

Research Article

Using the Internal Stress Concept to Assess the Importance of Moisture Sorption-induced Swelling on the Moisture Transport through the Glassy HPMC Films

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Abstract. The purpose of this research was to elucidate the significance of the changes in the mechanical and the volumetric properties on the moisture diffusivity through the polymer films. The internal stress concept was adapted and applied to estimate the relative impact of these property changes on the total stress experienced by a polymer film during storage. Hydroxypropyl Methylcellulose free films were used as a model material prepared at various conditions and stored at different relative humidities. The changes in the internal stress of these films due to the moisture sorption were studied. It was demonstrated that the stress-relaxation of the films increases at increasing moisture content. At the point when there is a definite loss of stress in the film, which is at moisture content higher than 6%, was shown to correlate with the significant increase of the moisture diffusivity. Further investigations revealed that the loss of stress is especially due to the swelling of the polymer rather than the changes in the inherent strain (the quotient between the tensile strength and the modulus of elasticity) of the HPMC films. This implies that the impact of the moisture sorption on the diffusivity is predominantly *via* volume addition rather than *via* altering the mechanical properties. Additionally, the approach presented here also brings up a new application of the internal stress concept, which in essence suggests the possibility to estimate the diffusion coefficient from the sorption isotherm and the mechanical analysis data.

KEY WORDS: HPMC; internal stress; mechanical properties; moisture diffusion; swelling.

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NOTATIONS: A , Film area [=] m²; C_{avg} , Average moisture content [=] %-weight; E , Young modulus of elasticity [=] MPa; P , Internal stress [=] MPa; S_{avg} , Average solubility of moisture in the total film [=] g/m³Pa; T_g , Glass transition temperature of the coating material [=] K; V , Original volume of the core [=] m³; WVP, Water Vapor Permeability [=] g/m.Pa.s; Δm , Moisture gain at certain permeation time [=] g; ΔP , Difference of partial pressure of water vapor at two sides of the coating film [=] Pa; ΔRH , Gradient of the relative humidity [=] %; Δt , Time [=] s; ΔT , Difference between the glass transition temperature of the coating and the temperature of the film during process and storage [=] K; ΔV , Volumetric changes of the core [=] m³; Δx , Film thickness; $\Delta\alpha_{(cubic)}$, Difference in thermal expansion coefficient of the core and the coating material [=] K⁻¹; ϵ_i , Internal strain [=] %; ϵ_f , Maximum strain before fracture [=] %; ϵ_{total} , Total strain [=] %; ϕ_R , Volumetric fraction of water retained in the film during storage [=] %; ϕ_S , Volumetric fraction of water at solidification point (during drying) [=] %; ν , Poisson ratio [=] -; ρ_{true} , True density [=] g/m³; σ , Stress [=] MPa; σ_f , Maximum tensile strength before fracture [=] MPa; φ , Degree of swelling [=] -.

INTRODUCTION

It is well known that hydrophilic polymers take up significant amounts of water e.g. during storage or processing (1). This presence of water modifies the rheological properties of the polymers, which can affect important aspects like the film functionalities for polymers used as coating materials. The plasticization effect of water has been demonstrated in the decrease of the glass transition temperature (2) and in the changes in the mechanical properties, such as the modulus of elasticity and the tensile strength (3). Simultaneously, the interaction with water also affects the physical state of these polymers, which extent is dependent on the glass transition temperature of the polymer itself and the amount of water bound to the polymer chains. For polymers with low glass transition temperature, the transition of the polymer phase from glassy to rubbery state occurs at lower water content than for polymers with high glass transition temperature. Obviously, when the polymer changes from glassy to rubbery state, the viscoelasticity and the volume of the polymer tremendously change. Additionally, some changes in these polymer properties may still be expected to occur with increasing moisture content even when the polymer is still in the glassy state. These alterations to any extent are important considering that the functionality of the coating material may be affected.

A glassy material is often chosen as a coating material, because it is able to provide a better barrier functionality. Nevertheless, less work has been done to investigate the extent of the alteration by moisture in the polymer properties in the glassy state. In this study, the viscoelasticity and volume changes of Hydroxypropyl Methylcellulose (HPMC) polymer (taken as a model material) by water was investigated and the effect of these changes on the permeability of HPMC for moisture (taken as an important functionality) was elucidated.

