

ARTICLE**Study of Hydrophilic Properties of Polysaccharides****Michael Ioelovich***

Designer Energy, Rehovot, 7670504, Israel

ARTICLE INFO*Article history*

Received: 08 December 2020

Accepted: 27 December 2021

Published Online: 30 December 2021

Keywords:

Polysaccharides
 Amorphous domains
 Structure
 Specific surface area
 Sorption of water vapor
 Enthalpy of wetting
 Hydrophilicity index
 Calculations

ABSTRACT

In this research, the structural characteristics, specific surface area, sorption of water vapor, and wetting enthalpy of various polysaccharides (cellulose, hemicelluloses, starch, pectin, chitin, and chitosan) have been studied. It was confirmed that crystallites are inaccessible for water, and therefore water molecules can interact only with polar groups in noncrystalline (amorphous) domains of biopolymers. The isotherms of water vapor sorption for various polysaccharides had sigmoid shapes, which can be explained by the absorption of water molecules in heterogeneous amorphous domains having clusters with different packing densities. The method of contributions of polar groups to sorption of water molecules was used, which allowed to derive a simple calculating equation to describe the shape of sorption isotherms. The wetting of biopolymers with water was accompanied by a high exothermic thermal effect, in direct proportion to the amorphicity degree. The sorption values and wetting enthalpies of amorphous domains of biopolymers were calculated, which allowed to find the hydrophilicity index and compare the hydrophilicity of the various polysaccharides.

1. Introduction

Polysaccharides are an important class of biopolymers synthesized in living organisms such as plants, animals, and microorganisms, from which these biopolymers can be extracted [1-3]. The polysaccharides can be amorphous or semicrystalline, and composed of the same (homo-polysaccharides) or different (hetero-polysaccharides) monomeric units; in addition, hydroxyl groups of these units can be substituted by other groups. Polysaccharides may comprise residues of various monosaccharides such as

glucose, fructose, mannose, galactose, xylose, etc. Depending on whether the monomeric unit contains 5 or 6 carbon atoms, polysaccharides are classified also into C5- and C6-polysaccharides.

Known types of polysaccharides are cellulose, starch, mannan, xylan, pectin, chitin, chitosan, and others. The most widespread polysaccharide in nature is cellulose [4]. Cellulose is a linear, stereoregular, high molecular, and semicrystalline biopolymer composed of repeating D-anhydroglucose units (AGU) linked by β -1,4-glycosidic bonds. This polysaccharide occurs in all terrestrial plants

**Corresponding Author:*

Michael Ioelovich,
 Designer Energy, Rehovot, 7670504, Israel;
 Email: ioelovichm@gmail.com

DOI: <https://doi.org/10.30564/opmr.v3i2.4181>

Copyright © 2021 by the author(s). Published by Bilingual Publishing Co. This is an open access article under the Creative Commons Attribution-NonCommercial 4.0 International (CC BY-NC 4.0) License. (<https://creativecommons.org/licenses/by-nc/4.0/>).

and many algae; in addition, cellulose is found in shells of certain marine creatures, and this biopolymer is synthesized by some microorganisms, e.g. *Gluconacetobacter xylinus*.

Mannan and xylan, also called hemicelluloses, are found in all terrestrial plants^[5]. They are low crystalline and low molecular biopolymers. Mannan is a polysaccharide containing mannose units linked by β -1,4-bonds. In addition to mannose, mannan may contain residues of glucose and galactose. Xylan consists of xylose units connected by β -1,4-bonds. This polysaccharide usually also contains 9%-10% residues of 4-O-methylglucuronic acid.

Starch is a complex polysaccharide consisting of two main components amylose and amylopectin^[6]. Amylose is a linear carbohydrate, glucose units of which are connected by α -1,4-glycosidic bonds. Amylopectin is a branched carbohydrate, containing α -1,4-glycosidic bonds in linear segments and α -1,6-glycosidic bonds in branches. Due to such structure, low crystallinity, and low degree of polymerization (DP), starch is soluble in hot water and turns into a gel when cooled.

The carboxylated polysaccharide, pectin, and the nitrogenized polysaccharides, chitin, and chitosan are also well known. Linear chains of pectin contain units of D-galacturonic acid joined by α -1,4-bonds. Pectin is an amorphous, low-molecular biopolymer that is soluble in hot water to form a gel.

Chitin is the most widespread nitrogen-containing polysaccharide in nature, which is present in exoskeletons and shells of some aquatic animals and insects, as well as in the cell walls of some fungi and microorganisms^[7]. Chitin is regarded as a nitrogenized derivative of cellulose, where the hydroxyl group at C2 atoms in each AGU is replaced with an acetyl amino group. Macromolecules of this natural polymer contain up to 10,000-15,000 units of 1,4- β -N-acetylglucosamine. Similar to cellulose, chitin is a linear semicrystalline biopolymer. Chitosan is a nitrogenized polysaccharide containing amino groups in glucosamine units of macromolecules. This biopolymer is produced mainly by deacetylation of chitin with hot sodium hydroxide. Like chitin, chitosan is a linear semicrystalline biopolymer. A distinctive feature of chitosan is easy dissolution in dilute acids and subsequent regeneration from the solutions after neutralization.

Despite the difference in structure and origin, almost all polysaccharides have such specific features as an affinity for water, i.e. they are hydrophilic polymers. To study hydrophilicity, various methods can be used, such as measuring the contact angle of a water drop on the surface, the degree of swelling, sorption of water vapor, enthalpy of wetting, and some others. However, to mea-

sure the contact angle, the surface of the sample must be flat, homogeneous, free of roughness and pores^[8,9], which in many cases is difficult to implement in practice. The measurement of the degree of swelling is not standardized and depends on the conditions of sample preparation, its external structure (powder, fiber, sheet, or film), and the method of removing the water excess, etc. The most accurate and reproducible methods for studying hydrophilicity are considered the sorption of water vapor and the enthalpy of wetting.

When studying the sorption isotherms of water vapor (WV) for cellulose and other polysaccharides it was found that these isotherms are S-shaped, i.e. they are type II. This type of isotherm is usually explained by multilayer surface adsorption of water molecules, which is described by BET, GAB, or some other adsorption equations^[10-12]. The analysis of the GAB equation showed that the common three-parametric GAB equation describes the sorption isotherms with low accuracy, especially at increased relative vapor pressures or water vapor activities^[13]. If the number of parameters of the GAB equation increases, the accuracy improves. However, in this case, the parameter of monolayer capacity becomes a variable value, and the calculations of the specific surface area of biopolymers become unreliable.

Park's sorption model provides the use of the Langmuir equation of monolayer surface adsorption at the initial stage, Henry's equation of WV dissolution in biopolymer at the middle stage, and a power-law equation describing the clustering of water molecules at the last stage of sorption^[14,15].

