

EFFECTS ACCOMPANYING WATER SORPTION IN CHITOSAN BLENDS

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Abstract

Growing interest in the applicability of chitosan in various branches of economy caused a development of research on chitosan modification, for example the production of new chitosan blends with specific properties.

In the paper, miscibility of two hydrophilic polymers, i.e. chitosan with hydroxypropyl-cellulose, is discussed. By analysis of microscopic and FTIR results of the blends, the interaction by hydrogen bonds of functional groups of both polymeric components were observed, leading to some miscibility and a structural packing into micron size domains.

The effect of hydroxypropylcellulose content in chitosan blends on water sorption isotherms was determined. In spite of the predicted presence of molecular interactions between components, the amount of sorbed water in various water activities is linearly proportional to the weight fraction of chitosan in blends. Similarly, physical GAB parameters describing isotherm curves show a linear dependence on blends composition. This fact can be explained by the process of substitution of weak hydrogen or ionic bonds existing between active groups of components by hydrogen bonds with a participation of water, especially after reaching a single molecular layer of water in mesopores of the polymer mixture.

Determined values of mesopore volumes decrease with chitosan content in the blends. The isosteric heat of water sorption (also of a single layer) shows an exponential decrease with increasing water content in the samples and depends on the composition of blends.

The relations for modeling sorption isotherm of chitosan-hydroxypropylcellulose blends as a function of alternating composition were also presented.

Introduction

Natural polymers such as chitosan and its blends in many areas supersede synthetic fibers which are environmental nuisance. Chitosan belongs to the class of modern high-tech biopolymers which find applications in technology, medicine, agriculture and biotechnology [1]. Due to their basic character it shows unique features such as bioactivity, biodegradability and biocompatibility, which distinguish it from other polysaccharides. These properties are a result of uniformly distributed amino groups in polyanhydro-glutamine chain. By physicochemical or chemical modification of chitosan a number of different practically important polymer forms are produced [2, 3]. In this paper results of sorption studies in relation to the discussion of interrelations on the domain boundary in the chitosan-hydroxypropylcellulose system in the presence of water are presented. The studies of water sorption by chitosan and its hydroxypropylcellulose blends [4] in the form of films

with different weight fractions of components are presented and thermal effects accompanying the sorption process are determined.

It is widely accepted in the literature [5, 6] that the shape of the sorption isotherms and the water partitioning within a mixture can be calculated from a weighted average of the sorption behavior of the individual components. Thus, the moisture content of the mixture of 2 components can be given by:

$$X_{mix} = (1 - w_f) \cdot X_1 + w_f \cdot X_2 \quad (1)$$

where X_{mix} is the equilibrium moisture content of the mixture at specific water activity, X_1 and X_2 are the equilibrium moisture components in the pure form at this water activity and w_f weight fraction of second component in the mixture.

From the sorption isotherms, water partitioning can be predicted at any water activity if we assume that: 1. the mixture is at equilibrium and so water activity of all components is the same and equal to the overall water activity of the mixture; 2. the sorption characteristics of each component in the mixture are unaltered by the presence of other components.

The moisture content of every component in the mixture at a particular water activity can be obtained from the sorption isotherm of the pure component.

Several mathematical equations have been proposed in the literature to describe the sorption isotherm. One of the most widely used models is the GAB model (equation (2)) [7-9] :

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

where: X – water content on a dry weight basis; X_m – the 'monolayer' moisture content; $a_w = p/p_s$ – water activity defined as the ratio of vapor pressure over water (p) to vapor pressure over the tested sample (p_s); $k = e^{d/RT}$ – parameter in the equation; d – energy needed to transport water inside a multimolecular absorbent layer; c – parameters of the GAB equation; T – process temperature; R – gas constant. The equation has been shown to successfully describe water sorption isotherms up to water activity of 0.9. Parameters of the equation should be then in the range: $0.24 < k \leq 1$ and $5.67 \leq c < \infty$ [10,11].

Parameter c in the GAB isotherm equation is used to calculate the mean heat of adsorption of the first layer of gas molecules (E_1) and pure molar heat of absorption q :

$$q = E_1 - E_L = R \cdot T \cdot \ln c \quad (3)$$

where E_L – molar heat of adsorptive vapor condensation.

