Adsorption (2014) 20:863–874
DOI 10.1007/s10450-014-9628-6

Water vapor adsorption equilibria and mass transport in unmodified and modified cellulose fiber-based materials

Alemayehu H. Bedane · Huining Xiao · Mladen Eić

Received: 2 September 2013 / Revised: 10 July 2014 / Accepted: 4 August 2014 / Published online: 13 August 2014

Abstract Water vapor adsorption isotherms of different unmodified and coated paper samples were studied to determine their suitability as water barrier packaging materials. The sorption behavior of these samples was compared with commercially available paper. The experimental data were analyzed using the Hailwood–Horrobin (H–H), Guggenheim–Anderson–De Boer (GAB) and BET models for extraction of isotherm parameters and determination of monolayer moisture contents. The H–H and GAB models were found to provide good fits to the experimental data. The monolayer moisture content of modified papers was less than 3.0 % (dry basis) as compared to unmodified paper samples (4.20 %), at saturation. It was also observed that the sorption behavior of modified paper samples differed with substrate type. Water vapor permeability (WVP) of unmodified and coated paper samples at the temperatures of 25 and 38 °C were also measured for a wide range of vapor partial pressure gradients. The permeabilities of the modified samples were found to be generally low compared to the unmodified (reference) paper sample. Among the investigated samples, PLA and PHBV coated paper samples showed higher mass transfer resistance to water vapor transport. Furthermore, the water vapor permeabilities of different samples were found to be relatively constant up to the modest relative humidity levels; however, at the higher humidity levels they showed increasing trend with the further increase in relative humidity. Results of this study confirmed that blocking of active surface sites by coating with PLA and PHBV is the most effective way to increase the water vapor barrier properties of modified papers, thus making them the appropriate candidates for green-based food packaging materials.

Keywords Adsorption isotherms and equilibrium models · Coated-paper · Moisture content · Cellulose fibers · Water vapor permeability · Solution-diffusion model

1 Introduction

Cellulose fiber based materials, like papers, can be potentially used as packaging materials because they are considered environmentally friendly due to their recyclability and biodegradation properties. A variety of paper-based packaging materials have been widely used for both food and non-food products. There are many industries where moisture control is critical, especially for food and pharmaceutical packaging. The moisture content of paper-based materials at different relative humidity of the surroundings, and water vapor barrier properties of the substrate material play a key role in maintaining food product quality. Adsorbed moisture on the paper could affect the physical and mechanical properties of the paper-based packaging materials (Twede and Selke 2005). Moisture sensitive foods and pharmaceuticals can be placed in packaging with controlled water vapor and gas transmission rates to achieve the required quality, safety, and shelf life (Ashley 1985; Del Nobile et al. 2006; Koide and Shi 2007).

Paper is made from chemical or mechanical pulps and has a network of natural cellulosic fiber made up of

Electronic supplementary material The online version of this article (doi:10.1007/s10450-014-9628-6) contains supplementary material, which is available to authorized users.

A. H. Bedane · H. Xiao · M. Eić (✉)
Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada
e-mail: meic@unb.ca

microfibrils which are composed of long chain cellulose molecules in a crystalline structure. The cellulose fiber possesses a high crystalline content, inaccessible to water molecules but also contains a para-crystalline component to which water molecules can gain access. The microfibril units have a high content of surface OH groups that is accessible to water. Paper-based packaging materials readily absorb moisture from the atmosphere due to the composition of highly porous cellulose fibers and OH sites in the basic unit of cellulose ($C_6H_{10}O_5$). The water molecules are adsorbed in the cell wall. These that are closely associated with OH groups form monolayer water, unlike those that are not intimately associated, and are forming polylayer water (Hill et al. 2009). Andersson (2008) reviewed new methodologies for improvement of functionality of fiber-based materials by surface treatment. Parker et al. (2006) reported sorption isotherm data for different unmodified paper samples, but no isotherm data were provided for coated paper samples. Hence, characterizing modified paper samples is essential for further improvement paper's barrier and isotherm properties, in order to increase its viability as a packaging material and quality paper.

Adsorption isotherm measurements of a material provide essential information about water vapor sorption mechanism and interaction of packaging materials with water vapor at different humid environments. Hailwood–Horrobin (H–H), GAB and BET models were primarily used in this study to determine the monolayer moisture contents of different paper samples. H–H model was also used to access the availability of the adsorbed water vapors to form polylayers on the paper surface. Monolayer moisture content has a significant effect on the physical and chemical stability of cellulose fiber materials. It is defined as the minimum moisture content, covering hydrophilic sites on the material surface, and is usually accepted as a criterion for achieving safe storage with minimum quality loss during long time exposures (Rhim and Lee 2009; Moreira et al. 2008). Determination of monolayer moisture content of cellulose fiber materials is essential to estimate shelf stability and maintain high functionality of packaging materials. The H–H model is used mostly in the area of wood fiber science to analyze the adsorption isotherm, but is less often applied for the analysis of paper packaging materials (Hill et al. 2009; Spalt 1958; Simpson 1980).

The permeability coefficients can be used to predict the rate of water vapor diffusion that takes place in response to a concentration gradient. They also provide a means of predicting the equilibrium water content that is available for hydrolysis (Siparsky et al. 1997). There are a few numbers of studies on the water vapour permeability of bio-films but a limited number of studies as a coating on cellulose-fiber material (Bertuzzi et al. 2007; Kuusipalo 2000; Siparsky et al. 1997; Shogren 1997; Tsuji et al. 2006). In this study, gravimetric-IGA system is used for accurate and fast measurements of water vapor transmission rates (WVTR's) and water vapor permeability (WVP) on the selected fibre samples.

The hydrophilic surface of cellulose has to be modified to be more compatible with non-polar or less polar polymer matrices. Biodegradable materials, such as polylactic acid or polylactide (PLA), poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) and zein have a significant potential as packaging materials. These bio-based polymers have also been used for modification of cellulose fiber materials in order to increases water barrier properties. Zein was used to fill gaps between fibers on the treated papers, thus making them less permeable for water vapor. On the other hand, PLA and PHBV were used to block active hydroxyl groups on surface areas of modified papers in order to achieve the same effects. Related to this, it is very important to understand the characteristic of physical and chemical treatments applied to paper surface on the influence of water adsorption capacity and water vapor transport properties. The main objectives of this study were:

- To investigate water vapor sorption behavior on unmodified and coated paper samples, and compare with commercially available papers.
- To measure and analyze the water vapor permeabilities (WVP's) on the selected cellulose fiber-based samples at different humidities, e.g., ΔRH, and ultimately determine the effects of different modification methods (pore filling or active surface blocking) on hydrophobic properties of modified papers.

