Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Carbohydrate Polymers 62 (2005) 42–49

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Kinetics of water sorption by chitosan and its blends with poly(vinyl alcohol)

M. Mucha*, S. Ludwiczak, M. Kawinska

Faculty of Process and Environmental Engineering, Lodz Technical University, ul. Wolczanska 215, 90-924 Lodz, Poland

Received 24 March 2005; revised 30 June 2005; accepted 12 July 2005
Available online 8 September 2005

Abstract

Gravimetric and spectrophotometric studies of the kinetics of water sorption from air of various water activities by chitosan of different deacetylation degrees (and molecular weights) and chitosan/poly(vinyl alcohol) blends were conducted.

Analysis of the presented results has shown a clear effect of the deacetylation degree of chitosan and the presence of poly(vinyl alcohol) in chitosan blends on water sorption rate. The character of sorption curves, calculated values of diffusion coefficients of water vapour and micropore volumes have shown that the higher chitosan deacetylation (and higher M_w) the lower the sorption of water vapour. The observed effect is explained by a rising ordering of molecular chains leading to an increase of structural packing in chitosan.

Modification of the chitosan structure in miscible blends with poly(vinyl alcohol) has been reflected in their sorptive properties which depend on the weight fraction of poly(vinyl alcohol) and water activity. Good compatibility of the components, resulting from the presence of hydrogen bonds between specific groups (hydroxyl, amide) of chitosan and poly(vinyl alcohol) chains, causes an increase in molecular packing and thus, a decrease of pore volume and a rate of water diffusion.

Keywords: Chitosan; Deacetylation degree; Chitosan/poly(vinyl alcohol) blends; Water sorption

1. Introduction

Recently, polymer biomaterials have been broadly applied both in industry and medicine. Analysis of water sorption by these materials is important because the presence of water has a primary effect on their physical properties and possible applications.

Chitosan is a copolymer consisting of β-(1-4)-2-acetamido-D-glucose) and β-(1-4)-2-amino-D-glucose units with the latter changing usually from 60 to 90% (degree of deacetylation). Chitosan is prepared from chitin by deacetylation in the presence of alkali.

Chitosan has been extensively used over a wide range of applications such as prevention of water pollution by chelating heavy metals or radioactive isotopes (Muzzarelli, 1977), membrane separation (Aiba, Izume, Minoura, & Fujiwara, 1986), in medicine and biotechnology, and in the food-related areas either as food packaging material because of its antimicrobial action (El Ghaouth, Arul, Ponnamplalan, & Boulet, 1991; Wong, Gastineau, Gregorski, Tillin, & Pavlath, 1992) or as dietary fiber and a potential medicine against hypertension thanks to its scavenging action for chloride ions (Furda & Brine, 1990; Ishikura, 1993; Muzzarelli, 1996; Muzzarelli & Muzzarelli, 2002; Okuda, 1995).

High-molecular polysaccharides, including chitosan, can absorb water easily, mainly by hydrogen bonds which are formed with hydroxyl and amide groups present in its structure (Chen, Lin, & Yang, 1994; Gocho et al., 2000).

Our previous study, (Mucha & Pawlak, 2002) on swelling of chitosan films in water with different deacetylation degrees (DD) showed that the rate of water sorption and kinetic water diffusion coefficient increased with a decrease of DD. Also thermal degradation of chitosan, by modifying the polymer structure, leads to a change in water sorption kinetics. This was explained by changing degrees of spatial packing of the chitosan.

Other authors (Kim, Kim, Lee, & Kim, 1992; Kim, Park, & Kim, 2003) found that the degree of chitosan swelling in water depended linearly both on deacetylation degree

---

* Corresponding author. Tel. +48 631 3785; fax: +48 42 365 663.
E-mail address: muchama@wipos.p.lodz.pl (M. Mucha).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.07.008

and molecular weight of the polymer, showing opposite tendencies. An increase of the deacetylation degree from 70 to 92% at constant $M_w = 7.4 \times 10^5$, resulted in a growth of chitosan crystallinity from 5 to 14%, and swelling degree from 48 to 60%. When the deacetylation degree remained constant and was 95%, the increase of molecular weight from 3×10^5 to 8×10^5 caused a decrease of crystallinity from 24 to 13% which was related to the increase of swelling from 28 to 46%.

Blending of chitosan with other synthetic hydrophilic polymers such as poly(vinyl alcohol), poly(vinyl pyrrolidone), hydroxypropylcellulose or natural polymers: starch, pectin, gelatine and collagen, has been suggested as a promising approach to producing polymers for specific uses (Arvanitoyannis, Psomiadou, & Nakayama, 1996; Arvanitoyannis et al., 1997; Arvanitoyannis, 1999; Blair, Guthrie, Law, & Turkington, 1987; Quarashi, Blair, & Allen, 1992; Yao et al., 1996).