By a direct analysis of experimental isotherms that describe water sorption by a given adsorbent at different temperatures, one can define thermal effect accompanying a transformation in isobaric conditions, i.e. the so-called isosteric heat of adsorption q_{st} . The isosteres are the lines representing the dependence of water activity on temperature at a constant amount of adsorbed gas.

Pure molar isosteric heat of adsorption can be calculated from slopes of the straight lines of particular isosteres, using the converted Clausius-Clapeyron equation:

$$q_{st}^o = -R \cdot \left(\partial \ln a_w / \partial \frac{1}{T} \right)_X \quad (4)$$

Taking into account Riedel relations which describes variations of water activity with temperature [12]:

$$\ln \left[\frac{a_w(T_2)}{a_w(T_1)} \right]_X = A_1 \cdot e^{(-A_2 \cdot X)} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

the isosteric heat of adsorption q_{st} is presented as a function of water content in material X according to the equation:

$$q_{st} = q_{st}^o + E_L = C \cdot e^{(-A \cdot X)} + E_L \quad (6)$$

where A and C are constants.

The characteristic curves of water sorption to material are related to the capillary structure of adsorbent and volume W of the liquid phase adsorbed in the pores. ($W = X/\rho_w$ where ρ_w – water

density). Volume W depends on water activity a_w . The following relation presenting dependence of W on water activity a_w was predicted [13] to determine the volume of mesopores:

$$W = W_o \cdot \exp \left[-bR^2T^2 \left(\ln \frac{1}{a_w} \right)^2 \right] \quad (7)$$

where: W_o – mesopore volume, R – gas constant, T – temperature, b – parameter related to capillary distribution of pore volume.

Material and Methods

Chitosan (CH) is a natural copolymer of glucosamine and N-acetylglucosamine; it is formed during deacetylation of chitin, a polysaccharide that occurs in the shells of crabs, shrimps, lobsters, insects and other crustaceans, and also in fungi parenchyma and cell walls of microorganisms.

An object of this study was a sample of chitosan (from krill) with deacetylation degree (DD) 78%, crystallinity degree 25% and $M_w=2.1 \cdot 10^5$ purchased from the Sea Fishery Institute in Gdynia, where it was produced.

Chitosan is insoluble in water, but with acetic acid it forms a water-soluble salt called chitosan acetate. Chitosan of deacetylation degree $DD = 78\%$ in the form of powder, was dissolved in 1% acetic acid to produce 2% solutions. The process of chitosan dissolution took place at room temperature (ca. 24°C) for about 48 h. Two samples of chitosan were prepared in the form of films: 1. chitosan acetate from acetic acid solution and 2. sample 1 treated with NaOH solution to get a chitosan film.

A polymer used for the physical modification of chitosan was hydroxypropylcellulose (HPC) of crystallinity degree 51% and $M_w=1 \cdot 10^5$ purchased from Sigma-Aldrich Chemie, Germany. Hydroxypropylcellulose (HPC) is an ester of cellulose obtained due to binding propylene oxide to hydroxyl groups of alkylcellulose.

Both polymers, as high-molecular polysaccharides, can sorb water easily by formed hydrogen bonds using hydroxyl and amide groups that exist in their structures.

In order to obtain blends of CH with HPC of proper weight fractions of the components, appropriate amounts of 2% chitosan acetic solution were mixed with 2% water solution of hydroxypropylcellulose. The solutions of chitosan CH, HPC and their blends (CH/HPC) were cast onto glass plates (left for 3 days to evaporate water) to produce films of comparable thicknesses equal to about 15 μm .

Spectrophotometric analyses of CH/HPC blends were made using a Genesis II FTIR spectrophotometer (Mattson). Basing on the FTIR analysis, functional groups present in macromolecules of the tested blend and corresponding absorption bands with defined wave number were identified. The spectra were collected at ambient temperature at the resolution 4 cm^{-1} and 16-time scanning.