2 Materials and experimental

2.1 Preparation of samples

Several types of paper samples that were prepared for this study are listed in Table 1. Unmodified paper samples were made from pure cellulose. Modified paper samples such as PLA and PHBV coated paper, with coating weight of 20–23 g/m^2 and base paper (95 ± 4 g/m^2), as well as zein grafted paper (8 wt% corn zein) were prepared according to the procedures further explained in this section. The PLA was purchased from NatureWorks LLC, and chloroform used as the solvent was purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd. All compounds were used without further purifications. The PLA coating solution was prepared by dissolving 0.25 g of PLA in 6 ml of chloroform and stirring with a magnetic stirrer (Rhim et al. 2007). Before processing, PLA was dried overnight at 60 °C under reduced pressure and stored under vacuum in

Table 1 Paper samples and their physical properties

Physical properties	Paper types					
	Unmodified paper	Zein grafted/ coated paper	PLA coated paper	PHBV coated paper	Commercial papers	
					Copy paper	Calendered coated paper
Grammage (g/m^2)	60	88	115	110	82	150
Density (kg/m^3)	543	628	907	967	820	1083
Thickness (mm)	0.110	0.140	0.127	0.120	0.099	0.140

the presence of a P_2O_4 desiccant. Completely dissolved coating solutions were cast onto printing paper (8.8 cm diameter), in three steps. In the first two steps, 1 ml of each solution was cast into the paper, and then the rest of solution was cast onto the paper to decrease the penetration into the paper substrate, which was mounted on a flat glass petri dish. PLA coating solutions were spread over on different printing papers by using a glass spoon-shape bar, and dried under ambient condition (23 ± 2 °C) for 24 h.

Poly-3-hydroxybutyrate-*co*-3-hydroxyvalerate, with a hydroxyvalerate content of 3 wt% was purchased from Sunrise Global, Inc. NJ. USA. PHBV coating solution was prepared at room temperature, under magnetic stirring by dissolving powder of PHBV in 6 ml of chloroform sonicated for 1 h. The coating solution was then spread onto paper (10 × 10 cm, thickness ca 90 μm) mounted on a Teflon sheet (10 × 10 cm), in the three step process. In each step 2 ml of solution was added using a glass spoon-shape bar with 1 min intervals, and dried under ambient conditions (23 ± 2 °C) for 24 h.

Zein, a class of prolamine protein-based natural products with highly hydrophobic and barrier properties, was grafted onto the paper consisting of sulphite fibre using Isophorone Diisocyanate (IPDI) as a coupling agent. The zein solution was prepared by dissolving a certain amount of zein powder in the mixture of 70 % acetone and 30 % water (v/v) (Yamada et al. 1996). Then the additive-free hand sheets were reacted with the diluted zein solution and the IPDI at the temperature of 50–60 °C, followed by a magnetic stirring for a few hours. The samples were finally washed several times and oven dried overnight at 100 °C before the characterization tests were carried out.

2.2 Water vapor adsorption isotherms

Water vapor adsorption isotherms were measured using Belsorp-Max (BEL JAPAN, INC., Osaka, Japan). The Belsorp-max is an automatic gas adsorption/desorption instrument using volumetric method to measure adsorption isotherm in the relative pressure range $p/po = 10^{-8}$–0.997. The adsorption isotherms of the samples used in this study were measured at 15, 25 and 35 °C.

2.3 Water vapor transport properties

Water vapor transmission rates (WVTR's) measurements on paper samples were performed using a state-of-the-art sorption apparatus, consisting of high sensitivity microbalance (0.1 μg) and turbomolecular high vacuum pumping system (IGA-003; Hiden-Isochema, Warrington, UK). The IGA instrument can be easily adapted to measure water vapor transfer rates, in accordance to the method described by ASTM E 96/E96M-05 standard (2005). The measurements were carried out at the relative humidity differences ranging from 10 to 90 % (*ΔRH* %) and temperature of 25 and 38 °C. In these experiments, sample (paper film) was first saturated at different RH using a salt solution ($MgCl_2$ (33 % *RH*), $Mg(NO_3)_2$ (52 % *RH*), NaCl (76 % *RH*), KNO_3 (92 % *RH*)) in the base of the sample holder. It was then, followed by desorption step using a flow of purge gas (nitrogen) partially saturated with water vapor, e.g., relative humidity of 2, 20 and 50 %, obtained by an automatic water vapor generator (HumidSys, InstruQuest Inc., USA), in order to study the effects of driving force (ΔRH) on the water vapor permeability. Two to three replicates were made per each RH depending on the variation of the results and the average values were taken for the analysis. Reproducibility of the results was within 5–10 % range.

3 Theory

3.1 Adsorption isotherm models

3.1.1 Hailwood–Horribon (H–H) model

In order to understand the formation of water vapor in the cellulose fiber based material, water vapor adsorption isotherms were studied by Hailwood–Horribon model. The model was primarily used to evaluate the form of water existing in chemically modified and unmodified cellulose fiber materials. According to the model postulates, adsorption of water vapor by porous material is governed by two sets of equilibria: the first is the formation of a solid solution of water in the material (polylayer water), and second is the formation of hydrates between water and active surface group of the fiber material (monolayer water). Based on the model postulations the three distinct regions in the cell wall are: unhydrated polymer (a unit of the hypothetical polymer molecule of dry fiber, which can adsorb one molecule of water to form a monohydrate), hydrated polymer (the bound moisture, described as a monohydrate), and polylayer water (the water molecules loosely bound to the cell wall in layers that superimpose to the water monolayer). Furthermore, these three formations are supposed to behave as an ideal solid solution. The H–H model examines the state of equilibrium existing between a vapor phase, a liquid phase and a solid solution (Hailwood and Horrobin 1946). The H–H theory predicts that plotting the ratio of the humidity to the uptake (h/M) against relative humidity (% h) should give a parabolic relationship of the form shown by the following equation:

$$\frac{h}{M} = A + B \times (h) - C \times (h)^2 \tag{1}$$

where h is the relative humidity (%); M is the equilibrium moisture content (%); and A, B, and C are the empirical parameters (Skaar 1988).

$$M = M_h + M_s = \frac{W}{18} \tag{2}$$

In terms of relative humidity, $H = 100h$, and percentage moisture content $M = 100m$:

$$\begin{aligned} M &= M_h + M_s \\ &= \frac{1800}{W}\left[\frac{K_1K_2H}{100 + K_1K_2H}\right] + \frac{1800}{W}\left[\frac{K_2H}{100 - K_2H}\right] \end{aligned} \tag{3}$$

$$\mathrm{A} = \frac{\mathrm{W}}{18} \times \left[\frac{1}{\mathrm{K_2(K_1 + 1)}}\right] \tag{4}$$

$$B = \frac{W}{1800} \times \left[\frac{K_1 - 1}{K_1 + 1}\right] \tag{5}$$

$$C = \frac{W}{1800} \times \left[\frac{K_1K_2}{K_1 + 1}\right] \tag{6}$$

The molecular mass of the dry cell wall material per adsorption site (W) gives a comparative indication of the susceptibility of the cellulose fiber material and can be calculated from the constants A, B and C in (1).

$$W = 1800\sqrt{B^2 + 4AC} \tag{7}$$

In the above equations M_h and M_s are the fractional moisture contents of the monolayer and polylayer water, respectively, and M is the total fraction of moisture content (all based on the dry weight of cell wall polymer), K_1 is the equilibrium constant related to the hydrate formation from dissolved water and dry cellulose fiber material, K_2 is the equilibrium constant between dissolved water and water vapor, W is the weight of dry wood per mole of sorption sites and $1/W$ indicates the amount of sorption sites.