Our last studies have focused on a physical modification of chitosan structure by blending it with water soluble polymers: such as poly(vinyl alcohol) and hydroxypropyl cellulose (Mucha, Marszalek, & Miśkiewicz, 2000; Mucha & Ludwiczak, 2005). Formation of strong, transparent films indicates good miscibility of components. Chitosan blends (also with starch) in the form of diluted solutions have been used recently for paper impregnation (Mucha & Miśkiewicz, 2000).

Chitosan blends with poly(vinyl alcohol) are prepared and widely discussed (Arvanitoyannis et al., 1999, Miya, Iwamoto, & Mima, 1983). They are also used in the form of hydrogels (Koyano, Minoura, & Nagura, 1998) and as membranes (Mucha, Marszalek, & Miśkiewicz, 2000; Wu Li-Guang, Zhu Chang-Luo, & Liu Moe, 1994).

The aim of this research was to identify the effect of chitosan deacetylation degree and contribution of poly(vinyl alcohol) in blends with chitosan on the kinetics of water sorption from the environment at different air humidities.

2. Experimental

2.1. Materials

A subject of present study was chitosan samples (from krill) of different deacetylation degrees (DD) and molecular weights (M_w) (Table 1) produced by the Sea Fishery Institute in Gdynia.

Here, M_w of chitosan was decreasing with an increase of DD. Such correlation between DD and M_w of chitosan is not usual.

Physical modification of chitosan structure was made by blending with poly(vinyl alcohol) (PVAL) prepared from PVAC of molecular weight $M_w = 72{,}000$.

The structure of crystalline PVAL was shown to be monoclinic (Hodge et al., 1996; Hodge, Edward, & Simon, 1996b). PVAL is a semicrystalline polymer of about 50% of crystallinity (Arvanitoyannis et al., 1997; Mucha & Ludwiczak, 2005).

Table 1
Description of samples of chitosan and chitosan/poly(vinyl alcohol) blends

Oznaczenie próbki	DD (%)	M_w?10^{-5} (g/mol)	w_f
CH59	59	5.7	1
CH73	73	4.5	1
CH78	78	2.1	1
CH86	86	1.05	1
CH67	67	5.1	1
CH67/PVAL/0,8			0.8
CH67/PVAL/0,6			0.6
CH67/PVAL/0,4			0.4
CH67/PVAL/0,2			0.2
PVAL		0.72	0

M_w, molecular weight; w_f, weight fraction of chitosan.

2.2. Film preparation techniques

Chitosan is insoluble in water, but with acetic acid it forms chitosan acetate, a water soluble salt. Chitosan with different deacetylation degrees (CH59, CH67, CH73, CH78, CH86) in the form of powder, was dissolved in 1% acetic acid to obtain 2% solutions. The process of chitosan dissolution took place at room temperature (ca. 24 °C) for about 48 h. The resultant bright yellow solutions with different viscosities were then carefully filtered to remove various types of dust.

To produce blends with poly(vinyl alcohol), chitosan with deacetylation degree equal to 67% was selected. In order to obtain blends of chitosan (CH67) with PVAL of proper weight fractions of the components, appropriate amounts of 2% chitosan solution were mixed with 5% (water) solution of poly(vinyl alcohol).

The solutions of chitosan with different deacetylation degrees, blends of CH67/PVAL and PVAL were casted onto glass plates and left for 3 days to evaporate and to produce films of comparable thicknesses equal to about 15 μm. Then, the chitosan films were etched in methanol to remove acid residues (the etching time was 24 h), and dried for 24 h.

2.3. Research methods

The kinetics of water sorption by tested samples was investigated by the gravimetric method using an analytical balance and by FTIR spectrophotometry (measurement of absorbance in hydroxyl group band), using a Genesis II spectrophotometer (Mattson).

Analysis of water sorption was carried out at the temperature 25 °C (±1 °C) in 9 desiccators equipped with a hygrometer and thermometer, each of them containing saturated solution of a different salt (Table 2) in order to obtain variable air humidity (water activity).

Before water sorption measurement, the tested samples were dried at the temperature 100 °C until constant mass

Table 2
Water activity (a_w) on saturated solutions of various salts

Salt	a_w
CH_3COOK	0.234
$MgCl_2$	0.329
K_2CO_3	0.443
$Mg(NO_3)_2$	0.536
$NaNO_2$	0.654
NaCl	0.765
KCl	0.846
$BaCl_2$	0.904
H_2O	1.000

was maintained. Next, the samples were placed in the desiccators containing saturated solutions of the mentioned salts. Every few minutes the samples were taken out, their mass and IR spectra were recorded. The measurements were continued until reaching the state of equilibrium (ca. 4 h). The estimated error of measurements was about 10% due to disturbing a thermodynamic equilibrium of the system by opening desiccators for a short time. The measurements were triplicated.

