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SORPTION PROPERTIES OF MODIFIED POTATO STARCH*

WŁAŚCIWOŚCI SORPCYJNE MODYFIKOWANEJ SKROBI ZIEMNIACZANEJ

Summary

Background. Starch is one of the biopolymers most commonly used in the food industry. In its native form its applications are limited. In contrast, its structure is relatively readily modified using various methods, producing starch derivatives of greatly diverse properties. The primary methods used to change characteristics of starch include acetylation and oxidation. Thus obtained raw materials are used as food additives. Stability of these raw materials and food products to a considerable extent depends on their composition and parameters characterizing storage facilities, i.e. relative humidity and temperature. One of the methods to specify adequate ambient conditions is based on water activity supplemented by sorption isotherms. As a result studies investigating correlations between water activity and moisture content are of importance for the optimization of storage conditions and design of certain food processing procedures. For this reason the aim of this study was to assess the effect of modification (oxidation, acetylation and their combination) on sorption properties (described based on sorption isotherms) of potato starch.

Material and methods. Analyses were conducted on potato starch and its derivatives produced by acetylation, oxidation and co-modification (acetylation coupled with oxidation). Starch was oxidized using sodium chlorate (I), while acetylation was run using anhydrous acetic acid. Sorption isotherms were determined by the static desiccator method. Results were described applying selected mathematical methods equipped with physical interpretations (BET and GAB) and empirical models (Halsey, Oswin, Henderson, Pelega, Lewicki, Blahovec-Yanniotis). Calculations were made using non-linear estimation.

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Results. The greatest water absorbability was found for native potato starch. Modifications caused a decrease in the amount of adsorbed water vapour, dependent on the applied modification. Acetylation resulted in significantly greater reduction of the amount of adsorbed water vapour in comparison to oxidation. Oxidation had a slight effect on sorption properties. The lowest hygroscopicity was recorded for co-modified starch, which resulted from the overlapping effect of oxidation and acetylation, reducing the capacity to adsorb water vapour. Four of the applied mathematical models (Pelega, Lewicki, GAB and Blahovec-Yanniotis) adequately reflected the course of isotherms and were characterized by comparable accuracy. Water contents in the monolayer ranged from 0.0738 to 0.0801 (the BET model) and from 0.0960 to 0.1010 (the GAB model). Based on the model proposed by Blahovec and Yanniotis it was found that modifications led to a decrease in the share of adsorbed water and an increase in the share of free water available for soluble components.

Conclusions. Sorption isotherms for all tested starch forms (native and modified) had a sigmoid shape. Analyzed modifications led to a decrease in starch hygroscopicity, with acetylation causing a markedly greater reduction of water vapour adsorbability in comparison to oxidation. Among the eight mathematical models used to describe sorption properties the Pelega model proved to be the best, although three other (the Lewicki, GAB and Blahovec-Yanniotis models) described experimental data with comparable accuracy. In most cases chemical modification of starch resulted in a reduced monolayer absorbability. An exception in this respect was connected with the value established based on the GAB model for oxidized starch. The results may be used to optimize storage conditions and to design products containing starch and its derivatives.

Key words: potato starch, modification, sorption properties, acetylation, oxidation

Introduction

Among numerous starch modification methods (Pietrzyk et al., 2013; Tharanathan, 2005; Witczak et al., 2016a) a significant role is played by oxidation and acetylation. As a result of oxidation carboxyl and/or aldehyde groups are substituted in starch. The number of these groups is influenced by such factors as the type of applied oxidant, reaction conditions as well as the botanical provenance of biopolymer. The oxidation reaction leads to a decrease of molecular mass and contents of substances accompanying starch such as fats, protein and phosphorus. The internal and external structure of starch grains were changed. All these factors affect water binding capacity and thus also sorption characteristics of starch (Pietrzyk et al., 2006). In turn, acetylated starch is produced in the reaction with acetic acid, its anhydride or their mixture (Tegge, 2010). At present a large variety of acetylated starch preparations are available for applications not only in food production, but also in the textile, pharmaceutical and biodegradable packaging industries (Golachowski et al., 2015). Properties of acetylated starch preparations depend on the type of starch, esterifying agent, reaction medium and reaction conditions (ratios of substrates, pH, temperature, catalyst, reaction time, pressure, etc.) (Golachowski et al., 2015).

