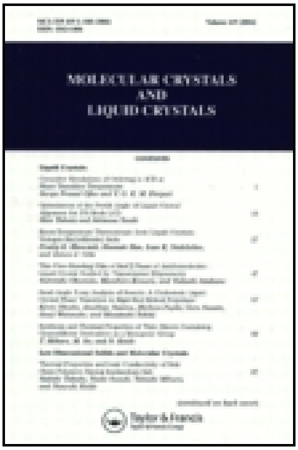

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# Dynamics of Water Sorption to Nanopores of Polymer Biomaterials

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# Dynamics of Water Sorption to Nanopores of Polymer Biomaterials

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*Gravimetric studies of the kinetics of water sorption from air of various water activities by chitosan of different deacetylation degrees (and molecular weights) and chitosan/hydroxypropyl cellulose blends were conducted.*

*Analysis of the presented results has shown a clear effect of the deacetylation degree of chitosan and the presence of hydroxypropyl cellulose in chitosan blends on the process rate. The character of sorption curves and calculated values of diffusion coefficients of water have shown that the higher chitosan deacetylation (and higher $M_w$) the worse are its sorptive properties. The observed effect is explained by a rising ordering of molecular chains leading to an increase of structural packing.*

*Modification of the chitosan structure in blends has been reflected in their sorptive properties which depend on the weight fraction of hydroxypropyl cellulose and water activity. Good compatibility of the components, due to the presence of hydrogen bonds between specific groups (hydroxyl, amide) of chitosan and hydroxypropyl cellulose chains, causes an increase of molecular packing and observed decrease of water diffusivity.*

*Assuming a capillary structure of free volume space of nano size, the total volume of the pores was calculated as a function of deacetylation degree of chitosan and weight fraction of HPC in chitosan blends. Curves of sorption isotherms show sigmoid shape which was discussed on the basis of GAB multilayer absorption theory.*

**Keywords:** chitosan; chitosan/hydroxypropyl cellulose blends; nanopores; polymer biomaterials; water sorption

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## INTRODUCTION

The sensitivity of some polymeric products to moisture determines physical properties of the materials and can be recognized on the basis of water sorption studies.

For a few years, our research has been focused on chitosan structure, properties and miscibility with water soluble polymers such as polyethylene oxide, polyvinyl alcohol, starch and hydroxypropyl cellulose [1–5]. Chitosan and all the polymers are hydrophilic. They can absorb water molecules from humid atmosphere making hydrogen bonds with the macromolecules.

The aim of our research was to determine the effect of chitosan deacetylation degree and the presence of hydroxypropyl cellulose in chitosan blends on the rate of water sorption from the environment with different air humidity and to specify on this basis material porosity and structural packing. Similar research carried out for blends of chitosan and polyvinyl alcohol is a subject of another publication [6].

## EXPERIMENTAL

### Materials

Chitosan (CH) is a copolymer, a partly deacetylated derivative of chitin coming from various natural sources. A subject of this study were the samples of chitosan (from krill) with different deacetylation degrees (DD) purchased from the Sea Fishery Institute in Gdynia, where they were produced.

The tested chitosan samples were characterized by $M_w$ value which here was decreased with an increase of DD (Table 1).

**TABLE 1** Determination of Chitosan and Chitosan Hydroxypropyl Cellulose Blends

| Sample | $M_w \times 10^{-5}$ | Sample | $w_f$ |
|---|---|---|---|
| CH59 | 5.7 | CH78 | 1 |
| CH67 | 5.1 | CH78/HPC/0.8 | 0.8 |
| CH73 | 4.5 | CH78/HPC/0.6 | 0.6 |
| CH78 | 2.1 | CH78/HPC/0.4 | 0.4 |
| CH86 | 1.05 | CH78/HPC/0.2 | 0.2 |
| HPC | 1 | HPC | 0 |

$M_w$ – molecular weight, $w_f$ – weight fraction of chitosan.

