

EFFECT OF PLASTICIZER LEVEL AND TEMPERATURE ON WATER VAPOR TRANSMISSION OF CELLULOSE-BASED EDIBLE FILMS¹

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ABSTRACT

This study was conducted to determine water sorption isotherms of cellulose-based films made from methyl cellulose (MC) and hydroxypropyl cellulose (HPC), and to evaluate the effect of plasticizer concentration and temperature on water vapor permeability coefficient in those films. The equilibrium moisture contents of MC film and HPC film increased slowly with an increase in water activity (a_w) up to 0.75, but increased greatly after 0.75 a_w . The water vapor permeability coefficient of HPC film increased as the concentration of polyethylene glycol (PEG) increased; however, the water vapor permeability coefficient of MC film which contained 0.22 ml PEG/g cellulose was lower than of films which contained no or higher PEG. An Arrhenius-type relationship was fitted to examine temperature dependence of water vapor permeability coefficients of cellulose films. The edible films studied exhibited relatively low activation energies (14.56-16.43 kJ/mol) compared with typical food packaging materials.

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INTRODUCTION

Controlling moisture exchange is a critical factor in extending the shelf-life of moisture sensitive foods (fresh fruits and vegetables), and processed products (frozen foods, candies, snacks and cookies). Edible coatings for fresh fruits and vegetables have been used to control moisture loss with the purpose of prolonging their shelf-life during storage (Erbil and Muftugil 1986; Risse *et al.* 1987; Smith and Stow 1984). Water loss in fresh fruits and vegetables can adversely affect their quality during the marketing period. Edible coatings can act as a moisture barrier. They can also create and allow the build-up of carbon dioxide level and reduction of oxygen level inside the fruit or vegetable tissue thus reducing respiration rate and potentially extending product shelf-life.

Concerns have been raised about transmigration of monomers from plastic films into foods when in contact (Park and Ashcraft 1989); for example, the monomer of polyvinyl chloride has been listed as a carcinogen. However, cellulose-based films are edible, biodegradable and fall under the GRAS (generally recognized as safe) category (Kester and Fennema 1986). The cellulose-based films may be used as packaging materials which come in contact with foods. Edible coatings for processed products also could be used as moisture barriers to extend product shelf-life during their marketing. Kester and Fennema (1989b) reported that the lipid-cellulose film placed at the interface of two components, bread and a tomato-based sauce, effectively retarded migration of moisture from sauce to bread during storage. Rico-Pena and Torres (1990a) used methyl cellulose-palmitic acid film in a simulated ice cream cone core as moisture-impermeable barrier and observed that the sample of sugar cone which contained this film showed no detectable moisture increase for 10 weeks at -23C and for 4 weeks at -12C.

Gas and water vapor permeation properties in edible films including cellulose are affected by several factors such as solvent type, plasticization, polymer material, and other film additives (Banker 1966; Banker *et al.* 1966; Pascat 1986). Gontard *et al.* (1993) recently published data on the effect of glycerin as a plasticizing agent on water vapor barrier properties of wheat gluten film and reported that the water vapor transmission rate increased as concentration of the plasticizer increased in the film. Park and Chinnan (1995) made cellulose-based films which contained two different concentrations of plasticizer and found that the gas and water vapor permeability coefficient increased with increasing plasticizer level. Overall, very limited work has been reported in the literature on the plasticizer effect on the water vapor barrier properties of cellulose-based films.

Several reports exist on determining the water vapor permeability coefficient and water vapor sorption isotherm in plastic films (Labuza and Contreras-Medellin 1981; Karel *et al.* 1959). Linear relationship between water

content and water activity (a_w) in the plastic films was observed (Karel *et al.* 1959). Water vapor permeation properties of cellulose-based films and protein-based films are different when compared with plastic films. The moisture isotherms of most edible films made from biopolymers are not linear over a wide range of a_w . Gontrad *et al.* (1993) reported that the slope of water vapor sorption isotherm of wheat gluten film increased linearly in the range of 0 to 0.68 a_w and then increased sharply beyond 0.68 a_w . However, data on water vapor sorption isotherm of cellulose-based films is not available.