3. Results and discussion

3.1. Sorption kinetics

Selected kinetic curves of water sorption are described by the dependence of moisture content of sample X (mass of water in the sample per 1 kg dry material) on time. These curves, obtained at different water activities, are shown in Fig. 1(a) for CH67/PVAL/0,2. The higher water activity the higher moisture content in the sample is measured. The similar behaviour of other blends of various PVAL content is observed. Fig. 1(b) illustrates the dependence of X on time at water activity equal to 0.329 for the chitosan samples of different deacetylation degrees and the blends CH67 with PVAL.

The moisture content depends strongly on deacetylation degree of the chitosan samples or PVAL fraction in the blend with chitosan.

Fig. 2(a) shows results obtained by the spectrophotometric method presented for chosen CH67/PVAL blend. Fig. 2(b) illustrates a selected FTIR spectrum of CH67 in the region of hydroxyl band at 3370 cm^{-1} whose absorbance value changes with increasing moisture content.

The kinetic curves of water sorption show a clear effect of the deacetylation degree of chitosan on this process. The lower the deacetylation degree the better sorption properties of the polymer are observed. This is confirmed by results obtained by both gravimetric and IR spectroscopy methods. We suppose that the observed dependence of chitosan moisture content on DD does not result from changing a chemical structure of this copolymer or a type and number of end groups, as other authors suggested (Gocho et al., 2000), but from differences in the spatial packing of chitosan chains. A big acetamide group present in chitin-like part of chitosan chain causes a steric resistivity of structured packing. The bigger voids are more easily filled with water aggregates. The chitosan sample CH59 that contains more acetamide groups than other samples absorbs much more water.

By the modification of chitosan in mixing with PVAL, a strong reduction of its sorption ability is observed. The higher PVAL content in the blends, the lower water absorptivity is found. Also the time for reaching sorption equilibrium is longer.

PVAL and chitosan are semicrystalline polymers consisting of amorphous and crystalline phases. Chitosan has a much lower crystallinity degree than PVAL. Thus, the water sorption occurring mainly in the amorphous phase of the polymeric system depends on the blend composition. Lower equilibrium moisture of PVAL and its blends with

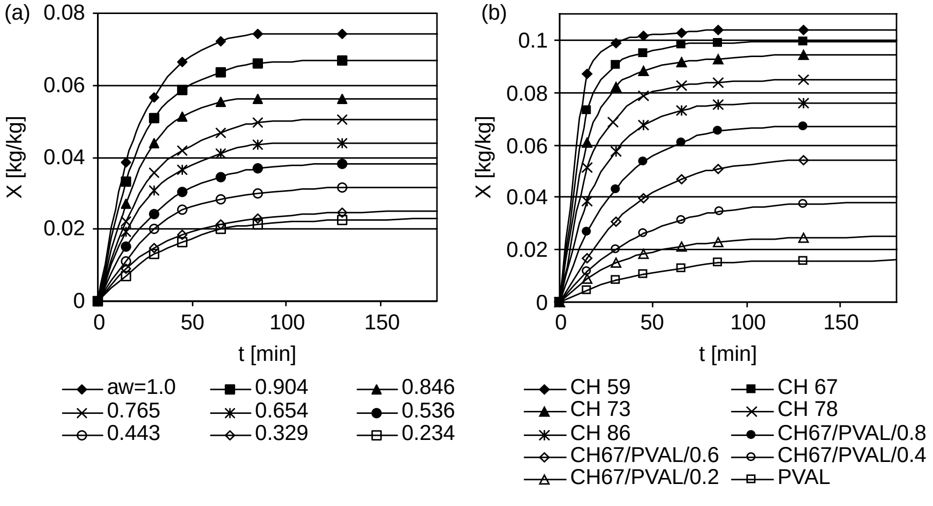

Fig. 1. Kinetics curves of water sorption obtained from gravimetric measurements: (a) CH67/PVAL/0,2 in various water activity a_w; (b) chitosan of various DD and CH67/PVAL blends ($a_w = 0.329$). X-water mass in a sample for 1 kg of dried material.

