

Gas Permeation Related to the Moisture Sorption in Films of Glassy Hydrophilic Polymers

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ABSTRACT: The purpose of this article is to elucidate the effect of integral sorption of moisture on gas permeation in glassy hydrophilic polymers. The oxygen and the simultaneous moisture sorption into various hydroxypropyl methylcellulose (HPMC) films were measured under a wide range of relative humidities using sorption analyzer equipment. Correspondingly, the oxygen permeability at different ambient conditions was measured using an oxygen detector. The solubility of oxygen in the HPMC film was found to be affected by the amount of water and therefore by the water state. At low moisture content, the water molecules are present as bound water, which promotes the sorption of oxygen in the HPMC films. At moisture content higher than 5%, water

clusters are rapidly formed, which increase the affinity of HPMC polymer towards water rather than towards oxygen molecules, resulting in a decrease of oxygen solubility in the polymer. This was found to be the governing factor for the reduction in the oxygen permeability in glassy HPMC films at high water activity. This proposes a specific interaction between moisture sorption and oxygen transport in coating films like HPMC, which is of important aspect in the coating design and formulation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3310–3317, 2010

Key words: adsorption; functionalization of polymers; gas permeation; hydrophilic polymers; polysaccharides

INTRODUCTION

Glassy hydrophilic polymers are often the materials of choice for functional encapsulation when protection of a core material is necessary. In terms of their barrier properties, glassy polymers are superior over rubbery polymers.¹ The film forming properties and the environmental and safety aspects of hydrophilic polymers are more favorable than the more hydrophobic counterparts that often form poor films and require the use of organic solvents during processing.^{2,3}

During processing and storage, moisture is often present next to other gases in the ambient air. For hydrophilic polymers, there is significant moisture sorption and simultaneous diffusion of moisture in a wide range of relative humidity, which will alter the polymer barrier properties against other compounds, such as oxygen.⁴ The fact that polymers in glassy

state are in a nonequilibrium situation leads to the complexity in the transport and sorption of gases in glassy polymers, where more than one mode of permeant transport may be present.^{1,5,6} From the perspective of product design, this makes glassy hydrophilic polymers challenging systems.

Hydroxypropyl methylcellulose (HPMC) polymers are typical examples of glassy hydrophilic polymers. They are edible, resistant to oils and fats, flexible, transparent, odorless, tasteless, water-soluble, moderate barriers to oxygen, and superior film forming materials with good strength.² For these reasons, they have widely been utilized as coating materials in various pharmaceutical as well as food applications.^{2,7} In these applications, the prevention of oxidation as well as moisture loss from the product is required. For pharmaceutical and food applications, the edibility of coating material is an important aspect. It is realized that edible coatings are poorer barriers to moisture and oxygen than synthetic polymers, e.g. PVOH, EVOH, PVDC, etc.^{8,9} To meet the requirement as barrier materials, many of edible films are used in combination with other polymers that compensate the limitation of one and another.

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HPMC polymers that form strong and flexible films provide excellent structural matrix to e.g. wax or fatty acids that are good water vapor barriers yet poor film forming materials. They are also applied as crispness and low-fat retainer coating for deep-fried food products.^{10,11} Due to their hydrophilic nature, HPMC polymers retain moisture and avoid the uptake of other components such as oil. With their emulsifying ability, HPMC polymers can also be used to encapsulate fish oil.¹² Besides HPMC, edible films, such as zein,^{13,14} starch,^{15–17} whey protein,^{18,19} and chitosan^{20,21} are also glassy polymer systems, which are also used as oxygen barrier materials. Compared to these polymers, HPMC polymers have higher glass transition temperature.^{22–24} This implies that HPMC polymers can contain more plasticizer components without immediately altered to rubbery systems. The wide range of utilization and properties makes HPMC polymers suitable model materials for our study.