Stability of food products to a considerable extent is determined by interactions between water and their other components (Sablani et al., 2004). To characterize these interactions and define product stability the concept of water activity is applied, which value is connected with microbial growth, fat oxidation, enzymatic activity, etc. In turn, the relationship of water activity and its content in the product expressed in sorption

isotherms are used to design and control food production processes (Sablani et al., 2004). The aim of this study was to assess the effect of modification (oxidation, acetylation and their combination) on sorption properties (described using sorption isotherms) of potato starch.

Material and methods

Material

Analyses were conducted on potato starch (SZ) produced by AVEBE (Holland), oxidized potato starch (SZu), acetylated potato starch (SZa) and co-modified potato starch (SZau). Starch was oxidized using sodium chlorate (I) in 40% aqueous starch suspension according to Forssell et al. (1995) at a temperature of $20 \pm 2^\circ\text{C}$. Starch suspension was mixed in an alkaline medium (pH = 10.0) for 50 min. Next the reaction mixture was neutralized with 1 M H_2SO_4 solution to pH = 7.0. The amount of NaOCl used in oxidation was equivalent to 20 g Cl/kg starch. Following neutralization starch was rinsed, dried at room temperature for 48 h, comminuted and sieved through mechanical screens (mesh size 0.2 mm). Acetylation was run following the methodology proposed by Mężyński (1972) in an aqueous starch suspension. A batch of 200 g starch (in terms of dry mass) was placed in a reactor and supplemented with distilled water to 560 g. The pH value of the suspension (pH 8–9) was regulated using 2% NaOH solution. Next 15 cm^3 anhydrous acetic acid was added mixing gently with constant velocity of 1 cm^3/min together with 2% NaOH solution in order to adjust pH of the mixture to 8–9. Following the introduction of acetic anhydride the suspension was mixed for 15 min and subsequently it was acidified with 10% HCl to pH 5.2–5.6. The produced starch was separated in a filter funnel with the sintered disc, rinsed with distilled water to remove reagent residue, dried at max. 30°C and screened. Efficiency of oxidation and acetylation was assessed by determining the contents of carboxyl groups (ISO 11214) and acetyl groups (Wurzburg, 1964). Obtained preparations contained 0.150% carboxyl groups (oxidized potato starch) and 1.270% (acylated potato starch) as well as 1.474% acetylated groups (oxidized acetylated potato starch).

Sorption isotherms

Native potato starch and modified starches were subjected to freeze drying in a lyophiliser (LAB CONCO Free Zone 6) and stored for two weeks over P_2O_5 for force drying. Next sorption isotherms were determined using the static desiccator method (Witczak et al., 2016b). Analytical samples of the preparation (approx. 0.5 g) were stored at 25°C over saturated saline solutions of varying water activity ranging from 0.11 to 0.91 until equilibrium moisture content was reached. Analyses were performed in two replications.

Modelling and statistical analyses

Sorption isotherms were described using eight models (Table 1). Two of them, i.e. BET and GAB, are based on the theory of adsorption and are physically interpretable.

