



Analysis of Water Adsorption on Chitosan and Its Blends with Hydroxypropylcellulose

Maria Mucha,^{1*} Kazimierz Wańkowicz,¹ Jacek Balcerzak¹

¹ Faculty of Process and Environmental Engineering, Technical University of Lodz ul. Wólczajska 213, 93-005 Lodz, Poland. Fax: +48-42-6365-663. E-mail: muchama@wipos.p.lodz.pl

(Received: 10 October, 2006; published: 7 February, 2007)

Abstract: Chitosan (CH) and hydroxypropylcellulose (HPC) adsorb water easily by hydrogen bonds formed with hydroxyl and amide groups present in their structures. Heat of adsorption is a thermodynamic parameter which is used to estimate the type of adsorbate molecule bond on a solid surface, among the others. Adsorption of water from vapour phase on chitosan, hydroxypropylcellulose and blends of both biopolymers in the form of films were carried out. Isotherms of water adsorption in the samples were described by the GAB equation. Correlations between mass fraction of chitosan in the sample (w_i) and the values of GAB coefficients were obtained. From parameter c in the GAB equation mean heat of adsorption of the first monomolecular layer of water molecules E_1 , and pure molar heat of adsorption q were determined.

Introduction

Chitosan (CH) is characterized by many valuable properties, first of all biodegradability, bioactivity, biocompatibility and non-toxicity. Additionally, it has very good adhesive properties and ability to sorb, chelate and bind metal ions and organic substances [1]. Bioactivity of chitosan is confirmed by binding of pathogenic bacteria or substances necessary for bacterial growth, biocompatibility with living cells, reduction of cholesterol content in serum, or agglutination of red blood cells. Chitosan hampers viral infections and growth of certain fungi, and also induces the synthesis of plant enzymes. Moreover, it can absorb and bind water [2]. The advantages of chitosan led to numerous applications of this polymer in various branches of industry [3], medicine [4-6], agriculture [7-8] and environmental protection [9-10]. Chitosan usually shows good miscibility with other water-soluble polymers. Particularly interesting is its good miscibility with another polysaccharide – cellulose and its derivatives, in this particular case hydroxypropylcellulose (HPC) [11]. The blends of chitosan and HPC in the form of water solutions, find application in paper impregnation [12].

Water adsorbed on pore surface of a macromolecule has an essential impact on its physical properties and causes hydrolysis of polymer chains. The presence of water molecules in the structure simplifies enzymes diffusion, which leads to polymer biodegradation. Depending on the type of water binding with a material, the thermal effect of adsorption process is different. Studies on water adsorption on polymeric materials and also an amount of heat of this process are useful in the determination of macromolecule structures and also in drying technologies of biomaterials.

In literature [13-14] there are many equations describing isotherms of water adsorption by biomaterials. A generally used equation that describes a multi-layer adsorption of vapours or gases was derived by Brunauer, Emmett and Teller (the BET equation) [15]:

$$\frac{X}{X_m} = \frac{c \cdot a_w}{(1 - a_w) \cdot [1 + (c - 1) \cdot a_w]} \quad (1)$$

where:

X – equilibrium content of adsorbate in the dry mass (d.m.) of adsorbent [$\text{kg}_{\text{adsorbate}}/\text{kg}_{\text{d.m.}}$]; X_m – amount of adsorbate forming a complete monomolecular layer on the adsorbent surface [$\text{kg}_{\text{adsorbate}}/\text{kg}_{\text{d.m.}}$]; c – parameter related to the heat of adsorption; a_w – water activity, i.e. a relative humidity over a sample (dimensionless)

The model of adsorption proposed by Brunauer, Emmett and Teller holds for water activity ranging from 0.05 to 0.35 (sometimes to $a_w = 0.5$). Above this limit the BET equation loses applicability because of capillary condensation which takes place beside physical adsorption.