A polymer used for physical modification of chitosan was hydroxypropyl cellulose of $M_w = 1 \cdot 10^5$ (HPC) purchased from the Sigma – Aldrich Chemie, Germany.

A water solution of 1% acetic acid was used as a chitosan solvent.

## Film Preparation Techniques

Chitosan is insoluble in water, but with acetic acid it forms a water-soluble salt called chitosan acetate. 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.

In order to obtain blends of chitosan (CH78) with HPC of proper weight fractions of the components, appropriate amounts of 2% chitosan solution were mixed with 2% (water) solution of HPC (Table 1).

The solutions of chitosan with different deacetylation degrees, blends of CH78/HPC and HPC were cast onto glass plates and left for 3 days to evaporate water. Strictly specified amounts of the solutions were used to produce films of comparable thicknesses equal to about 15 μm. Prior to the investigations, the chitosan films were etched in methanol to remove acid residues (the etching time was 24 h), and next air-dried for 24 h.

## Research Methods

The kinetics of water sorption by tested samples was investigated by the gravimetric method using an analytical balance.

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).

Prior to proper water sorption measurement, the tested samples were dried at the temperature around 100°C to constant mass. Next, they were placed in the desiccators containing saturated solutions of the above mentioned salts. Every several minutes the samples were taken out, their mass was measured (and IR spectra recorded – not shown here). The measurements were made until reaching the state of equilibrium (ca. 4 h). The estimated error of gravimetric measurements was about 10%. The error resulted primarily from the experimental method that consisted in taking the samples out from the desiccator to weight them which disturbed thermodynamic equilibrium of the system for a short time. Similar measurements were triplicated.

**TABLE 2** Water Activities over Saturated Solutions of Various Salts

| Salts | $a_w$ |
|---|---|
| $CH_3COOK$ | 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 |

$a_w$ – water activity.

# RESULTS AND DISCUSSION

## Water 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 ($a_w$) and for variable composition of CH/HPC blend, are shown in Figure 1.

The modification of chitosan by mixing it with HPC, much deteriorates its sorption abilities. The smaller is the HPC fraction in the blend and the higher water activity, the higher is water absorptivity and shorter is the time in which sorption equilibrium is settled.

Similar relations are observed in chitosan blends with PVAL. The effect of chitosan structure packing by adding PVAL macromolecules is evident [3,4,6]. Beside chitosan sorption, even a 20% fraction of PVAL affects significantly its other properties.

## Determination of Diffusion Coefficients

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

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where:

C – concentration
D – effective kinetic diffusion coefficient
t – time,
x – distance