It is known that internal stresses develop within a coating film on a core during film formation and during subsequent storage e.g. due to the shrinkage of the film after its solidification point as solvent evaporates from the system (4,5), through temperature variations (5) and relative humidity (RH) changes (6–8). Okutgen *et al.* (7) has combined these different mechanisms and formulated a model to estimate the internal stress (P) as described in Eq. 1.

$$P = \frac{E}{3(1-\nu)} \left[\left(\frac{\phi_S - \phi_R}{1 - \phi_R} \right) + \Delta\alpha_{(\text{cubic})}\Delta T + \frac{\Delta V}{V} \right] \quad (1)$$

This model basically depicts the internal stress induced by the volume changes due to the differences in moisture content at the solidification point and during the storage of the coating. It also considers the volume changes due to the difference in thermal and swelling behavior of the core and coating substrates. Thereby, the final changes in the coating volume are also corrected by the mobility of the polymer chains themselves to remain intact. Originally, this concept has been utilized to predict the incidence of internal stress related film coating defects (9,10). When the internal stresses exceed the tensile strength of the film, the adhesion and cohesion related film coating defects such as cracks, edge splitting and peeling are likely to occur.

In this work, this concept was adapted and the transition of the internal stress through water activity changes was monitored. The water vapor permeability (WVP) of HPMC films and the mechanical properties were measured at various RH's and correspondingly product water activities. It is known that water can act as a plasticizer in HPMC and cause the swelling of the HPMC films. This means that the influence of water on the WVP can be both *via* altering the viscoelasticity and the volume of the HPMC. As both the modifications in the viscoelasticity and the volume are comprised in the internal stress, the impact of water sorption should also be seen in the internal stress. Therefore, it is proposed here to use the internal stress concept to aid the understanding of the impact of moisture sorption on the water vapor permeability.

MATERIALS AND METHODS

Materials

Hydroxypropyl methylcellulose (HPMC) (Methocel E5, LV USP/EP premium grade) from Dow, supplied by Colorcon, UK, was used as a model coating polymer. Citric acid and sodium dihydroxyphosphate (NaH_2PO_4) were obtained from JT Baker, The Netherlands. The pigment used is Carmoisine (E122) from Pomona BV, The Netherlands, which is a water soluble food-grade dye.

Methods

Film Production

In this study, the free films were made by casting or spraying. HPMC was dissolved in cold water (5% *w/w* water) and was stirred for about 1 h to assure a homogeneous solution. Whenever applicable, the pigment was added during early stirring at concentration of 0.1% by solution weight. The HPMC solution was then poured into a mold made of High Density Polyethylene (HDPE), from which the HPMC film could be easily removed after drying. Three different drying temperatures were used, i.e. room temperature (25°C), 40°C and 60°C. Drying at room temperature, 40°C and 60°C lasted for 48 h, 16 and 8 h, respectively. The moisture contents retained in the films after these drying conditions were found to be 5.21%, 1.08% and 0.69%, respectively. These values were determined from the difference in the film weight after drying and the theoretical weight of the polymer in the film divided by the polymer weight. For sprayed films, the coating solution was sprayed by using a two-fluid nozzle normally utilized in thin layer chromatography using pressurized nitrogen flow at 1.5 bar. The coating solution was sprayed layer by layer onto a poly-tetrafluor-ethylene sheet, which put on top of a glass plate that was heated at 60°C. The films obtained had an average thickness of 80–100 μm .

The crosslinking process of the HPMC films was performed based on the formulation and conditions developed by Coma *et al.* (11). The cross-linking agent and catalyst used were citric acid and sodium dihydroxyphosphate (NaH_2PO_4), at concentrations of 15% and 7.5% by weight of HPMC respectively, in order to reach >95% degree of cross-linking (11). These agents were added to the film forming solution before molding or spraying. Initially, the films were dried at 60°C, before they were finally cross-linked at 190°C for 15 min.

Film Characterization

Film Thickness. The film thickness (Δx) was measured with Mitutoyo micrometer with an accuracy of 1 μm . For each film, the thickness was measured 5 times at different locations. The standard deviation of the thickness measurement for each film was less than 10%.

Sorption Isotherm. The sorption isotherms of different free films were obtained from the analysis performed in a sorption analyzer SPS11-100n from Projekt Messtechnik (Germany) at 25°C. The relative humidity (RH) inside the sorption chamber was conditioned by mixing a dry nitrogen gas flow with a gas flow saturated with water, programmed from 0 to 70% and from 70 to 0% at 10% steps. Each step lasted until equilibrium was reached, allowing the sorption and desorption to be prudently monitored. The mass of samples used was about 100 mg of each film and the results were reported as the equilibrium moisture content (in g/g film) at different RH's.