Regarding to its high interaction with other components in its surroundings, the examination of gas transport through a glassy hydrophilic coating material should not be separated from the accompanying transport and sorption of other permeants. To our knowledge, the determination of permeability has mostly been performed under pure gas environment. Moreover, the data presented are also not always in agreement with each other without any further clarity on the underlying mechanism that explains the differences.^{25–28}

Besides with water vapor, HPMC polymers also interact with many different substances that can influence their barrier properties, e.g. surfactants such as sorbitan monostearate and sucrose palmitate²⁹ and other components that act as plasticizer to HPMC polymers e.g. PEG and triacetin.³⁰ In high ionic strength environment, the barrier properties of HPMC polymer could also vary due to disintegration of the gel layer.^{31,32} This study focused on the effect of interaction between HPMC and moisture on the permeation of oxygen, which is a common phenomenon during the application of HPMC polymer. The determination of the oxygen permeability was performed under the atmospheric conditions with various relative humidities according to the method previously used by other workers.^{33–35} To provide a range of relative humidities, various salt solutions were used.^{36,37}

MATERIALS AND METHODS

Materials

HPMC (Methocel E5, LV USP/EP premium grade) from Dow, supplied by Colorcon UK, was used as a model coating material.

Experimental methods

Film production

In this study, the free films were made by a casting method. HPMC was dissolved in cold water and was stirred for about 1 h to assure a homogeneous solution. Three different concentrations (2, 5, and 10% w/w HPMC in water) and temperatures (25, 40, and 60°C) were used to investigate the influence of the initial coating solution concentration and temperature on the film properties. The HPMC solution was then poured into a mold made from High Density Polyethylene (HDPE), from which the formed film could be easily removed after drying. The drying times were 48, 16, and 8 h for films dried at 25, 40, and 60°C, respectively. The films obtained had an average thickness of around 80 μm .

Film characterizations

Film thickness. The film thickness (Δx) was measured with Mitutoyo micrometer with an accuracy of 1 μm . For each film, the thickness was measured five times at different locations. The standard deviation of the thickness measurement for each film was less than 10%.

Determination of oxygen permeability (OP). The oxygen permeability (OP) of the films was measured using the OxySense™ 210T. The OP through the HPMC films was determined at various relative humidities (RH's), using an experimental setup, which is schematically depicted in Figure 1. Seven saturated salt solutions (LiCl, MgBr₂, NaI, Mg(NO₃)₂, NaBr, KI, and KBr) were used to create various RH's ranging from 12 to 80% with interval steps around 10%. The OxyDot™ was glued inside a vial. This dot responds by emitting red light back to the detector, which intensity and fluorescent lifetime are reduced with the increasing concentration of oxygen in the

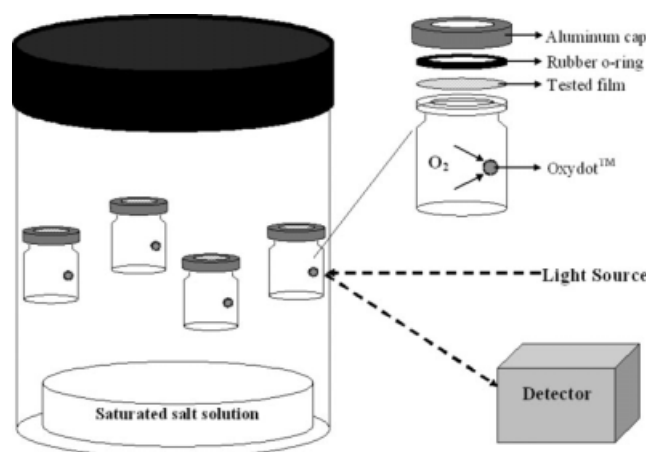


Figure 1 Schematic representation of the experimental set up for the oxygen permeability measurement.

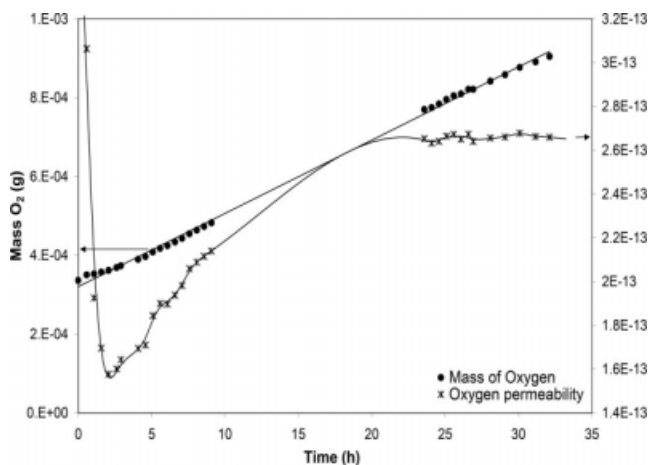


Figure 2 A typical measurement curve and the calculated oxygen permeability of HPMC E5 films (taken from the permeation of oxygen at 30% RH through the HPMC film made from 5% concentration and dried at 25°C).

