Food Sci. Biotechnol. Vol. 14, No. 1, pp. 68 ~ 72 (2005)

Food Science and Biotechnology

Relationship between Moisture Barrier Properties and Sorption Characteristics of Edible Composite Films

Sou Youn Ryu, Jong Whan Rhim[1], Won Jong Lee[2], Jung Ro Yoon[2] and Suk Shin Kim*

Department of Food Science and Nutrition, The Catholic University of Korea, Buchon 422-743, Korea

[1]Department of Food Engineering, Mokpo National University, Muangun, Chonnam 534-729, Korea

[2]Department of Food Science, Kangnung National University, Kangnung 210-702, Korea

Abstract Moisture sorption characteristics of edible composite films were determined and compared against moisture barrier properties. Edible composite films were Z1 (zein film with polyethylene glycol(PEG) and glycerol), Z2 (zein film with oleic acid), ZA1 (zein-coated high amylose corn starch film with PEG and glycerol), and ZA2 (zein-coated high amylose corn starch film with oleic acid). Z2 film showed the lowest equilibrium moisture content (EMC), monolayer value (W_m), water vapor permeability (WVP), and water solubility (WS). Surface structure of Z2 was relatively denser and finer than that of other edible films. GAB W_m and C values decreased, while K values increased with increasing temperature. Correlation coefficients of WS:EMC and WVP:EMC at Aw 0.75 were higher than those of WS: W_m and WVP: W_m, respectively. EMC values at Aw 0.75 appeared useful for evaluating or predicting moisture barrier properties of edible films.

Keywords: edible composite films, high amylose corn starch, zein, moisture barrier properties, sorption characteristics

Introduction

Films made of biological macromolecules such as polysaccharides, proteins, and lipids contribute to the protection of the environment from plastic wastes, because they are biodegradable as well as edible. High amylose corn starch (HACS) is one of the edible polysaccharides, which can produce films with higher barrier properties and physical strength than normal corn starch films (1). Zein is also an edible protein, which can produce films with heat-sealability and good barrier properties (2). However, the function of HACS and zein films as moisture barriers becomes poorer with the increased use of plasticizers. Therefore, combination of lipids such as fatty acids with polysaccharides and/or proteins is desirable to maximize advantages and minimize disadvantages of individual film-forming materials (3). Although several research works have been conducted on edible composite and edible multi-component films (4-8), there have been no or little reports on the composite films made from HACS, zein, and lipid layers.

In general, the moisture barrier properties of polymeric films are determined by evaluating their water vapor permeabilities. However, this approach may fail in cases of hydrophilic polymers such as edible films, because their barrier properties depend on both the diffusion coefficient and the solubility of water in the film matrix. The moisture sorption can thus be used to characterize the barrier properties of edible film (9-10), which is a type of dried food with a thin shape. However, only relatively few reports have been reported on the moisture sorption characteristics of edible films. Herber and Dietnar (11) reported sorption isotherms of HACS film, Gennadios and Weller(12) of corn zein and wheat gluten films, Gontard *et al.* (13) of wheat gluten film, Chinnan and Park(14) of cellulose-based film, Coupland *et al.* (9) of whey protein film, and Kim and Ustunol (15) of whey-protein-based film. However, no studies have been performed on the isotherms of edible composites composed of HACS and/or zein with or without lipid layers, nor on the relationship between moisture sorption characteristics and the moisture barrier properties.

Therefore, the objectives of this study were to determine the moisture sorption characteristics and compare them against the moisture barrier properties of the edible composites composed of HACS and/or zein with or without lipid layers.

Materials and Methods

Materials HACS (HYLON VII, amylose content 70%) was obtained from National Starch & Chemical Co. (Bridgewater, NJ, USA), and zein was from Showa Sangyo Inc. (Tokyo, Japan). Sorbitol was purchased from Cerestar NV/SA (Paris, France), 95% alcohol and oleic acid from DukSan Chemicals, and polyethylene glycol (PEG) 400 from Sigma Chemicals (St. Louis, MO, USA).