3.1.2 Brunauer, Emmett and Teller (BET) model

Brunauer, Emmett and Teller (BET theory) is the extended Langmuir's monolayer theory, which also considers formation of multilayers during adsorption. The BET model is used as a standard method to determine the surface area of adsorbents (Brunauer et al. 1938). The BET equation is shown below:

$$\frac{a_w}{M(1 - a_w)} = \frac{1}{M_hC} + \frac{(C - 1)a_w}{M_hC} \tag{8}$$

M_h is the moisture content in % corresponding to a mono-layer, a_w is water activity defined as (p/po), where p is the partial pressure and po is the saturation pressure of water vapor at a relevant temperature, M is the total equilibrium moisture content at a_w. The equilibrium constant C can be approximated (Moreira et al. 2008):

$$C = C_o \exp((H_M - H_N)/RT) \tag{9}$$

where H_M is the heat of adsorption of the first and H_N of the consecutive layers.

3.1.3 Guggenheim Anderson de Boer (GAB) model

GAB model has been used for predicting moisture sorption isotherms for cellulosic products. The GAB model is usually written in the form (Timmermann 2003):

$$M = M_h \times \frac{C \times K \times a_W}{(1 - K \times a_W)(1 - K \times a_W + C \times K \times a_W)} \tag{10}$$

where M is the moisture content of the material in (%), M_h is the content of water sorbed in the first layer (monolayer moisture content), a_W is the water activity (p/po), and K and C are the Guggenheim constants corresponding to the heat of sorption of the sorbed layer. C is a constant that relates to the strength of water molecule bindings to primary adsorption sites can be determined by Eq. 9, and K is related to the heat of multilayer sorption. The parameters M_h and K can also be calculated by Arrhenius equations as (Moreira et al. 2008):

$$M_h = M_{ho} \exp(\Delta H/RT) \tag{11}$$

$$K = K_o \exp((H_L - H_N)/RT) \tag{12}$$

where H_L is the average heat of condensation of water vapor and ΔH is the heat of adsorption. The parameters, H_M and H_N have the same physical meaning as in the BET model. The heat parameters: ΔH, H_M and H_N can be calculated from Eqs. (9)–(12), after extracting M_h, K and C parameters by fitting the GAB model to the experimental isotherm data.

3.2 Water vapor transport properties

At constant temperature and relative humidity gradient (ΔRH (%)), a steady state will be attained and at that condition WVTR can be directly calculated from the change in weight of the paper sample, at a specified time interval, and the area of exposed film, as described by Eq. 13:

$$WVTR = \frac{\text{Weight Change of sample}}{\text{Area} \times \text{time}} \tag{13}$$

WVTR refers to a specific sample configuration, e.g., thickness of the sample film. Water vapor permeability (WVP) can be calculated from WVTR as follows:

$$WVP = \frac{WVTR \times Z \times 100}{P^{sat} \times RH(\%)} \tag{14}$$

where Z is film thickness, P^{sat} is water vapor saturation pressure at the experimental temperature, and ΔRH (%) is percentage relative humidity gradient.

4 Results and discussion

4.1 Water vapor adsorption equilibria

Water vapor adsorption isotherms of unmodified paper (control sample) and PLA coated paper samples at three different temperatures (15, 25 and 35 °C) are shown in Fig. 1a (additional figures are available in supplementary material). All isotherms are of type IV according to IUPAC classification. It should be noted that dry, non-treated paper belongs to category of nonporous materials with typical BET surface area about 0.5 m^2/g. However in the presence of water vapor paper samples create relatively high BET areas due to swelling, e.g., over 100 m^2/g, which is a characteristic of porous materials (Bismarck et al. 2002). As expected, the equilibrium moisture content increased with an increase in relative water vapor pressure (relative humidity) at constant temperature. At the lower relative humidity, the isotherms show a rapid change, due to stronger sorbate–adsorbent interactions, leading to monolayer formation. At the intermediate relative humidities, corresponding to the multilayer sorption region, a more modest adsorption uptake increase is noticeable, whereas at higher relative humidity region, corresponding to the capillary condensation region, the adsorption uptake increases rapidly for unmodified samples. All samples generally show effects related to capillary condensation, in particular the isotherms at 15 °C. The smallest effects are observed for PLA coated paper at 35 °C, but at this temperature the experimental data at the highest RH's are most constrained (no data available beyond 90 % RH). However, even for these cases there is, at least, indication that the capillary condensation may exist (change of the slope is noticeable), except for the PLA coated sample. The absence of capillary condensation in PLA coated paper could be due to the variations in pore volume and pore size distribution of the coated paper samples (Chow et al. 1999). In addition to the pore size distribution, the shape of the vapor adsorption isotherm can also be affected by the degree of crystallinity (Parker et al. 2006; Newman 1995). Paper with high crystalline cellulose content has the lowest adsorption capacity (Ciolacu et al. 2011; Parker et al. 2006). Wadsworth and Cuculo (1978) showed, using XRD analysis, that water molecules do not penetrate the crystalline region, thus indicating that the moisture is adsorbed in the amorphous regions and on the surface of crystallites. Water vapor adsorption isotherms vary with temperature and, as expected, the moisture equilibrium content decreases with increase in temperature at the constant vapor pressure, as shown in Fig. 1a. Similar results were reported for cellulose fiber and cellulose fiber-based materials in other studies (Rhim and Lee 2009; Wahba and Nashed 1957).

The adsorption–desorption isotherms of water vapor for unmodified and PLA coated paper samples are depicted in Fig. 1b. From the figure, the existence of H3 hysteresis loops is noticeable with the adsorption and desorption branches nearly parallel for the entire range of relative humidities. The existence of this kind of hysteresis loop related to water vapor adsorption/desorption isotherms on cellulose-fiber and wood was reported by others (Hill et al. 2009; Morrison and Dzieciuch 1959). During water vapor adsorption a significant increase of the surface area occurs, due to the swelling effect of fibers leading to strong interaction of water molecules with active surface sites. This creates conditions for the hysteresis loop during desorption, e.g., the water molecules are strongly attached to the adsorption sites rendering the vapor pressure during desorption lower for the same amount of water being adsorbed during the adsorption step of isotherm measurement (Morrison and Dzieciuch 1959).