Labuza and Contreras-Medellin (1981) found that water vapor gas permeability coefficients increased in plastic films as temperature increased. Temperature effect on oxygen permeability coefficients of protein-based films was reported by Gennadios *et al.* (1993), and Arrhenius plots were fitted by them in the temperature range of 7 to 35C. However, the authors of this study are not aware of any study reporting the effect of temperature on water vapor barrier properties of cellulose-based films.

The objectives of this study were to (1) determine the water vapor sorption isotherms of cellulose-based films, and (2) evaluate the effect of plasticizer concentration and temperature on water vapor permeability coefficients in those films.

THEORETICAL CONSIDERATION

Fick's first law can be applied to the water vapor permeation process when it is assumed that the diffusion is in a steady state and there is a linear concentration gradient through the film. Then, the flux (J) is given by

$$J = D \cdot \Delta C/X = Q/(A \cdot t) \quad (1)$$

where, J is flux ($\text{g}/\text{m}^2 \cdot \text{s}$), D is diffusion coefficient (m^2/s), ΔC is concentration difference across the film (g/m^3), X is thickness of the film (m), Q is amount of water diffusing through the film (g), A is area of the film (m^2) and t is time (s) (Crank 1975).

The driving force needs to be expressed in terms of partial pressure difference, rather than the concentration difference because it is easier to measure pressure difference and then correlate to concentration difference. Therefore, Henry's law, where the vapor pressure of the solute varies with concentration in a linear manner, could be applied. A rearrangement of terms yields the following equation in terms of permeability coefficient and partial pressure difference (Crank 1975).

$$D \cdot S \cdot (p_2 - p_1)/X = P \cdot (p_2 - p_1)/X = Q/(A \cdot t) \quad (2)$$

where, S is the Henry's law solubility coefficient ($\text{g}/\text{m}^3 \text{ Pa}$), $p_2 - p_1$ is the partial pressure difference across the film (Pa) and P is the permeability coefficient ($\text{g}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$). It may be noted that Henry's law is not applicable in those packaging materials which exhibit nonlinear moisture sorption isotherm (Karel *et al.* 1959; DeLeiris 1986); however, it is often applied to such materials (e.g., edible films). In situations when Henry's law is applied for determining permeability coefficients, the resulting values are effective or average permeability coefficients and valid only for the conditions of the experiment.

MATERIALS AND METHODS

Materials

The materials used to prepare the cellulose films were: methyl cellulose (25 cp), hydroxypropyl cellulose (370,000 mw), polyethylene glycol (400 mw) (Aldrich Chemical Company, Inc., Milwaukee, WI); and ethanol, 95% (Fisher Scientific, Pittsburgh, PA). All the salts for saturated salt solutions to obtain moisture isotherms are listed in Table 1 and were acquired from Fisher Scientific (Pittsburgh, PA).

TABLE 1.
RELATIVE HUMIDITY (%) OF VARIOUS SALTS SOLUTIONS¹

Salts	Relative humidity ¹	
	5C	21C
Potassium acetate	25	23
Magnesium chloride	33	33
Magnesium nitrate	54	52
Cupric chloride	65	68
Sodium chloride	76	75
Ammonium sulfate	81	79
Lithium sulfate	84	85
Potassium sulfate	98	97

¹Rockland (1960).

Preparation of the Cellulose-Based Films

Methyl cellulose (MC) and hydroxypropyl cellulose (HPC) based film solutions were prepared by dissolving 9 g of each cellulose in a solvent mixture

containing 200 ml of ethanol and 100ml of distilled water (Kamper and Fennema 1984; Park and Chinnan 1995). Three solutions were prepared for each cellulose type containing polyethylene glycol (PEG) as plasticizer at levels of 0, 0.11, 0.22 and 0.33 ml PEG/g cellulose. Brinkmann homogenizer (Westbury, NY) was used to mix the film solution. For degassing, solution was heated until it started boiling. The degassed solution was poured onto a glass plate and dried. The film thus formed was carefully detached from the glass plate and used for determining moisture sorption isotherm and water vapor permeability coefficient properties.

Thickness Measurement

A micrometer was used to measure the film thickness to an accuracy of 0.0025 mm. Ten measurements were made at random positions on each film.