Water Vapor Permeability (WVP) and Diffusivity of Water Vapor (D). The WVP was measured at 25°C by using a permeation cell inside a sorption analyzer SGA-100 from

VTI (Hialeah, USA). The permeation cell used is a cup with a wide top-edge to where the free films were attached. The diameter of free films available for the permeation process is 14.80 mm and the permeation cell is 4.33 mm in depth. The saturated salt solution was placed in the permeation cell providing a constant RH gradient from outside to inside of the permeation cell during the permeation of moisture. Different salts were chosen, according to the desired RH outside the permeation cell (inside the sorption chamber), so that the gradient of RH of each permeability measurement was always between 15–20%. The type of salts and their corresponding RH are listed in Table I. The WVP was calculated according to Eq. 2 (12). The WVP was taken as the slope of the plot between the mass increase (Δm) due to the moisture transfer into the permeability cell and the product of time (Δt), area of coating film (A) and the differential partial pressure (ΔP), divided by the film thickness (Δx).

$$\Delta m = WVP \frac{\Delta t \cdot A \cdot \Delta P}{\Delta x} \quad (2)$$

Furthermore, the diffusivity of water vapor through the HPMC films was determined by dividing the WVP with the solubility of the water vapor in the film. Solubility is defined as the concentration of the moisture within the film equilibrated at certain partial pressure (ΔP) and temperature. In our situation, an average solubility was used, as there was a difference in the water activity at the two surfaces of the film during the determination of the WVP. Therefore, the average value of relative humidity of outside and inside the permeation cell was used and the corresponding moisture uptake at this average relative humidity was taken as the average moisture content in the film C_{avg} . Subsequently, the solubility of the water vapor in the film was determined according to Eq. 3. The solubility of water vapor was defined in the volume unit of the polymer. Here, the true density of the HPMC E5 polymer was taken as $1.328 \times 10^6 \text{ g/m}^3$ during calculation, which was measured in a gas pycnometer (Micromeritics type Accupyc 1330) with nitrogen as the inert gas.

$$S_{\text{avg}} = \frac{C_{\text{avg}} \times \rho_{\text{true}}}{\Delta P} \quad (3)$$

Mechanical Analysis. The mechanical analysis was performed using a tensometer LR5K (Lloyd instruments) with crosshead speed of 2.5 mm/min. The free films were cut

using an ASTM D.638T.4 stamp and equilibrated at different RH. The initial sample length and the width of the sample are respectively 55 and 6.7 mm. During analysis, the stress and the strain were measured and from the slope of the plot, the Young modulus of elasticity can be determined, as defined in Eq. 4.

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon} \quad (4)$$

Stress and strain have been defined elsewhere (13). Furthermore, the maximum tensile strength (σ_f) was determined from the maximum stress applied before the film starts to break.

Glass Transition Temperature. The glass transition temperature was determined using a Differential Scanning Calorimetry (DSC). The Modulated DSC scans were made from 25°C to 250°C on a Mettler Toledo DSC 822e with a scan rate of 5°C/min, period of 1 min, and amplitude of 0.5°C, with continuous flow of nitrogen at 40 ml/min. The films were cut using a 4-mm hollow-punch to fit into the crucible and then were equilibrated at different relative humidities. The sample films weighed between 3–6 mg and were hermetically sealed in 40 μl aluminum crucibles. The DSC cell was calibrated with indium, which melt temperature of 429.6 K and fusion enthalpy of 28.54 J/g. The glass transition temperatures were determined from the reversible heat curve, taken as the mid-point value.

Degree of Swelling. The degree of swelling (φ) of the HPMC free films was measured optically using a stereo microscope (Olympus SZ40, Olympus, Zoeterwoude, The Netherlands), equipped with a Sanyo CCD color camera to capture the images. Images of film samples (having a similar dimension as the ones used for the determination of the glass transition temperature) were taken before and after equilibrated at different RH's. The obtained images are 700×525 pixels and have a resolution of 10 μm per image pixel. The area of the respective films before (A_o) and after equilibrated at different RH's (A_{RH}) were determined using image processing toolbox provided in MATLAB R2007a. An average diameter could be calculated from the determined area, assuming a circle shape of the film sample. The degree of swelling was defined as the ratio between the increase in diameter ($D_{\text{RH}} - D_o$) and the original diameter (D_o) of the film sample, as given in Eq. 5. The results are shown in Table II.

$$\varphi = \frac{D_{\text{RH}} - D_o}{D_o} = \frac{\left(\frac{A_{\text{RH}}}{\pi}\right)^{0.5} - \left(\frac{A_o}{\pi}\right)^{0.5}}{\left(\frac{A_o}{\pi}\right)^{0.5}} \quad (5)$$