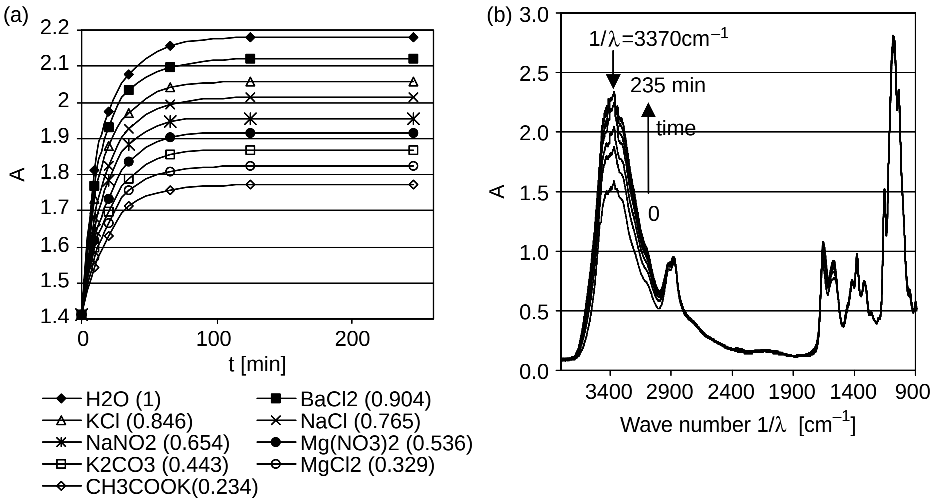

Fig. 2. (a) Kinetic curves of water sorption obtained using spectrophotometric method for CH67/PVAL/0,8 in various water activity a_w; (b) absorbance change in the time of water sorption process for chitosan of DD=67% ($a_w = 1$) A-absorbance in $1/\lambda = 3370\ \mathrm{cm}^{-1}$.

chitosan of higher PVAL content results perhaps from the crystallinity effect. No PVAL separation from the chitosan blends up to 20–30% content of PVAL is recognised. T_m and T_g of PVAL in DSC measurement are not observed (Arvanitoyannis et al., 1997; Mucha & Pawlak, 2005).

The effect has been attributed to good dilution of PVAL in chitosan structure—good miscibility of the system due to intermolecular interactions.

3.2. Determination of diffusion coefficients

To analyse the presented sorption curves, second Fick's law describing the rate of unidirectional mass transport due to unsteady diffusion was used:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C, concentration; D, effective kinetic diffusion coefficient; t, time; x, distance.

Solution of Eq. (1) is given in formula (2) (Crank, 1975; Fukuda, 1996; Perrin & Manley, 1995):

$$\frac{X_t}{X_\infty} = 1 - \sum_{0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[-\frac{D\pi^2}{L^2}(2n+1)^2 t\right] \qquad (2)$$

where L, sample thickness; n, natural number (in calculation $n=10$ was assumed); X_t, water mass in time t; X_∞, final water mass (in saturated state).

Eq. (2) is only valid when a gas or water vapour penetrates polymer undirectionally from the plane surface. Since, our samples are very thin films (15–20 μm), the penetration of water vapour by the edges can be negligible.

The criteria for selecting parameter n and estimating coefficient D were based on the nonlinear regression method, fitting experimental curves to Eq. (2). Assuming the value of n higher than 10, no significant changes were found in the description of results.

Fig. 3 shows the examples of theoretical curves (lines) described by Eq. (2) fitted to experimental data (points)

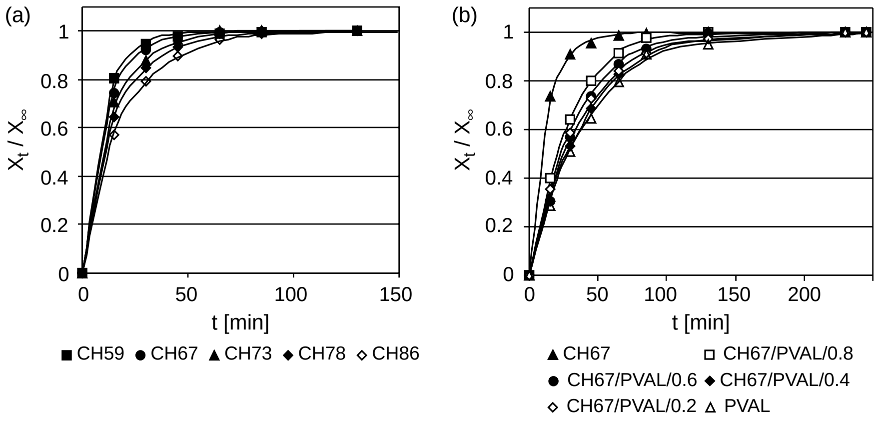

Fig. 3. Presentation of theoretical curves fitting, according to Eq. (2) (lines) to the experimental points of water sorption process: (a) chitosan of various DD ($a_w = 0.654$); (b) CH67/PVAL blends of various w_f ($a_w = 0.329$).