Preparation of films Four kinds of edible composite films, Z1 (zein film with PEG and glycerol), Z2 (zein film with oleic acid), ZA1 (zein-coated HACS film with PEG and glycerol), and ZA2 (zein-coated HACS film with oleic acid), were made.

When making Z1 and Z2 films, zein (16.7 g) and glycerol : PEG 400 (1:1) (3.34 g), and zein (16.7 g) and oleic acid (3.34 g), respectively, were weighed in 100 g of 95% ethanol and dissolved by heating at 85°C for 20 min. The mixture was cast on a polystyrene plate (120 mm × 120 mm, 10 mm depth) and dried at 50°C.

Prior to making ZA1 and ZA2 films, suspension of 3 g

*Corresponding author: Tel: 82-2-2164-4316, Fax: 82-2-2164-4316
E-mail: kimsukshin@catholic.ac.kr

Received August 19, 2004; accepted January 5, 2005

HACS with 0.6 g sorbitol in 100 g water was preheated at 100°C for 30 min, gelatinized at 160 ± 5°C in an oil bath for 30 min, cooled to 80°C, cast on polypropylene plate (300 mm diameter and 10 mm depth), and dried at 50°C for 24 hr. ZA1 and ZA2 films were then prepared by dipping the HACS films prepared above in 100 g alcoholic solution (85°C), either with zein (16.7 g) and glycerol : PEG400 (1;1) (3.34 g) in the case of ZA1, or zein (16.7 g) and oleic acid (3.34 g) in the case of ZA2, and drying at 50°C for 4 hr.

Moisture sorption isotherms Moisture sorption isotherms of edible composite films were measured using saturated salt solutions at 5, 20, and 35°C. Before each measurement, each film sample was equilibrated in a 0% relative humidity (RH) desiccator for three days at each testing temperature (11). The moisture and solid contents of films were determined by vacuum-drying for 24 hr at 70°C and 100 mmHg pressure. All samples reached equilibrium within four weeks, at which time their equilibrium moisture contents were measured. RH of saturated salt solutions were directly measured with a water activity meter (Rotronic-Hygroskop BT, CH-8040 Zurich, Switzerland) (Table 1).

Model for moisture sorption isotherms Guggenheim-Anderson-de Boer (GAB) model (16) was used to fit the experimental sorption data:

$$W/W_m = CKA_w/[(1 - KA_w)(1 - KA_w + CKA_w)] \quad (1)$$

where, A_w is water activity, W is moisture content on dry basis, W_m is monolayer water content, C is GAB constant related to monolayer properties, and K is GAB constant related to multilayer properties.

Measurement of water vapor permeability and water solubility Water vapor permeability (WVP) (17) was measured using the modified ASTM Standard Method E96-95 (18) at 25°C and 50% RH using polymethylacrylate cup (46 mm ID, 87 mm OD and 21 mm depth) (19). The cup was filled to a depth of 11 mm with distilled water and covered with a test film sample. The lid was fixed using four screws. Vacuum grease was used between the lid and the cup to seal the film specimens. After the film specimens were equipped, the assembly was weighed and placed in a chamber conditioned at 25°C and 50% RH.

Table 1. Values of the equilibrium relative humidity (%ERH) of selected saturated salt solutions

Saturated salt solutions	Equilibrium Relative humidity (%)		
	5°C	20°C	35°C
Lithium brimide	0.5	5.4	9.7
Lithium chloride	3.2	9.3	15.2
Potassium acetate	19.2	23.7	29.5
Chromium trioxide	33.1	38.9	44.4
Magnesium nitrate	52.2	53.3	55.6
Sodium acetate	82.7	74.8	71.0
Ammonium sulfate	87.0	81.4	79.9
Ammonium dihydrogen phosphate	98.2	92.4	90.4

Weight loss of cups against time was measured and plotted. The slope of the straight line was calculated based on the(?) linear regression. Water vapor transmission rate (WVTR) was calculated by dividing the slope by the open area of the cup and corrected for the resistance of stagnant air gap between the underside of film samples on cups and the surface of water inside the cups according to the method of Gennadios *et al.* (12). WVP was calculated as follows:

$$WVP = WVTR \times L/\Delta P \quad (2)$$

where, L is film thickness (m) and ΔP is corrected water vapor partial pressure difference across the film (Pa).