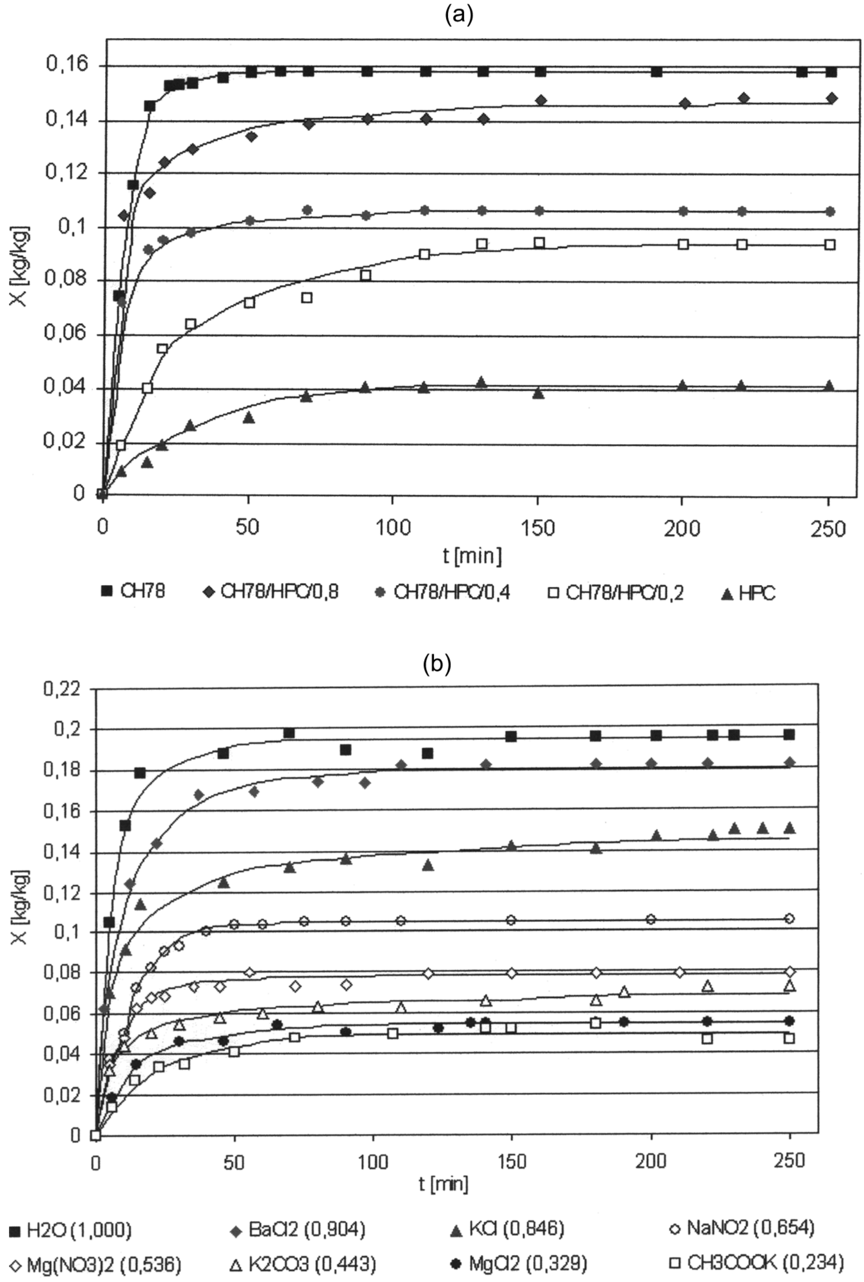

**FIGURE 1** Kinetic curves of water sorption for a) chitosan, HPC and its blends with CH/HPC ($a_w = 0.765$); b) CH/HPC/0.6 blends at different water activities ($a_w$); X – mass of water in the sample per 1 kg dry material.

Solution of Eq. (1) is given in formula (2):

$$\frac{X_t}{X_\infty} = 1 - \sum_0^\infty \frac{8}{(2n+1)^2\pi^2} \exp\left[-\frac{D\pi^2}{L^2}(2n+1)^2 t\right] \tag{2}$$

where:

L – sample thickness
n – natural number (in calculation n = 10 was assumed)
$X_t$ – water mass in the sample in time t,
$X_\infty$ – final water mass in the sample (in saturated state).

Figure 2 shows the examples of theoretical curves (lines) described by Eq. (2) fitted to experimental data (points) obtained for the following samples chitosan blends with HPC of different weight fractions of chitosan. The best fitting allowed us to estimate kinetic diffusion coefficients D, whose dependence on chitosan weight fraction $w_f$ in blends is shown in Figure 3.

The effective water diffusion coefficient D in CH78/HPC blends increases with water activity and is the highest for pure chitosan.

