European Journal of Wood and Wood Products
https://doi.org/10.1007/s00107-023-01976-x

ORIGINAL ARTICLE

Sorption properties of paper treated with silane-modified starch

Jerzy Majka[1] · **Waldemar Perdoch**[1] · **Łukasz Czajkowski**[1] · **Bartłomiej Mazela**[1] · **Wiesław Olek**[1]

Received: 4 January 2023 / Accepted: 28 July 2023

Abstract

Sorption properties of paper products are important when applying paper as the packaging material. Hydrophobicity, i.e. reduced affinity of paper surface to liquid water, is of particular importance from the point of view of the direct impact on packed goods. However, hygroscopicity of the material is significant during storage of goods. The analysis of changes in the hygroscopic properties of paper products induced by the treatment with silane modified starch was presented. The results on the hygroscopicity of treated paper were related to the previously published results on the hydrophobicity. The discrete values of equilibrium moisture content allowed constructing adsorption and desorption isotherms. The three-parameter Guggenheim, Anderson, and De Boer (GAB) model, the four-parameter Generalized D'Arcy and Watt (GDW), and Yanniotis and Blahovec (Y-B) sorption isotherm models were used to quantify the hygroscopic properties for all options of untreated and modified paper samples. The effectiveness of silanes for improving hygroscopic properties was determined and compared to their impact on hydrophobicity of the studied materials. It was found that 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane was the only silane improving hydrophobic and hygroscopic properties. The analysis of the applied models of sorption isotherms depicted that the GAB model was not valid for describing water sorption isotherms in the case of the tested materials, while the GDW and Y-B models provided a much more realistic description of water sorption mechanisms. The evaluation of the results of fitting the GDW model indicated that water molecules bonding to the primary sites was the dominating mechanism of sorption.

1 Introduction

Due to its availability, strength properties, and biodegradability, the use of cellulose is widespread in many industries. An essential feature of cellulose materials, resulting from their chemical composition and capillary-porous structure, is their water affinity. The feature is not beneficial. Water, penetrating between amorphous areas of cellulose and entering the capillary spaces of the fiber cell walls, causes them to swell. Moreover, water bridges are formed, which replace hydrogen bonds reducing the material's overall mechanical strength. Commonly used methods of cellulose surface modification are aimed at limiting the access of water molecules to the fibers through hydrophobization, i.e., increasing liquid water repellency. The cellulose hydroxyl groups are often replaced with other functional groups that do not interact with water molecules (e.g., Rodríguez-Fabià et al. 2022). Another method is to create an additional cellulose-encrusting net (shell) that physically blocks the ability to link water, i.e., by alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Both agents are dedicated to bulk and surface hydrophobization under neutral or alkaline pH conditions (Holik 2006). The hydrophobization agents are often dosed in the presence of starch, i.e., the most widely used substance to improve the strength of paper in dry conditions (Hubbe 2007; Biricik et al. 2011). Starch physically blocks pores on paper surface. However, since it is a hydrophilic, water-soluble substance, it does not provide sufficient water protection to the papermaking products. Therefore, starch is often modified by adding styrene maleic anhydride (SMA), styrene-acrylic copolymer (SA), polyurethanes (PU), or previously mentioned AKD or ASA.

The other promising method for cellulose hydrophobization is the application of organosilicon compounds, which are already in the wood and textile industry (Sèbe and Brook 2001). The concept of silicone compounds resulted from their hydrophobic nature and low environmental toxicity (De Vetter et al. 2010). Organosilicone compounds consist of reactive organic groups and silane groups. Organic groups

