

Water Vapor Permeability and Moisture Sorption of Soy Protein Isolate/Poly (Vinyl Alcohol) Packaging Films

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Abstract: Packaging films based on agricultural materials have received much attention as potential packaging materials, principally because such biodegradable films are considered to be a promising solution to environmental impacts of synthetic polymer packaging. The aim of the present work was to investigate the moisture sensitivity of films of soy protein isolate (SPI) blended with poly (vinyl alcohol) (PVA) and plasticized with glycerol. Moisture adsorption and sorption isotherm data of SPI/PVA/glycerol were mathematically fitted to the GAB model. With increasing PVA content, the equilibrium moisture content (EMC) of film samples clearly decreased. That trend indicates that the addition of PVA decreased the ability of SPI protein molecules to absorb and accept water. EMC data and contact angle measurements showed that the addition of plasticizer not only loosened the microstructure of blended films, but also increased the hydrophilicity by exposing their hydroxyl groups. Water vapor permeability (WVP) and moisture sorption were measured based on the PVA and glycerol content of the films. WVP values of SPI/PVA films with and without glycerol were in the range 8.25 and 10.9 g mm (m² h kPa)⁻¹, and were significantly affected by both PVA and glycerol. WVP values decreased with increasing PVA content. XRD analysis confirmed that the glycerol can enter the macromolecular blend structure and destroy the crystallinity of the blends. Cross-linking between glycerol molecules and SPI reduced the interstitial spaces in the protein matrix, thus decreasing the rate of diffusion of water molecules through the films.

Keywords: Soy Protein Isolate; Poly (vinyl alcohol); Water Vapor Permeability; Moisture Sorption; Packaging Films

1. Introduction

Biodegradable materials derived from natural products offer an outlet for overflowing solid waste streams. In recent years, soy protein isolate (SPI) has been considered as a promising biodegradable plastic with the advantages of low cost and easy availability. In the packaging materials field, SPI has been used to fabricate food trays, containers, flatware, edible films and packaging films [1]. In particular, SPI-based packaging films have been extensively studied as a potential replacement for petroleum-based plastic films. To date, many attempts have been made to modify the poor mechanical properties and relatively high moisture sensitivity of SPI films by physical, enzymatic, chemical and physicochemical methods. However, as SPI contains 58% polar amino acids that cause its hydrophilicity, its moisture sensitive is difficult to eliminate. At the same time the barrier properties against oxygen and oil are greatly affected by the relative humidity. Moisture sensitive foods or pharmaceuticals are usually put into sealed packaging films with controlled water vapor permeability to obtain the required quality, safety and shelf-life. Consequently, being able to produce SPI-based films with improved moisture resistance is now a major concern for SPI plastics,

and a key issue for their competitiveness as a new packaging material.

Previous studies have reported that the moisture sensitivity problem can be overcome to some extent through two approaches. One straightforward approach is to add hydrophobic plasticizers to films. Another approach to modifying the moisture sensitivity of SPI films is to blend other natural or synthetic polymers with SPI materials [2]. A novel film fabricated from SPI and PVA and plasticized by glycerol was reported in our previous studies [3]. The results showed that the SPI/PVA blends of biocompatible polymers combined the advantages of both components, and sharply improved the flexibility. In addition, glycerol increased the compatibility and/or modified the interfacial adhesion of the blend. To be successfully applied as a biodegradable film in the packaging field, SPI/PVA/glycerol film should resist moisture transfer through the inside and the outside of packaging. Based on the above-mentioned background, and the drive of fundamental research and industrial applications of packaging films, the objective of the present study was to measure the water vapor permeability and moisture sorption properties of SPI/PVA films. The scope of this study was the effect of PVA content and glycerol addition on the moisture sensitivity of these films.

2. Experimental

2.1. Materials

PVA ($M_w \approx 1.0 \times 10^5 \text{ g mol}^{-1}$, minimum degree of hydrolysis $\approx 87\%$) was purchased from SINPEC Shanghai Petrochemical Co. Ltd. SPI powder (Type C[®]), prepared by acid precipitation, was provided by Harbin High-technology Soy Protein Co. Ltd. It contained $>90\%$ protein and $<5.0\%$ moisture. Both PVA and SPI were vacuum-dried at 50°C for 24 h before use. Analytical grade glycerol (1,2,3-propanetriol) with 95% purity was purchased from Tianjin Chemical Co. Ltd. Analytical grade sodium hydroxide (NaOH) pellets were used to prepare a 2.0 mol L^{-1} solution at room temperature.