Table 1. Sorption models used in this study
Tabela 1. Modele sorpcyjne wykorzystane w pracy

Model	Equation – Równanie
BET (Brunauer et al., 1938)	$u = \frac{u_0 \cdot C \cdot a_w}{(1 - a_w) \cdot (1 + (C - 1) \cdot a_w)}$
Blahovec-Yanniotis (Blahovec and Yanniotis, 2009)	$u = \frac{a_w}{a_1 + b_1 a_w} + \frac{a_w}{a_2 - b_2 a_w}$
GAB (Guggenheim, 1966; Anderson, 1946; de Boer, 1953)	$u = \frac{u_0 \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C \cdot K \cdot a_w)}$
HALSEY (Halsey, 1948; Iglesias and Chirife, 1976)	$u = \left(-\frac{S}{\ln a_w} \right)^{1/n}$
HENDERSON (Henderson, 1952)	$u = \left[\frac{\ln(1 - a_w)}{-P} \right]^{1/m}$
LEWICKI (Lewicki, 1998)	$u = F \cdot \left[\frac{1}{(1 - a_w)^G} - \frac{1}{(1 + a_w^H)} \right]$
OSWIN (Oswin, 1946)	$u = h \cdot \left(\frac{a_w}{1 - a_w} \right)^z$
PELEG (Peleg, 1993)	$u = A \cdot a_w^D + B \cdot a_w^E$

u – equilibrium water content (g H₂O per 1 g d.m.), a_w – water activity, u_0 – monolayer water content (g H₂O per 1 g d.m.), $C, a_1, b_1, a_2, b_2, K, S, n, m, P, F, G, H, h, z, A, D, B, E$ – constants of respective equations.

u – równowagowa zawartość wilgoci (g H₂O w 1 g s.m.), a_w – aktywność wody, u_0 – zawartość wody w monowarstwie (g H₂O w 1 g s.m.), $C, a_1, b_1, a_2, b_2, K, S, n, m, P, F, G, H, h, z, A, D, B, E$ – stałe odpowiednich równań.

The other models represent empirical dependencies and they are applied mainly to reliably reflect experimental data. Sorption models were fitted using the non-linear estimation module (the Marquardt-Levenberg method) of the Statistica 9.0 software package (Statsoft, Inc., USA). The coefficient of determination R^2 and the root mean square (RMS) were used as assessment criteria (Ciurzyńska and Lenart, 2010).

Results and discussion

Sorption isotherms

Figure 1 presents sorption isotherms of tested starches. The greatest water absorbability was recorded for potato starch. Modifications caused a decrease in adsorbed water vapour. The analyzed isotherms were sigmoid in shape, which classifies them to type II