Moisture Sorption Isotherms

Dried HPC film and MC film were cut into small pieces (less than 0.015 g), weighed, and then placed over saturated salt solutions in desiccators at constant temperature (5C and 21C) to provide water activities in the range 0.23-0.97 (Table 1). Final moisture contents were determined after moisture had equilibrated which was verified by periodic weight measurements. Samples were dried overnight at 100C under vacuum to determine moisture content as described in AOAC (1980) method 23.002 for gelatin. Tests were conducted in triplicate.

Water Vapor Permeability Coefficient (WVP)

Three plastic cups of high density polyethylene (3 mm thick) filled with desiccant and covered with HPC film and MC film to be tested were placed individually in two desiccators, one was 33%RH ($MgCl_2$) and the other was 75%RH (NaCl), at 5, 13, 21C, respectively. The change in weight of the cups against time was recorded every two hours. The permeability coefficient was calculated from Eq. 2; where water vapor pressure (p_1) on the desiccant side of the film was assumed to be zero and the water vapor pressure (p_2) in the desiccator due to $MgCl_2$ or NaCl salt solution was calculated from the vapor pressure of pure water at respective selective humidities. It is to be noted that no forced air movement was provided and we did not specifically follow the ASTM E96-80 method for determination of WVP. However, we did follow the procedures published by other researchers and the authors of this study (Kamper and Fennema 1984; Aydt *et al.* 1991; Park and Chinnan 1995).

RESULTS

Moisture Sorption Isotherms

Sorption isotherms of the MC film and HPC film at 5 and 21C are shown in Fig. 1 and 2, where moisture content was plotted against water activity. At higher temperatures, less moisture was absorbed at a given water activity. This trend is well documented in literature for most food materials. The sorption isotherm curves of MC film and HPC film (Fig. 1 and 2) can be viewed as two distinct segments indicating that the equilibrium moisture increases slowly with an increase in water activity up to 0.75, beyond which there was a sharp increase in equilibrium moisture of the films tested. Linear regression analysis of moisture content and water activity (a_w) data for a_w from 0 to 0.75 yielded R^2 values greater than 0.98 (Table 2). Including a_w values beyond 0.75 drastically reduced R^2 values.

The shape of sorption isotherm of the MC film was similar to that of methyl cellulose-palmitic acid film, reported by Rico-Pena and Torres (1990b), which had weight ratio of 3:1 at 24C. The equilibrium moisture of MC film was slightly higher than that of HPC film at a given water activity. Moisture isotherms were not determined at 13C, although the water vapor permeability coefficients were measured at 13C in addition to 5 and 21C. Observing the similarity in shapes of 5 and 21C isotherms, it was not believed necessary to obtain 13C isotherm for our study.

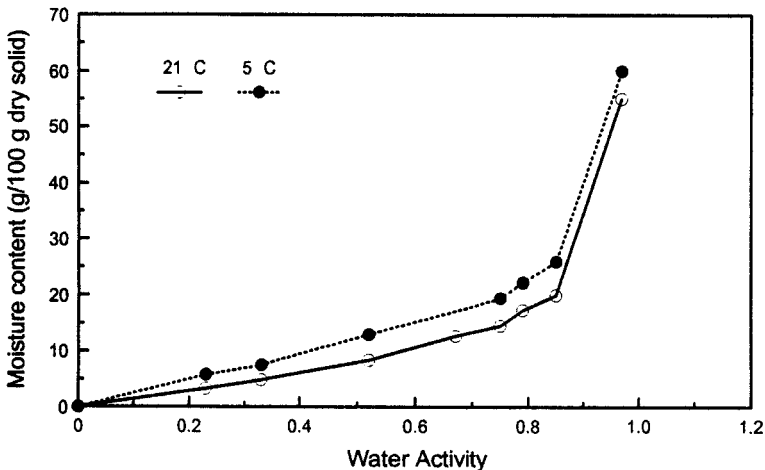


FIG. 1. MOISTURE SORPTION ISOTHERMS OF METHYL CELLULOSE FILM WITHOUT PLASTICIZER AT 5 AND 21C.