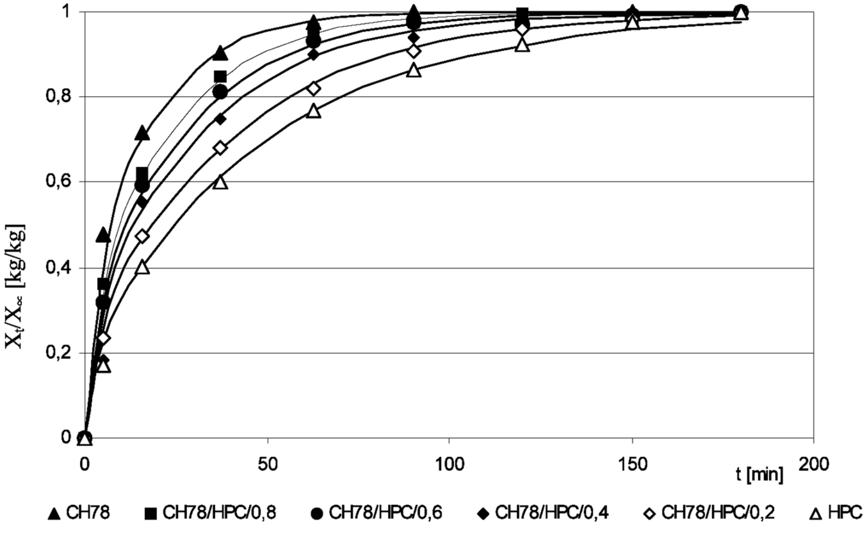

**FIGURE 2** Theoretical curves of Eq. (2) (lines) fitted to experimental points obtained during sorption (CH78/HPC blends with different $w_f$, $a_w = 0.329$).

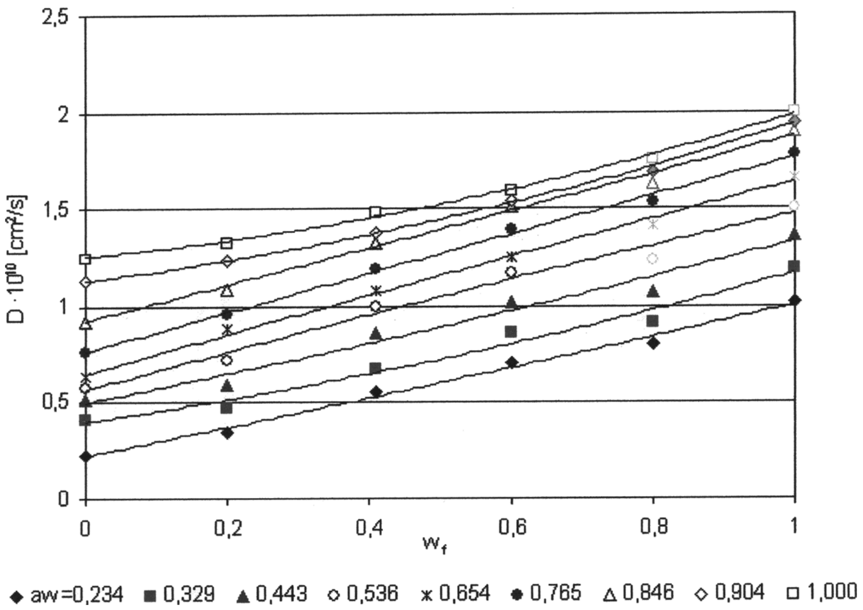

**FIGURE 3** Dependence of the effective diffusion coefficient D on weight fraction of chitosan $w_f$ in CH78/HPC blends for different water activities $a_w$.

## Estimation of the Pore Volume

Assuming that the characteristic curves of water sorption to materials are related to the capillary structure of an adsorbent and the volume of liquid phase adsorbed in the pores W depends on water activity $a_w$, the following relation can be used to determine the volume of pores:

$$W = W_0 \exp\left[-bR^2T^2\left(\ln\frac{1}{a_W}\right)^2\right] \tag{3}$$

where:

$W_o$ – pore volume,
R – gas constant,
T – temperature,
b – parameter related to capillary pore volume distribution.