surroundings of the dot. Initially, the vials were purged with nitrogen flow to decrease as much as possible the oxygen content inside the vials. While purging with nitrogen, the vials were carefully sealed with the test films, which were pre-equilibrated at the relevant RH. The test films were clamped to the vial by an aluminum cap, as depicted in Figure 1. Subsequently, the vials were placed inside a jar, which contained a saturated salt solution, giving a certain RH at room temperature. For each relative humidity, a new film sample was used from each film formulation. The OP was measured in twofold for each HPMC film.

After the prepared vials were placed in the jar, the jar was purged with nitrogen for 24 h to allow the film to reach the equilibrium without any presence of oxygen, and afterwards with air for 5 min to supply back the oxygen inside the jar. Thereafter, the measurement of the oxygen permeation started. Subsequently, the oxygen concentration (%) inside the vial was measured, every 30 min during the first day and each hour on the second day.

The amount of oxygen transfer from the jar to the vial is considerably low during the respective measurement time. For this reason, the oxygen content in the jar was assumed to be constant.

A typical measurement curve of the oxygen permeability (OP) of the HPMC films is shown in Figure 2. The OP values were calculated according to eq. (1), where Δm , Δt , Δx , A , ΔP are the increase of the oxygen mass inside the vial (Δm), time interval, film thickness, film area, and the difference in the partial vapor pressure of oxygen, respectively. The oxygen analyzer measured the oxygen concentration ($[O_2]_t$) in percentage, instead of the oxygen mass. Therefore, the Δm was calculated according to eq. (2), where V_v and ρ_{O_2} are the vial volume and the

oxygen density, respectively. The difference in the partial pressure (ΔP) was computed using eq. (3), where $[O_2]_t$ is the oxygen concentration inside the vial at time t , while $[O_2]_i$ is the initial vial oxygen content. The total pressure (P_{tot}) was calculated by taking into account the influence of the temperature (T) on the saturation pressure of water vapor ($P_{H_2O}^{sat}$) and the relative humidity (RH) as shown in eq. (4). The $P_{H_2O}^{sat}$ was calculated using an established correlation.³⁸ The values of different properties used for the calculation of oxygen permeability are listed in Table I.

$$OP = \frac{\Delta m \cdot \Delta x}{\Delta t \cdot A \cdot \Delta P_{O_2}} \quad (1)$$

$$\Delta m = [O_2]_t \cdot V_v \cdot \rho_{O_2} \quad (2)$$

$$\Delta P_{O_2} = ([O_2]_t - [O_2]_i) \cdot P_{tot} \quad (3)$$

$$P_{tot} = P_{atm} - (P_{H_2O}^{sat} \cdot RH) \quad (4)$$

In the beginning of the measurement, the oxygen permeability varied in time, due to the time needed for the film and the system to reach steady state. After the steady state was reached (which was on the second day of measurement), the oxygen permeability value became constant, as illustrated in Figure 2. Therefore the oxygen permeability was taken as the average of the oxygen permeability measured under the steady state condition.

Determination of sorption of moisture and oxygen and solubility of Oxygen. The equilibrium moisture contents and the solubilities of oxygen in different HPMC free films were determined from the analysis performed in a sorption analyzer SPS11-100n from Projekt Messtechnik (Germany) at 25°C. This apparatus is able to handle two types of carrier gases through the sorption chamber: nitrogen and air. The saturated water vapor and either nitrogen or air flow are mixed. Initially, the sorption isotherm was determined using the nitrogen and water vapor mixture and thereafter using air and water vapor mixture as ambient. Air was considered to contain 79% of nitrogen and 21% of oxygen. In these two different ambient gas mixtures, the amount of water vapor and nitrogen sorbed into the film is assumed