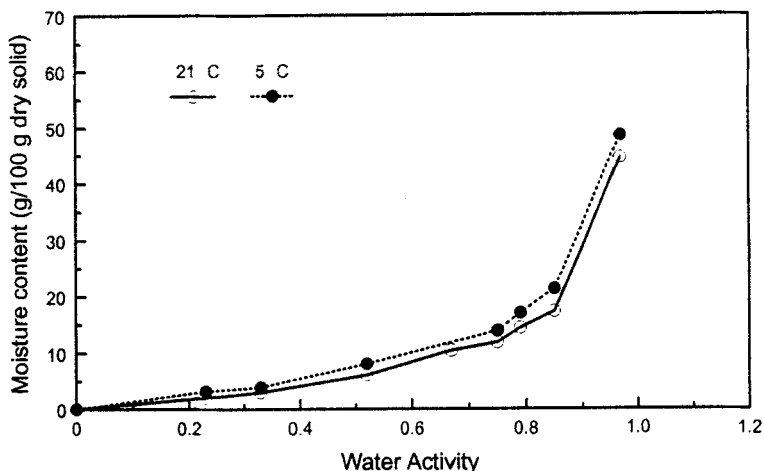


FIG. 2. MOISTURE SORPTION ISOTHERMS OF HYDROXYPROPYL CELLULOSE FILM WITHOUT PLASTICIZER AT 5 AND 21°C

TABLE 2.
REGRESSION ANALYSIS OF MOISTURE ISOTHERM DATA OF METHYL CELLULOSE (MC) AND HYDROXYPROPYL CELLULOSE (HPC) FILMS

Film	Temperature (C)	Relative humidity-Data Range (%)	Regression analysis statistics	
			Slope	R ²
MC	5	0-33	23.1	0.995
		0-75	24.6	0.995
	21	0-33	14.4	0.999
		0-75	19.6	0.980
HPC	5	0-33	12.4	0.988
		0-75	15.3	0.973
	21	0-33	8.95	0.999
		0-75	16.5	0.949

Water Vapor Permeability Coefficient (WVP)

WVPs of cellulose films, MC and HPC, were considerably greater than those of commonly used plastic films such as polyethylene (PE) and polyvinyl chloride (PVC) in Table 3. Without any plasticizer, WVP of HPC film was expected higher than that of MC film because HPC has a hydroxyl group in hydroxypropyl functional groups. But WVP of HPC film was lower than that of methyl cellulose. Reduction of WVP of HPC film could be attributed to formation of hydrogen bond between HPC polymers (Banker *et al.* 1966).

TABLE 3.
WATER VAPOR PERMEABILITY COEFFICIENTS OF SELECTED FILMS

Film	Thickness (mm)	Relative humidity difference(%)	Permeability ^a
Cellulose film in this study ^b			
HPC	0.08	75	68.5 ± 2.7
		33	51.6 ± 4.4
MC	0.11	75	154.4 ± 4.1
		33	113.5 ± 5.7
Cellulose films from the literature			
C 18-C 16 HPMC ^c	0.04	97	4-22
C18-C16 MC/HPMC ^c	0.02	97	3-16
HPMC ^d	0.01-0.04	85	15-200
Other films from the literature			
PE ^c	-	100-90	0-7
PVC ^c	-	100-90	0.6

^a Unit of permeability is in $\text{pg}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ at 21°C; p is an abbreviation of pico (10^{-12}).

^b Cellulose films without plasticizer.

^c Kester and Fennema (1989a); C18 (stearic acid), C16 (palmitic acid), MC (methyl cellulose), HPMC (hydroxypropylmethyl cellulose), PE (Polyethylene, low density) and PVC (Polyvinyl chloride).

^d Hagenmaier and Shaw (1990).