---

✉ Wiesław Olek
wieslaw.olek@up.poznan.pl

[1] Faculty of Forestry and Wood Technology, Poznań University of Life Sciences, Poznań, Poland

have a high potential for interaction with the substrate, and silane groups can give the material the desired properties, e.g., increasing hydrophobicity, dimensional stability, and durability (Tshabalala and Gangstad 2003; Hill et al. 2004; Ratajczak et al. 2010; Xie et al. 2010; Siuda et al. 2019). There are already known methods of paper hydrophobization using alkoxysilanes with isocyanate substituents or chlorine (Cunha et al. 2010a, b), which guarantee the formation of silane-cellulose bonds. The form-forming properties of starch, which is applied to paper in the form of a colloidal solution, can be used to evenly distribute alkoxysilanes on the surface of paper products (Ganicz and Rozga-Wijas 2021; Nowak et al. 2022). The hydroxyl groups of glucose units in starch make it possible to form starch-silane bonds and obtain a consolidated hydrophobic layer. Ganicz et al. (2020) reported high efficiency of surface hydrophobization of paper with methyltriethoxysilane-modified starch, i.e., high values of surface contact of 114° were found, and the water Penetration Dynamics Analysis test confirmed the barrier properties.

The interaction of paper with water vapor or, more precisely, with moist air is substantially rarely studied as compared to the analyses on hydrophobization of lignocellulosic materials, i.e., improving the properties dependent on the liquid water action. Water vapor sorption significantly influences the quality and properties of paper products. The adsorption processes are responsible for paper hygroexpansion and dimensional instability. The strength properties of paper are substantially affected by water vapor sorption, while cyclic changes of air relative humidity induce mechanosorptive creep (e.g., Fellers 2009). Therefore, a reduction in paper hygroscopicity has to be considered.

Camargo and Garcia (2011) studied adsorption and desorption isotherms as well as sorption hysteresis of the cellulose II:SiO_2 composites. The reduction of hygroscopic properties was found only for one level of silicification, i.e., 20%. It was also revealed that the silicification promoted the primary water sorption as compared to the secondary water. Mohammadzadeh et al. (2020) analyzed the hygroscopic properties of cellulose-based paper treated with commercial products, including hydrophobic and oleophobic agents. The moisture sorption isotherms for untreated and chemically modified paper sheets were studied and analyzed in light of the GAB model. The applied chemical treatments resulted in a reduction in hygroscopicity and an increase in the dimensional stability of paper. Because of the unknown composition of silane in commercial products, it was not easy to discuss the influence of the chemical nature on treated materials.

The objective of the present study was to determine changes in the hygroscopic properties of paper due to its surface treatment with wheat starch as modified with silane coupling agents. The hygroscopicity of the modified paper was also compared to the hydrophobization effectiveness of the applied treatment options.

2 Materials and methods

2.1 Materials

Bleached softwood Kraft fibers (Södra Black R, Sweden) with average length and width of 2100 and 30.0 µm, respectively, were used as the raw material. The cellulose fibers were characterized by the coarseness of 135 µg/m, ash content of 0.25%, brightness of 89.5%, and pH of 4.8.

Wheat starch (C*Flex 20002, Minneapolis, MN, USA) was used as a functional additive in the study. The starch was characterized by the amylose content of 31.2 ± 0.16%, the lipid content of 0.25 ± 0.02%, and the protein content of 0.30 ± 0.01%. An aqueous solution of starch (concentration of 5%) was stirred at 70 ± 3 °C in the presence of 0.5% sodium hydroxide (CAS no, 1310-73-2, ChemPur, Poland) to reduce the temperature of starch gelatinization (Kolpak et al. 1978; Okano and Sarko 1985). The starch was separately modified with four silane coupling agents, i.e. methyltrimethoxysilane (MTMS) (Sigma Aldrich, CAS no, 1185-55-3, St. Louis, MO, USA), tetraethyl orthosilicate (TEOS) (Sigma Aldrich, CAS no, 78-10-4, St. Louis, MO, USA), n-octyltriethoxysilane (NOTES) (Sigma Aldrich, CAS no, 2943-75-1, St. Louis, MO, USA) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (WR) (Sigma Aldrich, CAS no, 51851-37-7, St. Louis, MO, USA).

2.2 Production of paper sheets

Before paper manufacturing, either as native or in a modified form, cellulose fibers were immersed in deionized water for 24 h for better defibrillation during paper sheet production. A lubricancy of diluted suspension of pulp was measured by the Schopper-Riegler apparatus (Labormex, Poland) according to SIST PN-EN ISO 5267-1:2000/AC: 2003. Pulp suspension in water in terms of the Schopper-Riegler number was 14 ± 0.8. The Rapid-Köthen sheet former (Labormex, Poland) was applied to prepare paper sheets with a diameter of 200 ± 0.1 mm and an average thickness of 0.5 ± 0.02 mm. The paper sheets were vacuum dried in the Rapid-Köthen sheet former for 600 s at a temperature of 95 ± 1 °C. Then the sheets were conditioned at the set temperature of 18 °C and relative humidity of 50%.