The kinetics of water sorption by tested samples was investigated by the gravimetric method using an analytical balance. Water sorption was analyzed at the temperatures 25°, 35° and 45°C ($\pm 1^\circ\text{C}$) in 9 desiccators equipped with a hygrometer and thermometer, each of them containing saturated solution of a different salt 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 various salts. The measurements were made after reaching the state of equilibrium (ca. 4 h). The estimated error of gravimetric measurements was about 10%. The measurements were triplicated.

Results and Discussion

Morphological structure

Chitosan hydroxypropylcellulose blends obtained from a solution are characterized by good miscibility of components on the level of domain dimensions of the order of a wavelength of visible light. The films are transparent, with slightly bluish color in the transmitted light. The DSC and DMTA analyses showed [14] that there were two glass transition temperatures characteristic of both

components which indicated that the polymers despite similarities of chemical structure were immiscible on molecular level.

Figures 1 a and b show microphotographs of the structure of CH/HPC blends with weight fraction HPC $w_f = 0.4$, both dry and containing about 40% water (after equilibrium water sorption at activity $a_w = 1$). A visible increase of domain sizes (first of all of chitosan, which sorbs more water than HPC) and good miscibility of both components on the domain level, which leads to good packing of the structure, are observed.

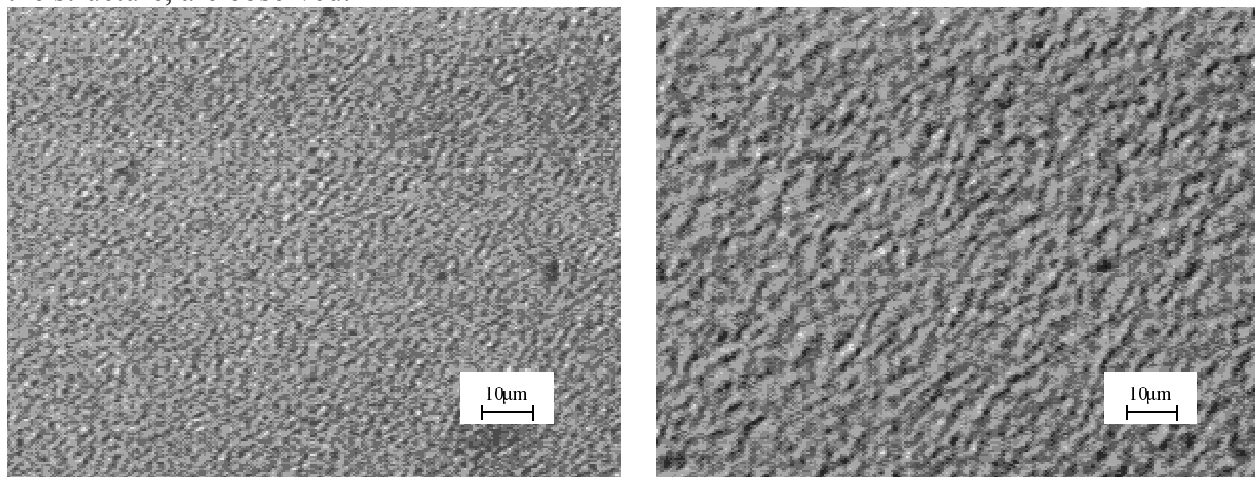


Figure 1 : Morphology of CH/HPC blend with $w_f = 0.4$; temp. 25°C a) dry sample, b) after water sorption at $a_w=1$