TABLE I
Data of Properties Used to Calculate the Oxygen Permeability

Variables	Value
Volume of the vial (V_v)	$17.424 \times 10^{-3} \text{ cm}^3$
Density of oxygen (ρ_{O_2}) ²⁴	0.001331 g / m^3
Atmospheric pressure (P_{atm})	101325 Pa
Saturation pressure of water vapor ($P_{H_2O}^{sat}$) ¹¹	$P_{H_2O}^{sat} = 190.2 \cdot T(^{\circ}\text{C}) - 1536.7 \text{ (Pa)}$
Film Area (A)	$1.23 \times 10^{-4} \text{ m}^2$
Room temperature (T)	25°C

to be constant. As a result, the difference between the mass gain fraction (ω) during sorption under nitrogen–water vapor and air–water vapor ambient was assumed to be due to the oxygen sorption into the film, as illustrated in eq. (5).

$$\begin{aligned}\omega_{O_2} &= \omega_{\text{air-H}_2\text{O}} - \omega_{\text{N}_2\text{-H}_2\text{O}} \\ &= (\omega_{\text{N}_2} + \omega_{\text{O}_2} + \omega_{\text{H}_2\text{O}}) - (\omega_{\text{N}_2} + \omega_{\text{H}_2\text{O}})\end{aligned}\quad (5)$$

For each kind of ambient mixture, i.e. humid air or humid nitrogen, the RH inside the sorption chamber was set from 0–80% with 10% steps. The conditions at each step were held constant until equilibrium was reached. The mass of samples used was about 4–5 g for each film. The equilibrium moisture contents in the films were taken as the final (equilibrium) mass gain during sorption under nitrogen and water vapor mixture.

Furthermore, the solubility of oxygen (S_{O_2}) can be calculated according to eq. (6), defined as the concentration of the oxygen within the film equilibrated at certain partial pressure of oxygen (ΔP_{O_2}) and temperature. ρ_{true} is the true density of the HPMC E5, which was used for this calculation to convert the mass–mass ratio of O_2 to the mass–volume ratio to polymer film.

$$S_{O_2} = \frac{\omega_{O_2} \cdot \rho_{\text{true}}}{\Delta P_{O_2}}\quad (6)$$

RESULTS AND DISCUSSION

Oxygen sorption in HPMC films containing moisture

The relationship between the amount of oxygen sorbed in the HPMC films and the moisture content is presented in Figure 3. The present HPMC films are heterogeneous matrices, comprising HPMC polymer, sorbed moisture, and oxygen. Furthermore, the films can contain different amount of voids and defects, such as cracks resulted from e.g. drying of films with different solid concentration and drying temperature. Differences in the film structure can also lead to the variation of the oxygen sorption in the films, as shown in Figure 3. Higher oxygen sorption would most likely occur in films containing more voids.

At the first place, the effect of HPMC concentration used in the coating formulation and the drying temperature on the oxygen sorption seemed to be inconsistent. This was mainly due the opposite effect of these factors on the film formation and therefore on the obtained film structure. With the increase of the solid concentration, the polymer chains were closer with each other and at the same time, the dry-

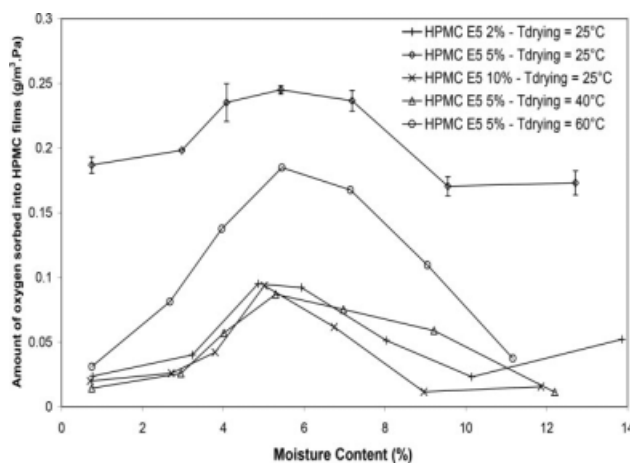


Figure 3 Relationship between the solubility of oxygen and the moisture content in the HPMC E5 films.