4.1.1 Hailwood–Horrobin data analysis

The ratio of humidity to the equilibrium uptake versus equilibrium uptake gives parabolic curves as shown in the Fig. 2, in accordance to the Hailwood–Horrobin (H–H) model prediction (Hailwood and Horrobin 1946). The fitting of H–H model to the experimental data for five samples is shown in the same figure. The monolayer and polylayer moisture contents of the paper samples were

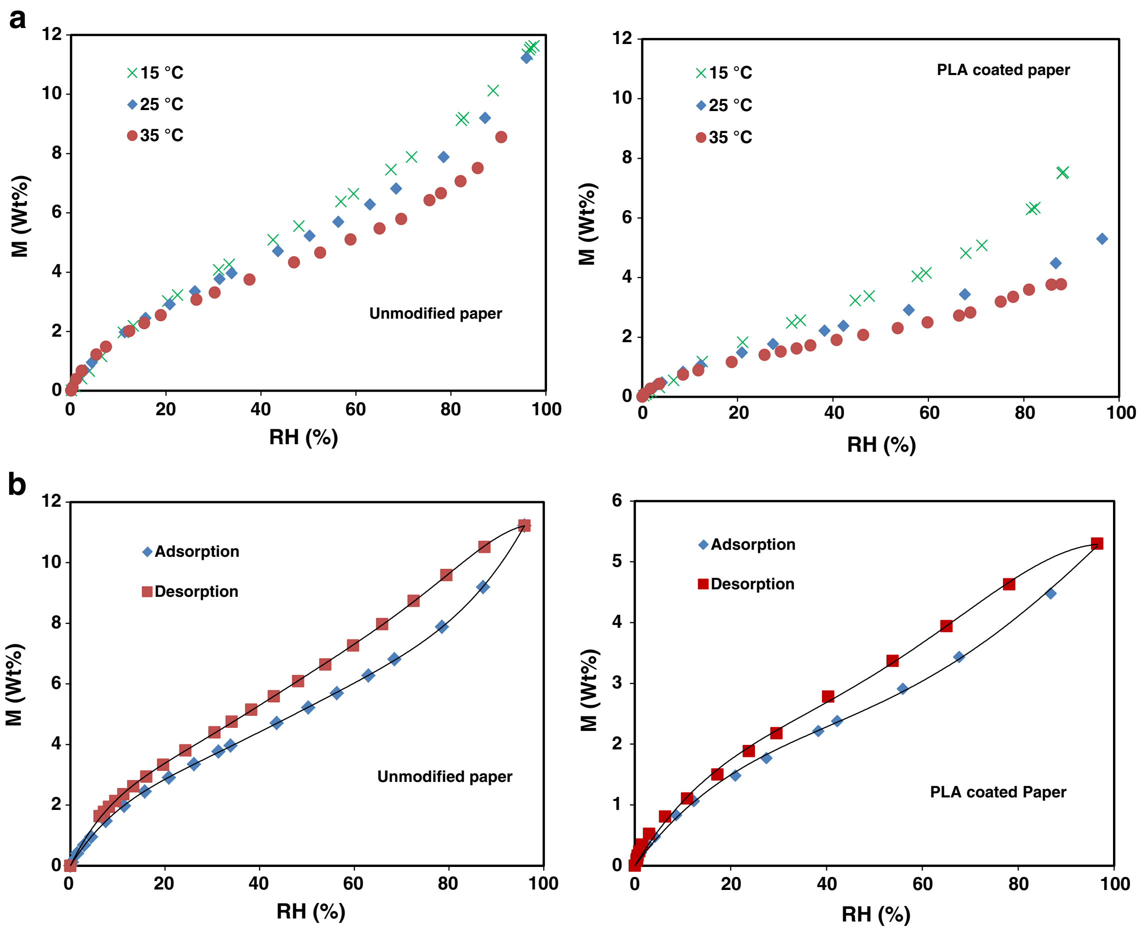

Fig. 1 **a** Adsorption isotherm of different paper samples at 15, 25 and 35 °C. **b** Adsorption/desorption isotherm of different paper samples at 25 °C

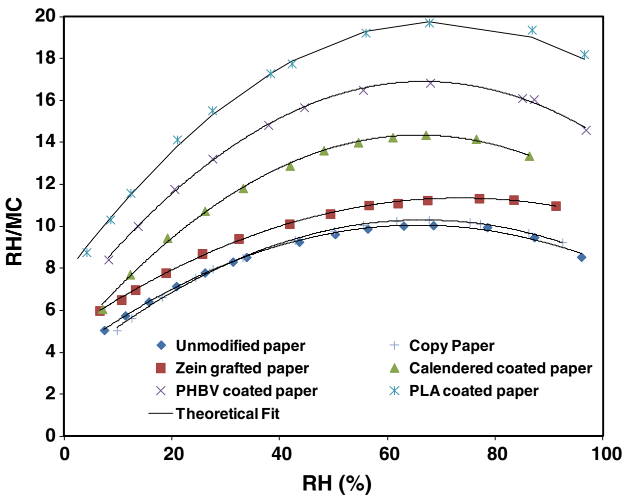

Fig. 2 Parabola predicted by H–H theory and observed experimentally

determined using the model Eqs. (1)–(5). Summary of the H–H parameters $(A, B, C,\ K_1, K_2$ and $W)$ of different investigated paper samples are provided in Table S1 of the supplementary material. The results from the H–H analysis (M_h and M_s contents) for two samples are also graphically displayed in Fig. 3 (additional diagrams are provided in Figure S2 of the supplementary material).

The total adsorbed water content is divided into monolayer and polylayer contents that are referred as hydrate and dissolved water, respectively. The results reveal that for low relative humidities (pressures), adsorption on primary sites dominates while, with increasing RH, adsorption on secondary sites (multilayer formation) gains in significance. The monolayer fraction (M_h) is of a particular interest, as it indicates the amount of water that is strongly adsorbed to specific sites. It is considered an optimum moisture content for food products, because it increases food stability and also at this condition, the rates of spoilage reactions are minimal (Moreira et al. 2008). Therefore, at a given temperature, the safest water activity level or relative humidity condition corresponds to monolayer moisture content or lower. Low monolayer moisture content (low hygroscopicity of the paper) is also beneficial in maintaining the high functionality of paper-based

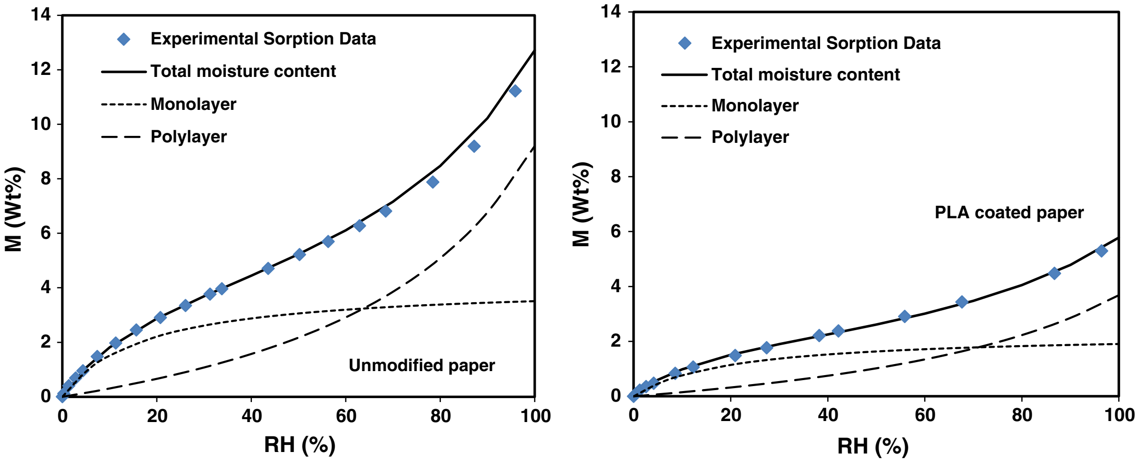

Fig. 3 Water vapor adsorption experimental data showing agreement with H–H theory of multi-stage adsorption at T = 25 °C

packaging materials. Although the H–H model cannot be used to determine moisture content due to the capillary condensation, nevertheless it provides useful information regarding the monolayer water content, i.e., strongly bound water molecules to the surface of the paper, as well as multilayer water vapor content below 80 % RH. At very high humidity (>80 % RH) conditions, the water vapor condenses in the capillary or pores of the materials. At this region, mechanism of capillary condensation plays an important role and the pore size distribution on the paper surface determines the equilibrium moisture content (Parker et al. 2006). Equilibrium moisture contents of modified paper samples were reduced at each relative humidity level compared to the untreated paper, indicating the reduction in the hygroscopicity of paper.