Internal Stress. The terms $\Delta\alpha_{(\text{cubic})} \Delta T$ and $\frac{\Delta V}{V}$ in Eq. 1 contribute to the total internal stress when there is a difference in the coefficients of thermal expansion and the volumetric changes between the core and the coating film during process and storage, respectively. As the internal stress was studied on free films, these terms became irrelevant to our situation. Therefore, in this study, the internal stress was calculated based only on the stress induced by the difference

Table I. Saturated Salt Solutions Used to Provide Various Humidity Levels in This Study

Saturated salt solutions	Relative humidities
SiO ₂	0%
LiCl	12%
CH ₃ COOK	22%
MgCl ₂	33%
K ₂ CO ₃	43%
Mg(NO ₃) ₂	54%
NaNO ₂	64%
NaCl	75%

Table II. Influence of the Relative Humidity During Storage on the Degree of Swelling of HPMC Films Made at Various Drying Temperatures

RH _{storage}	T _{drying}		
	25°C	40°C	60°C
22%	0.65%	0.10%	0.06%
43%	1.29%	0.89%	0.41%
64%	3.25%	2.95%	1.68%
75%	23.89%	22.74%	22.28%

of the moisture content in the film during the storage and solidification point (as given in Eq. 6).

$$P = \frac{E}{3(1-\nu)} \left(\frac{\phi_S - \phi_R}{1 - \phi_R} \right) \quad (6)$$

Adapted from Okutgen *et al.* (1995) and Okhamafe and York (1985), this equation can be compared to the mechanical strength of the material (the tensile strength, σ_f), in order to estimate the excess of stress in the film, given in Eq. 7. If the internal stress within the film is equal to or greater than the mechanical strength of the film ($P > \sigma_f$), cracks and other defects may occur. This equation has been successfully used to predict the failure of the film (7,9,10).

$$\text{Excess of Stress} = \frac{1}{3(1-\nu)} \left(\frac{\phi_S - \phi_R}{1 - \phi_R} \right) - \frac{\sigma_f}{E} \quad (7)$$

In this study, the loss of stress (an inverse of Eq. 7, rewritten as Eq. 8) was used rather than the excess of internal stress, as it is our purpose to assess the physical phenomena when the internal stress is reducing due to impact of higher moisture content.

$$\text{Loss of Stress} = \frac{\sigma_f}{E} - \frac{1}{3(1-\nu)} \left(\frac{\phi_S - \phi_R}{1 - \phi_R} \right) \quad (8)$$

For every film equilibrated at fixed RH, the losses of stress were calculated using the measured maximum tensile strength and Young modulus of elasticity, both derived from the mechanical analysis data, and the volume fraction of moisture retained in the film, which was taken from the sorption isotherm.

The Poisson's ratio of the HPMC films was taken as 0.35, which is a common approximation value for many polymeric materials (4, 14, 15). Due to the difficulties of the determination of the fraction of moisture at solidification point, in this study a value of 0.12 was taken, while Croll (1979) suggested a value of 0.162 for polyisobutyl methacrylate. Despite this arbitrariness, the trend of the correlation between the excess of internal stress and the moisture content remains the same and the estimated internal stresses are in the same order of magnitude as the values reported by others (7).

RESULTS AND DISCUSSION

In Fig. 1, the sorption isotherms of different HPMC E5 free films are presented. It is shown that the sorption behavior is merely a material property, as the differences in the film production methods and conditions barely affect the moisture uptake. Furthermore, the moisture sorbed in the HPMC films causes the plasticization of the film, as signified in the decrease in the glass transition temperature (T_g) of HPMC films with the increase of moisture content (Fig. 2). However, even at moisture content higher than 10%, the T_g of the HPMC films is not lower than 120°C, which is clearly higher than the room temperature. This means that the HPMC films containing different moisture contents tested in this study are still in their glassy state.

The water vapor permeabilities (WVP) and the diffusivities of moisture through the HPMC free films at different humidity levels were determined. The WVP is directly related to the diffusivity of the moisture through the films. Therefore,