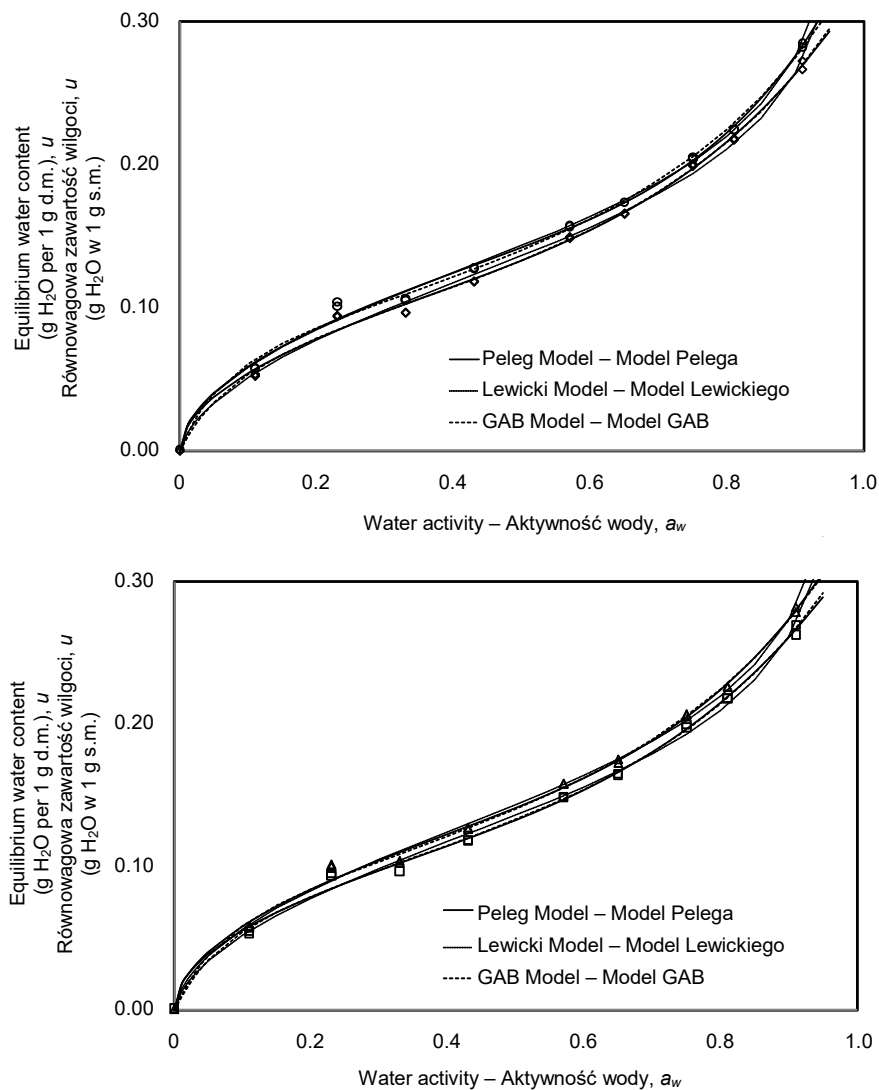


Fig. 1. Sorption isotherms of analysed starches (○ – potato starch, ◇ – acetylated potato starch, △ – oxidized potato starch, □ – acetylated and oxidized potato starch)
 Rys. 1. Izotermy sorpcji badanych skrobi (○ – skrobia ziemniaczana, ◇ – skrobia ziemniaczana acetylowana, △ – skrobia ziemniaczana utleniona, □ – skrobia ziemniaczana acetylowana i utleniona)

isotherms according to the classification proposed by Brunauer et al. (1938). These results are consistent with those recorded previously for native and modified starches of various botanical origin (Al-Muhtaseb et al., 2004a; Pałacha and Chrzanowski, 2013).

Sorption properties of tested starches depended on the applied modification. Acetylation caused a significantly greater decrease in the amount of adsorbed water vapour in comparison to oxidation. Oxidation had a limited effect on sorption properties. However, as a result the lowest hygroscopicity was found for co-modified starch, which results from the overlapping effect of oxidation and acetylation, reducing the capacity to adsorb water vapour. However, this effect was not additive. At lower values of water activity this decrease was smaller than the total decrease resulting from oxidation and acetylation, while at higher values it was greater than that for the sum of single modifications. The smallest capacity to adsorb water vapour for acetylated starch was also reported by Pałacha and Chrzanowski (2013) when comparing sorption properties of potato starch and modified starches. According to Al-Muhtaseb et al. (2004b), potato starch shows higher values of heat of adsorption and desorption in comparison to other starches. According to those authors this suggests that potato starch is more polar on the surface and thus bond energy of water molecules on the starch surface is greater. However, it needs to be remembered that the starch granules have a complex structure, composed of amorphous and crystalline zones. The former may be plasticized by water, while the latter are relatively resistant to the action of water vapour (Fornal et al., 2012, Al-Muhtaseb et al., 2004b). Thus water binding capacity to a considerable degree depends on the degree of crystallinity and position of the above-mentioned structures in relation to one another.

Observed dependencies were described using selected mathematical models (Table 1). Equation parameters are given in Table 2. Most applied models correctly described the course of sorption isotherms. In this respect the Halsey and BET models were least accurate. Slightly higher RMS values in relation to the other models were also obtained for the Oswin and Henderson model. In turn, the Pelega, Lewicki, GAB and Blahovec-Yanniotis models reflected the course of the isotherms with comparable accuracy (RMS ranging from 4.39% to 5.35%). A similar dependency, although with lower RMS values, was obtained by Pałacha and Chrzanowski (2013). According to those authors water vapour adsorption isotherms for starch were best described by the model proposed by Pelega. Similar conclusions were earlier reached by Al-Muhtaseb et al. (2004a) when determining sorption isotherms for potato starch at various temperatures.