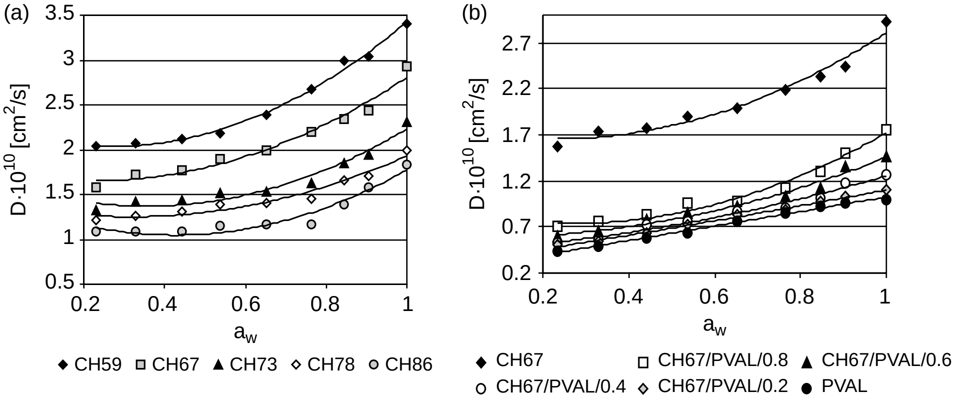

Fig. 4. Plots of water diffusion coefficient D versus water activity a_w for (a) chitosan of various DD; (b) CH67/PVAL blends of various w_f.

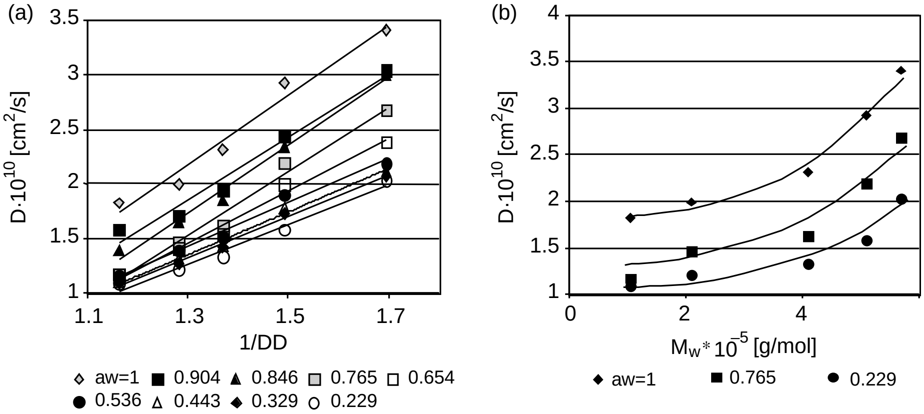

Fig. 5. Plots of water diffusion coefficient D versus (a) reciprocal deacetylation degree (1/DD) of chitosan (various M_w) for various water activity a_w; (b) molecular weight M_w of chitosan (various DD) for chosen a_w.

obtained for the following samples: (a) chitosan with different deacetylation degrees and (b) chitosan blends with various weight fractions of PVAL. Good fitting of theoretical curves to experimental results confirms the agreement with Fick's law. Fig. 4(a) and (b) show the values of water diffusion coefficient D for chitosan and CH67/PVAL blends vs. water activity a_w.

The estimated value of diffusion coefficient D of water for the tested samples of chitosan depends both on deacetylation degree (DD) and molecular weight (M_w) of the polymer. The dependence of D on the inverse of deacetylation degree (1/DD) of chitosan at different water activities (a_w) is shown in Fig. 5(a), and on M_w for three values of a_w in Fig. 5(b).

A linear dependence of water diffusion coefficient D on weight fraction of chitosan in CH67/PVAL blends shown in Fig. 6(a) can be described by Eq. (3) in the range of $w_f < 0.8$:

$$D = \left(\frac{\partial D}{\partial w_f}\right) w_f + D_{\mathrm{PVAL}} \qquad (3)$$

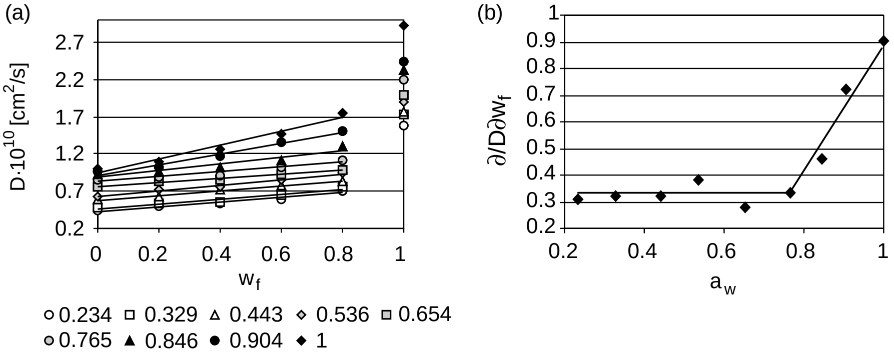

Fig. 6. (a)Plots of water diffusion coefficient D on weight fraction w_f of chitosan in CH67/PVAL blends in various water activity a_w; (b) $\partial D/\partial w_f$ coefficient of Eq. (4) plots versus a_w.