ing process was slower due to the higher viscosity of the solution. For films made of 10% of solid concentration, the first aspect was most likely to be more dominant, which led to a denser film as the polymer chains were at the closest proximity with each other. For films made of 2% of solid concentration, the faster drying would lead to more complete drying of the films, leaving less voids in the films. For this reason, comparable oxygen sorption was found in films made of 2 and 10% of solid concentration. A deep point was found for films made of 5% of solid concentration, where the two aspects competed with each other and resulted in poorer film structure (more voids due to slower drying and that the polymer chains were not sufficiently close with each other). By increasing the drying temperature, a denser film structure was expected yet the formation cracks would also become significant, due to the increase of internal stress in the film (big gradient of relative humidity in and around the film).³⁹ It appeared that such crack formation was more significant in films dried at 60°C and caused higher oxygen sorption than films dried at 40°C.

Considering the components in the HPMC films, the total amount of oxygen sorbed in the films can be counted as the total amount of oxygen sorbed in HPMC polymer itself and dissolved in moisture. The amount of oxygen dissolved in water (at 25°C) is much lower (4.036×10^{-4} g/m³Pa, calculated from the empirical equation given in Standard Methods for the Examination of Water and Wastewater⁴⁰) than the amount of oxygen sorbed in the HPMC polymer ($\sim 1.4\text{--}24.5 \times 10^{-2}$ g/m³Pa, this study). For this reason, the amount of oxygen dissolved in the moist HPMC films can be considered as the oxygen dissolved in the polymer only. Nevertheless, the influence of moisture content on the amount of oxygen sorbed in the HPMC films is apparent, as it can be seen in Figure 3. This implies that water

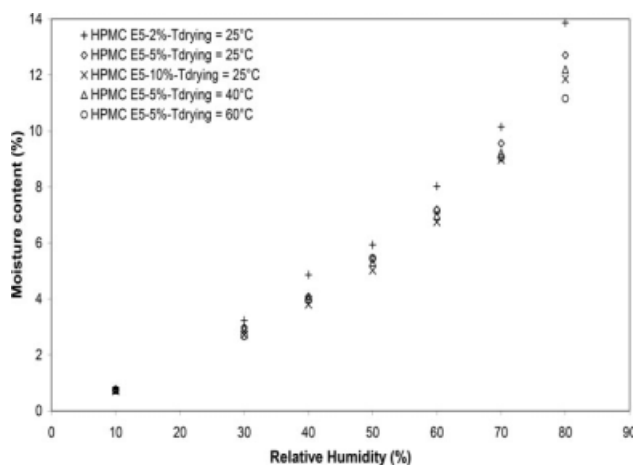


Figure 4 Moisture sorption isotherms of HPMC films.

influences the oxygen sorption in the HPMC film in certain manner, logically via altering the properties of the polymer.

As shown in Figure 3, at low moisture content, the amount of oxygen sorbed increases with the moisture content in the HPMC films, while at moisture levels above 5%, the amount of oxygen sorbed decreases with increasing moisture content in the film. This dual effect of moisture content on the oxygen sorption can be related to the state of water in the films, which also varies through different water activities.

The water molecules sorbed in polymer matrix are present as "bound" and "free" water.⁴¹ In this study, the "bound" water is defined as the monolayer water on the adsorption sites of the polymer while the "free water" is defined as those water molecules that do not come into direct contact with the polymer matrix. The monolayer water can be estimated by fitting the sorption-isotherm data with the Guggenheim-Anderson-de Boer (GAB) equation, given in eq. (7).^{42–44} This model describes multilayer adsorption, which is suitable for the moisture sorption in the HPMC films. In Figure 4, the moisture sorption isotherms of the HPMC films tested in this study are given. In this equation, w and a_w are the amount of the sorbed molecules and the water activity, respectively, whereas c_g , w_m , and k are the GAB parameters, which represent the energy of adsorption, the monolayer capacity and the state of the sorbed molecules above the first layer relative to bulk water, respectively. The values of these parameters derived from the fitting process are given in Table II. The maximum water bound to the polymer sites could then be estimated from the monolayer capacity (w_m), which is approached when the moisture content in the film is around 6%.