Two basic models of sorption isotherms are referred to as BET and GAB. The GAB model is based on the theory of multiple layer adsorption. Its parameters are physically reliable and in contrast to the BET model (being its modification) it may be applied within a broader range of water activity values ranging from 0 to 0.9. Both these models make it possible to calculate water contents in the monolayer. In the analyzed case this content ranged from 0.0738 to 0.0801 (BET) and from 0.0960 to 0.1010 (GAB). These values were slightly higher than those reported by Pałacha and Chrzanowski (2013), amounting for potato starch to 0.072 (BET) and 0.085 (GAB). However, these differences may be ascribed to the variability of properties in the case of potato starch.

Values of constants C and K for the GAB model were found within the ranges described by Lewicki (1997). According to that author, the value of the C constant should be greater than 5.67, while that of the K constant should be within the range of 0.24 to 1. Otherwise this model does not produce the sigmoid shape or it leads to high discrepancies (the error exceeding 15.5%) between the actual water content in the monolayer and that calculated based on the above-mentioned model (Lewicki, 1997).

Table 2. Parameters of sorption models
Tabela 2. Parametry modeli sorpcyjnych

Model	Parameter Parametr	SZ (PS)	SZa (PSa)	SZu (PSo)	SZau (PSao)
BET ¹	u_0	0,0801	0,0740	0,0789	0,0738
	C	19,86	19,26	20,44	20,91
	R^2	0,976	0,977	0,978	0,977
	RMS	9,23	9,19	8,86	9,02
GAB	u_0	0,0987	0,0960	0,1010	0,0962
	C	17,12	13,90	15,47	14,50
	K	0,724	0,721	0,714	0,717
	R^2	0,997	0,997	0,997	0,997
	RMS	5,35	4,93	4,82	4,79
OSWIN	h	0,140	0,132	0,140	0,133
	z	0,316	0,324	0,315	0,320
	R^2	0,993	0,990	0,991	0,989
	RMS	7,61	8,25	7,81	7,99
PELEG	A	0,202	0,181	0,196	0,177
	D	0,534	0,523	0,525	0,500
	B	0,157	0,146	0,147	0,145
	E	5,742	4,401	4,875	4,151
	R^2	0,997	0,997	0,997	0,997
	RMS	4,89	5,13	4,82	5,06
LEWICKI	F	0,267	0,261	0,274	0,262
	G	0,190	0,185	0,180	0,181
	H	0,602	0,667	0,637	0,658
	R^2	0,997	0,996	0,997	0,995
	RMS	4,98	5,16	4,82	5,15
HALSEY	S	0,00429	0,00417	0,00420	0,00389
	n	2,55	2,49	2,56	2,53
	R^2	0,962	0,954	0,956	0,953
	RMS	12,01	12,91	12,34	12,59
HENDERSON	P	28,87	28,25	28,91	29,97
	m	1,93	1,86	1,93	1,89
	R^2	0,994	0,995	0,995	0,995
	RMS	6,17	6,02	5,73	5,99
BLAHOVEC- -YANNIOTIS	a_1	1,15	1,17	1,10	1,08
	b_1	7,59	9,94	8,56	10,38
	a_2	20,64	15,19	16,60	14,52
	b_2	16,82	11,16	12,61	10,41
	R^2	0,996	0,995	0,996	0,995
	RMS	4,39	4,82	4,46	4,79

¹ In the water activity range of 0 to 0.43.

¹ W zakresie aktywności wody od 0 do 0,43.

Values of the C constant obtained for the BET and GAB models were greater than those in a study by Pałacha and Chrzanowski (2013), while they were similar to those reported by Al-Muhtaseb et al. (2004a) for potato starch. In turn, the K constant had lower values in comparison to both these studies.