Table 2 and Fig. 4 summarize the results obtained by H–H theory at 25 °C. From Fig. 4, it is clear that the contribution of polylayer water is insignificant at low relative humidities, but at higher RH values ($>RH = 75$ %) the contribution is significant for all the samples. It can also be seen that the application of the PLA and PHBV on coated paper sample reduces the total sorption by 54.4 % for PLA and 45.4 % for PHBV compared to the control sample. Monolayer moisture sorption is reduced by 48.4 and 41.03 % and polylayer moisture sorption by 56.74 and 47.1 % for PLA and PHBV respectively compared to the control sample. These paper samples also show lower monomolecular sorption compared to the commercial calendered coated paper. From the H–H analyses, it can be asserted that grafting zein on the paper has no influence in reducing the monolayer moisture content. It is plausible that it does not block the primary surface groups, but only fills the pores of the paper, thus only reducing the equilibrium moisture content at higher relative humidity due to polylayer formation. In general, surface coating (using PLA and PHBV) reduces the active sites on the cellulose fibers, resulting in a significant change of monolayer moisture content. Effects of temperature on monolayer and polylayer moisture content of paper samples are explained in Section S1.3 of the supplementary material.

4.1.2 GAB model

Summary of the GAB model fittings of experimental isotherms is shown in Fig. 5. As can be clearly observed from that figure, the model provides good fits for all experimental isotherms. The largest adsorption was observed for the unmodified paper sample with moisture content of 11 wt% at RH = 96 %. It was reported in earlier studies that the equilibrium moisture content of cellulose was around 15 and 17 wt% at RH = 95 %, at 25 and 20 °C, respectively (Morrison and Dzieciuch 1959; Wahba and Nashed 1957). Rhim and Lee (2009) reported the equilibrium moisture content of kraft paper to be around 15 wt% at RH = 95 % and 25 °C. In this study, PLA and PHBV coated papers showed the lowest water vapor adsorption, e.g., equilibrium moisture contents of less than 6 wt% at RH = 96 % and 25 °C, as shown in Fig. 5. PHBV is more crystalline than PLA (Shogren 1997), and for that reason it was expected to exhibit a lower adsorption capacity than PLA coated paper; however, contrary to the expectation, this was not found in this study. The method of preparation and the hydrophilic properties of hydroxyvalerate content in the PHBV might have caused slightly higher water vapor adsorption than in the PLA coated paper. To the best knowledge of the authors, there is no information available in the open literature on the water vapor adsorption isotherms for polymer coated papers. Zein grafted and commercial copy paper showed lower vapor adsorption capacities compared to unmodified papers because the zein

Table 2 Values of monolayer (M_h) and polylayer (M_s) water derived from Hailwood Horrobin fits at 100 % relative humidity and T = 25 °C

Paper samples	Monomolecular (M_h) (%)	Polymolecular (M_s) (%)	Total ($M_h + M_s$) (%)	Total sorption percentage reduction (%)
Unmodified Paper	3.51	9.20	12.71	–
Commercial copy paper	3.42	8.39	11.81	7.10
Zein grafted paper	3.46	6.03	9.49	25.30
Calendered coated pap.	2.32	4.80	7.12	44.00
PLA coated paper	1.81	3.98	5.79	54.40
PHBV coated paper	2.07	4.87	6.94	45.40

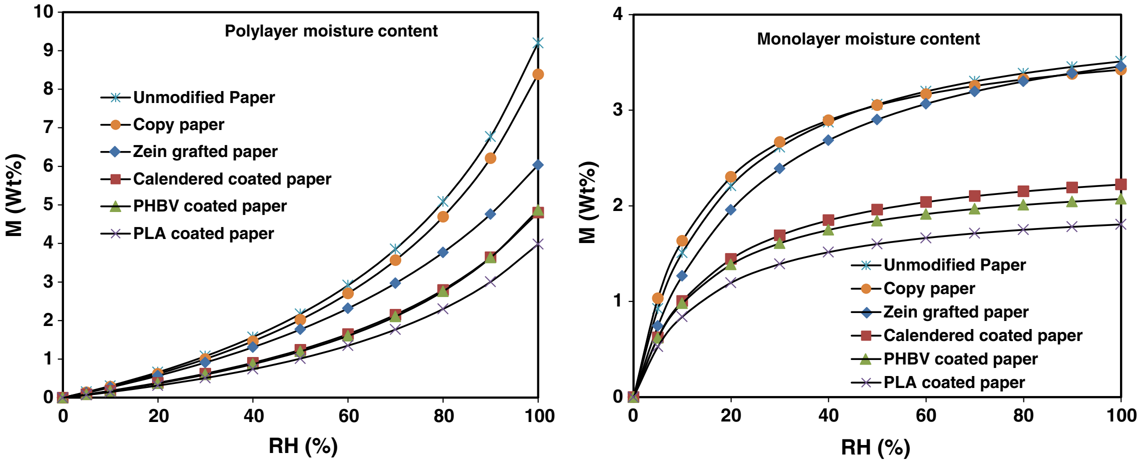

Fig. 4 Monolayer and polylayer moisture content of different paper samples at T = 25 °C

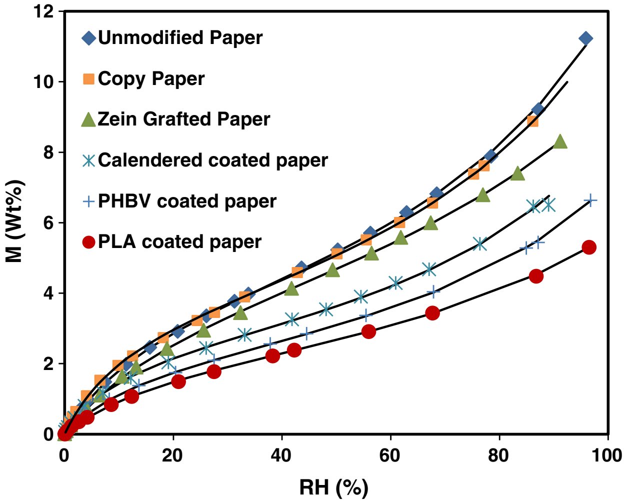

Fig. 5 Experimental data and GAB-predicted adsorption isotherms at 25 °C

in the grafted paper and calcium carbonate fillers in the copy papers contribute to the reduction of equilibrium moisture contents due to pore filling effects. On the other hand, PLA and PHBV coated papers showed the lowest adsorption capacities, i.e., the highest hydrophobicity, thus confirming that active site blocking is more effective in increasing hydrophobicity of papers than the pore filling. The addition of sizing agents and fillers, are also expected to change the pore size distribution (Kinoshita et al. 1998). Moreover, fillers tend to decrease the overall moisture content, because of their lower hygroscopicity (Newman 1995).

