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Modeling of water sorption isotherms of chitosan blends

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ABSTRACT

The blends obtained on the basis of biodegradable chitosan were investigated taking into consideration possible miscibility of their components due to the presence of hydrogen bonds leading to formation of complexes. However, the components of chitosan blends with hydroxypropyl cellulose, poly(ethylene oxide), poly(vinyl alcohol) and starch show good miscibility only on a domain scale of micron or less size.

The Authors proposed the formula which considers the dependence of moisture content on the weight fraction of the blend components and taking into account the observed lack of additivity resulting from the presence of some molecular interactions (the parameter ∂) of functional groups in the presence of water.

Modelling of water sorption isotherms of polymer blends using the parameter ∂ leads to good correlations with the experimental results simultaneously indicating that the greatest deviation from the moisture additivity occurs in case of high water activity (water humidity).

1. Introduction

Due to its nature, water interacts with hydrophilic polymers as a result of the interactions of the type of hydrogen bonds. Therefore, the physico-chemical properties of those polymers depend on the presence of water in their structure (Pu, Wirsen, & Albertson, 2000). Moisture content present in polymers plays a key role in such properties as the electrochemical and biological activity of polymer membranes and their resistance to hydrolysis and biodegradation.

In hydrophilic polymers part of adsorbed water is strongly bound to the individual places of structure, i.e. the active groups. This is a so-called bound water which is non-freezing and forming a mono-layer. The closest layers of water in which particles are not utterly free form the so-called partially bound water which is freezing. The so-called free water is this part of water which has not contacted with a solid body, filling its pores in a capillary form. This is freezing water and it may be removed by centrifugation.

Polymer blends comprising one hydrophylic component are materials of potentially better biodegradability with regard to the possibility of diffusion of water together with enzyme to the internal structure of the material (Mucha & Pawlak, 2002).

Mixing of polymers is one of the most effective methods applied to obtain materials of new properties, for instance, for biomedical and technical applications.

Due to its properties chitosan is a polymer which is widely investigated and frequently applied to obtain new blends. Chitosan is physically and/or chemically modified in order to improve its mechanical strength, chemical and thermal stability as well as modification of hydrophilicity. Modification of chitosan with other polymers is a widely examined problem. As adblends to chitosan there are applied the following compounds: poly(vinyl alcohol) (Fambri, Pegoretti, Fenner, Incardona, & Migliaresi, 1997; Kim, Oark, & Kim, 2003; Mucha, Ludwiczak, & Kawińska, 2005; Schellekens & Bastiansen, 1991; Zhao et al., 2003) as well as polylactide and poly(lactid acid) (Messai et al., 2005; Peesan, Supaphal, & Rujiravanit, 2005). Great hopes are connected with chitosan blends containing cellulose and its derivatives (Hasagawa, Isogai, Onabe, Usuda, & Atalla, 1992; Twu, Huang, Chang, & Wang ,2003) and with poly(ethylene oxide) (Amiji, 1995; Wrzyszczyński et al., 1995; Mucha, Piekielna, & Wieczorek, 1999). The following systems: chitosan/starch and chitosan/pullulan are also investigated (Lazaridon & Biliadderis, 2002) as well as many others.

To describe water sorption isotherms a popular GAB equation was applied (Anderson, 1946; Lewicki, 1997) and the parameters of this equation k, C and X_m were determined on the way of adjustment of the curves of the equation with the experimental results.

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

where:

a_w – the activity of water above the solution and sample;

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X – the quantity of an adsorbed substance (adsorbate) remaining in the equilibrium state with the pressure of the adsorbate in a gas phase in g/g of an adsorbent;
X_m – indispensable amount of adsorbate for covering the adsorbent with a mono-molecular layer;
C – the constant of GAB equation is connected with pure adsorption heat;
k – the coefficient of GAB equation connected with the energy which is essential to transport one mole of a liquid into the adsorbate layer which has already existed.