Analysis of FTIR spectra

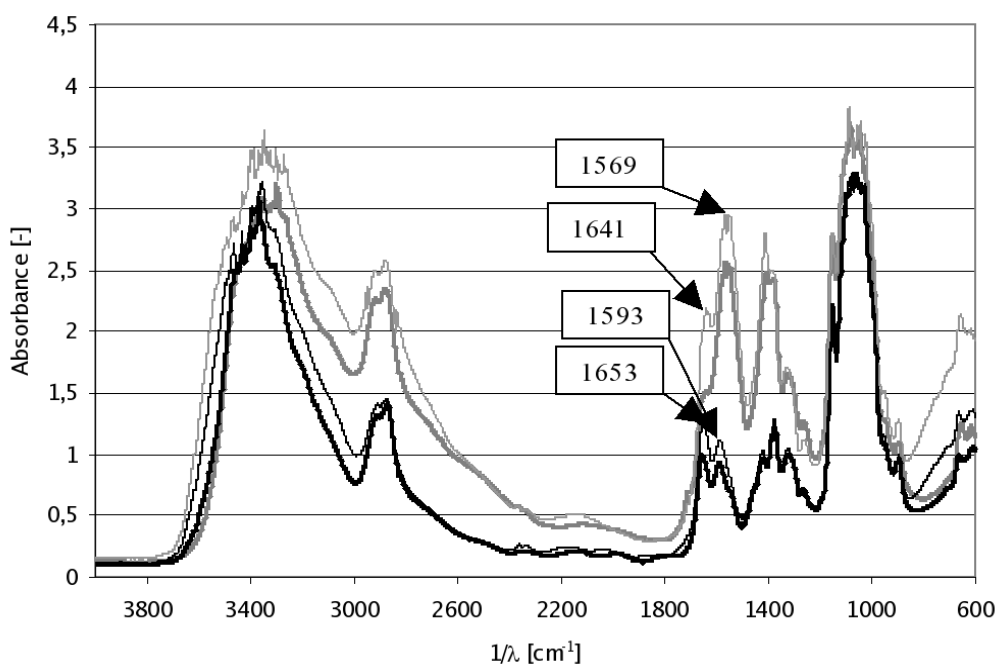


Figure 2 : FTIR spectra of the following films: — - chitosan acetate after water sorption ($a_w = 1.0$); — - dry chitosan acetate; — - chitosan after water sorption ($a_w = 1.0$); — - dry chitosan. Numbers mean the wavelength frequencies (in cm^{-1})

When analyzing absorption spectra (Fig. 2) of chitosan and chitosan acetate in the dry state, a decrease of absorbency of the absorption band of amino group NH_2 (1593 cm^{-1}) is observed as compared to the absorbency of chitosan acetate. The position of peak also changes – there is a shift of the wave number to lower values from 1593 to 1569 cm^{-1} .

In both samples the presence of water does not cause peak shift and is reflected by growth first of all in the bands of amide groups and hydrogen groups.

Figure 3 shows absorption spectra of chitosan acetate, hydroxypropylcellulose and CH/HPC blend with weight fraction $w_f = 0.4$. It can be observed that the presence of HPC in the blend with chitosan acetate does not induce any significant change in the position of amide group peak (a slight decrease of the wave number from 1569 to 1563 cm^{-1}). In the range of OH hydrogen group relations (3400-3300 cm^{-1}) occurring in both polymers, absorptency bands in the mixture are modified.