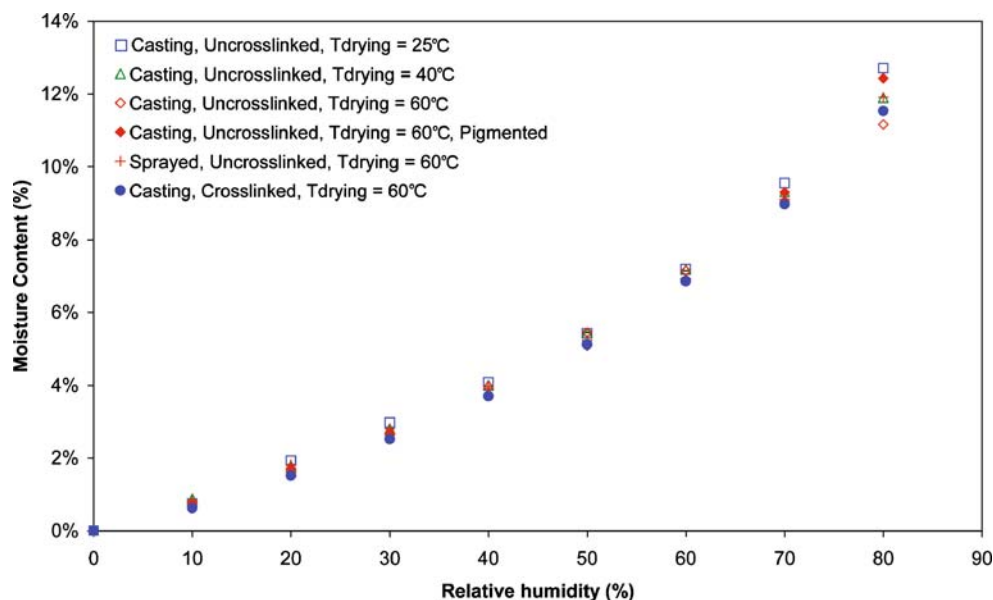


Fig. 1. Sorption isotherms of HPMC E5 free films produced by different methods and conditions

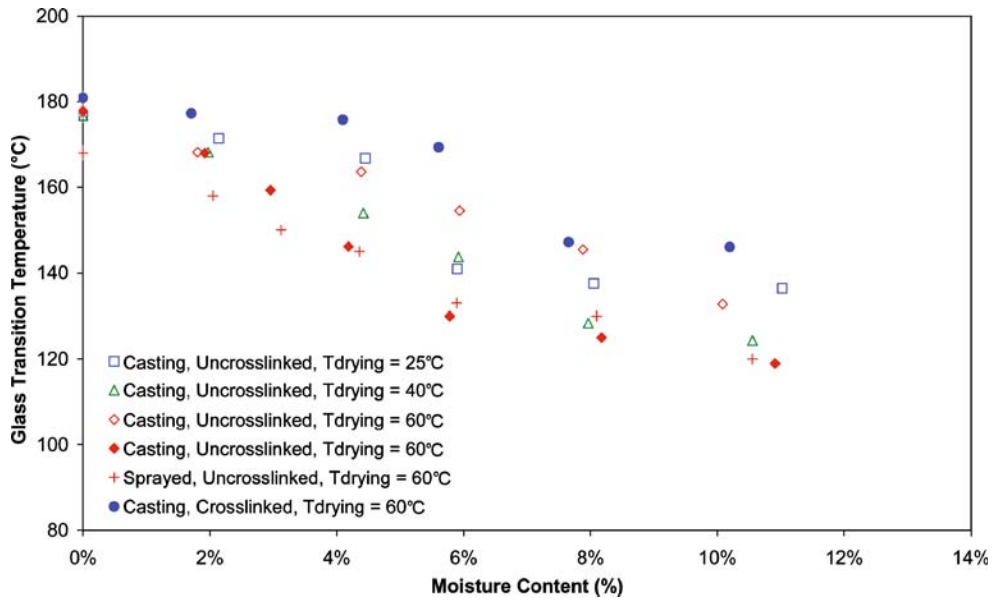


Fig. 2. The glass-rubber transition temperature of different HPMC E5 free films at different moisture contents

currently only the moisture diffusivity data are presented and shown in Fig. 3. It is shown in this figure that the moisture diffusivity through the HPMC films increases significantly with the moisture content at moisture content higher than 6%. Below this value the moisture diffusivity is hardly changed. This stepwise impact of the moisture sorption on the moisture diffusivity is (1) due to the alteration in the physical state of the HPMC polymer and (2) due to the water state in the polymer at high moisture content. This study focuses especially on the first aspect. The swelling behavior of the HPMC polymer family upon contact with water is extensively known in literature (e.g. 16–18). Also the swelling occurrence of the HPMC polymer under humid condition has been reported (19). However, an accurate measurement of

the degree of swelling of a polymer upon contact with water vapor is rather difficult as an *in situ* measurement is required. In our approach for measuring the degree of swelling, the films were exposed to the room ambient for a short period of time while taking the images. During this time, there might be some moisture sorption or evaporation. Despite the experimental error that has been introduced, our results confirmed the significant swelling occurrence of the HPMC films at high moisture content (at RH>64%), as shown in Table II. This finding implicates that the influence of moisture on the transport properties of the glassy HPMC films may also be *via* other manner, i.e. causing the polymer swelling rather than only *via* changing the mechanical properties of the HPMC films.