The condition of solubility of a macromolecule in a solution as well as the miscibility of both polymers is a negative value of free enthalpy of mixing:

$$\Delta G = \Delta H - T\Delta S < 0 \tag{2}$$

Due to the fact that $\Delta S > 0$ and in case of the polymer it attains a rather low value, the value ΔH should also be low to fulfill the condition. In accordance with the Flory–Huggins' law the free enthalpy of the blend ΔG_m may be defined by the following equation:

$$\Delta G_m = \frac{RTV}{V_s}\left(\frac{x_1}{z_1}\ln x_1 + \frac{x_2}{z_2}\ln x_2 + \chi x_1 x_2\right) \tag{3}$$

where:

x_i – volumetric or mass fraction of i-component;
V – volume of the blend;
V_s – reference volume equal to the molar volume of mer;
z_i – degree of polymerization of i-polymer;
R – the gas constant;
T –temperature;
χ – the parameter of interaction (Flory–Huggins) polymer–polymer.

In case of good miscibility of two polymers, parameter χ should attain the negative values.

Analyzing water sorption isotherms of the investigated blends from the point of view of components' interactions in the presence of water the occurrence of deflection of the adsorbed moisture content value by the blends from the additivity was found. Writing Eq. (4), which indicates this deflection from the additivity resulting from the components fraction, parameter ð dependent on a_w was calculated:

$$X = w_f X_1 + (1 - w_f)X_2 + \eth w_f(1 - w)f) \tag{4}$$

where:

X_1 – the quantity of moisture adsorbed by the first polymer (chitosan) in the investigated water activity (a_w),
X_2 – the quantity of moisture adsorbed by the second polymer in the investigated water activity (a_w),
w_f – weight fraction of the first blend component (chitosan);
ð – the so-called parameter of interaction in the presence of water, derived by an analogy to parameter χ from the Flory–Huggins Eq. (3),
$\eth w_f(1\text{-}w_f)$ – the factor of deflection of moisture content from the additivity.

2. Experimental

2.1. Materials

Chitosan (CH) was produced at the Sea Fisheries Institute in Gdynia. Blends on the basis of chitosan of a deacetylation degree DD = 78,40% and molecular mass $M_w = 2{,}10 \times 10^5$ g/mol were investigated.

Poly(vinyl alcohol) (PVAL) of molecular mass $7{,}2 \times 10^4$ g/mol was purchased at the Polish Chemical Reagents company.

Hydroxypropylcellulose (HPC) of molecular mass 10×10^4 g/mol, produced by Sigma–Aldrich Chemie GmbH, Germany.

Potato starch (S) of moisture content 15,6%, of grain size 20 μm, meeting the Polish norm PN–93/A–74710, produced by PPZ "Trzemeszno" Ltd.

Poly(ethylene oxide) of molecular mass 2×10^4 g/mol originated from the Polyscience Inc.

Blends of chitosan acetate (CH78) with HPC, PVAL, PEO and S in the form of films of various weight fractions were obtained. To reach that goal the following solutions were mixed: 2% solution of chitosan in 1% acetic acid with: 2% water solution HPC (solving time 3 days), 5% water solution PVAL (solving time 3 days), 2% water solution PEO (solving time 1 day), 2% water solution of gellified starch (solving at the temperature 55 °C with simultaneous mixing to obtain gel of low viscosity).

Homogenous blends of the solutions of proper components ratio were cast on a glass or Teflon plate. After vapourization of the solvent the films CH78/HPC, CH78/PEO and CH78/PVAL of thickness ~13 μm and CH78/S of thickness ~22 μm were obtained. In Table 1 the assignment and composition of blends are presented.

2.2. Methods

Water sorption investigations in various water activities (the air humidities) were carried out in the desiccators at ambient temperature of about 23 °C. The desiccators with adjusted covers were equipped with perforated inserts made of net on which the films subjected to sorption were placed. Table 2 presents water activities a_w above saturated solutions of various salts in particular desiccators.

The examined films of chitosan acetate and its blends were dried at the temperature of about. 95 °C for about 30 min to obtain the constant mass. The dry samples were placed in the desiccators. The measurements of mass were performed up to constant value – the moment of equilibrium state (sorption isotherms). Measurement error of mass was estimated to be equal 8%.