Anderson [16] modified the BET equation to increase its applicability. By introducing additional coefficient k , Anderson obtained an equation that became a prototype of the model of sorption, known generally as GAB (Guggenheim, Anderson, de Boer):

$$\frac{X}{X_m} = \frac{c \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot [1 + (c - 1) \cdot k \cdot a_w]} \quad (2)$$

where:

$k = e^{d/RT}$ – GAB parameter correcting the real value of water activity, related to thermal effect of adsorption, can assume values ranging from 0 (for $d \rightarrow -\infty$) to 1 (for $d = 0$); d – energy needed to transport the mole of adsorptive into the few layers of adsorbed molecules which are on the adsorbent surface [kJ/mol]; The GAB model describes sigmoidal isotherms (II BET type) at water activity up to around 0.9. It has been successfully applied to describe water adsorption on chitosan-based blend films [17-18] and other biopolymers [19-20].

Many definitions of the heat of adsorption result from different methods for the determination of thermal effect of the process and conditions in which the adsorption takes place.

According to the BET theory based on the model multi-layer adsorption, on the monomolecular adsorbate layer formed with a release of adsorption heat (E_1), condensation of subsequent gas layers with heat equal to the heat of gas condensation (E_L) is possible:

$$E_2 = E_3 = \dots = E_i = E_L \quad (3)$$

The behaviour of each separate adsorbed layer corresponds to Langmuir's concept of the localised adsorption and lack of interactions between adsorbate molecules.

Parameter c in the BET (and GAB) equation is used to calculate the mean heat of adsorption of the first layer of gas molecules (E_1):

$$c = \frac{a_1 \cdot b_2}{b_1 \cdot a_2} \cdot e^{(E_1 - E_L)/RT} \quad (4)$$

where:

a_1, a_2, b_1, b_2 – constants related to adsorption/desorption of water molecules.

The term $\frac{a_1 \cdot b_2}{b_1 \cdot a_2}$, called the entropy factor, is close to unity, hence, the formula for pure molar heat of adsorption (q), corresponding to the difference of the heat of adsorption in the first layer and molar heat of condensation of adsorptive vapours, is as follows:

$$q = E_1 - E_L = R \cdot T \cdot \ln(c) \quad (5)$$

where:

$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ – gas constant; T – temperature of adsorption [K].

When transforming adsorption isotherms prepared for the process at different temperatures into isosteres in $\ln(a_w)=f(1/T)$ system, the so-called isosteric heat of adsorption can be determined using the Clausius-Clapeyron equation [21]. Results of the calculation of isosteric heat of water adsorption by CH/HPC films are given in a previous study [22].

Chitosan (CH) and hydroxypropylcellulose (HPC) as high-molecular polysaccharides adsorb water easily by hydrogen bonds formed with hydroxyl and amide groups present in their structures. The aim of this research was to analyse adsorption of water from vapour phase on blends of chitosan and hydroxypropylcellulose in the form of films. Studies of the influence of CH/HPC blend composition and process temperature on thermal effect of water adsorption are also presented in this paper.

Results and Discussion

In the description of experimental data for water sorption from vapour phase at different water activities determined by the gravimetric method, the GAB model was used. Experimental data represented by the amount of adsorbed water vapour (X) at given water activities (a_w) were introduced to the linear form of the isotherm equation:

$$\frac{a_w}{X \cdot (1 - k \cdot a_w)} = \frac{1}{X_m \cdot c \cdot k} + \frac{c - 1}{X_m \cdot c} \cdot a_w \quad (6)$$

Coefficients $\frac{c - 1}{X_m \cdot c}$ and $\frac{1}{X_m \cdot c \cdot k}$ in equation (6) were determined by means of linear regression method, and next the values of X_m and c were defined. Coefficient k was assumed using the iterative selection method in the range $0.24 < k \leq 1$, for every water-adsorbent system separately.

Table 1 gives the coefficients of GAB equation determined in the above method for particular water-polymer film systems. Water adsorption isotherms obtained for CH/HPC blends of compositions given in Table 1 are presented elsewhere [22-24] and in Fig. 1A. Variation of parameters X_m and c with changes in the polymer film composition is described by linear relations (Figs. 1 and 2).