Water solubility (WS) of film (13, 20) was measured as a percentage of dry matter of the film solubilized in water for 24 hr. The initial dry matter of each film was determined by drying at 100°C for 24 hr. The films were cut into 40 × 40 pieces, weighed, immersed in 50 mL distilled water containing 0.02% sodium azide (W/V) to prevent the growth of microorganisms, sealed using parafilm, and periodically agitated for 24 hr at 25°C in a shaking incubator (Model VS-8480SL, Vision Scientific Co., Korea). The films not solubilized in water were removed and dried to determine the weight of dry matter. Tests were performed in triplicates, and the solubility was calculated as follows:

$$\text{Water solubility } (\%) = 100 \times (DM_o - DM_{24})/DM_o \quad (3)$$

where, DM_o and DM_{24} are initial dry matter of the films and dry matter of the water-insoluble films, respectively.

Surface structure Film samples were mounted on a copper stub with double-sided carbon tape, and ion-sputtered (gold deposit). Cross sections and surfaces of the films were examined using a scanning electron microscope (JEOL Scanning Microscope, model JSM-5410LV, JEOL USA, Inc., Peabody, MA, USA).

Statistical analysis The linear regression and analysis of statistical differences ($p<0.05$) were performed using the statistical analysis program of SigmaPlot version 5.00 (SPSS Inc., Chicago, IL, USA).

Results and Discussion

Moisture sorption isotherms (MSI's) of edible composite films Figure 1 shows experimental MSI's at 5°C and the MSI's calculated from the GAB model of edible composite films Z1, Z2, ZA1, and ZA2. MSI's were sigmoid-shaped and similar to those of most bio-polymers. Bader and Goritz (21) reported similar MSI's of HACS film at 20°C, and Gennadios and Weller (12, 22) reported MSI's of three protein-based edible films at 25°C.

Both experimental and calculated MSI's of Z2 exhibited the lowest equilibrium moisture contents (EMC) throughout the A_w range investigated. This implies that Z2 film is the least sensitive to environmental relative humidity due to the hydrophobic nature of zein and oleic acid. In contrast, no significant differences in EMC values were observed among the other three MSI's of Z1, ZA1, and ZA2, which showed much higher EMC than Z2 MSI's. This may be due to the hydrophilic nature of the film-forming materials

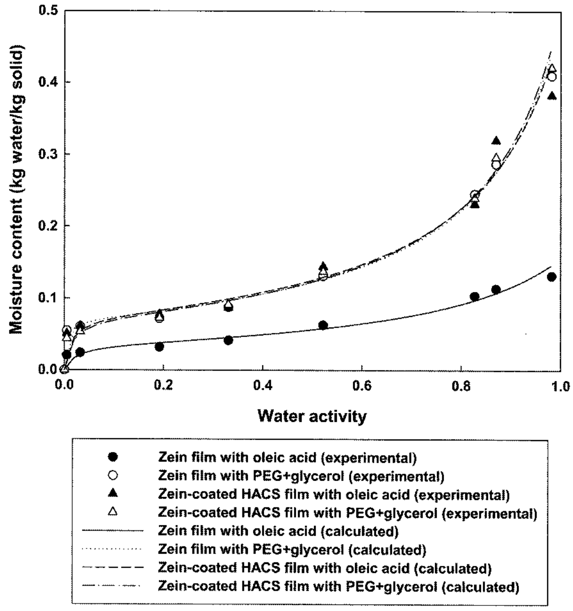

Fig. 1. Moisture sorption isotherms of edible composite films at 5°C

of Z1, ZA1, and ZA2. Z1 and ZA1 were made of hydrophilic plasticizers such as PEG and glycerol, and ZA1 and ZA2, even-coated with zein and/or oleic acid, remained hydrophilic, because the hydrophilic HACS was the major and the hydrophobic zein and oleic acid were the minor components.