3. Results and discussion

3.1. Morphology

Chitosan creates semi-miscible systems with polymers soluble in water such as: poly(vinyl alcohol) PVAL and hydroxypropylcel-

Table 1
Designation of the samples of blends CH78 with HPC, PVAL, PEO and S.

Name of polymer	Weight fraction of chitosan in a blend (w_f)	Designation of the blend
Hydroxypropyl cellulose HPC	0,8	CH78/HPC–0,8
	0,6	CH78/HPC–0,6
	0,4	CH78/HPC–0,4
	0,2	CH78/HPC–0,2
Poly(vinyl alcohol) PVAL	0,8	CH78/PVAL–0,8
	0,6	CH78/PVAL–0,6
	0,4	CH78/PVAL–0,4
	0,2	CH78/PVAL–0,2
Poly(ethylene oxide) PEO	0,8	CH78/PEO–0,8
	0,6	CH78/PEO–0,6
Gellified starch S	0,85	CH78/S–0,85
	0,75	CH78/S–0,75
	0,65	CH78/S–0,65
	0,55	CH78/S–0,55

Table 2
Water activities a_w over saturated solutions of various salts in desiccators.

Salt	Water activity (a_w)
$MgCl_2$	0,329
K_2CO_3	0,443
$Mg(NO_3)_2$	0,536
$NaNO_2$	0,654
NaCl	0,765
$BaCl_2$	0,904
H_2O	1,000

lulose (HPC) in the whole range of compositions as a result of formation of complexes (Mucha & Pawlak, 2003). The microscopic examinations of films CH78 and CH78/PVAL blends indicate the homogenous structure. The films were transparent and did not display any over-molecular structure on the level of observation in an optical microscope. Films CH78/HPC were transparent of slightly milky colour and transparent blue glow. The study on glass temperature indicates the components separation by annealing and creation of two separate glass transition temperatures (Mucha & Pawlak, 2005).

In Fig. 1a and b microphotographs of the structure of the blend CH78/HPC-06, of a dry sample and of the one containing about 40% of water (after the equilibrium water sorption in the conditions of water activity $a_w = 1$) are presented. A visible increase of domain size is observed and a miscibility of both components on a domain level leading to an observed structure packing occurs.

The microscopic results of the CH78/PEO blends are demonstrated in Fig. 2a and b. Poly(ethylene oxide) is a crystallizing polymer. It crystallizes from the solution in the form of spherulites.

The presented microphotographs of morphology of CH78/PEO blends show a clear modification of the morphological PEO structure with the increasing content of CH in the blend. The spherulitic structure of PEO is visible up to 0.8 chitosan fraction in the samples. The presence of chitosan limited the nucleation process of PEO which is reflected in a decrease of the number of spherulites and an increase of their size. Chitosan is embedded into the interlamellar structure of crystallites in PEO spherulites.

Microphotograph of morphology of chosen sample of CH78/S blends is demonstrated in Fig. 3. They present as like fibrillar starch structure well distributed in the chitosan matrix. The CH78/S blends of lower starch concentration have similar more packed structure.