The tested polymers are adsorbents of porous, nonhomogeneous structure. At low water activities, water fills up the pores of the

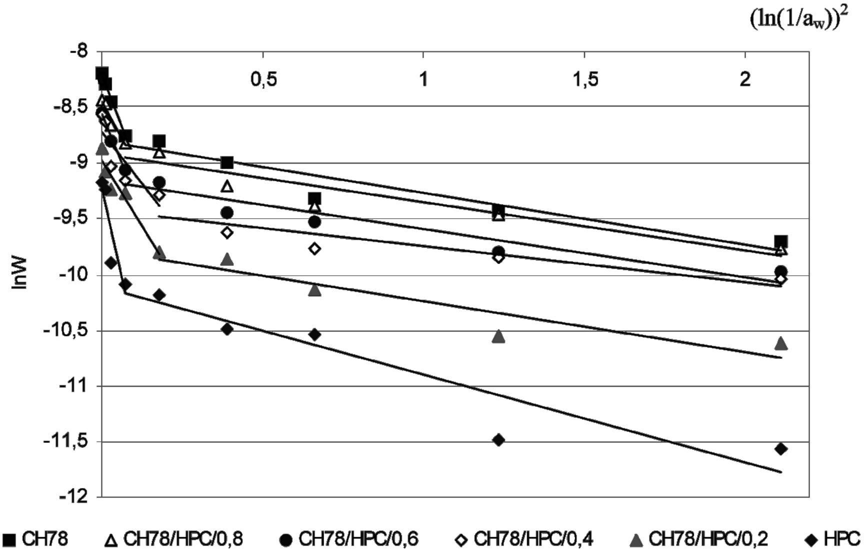

**FIGURE 4** Dependence of lnW on $(\ln 1/a_w)^2$ for CH78, CH/HPC blends and HPC.

smallest diameters. With growing $a_w$, in the gas phase pores of bigger diameters are filled up.

Basing on Eq. (3), porosity of tested films was determined. The value of $W = X/\rho_w$ ($\rho_w$ – water density) was calculated and dependence of lnW on $(\ln(1/a_w))^2$ was determined, as shown in Figure 4. Measuring points shown in the diagram, are arranged along two lines. By extrapolating straight lines to $(\ln(1/a_w))^2 = 0$, the pore volumes $W_{01}$ and $W_{02}$ were obtained. 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 $a_w > 0.7$.

Dependence of $W_{01}$ and $W_{02}$ on the weight fraction of chitosan in the blend with HPC is illustrated in Figure 5. A modification of chitosan by mixing it with hydroxypropyl cellulose causes a decrease of porosity as a result of good packing of HPC molecules in a quite loose structural volume of chitosan.

## The Sorption Isotherms

The sorption isotherms can be divided into three parts, analyzing the type of moisture bonds with the material and the character of the interactions. In region I ($a_w < 0.2$) moisture molecules adsorbed are on polar components of the material – monomolecular adsorption.

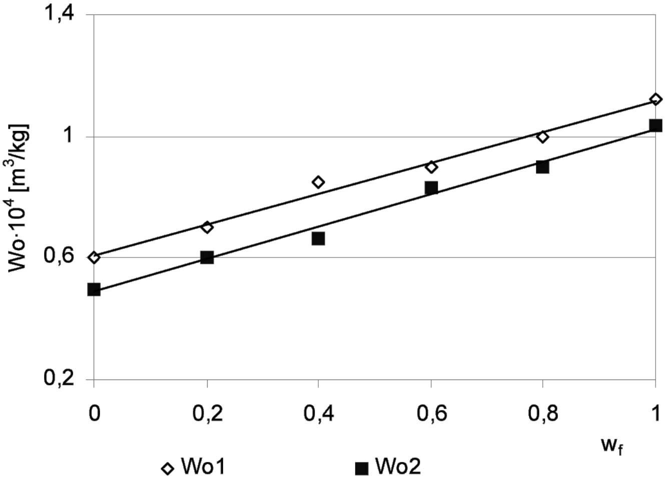

**FIGURE 5** Dependence of $W_o$ on chitosan weight fraction in CH78/HPC blend.

Region II is characterized by a polymolecular adsorption. In region III moisture fills up the pores in the material structure – capillary condensation [7].