MSI's at 20 and 35°C (Figs. 2 and 3, respectively) also showed similar patterns to those of Fig. 1, which indicates that both hydrophobic and hydrophilic natures cannot be altered through changes in the temperature.

GAB parameters and temperature dependencies of edible composite films The GAB parameters of edible composite films Z1, Z2, ZA1, and ZA2 at 5, 20, and 35°C are listed in Table 2. Z2 showed the lowest monolayer (W_m) values; while, those of Z1, ZA1, and ZA2 were not significantly different. The lowest W_m values of Z2 implies that Z2 is much more hydrophobic than the other three films due to the presence of zein and oleic acid. The GAB W_m and C values decreased with increase in temperature; while K values increased. Kim and Bhowmik (23) also reported similar patterns in yogurt powders.

The temperature dependency of Z2 film MSI's is shown in Fig. 4. All EMC values in the entire A_w range decreased as the temperature increased. The MSI's of Z1, ZA1, and ZA2 also showed similar temperature dependencies (Data not shown).

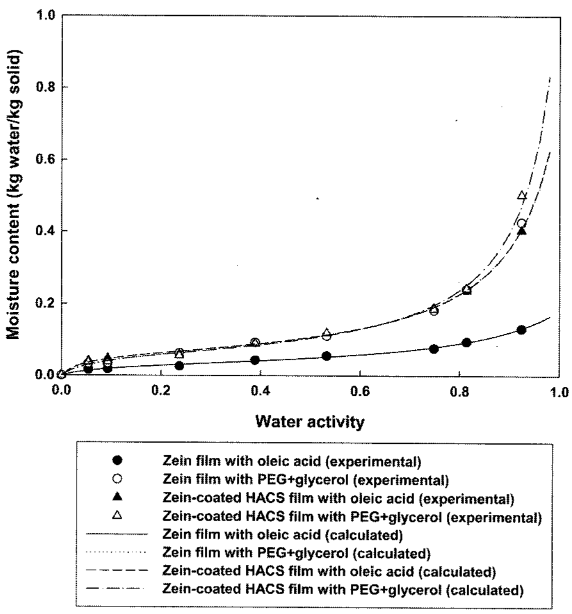

Fig. 2. Moisture sorption isotherms of edible composite films at 20°C

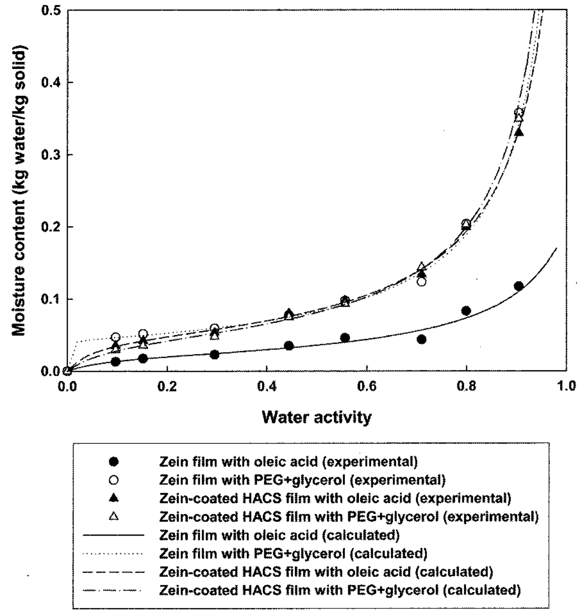

Fig. 3. Moisture sorption isotherms of edible composite films at 35°C

Table 2. GAB parameters for moisture sorption isotherms of edible composite films