The following equations describing the linear dependence of parameter X_m on polymer film composition were obtained for the analysed temperatures:

$$T = 25^\circ\text{C}: \quad X_{m25} = 0.043 \cdot w_f + 0.026 \quad (7)$$

$$T = 45^\circ\text{C}: \quad X_{m45} = 0.040 \cdot w_f + 0.020 \quad (8)$$

Dependence of parameter c on polymer film composition (w_f) is described by the equations:

$$T = 25\text{ }^{\circ}\text{C}: \quad c_{25} = 46.5 \cdot w_f + 2.5 \quad (9)$$

$$T = 45\text{ }^{\circ}\text{C}: \quad c_{45} = 59.7 \cdot w_f + 2.1 \quad (10)$$

Tab. 1. Coefficients in the GAB adsorption isotherm equation.

Sorption temperature	Sample characteristic	k	X_m [kg _{H2O} /kg _{d.m.}]	c
25°C	HPC	0.90	0.028	3.4
	CH/HPC/0.2	0.89	0.034	8.5
	CH/HPC/0.4	0.88	0.039	23.8
	CH/HPC/0.6	0.85	0.053	30.4
	CH/HPC/0.8	0.87	0.058	40.3
	CH	0.86	0.071	48.0
45°C	HPC	0.93	0.019	3.9
	CH/HPC/0.2	0.82	0.031	9.1
	CH/HPC/0.4	0.82	0.034	27.8
	CH/HPC/0.6	0.83	0.041	40.1
	CH/HPC/0.8	0.83	0.050	50.9
	CH	0.84	0.062	59.9

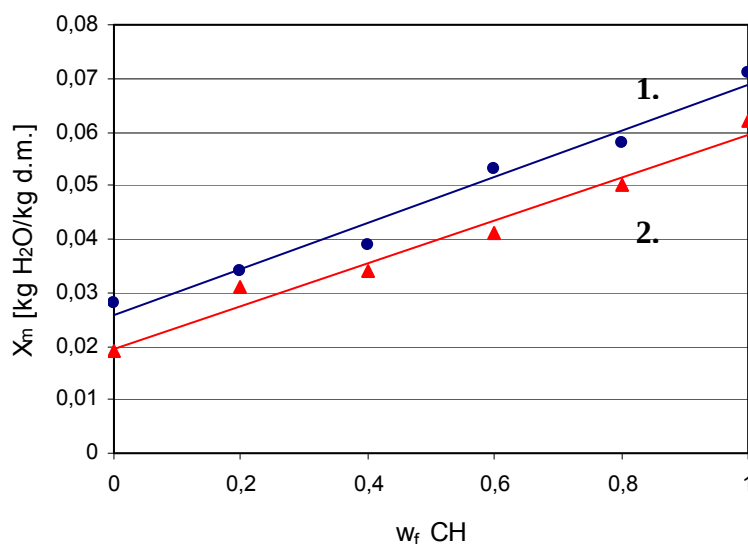


Fig. 1. Dependence of parameter X_m in the GAB equation on blend composition (1. $T=25^{\circ}\text{C}$, 2. $T=45^{\circ}\text{C}$); points – experimental data; lines – function $X_m=f(w_f)$; w_f – mass fraction of chitosan in the blend; d.m. – dry mass.

For water adsorption on CH/HPC blends at two analysed temperatures, the mean value of parameter k was determined. In determination of k_{av} the values of this coefficient corresponding to water adsorption on HPC films were neglected; these values differ significantly from other ones. This is caused most probably by good

solubility of HPC in water. The adsorbed water changes the structure of HPC film and causes its swelling. The values of parameter k of the GAB equation obtained in this way are given in Table 2.