However, the problem is that in reality the equations of monolayer and multilayer surface adsorption of WV are unsuitable for calculating the structural parameters of polar hydrophilic biopolymers since the sorption mechanism is not the adsorption of sorbate molecules on the surface of pores, but the absorption of polar water molecules inside the noncrystalline (amorphous) domains of the polar polymers^[16-18]. In this case, to calculate the isotherms of WV for biopolymers, it is necessary to use the thermodynamic equation^[19] or other equations describing the absorption process such as Henry, Hailwood Horrobin, etc.^[15,16,20].

Discussing Park's model it should be noted that the presence of a linear dissolution process of WV in polysaccharides following Henry's law is unlikely since this law is observed only for ideal solutions, to which the polysaccharide-water system does not belong. In addition, the clustering of water molecules in hydrophilic biopolymers at the last stage of sorption was not found. Moreover, to describe each isotherm, Park's model

requires the determination of at least five parameters^[15]. If it is necessary to describe the isotherm of WV for another biopolymer sample, then the new five parameters must be recalculated. Thus, Park's model is mathematically adapted to the experimental isotherm without proof of the sorption mechanism.

The Hailwood and Horrobin model postulated the dissolution of VW in the internal structure of biopolymer during the sorption process with the formation of monohydrates and polyhydrates^[20]. However, this hypothesis is doubtful since polysaccharides cannot form chemical compounds with water such as monohydrates. It has also not been proven that the formation of polyhydrates should actually lead to a hyperbolic increase in the amount of sorbed water. The parameters of Hailwood and Horrobin's equation are selected in such a way as to achieve the best agreement with the experimental isotherm. This assists to adapt the model to the experiment but does not provide arguments about the real sorption mechanism.

Many arguments are indicating the absorption mechanism of the interaction of water molecules with polysaccharides. For example, it is known that cellulose and other carbohydrates in the dry state are low-porous sorbents, whose specific surface measured by the sorption of inert gases and vapors is several square meters per gram^[21,22]. In this case, the value of surface adsorption should be very low and cannot exceed one percent. However, in reality, the amount of WV sorbed by biopolymers reaches several tens and even several hundred percent.

If such polysaccharide as natural cellulose is mercerized or dissolved in a solvent and then regenerated from the solution, the specific surface area of the obtained samples decreases^[19]. Despite this fact, the sorption capacity of the samples for WV after these treatments, on the contrary, increases sharply, which is caused by amorphization of the biopolymer and increase in the content of amorphous domains providing higher accessibility of polar water molecules to the internal structure of polar sorbent^[23].

In addition, the process of WV sorption by polysaccharides is accompanied by such phenomena as a swelling, partial dissolving of water-soluble biopolymers, decrease of the glass transition temperature and even melting point, and recrystallization of amorphized biopolymers, etc.^[24,25]; furthermore, when these polysaccharides are wetted, a significant amount of thermal energy is released^[26]. All these phenomena are obvious evidence for the absorption of water molecules by biopolymers.

Taking into consideration the absorption mechanism, in this article, a comparative study of the hydrophilicity

of various polysaccharides was carried out by measuring the sorption of WV and the enthalpy of wetting. Since the crystallinity strongly affects the sorption capacity, to compare the hydrophilicity of samples with different crystallinity, it is necessary to use hydrophilic characteristics of amorphous domains of semicrystalline biopolymers. After that, the relative hydrophilicity index of various polysaccharides was calculated.

2. Materials and Methods

2.1 Materials

The following cellulose samples were investigated:

- Fine powder of microcrystalline cellulose (MC) Avicel PH-301 of FMC BioPolymer Co.
- Sheets of pure chemical-grade cotton cellulose (CC) of Hercules Co.
- Sheets of bleached spruce Kraft pulp (KP) of Weyerhaeuser Co.
- Fibers of mercerized Kraft pulp (MP) prepared by treatment with 20% NaOH and following washing and drying
- Yarn of viscose fibers (VF) of Rayonier Inc.

Purified powders of chitin (CT) from crab shells (degree of acetylation DA=94%) and chitosan (CS) (degree of deacetylation DDA=85%), potato starch (ST), citrus pectin (PC), birch xylan (XL), and mannan (MN) from *Ceratonia siliqua*, were acquired from Sigma-Aldrich.

2.2 Wide-angle X-ray Scattering (WAXS)

Wide-angle X-ray scattering (WAXS) studies were carried out using diffractometer Rigaku Ultima Plus in the 2θ angle range from 5° to 80° . $\text{CuK}\alpha$ radiation had wavelength $\lambda = 0.15418$ nm. Collimation included a system consisting of vertical slits and Soller slits. The procedure of 0.02° step-by-step scanning was used to determine the exact position of the peaks. The weak peaks were identified by a step-by-step scanning method with the accumulation of impulses at each step. A few of the diffractograms of the same biopolymer sample were recorded to obtain more reliable results. The incoherent background was subtracted from diffractograms. Then profiles of the isolated peaks were improved using corrections on absorption, combined PL factor, and Rietveld refinement. The angular positions of the peaks were checked using a narrow line of NaF standard at 2θ of 38.83° . Overlapped peaks were separated using the least-squares program.

The degree of crystallinity (X) of the biopolymer samples was calculated by the following equation^[27]:

$$X = \int Jc \, d\theta / \int Jo \, d\theta \quad (1)$$

where Jc and Jo are the corrected and normalized intensities of X-ray diffraction from crystalline domains only and whole polymer sample, respectively.

In addition, the amorphicity degree (Y) of the samples was calculated, as follows:

$$Y = 1 - X \quad (2)$$

2.3 Sorption of Vapors

The sorption experiments were carried out at 25 °C on a vacuum Mac-Ben apparatus having helical spring quartz scales. Sorbates were water and n-hexane. Before starting the experiments the samples were dried at 105 °C up to constant weight and additionally degassed under vacuum in the sorption device. Three of the same samples were tested to calculate an average sorption value and standard deviation that was in the range ± 0.002 g/g. The value of s_m (g/g) corresponding to the inflection point of the isotherms was found, after which the specific surface value (S_{sp} , m²/g) was calculated, as follows.

$$\text{In the case of n-hexane vapor: } S_{sp}(H) = 2087 s_m \quad (3)$$

$$\text{In the case of water vapor: } S_{sp}(W) = 3516 s_m \quad (4)$$

2.4 Enthalpy of Wetting

The enthalpy of wetting of biopolymers ($\Delta_w H$) was studied at 25 °C by the method of precise microcalorimetry using a TAM III calorimeter [28]. The samples were preliminarily dried at 105 °C in a vacuum chamber to constant weight. Three of the same samples were tested to calculate an average enthalpy value and standard deviation that was in the range ± 0.02 J/g.

3. Results

3.1 WAXS Studies of Polysaccharides

The study of X-ray diffraction showed that such samples as CT, KP, MC, and CC had intensive and narrow crystalline peaks, which is a sign of the quite high crystallinity of these samples (see e.g. Figure 1, Table 1). Samples of CS, MP, and VF exhibited broader crystalline peaks of medium intensity indicating their medium crystallinity (see e.g. Figure 2, Table 1).