2.2. Preparation and Characterization of films

Fabrication of SPI/PVA films was based on a solution casting and evaporation method [4].

The films were kept at room temperature in a conditioning desiccator at 43% relative humidity (produced by a saturated K_2CO_3 solution) for 3 days before being tested. Samples were cut to the required sizes for investigation of morphology and mechanical properties. A series of SPI/PVA films coded as P-0, P-5, P-10, P-15, P-20, P-25, P-30 and P-40 were made up with SPI:PVA weight ratios 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30 and 60:40, respectively. Another series of SPI/PVA films was prepared using the method above, with addition of glycerol. These films were coded as P-PVA-n, where n is the weight percent of glycerol relative to SPI. For example, P-10-2 means the weight ratio of SPI to PVA was 90:10 in the blend film, and the glycerol content relative to SPI was 2.0 wt. %.

Water sorption isotherms were measured according to the procedure described by Chang [5]. Film samples were cut into small pieces (5.0x5.0 mm) and dried in a vacuum desiccator over P_2O_5 at 25°C for 3 days. The dried samples were weighed to 0.0001 g into pre-weighed bottles and equilibrated with salt solutions of known water activity (a_w) at 5, 25, 35 and 45°C [6]. Saturated solutions of LiCl, CH_3COOK , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NaBr, NaCl and KCl, contained in vacuum desiccators at 25°C , were used to give relative vapor pressure (RVP) 11, 24, 33, 44, 54, 66, 76 and 86 %, respectively. Table 1 lists a_w data for all saturated solutions at different temperatures, covering the water activity range from 0.10 to 0.90 [7]. For details of the equilibration procedure refer to Bertuzzi [8]. Film samples were placed on a stainless steel lattice supported on a tripod inside the sorbostats containing the saturated salt solutions, then the sorbostats were sealed. The sorbostats were moved into an environmental chamber maintained at constant temperature. While being equilibrated in the sorbostats, the sample weights were recorded every day. Equilibrium was considered to be achieved when the difference between two consecutive sample weights was

$<1.0 \text{ mg per g}$ of dry solid. Moisture sorption (MS) at equilibrium for each sample was calculated as g water sorbed per 100 dry film at a range of relative humidities. MS data were then determined by vacuum drying at 70°C and pressure $<1 \text{ mmHg}$ for 24 h. MS_i was evaluated from Eqs. (1),

$$\text{MS}_i = \frac{W_i - W_{i0}}{W_{i0}} \times 100\% \quad (1)$$

where W_{i0} , W_i and MS_i are the original weight, weight after moisture sorption and moisture sorption, respectively, for a sample. MS is the average value of moisture sorption from triplicate measurements of MS_i , which were obtained for each type of film with individually prepared films as replicated experimental samples, and three specimens from each sample.

Table 1. Water activity values (a_w) of saturated solutions at different temperatures.

Salt	a_w (5°C)	a_w (25°C)	a_w (35°C)	a_w (45°C)
LiCl	0.129	0.114	0.108	0.103
CH_3COOK	0.292	0.237	0.216	0.198
MgCl_2	0.354	0.329	0.318	0.308
K_2CO_3	0.459	0.443	0.436	0.430
$\text{Mg}(\text{NO}_3)_2$	0.584	0.536	0.516	0.497
NaBr	0.682	0.653	0.638	0.624
NaCl	0.805	0.762	0.743	0.726
KCl	0.934	0.855	0.821	0.791

3. Results and discussion

Fig.1 shows water sorption isotherms for SPI/PVA films (P-0, P-10, P-20 and P-30) at 5, 25, 35 and 45°C , respectively. Because moisture content of the film increases at elevated water activity (a_w), the time to reach equilibrium moisture content (EMC) at lower humidity is longer than that at higher humidity [9]. The EMC increased with increasing temperature, at the same a_w , for each sample. In Fig.1 (a), the slope of the isotherms for pure SPI film (P-0) was smaller at lower a_w : with increase in a_w the slope increased rapidly. In addition, high temperature enhanced the water sorption ability of pure SPI films. Compared to P-0, the EMC values for samples P-10, P-20 and P-30 were smaller in the a_w range 0.1 to 0.6, as shown in Fig.1 (b-d). This trend indicates that the addition of PVA decreased the ability of SPI protein molecules to absorb and accept water. This result is in accordance with a previously reported conclusion [4]. However, the temperature did not greatly affect the EMC for films in the a_w range 0.1 to 0.6, possibly due to the lower weight ratios of hydrophilic SPI in these films and the dense blend structure of SPI/PVA. For $a_w > 0.6$, the EMC decreased with both temperature and increasing PVA content.