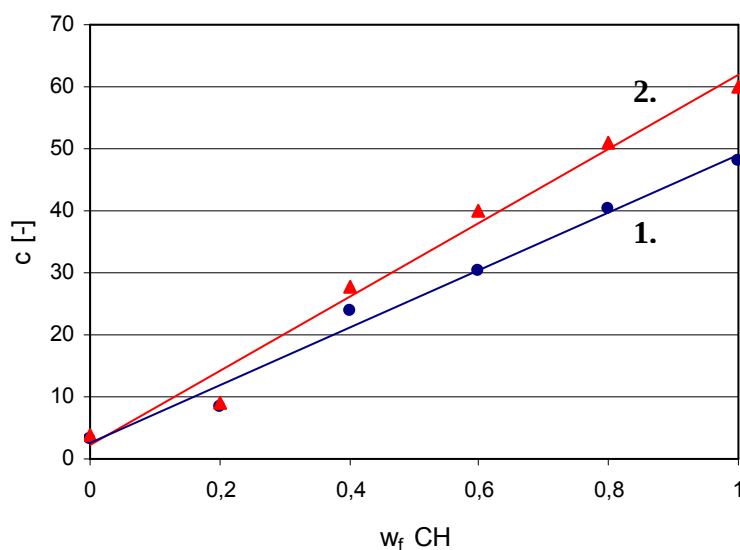


Fig. 2. Dependence of parameter c in the GAB equation on blend composition (1. $T=25$ °C, 2. $T=45$ °C); points – experimental data; lines – functions $c=f(w_f)$; w_f – mass fraction of chitosan in the blend.

Tab. 2. Values of coefficient k in the GAB equation.

Sorption temperature	k_{HPC}	k_{av}
25 °C	0.90	0.87
45 °C	0.93	0.83

k_{HPC} – for water adsorption on HPC;

k_{av} – arithmetic mean calculated for water adsorption on CH and CH/HPC blends.

Next, the GAB equation describing the isotherms of water adsorption on films made from chitosan and its blends with HPC was modified by substituting coefficients X_m and c by chitosan mass fraction in the blend (w_f) according to equations (7)-(10), assuming the values of k_{av} in Table 4. The following relations $X = f(a_w, w_f)$ were obtained for two temperatures:

$T = 25$ °C:

$$X^{25} = \frac{(1,74 \cdot w_f^2 + 1,15 \cdot w_f + 0,06) \cdot a_w}{(1 - 0,87 \cdot a_w) \cdot (1 + (40,46 \cdot w_f + 1,31) \cdot a_w)} \quad (11)$$

$T = 45$ °C:

$$X^{45} = \frac{(1,98 \cdot w_f^2 + 1,06 \cdot w_f + 0,03) \cdot a_w}{(1 - 0,83 \cdot a_w) \cdot (1 + (49,55 \cdot w_f + 0,91) \cdot a_w)} \quad (12)$$