Samples of PC, ST and hemicelluloses were characterized by broad and low intensive diffraction, which indicates an amorphized low-crystalline structure (see e.g. Figure 2, Table 1).

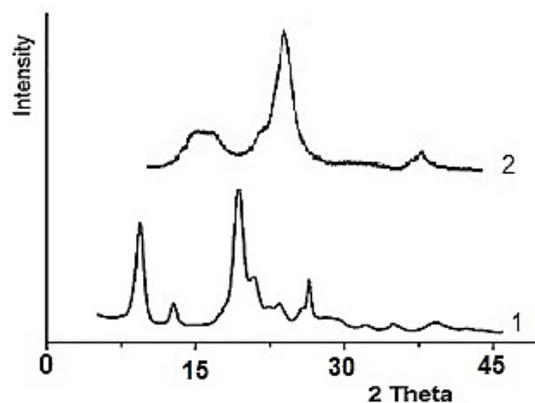


Figure 1. X-ray diffractograms for samples of CT (1) and KP (2)

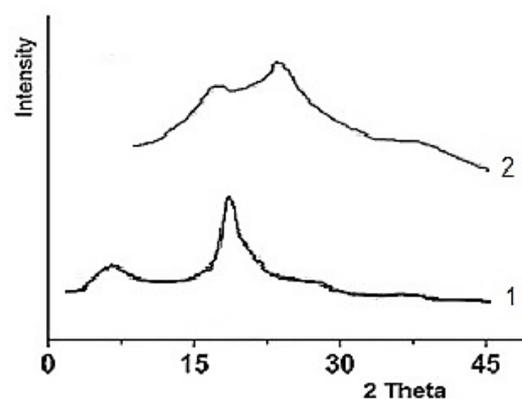


Figure 2. X-ray diffractograms for samples of CS (1) and PC (2)

3.2 Estimation of the Specific Surface Area of Polysaccharides

Sorption isotherms of n-hexane vapor for dry samples of MC and ST resemble isotherms of I (b) type, which have an initial steep part and then a gentle plateau (Figure 3). Therefore, to find s_m value the Langmuir equation was used

Despite higher crystallinity ($X=0.75$), the MC sample has a higher sorption value than the less crystalline ST sample ($X=0.28$). As a result, fine MC powder exhibits a higher specific surface area, $S_{sp}(H)$, than starch grains (Table 1). Nevertheless, in all cases, the sorption value of n-hexane for biopolymer samples was relatively small, several milligrams per gram of dry sorbent. These features indicate the adsorption mechanism sorption of the inert sorbate molecules on the surface of low-porous biopolymers.

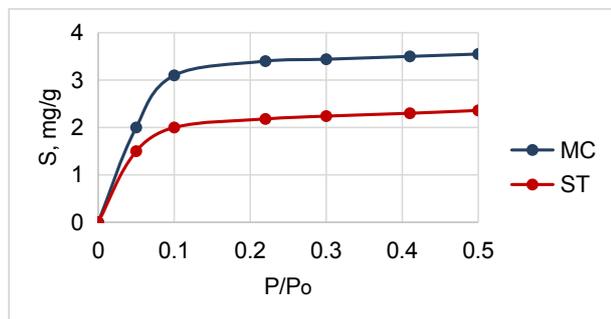


Figure 3. Sorption isotherms of n-hexane vapor for dry samples of MC and ST

Table 1. Specific surface area of polysaccharides measured by sorption of n-hexane [$S_{sp}(H)$], and water vapors [$S_{sp}(W)$]

Sample	X	Y	$S_{sp}(H)$, m ² /g	$S_{sp}(W)$, m ² /g
MC	0.75	0.25	7.1	84
CC	0.70	0.30	5.4	100
KP	0.64	0.36	6.3	122
MP	0.53	0.47	3.7	161
VF	0.36	0.64	3.0	200
ST	0.28	0.72	4.6	231
MN	0.26	0.74	6.5	242
XL	0.23	0.77	6.8	216
PC	0.20	0.80	6.0	232
CT	0.68	0.32	5.6	90
CS	0.46	0.54	5.2	180

In contrast to isotherms of type 1(b) characteristic for surface adsorption of inert sorbates (n-hexane), the sorption isotherms of water vapor for various samples had sigmoid shapes, and therefore they can be classified as type II (Figure 4). Isotherms of this type have an initial steep part, after which a gradual increase in sorption is observed, and finally, at high relative vapor pressures, a sharp increase in the sorption of WV occurs.

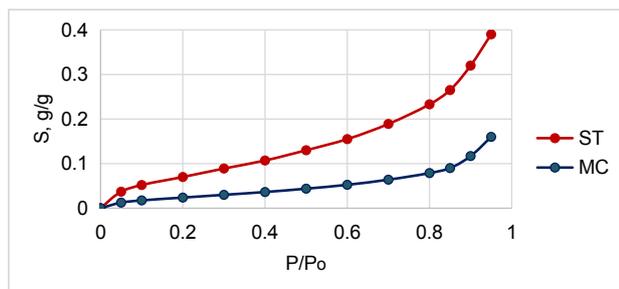


Figure 4. Sorption isotherms of water vapor for dry samples of MC and ST

In the coordinates of the BET equation, $Z = \phi / [(S(1-\phi))] = F(\phi)$, where $\phi = P/P_0$, the sorption isotherms of WV are generally nonlinear (Figure 5). To find s_m , the linear sec-

tion of the BET isotherms was used in the ϕ range from 0.1 to 0.5. The specific surface area of biopolymers, $S_{sp}(W)$, calculated from the BET sorption isotherms of WV is very high and reaches several hundred square meters per gram despite the fact that all studied samples in the dry state were low-porous (Table 1). Moreover, the study showed, there is no correlation between $S_{sp}(W)$ and $S_{sp}(H)$.

On the other hand, the linear correlation between the $S_{sp}(W)$ value and the degree of amorphicity (Y) of samples is observed (Figure 6), which evidences the absorption mechanism sorption of WV in amorphous domains of various polysaccharides.

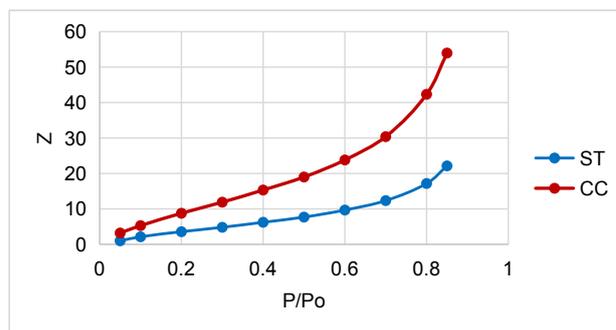


Figure 5. Sorption isotherms of water vapor by CC and ST in coordinates of BET equation

Thus, the $S_{sp}(W)$ value does not characterize the porous structure of polysaccharides. In fact, the high value of $S_{sp}(W)$ is an index of the accessibility of the internal structure of biopolymers to water vapor, which depends on the degree of amorphicity.