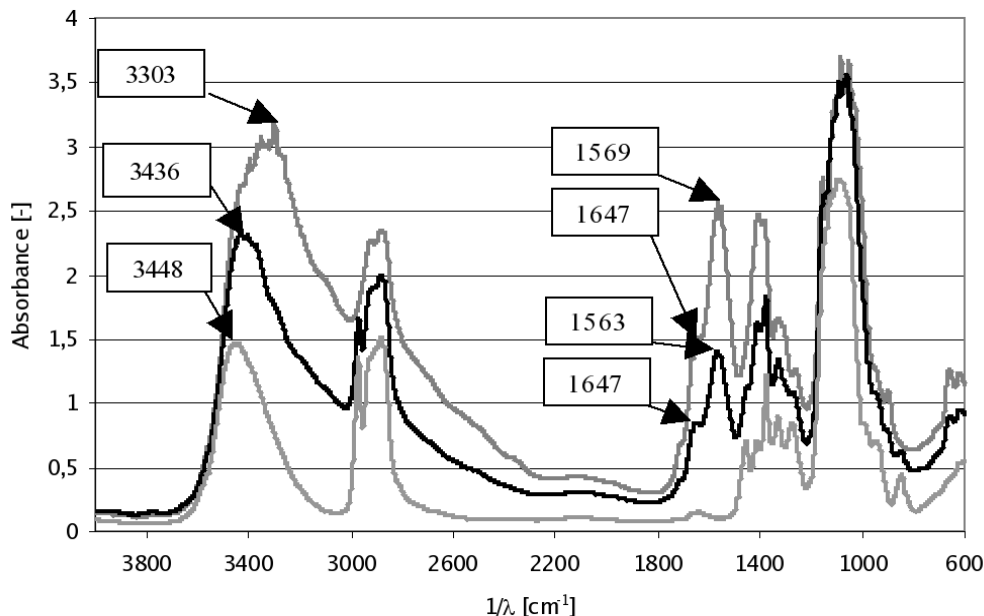


Figure 3 : FTIR spectra of dry samples: — - chitosan acetate ($w_f=0$); — - CH/HPC ($w_f=0,4$); — - HPC ($w_f=1$). Numbers mean the wavelength frequencies (in cm^{-1})

Analysis of sorption isotherms

Analysis of curves – sorption isotherms, with the use of linearization method of the GAB equation enabled the determination of physical parameters of the equation X_m , c , k .

Coefficient k reached similar values for each temperature and composition and was equal to 0.85. Dependence of coefficients c and X_m on the weight fraction of HPC appeared to be rectilinear. They are described by equations (8-11) given in Table 1.

Equations (12) and (13) given in Table 1 enable modeling of sorption isotherms of the CH/HPC blend as a function of its variable composition, taking into account the dependence of GAB coefficients on the weight fraction of HPC in the blend with CH.

Table 1: Functions coefficients of the GAB equation and sorption isotherms

Temp.	X_m	c	X
25°C	$X_m = -0.043w_f + 0.069$ (8)	$c = -46.5w_f + 49$ (10)	$X = \frac{(1.74 \cdot w_f^2 - 4.63 \cdot w_f + 2.95) \cdot a_w}{(1 - 0.87 \cdot a_w) \cdot (1 - (40.46 \cdot w_f - 41.77) \cdot a_w)}$ (12)
45°C	$X_m = -0.040w_f + 0.060$ (9)	$c = -59.7w_f + 61.8$ (11)	$X = \frac{(1.98 \cdot w_f^2 - 5.02 \cdot w_f + 3.07) \cdot a_w}{(1 - 0.83 \cdot a_w) \cdot (1 - (49.55 \cdot w_f - 50.46) \cdot a_w)}$ (13)

Analysis of the results indicates that there is a distinct effect of weight fraction of components in the CH/HPC blend on the process of sorption and the obtained isotherms.

Figure 5a shows the dependence of the amount of absorbed water X at different activities on the weight fraction of HPC in the blend with CH. This dependence is rectilinear thus indicating a heterogeneous character of the blend structure. Water penetrating the capillary structure of films (acting like a plasticizer plays the main role in transmission of the component interactions. Figure

5b shows dependence of the amount of moisture in HPC as a function of total moisture content. Continuous curves correspond to sorption isotherms according to the GAB equation.