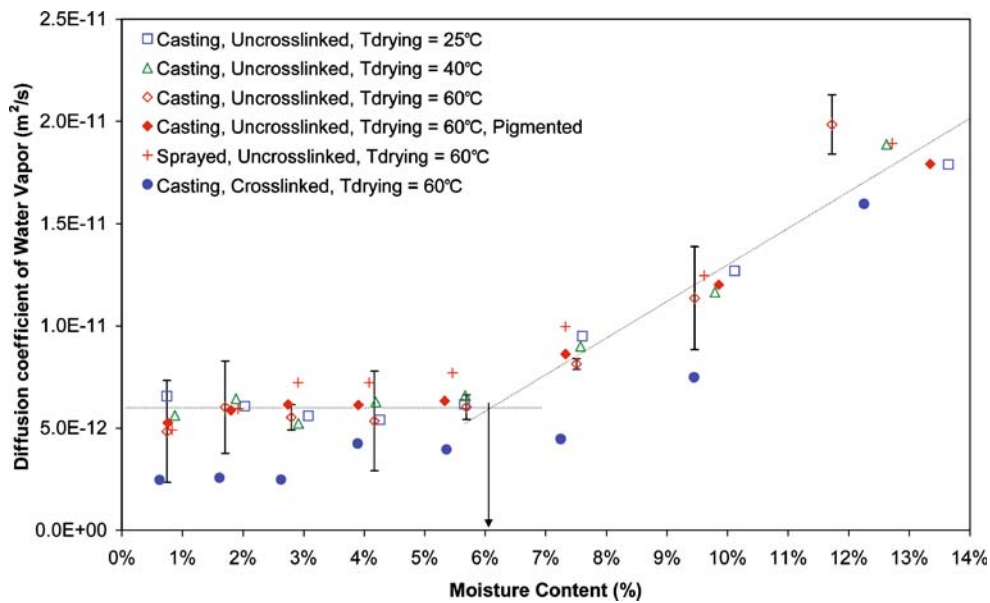


Fig. 3. Correlation between the moisture content and the diffusion coefficient of moisture through the HPMC films

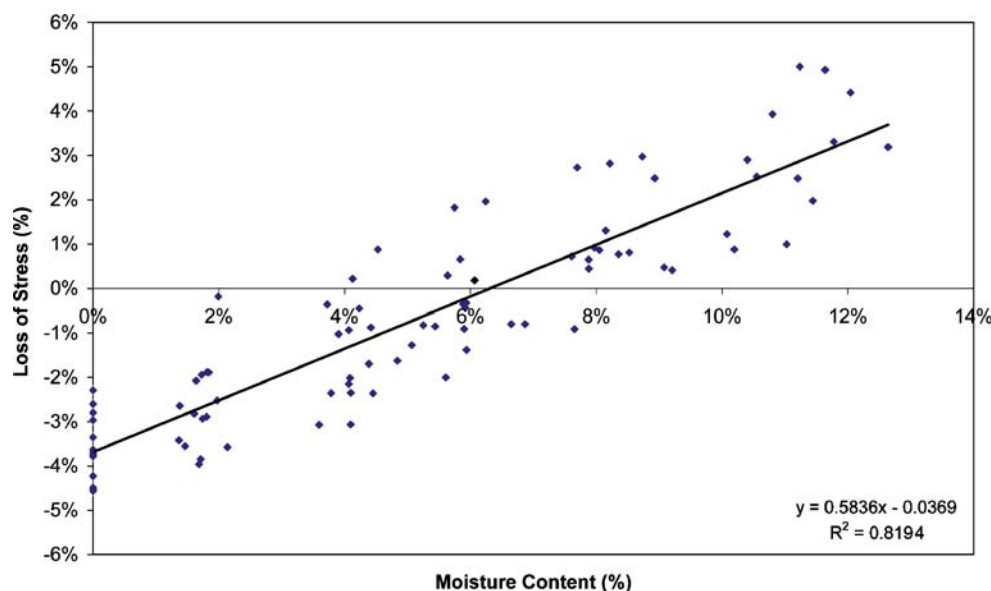


Fig. 4. Transition in the loss of stress with increasing moisture content

Furthermore, the internal stress concept was assessed, by which both impacts of the changes in the mechanical properties and in the volume of the HPMC films by moisture sorption on the diffusivity of moisture through the HPMC films can be elucidated. The loss of stress was estimated according to Eq. 8 and plotted against the moisture content (Fig. 4). The influence of the film preparation conditions on the correlation between the loss of stress and the moisture content is negligible. This is also confirmed by the fact that the total data was well fitted into one correlation with the moisture content in the film (see Fig. 4). In this figure, it can be seen that there is a transition in the loss of stress with the increase of moisture content: from a negative (i.e. excess of stress) to a positive value. Equation 8 comprises 2 terms, where the first term corresponds to the mechanical properties of the HPMC films, while the second term corresponds to the volume change in the HPMC films, which both are affected by moisture sorption. As derivation, the first term can also be considered as the maximum strain before fracture (ε_f), while the second term can be considered as the internal strain (ε_i). Therefore, Eq. 8 can be rewritten as Eq. 9.