The cellulose fibers were modified after forming paper sheets, i.e. the additives were applied at both surfaces of already produced sheets. An aqueous solution of wheat starch (concentration of 5%) was first stirred at 70 ± 5 °C in the presence of 0.5% sodium hydroxide to reduce the starch gelatinization temperature. The starch structure was loosened to make it easier for silanes to penetrate amylose and amylopectin chains. The obtained suspension was cooled down to 25 ± 5 °C, and while mixing, 2.5% concentration of organosilicon compounds (i.e. MTMS, TEOS, NOTES, or WR) was added. The prepared formulations were applied as coatings using 100 g/m^2 for paper sheets produced according to the Rapid-Köthen sheet former procedure. After modification, sheets were conditioned for 7 days in a laboratory chamber at temperature of 18 ± 1 °C and relative humidity of 50%. Five paper sheets were produced for each option of modification.

The application of the additives resulted in the following options of the investigated materials, i.e. Control—untreated paper, WS—paper treated with wheat starch only, WS + MTMS—paper treated with starch modified with MTMS, WS + TEOS—paper treated with starch modified with TEOS, WS + NOTES—paper treated with starch modified with NOTES, WS + WR—paper treated with starch modified with WR. For each option of materials, 5 samples were prepared.

2.3 Sorption experiments

The samples of dimensions of $0.5 \cdot 50 \cdot 30$ mm were used for investigating hygroscopic properties. The dimensions and the number of samples for each option of the examined material resulted from the error analysis based on the total differential method (e.g. Taylor 1997). It was assumed that the relative error of the equilibrium moisture content determination should not exceed 2% for the lowest level of air relative humidity. Before starting sorption experiments, all samples were stored for 3 weeks in closed containers over phosphorus pentoxide to approach the dry state. The experimental set-up consisted of two chambers, as described by Majka and Olek (2007; 2008). The outer chamber encased the inner chamber to stabilize air temperature inside the set-up. The samples for all options of the examined material were placed in the inner chamber, and a fan forced airflow. The air relative humidity was controlled by saturated salt solutions listed in Table 1. The weighing procedure was repeated until the difference between the subsequent mass readings was not exceeding 0.001 g. It indicated that the hygroscopic equilibrium was approached. During the weighing phase of the samples, the upper part of the outer chamber was removed and the balance was placed on the top of the inner chamber. A string was used to link the balance and a pan which was placed inside the inner chamber. Therefore, the air exchange between the inner and outside chambers was minimized and limited to the weighing phase only. The sorption experiments were performed at a temperature of 22 ± 1 °C for both adsorption and desorption modes. The stability of air parameters during the sorption experiments was controlled by measuring temperature and relative humidity with an electronic thermohygrometer (LB 706, LAB EL, Poland). The samples were weighed at least twice at each relative humidity level specified in Table 1. After completing sorption experiments, the samples were placed in a laboratory dryer at a temperature of 103 °C to determine the oven-dry mass. Each equilibrium moisture content value was determined as the average of five observations for each material option.

Table 1 Salt solutions and chemicals applied in sorption experiments and recorded values of relative humidity at a temperature of 22 ± 1 °C

Salt solutions and chemicals	Relative humidity	
	Adsorption	Desorption
KNO_3	0.954	0.954
KCl	0.899	0.889
NaCl	0.778	0.791
NaBr	0.600	0.621
K_2CO_3	0.451	0.463
$CaCl_2 \cdot 6H_2O$	0.324	0.382
CH_3COOK	0.246	0.303
LiCl	0.115	0.116
P_2O_5	0.003	0.001

2.4 Modeling sorption isotherms

As obtained for all options of the investigated material, the adsorption and desorption isotherms were parametrized with three structural models. The first equation was the three-parameter Guggenheim, Anderson, and De Boer (GAB) model, still the most frequently applied equation for describing sorption isotherms in wood science. The GAB model was used in the following formula:

$$EMC = M_m \frac{K_{GAB} \cdot C_{GAB} \cdot RH}{(1 - K_{GAB} \cdot RH) \cdot (1 - K_{GAB} \cdot RH + C_{GAB} \cdot K_{GAB} \cdot RH)}, \quad (1)$$

where EMC; kg/kg—equilibrium moisture content, RH—air relative humidity, M_m; kg/kg—monolayer capacity, C_{GAB}—equilibrium constant related to the monolayer sorption, K_{GAB}—equilibrium constant related to the multilayer sorption.