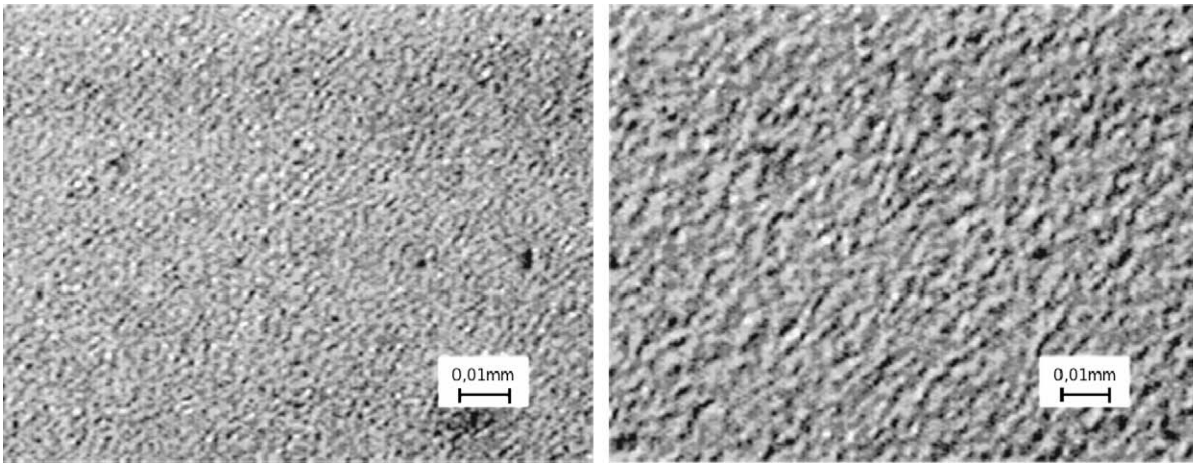

Fig. 1. Microphotograph of the morphology of CH78/HPC blend $w_f = 0.4$; (a) a dry sample, (b) after water sorption in $a_w = 1$.

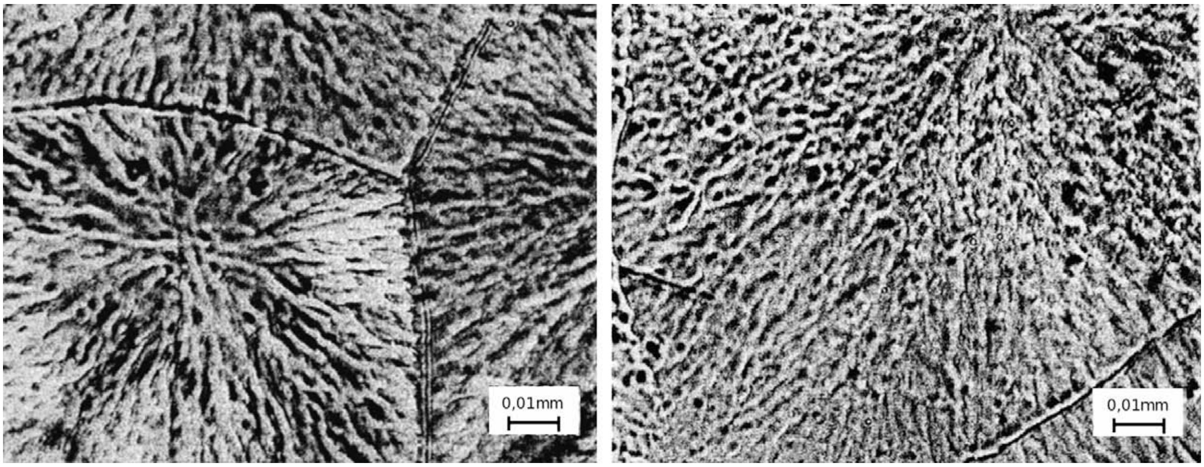

Fig. 2. Microphotograph of the blend (a) CH78/PEO–0.6 (b) CH78/PEO–0.8 (dry samples).

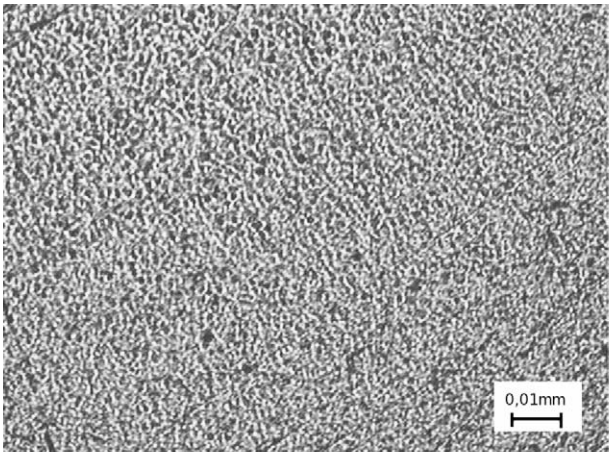

Fig. 3. Microphotograph of the blend CH78/S–0.65 (dry sample).