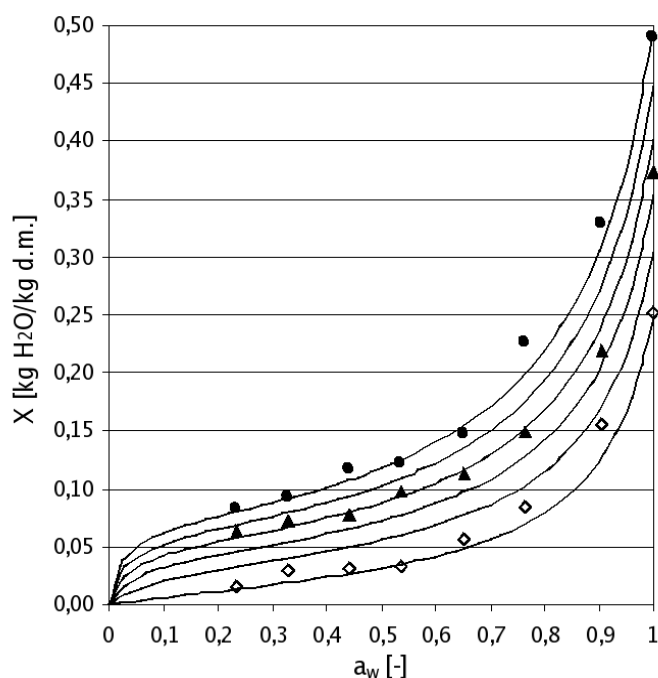


Figure 4 : Water sorption isotherms at the temperature 25°C modeled according to eq. (12) ($w_f=0, 0.2, 0.4, 0.6, 0.8, 1.0$). Points represent selected experimental data obtained for the blend of $w_f=0.4$ ▲, HPC ◇ and chitosan (acetate) ●; w_f — weight fraction of HPC; d.m.-dry mass.

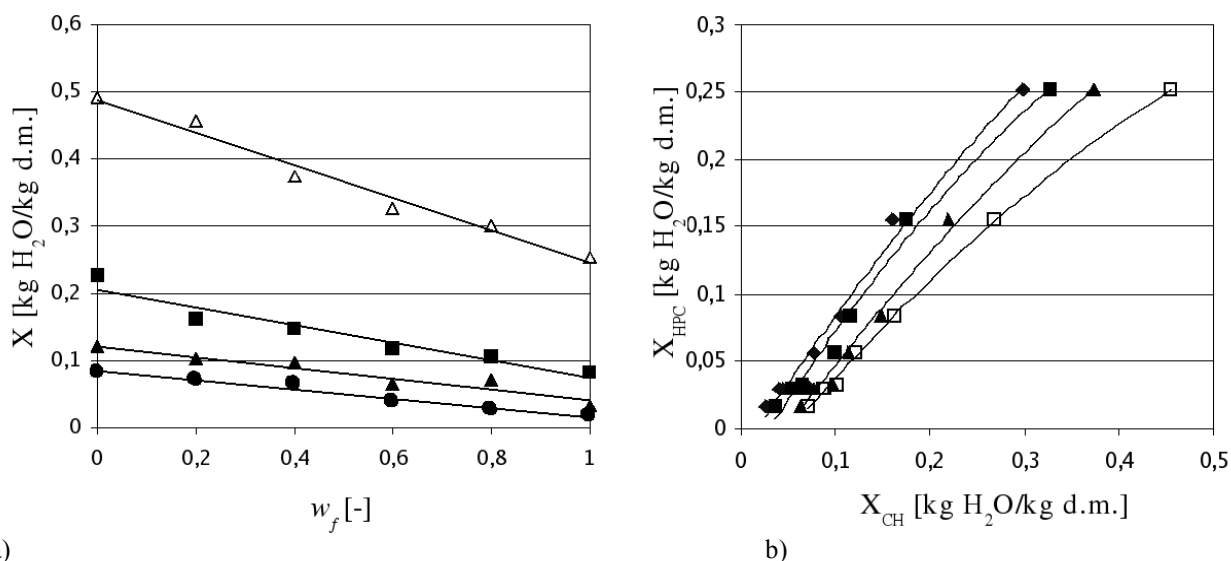
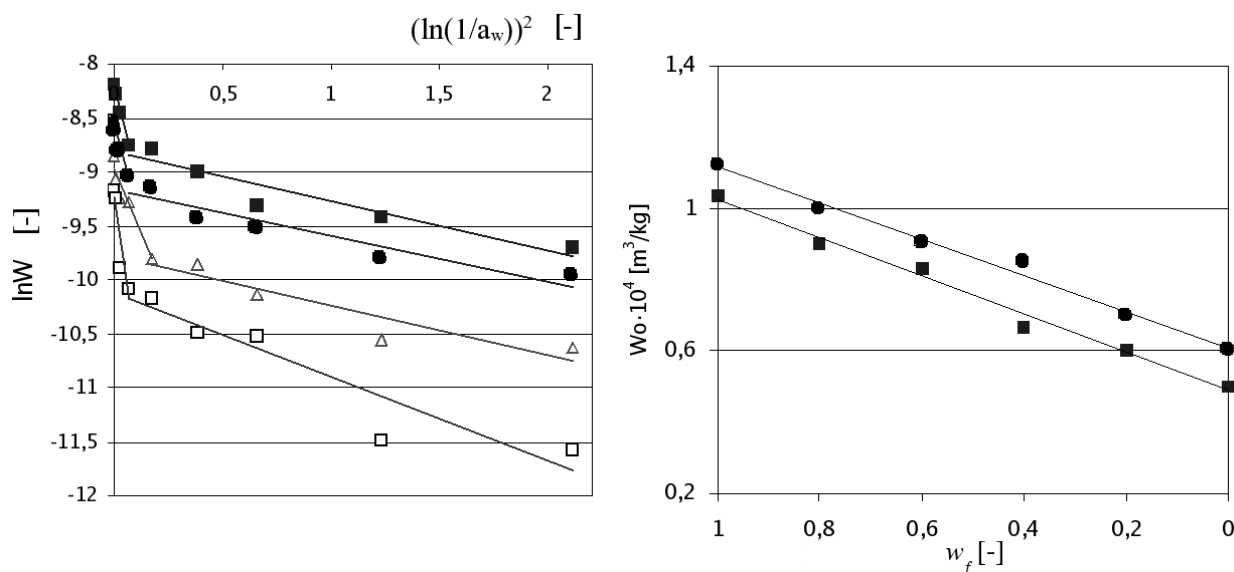