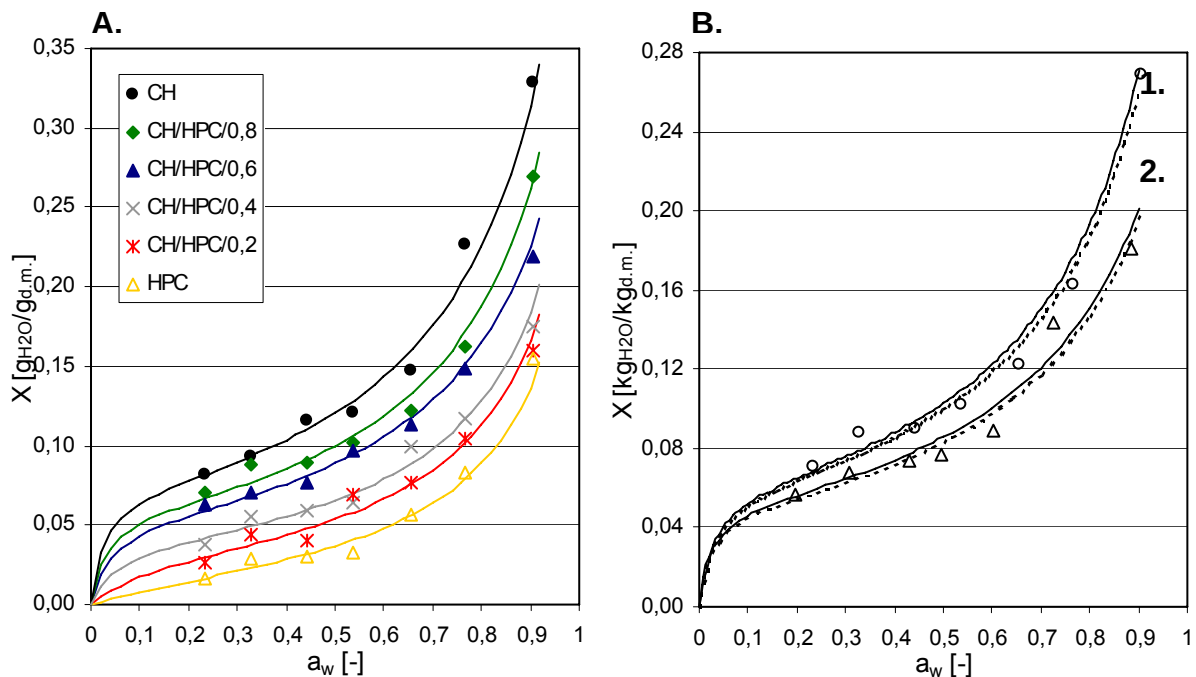


Fig. 3. Water adsorption isotherms for CH/HPC blends: **A.** at $T=25^\circ\text{C}$, experimental results [22]. **B.** sample CH/HPC/0.8 (1. $T=25^\circ\text{C}$, 2. $T=45^\circ\text{C}$); points – experimental data; broken lines – curves from GAB linearization; solid lines – functions $X = f(a_w, w_f)$ Eq. (12) and (13); d.m. – dry mass.

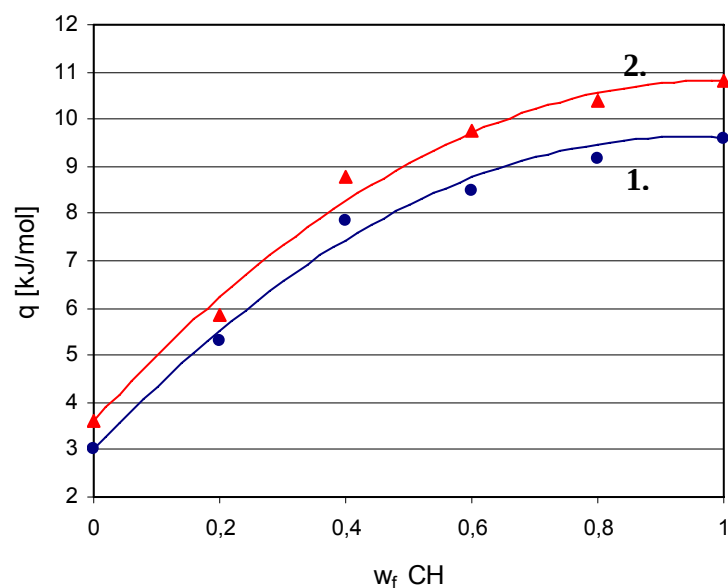


Fig. 4. Dependence of pure molar heat of water adsorption (q) on blend composition, at the temperatures 25°C (1.) and 45°C (2.); points – values calculated from equation (5), lines – function $q=f(w_f)$; w_f – mass fraction of chitosan in the blend ($w_f=0$ is pure HPC, $w_f=1$ is pure CH).

As follows from Fig. 3B (an example of one blend, adsorption at both temperatures), with equations (11) and (12) one can describe with acceptable accuracy the

adsorption of water on chitosan blends with HPC containing various mass fractions of components.

Results of calculation of q and E_1 from parameter c in the GAB equation, at both temperatures 25 °C and 45 °C, according to equation (5) are presented in the form of functions $q = f(w_f)$ and $E_1 = f(w_f)$ in Figs. 4 and 5. Curves shown in Fig. 4 indicate that pure molar heat of water adsorption q increases with the temperature growth. A bigger effect of temperature on q values can be observed when water is adsorbed on blends with a prevailing weight fraction of chitosan (w_f). Mean heat of adsorption of the first layer of water molecules (E_1) attains values close to these of CH/HPC blends up to fraction $w_f = 0.5$ at both analysed temperatures (Fig. 5). Above this value the curves become divergent.