GAB model was also used to determine monolayer moisture content (M_h). From the model analysis, PHBV and PLA coated paper showed the lowest monolayer moisture content values. Monolayer moisture content and extracted constant parameters (K and C) are provided in Table S2 of the supplementary material. According to the GAB model, the monolayer moisture content of zein grafted paper is higher than the unmodified (control) sample. On the other hand, according to H–H model, almost the same monolayer water content was obtained for both of the above referenced samples, as shown in Table 2. The M_h values obtained using GAB model for the control samples is similar to mould fiber (untreated cellulose) at 25 °C as reported by Sorensen and Hoffmann (2003).

4.1.3 *Comparison of models*

Table 3 shows comparison of H–H, GAB and BET models that were used to determine the monolayer moisture contents from the experimental isotherms. GAB model revealed comparatively higher monolayer moisture contents than others, while BET showed the lowest monolayer moisture contents for all samples. Timmermann (2003) reported that the GAB model always over predicts monolayer content compared to the BET model, and provided mathematical expression and physical reasons for the difference. The inequalities of the monolayer values are due to the effect of constant parameter (K) that measures the difference between the standard chemical potentials of the molecules in the second sorption level and in the pure liquid state (Brunauer et al. 1969; Timmermann 2003). The GAB equation reduces to the BET equation when $K = 1$, but when K is less than 1, a higher sorption is predicted than by the BET model. The other GAB constant, denoted by C, are energy constant but with slightly different physical meanings compared to the BET constant, C. The BET constant, C, is related to the difference between the chemical potential of the sorbate molecules in the pure liquid state and in the monolayer sorption. On the other hand, the GAB constant, C, is related to the difference of this magnitude in the upper layers and in the monolayer, while the constant K is related to this difference in the sorbate's pure liquid state and in the upper layers. The BET model generally has a difficulty to fit the isotherm data at the higher water vapor pressures (humidities) due to the formation of multi-layers. The GAB model is generally considered to provide better reproducibility of isotherm data and evaluation of the amount of water tightly bound to the primary adsorption sites (Timmermann 1989, 2003). The obtained monolayer moisture values from H–H model were also higher than BET model but slightly lower than GAB model as shown in Table 3. In general, the GAB and H–H models can be recommended as the best models from this study for fitting experimental isotherm data in order to determine the monolayer moisture content. Based on the BET theory, a monolayer of immobilized water molecules is completed well before relative pressure of 0.5 is reached, after which an upward deviation is observed. In this study, monolayer moisture contents were done from the analysis of experimental data up to the relative pressures of 0.5. The BET monolayer water content for cellulose was also found to be 3.19 % (Morrison and Dzieciuch 1959).

4.2 Water vapor transport properties

Table 3 Comparison of monolayer moisture contents derived from H–H, BET and GAB models

Paper samples	H–H model (M_h) (%)	BET-model (M_h) (%)	GAB model (M_h) (%)
Unmodified paper (Control)	3.51	3.27	4.12
Commercial copy paper	3.42	2.99	3.38
Zein grafted paper	3.46	2.36	4.32
Calendered coated pap. (Commercial)	2.32	2.03	2.70
PLA coated paper	1.81	1.57	2.29
PHBV coated paper	2.07	1.79	2.44

Water vapor transmission rates (WVTR's) of unmodified and coated paper samples at temperatures of 25 and 38 °C (corresponding to standard tropical condition) were calculated for different relative humidity gradients using Eq. 13. The summary of results is shown in Table 4. As expected, WVTR's are dependent on the relative humidity difference (driving force) and temperature. Zein grafted paper samples showed lower WVTR than reference sample, but higher WVTR value than coated paper samples. Zein grafting facilitates the closing of surface pores in the fiber network but does not have significant effect in reducing water solubility in the sample, as discussed in the previous section. The surface coating of papers (using PLA and PHBV) decreases WVTR's much more than using filler (zein) alone. It is plausible that coating plays a significant role in reducing both water vapor solubility and mobility (diffusion) in the modified samples. PHBV coated samples showed much lower WVTR's than other paper samples. Shogren (1997) reported that the WVTR's values of PLA and PHBV films are 172 and 21 g/m^2/day at T = 25 °C and ΔRH = 100 %, respectively. The WVTR's values of PLA and PHBV coated paper films found in this study were higher than the values reported for the pure PLA and PHBV films. This is probably due to the deficiency of continuous film formation during coating process and possibly using thinner films for the coatings. The percentage of crystallinity in the film also affects the water vapor transmission rate. Shogren (1997) and Tsuji et al. (2006)showed that WVTR's decreases with increased crystallinity of the film. The WVTR's decreases monotonically with increased in crystallinity from 0 to 20 % and levels off when crystallinity exceeds 30 %. They suggested that the change was due to the higher resistance of restricted amorphous regions to water vapor permeation compared to the free amorphous regions. According to Thygesen et al. (2005), the cellulose crystallinity from wood based fibers ranged between 60 and 70 % of cellulose content and the crystallinity of the filter paper was 57 % of the sample weight.

Water vapor permabilities (WVP's) of unmodified and coated samples at 25 and 38 °C were calculated using Eq. 14. Figure 6 shows the WVP's of the samples at different relative humidity gradients (ΔRH). As can be seen from the figure, WVP's increase slightly with the temperature. They stay relatively constant at lower relative

Table 4 WVTR, normalized to Z = 100 μm, and permeabilities (WVP) of different paper sample films at P = 100 kPa and T = 25 & 38 °C

Paper samples	WVTR (g/m^2 day) (25 °C)			WVTR (g/m^2 day) (38 °C)		
	ΔRH = 33 %	ΔRH = 50 %	ΔRH = 90 %	ΔRH = 33 %	ΔRH = 50 %	ΔRH = 90 %
Unmodified paper (60 g/m^2)	190	257	822	536	1600	2473
Calendered coated paper (commercial)	127	187	550	322	209	1275
Zein grafted paper	–	143	335	–	–	1800
PLA coated paper	58	95	250	99	189	647
PHBV coated paper	11	22	82	196	78	196