It may be noted that Eq. 2 can be used to calculate the WVP in linear portion of moisture sorption isotherm for hydrophilic films because of Henry's law (Karel *et al.* 1959; DeLeiris 1986). WVPs of MC and HPC films in this study were measured at a_w differences by 0-0.33 and 0-0.75 which are linear portions in moisture sorption isotherms curves of the films. Therefore, the permeability of the films are theoretically same if these are measured inside of linear portion of moisture sorption isotherms curves. However, slopes of moisture content and a_w data for a_w from 0 to 0.75 in moisture sorption isotherms curves were higher than those of a_w from 0 to 0.33, which can cause

higher WVPs in the films. Kester and Fennema (1989a) also reported that the WVPs of cellulose films measuring at 0-97% relative humidity (RH) gradient were lower than those of films measuring at 67-95% RH gradient in cellulose films. Higher slopes of moisture content and a_w data for a_w from 67-95 than those of the slopes for a_w from 0-95 in moisture sorption isotherms of methyl cellulose films (Rico-Pena and Torres 1990b) would contribute to higher WVPs of the cellulose films measuring at 67-95% RH gradient in Kester and Fennema work (1989a). Labuza and Contreras-Medellin (1981) also reported that many hydrophilic films show a change in WVP depending on vapor pressure conditions. The HPC film was more flexible than MC film, which is probably attributed to HPC polymer having longer side chains than MC. WVPs of cellulose films of Kester and Fennema (1989a) contained stearic and palmitic acids and were lower than those of cellulose films prepared in our laboratory, which could be attributed to fatty acids in the former films (Table 3). WVP of plastic films were 2 orders of magnitude lower than those of cellulose films.

Plasticizer Effect. The effect of plasticizer concentration on WVP of cellulose films is shown in Fig. 3. WVP of HPC film increased as the concentration of polyethylene glycol (PEG) increased from 0 to 0.33 ml PEG/g cellulose. However, the WVP of MC film showed a different trend compared to HPC film. The WVP of MC film containing 0.22 ml PEG/g cellulose was lower than those of MC films which contained 0, 0.11 and 0.33 ml PEG/g cellulose. Banker *et al.* (1966) observed that the plasticizer could enhance or retard moisture permeation of cellulose films, depending upon its concentration. Park and Chinnan (1995) reported that the WVP of HPC film and MC film increased as the concentration of PEG increased from 0.11 to 0.33 ml PEG/g cellulose. In wheat gluten film, WVP increased linearly as concentration of the plasticizer, glycerin, increased in the range of 16 to 33 g glycerin/100 g protein (Gontard *et al.* 1993). The surfaces of cellulose films containing higher level of plasticizer had smoother appearance than the films with low level of plasticizer.

Temperature Dependence. Temperature dependence of WVP of HPC and MC films is illustrated in Fig. 4. An Arrhenius-type relationship given below was fitted to data.

$$P = A \cdot \exp(-E_a/R \cdot T) \quad (3)$$

where P is permeability coefficient ($\text{g} \cdot \text{m} / \text{m}^2 \cdot \text{s} \cdot \text{Pa}$), A is constant, E_a is activation energy (J / mol), R is gas constant ($8.314 \text{ J} / \text{mol} \cdot \text{K}$) and T is absolute temperature (K). After logarithmic transformation, Eq. 3 is written as

$$\ln(P) = \ln(A) - (E_a/R) \cdot (1/T) \quad (4)$$

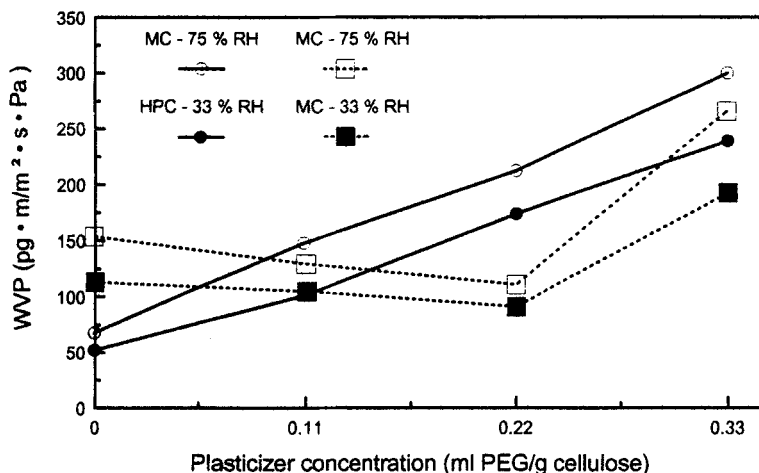


FIG. 3. PLASTICIZER EFFECT ON WATER VAPOR PERMEABILITY COEFFICIENT (WVP) OF HYDROXYPROPYL AND METHYL CELLULOSE FILMS
 HPC-75% RH (HPC film, WVP measured with 75% RH difference)
 HPC-33% RH (HPC film, WVP measured with 33% RH difference)
 MC-75% RH (MC film, WVP measured with 75% RH difference)
 MC-33% RH (MC film, WVP measured with 33% RH difference)
 PEG (polyethylene glycol), HPC (hydroxypropyl cellulose)
 and MC (methyl cellulose).