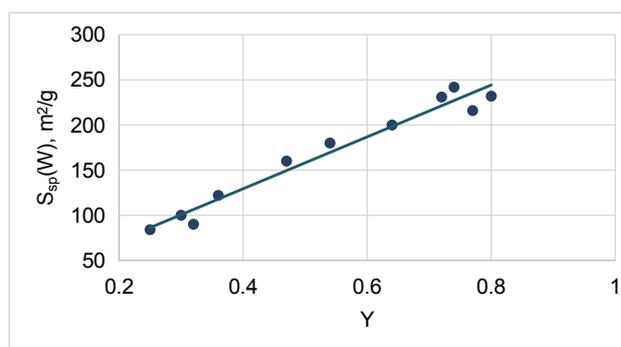


Figure 6. Linear correlation $S_{sp}(W) = F(Y)$

3.3 Water Sorption Ability of Functional Groups of Amorphous Biopolymers

To calculate the sorption isotherms of water vapor for amorphous polymers or amorphous domains of semicrystalline polymers at 25 °C, Van Krevelen proposed the contributions of various functional groups of polymers to the sorption of water molecules at several values of the relative vapor pressure, $\phi = P/P_0$ [29]. It was found that only

polar groups are capable of attaching water molecules, while the contribution of non-polar aliphatic and aromatic groups to the sorption of WV was close to zero.

Calculations by the Van Krevelen method showed good agreement with the experiments. However, this method has also limitations. The first limitation is that the method of Van Krevelen allows one to reliably find only three to four points of the isotherm, which is insufficient for plotting the full isotherm. The second limitation is that the group contributions at high ϕ -values, 0.9 and 1, contain not only water molecules sorbed by functional groups, but also capillary condensed water, and therefore the contribution values need to be corrected.

To overcome the mentioned limitations of the Van Krevelen method, in this study an Equation (5) was derived for calculating the contributions of different polar functional groups to the sorption of WV over the all ϕ -range, from 0 to 1 (Table 2).

$$a_i = a_{o,i} (1 - K \ln \phi)^{-1} \quad (5)$$

where a_i and $a_{o,i}$ are contributions of polar groups to the sorption of WV at a certain ϕ and $\phi=1$, respectively; moreover, a_i and $a_{o,i}$ have the dimension of mol H₂O per mol group, while K is coefficient.

Table 2. Parameters of Equation (5)

Polar functional groups	$a_{o,i}$ mol/mol	K
-OH, -NH ₂ , -NHCO-	1.44	2.6
-COOH	1.31	5
-C=O	0.30	6
-COO-	0.24	7
-O-	0.12	16

Parameters of Equation (5) allow calculation of the sorption values (A_a , mol/mol) of WV for amorphous domains (AD) of semicrystalline polysaccharide at various ϕ , knowing only the chemical formula of the repeating unit (RU) of this biopolymer including the type and content (n_i) of polar groups, as follows:

$$A_a = \sum n_i a_i \quad (6)$$

Moreover, the maximum amount of water molecules ($A_{o,a}$) absorbed by AD of polysaccharides at $\phi=1$, can be also calculated (Table 3).

Table 3. Maximum amount of water ($A_{o,a}$, mol/mol) absorbed by AD of various polysaccharides

Polysaccharides	Formula of RU	MW	N_p	$A_{o,a}$
C5-Polysaccharides (C5P)	C ₅ H ₆ O ₂ (OH) ₂	132	4	3.00
C6-Polysaccharides (C6P)	C ₆ H ₇ O ₂ (OH) ₃	162	5	4.56
Amino C6P (CS)	C ₆ H ₇ O ₂ (OH) ₂ NH ₂	161	5	4.56
Acetylamin of C6P (CT)	C ₆ H ₉ O ₄ (NHCO)CH ₃	203	5	4.51
Carboxylated C6P (PC)	C ₅ H ₅ O ₃ (OH) ₂ COOH	176	5	4.30

MW is the molecular weight of RU of polysaccharide

N_p is a number of polar groups in repeat unit (RU) of AD

From the theoretical calculations, it follows that each repeating unit of AD of studied polysaccharides can attach from 3 (for C5P) to 5 (for C6P) water molecules, i.e. one polar group of the RU in AD sorbs a maximum of one water molecule. This conclusion is confirmed by the literature data [16,30]. Thus, monomolecular absorption of water molecules in AD of biopolymers is achieved only at a maximum vapor pressure $\phi=1$. This behavior distinguishes the polar hydrophilic biopolymers from porous low- and non-polar polymers, in which water molecules cover the surface of pores with a monomolecular layer at a low vapor pressure, usually below $\phi = 0.3$.

The sorption values (S_a) at various ϕ for AD of the polysaccharide expressed in gH₂O/g sorbent also can be calculated, as follows:

$$S_a \text{ (g/g)} = A_a \text{ (mol/mol)} \times (18/MW) \quad (7)$$

As an example, it can calculate the sorption isotherm of WV for AD of C6-polysaccharide (C6P) having the formula of repeating unit C₆H₇O₂(OH)₃. Such a polysaccharide can be cellulose, starch, mannan, and other hexoses. The RU of such polysaccharides contains two ether groups and three hydroxyl groups. The results of calculations of the a_i -values for these polar groups using Equation (5) and sorption values (A_a) for AD of C6P at various ϕ are shown in Table 4.

Table 4. Calculated sorption values of WV for AD of C6P

ϕ	$2a_e$	$3a_h$	A_a	S_a
0	0	0	0	0
0.05	0.005	0.490	0.495	0.054
0.1	0.006	0.618	0.624	0.069
0.2	0.009	0.833	0.842	0.094
0.3	0.012	1.046	1.058	0.117
0.4	0.015	1.277	1.292	0.144
0.5	0.020	1.542	1.562	0.174
0.6	0.026	1.855	1.881	0.209
0.7	0.036	2.240	2.276	0.253
0.8	0.052	2.734	2.786	0.310
0.9	0.089	3.391	3.480	0.387
1.0	0.240	4.320	4.560	0.506

$2a_e$ is the contribution of two ether groups

$3a_h$ is the contribution of three hydroxyls groups

A_a is the amount of WV absorbed by AD of C6P (mol/mol) at various ϕ

S_a is the amount of WV absorbed by AD of C6P, (g/g) at various ϕ

Based on the parameters of Equation (5) (Table 2), the isotherm of VW for AD of biopolymers, e.g. for C6P, can be drawn (Figure 7).

Further, this isotherm of VW for AD can be presented

in a linear form, as shown in Figure 8. Extrapolation of the linear plot $1/S_a = F(-\ln\phi)$ to $\ln\phi = 0$ gives the value $1/S_{0,a}$, from which the maximum sorption value, $S_{0,a}$, can be found. In addition, the slope coefficient (k) of the plot can be also determined. As a result, the following equation of the isotherm was obtained:

$$S_a = S_{0,a} (1 - C \ln\phi)^{-1} \quad (8)$$

where $S_{0,a}$ is the maximum amount of water molecules absorbed by AD at $\phi=1$, and coefficient $C=k S_{0,a}$. For C6P $S_{0,a} = 0.506$ (g/g), while $C=2.7$.