Fig. 6(b) shows how $\partial D/\partial w_f$ depends on a_w. In the first range, up to $a_w < 0.8$, the value of $\partial D/\partial w_f$ is constant. The second one $a_w > 0.8$ is characterised by a fast growth of $\partial D/\partial w_f$ which indicates a change in the mechanism of water sorption process in the material. The mechanism of water sorption to these materials, through the analytical assessment of the parameters of sorption isotherms is discussed in our paper submitted for publication (Mucha & Ludwiczak, 2005).

3.3. Estimation of the volume of micropores

Assuming that the characteristic curves of water sorption to materials are related to the capillary structure of adsorbent and the volume of liquid phase adsorbed in the micropores. W depends on water activity a_w, the following relation (Dubinin, 1975) can be used to determine the volume of micropores:

$$W = W_0 \exp\left[-bR^2T^2\left(\ln\frac{1}{a_W}\right)^2\right] \qquad (4)$$

where W_o, micropore volume; R, gas constant; T, temperature; b, parameter related to capillary pore volume distribution.

The tested polymers are the adsorbents of porous, nonhomogeneous structure. At low water activities, water fills up the pores of the smallest diameters. With growing a_w, in the gas phase pores of bigger diameters are filled up.

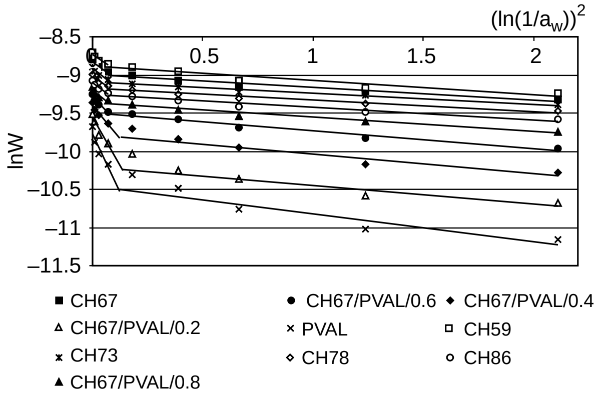

Fig. 7. Dependence of ln$W$ on $(\ln(1/a_w))^2$ for chitosan and CH67/PVAL blends.

Basing on Eq. (4), the porosity of the tested films was determined. The value of $W = X/\rho_w$ (ρ_w-water density) was calculated and dependence of ln$W$ on $(\ln(1/a_w))^2$ was determined, and drawn as shown in Fig. 7. Experimental points shown in Fig. 7, are arranged along two lines. By extrapolating straight lines to $(\ln(1/a_w))^2 = 0$, the micropore volumes W_{01} and W_{02} were determined. At $a_w < 0.7$ smaller pores of volume W_{02} are filled up, while bigger pores of volume W_{01} are filled up at $a_w > 0.7$.

Plots of W_{01} and W_{02} as on function of DD and the weight fraction of chitosan in the blends are shown in Fig. 8(a) and (b). It follows from the analysis of Fig. 8 that the volume of micropores in chitosan decreases with increase of its deacetylation degree (also with a decrease of molecular weight of the polymer). It is assumed to be a result of differences in spatial packing of the macromolecular chains (the spatially extended and statistically distributed acetamide group in chitosan comonomer is arranged asymmetrically). Chitosan modification by blending with poly(vinyl alcohol) causes a decrease of porosity due to good packing of PVAL molecules in a free volume of chitosan structure.

The observed differences in molecular packing of chitosan of variable DD was reflected in changing susceptibility to hydrolysis and biodegradation of this polymer. It was observed (Pawlak, 2004) that the rate of hydrolysis and biodegradation increased with decreasing DD of chitosan. It was related to various rates of water sorption transferring enzymes. A glycosidic bond of the polymer chains is scissioned first in the vicinity of amide group. The crystallinity degree of chitosan was found relatively low, from 5 to 24% (Wan, Creber, Peppley, & Tam Bui, 2003) depending on deacetylation degree and molecular weight. Chitosan of a lower deacetylation degree has a more irregular molecular structure and its crystallisation is more difficult. Moreover, the crystallity degree, statistical distribution of amino groups in the chitosan chain and its molecular weight should be recognised as having an influence on water sorption ability of the polymer. It results from a change in the chain flexibility and in supermolecular