Water sorption isotherms for films as a function of temperature (25°C) and plasticizer concentration showed behavior that is typical of hydrophilic materials. Fig.2 shows water sorption isotherms for P-5, P-10, P-20 and

P-30 with glycerol contents 1.0-3.0 wt.%, at 25°C. It is apparent that films with a higher proportion of glycerol absorbed more moisture at a given a_w . This observation is in accordance with the reported results that glycerol not only loosens the microstructure of blended films, but also increases their hydrophilicity by exposing their hydroxyl groups [10]. As glycerol is a small (92 g mol⁻¹) molecular plasticizer, it easily inserts the SPI film structure. This explanation is also appropriate for other protein (whey, zein and wheat) films [11]. Another feasible explanation is that with addition of glycerol, the free volume of the molecular network is increased by the increased mobility of the polymeric chains.

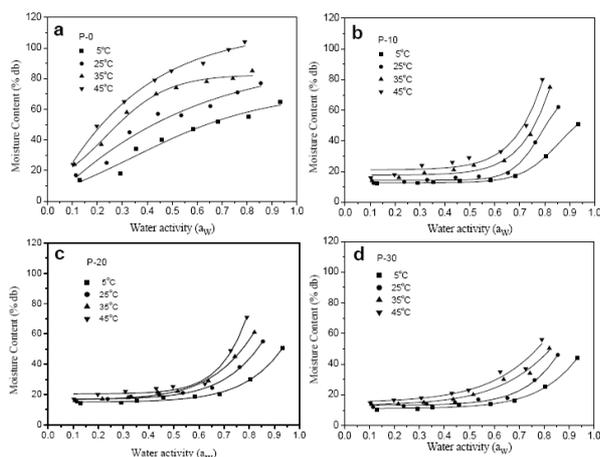


Figure 1. The water sorption isotherms of film samples under temperatures of 5°C, 25°C, 35°C and 45°C: (a) P-0 (pure SPI film), (b) P-10, (c) P-20 and (d) P-30.

The GAB model gives Eq. (2)

$$EMC = \frac{W_m C k \alpha_w}{(1 - k \alpha_w)(1 - k \alpha_w + c k \alpha_w)} \quad (2)$$

$$r^2 (\%) = \frac{100}{n} \sum_{i=1}^n \left(\frac{M_e - M_c}{M_e} \right)^2 \quad (3)$$

where EMC is the equilibrium moisture content on a dry film basis, W_m is BET monolayer moisture content and represents the water content corresponding to the saturation of all primary adsorption sites by one water molecule, C is the Guggenheim constant, and k is a factor correcting the properties of multilayer molecules corresponding to the bulk liquid. The criterion used to evaluate goodness of fit of experimental sorption data was the root mean square error (r^2 , %), where n is the number of experimental points, and M_e and M_c are the experimental and calculated EMC values, respectively.

Table 2 lists the values of r^2 and the GAB model constants (W_m , C and k) for different films. At 25°C, the high

r^2 values ($r^2 > 0.97$) confirm that the GAB model is a good representation of the experimental data. The reported ranges of applicability of a_w for the isotherm models lies between 0.1 and 0.4 (monomolecular layer) for the BET model, and between 0.3 and 0.9 (multimolecular and capillary condensation layers) for other models [12]. Consequently, the water sorption behavior can be understood by analyzing the constants for the GAB model. Moreover, this model has an important advantage because it leads to an equation that contains parameters with physical significance [13].