The Equation (8) is similar to the equation presented in [19], which was derived from the Gibbs-Duhem relationship for the thermodynamic equilibrium in a binary sorbent-sorbate system.

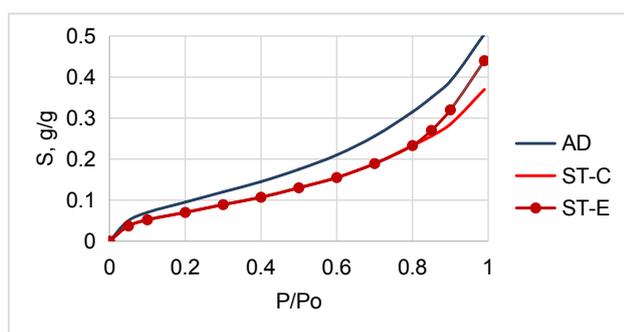


Figure 7. Calculated isotherms of WV for AD of C6P (AD) and sample of semicrystalline ST (ST-C); ST-E is experimental isotherm of ST sample

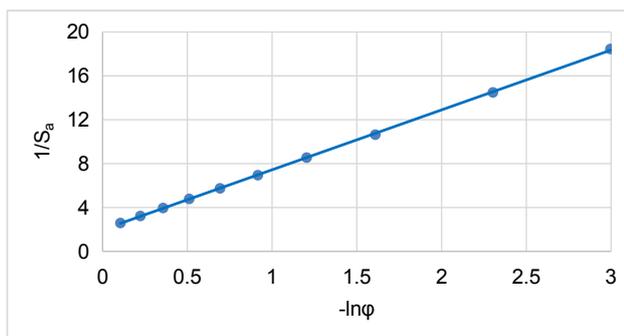


Figure 8. Linear form of sorption isotherm of WV for AD of C6P

To obtain the equation of sorption isotherm for a semicrystalline sample with a degree of amorphicity (Y), it is enough to introduce the Y -value in the Equation (8).

$$S = Y S_{0,a} (1 - C \ln\phi)^{-1} \quad (9)$$

An example of the isotherm calculated for a semi-crystalline sample, ST-C, having $Y = 0.72$ is shown in Figure 7. The experimental isotherm of this sample, ST-E, is also presented. Comparison of the experimental and calculated isotherms for ST shows that in the ϕ -range from 0 to 0.8, these isotherms are practically identical. However, at $\phi > 0.8$, a de-

viation of the experimental isotherm from the calculated one is observed. This phenomenon is caused by the known fact that at high relative vapor pressures, along with molecular sorption of water by polar groups of a low-porous hydrophilic polymer, also capillary condensation of WV occurs, which increases the amount of water in this polymer [16,30,31]. Using calculations by the Equation (9) it is possible to separate the molecularly sorbed water (Figure 7, red line) from the capillary water (Figure 7, brown line) at $\phi > 0.8$.

3.4 Sorption of Water Vapor by Cellulose Samples and Other Unsubstituted Polysaccharides

The isotherms of WV sorption by semicrystalline cellulose samples have a sigmoid shape typical of hydrophilic biopolymers (Figure 9). To separate capillary-condensed water, the sections of isotherms above $\phi=0.8$ were calculated using Equation (9). As a result, isotherms only molecularly sorbed water were obtained. Next, the isotherms also for other polysaccharides will include only molecularly sorbed water.

Studies have shown that the sorption ability (S) increases in direct proportion to the amorphicity degree (Y) of the sample (see e.g. Figure 10). Thus, it is confirmed that the process is performed via absorption of water molecules by amorphous domains of cellulose samples.

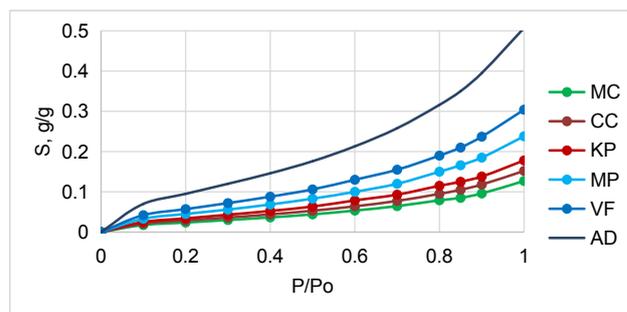


Figure 9. Sorption isotherms of WV for semicrystalline cellulose samples and AD of this biopolymer

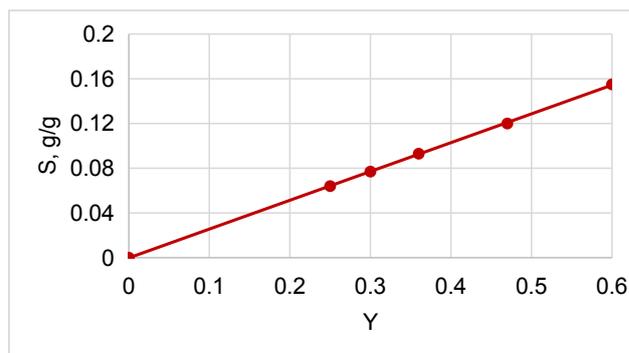


Figure 10. Dependence of sorption value at $\phi=0.7$ on amorphicity degree of cellulose samples

If the sorption values at various ϕ to divide by the degree of amorphicity of the sample, then it is possible to obtain the sorption isotherm for AD that is general for all cellulose samples (Figure 9). This general isotherm is identical to AD isotherm in Figure 7 calculated by Equation (5) and (8) for AD of C6P, to which cellulose also belongs. This confirms the validity of the Van Krevelen method, on which these equations are based.

The sorption of WV by ST sample and its AD has been already discussed (see Figures 7 and 8). Another C6P biopolymer, such as MN, has sorption properties similar to ST.

Xylan, XL, belongs to C5P, therefore its sorption characteristics differ from those of biopolymers belonging to C6P. Since the repeating unit of isolated XL has only two OH-groups, the sorption capacity of its AD is lower than that AD of C6P, the repeating unit of which contains three OH-groups (Figure 11).

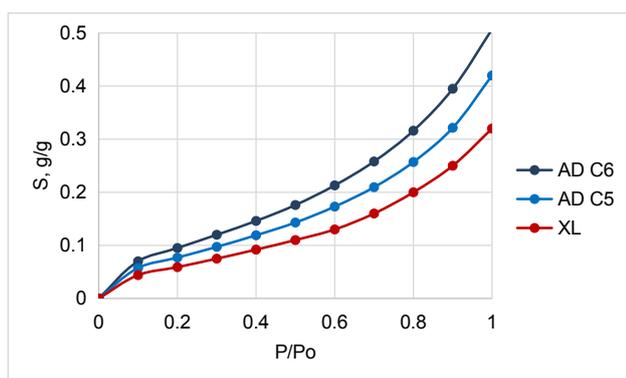


Figure 11. Sorption isotherms of WV for semicrystalline sample of isolated XL, AD of XL (AD C5) and AD of C6P (AD C6)

3.5 Sorption of Water Vapor by Substituted C6-polysaccharides

In this study, such substituted C6P as CT, CS, and PC were used. Since these samples were semicrystalline, their sorption values were understated (Figure 12).