3.2. Modelling of sorption isotherms in the function of blends composition

Fig. 4 presents plots of moisture content X on the chitosan weight fraction for chosen water activities a_w. The parameters $\eth$ are calculated by the adjustment of the curves to Eq. (4).

The curves in Fig. 4 are of shape closer to rectilinear for low values of a_w. Then, the parameter $\eth$ attains the values close to zero, which proves the additivity of the water quantity absorbed by two polymers in the blend which is due to the formation of a water mono-layer. The parameter $\eth$ decreases with the increasing water activity. Thus, the molecular interaction between the components

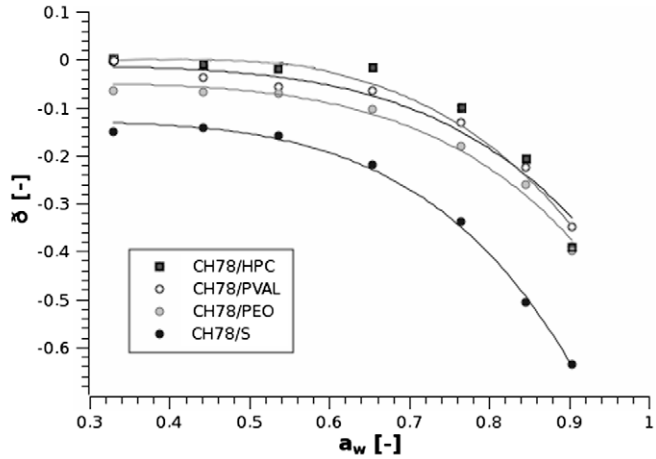

Fig. 5. Dependence of the parameter $\eth$ on a_w for the investigated systems.