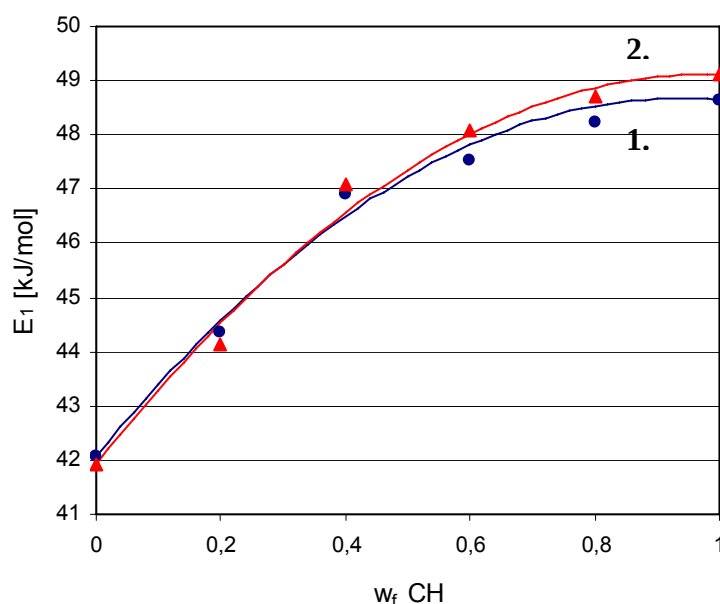


Fig. 5. Dependence of mean heat of adsorption of the first layer of water molecules (E_1) on blend composition at the temperatures 25 °C (1.) and 45 °C (2.); points – values calculated from equation (5); lines – function $E_1 = f(w_f)$; w_f – mass fraction of chitosan in the blend ($w_f = 0$ is pure HPC, $w_f = 1$ is pure CH).

The effect of mass fraction of chitosan (w_f) on pure molar heat of water adsorption in the blend for given process temperatures are described by the relations (13)-(16):

$$q(w_f) = E_1(w_f) - E_L \quad (13)$$

$$q(w_f) = E_{1(CH)} \cdot w_f + E_{1(HPC)} \cdot (1 - w_f) + w_f(1 - w_f) \cdot \varphi - E_L \quad (14)$$

where:

$E_{1(CH)}$ – mean heat of adsorption of the first layer of water molecules on CH [kJ/mol];
 $E_{1(HPC)}$ – mean heat of adsorption of the first layer of water molecules on HPC [kJ/mol];
 φ – parameter representing the excess function characterising relationships between blend components and water [kJ/mol].

By fitting experimental results (Fig. 4, 5) to relations (13-14) parameter φ was calculated. Thus, the relations between q and w_f at two temperatures can be presented as follows:

$$T = 25\text{ }^{\circ}\text{C}: \quad q_{25} = 48.7 \cdot w_f + 42.1 \cdot (1-w_f) + w_f \cdot (1-w_f) \cdot 7.5 - 39.1 \quad (15)$$

$$T = 45\text{ }^{\circ}\text{C}: \quad q_{45} = 49.1 \cdot w_f + 41.9 \cdot (1-w_f) + w_f \cdot (1-w_f) \cdot 7.4 - 38.3 \quad (16)$$

where:

$$E_{1(CH)} = 48.7\text{ kJ/mol } (T=25^{\circ}\text{C}) \quad E_{1(CH)} = 49.1\text{ kJ/mol } (T=45^{\circ}\text{C})$$

$$E_{1(HPC)} = 42.1\text{ kJ/mol } (T=25^{\circ}\text{C}) \quad E_{1(HPC)} = 41.9\text{ kJ/mol } (T=45^{\circ}\text{C})$$

$$\varphi = 7.5\text{ kJ/mol } (T=25^{\circ}\text{C}) \quad \varphi = 7.4\text{ kJ/mol } (T=45^{\circ}\text{C})$$

Values of heat of water vapour condensation were taken from literature as follows: E_L = 39.1 kJ/mol ($T=25^{\circ}\text{C}$) and 38.3 kJ/mol ($T=45^{\circ}\text{C}$).