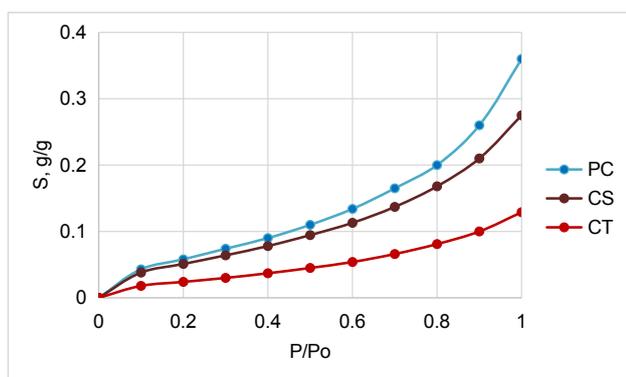


Figure 12. Sorption isotherms of WV by semicrystalline samples of PC, CS and CT

However, if consider sorption of WV by AD of these biopolymers, then the sorption capacity will be determined only by the type and content of polar groups. In the repeating unit of CS, one amino group substitutes one hydroxyl group at C2 present in C6P. The contribution of the amino group to sorption is close to the contribution of the hydroxyl group, therefore, the sorption isotherms for AD of CS and AD of C6P will be similar.

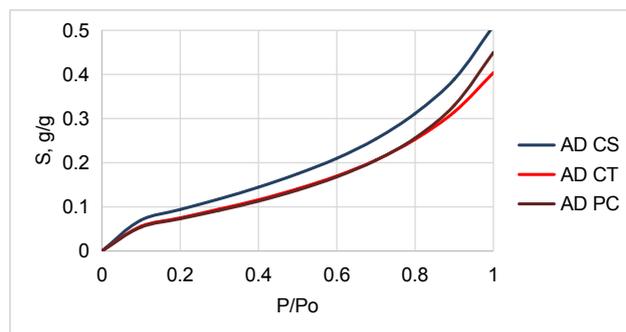


Figure 13. Sorption isotherms of WV for AD of CS (AD CS), CT (AD CT) and PT (AD PT)

Since the repeating unit of CT has a higher molecular weight than CS and contains low-polar acetyl groups, the sorption capacity for AD of CT will be lower than that for AD of CS and AD of C6P containing highly-polar amino- and hydroxyl groups. The same phenomenon is observed for AD of PC, the repeating unit of which contains a low-polar carboxyl group (Figure 13).

3.6 Enthalpy of Wetting

Calorimetric studies revealed (Table 5) that the interaction of various polysaccharides with water is accompanied by exothermic heat effects called the enthalpy of wetting ($\Delta_w H$).

Table 5. Enthalpy of wetting for samples of various polysaccharides

Sample	X	Y	$-\Delta_w H$, J/g
MC	0.75	0.25	42
CC	0.70	0.30	50
KP	0.64	0.36	61
MP	0.53	0.47	79
VF	0.36	0.64	108
ST	0.28	0.72	121
MN	0.26	0.74	124
XL	0.23	0.77	106
PC	0.20	0.80	118
CT	0.68	0.32	43
CS	0.46	0.54	92

For the same polysaccharide type, e.g. C6P, samples of which have different crystallinity and amorphicity, the enthalpy of wetting is directly proportional to the

amorphicity degree (Figure 14).

Such dependence confirms that the interaction occurs by volume absorption of water in AD of the polysaccharides. The slope factor of the straight line in Figure 14 gives the value $\Delta_w H_a = -168$ (J/g), which is the wetting enthalpy of the amorphous phase of C6P.

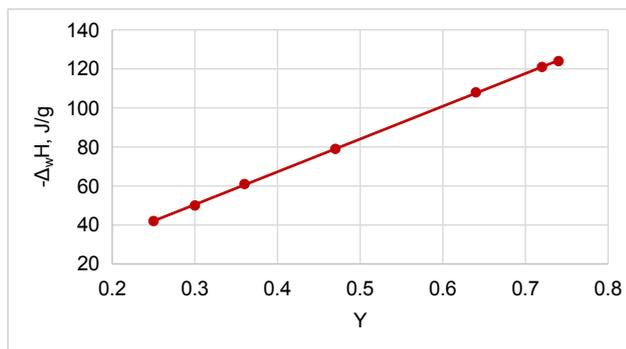


Figure 14. Dependence of enthalpy of wetting on amorphicity degree for samples of C6P

Values of $\Delta_w H_a$ for other samples can be found by dividing the experimental value of the wetting enthalpy for the sample by its amorphicity degree (Table 6).

4. Discussion

To describe the sorption isotherms of water vapor for hydrophilic biopolymers, including polysaccharides, the equations of multilayer surface adsorption such as BET and GAP are mostly used in the literature [10-13,16,32-34]. Using these equations, the value of the monolayer adsorption, specific surface area, and the constants of these equations are calculated. However, it has been proven that polysaccharides and other hydrophilic biopolymers interact with water by the absorption mechanism. Therefore, the calculations of adsorption characteristics for absorbing sorbents using BET or GAP equations have no physical meaning.

To describe the absorption process, the Flory-Rehner, Hailwood Horrobin, and some other equations can be used [16]. However, the studies revealed that the best conformity with experiments gives the use of the equation of type (9): $S = Y S_{o,a} (1 - C \ln \phi)^{-1}$, parameters of which for samples of various polysaccharides are presented in Table 6.

Table 6. Parameters of Equation (9)

Polysaccharides	C	$S_{o,a}$, g/g	$-\Delta_w H_a$, J/g
C5P	2.7	0.410	137
C6P	2.7	0.506	168
CS	2.7	0.510	170
CT	2.7	0.400	134
PT	3.1	0.440	147

It has been found that crystallinity strongly affects the sorption capacity and wetting enthalpy. Therefore, to compare the hydrophilicity of various polysaccharides with different crystallinity, it is necessary to use hydrophilic characteristics of amorphous domains of semicrystalline biopolymers. After that, the relative hydrophilicity index (HI) of various polysaccharides can be calculated. For this purpose, the following ratios were calculated:

$$HI_s = S_{o,a}(P)/S_{o,a}(C6P) \text{ and } HI_e = \Delta_w H_a(P)/\Delta_w H_a(C6P) \quad (10)$$

where HI_s and HI_e are hydrophilicity indexes measured by sorption, and wetting enthalpy, respectively; $S_{o,a}(P)$ and $S_{o,a}(C6P)$ are maximum sorption values for AD of tested polysaccharide (P), and C6P, respectively; $\Delta_w H_a(P)$ and $\Delta_w H_a(C6P)$ are wetting enthalpies for AD of tested polysaccharide (P), and C6P, respectively.