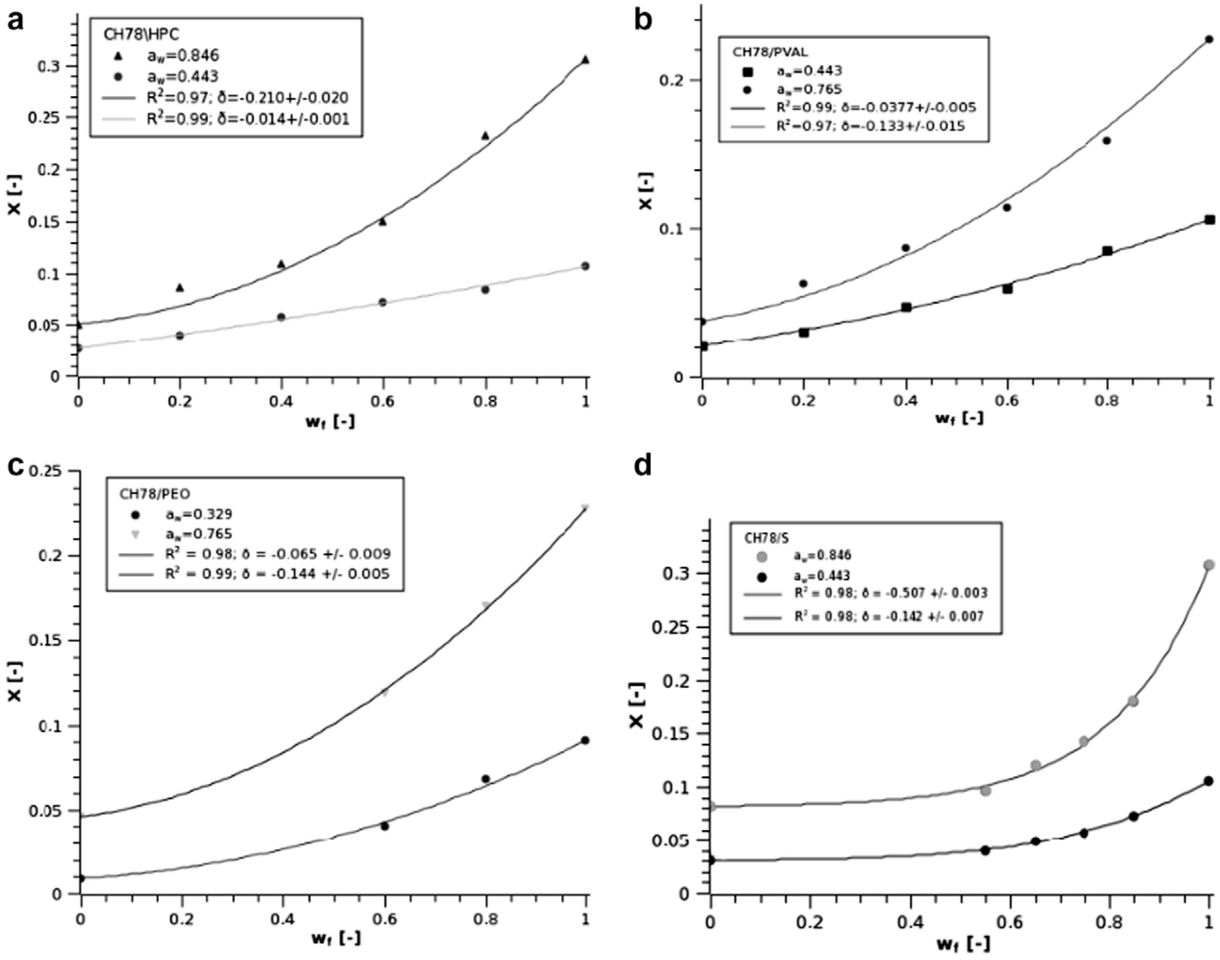

Fig. 4. Dependence of the absorbed moisture X on chitosan weight fraction w_f in blend: (a) CH78/HPC in $a_w = 0.443$ and 0.846 (b) CH78/PVAL in $a_w = 0.443$ and 0.765 (c) CH78/PEO in $a_w = 0.329$ and 0.765 (d) CH78/S in $a_w = 0.443$; 0.536 and 0.846.