The model was often transformed into another mathematical form in which the ratio of relative humidity and equilibrium moisture content was the parabolic function of relative humidity (e.g., Babiak 2007; Skaar 1988; Thybring et al. 2021):

$$\frac{RH}{EMC} = a + b \cdot RH - c \cdot RH^2, \quad (2)$$

where a, b, c—fitted parameters are functions of the original coefficients of the GAB model.

The GAB equation assumes binding water onto primary sorption sites and forming the monolayer of water, i.e., the primary water. These water molecules are converted into the secondary sorption sites, and additional layers of water are sorbed, i.e., the secondary water. The model assumes that the molecules of the secondary water are less strongly sorbed than the ones of the monolayer water. The application of the GAB model in wood science was questioned due to (a) deviation of empirical data from the parabolic relation (e.g Nakano 2006; Olek et al. 2013), (b) the decrease in the ratio of primary and secondary water contents with temperature (Zelinka et al. 2018), (c) the prediction of too low monolayer capacity and the capacity decreases with increasing temperature (Thybring et al. 2021).

It was already postulated to develop and apply new models describing sorption isotherms (e.g., Zelinka et al. 2020). Therefore, the four-parameter Generalized D'Arcy and Watt (GDW) equation developed by Furmaniak et al. (2007a, b) was utilized as the second model in the present study. The GDW equation assumes the existence of the primary sorption sites on solid surfaces and postulates that each active site can adsorb only one water molecule. The already adsorbed water molecules can be converted into the secondary sorption sites. The most important feature of the GDW model is related to three possible scenarios of the secondary water sorption resulting from the mathematical structure of the equation:

$$EMC = \frac{m_{GDW} \cdot K_{GDW} \cdot RH}{\left(1 + K_{GDW} \cdot RH\right)} \cdot \frac{1 - k_{GDW} \cdot (1 - w) \cdot RH}{\left(1 - k_{GDW} \cdot RH\right)}, \quad (3)$$

where EMC; kg/kg—equilibrium moisture content, RH—air relative humidity, m_{GDW}; kg/kg—monolayer water content (the maximum content of water bound to the primary sites), K_{GDW}—kinetic constant related to sorption on the primary sites, k_{GDW}—kinetic constant related to sorption on the secondary sites, w—ratio of water molecules bound to the primary sites and converted into the secondary sites.

The mentioned three scenarios of the secondary water sorption depend on possible values of the w parameter: (a) $w < 1$—water molecules bound on the primary sites are not completely converted into the secondary sorption sites (i.e., the number of the secondary sites is lower than the primary sites), (b) $w = 1$—all primary water molecules are converted into the secondary sorption sites, and the GDW model is reduced to the GAB model (Furmaniak et al. 2007a), (c) $w > 1$—each primary water molecule is statistically converted into more than one secondary sorption site, and the higher w values are obtained, the more intensive process of water cluster formation occurs.

The third applied equation was the four-parameter model proposed by Yanniotis and Blahovec (2009) and denoted here as the Y-B model. It assumes that the primary water is sorbed according to the Langmuir mechanism. In contrast, the remaining water is less strongly bound due to the solution formation according to the modified Raoult's law. The following form of the model is given:

$$EMC = \frac{RH}{a_1 + b_1 \cdot RH} + \frac{RH}{a_2 - b_2 \cdot RH}, \quad (4)$$

where a_1, a_2, b_1, b_2 are the coefficients to be fitted. The first component of the sum is recognized as the content of water sorbed on active sorption sites, while the second one involves the content of water forming solution with the solid. The solution formation mechanism is less realistic than the water cluster arrangement according to the GDW model. However, Yanniotis and Blahovec (2009) proposed a method for classifying water vapor sorption isotherms. The fitted coefficients of the model were used to calculate additional parameters, which were originally denoted as D_{10}, R_{fi}, and X_4. The relations of positive or negative values of the additional parameters were the criteria for the isotherms classification (Table 2).