The calculations showed that the values of HI_s and HI_e are equal; therefore, the common hydrophilicity index (HI) was subsequently used. As follows from Figure 15, chitosan is the most hydrophilic polysaccharide type among the studied biopolymers, while other substituted polysaccharides, pectin, xylan, and chitin showed less hydrophilicity.

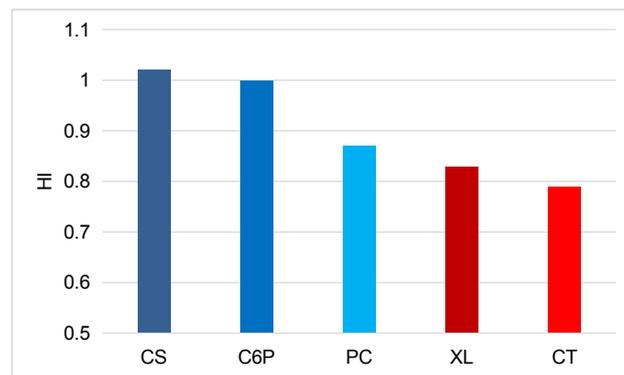


Figure 15. Hydrophilicity index of various polysaccharides

Since the contribution of the amino group of chitosan and the hydroxyl group of C6-polysaccharides to sorption are close, it can be expected that the HI for CS and C6P will be similar. However, in reality, the HI for CS is slightly higher than for C6P. This can be explained by the fact that the binding energy of water molecules with the nitrogen atoms of the amino groups of CS is greater than with the oxygen atoms of hydroxyl groups of C6P [35].

The decreased HI for PC, XL, and CT is because repeating units of these polysaccharides contain two unsubstituted hydroxyl groups instead of three in C6P. An additional reason for the low HI of CT is that, firstly, repeating unit

of this biopolymer contains a low-polar acetyl group; and secondly, the molecular weight (MW) of the repeating unit of CT is the largest of all the studied polysaccharides (Table 3), thus relative sorption value expressed in gram H₂O per gram biopolymer will be the smallest.

Discussing the process of water vapor sorption by polysaccharides, an additional problem arises because the amorphous domains of all these biopolymers are in a glassy state at room temperature. Since all these polymers are low-porous, then theoretically the sorption of water vapor in glassy AD of the biopolymers at the low and middle ϕ -ranges should be absent, and begins only at increased vapor pressures, when as a result of the plasticizing action of water the glass transition temperatures decrease below the temperature of sorption experiment, 25 °C. However, the experiments do not support this theory, which requires an explanation.

The explanation is that amorphous domains of biopolymers have heterogeneous packing since they consist of clusters with different packing densities and energies of hydrogen bonds^[36]. Despite the glassy state of densely packed clusters, in less densely packed clusters, local mobility of small segments is possible, which creates a free volume sufficient for the penetration of small water molecules. For example, it was calculated that the free volume of loosely packed clusters in AD of such C6P as cellulose is $V_f = 3.32 \times 10^{-23} \text{ cm}^3$ per one monomeric unit, which exceeds the volume of a water molecule, $V_w = 2.99 \times 10^{-23} \text{ cm}^3$.

As a result, at the initial sorption stage, water molecules can penetrate in loosely packed clusters of AD and intensively sorb by polar groups of these clusters. This initial sorption stage is accompanied by a high exothermic heat effect^[16]. The beginning sorption leads to a weakening of the H-bonds of neighboring clusters, which promotes further gradual sorption of water molecules at the middle ϕ -range. This process continues until the densely packed clusters soften at increased relative vapor pressures due to the plasticizing effect of the absorbed water, which leads to a sharp increase in further sorption of water vapor at $\phi > 0.8$ ^[16,36].

When the polysaccharides are wetted with water, their amorphous domains soften and pass into a viscoelastic state, which provides fast and complete absorption of water molecules in AD accompanied by an exothermal wetting effect, i.e. enthalpy.

5. Conclusions

The specific surface area, sorption of water vapor, and wetting enthalpy of various polysaccharides (cellulose,

hemicelluloses, starch, pectin, chitin, and chitosan) have been studied. It was found that the specific surface area of the dry samples measured by sorption of inert vapor of n-hexane was low indicates the low-porous structure of these polysaccharides. As opposite, the specific surface area measured by sorption of active water vapor was 20-80 times higher and correlates with the amorphicity degree of the samples. It was shown that crystallites are inaccessible for water, and therefore water molecules can interact only with polar groups in noncrystalline (amorphous) domains of biopolymers. The isotherms of water vapor sorption for various polysaccharides had sigmoid shapes, which can be explained by the absorption of water molecules in heterogeneous amorphous domains having clusters with different packing densities. The method of contributions of polar groups to sorption of water molecules was used, which allowed to derivate a simple calculating equation to describe the shape of sorption isotherms. The wetting of biopolymers with water was accompanied by a high exothermic thermal effect, in direct proportion to the amorphicity degree. The sorption values and wetting enthalpies of amorphous domains of biopolymers were calculated, which allowed to find the hydrophilicity index and comparing the hydrophilicity of the various polysaccharides. The calculations showed that the amino-polysaccharide, chitosan, is the most hydrophilic among the studied biopolymers, while other substituted polysaccharides, pectin xylan, and chitin are characterized by reduced hydrophilicity.

References

- [1] Thomas, S., Ninan, N., Mohan, S., Francis, E., 2012. Natural Polymers, Biopolymers, Biomaterials, and Their Composites, Blends, and IPNs. Academic Press: New York. pp. 444.
- [2] John, M.J., Thomas, S., 2012. Natural Polymers. RCS Publishing: Landon. pp. 313.
- [3] Kantappa, H., Kim, H.J., Birajdar, M., et al., 2016. Recently developed applications for natural hydrophilic polymers. J. Ind. Eng. Chem. 40, 16-22. DOI: <https://doi.org/10.1016/j.jiec.2016.06.01>.
- [4] Ioelovich, M., 2021. Adjustment of hydrophobic properties of cellulose materials. Polymers. 13(8), 1241-1252. DOI: <https://doi.org/10.3390/polym13081241>.
- [5] Scheller, H.V., Ulvskov, P., 2010. Hemicelluloses. Ann. Rev. Plant. Biol. 61, 263-89. DOI: <https://doi.org/10.1146/annurev-arplant-042809-112315>.
- [6] Cornejo-Ramírez, Y.I., Martínez-Cruz, O., Del Toro-Sánchez, C.L., et al., 2018. The structural char-