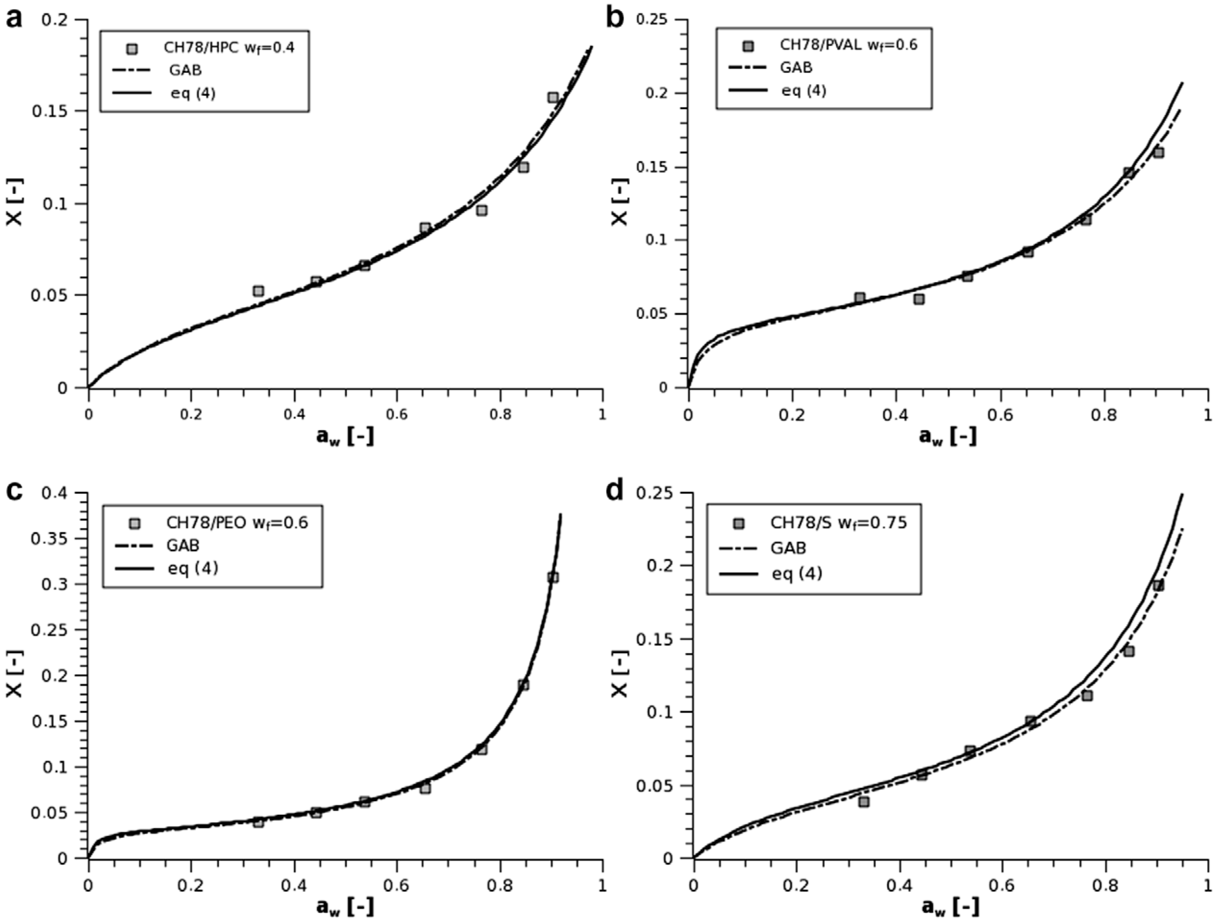

Fig. 6. Sorption isotherms derived from Eq. (4) with the parameter ð (dotted line) and the model GAB (continuous line) calculated for the blends: (a) CH78/HPC, (b) CH78/PVAL, (c) CH78/PEO and (d) CH78/S. Points – experimental data.

of the blends and the components with water change with the increasing moisture content in the sample.

The dependence of the parameter ð on the water activity a_w is demonstrated in Fig. 5.

The sorption isotherms of blends presented in Fig. 6 and determined in accordance with Eq. (4) using the parameter ð, well define the experimental relation $X = f(a_w)$ and they present a good agreement with the model GAB.

The values of parameters k, C and X_m of GAB model determined for the examined systems were presented and discussed in other publications (Balcerzak & Mucha, 2008; Mucha et al., 2005).

4. Conclusions

Water sorption isotherms of blends obtained on the basis of biodegradable chitosan were investigated. A miscibility on a domain scale of micron size by the components of blends CH78/HPC, CH78/PVAL, CH78/PEO, CH78/S is observed.

The dependence describing the moisture content in a blend which considers the molecular interaction of components is proposed. It allows to model the sorption isotherms of a given blend in the function of its changing composition. The formula takes into consideration the dependence of the quantity of the adsorbed moisture content by the blend components not only as a function of their weight fraction in the sample and also defines the parameter ð between the components in the presence of water.

The presented results of well fitting of Eq. (4) to the experimental data pinpoint the complexity of the parameter ð, which comprises the molecular interaction of both polymers with the participation of water (depending on a_w). At high a_w the content of the adsorbed water (moisture) influences the hydrogen bonds between the polymeric components. For $a_w \rightarrow 0$, ð one should respond to the molecular interactions polymer/polymer in the system without moisture content. Such a state practically does not occur in case of hydrophilic polymers. For example, at a typical relative humidity of air equal to 50% the moisture content in chitosan is equal to 16% (Ratto, Jo, Hatakeyama, and Blumstein, 1995; Balcerzak & Mucha, 2008).

The dependence of the parameter ð of the investigated system upon a_w (Fig. 5) indicates that with the increasing water activity (which leads to the increasing moisture content) the deflection of sorption isotherms of polymer blends from the additivity connected with the participation of the components increases.

Modelling of water sorption isotherms of polymer blends with the participation of the parameter of interaction ð in the presence of water leads to a good correlation with the experimental results and GAB model (Fig. 6).

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