Figure 5 : Dependence of a) amount of absorbed water X on w_f at different water activities: a_w : Δ - 1, ■ - 0.765, ▲ - 0.536, ● - 0.234; b) Dependence of moisture content of the HPC X_{HPC} in blends HPC/CH of w_f equal to: ◆ - 0.8, ■ - 0.6, ▲ - 0.4, □ - 0.2; versus overall moisture content X . The solid lines are obtained from GAB equation of sorption isotherm; w_f — weight fraction of HPC; d.m.-dry mass.

Pore size

Figure 6 shows analysis of pore volume in the CH/HPC blend made on the basis of equation (6). The dependence of $\ln W$ on $(\ln(1/a_w))^2$ shown in Fig. 6a was determined. Measuring points in the diagram are arranged along two lines. Basing on the extrapolation of straight lines to $(\ln(1/a_w))^2=0$ mesopore volumes W_{01} and W_{02} were calculated. Their values presented as a function of the weight fraction of HPC in the blend are shown in Fig. 6b. For $a_w < 0.7$ smaller pores of volume W_{02} , while for $a_w > 0.7$ bigger pores of volume W_{01} are filled. Modification of chitosan by blending it with hydroxypropylcellulose causes a decrease of porosity as a result of good packing of HPC chains in

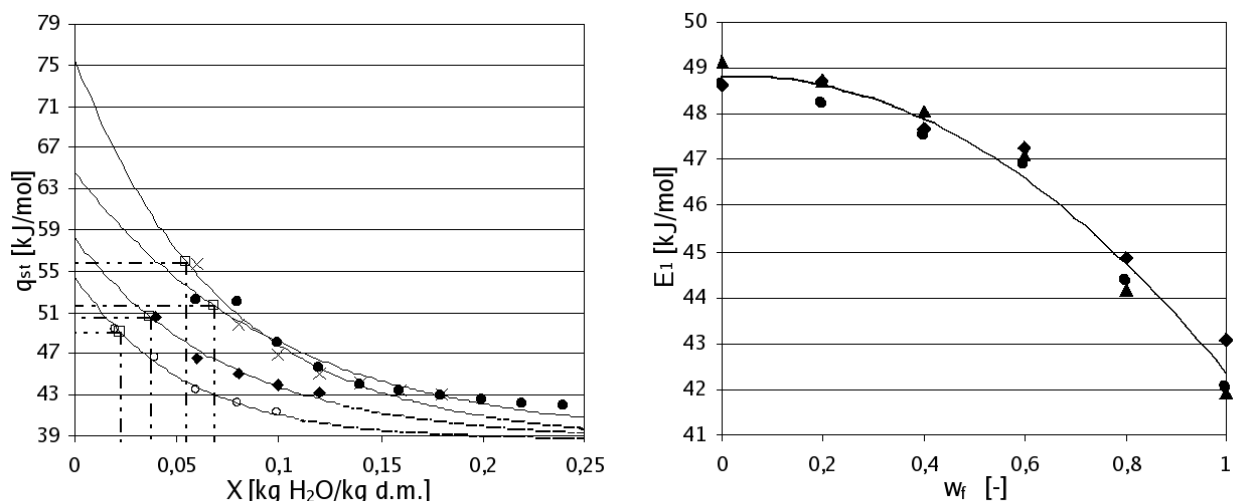
loose structural volume of chitosan. The volume of mesopores in chitosan is about 3 times bigger than in HPC.