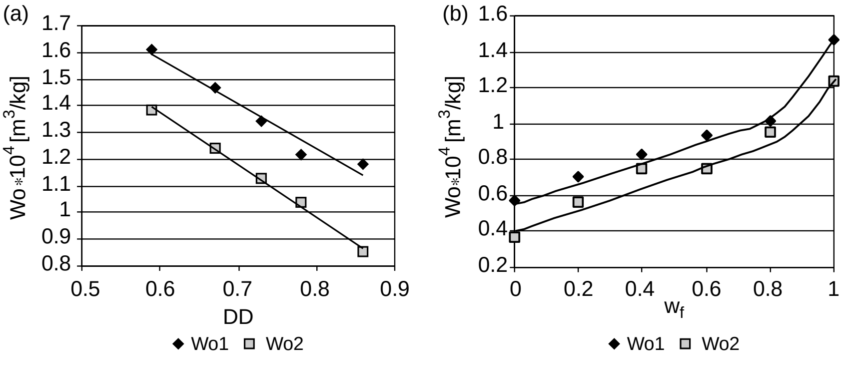

Fig. 8. Dependence of micropores volumes W_o on (a) deacetylation degree DD of chitosan; (b) weight fraction of chitosan in CH67/PVAL blends.

structure which is related to the ability of packing and ordering of its chains. Higher crystallinity of chitosan films with bigger DD causes a reduction in the content of water adsorbed in the polymer structure (Wan et al., 2003).

The values of coefficient D and micropore volume are the higher, the lower is DD of chitosan and the bigger is the weight fraction of chitosan in the CH67/PVAL blend due to good packing of PVAL in the porous volume of chitosan (good dilution). The diffusion coefficient D of water in chitosan and CH67/PVAL blends increases with water activity.

4. Conclusions

Analysis of the presented results on water sorption by chitosan and its blends at different activities a_w, carried out by the gravimetric and spectroscopic method shows that the process rate depends evidently on the deacetylation degree of chitosan and the fraction of poly(vinyl alcohol) in chitosan blends.

Sorption curves and determined process parameters, including water diffusion coefficients and micropore volumes show that the lower deacetylation degree of chitosan (also higher M_w), the better water sorptivity. The observed effect is explained by lower ordering of the polymer.

The modification of chitosan structure in PVAL blends leads to a limitation of its water sorptivity which depends on the fraction of PVAL. Good miscibility of the components, resulting from interactions of specific functional groups (hydroxyl, amide) present in CH and PVAL macromolecules, causes that a structural packing of the system increases.

Acknowledgements

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

References

Aiba, S., Izume, M., Minoura, N., & Fujiwara, Y. (1986). Chitosan based membranes for separation processes. In R. A. A. Muzzarelli, C. Jeuniaux, & G. M. Gooday (Eds.), *Chitin in nature and technology* (pp. 396–398). New York: Plenum Press.

Arvanitoyannis, I. (1999). Totally-and-partially biodegradable polymer blends based on natural and syntethic macromolecules: Preparation and physical properties and potential as food packaging materials. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*, *C39*(2), 205–271.

Arvanitoyannis, I., Kolokuris, I., Nakayama, A., Yamamoto, N., & Aiba, S. (1997). Physico–chemical studies of chitosan-poly(vinyl alcohol) blends plasticized with sorbitol and sucrose. *Carbohydrates Polymers*, *34*(1/2), 9–19.

Arvanitoyannis, I., Psomiadou, E., & Nakayama, A. (1996). Edible films made from sodium caseinate, staerches, sugers or glycerol, Part 1. *Carbohydrates Polymers*, *31*, 179–192.

Blair, H. S., Guthrie, J., Law, T.-K., & Turkington, P. (1987). Chitosan and modified chitosan membranes. I. Preparation and characterization. *Journal of Applied Polymer Science*, *33*, 641–656.

Chen, P. h., Lin, J. H., & Yang, M. H. (1994). Relationships between the chain flexibilities of chitosan molecules and the physical properties of their cased films. *Carbohydrates Polymers*, *24*, 41–46.

Crank, J. (1975). *The mathematics of diffusion*. Oxford: Clarendon Press.

Dubinin, M. M. (1975). *Adsorpcja i porowatosc*. Warszawa: PWN.

El Ghaouth, A., Arul, J., Ponnamplalan, R., & Boulet, M. (1991). Chitosan coating effect on storability and quality of fresh strawberris. *Journal of Food Science*, *56*, 1618–1624.

Fukuda, M. (1996). Diffusion of moisture in poly(p-phenylene terephthalamide) film: Analysis by the adsorption-controlled diffusion equation. *Polymer Engineering and Science*, *36*, 558–567.

Furda, I., & Brine, C. J. (1990). *New developments in dietary fiber*. New York: Plenum.

Gocho, H., Shimizu, H., Tanioka, A., Chou, T. J., & Nakajima, T. (2000). Effect of polymer chain end on sorption isotherm of water by chitosan. *Carbohydrates Polymers*, *41*, 87–90.