2.5 Static water contact angle analysis

The sessile droplet contact angle was measured at the standard conditions, i.e., at temperature of 20 ± 1 °C and air relative humidity of 50%, using a Kruss contact angle measuring device (Kruss, Germany). A water droplet of 4.0 µL volume was placed on the surface, and a camera took a picture of the droplet within 30 s. Every sample was evaluated in five repetitions.

Table 2 Relations of the additional parameters for sorption isotherms classification according to Yanniotis and Blahovec (2009)

Type of isotherm	D_{10}	R_{fi}	X_4
Langmuir-like (type I)	Positive	Positive	Positive
Sigmoid more to the Langmuir-like (type IIa)	Positive	Negative	Negative
Sigmoid more to the solution-like (type IIb)	Positive	Negative	Positive
Solution-like (type III)	Negative	Positive	Negative

3 Results and discussion

The obtained discrete values of equilibrium moisture content were used to construct adsorption and desorption isotherms for all treatment options of the studied paper sheets. The isotherms were plotted after their parameterization with the GDW model (Fig. 1a–d). Each plot presents three sets of isotherm loops, i.e., for untreated paper sheets, paper treated with wheat starch only, and paper coated with starch modified by one of the options of organosilicon compounds. The surface application of unmodified wheat starch caused some increase in equilibrium moisture content for both adsorption and desorption modes. The observed increase was primarily due to the higher hydrophilicity of starch compared to cellulose (e.g., Peleg 2020). The paper treatment with coatings consisting of starch modified with organosilanes invoked a diverse influence on the hygroscopic properties of the material. The application of starch modified with MTMS or TEOS induced an additional increase in equilibrium moisture content (Fig. 1a, b) compared to the coating made of unmodified wheat starch. The highest increase in hygroscopicity was found for paper coated with starch modified with NOTES (Fig. 1c). The paper coating with starch modified with WR was the only treatment option resulting in a significant reduction in hygroscopicity for air relative humidity above 0.6 (Fig. 1d).

The three-parameter GAB, four-parameter GDW, and Y-B sorption isotherm models were fitted separately for