An interesting model is provided by a dependence presented by Blahovec and Yanniotis (2009). That equation was applied with satisfactory results to describe sorption in such food products as starch, fruit, vegetables, etc. (Blahovec and Yanniotis, 2009; Červenka et al., 2012). According to the assumptions of this model, the total water content in the product at a specific activity may be divided into water which is sorbed by insoluble components and which forms the monolayer, and water available for soluble components. Such a dependence is presented in Figure 2. As it may be seen, the content of water participating in dissolution is slight at low activities and it increases gradually, reaching high values at high activities. Chemical modification caused a reduction of the share of adsorbed water and an increase in the amount of water available for soluble components.

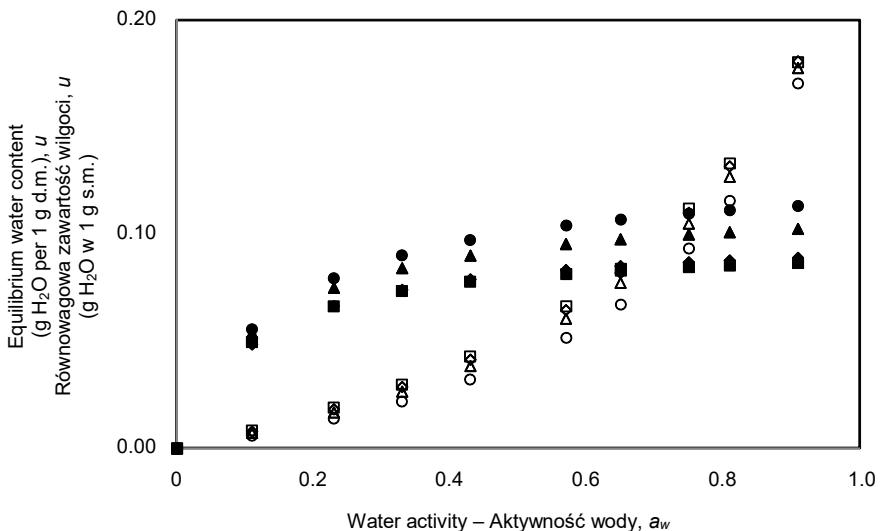


Fig. 2. Bound water (solid symbols) and unbound water (open symbols) determined on the basis of the Blahovec-Yanniotis model (○ – potato starch, ◇ – acetylated potato starch, △ – oxidized potato starch, □ – acetylated and oxidized potato starch)

Rys. 2. Woda związana (pełne symbole) i niezwiązana (puste symbole) wyznaczona na bazie modelu Blahoveca-Yanniotisa (○ – skrobia ziemniaczana, ◇ – skrobia ziemniaczana acetylowana, △ – skrobia ziemniaczana utleniona, □ – skrobia ziemniaczana acetylowana i utleniona)

Conclusions

1. The course of isotherms for all the tested starches (native and modified) was sigmoid, corresponding to type II isotherms according to the classification presented by Brunauer et al.

2. All tested modifications led to a decrease in starch hygroscopicity, with acetylation causing a markedly greater loss of water vapour absorbing capacity in comparison to oxidation.

3. Of the eight analyzed models that proposed by Pelega proved to be the best, although three other (Lewicki, GAB and Blahovec-Yanniotis) described experimental data with similar accuracy.

4. In most cases chemical modification resulted in a decrease in monolayer capacity. An exception in this respect was found for the value determined from the GAB model for oxidized starch.