Hodge, R. M., Bastow, T. J., Edward, G. H., Simon, G. P., & Holl, A. J. (1996). Free volume and the mechanism of plasticization in water swollen poly(vinyl alcohol). *Macromolecules*, *29*, 8137–8143.

Hodge, R. M., Edward, G. H., & Simon, G. P. (1996). Water absorption and states of semicrystalline poly(vinyl alcohol) films. *Polymer*, *37*, 1371–1376.

Ishikura, S. (1993). Chitin and chitosan. *Gekkan Fudo Kemikaru*, *9*, 62–64.

Kim, J. H., Kim, J. Y., Lee, Y. M., & Kim, K. Y. (1992). Properties and swelling characteristics of cross-linked poly(vinyl alcohol) /chitosan blend membrane. *Journal of Applied Polymer Science*, *45*, 1711–1717.

Kim, S. T., Park, S. J., & Kim, S. J. (2003). Swelling behaviour of interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and chitosan. *Reactive and Functional Polymers*, *55*, 53–59.

Koyano, T., Minoura, N., & Nagura, M. (1998). Anti-bacterial and anti-fungal activities of poly(vinyl alcohol)/chitosan blended hydrogels. *Japanese Journal of Polymer Science and Technology*, *55*(10), 628–631.

Miya, M., Iwamoto, R., & Mima, S. (1983). Highly acetylated chitosan and its properties. *Journal of Applied Polymer Science*, *285*, 1909–1917.

Mucha M., & Ludwiczak S. (2005), Isotherms of water sorption in biomaterials based on chitosan, advances in chitin science, (in press) .

Mucha M., Marszalek J., & Miśkiewicz D. (2000), Bioblends containing derivatives of chitin and their some applications, Proceedings of 3rd International Symposium on Natural Polymers and Composites-ISNaPol/2000, Edit. Embrapa Instrumentacao Agropecuaria, Sao Carlos, Brazil, pp. 537–542. advances in chitin science, vol. 5, Proceedings of 5th Asia Pacific Chitin and Chitosan Symposium, Thailand, pp. 221–225.

Mucha, M., & Miśkiewicz, D. (2000). Chitosan blends as fillers for paper. *Journal of Applied Polymer Science*, *77*, 3210.

Muncha, M., & Pawlak, A. (2002). Study of water absorption in Chitosan Films: The Effect of Degradation, Conference proceeding, (5 th Asia Pacific Chitin–Chitosan Symp.), Thailand.

Mucha, M., & Pawlak, A. (2005). Thermal analysis of chitosan and its blends. *Thermochemica Acta*, *427*, 69–76.

Muzzarelli, R. A. A. (1977). *Chitin*. Oxford: Pergamon Press.

Muzzarelli, R. A. A. (1996). Chitosan-based dietery foods. *Carbohydrates Polymers*, *29*, 309–316.

Muzzarelli, R. A. A., & Muzzarelli, C. (2002). *Chitosan in pharmacy and chemistry*. Italy: Atec.

Okuda, H. (1995). Blood pressure control and role of chitosan. *Gekkan Fudo Kemikaru*, *11*, 33–38.

Pawlak A. (2004), Kinetyka degradacji ukŁadów polimerowych zawierających chitozan, (Kinetics of degradation of polymeric systems containing chitosan), PhD thesis 2004, Faculty of Process and Environmental Engineering Lodz Technical University.

Perrin, L., & Manley, R. S. J. (1995). Carbon dioxide sorption and transport in miscible cellulose/poly(vinyl alcohol) blends. *Macromolecules*, *28*, 5793–5798.

Quarashi, M. T., Blair, H. S., & Allen, S. J. (1992). Studies on modified chitosan membranes. II. Dialysis of low molecular weight metabolites. *Journal of Applied Polymer Science*, *46*, 263–269.

Wan, Y., Creber, K. A. M., Peppley, B., & Tam Bui, V. (2003). Ionic conductivity of chitosan membranes. *Polymer*, *44*, 1057–1065.

Wong, D. W. S., Gastineau, F. A., Gregorski, K. S., Tillin, S. J., & Pavlath, A. E. (1992). Chitosan lipid films: Microstructure and surface energy. *Journal of Agricultural and Food Chemistry*, *40*, 540–544.

Wu, L. G., Zhu, C. L., & Liu, M. (1994). Study of a new pervaporation membrane, Part 1. Preparation and characteristics of the new membrane. *Journal of Membrane Science*, *90*(3C), 199–205.

Yao, K. D., Liu, j., Cheng, G. x., Lu, X. D., Tu, h. L., & Silva, J. A. L. (1996). Swelling behaviour of pectin/chitosan complex films. *Journal of Applied Polymer Science*, *60*, 279–283.