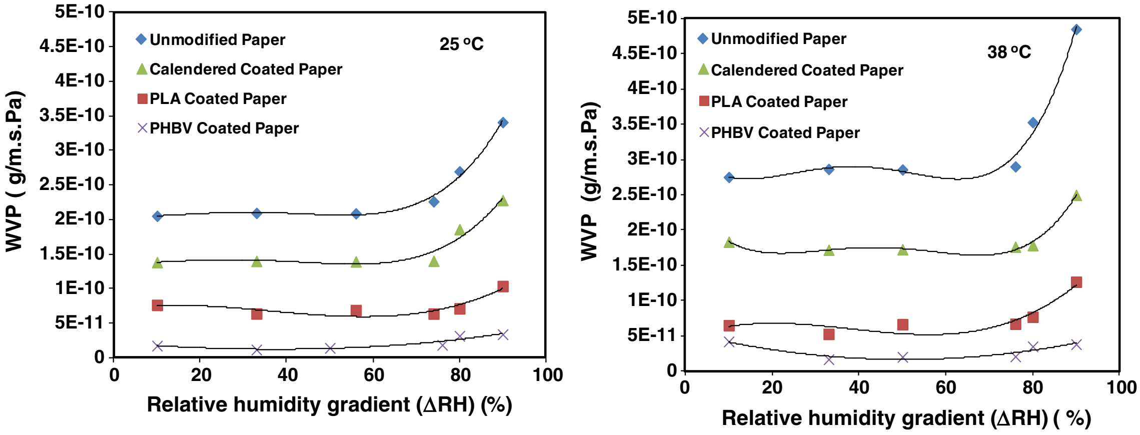

Fig. 6 WVP of different paper samples at 25 and 38 °C

humidity gradients, but at the higher gradients, the WVP's showed upward trends. This can be due to the dependency of diffusivity on moisture content of the sample and/or different transport mechanisms prevalent at different RH's, as reported in our previous study (Bedane et al. 2012). At the lower RH region, molecular and/or Knudsen diffusion mechanism controls the water vapor transport behavior in the pores of the cellulose network, and the diffusivity is nearly independent of the moisture content of the sample. However, as the relative humidity increases, the surface diffusivity becomes the dominant transport mechanism, and the diffusivity increases consequently by reaching the maximum value, after which it starts to decrease due to formation of water vapor cluster at the higher humidity, as reported in our previous study (Bedane et al. 2012). According to the solution-diffusion (S-D) theory, which was proposed for the water vapor permeability through paper samples (films), permeability depends on both the solubility and diffusivity of water vapor. PHBV coated paper exhibits lower water vapor permeability than PLA coated paper, as can be seen from Fig. 6, even though the PHBV coated paper has higher water adsorption capacity than its PLA counterpart, i.e., higher solubility, as discussed in the Sect. 4.1 and shown in Fig. 5. This result could be interpreted by applying the combined solution-diffusion effect, as per the S-D theory, for the case when diffusivities of water vapor through these films are more dominant than their solubilities (Bedane et al. 2012).

Moreover, PHBV and PLA coated paper samples showed much lower water vapor permeability than unmodified and commercial calendered coated paper samples, as also shown in Fig. 6. Their permeability values are slightly higher than for the pure PHBV and PLA films, as reported by Tsuji et al. (2006), who found the WVP's of PLA films in the range of 1.69–2.08 × 10^{-11} g/m s Pa, and Sanchez-Garcia et al. (2008), who found the WVP's of PHBV films in the range of 0.32–1.27 × 10^{-11} g/m s Pa. This is expected due to less hydrophilic nature of PHBV and PLA films compared to the overall hydrophilicity of PHBV and PLA coated paper samples, and it also depends on the coating film thickness of the paper samples. The water vapor permeabilities of amorphous PLA and PHBV films vary from 1.8 to 2.3 × 10^{-11} g/m s Pa and 1.0 to 2.0 × 10^{-11} g/m s Pa at 25 °C, respectively, which are equivalent to PLA and PHBV coated papers (Sanchez-Garcia et al. 2008; Kalia and Avérous 2011; Tsuji et al. 2006; Siparsky et al. 1997). WVP's of zein coated paper was found in this study to be 1.35 × 10^{-10} g/m s Pa at

T = 25 °C and ΔRH = 90 %, which is higher than for PLA and PHBV coated paper samples. However, WVP of zein coated paper from this study is lower than for pure starch films, which was reported in other studies to be in the range of 3–117 × 10^{-10} g/m s Pa (Bertuzzi et al. 2007; Ryu et al. 2002). This could be due to the strong hygroscopicity of starch films. The solubility of water in the starch film is also higher than in cellulose fiber, as reported by Bertuzzi et al. (2007).

5 Conclusions

The sorption behavior of different modified paper samples was determined from their water vapor adsorption isotherms at 15, 25 and 35 °C. The type II isotherms measured experimentally at 25 °C were mathematically modeled using H–H, GAB and BET equations. The monolayer moisture content of each sample was determined from these models. The values of monolayer moisture content, obtained from the H–H and GAB model fittings of the experimental data, are in the close agreements for all paper samples investigated in this study and are recommended as the best models for monolayer water vapor determinations. The isotherm, according to the H–H model, can be conveniently divided into monolayer and polylayer parts for a given relative humidity. From that analysis, it was shown that zein grafted paper did not exhibit reduction in the monolayer moisture content, but showed decreased multilayer moisture content when compared to unmodified (reference) paper sample. The monolayer moisture contents of PLA and PHBV coated paper samples are lower compared to unmodified paper samples and commercial calendered coated samples. The application of the PLA and PHBV films on coated paper samples reduce the total sorption by 54.4 and 45.4 %, respectively compared to the control sample, clearly indicating that coating has to be implemented on the substrate to obtain superior barrier properties. The amount of sorption (formation of monolayer and polylayer moisture contents) decreases as the temperature increases, in particular for the monolayer moisture contents. At low relative humidities (vapor pressures), adsorption on primary sites dominates, while with increasing RH above 75 % adsorption on secondary sites (multilayer formation) gains in significance.

WVP's of unmodified and coated paper samples at the temperatures of 25 and 38 °C were calculated from WVTR's, which were measured at a wide range of vapor partial pressure gradients. PHBV and PLA coated paper samples showed much lower WVP's than unmodified and commercial calendered coated paper samples. The water vapor permeabilities for different samples were found to be relatively constant up to the modest relative humidity levels; however, at the higher levels they showed an increasing trend. This behavior is attributed to an increase in the surface diffusivities of water vapor at the higher moisture contents according to the solution-diffusion theory.

Based on the overall investigation performed in this study PHBV and PLA coated paper samples showed the best barrier properties to water vapor and could be considered the most appropriate candidates for packaging applications.

Acknowledgments The authors gratefully acknowledge financial support from Natural Sciences and Engineering Research Council of Canada (NSERC) Strategic Green Fiber Network program. We also thank Dr. Xiao's graduate students, Mr. Madjid Farmahini-Farahani and Ms. Zhaoping Song for preparation of the samples in the UNB Limerick pulp and paper laboratory. Last but not least, our thanks are due to Mr. Nikola Mijatovic, the summer student, who was assisting us in the experimental work during the course of this project.