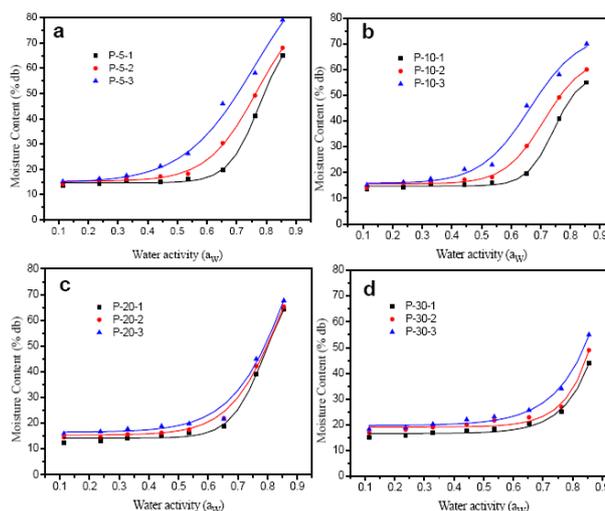


Figure 2. Water sorption isotherms of film samples at 5, 25, 35 and 45°C: (a) P-0 (pure SPI film), (b) P-10, (c) P-20 and (d) P-30.

Table 2. GAB Model Constants and root mean square error (r^2 , %) of the Fitting for SPI/PVA films (P-0, P-5, P-10 and P-20) with/without glycerol.

Film Samples	GAB model constants			r^2 (%)
	W_m	C	k	
P-0	7.01 d	3.31 a	0.95 d	97.8
P-5	7.03 d	4.25 ab	0.84 dc	97.1
P-5-1	7.21 d	4.30 b	0.86 c	97.0
P-5-2	7.35 d	4.21 b	0.89 c	97.4
P-5-3	7.47 cd	4.00 b	0.90 bc	97.7
P-10	6.49 b	4.67 a	0.79 b	97.5
P-10-1	6.30 b	4.35 c	0.81 b	98.6
P-10-2	6.34 b	4.75 c	0.83 b	98.5
P-10-3	6.20 b	7.82 d	0.87 b	98.5
P-20	6.30 a	5.12 a	0.71 a	99.7
P-20-1	6.46 a	5.09 c	0.75 a	99.5
P-20-2	6.49 a	4.95 d	0.76 a	99.6
P-20-3	6.51 a	7.90 d	0.79 a	99.7

Means values were determined in five replicates. Alphabets in a column indicate significant difference at $P < 0.05$ by Duncan's multiple range tests.

WVP is a measure of the amount of water vapor passing through unit area of material per unit time. For hy-

drophobic polymeric films such as polyethylene (PE) or polypropylene (PP), WVP is a proportionality constant that is assumed to be independent of the water vapor pressure gradient applied across the films. However, natural materials are hydrophilic materials with polar groups in their molecular structures, and the interactions of polar groups with permeating water molecules causes the WVP to depart from ideal behavior [14]. The deviation from ideal behavior is attributed to the variation of structure of the materials. The deviation was believed to be governed by free volume theory. Water increases the polymer free volume, allowing the polymeric chain segments to increase their mobility. Higher segment mobility results in higher WVP.

Table 3. WVP values of SPI/PVA films with and without glycerol.

Weight of PVA (100g/g SPI/PVA)	WVP (g mm/m ² h kPa)				
	0% glycerol	1% glycerol	2% glycerol	3% glycerol	4% glycerol
P-0	10.1±0.81d	10.0±0.70d	9.7±0.87d	9.6±0.48d	9.4±0.84d
P-10	9.7±0.77cd	9.5±0.66c	9.0±0.81c	8.4±0.42c	8.2±0.73c
P-20	9.5±0.76b	9.0±0.63c	8.5±0.76c	8.0±0.40c	7.3±0.65c
P-30	10.0±0.80b	10.1±0.70c	10.0±0.90c	9.9±0.49c	9.0±0.81c
P-40	11.0±0.88ab	10.9±0.76b	10.0±0.90b	10.5±0.52b	11.0±0.99b
P-50	12.5±1.00a	12.0±0.84a	12.5±1.12a	13.0±1.46a	13.5±1.21a