a) b)
Figure 6 : Dependence of a) $\ln W$ on $(\ln(1/a_w))^2$ for chosen CH/HPC blends. a_w – water activity, W – water volume in the tested material; ■ – various w_f , ● – 0.4, Δ – 0.8, □ – 1 b) Dependence of W_o on; ● – W_o on; ■ – W_o2 ; w_f – weight fraction of HPC

Thermal effects accompanying water sorption

Values of pure differential isosteric heat of water adsorption q_{st}^0 was determined by transforming water sorption isotherms through polymer films into isosteres in the system: $\ln(a_w) = f(1/T)X$. Reading of the angles of inclination of particular isosteres allows us to calculate q_{st}^0 according to eq. (5). Since adsorption is accompanied by vapor condensation, total isosteric heat $q_{st} = q_{st}^0 + E_L$, where E_L – heat of condensation equal in the tested temperature range (25–45°C) 38.7 kJ/mol. Curves $q_{st} = f(X)$ for selected CH/HPC blends are illustrated in Fig. 7a. Additionally, in the diagram the values of q_{st} corresponding to the monomolecular water layer in the region of porous structure of CH/HPC films are marked.



a) b)
Figure 7 : Dependence of a) q_{st} on the amount of adsorbed water X ; □ – q_{st} of the first layer at $X = X_m$ for w_f : ● – 0; × – 0.2; ◆ – 0.6; ○ – 1; b) E_1 on w_f at temp: ● – 25°C, ◆ – 35°C, ▲ – 45°C; w_f – weight fraction of HPC; d.m. – dry mass.

Relation $q_{st} = f(X)$ shows that the largest thermal effect occurs at the beginning of the process, when the first water layer connected directly with the polymer is filled up. In this way it decreases

exponentially with an increase of the adsorbed water layers, because the contribution of water vapor condensation in the process increases which is characterized by approximately constant heat value EL for the analyzed temperature range. Curves representing dependence of the heat of adsorption of the first layer of water molecules E_1 on w_f drawn according to eq. (6) have a parabolic shape (Fig. 7b). Hence, the effect of weight fraction of HPC on the values of E_1 at process temperature (25°C) can be described by the following function characterizing relations shown in Fig. 7b:

$$E_1 = 42.4 \cdot w_f + 48.8 \cdot (1 - w_f) + w_f \cdot (1 - w_f) \cdot \varphi \quad (14)$$

where: $E_{1\text{HPC}} = 42.4$ kJ/mol – mean heat of adsorption of the first layer of water molecules by HPC; $E_{1\text{CH}} = 48.8$ kJ/mol – mean heat of adsorption of the first layer of water molecules by CH; $\varphi = 7$ kJ/mol – parameter representing the excess function characterising relationships between blend components and water.

Conclusions

Chitosan (and strictly speaking chitosan acetate) blends with hydroxypropylcellulose have a regular domain structure of micron sizes. Good miscibility of both components is probably a result of hydrogen relationships between functional groups and ion relations in polymer chains.

The effect of HPC content in the blend with chitosan on water sorption isotherms was determined and described by equations. The GAB equation was used successfully to describe isotherms. Equation parameters were determined as a function of the blend composition.

The volume of mesopores as a function of HPC content in the blend was determined. It was found that chitosan had about 3-times bigger pore volume and its structure was less packed.

Isosteric heat of sorption was determined as a function of blend composition and the amount of adsorbed water. The dependence of heat of adsorption of the first layer of water molecules being 48.8 kJ/mol for chitosan, and 42.4 kJ/mol for HPC, on the composition was presented.

Acknowledgements

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

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