References

Andersson, C.: New ways to enhance the functionality of paperboard by surface treatment—a review. Packag. Technol. Sci. (2008). doi:10.1002/pts.823

Ashely, R.J.: Permeability and plastic packaging. In: Comyn, J. (ed.) Polymer Permeability, pp. 269–308. Elsevier Applied Science, London (1985)

ASTM Standard E96/E96M-05: Standard test methods for water vapor transmission of materials: ASTM International, West Conshohocken, PA, USA (2005). doi: 10.1520/E0096_E0096M-05

Bedane, A.H., Qinglin, H., Xiao, H., Eić, M.: Mass transfer of water vapor, carbon dioxide and oxygen on modified cellulose fiber-based materials. J. Nord. Pulp Pap. Res. **27**(2), 409–417 (2012)

Bertuzzi, M.A., Castro Vidaurre, E.F., Armada, M., Gottifredi, J.C.: Water vapor permeability of edible starch based films. J. Food Eng. **80**, 972–978 (2007)

Bismarck, A., Aranberri-Askargorta, I., Springer, J.: Surface characterization of flax, hemp and cellulose fibers; surface properties and the water uptake behavior. Poly. Compos. **23**(5), 872–894 (2002)

Brunauer, S., Emmett, P., Teller, E.: Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. **60**, 309–319 (1938)

Brunauer, S., Skalny, J., Bodor, E.E.: Adsorption on nonporous solids. J. Colloid Interface Sci. **30**, 546–552 (1969)

Ciolacu, D., Ciolacu, F., Popa, V.I.: Amorphous cellulose—structure and characterization. Cellul. Chem. Technol. **45**, 13–21 (2011)

Chow, G.-M., Ovid'ko Ilya, A., Tsakalakos, T.: Nanostructured films and coatings, vol. 78, pp. 55–61. Kluwer Academic Publisher, The Netherlands, (1999)

Del Nobile, M.A., Baiano, A., Benedetto, A., Massignan, L.: Respiration rate of minimally processed lettuce as affected by packaging. J. Food Eng. **74**, 60–69 (2006)

Hailwood, A., Horrobin, S.: Absorption of water by polymers: analysis in terms of a sample model. Trans. Faraday Soc. **42B**, 84–102 (1946)

Hill, C.A.S., Andrew, N., Gary, N.: The water vapor sorption behavior of natural fibers. J. Appl. Polym. Sci. **112**, 1524–1537 (2009)

Kalia, S. and Avérous, L.: Characteristics and Applications of Poly (lactide). Biopolymers: Biomedical and Environmental applications, pp.183-224. Scrivener Publishing LLC, Salem, Massachusetts, (2011)

Kinoshita, N., Noda, H., Toyotake, Y., Katsuzawa, H.: The effects of filler contents and beating on the porous structure of high-filler-containing papers. Sen'I Gakkaishi **54**(1), 46–53 (1998)

Koide, S., Shi, J.: Microbial and quality evaluation of green peppers stored in biodegradable film packaging. Food Control **18**, 1121–1125 (2007)

Kuusipalo, J.: PHB/V in extrusion coating of paper and paperboard-study of functional properties (Part-II). J. Polym. Environ. **8**, 49–57 (2000)

Moreira, R., Chenlo, F., Torres, M.D., Vallejo, N.: Thermodynamic analysis of experimental sorption of loquat and quince fruit. J. Food Eng. **88**, 514–521 (2008)

Morrison, J.L., Dzieciuch, M.A.: The thermodynamics properties of the system cellulose–water vapor. Can. J. Chem. **37**, 1379–1390 (1959)

Newman, R.H.: Adsorbed and Absorbed Moisture in Bleached KRAFT Pulp. Industrial Research Ltd., Lower Hutt (1995)

Parker, M.E., Bronlund, J.E., Mawson, A.J.: Moisture sorption isotherms for paper and paperboard in food chain conditions. Packag. Technol. Sci. **19**, 193–209 (2006)

Rhim, J.-W., Lee, J.-H., Hong, S.-I.: Increase in water resistance of paper board by coating with poly (lactide). Packag. Technol. Sci. **20**, 393–402 (2007)

Rhim, J.-W., Lee, J.H.: Thermodynamics analysis of water vapor sorption isotherms and mechanical properties of selected paper-based food packaging materials. J Food Sci. **74**, 502–511 (2009)

Ryu, S.Y., Rhim, J.W., Roh, H.J., Kim, S.S.: Preparation and physical properties of zein-coated high-amylose corn starch film. Food Sci. Technol. **35**, 680–686 (2002)

Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M.: Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. Carbohydr. Polym. **71**, 235–244 (2008)

Shogren, R.: Water vapor permeability of biodegradable polymers. J. Environ. Polym. Degrad. **5**, 91–95 (1997)

Simpson, W.: Sorption theories applied to wood. Wood Fiber **12**, 183–195 (1980)

Siparsky, G.L., Voorhees, K.J., Dorgan, J.R., Schilling, K.: Water transport in polylactic acid (PLA), PLA/polycaprolactone copolymers, and PLA/polyethylene glycol blends. J. Environ. Polym. Degrad. **5**, 125–136 (1997)

Skaar, C.: Wood–Water Relation. Springer, Berlin (1988)

Sorensen, G., Hoffmann, J.: Moisture sorption in moulded fibre trays and effect on static compression strength. Packag. Technol. Sci. **16**, 159–169 (2003)

Spalt, H.A.: The fundamentals of water vapor sorption by wood. For. Prod. J. **8**, 288–295 (1958)

Timmermann, E.O.: A B.E.T.-like three sorption stage isotherm? J. Chem. Soc. Faraday Trans. **85**, 1631–1645 (1989)

Timmermann, E.O.: Multilayer sorption parameters: BET or GAB values? Colloids Surfaces A **220**, 235–260 (2003)

Timmermann, E.O., Chirife, J., Iglesias, H.A.: Water sorption isotherms of foods and food stuffs: BET or GAB parameters? J. Food Eng. **48**, 19–31 (2001)

Thygesen, A., Oddershede, J., Lilholt, H., Thomsen, A.B., Stahl, K.: On the determination of crystallinity and cellulose content in plant fibres. Cellulose **12**, 563–576 (2005)

Tsuji, H., Okino, R., Daimon, H., Fujie, K.: Water vapor permeability of Poly (lactide)s: effect of molecular characteristic and crystallinity. J. Appl. Polym. Sci. **99**, 2245–2252 (2006)

Twede, D. and Selke, S.E.M.: Cartons, Crates and Corrugated Board. Handbook of Paper and Wood packaging Technology. DEStech Publications, Inc., Lancaster (2005)

Wadsworth, L.C., Cuculo, J.A.: Determination of accessibility and crystallinity of cellulose. In: Rowell, R.M., Young, R.A. (eds.) Modified cellulosics, pp. 117–196. Academic Press Inc, New York (1978)

Wahba, M., Nashed, S.: Moisture relations of cellulose. III. Sorption hysteresis and the effect of temperature. J. Text. Inst. Trans. **48**, 1–20 (1957)

Yamada, K., Noguchi, A., Takahashi, H.: Effects of the solvents on properties of zein. Nippon Shokuhin Kagaku Kaishi **43**, 306–312 (1996)