Fims	Temp. (°C)	W_m (kg water/kg solid)	C	K
Z1[1)]	5	0.0703	22.8926	0.8561
	20	0.0622	15.1979	0.9185
	35	0.0427	6.7811	0.9671
Z2[2)]	5	0.0355	56.1400	0.7738
	20	0.0317	14.5517	0.8289
	35	0.0217	13.6789	0.8912
ZA1[3)]	5	0.0715	78.8266	0.8569
	20	0.0585	18.3081	0.9490
	35	0.0454	11.7838	0.9718
ZA2[4)]	5	0.0734	89.0408	0.8452
	20	0.0607	24.9293	0.9218
	35	0.0469	19.2613	0.9514

[1)]Z1=zein film with polyethylene glycol(PEG) and glycerol
[2)]Z2=zein film with oleic acid
[3)]ZA1=zein-coated high amylose corn starch film with polyethylene
[4)]glycol(PEG) and glycerol
[5)]ZA2=zein-coated high amylose corn starch film with oleic acid

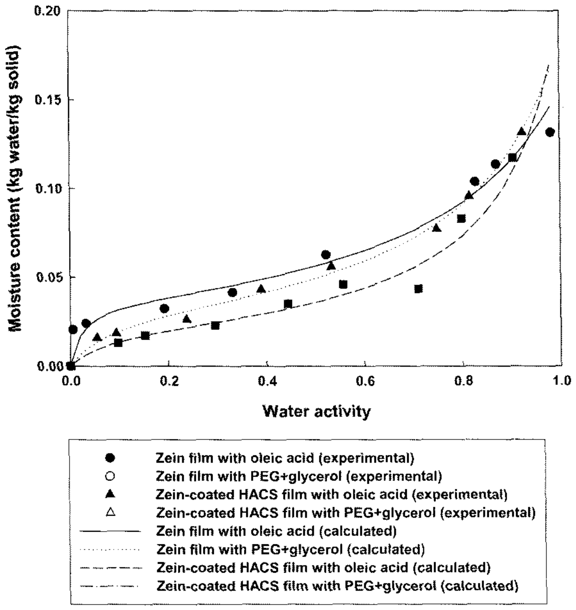

Fig. 4. Moisture sorption isotherms of zein film with oleic acid at 5°C, 20°C, and 35°C.

Table 3. Water vapor permeability and water solubility of edible composite films[1)]

Edible films	Water vapor permeability (10^{-9} g/m·s·Pa)	Water solubility (%)	Thickness (m)
Z1[2)]	10.14±1.30	1.84±0.55	119±5
Z2[3)]	5.91±1.44	1.04±0.04	118±6
ZA1[4)]	16.93±2.44	6.57±0.60	121±8
ZA2[5)]	14.83±2.41	8.38±0.37	120±8

[1)]Means ± standard deviations.
[2)]Z1=zein film with PEG and glycerol
[3)]Z2=zein film with oleic acid
[4)]ZA1=zein-coated high amylose corn starch film with PEG and glycerol
[5)]ZA2=zein-coated high amylose corn starch film with oleic acid

Correlation between moisture barrier properties and sorption characteristics of edible composite films Water vapor permeability (WVP) and water solubility (WS) of edible composite films are listed in Table 3. Z2 showed the lowest WVP, followed by Z1, ZA2, and ZA1, whereas WS of Z2 was the lowest, followed by Z1, ZA1, and ZA2; however, differences in WVP and WS were not significant between ZA1 and ZA2.

Figure 5 shows the correlation coefficients between moisture barrier properties and sorption characteristics of edible composite films. The coefficient was the highest between W_m and EMC (W_m:EMC), followed by WVP: EMC, and WS:EMC. The correlation coefficients increased as Aw decreased from 0.92 to 0.75; below Aw 0.75, however, the coefficients did not show any correlation with Aw. The coefficients of WS:EMC and WVP:EMC at Aw 0.75 were higher than those of WS: W_m and WVP: W_m, respectively. This suggests that, particularly at Aw 0.75, which can be easily obtained using saturated NaCl solution, EMC value is the most useful sorption parameter for evaluating or predicting the moisture barrier properties of edible films.