$$w = \frac{w_m c_g k a_w}{(1 - k a_w)(1 - k a_w + c_g k a_w)} \quad (7)$$

TABLE II
GAB Fitting Parameters Taken from Water Sorption Isotherm of HPMC E5 Films Made at Different Concentrations and Drying Temperatures

[HPMC] (%w/w)	T_{drying} (°C)	C_g	k	w_m	R^2
2%	25	2.203	0.8156	0.05955	0.9981
5%	25	1.726	0.7928	0.06211	0.9969
10%	25	1.747	0.7935	0.05768	0.9996
5%	40	1.342	0.7076	0.08138	0.9999
5%	60	1.791	0.8647	0.05025	0.9960

Due to the presence of previously sorbed water in the polymer, the extent of moisture sorption is dependent on the affinity of water either towards polymer or towards water itself.⁴⁵ When the affinity of water towards polymer is lower relative to water cohesion, clustering of water molecules will occur. This clustering phenomenon has been reported earlier in literature in particular for very hydrophilic or very hydrophobic glassy polymers, where the clustering of water is likely to occur at high water activity.⁴⁶

Clustering criteria of water have been proposed by Zimm and Lundberg⁴⁷ using a parameter $C_1 G_{11} + 1$, which represents the average number of water molecules in a cluster and it correlates to the relative humidity (RH) and the volumetric fraction of water (V) in the polymer [eq. (8)]. During calculation, the density of HPMC polymer was taken as 1.328 g/cm³.³⁹ When $C_1 G_{11} + 1$ is larger than 1, clustering of water molecules occurs.⁴⁸

$$C_1 G_{11} + 1 = (1 - V) \left(\frac{\partial \ln V}{\partial \ln a_w} \right) \quad (8)$$

Using the water sorption isotherm data of HPMC films, this parameter was calculated. The results are presented in Figure 5. It is found that clustering of

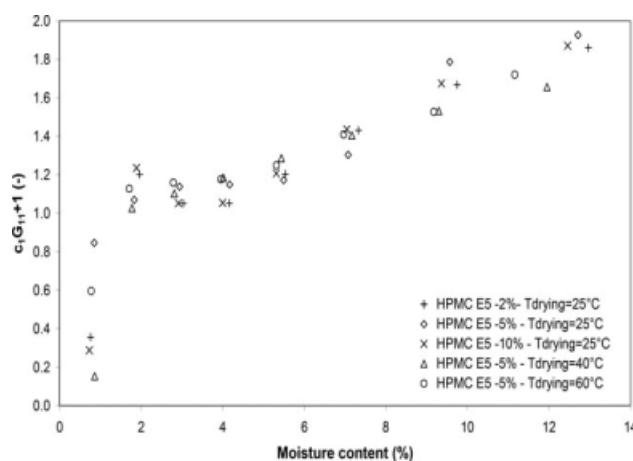


Figure 5 Average cluster size of water at different moisture contents.

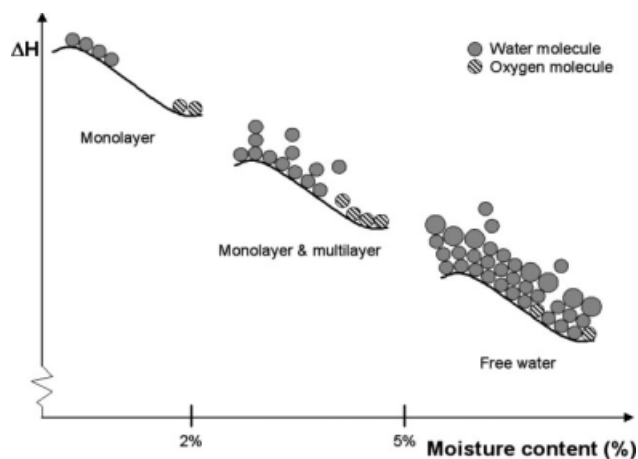


Figure 6 Illustration of the sorption mode of moisture to HPMC films at different moisture content and its effect on the sorption of oxygen. ΔH represents the heat of water sorption.

water molecules starts to occur at around 2% of moisture content. The monolayer capacity of HPMC films is reached at 6% of moisture content. This suggests that below this level, the water molecules can either be sorbed to the first layer or to the above layers. Close to the polymer surface, the water tends to be deconstructed.⁴⁹ Therefore, as long as the entire first layer has not been filled, water clustering (multilayer sorption) is counterbalanced with the monolayer sorption. This explains the rather constant (average) water cluster size ($C_{11}G_{11} + 1$) between 2 and 5% of moisture content. Above this level, the sorption of water will only take place on the presorbed water and bridging of small water clusters occurs. This is confirmed in the significant increase in the water cluster size above 5% of moisture content (Fig. 5).