Conclusions

The equilibrium of water adsorption from vapour phase on polymer CH/HPC blend films with different mass fractions of components at the temperatures 25 °C and 45 °C was described by the GAB model. A linear dependence of parameters X_m and c of the GAB isotherm on mass fraction of chitosan in the blend (w_f) and a decrease of both coefficients with adsorption temperature growth were observed. After averaging the values of parameter k , the equation of adsorption isotherm was modified and curves $X=f(a_w, w_f)$ were obtained. Approximation of the experimental data with this model is satisfactory in the case of adsorption carried out at the temperature 25 °C and 45 °C.

From the values of parameter c in the GAB equation pure molar heat of water adsorption (q) and mean heat of adsorption of the first layer of water molecules (E_1) on thin chitosan and HPC films were determined. Determinated values of E_1 are comparable to values of isosteric heat of adsorption of first monomolecular layer of water (calculated on the base of Clausius-Clapeyron eq.) found for various hydrophylic food compounds [25] and granules of starch [26]. The heat effect accompanying the process of water adsorption on CH/HPC blends decreased with an increase of hydroxypropylcellulose fraction which is probably caused by some sort of a porous structure of CH and HPC leading to their swelling. Dependence of E_1 and q on polymer blend composition has not been determined in the literature so far. Pure molar heat of water adsorption increases with the temperature growth.

Curves representing the dependence of q and E_1 on w_f at both analysed temperatures of adsorption are described by proposed equation (14) from which coefficient φ representing relations between blend components was identified. The coefficient was equal to 7.4-7.5 kJ/mol.

Experimental

The CH/HPC blends were obtained by mixing chitosan solution with deacetylation degree $DD = 78.5\%$, molecular weight $M_w = 4.3 \cdot 10^4$ g/mol and viscosity 127 mPas, purchased from the Sea Fishery Institute in Gdynia, in 1% acetic acid with water solution of HPC ($M_w = 1 \cdot 10^5$ g/mol) (SIGMA-ALDRICH Chemie GmbH, Steinheim, Germany) in adequate volume ratios.

Mass fraction of CH in the blends is given in Table 3. Polymer films prepared from CH/HPC blends were formed by casting the solutions onto levelled Perspex plates. Once the solvents were evaporated (3-4 days) transparent films 20 to 30 μm thick were obtained.

Tab. 3. List of prepared samples.

Mass fraction of chitosan in sample (w_f)	Sample
0	HPC
0,2	CH/HPC/0,2
0,4	CH/HPC/0,4
0,6	CH/HPC/0,6
0,8	CH/HPC/0,8
1,0	CH

After drying the films to constant mass at the temperature 110 °C, samples were placed in sorption desiccators with saturated water solutions of various salts (Table 4). The process of water vapour adsorption on the films was carried out for 4 h at two temperatures: 25 °C and 45 °C.

Tab. 4. Content of sorption desiccators [23].

No.	Salt	Water activity (a_w) over saturated salt solution [-]	
		T=25 °C	T=45 °C
1	CH ₃ COOK	0.234	0.197
2	MgCl ₂	0.329	0.308
3	K ₂ CO ₃	0.443	0.430
4	Mg(NO ₃) ₂	0.536	0.497
5	NaNO ₂	0.654	0.601
6	NaCl	0.765	0.726
7	BaCl ₂	0.904	0.885

When the equilibrium state between vapour phase and water adsorbed by blend films was reached, the samples were removed from desiccators and precisely weighed by analytical mass balance. The amount of water adsorbed (X) was determined according to equation (17):

$$X = \frac{m_s - m_D}{m_D} \quad (17)$$

where:

m_s – sample mass after adsorption process [kg]; m_D – dry sample mass [kg].