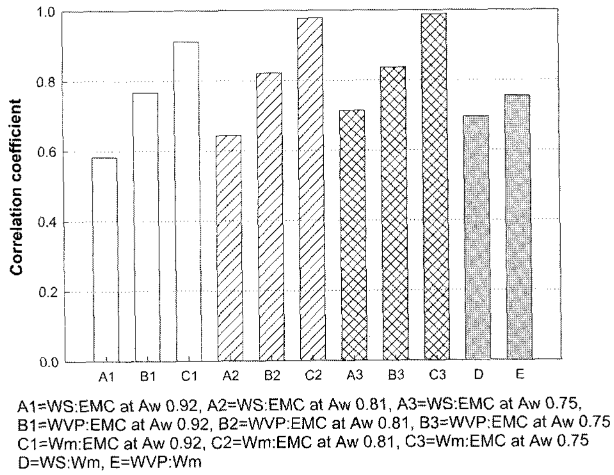

Fig. 5. Correlation coefficients of moisture barrier properties and sorption characteristics of edible composite films.

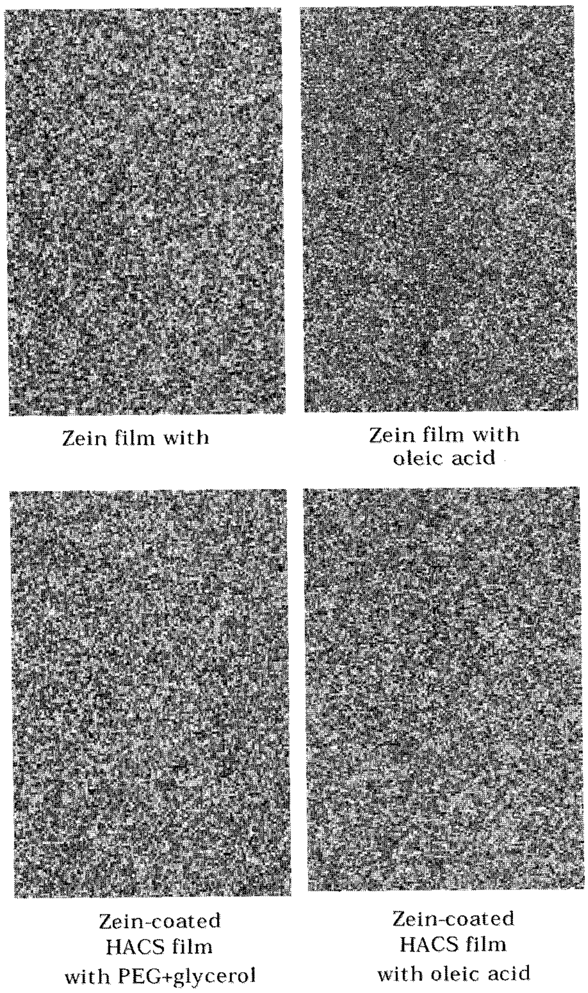

Fig. 6. SEM of surface of edible composite films at 1200 magnifications.

Surface structure of edible composite films Figure 6 shows the surface structures of the four edible composite films. The surface structure of Z2 was relatively dense and fine; while the other edible films had loose and rough structures. The dense surface of Z2 appeared to be responsible for the relatively high moisture barrier properties as compared to the other edible composite films.

Conclusion

The monolayer values and equilibrium moisture content of four edible composite films were compared against their vapor permeability and water solubility. The zein film with oleic acid showed the lowest monolayer value, equilibrium moisture content, WVP, and WS. Oleic acid appeared to be advantageous to the zein film, because it could effectively improve the moisture barrier properties of the composite film. The EMC value, particularly at Aw 0.75, proved to be the most useful sorption parameter and can be used to correlate with the moisture barrier properties of edible composite films.

Acknowledgments

This study was funded by Korean Council for University Education, Support for 2003 Domestic Faculty Exchange.