Figure 6 summarizes the mechanisms of moisture sorption in the HPMC films at different water activities and illustrates the possible effect on the oxygen sorption. This mechanism is proposed based on the understanding obtained from the evaluation performed on both the water state and the GAB moisture sorption. The specific mechanism of moisture sorption to HPMC films also explains the shifting effect of moisture content on the oxygen sorption in the HPMC films shown in Figure 3.

The high preferential sorption of water molecules above the precursor water molecules in the HPMC films provides the sorption mechanism for oxygen molecules through the polymer matrix region. Via changing the availability of these sorption sites, the simultaneous moisture sorption alters the affinity of the HPMC films towards oxygen through different relative humidities. At very low moisture content (<2%), the effect of moisture sorption is insignificant. Therefore, oxygen molecules are sorbed on the

first layer of the polymer interaction sites, by which mode water molecules are also sorbed. At moisture content between 2–5%, the water molecules bound tightly to the polymer surface, causing plasticization, i.e. relaxation of the polymer chains. This helps the mobility of oxygen molecules to allocate to the sorption sites, shown in the increase of oxygen solubility in the HPMC films at moisture content lower than 5%. At high moisture content (above 5%), big water clusters (free water) are formed. Unlike the “bound” water, which is integrated in the HPMC matrix, big water clusters can be considered as discrete elements in the HPMC polymer providing a different mechanism for the solubilization of oxygen. The solubility of oxygen in water is significantly lower than in the HPMC polymer, therefore the increasing amount of oxygen dissolving in the water clusters is negligible. Big water clusters are formed away from the polymer surface. This means that oxygen molecules have to diffuse through the layers of water clusters first, before they can come into contact with the polymer sorption sites. Water is a poor solvent for oxygen. Consequently the amount of oxygen sorbed to the polymer (oxygen solubility) decreases with the increasing fraction of water clusters at moisture content higher than 5% shown in Figure 3.

Oxygen permeability in HPMC films containing moisture

The dual effect of water on the sorption of oxygen has clear impact on the oxygen permeation, as shown in Figure 7. It was difficult to obtain robust films at low relative humidity. In this condition, the films are very brittle, resulting in high occurrence of cracks in the films. This caused high variability of the oxygen permeability measured in films under very dry conditions. For this reason, only the measurement results of the oxygen permeability at

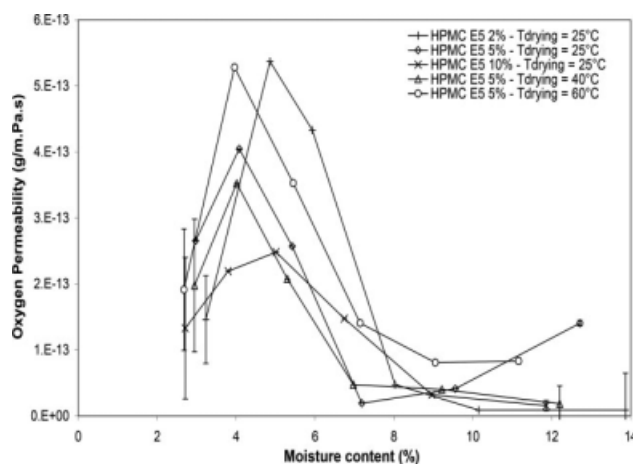


Figure 7 Influence of moisture content on the oxygen permeability.

relative humidity above 12% and correspondingly when the moisture content in the film is above 2% are further discussed. With the increase of moisture content, the integrity of the film increases. This was demonstrated by the lower variability in the experimental values of the oxygen permeability at high moisture content compared to those at low moisture content.