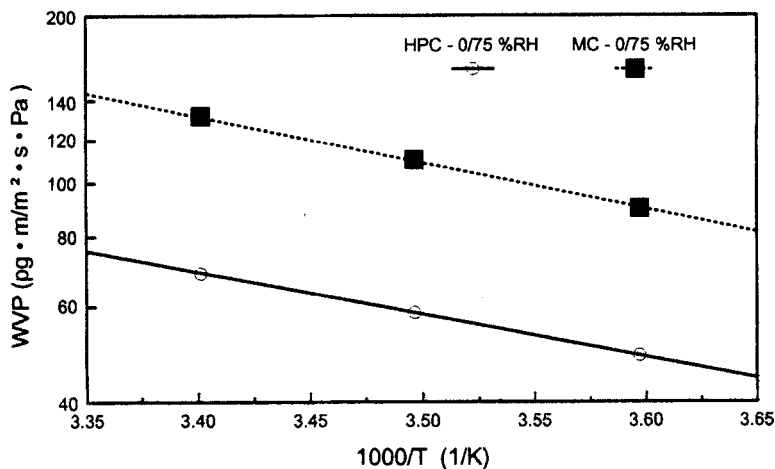


FIG. 4. TEMPERATURE DEPENDENCE OF THE WATER VAPOR PERMEABILITY COEFFICIENT (WVP) OF HYDROXYPROPYL AND METHYL CELLULOSE FILMS WITHOUT PLASTICIZER
 HPC-75% RH (HPC film, WVP measured with 75% difference)
 HPC (hydroxypropyl cellulose).

Slope of the fitted regression line allowed calculation of an apparent activation energy E_a . The same procedure described above was applied to calculate activation energy of MC film. The activation energies of HPC and MC films which had no plasticizer were 14.56 and 16.43 kJ/mol, respectively. These are relatively low activation energies, when compared with various packaging films such as polyvinylidene chloride, polypropylene, polyvinyl chloride and polyethylene (Labuza and Contreras-Medellin 1981; Myers *et al.* 1961). Kester and Fennema (1989a) observed a large value for activation energy (59.4 kJ/mol) in a waxed laminated cellulose film, this is probably due to heterogeneity of the laminated film. Gennadios *et al.* (1993) reported that activation energies of protein films such as corn-zein, wheat gluten and wheat and soy protein isolate films ranged from 46 to 50 kJ/mol (11 to 12 Kcal/mol), which is several fold greater than the cellulose films investigated here.

SUMMARY AND CONCLUSIONS

The sorption isotherm curves of MC film and HPC film indicated that the equilibrium moisture content increases slowly with an increase in water activity (a_w) up to 0.75, but increases sharply after a_w of 0.75. The equilibrium moisture of MC film was slightly higher than that of HPC film at a given water activity. The water vapor permeability coefficient of cellulose films were 2 orders of magnitude greater than those of typical plastic films, polyethylene and polyvinyl chloride. The water vapor permeability coefficient of HPC film increased as the concentration of polyethylene glycol (PEG) increased; however, the water vapor permeability coefficient of MC film which contained 0.22 ml PEG/g cellulose was lower than those of MC films which contained 0, 0.11 and 0.33 ml PEG/g cellulose. Temperature dependence of the water vapor permeability coefficient of HPC film and MC film followed an Arrhenius type relationship. The activation energies of HPC film and MC film containing no plasticizer were 14.56 and 16.43 kJ/mol, respectively; these are relatively low active energies compared with typical food packaging materials such as polyvinylidene chloride, polypropylene, polyvinyl chloride and polyethylene. Additional observations about these cellulose based films indicate that they have appearance and surface characteristics similar to those of plastic films. They are also transparent, without any odor and taste.

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