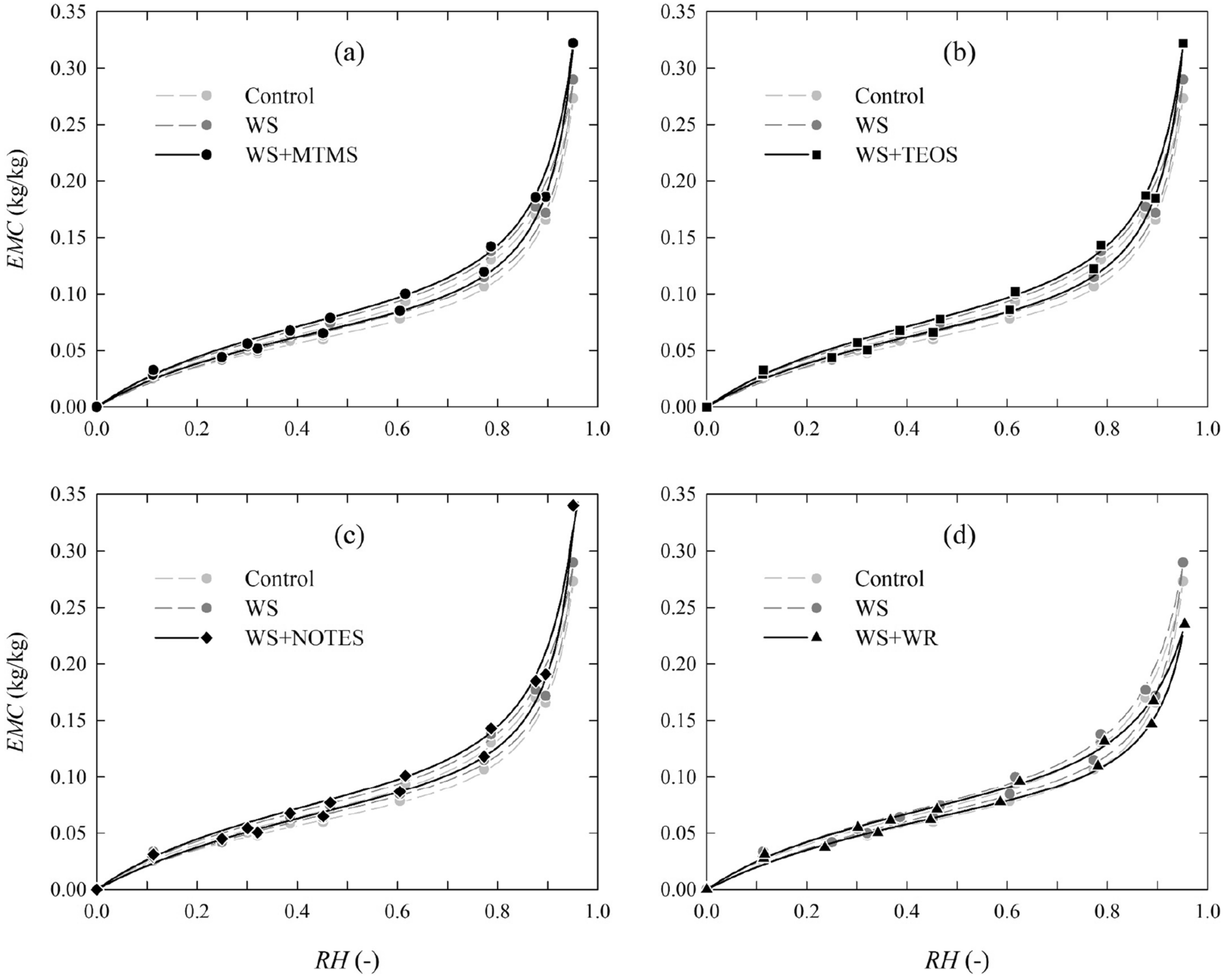

Fig. 1 Adsorption and desorption isotherms of the tested paper sheets at a temperature of 22 ± 1 °C. Each plot contains results for untreated paper (Control), surface treated paper with wheat starch only (WS), (**a**) paper treated with starch modified with MTMS, (**b**) paper treated with starch modified with TEOS, (**c**) paper treated with starch modified with NOTES, (**d**) paper treated with starch modified with WR. The isotherms parametrized with the GDW model, symbols represent experimental data separately measured for each option of the tested materials

all options of untreated and modified paper sheets. The coefficients of the best-fit of the sorption models were estimated using the Levenberg–Marquardt algorithm with SigmaPlot 9.0 software.

3.1 The Guggenheim, Anderson, and De Boer (GAB) model

The results of the model parametrization are presented in Table 3. The obtained values of the monolayer capacity (M_m), as reported for adsorption, were very low (ca. 0.04 kg/kg) and practically equal for all options of the treated material. It might suggest that the majority of absorbed water molecules were linked to the secondary sorption sites. Such exceptionally low values of the monolayer capacity are contrasted to the availability of sorption sites determined with the deuterium exchange method. Recently, Thybring et al. (2021) analyzed values of the monolayer capacity as predicted from different parabolic models of water sorption isotherms in beech and spruce wood (incl. the GAB equation) and experimentally obtained data on the accessibility of sorption sites. It was found that the measured values of accessibility were 2–5 times higher as compared to the predicted ones. Therefore, it was stated that the monolayer capacity values obtained from the analyzed sorption isotherms models, incl. the GAB equation, are not physically correct. The deuterium exchange method was also applied to quantifying available sorption sites in cellulosic pulps (e.g., Väisänen et al. 2018). The content of the accessible hydroxyl groups in kraft pulp obtained from spruce and pine wood was equal to 11.0 mol/kg. It had to result in the monolayer capacity as high as 0.2 kg/kg and suggests that the Langmuir mechanism governs the majority of sorption, and an only minor portion of water molecules is linked to the secondary sorption sites. Such a scenario will be verified within this study when analyzing the fitting results of the applied four-parameter GDW and Y-B sorption isotherm models.