A similar effect of moisture sorption on the oxygen permeability has been reported by Hu et al.,⁵⁰ who demonstrated the reduction of oxygen permeability of aromatic polyamides at high RH. It is also apparent that clustering of water also occurs in this type of polymer, which explains the similarity of the effects water sorption on the oxygen transport through the film.

According to Fick's first law of diffusion, the flux of permeant J is proportional to the diffusivity and the gradient of permeant activity c through the thickness of the polymer film x like shown in eq. (9).

$$J = -D \frac{\partial c}{\partial x} \quad (9)$$

Because the oxygen permeability measurements have been performed under more or less constant oxygen pressure, the oxygen sorption is a good representation of the oxygen activity. In this situation, Henry's law [eq. (10)] applies, as the sorption of oxygen occurs predominantly in the dense phase of the HPMC matrix. In this equation, S and P are the solubility and the partial pressure, respectively. As a result, eq. (11) can be derived by substituting eq. (10) to eq. (9).

$$c = S \times P \quad (10)$$

$$J = -DS \frac{dP}{dx} \quad (11)$$

The product of the effective diffusivity D and solubility S is also known as the permeability. Thereby, the results in Figure 3 were combined with those in Figure 7 making it possible to calculate the effective diffusion coefficient of oxygen in the film, shown in Figure 8. It can be seen that the variation of diffusion coefficient through different moisture contents is relatively small considering the large variation in the diffusivity values measured.

The previous section revealed that the oxygen sorption in the film correlates with the water state, which varies in a wide range of water content. Therefore, the influence of the moisture content shown on the oxygen permeability through the HPMC films is in fact mainly via altering the activity of oxygen in the HPMC film-humid air system, reflecting the changes in the affinity of the HPMC film towards oxygen.

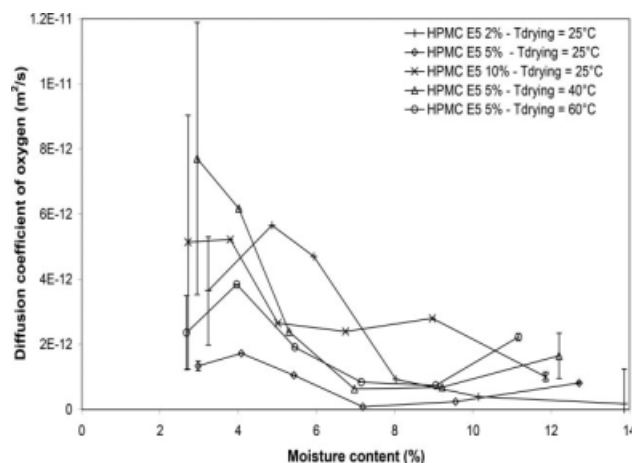


Figure 8 Relationship between the moisture content and the diffusivity of oxygen through HPMC films.

In Figure 7, it can be seen that the oxygen permeability slightly varies with the variation of the formulation and production condition of the HPMC films. It is apparent that the films made using higher concentration of HPMC solution have lower oxygen permeability at different relative humidities. The effect of drying temperature seems to increase the oxygen permeability. Despite this variation, unless they produce coating defects (present in dry films), the effect of moisture sorption on the oxygen permeability in the HPMC films seems to be larger than the effect of coating formulation and film production conditions. The effect is also consistent for the variety of films tested.

CONCLUSIONS

The sorption and transport of oxygen through glassy HPMC films containing moisture have been demonstrated to be influenced by the state of the water, which is dependent on the extent of the water sorbed in the polymer matrix. At low moisture content, most of the water molecules are present as bound water, which acts as plasticizer in the HPMC film promoting the sorption of the oxygen in the film. At high moisture content (>5%), water clusters are progressively formed, blocking the sorption sites for oxygen molecules. It has also been shown that oxygen permeability is primarily governed by the dissolution of oxygen in the polymer matrix. Therefore, low oxygen permeation occurs through films containing high moisture content and therefore low oxygen activity. This unique impact of moisture sorption on the oxygen permeability also implicates the feasible application of glassy hydrophilic polymers in the multilayer coating system for protection purpose.

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