$$\text{Total strain} = \varepsilon_f - \varepsilon_i \quad (9)$$

According to original application of this model, the internal strain is generally perceived as the shrinkage of the film e.g. due to solvent evaporation during film formation and storage. This can also be seen in the negative sign of the internal strain in Eq. 9, showing its negative contribution to the total strain. Looking at the second term in Eq. 8: $\frac{1}{3(1-\nu)} \left(\frac{\phi_S - \phi_R}{1 - \phi_R} \right)$, the value of this term reduces linearly with the increase of moisture content in the film (ϕ_R). This means that with increasing moisture content, the shrinkage of the film is gradually compensated with the swelling of the film, giving a lower value of the internal strain. When the value of this term is lower than $\frac{\sigma_f}{E}$, the loss of stress is shifted from a negative to a positive value. Assuming that the swelling of the film is similar in every direction, this total strain can be regarded as the volumetric

change in the film. Therefore, it can be suggested that the point when the loss of stress (or total strain) passes the zero value may be related to the start of significant swelling of the film matrix.

In this work, in spite of the decrease of the modulus of elasticity with increasing moisture content (shown in the left-corner of Fig. 5), the value of $\frac{\sigma_f}{E}$ changes very little with moisture content and can be considered constant (as it is still within the 95% of confidence limits of the real slope of correlation, displayed in Fig. 5). This constancy is also valid for films made with different conditions (therefore, the mechanical properties from various HPMC films were not clustered during plotting). This leads to the conclusion that the loss of internal stress is mainly influenced by the changes in the second term due to the direct contribution of moisture i.e. *via* volume addition. Furthermore, this explains the good correlation between the loss of stress and moisture content described in Fig. 4.

The feasibility of using the internal stress concept to indicate swelling from the loss of stress (reduction of internal stress) data has been further examined. For this purpose, the plot between the diffusion coefficient and the loss of stress was made, presented in Fig. 6. From this figure, it can be seen that the transition in the diffusivity of moisture through the glassy HPMC films (from almost constant to an increase) is also related to the transition in the loss of stress. At the point that the loss of stress is around zero, the diffusion coefficient starts to increase significantly, which is due to the swelling in the film. Eventually, this finding also verifies the plausibility of using the internal stress concept to indicate the moisture sorption-induced swelling occurrence, which significantly affects the diffusion coefficient. Considering this relationship between the diffusivity of moisture and the loss of stress and the factors influencing the loss of stress discussed before, it can be signified that in the glassy state, the impact of the changes in the mechanical properties on the transport properties is relatively smaller than the direct impact of the moisture in affecting the volume of the coating material.

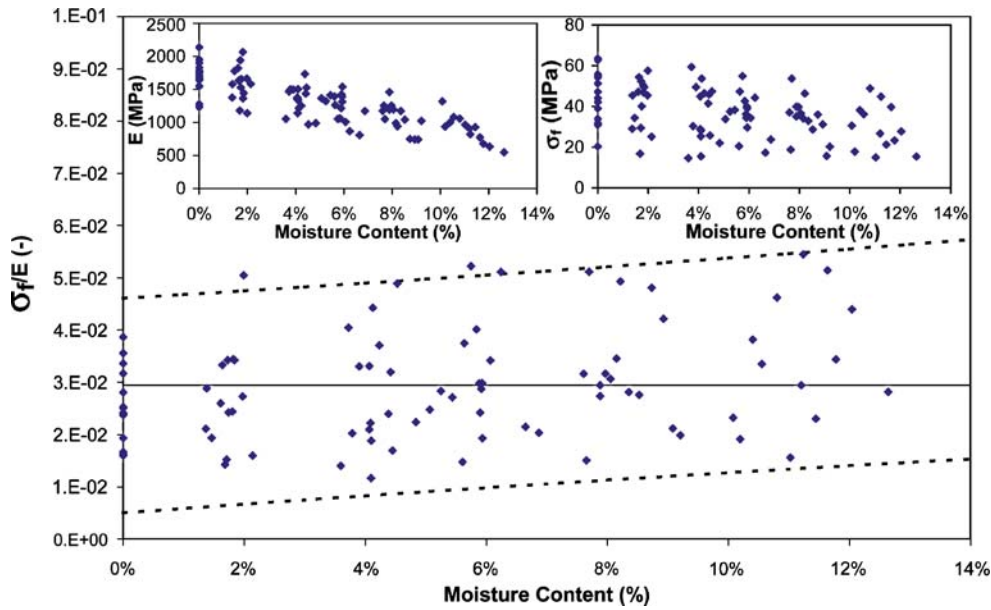


Fig. 5. The quotient between the tensile strength and the modulus of elasticity of various HPMC films at increasing moisture content