References

1. Kester JJ, Fennema OR. Edible films and coatings: a review. Food Technol. 40(12): 47-59 (1986)
2. Park HJ, Chinnan MS, Shewfelt RL. Edible corn zein film coatings to extend storage life of tomatoes. J. Food Process. Preserv. 18: 317-331 (1994)
3. Gennadios A, Weller CL, Park HJ. Environmental effects on tensile strength of edible films. Trans. ASAE 36(6): 21-24 (1992)
4. Mallikarjunan P, Chinnan MS, Balasubramaniam VM, Phillips RD. Edible coatings for deep-fat frying starchy products. Lebens. Wiss. U-Technol. 30: 709-714 (1997)
5. Lerthanangkul S, Krochta JM. Edible coating effects on postharvest quality of green bell peppers. J. Food Sci. 61: 176-179 (1996)
6. Park JW, Park HJ, Jung ST, Rhim JW, Park YK, Hwang KT. Corn zein laminated carrageenan film for packaging minced mackerels. Korean J. Food Sci. Technol. 30: 1381-1387 (1998)
7. Kim JN, Rhin, JW. Kinetics of water vapor adsorption by sweet potato starch-based edible films. Food Sci. Biotechnol. 13: 616-621 (2004)
8. Rhim JW. Increase in water vapor barrier property of biopolymer-based edible films and coatings by compositing with lipid materials. Food Sci. Biotechnol. 13: 528-535 (2004)
9. Coupland JN, Shaw NB, Monahan FJ, ORiordan ED, OSullivan M. Modelling the effect of glycerol on the moisture sorption behavior of whey protein edible films. J. Food Eng. 43: 25-30 (2000)
10. Del Nobile MA, Fava P, Piergiovanni L. Water transport properties of cellophane flexible films intended for food packaging applications. J. Food Eng. 53: 295-300 (2002)
11. Herbert GB, Dietnar G. Investigations on high amylose corn starch films-Part 2: water vapor sorption. Starch/Stärke 46: 249-252 (1994)
12. Gennadios A, Weller CL. Moisture adsorption by grain proten films. Trans. ASAE 37: 353-359 (1994)
13. Gontard N, Guilbert S, Cuq JL. Edible wheat gluten films: influence of the main process variables on film properties using response surface methodology. J. Food Sci. 57: 190-195, 199 (1992)
14. Chinnan MS, Park HJ. Effect of plasticizer level and temperature on water vapor transmission of cellulose-based edible films. J. Food Process Eng. 18: 417-429 (1995)
15. Kim SJ, Ustnol Z. Solubility and moisture sorption isotherms of whey-protein-based edible films as influenced by lipid and plasticizer incorporation. J. Agr. Food Chem. 49: 4388-4391 (2001)
16. Bizot H. Using the 'G.A.B.' model to construct sorption isotherms. pp. 43-54. In: Physical Properties of Foods. Jowitt R, Escher J, Hallstrom B, Meffert HFT, Spiess WEL, Vos G. (eds). Applied Science, New York, NY, USA (1983)
17. Gontard N, Guilbert S, Cuq J. Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. J. Food Sci. 58: 206-211 (1993)
18. ASTM. Standard test methods for water vapor transmission of materials. Annual book of ASTM standards, Destination : E96-80 (1989)
19. Park JW, Testin RF, Park HJ, Vergano PJ, Weller CL. Fatty acid concentration effect on tensile strength, elongation and water vapor permeability of laminated edible films. J. Food Sci. 59: 916-919 (1994)
20. Rhim JW, Park JW, Jung ST, Park HJ. Formation and properties of corn zein coated κ-carrageenan films. Korean. J. Food Sci. Technol. 29: 1184-1190 (1997)
21. Bader HG, Goritz D. Investigation on high amylose corn starch films. Part 2: water vapor sorption. Starch/Stärke 46: 249-252 (1994)
22. Gennadios A, Weller CL. Moisture sorption isotherms of edible films. Trans. ASAE 35(12): 17-20 (1991)
23. Kim SS, Bhowmik SR. Moisture sorption isotherms of concentrated yogurt and microwave vacuum dried yogurt powder. J. Food Eng. 21: 157-175 (1994)