, 53-57.

27. Boki, K., Ohno, S., and Shinoda, S. (1990). Moisture sorption characteristics of kudzu starch and sweet potato starch, **Journal of Food Science**, 53, 232-235.

28. Boki, K. and Ohno, S., (1991). Equilibrium isotherm equations to represent moisture sorption on starch, **Journal of Food Science**, 56, 1106-1110.

29. Cho, S.Y. and Rhee, C., (2001). Sorption characteristics of soy protein films and their relation to mechanical properties. College of Life and Environmental Sciences.

30. Mahmoud, R. and Savello, P.A., (1992). Mechanical properties of and water vapor transferability through whey protein films. **Journal of Dairy Science**, 75, 942-946.

31. Strauss, U.P., Porcja, R.J. and Chen, Y. (1991). Volume effects of starch water interactions, In: Water Relationships in Foods (Levine, H. and Slade, L. eds.), Plenum Press, New York.

32. Timmermann, E.O., Chirife, J. and Iglesias, H.A. (2001). Water sorption isotherms of foods and foodstuffs: BET or GAB parameters. **Journal of Food Engineering**, 48, 19-31.

33. Arevelo-Pinedo, A., Giraldo-Zuniga, A.D., Santos, F.L., Arevalo, S.D.S. and Arevelo, R.P. (2004). Application of mathematical models of two and three parameters in the prediction of sorption isotherms for Inga (*Inga edulis*) pulp. Drying 2004 – Proceedings of the 14th International Drying Symposium, A: 628-633.

34. Muller, C.M.O., Yamashita, F. and Laurindo, J.B. (2008). Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach, **Carbohydrate Polymers**, 72, 82-87.

35. Oswin, C.R. (1946). The kinetics of packing life III. The isotherm, **J. Chem. Ind.**, 65: 419-423.

36. Villalobos, R., Chanona, J., Hernández, P., Gutiérrez, G. and Chiralt, A. (2005). Gloss and transparency of hydroxypropyl methylcellulose films containing surfactants as affected by their microstructure. **Food Hydrocolloids**, 19, 53-61.