Figure 6(a–b) presents the sorption isotherm obtained for a) chitosan of various deacetylation degrees (DD), b) CH78, CH78/HPC and HPC blends. For each film at every water activity the equilibrium moisture content X was estimated and drawn versus water activity $a_w$.

Analyzing the medium hygroscopic shape of isotherm curves one observes good fitting to the GAB [8] equation:

$$\frac{X}{X_m} = \frac{Cka_w}{(1 - ka_w)(1 - ka_w + Cka_w)} \tag{4}$$

where: $X_m$, C and k – parameters of the GAB equation.

The GAB multilayer absorption theory predicts that for the first layer, the water molecules are absorbed by the polar groups on the polymer chains and the next nth layer corresponds to the water molecules successively condensed on the first layer. It allows us to find the equation parameters and to calculate a heat of water sorption in the materials.

Estimated GAB parameters $X_m$, C and k are introduced in Table 3. The values of GAB parameters C and $X_m$ change with DD of chitosan and weight fraction $w_f$ of chitosan in blends. C and $X_m$ increase with a

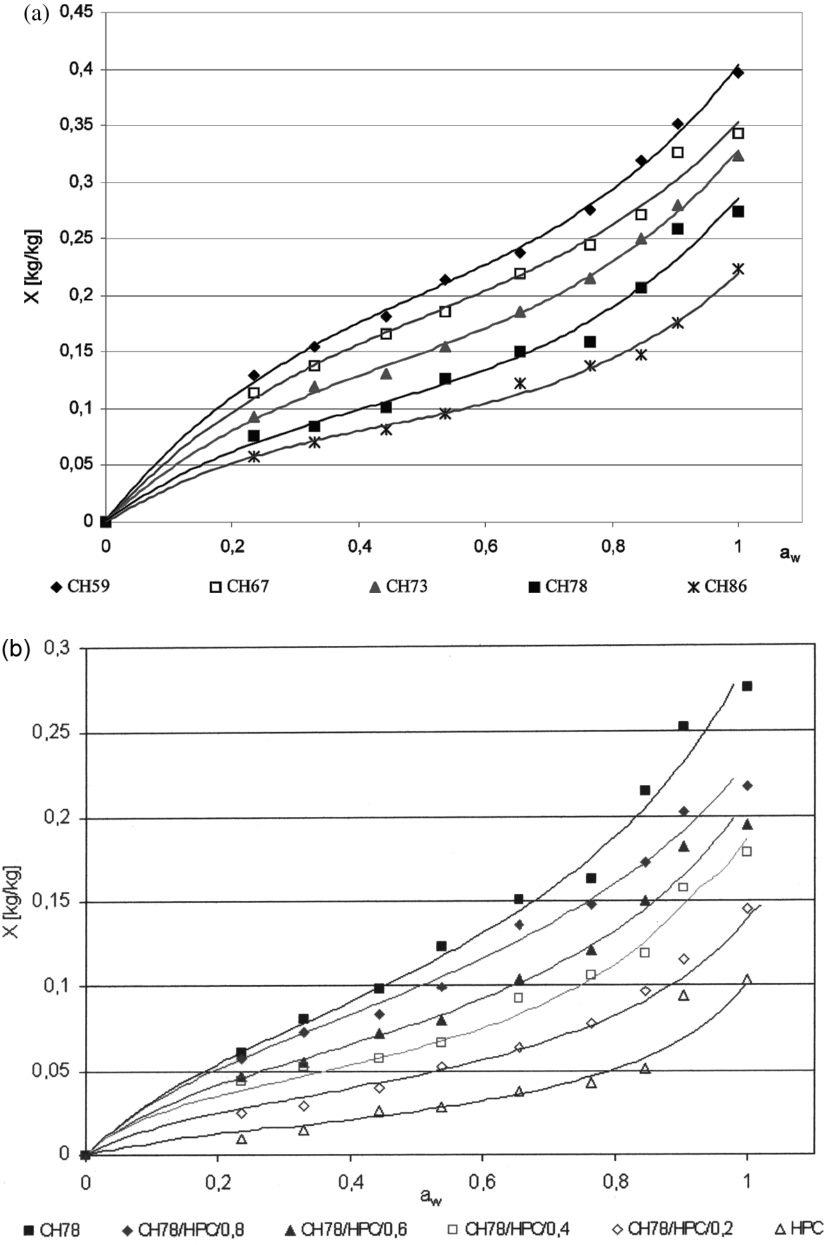

**FIGURE 6** Sorption isotherms for films made from a) chitosan of different deacetylation degree, b) chitosan CH78, CH78/HPC blends and HPC (points – experimental results, curve – GAB equation).

**TABLE 3** Parameters $X_m$, C, k in the GAB Equation

(a) Chitosan of Various Deacetylation Degrees (DD)

| Sample | DD | $X_m$ | C | k |
|---|---|---|---|---|
| CH59 | 59 | 0.16 | 13.25 | 0.62 |
| CH67 | 67 | 0.15 | 11.68 | 0.61 |
| CH73 | 73 | 0.11 | 12.31 | 0.67 |
| CH78 | 78 | 0.09 | 10.01 | 0.70 |
| CH86 | 86 | 0.07 | 9.84 | 0.65 |

(b) Chitosan Blends with Hydroxypropyl Cellulose of Various Weight Fractions of Chitosan ($w_f$)

| $w_f$ | Sample | $X_m$ | C | k |
|---|---|---|---|---|
| 1 | CH78 | 0.09 | 10.01 | 0.70 |
| 0.8 | CH/HPC/0.8 | 0.09 | 9.02 | 0.65 |
| 0.6 | CH/HPC/0.6 | 0.06 | 8.00 | 0.72 |