In this study, WVP were investigated to understand the effect of PVA and glycerol contents on blend films. Table 3 lists the WVP values of SPI/PVA films P-0, P-10, P-20, P-30, P-40 and P-50 with and without glycerol. WVP data were in the range 7.30 to 13.5 g mm (m² h kPa)⁻¹, and were significantly affected by either PVA or glycerol contents. Pure SPI film had WVP value 10.1 g mm (m² h kPa)⁻¹ which was not significantly decreased by adding 1.0-4.0 wt. % glycerol. Initially the WVP values decreased with increasing PVA content. For P-20, the minima were 7.3, 8.0, 8.5, 9.0 and 9.5 g mm (m² h kPa)⁻¹ corresponding to 0, 1.0, 2.0, 3.0 and 4.0 wt.% glycerol, respectively. Subsequently WVP values increased with increasing PVA content. In particular, P-20-4 with 4.0% glycerol had WVP value 7.3 g mm (m² h kPa)⁻¹, which is 140% higher than the value for pure SPI. By contrast, glycerol (1.0-4.0 wt.%) greatly reduced the WVP of SPI/PVA films while increasing film extensibility. A contrary view is that the consequences of the plasticizing action of glycerol are favorable to adsorption and absorption of water molecules by the film, so WVP will be substantially increased [15]. These results might be attributed to saturation by water reducing the interstitial spaces in the protein matrix, and consequently decreasing the rate of diffusion of water molecules through the films.

Fig.3 (a, b) shows the X-ray patterns of pure PVA powder and pure SPI powder. PVA has a strong characteristic peak at 2θ=20°, which agrees with the result obtained by Kaczmarek [16] working with pure PVA films, and with our previous work [3, 4]. It was that PVA pos-

sesses a flexible structure that favors close molecular packing and crystallization. Pure SPI has a strong characteristic peak at a 2θ value around 22°. It has been reported that composites of PVA and natural polymers (including starch, cellulose, chitin, chitosan, wheat protein, egg protein, lignin and sodium alginate) have good compatibility. In the present study, P-5 was found to have two strong reflections at 19 and 22°. The intensities of the reflections decreased substantially compared with the reflections of pure PVA and SPI, indicating that the crystalline structure of either PVA or SPI collapsed after blending of the two polymers. A similar result has been reported previously: XRD patterns of gelatin/PVA films showed multiple peaks. The intensity of the XRD peaks gradually decreased with increasing PVA content in films P-10, P-15 and P-20 (Fig.3 (d-f)). However, the XRD peaks had almost the same 2θ value (22°). To understand the effect of glycerol on the blend crystalline structure, XRD patterns of P-10-1, P-10-2 and P-10-3 are shown in Fig.3 (g-j). The XRD peaks are less intense with increased glycerol content of the blend films, indicating that the presence of glycerol reduces the crystallinity of PVA/SPI blends. Summarizing these results, it is believed that the SPI/PVA blend films are partially crystalline materials, and glycerol can enter the crystalline structure and regulate the microstructure of SPI/PVA blends. Lu [17] has reported the similar result that glycerol enters the macromolecular blend structure and destroys the crystallinity of blends. Moreover, the addition of glycerol to SPI/PVA blends compacts the components and increases the toughness by decreasing the degree of crystallinity.

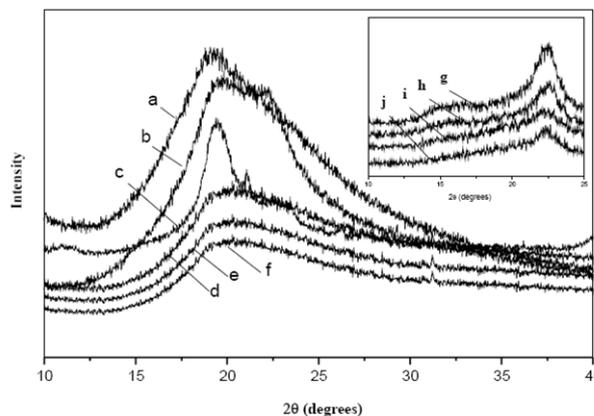


Figure 3. X-ray patterns of (a) pure PVA powder, (b) pure SPI powder; film samples of (c-f): P-5, P-10, P-15 and P-20; and filmsamples with glycerol, (g-j): P-10-1, P-10-2, P-10-3 and P-10-4.

4. Conclusion

Moisture adsorption and sorption isotherm data of SPI/PVA/glycerol were mathematically fitted to the GAB model. Blending with PVA improves the moisture

barrier properties and decreases the water sorption ability of SPI films. Because glycerol is hydrophilic, more water is absorbed by and retained in films with higher proportions of glycerol plasticizer, at a particular temperature and relative humidity. Water increases the polymer free volume, allowing the polymeric chain segments to increase their mobility. Higher segment mobility results in higher WVP. Glycerol (1.0-4.0 wt.%) greatly reduced WVP of SPI/PVA films while increasing film extensibility. Higher proportions of glycerol in films facilitate penetration of water molecules.

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