It can further be seen that the diffusion coefficient and the loss of stress are consistently correlated for HPMC films made at different drying temperatures. This means that it may later be possible to develop a model to estimate the diffusion coefficient for different kind of films based on the loss of stress data, which is easier than to measure the permeation properties directly. Also, it can be noticed that the diffusion coefficient of the cross-linked films are significantly lower than the diffusion coefficient of uncrosslinked films, although the correlation between the diffusion coefficient of cross-linked films and the relative humidity is similar with that of uncrosslinked films. This implies that other factors may also play a role in influencing the diffusion coefficient, such as the porosity, as it has been reported by Coma *et al.* (11). These

variables, which are altered by process conditions such as cross-linking should also be included in order to improve the model.

Considering that the determination of water vapor permeability is much more time consuming than the mechanical and sorption isotherm analysis, this application of the internal stress model may be promising for formulation purposes. At least, the transport properties may only have to be determined at a certain RH while the other values at elevated RH's may further be estimated. *Via* this approach, the swelling of film coating may also be estimated quite simply but more accurately than with other methods e.g. from the measurement of the film thickness before and after storage at different RH. Furthermore, the calculation is

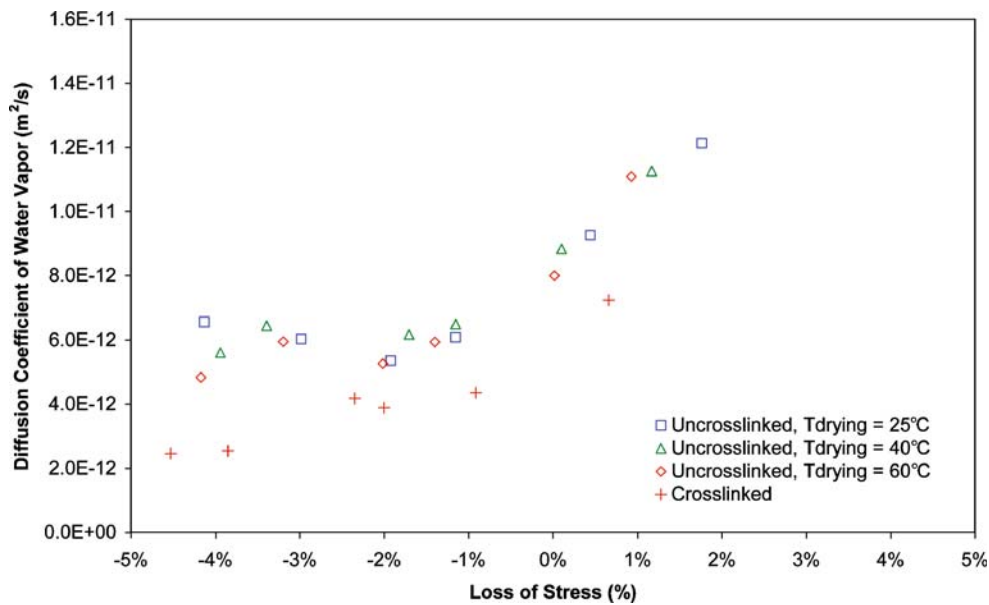


Fig. 6. Correlation between the diffusion coefficient of moisture through the HPMC films and the loss of stress calculated from the internal stress model

rather simple and requires parameters that can generally be found in literature.

CONCLUSIONS

Both swelling and the changes in the mechanical properties were observed in the HPMC films due to different levels of moisture sorption. The assessment of the internal stress of the HPMC films has shown that the significant increase of the moisture diffusivity at high (>6%) moisture content is correlated with the loss of stress in the films. Further assessment revealed that the loss of stress is mainly due the swelling occurrence rather than the changes in the mechanical properties of the films. This concludes to the predominant impact of the moisture-induced swelling on the transport properties of HPMC films in the glassy state. This also indicates the benefit of using the presented approach, which enables the estimation of swelling for the prediction purpose of the moisture diffusivity through a coating film.

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