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WŁAŚCIWOŚCI SORPCYJNE MODYFIKOWANEJ SKROBI ZIEMNIACZANEJ

Streszczenie

Wstęp. Skrobia należy do najczęściej wykorzystywanych w przemyśle spożywczym biopolimerów, jednak w formie natywnej ma ograniczone zastosowanie. Jej budowa sprawia, że stosunkowo łatwo ulega różnorodnym modyfikacjom, prowadzącym do powstania jej pochodnych o bardzo zróżnicowanych właściwościach. Do podstawowych metod stosowanych w celu zmiany charakterystyki skrobi należą acetylacja i utlenianie. Uzyskiwane dzięki temu surowce są stosowane jako dodatki do żywności. Stabilność tych surowców oraz produktów spożywczych z ich udziałem silnie zależy od ich składu oraz parametrów charakteryzujących miejsce przechowywania – wilgotności względnej i temperatury. Jedną z metod określania właściwych warunków charakteryzujących otoczenie opiera się na pojęciu aktywności wody, a następnie izotermach sorpcji. Sprawia to, że badania prowadzące do powiązania aktywności i zawartości wody są ważne z punktu widzenia optymalizacji warunków przechowywania oraz projektowania niektórych procesów przetwórstwa żywności. Celem niniejszej pracy była zatem ocena wpływu modyfikacji (utlenianie, acetylacja oraz ich połączenia) na właściwości sorpcyjne (opisane z wykorzystaniem izoterm sorpcji) skrobi ziemniaczanej.

Material i metody. Badaniom poddano skrobię ziemniaczaną oraz jej pochodne uzyskane w wyniku acetylacji, utleniania oraz podwójnej modyfikacji – acetylacji i utleniania. Utlenianie skrobi prowadzono z zastosowaniem chloranu (I) sodu, a acetylację – z wykorzystaniem bezwodnika kwasu octowego. Izotermę sorpcji wyznaczono metodą statyczno-eksykatorową. Uzyskane wyniki opisano wybranymi modelami matematycznymi, posiadającymi interpretację fizyczną (BET i GAB), oraz empirycznymi (Halseya, Oswina, Hendersona, Pelega, Lewickiego, Blahovca-Yanniotisa). Obliczenia wykonano z wykorzystaniem estymacji nieliniowej.

Wyniki. Największą zdolnością absorpcji wody charakteryzowała się natywna skrobia ziemniaczana. Modyfikacje powodowały spadek ilości adsorbowanej pary wodnej, zależny od rodzaju zastosowanej modyfikacji. Acetylacja powodowała istotnie większe ograniczenie ilości adsorbowanej pary wodnej niż utlenianie. Utlenianie wpływało na właściwości sorpcyjne w nieznaczny sposób. Najmniejszą higroskopijnością charakteryzowała się skrobia podwójnie modyfikowana, co wynikało z nakładania się efektu utleniania i acetylacji, zmniejszającego zdolność adsorpcji pary wodnej. Cztery z zastosowanych modeli matematycznych (Pelega, Lewickiego, GAB oraz Blahovca-Yanniotisa) dobrze odzwierciedlały przebieg izoterm, z podobną dokładnością. Zawartość wody w monowarstwie zmieniała się w zakresie od 0,0738 do 0,0801 (model BET) oraz od 0,0960 do 0,1010 (model GAB). Na podstawie modelu Blahovca i Yanniotisa stwierdzono, że modyfikacje prowadziły do spadku udziału wody adsorbowanej i zwiększenia udziału wody dostępnej dla składników rozpuszczalnych.

Wnioski. Izotermę sorpcji wszystkich badanych skrobi (natywnej i modyfikowanych) charakteryzowały się sigmoidalnym kształtem. Analizowane modyfikacje prowadziły do spadku higroskopijności skrobi, przy czym acetylacja powodowała zdecydowanie większy spadek zdolności adsorbowania pary wodnej niż utlenianie. Z ośmiu modeli matematycznych zastosowanych do opisu właściwości sorpcyjnych za najlepszy uznano model Pelega, chociaż trzy inne (Lewickiego, GAB oraz Blahovca-Yanniotisa) opisywały dane eksperymentalne z podobną dokładnością. W większości przypadków modyfikacja chemiczna skrobi prowadziła do zmniejszenia pojemności monowarstwy. Wyjątek stanowiła wartość wyznaczona z modelu GAB dla skrobi utlenionej. Uzyskane wyniki mogą zostać wykorzystane do optymalizacji warunków przechowywania i projektowania produktów z udziałem skrobi i jej pochodnych.

Słowa kluczowe: skrobia ziemniaczana, modyfikacja, właściwości sorpcyjne, acetylacja, utlenianie

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