| 0.4 | CH/HPC/0.4 | 0.04 | 7.53 | 0.79 |
| 0.2 | CH/HPC/0.2 | 0.03 | 7.04 | 0.75 |
| 0 | HPC | 0.02 | 5.69 | 0.82 |

lowering value of DD. In the case of CH/HPC blends, $X_m$ and C values increase with a rising weight fraction of chitosan.

## CONCLUSIONS

The kinetic curves of water sorption in chitosan indicate a strong effect of deacetylation degree on this process. The lower the deacetylation degree, the better are the polymer sorption properties.

The observed dependence of moisture content in chitosan (and the character of isotherm curves) on its DD is not only a result of a variable chemical structure of the co-polymer and its molecular weight, but also of differences in spatial packing of chains and differences in crystallinity degrees [1,9,10].

A big acetamide group present in chitin part of chitosan macromolecule causes steric limitations of structure packing; voids of molecular sizes (nanopores) appear which can be filled with water molecules and their aggregates.

Water diffusion coefficient D in chitosan increases with water activity. The higher the chitosan deacetylation degree, the lower is the value of water diffusion coefficient and the smaller the pore volume in the polymer structure [6].

Modification of chitosan due to mixing with HPC causes a significant deterioration of its sorption properties. The lower is the fraction of HPC in the mixture and the higher water activity, the higher is water absorptivity and the shorter is the time required to settle sorption equilibrium.

The bigger is the weight fraction of chitosan in CH/HPC blend the higher coefficient D and pore volume is observed. It is due to good HPC packing in the porous chitosan volume.

The GAB equation well describes sorption isotherms of studied polymer biomaterials based on chitosan. Parameters C, k and $X_m$ will be a subject of further structural analysis of biomaterials [8].

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