- acteristics of starches and their functional properties, *CyTA - Journal of Food*. 16(1), 1003-1017.
DOI: <https://doi.org/10.1080/19476337.2018.1518343>.
- [7] Elieh-Ali-Komi, D., Hamblin, M.R., 2016. Chitin and Chitosan: Production and Application. *Int. J. Adv. Res.* 4(3), 411-427.
- [8] Marmur, A., 2009. Solid surface characterization by wetting. *Ann. Rev. Mater. Res.* 39(1), 473-489.
DOI: <https://doi.org/10.1146/annurev.matsci.38.060407.132425>.
- [9] El-Saftawy, A.A., Abd El Aal, S.A., Badawy, Z.M., Soliman, B.A., 2014. Investigating wettability and optical properties of PADC polymer irradiated by low energy Ar ions. *Surface and Coatings Technol.* 253, 249-254.
DOI: <https://doi.org/10.1016/j.surfcoat.2014.05.048>.
- [10] Timmermann, E.O., 2003. Multilayer sorption parameters: BET or GAB values. *Colloid Surface A*. 220, 235-260.
DOI: [https://doi.org/10.1016/S0927-7757\(03\)00059-1](https://doi.org/10.1016/S0927-7757(03)00059-1).
- [11] Czepirsky, L., Komarowska-Czepirska, E., Szymonska, J., 2002. Fitting of different models for water vapor sorption on potato starch granules. *Appl. Surface Sci.* 196(1-4), 150-153.
DOI: [https://doi.org/10.1016/S0169-4332\(02\)00050-8](https://doi.org/10.1016/S0169-4332(02)00050-8).
- [12] Brousse, M.M., Linares, R.A., Vergara, M.L., Nieto, A.B., 2017. Adsorption isotherm of dehydrated mashed cassava from different varieties. *RECyT*. 19(28), 29-37.
- [13] Blahovec, J., Yanniotis, S., 2008. GAB generalized equation for sorption phenomena. *Food Bioprocess Technol.* 1, 82-90.
DOI: <https://doi.org/10.1007/s11947-007-0012-3>.
- [14] Park, G.S., 1986. Transport Principles-Solution, Diffusion and Permeation in Polymer Membranes. In: Bungay P.M., Lonsdale H.K., de Pinho M.N. (eds) *Synthetic Membranes: Science, Engineering and Applications*. NATO ASI Series C: Mathematical and Physical Sciences, vol 181. Springer: Dordrecht. pp. 57-108.
- [15] Bessadok, A., Langevin, D., Gouanvé, F., et al., 2009. Study of water sorption on modified Agave fibres. *Carbohydr. Polym.* 76, 74-85.
DOI: <https://doi.org/10.1016/j.carbpol.2008.09.033>.
- [16] Papkov, S.P., Fainberg, E.Z., 1976. Interaction of Cellulose and Cellulosic Materials with Water. *Chemistry: Moscow*. pp. 232.
- [17] Zografia, G., Kontnya, M.J., Yangb, A.Y.S., Brennerb, G.S., 1984. Surface area and water vapor sorption of microcrystalline cellulose. *Int. J. Pharm.* 18(1-2), 99-116.
DOI: [https://doi.org/10.1016/0378-5173\(84\)90111-X](https://doi.org/10.1016/0378-5173(84)90111-X).
- [18] Ioelovich, M., 2009. Accessibility and crystallinity of cellulose. *Bioresources*. 4(3), 1168-1177.
DOI: <https://doi.org/10.15376/BIORES.4.3.1168-1177>.
- [19] Ioelovich, M., Leykin, A., 2011. Study of sorption properties of cellulose and its derivatives. *Bioresources*. 6(1), 178-195.
DOI: <https://doi.org/10.15376/biores.6.1.178-195>.
- [20] Hill, C.A.S., Norton, A., Newman, G., 2009. The water vapor sorption behavior of natural fibers. *J. Appl. Polym. Sci.* 112, 1524-1537.
DOI: <https://doi.org/10.1002/app.29725>.
- [21] Bismarck, A., Aranberri-Askargorta, I., Springer, J., et al., 2002. Surface characterization of flax, hemp and cellulose fibers; surface properties and the water uptake behavior. *Polymer composites*. 23(5), 872-894.
DOI: <https://doi.org/10.1002/pc.10485>.
- [22] Chirkova, J., Andersons, B., Andersons, I., 2007. Study of the structure of wood-related biopolymers by sorption methods. *Bioresources*. 4(3), 1044-1057.
- [23] Takur, V.K., Takur, M.K., 2016. *Handbook of Sustainable Polymers: Structure and Chemistry*. PAN Stanford Publ: New York. pp. 988.
- [24] Ago, M., Endo, T., Hirotsu, T., 2004. Crystalline transformation of native cellulose from cellulose I to cellulose II polymorph by a ball milling method with a specific amount of water. *Cellulose*. 11(2), 163-167.
DOI: <https://doi.org/10.1023/B:CELL.0000025423.32330.fa>.
- [25] Paes, S.S., Sun, Sh., MacNaughtan, W., et al., 2010. The glass transition and crystallization of ball milled cellulose. *Cellulose*. 17(4), 693-709.
DOI: <https://doi.org/10.1007/s10570-010-9425-7>.
- [26] Ioelovich, M., 2016. Physico-chemical methods for determination of cellulose crystallinity. *ChemXpress*. 9(3), 245-251.
- [27] Ioelovich, M., 2016. Models of supramolecular structure and properties of cellulose. *Polymer Sci. A*. 58(6), 925-943.
DOI: <https://doi.org/10.1134/S0965545X16060109>.
- [28] Ioelovich, M., 2016. Study of thermodynamic properties of various allomorphs of cellulose. *ChemXpress*. 9(3), 259-265.
- [29] Van Krevelen, D.W., Nijenhuis, K., 2009. *Properties of Polymers: Correlations with Chemical Structure*. Elsevier: Amsterdam. pp. 1004.
- [30] Engelund, E.T., 2011. *Wood - water interactions: Linking molecular level mechanisms with macroscopic performance*. University Press: Copenhagen. pp. 171.

- [31] Shi, J., Avramidis, S., 2017. Water sorption hysteresis in wood: III physical modeling by molecular simulation. *Holzforschung*. 71, 733-741.
DOI: <https://doi.org/10.1515/hf-2016-0231>.
- [32] Agrawal, A.M., Manek, R.V., Kolling, W.M., Neau, S.H., 2004. Water distribution studies within microcrystalline cellulose and chitosan using differential scanning calorimetry and dynamic vapor sorption analysis. *J. Pharma. Sci.* 93(7), 1766-1779.
DOI: <https://doi.org/10.1002/jps.20085>.
- [33] Manek, R.V., Builders, P.F., Kolling, W.M., et al., 2012. Physicochemical and binder properties of starch obtained from *Cyperus esculentus*. *AAPS Pharm. Sci. Tech.* 13(2), 379-388.
DOI: <https://doi.org/10.1208/s12249-012-9761-z>.
- [34] Bertolin, Ch., Ferri, L., Strojceki, M., 2020. Application of the Guggenheim, Anderson, de Boer (GAB) equation to sealing treatments on pine wood. *Proc. Struct. Integ.* 26, 147-154.
DOI: <https://doi.org/10.1016/j.prostr.2020.06.018>.
- [35] Grinberg, N., Grushka, E., 2018. *Advances in Chromatography*. Vol. 54. CRC Press: Boca Raton. pp. 182.
- [36] Ioelovich, M., 2016. Isophase transitions of cellulose - A short review. *Athens J. Sci.* 3(4), 309-322.