Acknowledgements

The authors gratefully thank the Polish State Committee for Scientific Research (KBN) for support under grant no. 3 T09C 028 26.

References

- [1] Ravi Kumar, M.N.V. *React. Funct. Polym.* **2000**, 46, 1-27.
- [2] Struszczyk, M.H. *Polimery* **2002**, 47, 316-325.
- [3] Imeri, A.G.; Knorr, D. *J. Food Sci.* **1988**, 53, 1707-1710.
- [4] Illum, L. *Pharm. Res.* **1998**, 15, 1326-1331.
- [5] Dodane, V.; Vilivalam, V.D. *Pharm. Sci. Technol. Today* **1998**, 1, 246-253.
- [6] Karavas, E.; Georgarakis, E.; Bikiaris D. *J. Therm. Anal. Cal.* **2006**, 84, 125-133.
- [7] Bittelli, M.; Flury, M.; Campbell, G.S.; Nichols, E.J. *Agric. For. Meteorol.* **2001**, 107, 167-175.
- [8] Bautista-Banos, S.; Hernandez-Lauzardo, A.N.; Velazquez-del Valle, M.G.; Hernandez-Lopez, M.; Ait Barka, E.; Bosquez-Molina, E.; Wilson, C.L.; Crop Prot. **2006**, 25, 108-118.
- [9] Peniche-Covas, C.; Alvarez, L.W.; Arguelles-Monal, W. *J. Appl. Polym. Sci.* **1992**, 1147-1150.
- [10] Mitani, T.; Nakalima, C.; Sungkano, I.E.; Ishii, H. *J. Environ. Sci. Health Part A. Environ. Sci. Eng. Toxic* **1995**, 30, 669-674.
- [11] Suto, S.; Ui, N. *J. Appl. Polym. Sci.* **1996**, 61, 2273-2278.
- [12] Mucha, M.; Miskiewicz, D.; Pawlak, A. *Przemysł Chemiczny* **2003**, 82, 1139-1142. (in Polish)
- [13] Lewicki, P.P. *J. Food Eng.* **2000**, 43, 31-40.
- [14] Arslan, N.; Togrul, H. *J. Stored Products Research* **2006**, 42, 112-135.
- [15] Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, 60, 309-319.
- [16] Anderson, R. B. *J. Am. Chem. Soc.* **1946**, 68, 686-691.
- [17] Srinivasa, P.C.; Ramesh, M.N.; Kumar, K.R.; Tharanathan, R.N. *Carbohydr. Polym.* **2003**, 53, 431-438.
- [18] Mucha, M.; Ludwiczak, S. *Carbohydr. Polym.* **2005**, 62, 42-49.
- [19] Lewicki, P.P. *Int. J. Food Sci. Technol.* **1997**, 32, 553-557.
- [20] Velazquez de la Cruz, G.; Torres, J. A.; Martin-Polo, M. O. *J. Food Eng.* **2001**, 48, 91-94.
- [21] Soysal, Y.; Oztekin, S. *J. Agric. Eng. Res.* **2001**, 78, 159-166.
- [22] Balcerzak, J. *Master Thesis*, Faculty of Process and Environmental Eng., Technical University of Lodz **2006**.
- [23] Kaminski, W.; Kudra, T. *Drying Technology in Agriculture and Food Sciences*, Science Publishers, USA, Chapter 1. Equilibrium moisture relations for food and biomaterials; **2000**, p 1-28.
- [24] Mucha, M.; Ludwiczak, S.; In: Struszczyk, H.; Peter, M.G.; Domard, A.; Pospieszny, H.; editors; *Advances in Chitin Science vol. VIII*, Institute of Plant Protection, Poznan, Poland; **2005**, p 85-90.
- [25] Mulet, A.; Garcia-Pascual, P.; Sanjuan, N.; Garcia-Reverter, J. *J. Food Eng.* **2002**, 53, 75-81.
- [26] Calzetta Resio, A.; Aguerre, R.J.; Suarez, C. *J. Food Eng.* **1999**, 42, 51-57.