The values of the C_{GAB} coefficient of the GAB model are referred to sorption enthalpy of the monolayer water and are used for classifying sorption isotherms. The necessary condition for ranking the isotherms as sigmoidal ones (i.e., type II isotherms) is to obtain values of C_{GAB} higher than 2. The condition was satisfied for all treatment options and sorption phases (Table 3). However, Lewicki (1997) enhanced the condition and defined the following system of inequalities: $5.57 \le C_{GAB} < \infty$ and $0.24 < K_{GAB} \le 1$. The additional condition was again satisfied for all treatment options and sorption phases. Therefore, all isotherms were fully classified as sigmoidal ones. The observed values of C_{GAB} were much higher than K_{GAB} for all examined treatment options. The relation indicates that water molecules directly bound to active primary sites are much stronger linked to the sorption centers than the secondary water. However, the changes in C_{GAB} values could not be related to the applied treatment options.

The K_{GAB} coefficient denotes the difference between the free enthalpy of polymolecular and bulk water (Timmermann 2003). The reported values of the coefficient were somewhat lower than 1 and practically the same for all treatment options and sorption phases (Table 3). It can be concluded that neither the treatment option nor the sorption phase influenced the binding energy of water molecules during polymolecular sorption.

3.2 The Generalized D'Arcy and Watt (GDW) model

The results of fitting the GDW model to all treatment options and sorption phases are given in Table 4. The predicted maximum water content bound to the primary sites (m_{GDW}) was always over 0.1 kg/kg for the adsorption mode. Comparing the m_{GDW} value to registered values of the equilibrium

Table 3 Estimated coefficients of the GAB model

Treatment option	Sorption phase	a	b	c	R^2	M_m (kg/kg)	K_{GAB}	C_{GAB}
Control	Adsorption	1.92	22.60	− 21.34	0.9339	0.039	0.879	15.419
	Desorption	1.77	19.02	− 17.72	0.9590	0.045	0.863	14.491
WS	Adsorption	1.77	21.48	− 20.26	0.9394	0.041	0.880	15.762
	Desorption	1.52	18.33	− 16.93	0.9611	0.048	0.862	15.961
WS + MTMOS	Adsorption	1.54	21.78	− 20.71	0.9472	0.041	0.894	17.792
	Desorption	1.57	17.41	− 16.25	0.9404	0.050	0.866	14.812
WS + TEOS	Adsorption	1.60	21.43	− 20.43	0.9522	0.041	0.894	16.980
	Desorption	1.57	17.25	− 16.11	0.9485	0.050	0.866	14.710
WS + NOTES	Adsorption	1.37	22.58	− 21.52	0.9441	0.040	0.904	20.250
	Desorption	1.80	17.02	− 16.21	0.9296	0.050	0.872	12.825
WS + WR	Adsorption	2.13	20.63	− 18.89	0.9196	0.041	0.842	13.502
	Desorption	1.86	16.91	− 14.96	0.9691	0.050	0.812	13.194

Table 4 Estimated coefficients of the GDW model

Treatment option	Sorption phase	m_{GDW} (kg/kg)	K_{GDW}	k_{GDW}	w	R^2
Control	Adsorption	0.1026	2.466	0.9906	0.1723	0.9997
	Desorption	0.1043	2.843	0.9576	0.2536	0.9987
WS	Adsorption	0.1370	1.722	0.9987	0.1272	0.9991
	Desorption	0.1143	2.768	0.9638	0.2268	0.9985
WS + MTMOS	Adsorption	0.1141	2.390	0.9963	0.1699	0.9995
	Desorption	0.1251	2.559	0.9789	0.1950	0.9994
WS + TEOS	Adsorption	0.1387	1.766	1.0001	0.1392	0.9990
	Desorption	0.1248	2.587	0.9763	0.2024	0.9993
WS + NOTES	Adsorption	0.1060	2.720	0.9984	0.1837	0.9995
	Desorption	0.1706	1.527	0.9942	0.1364	0.9992
WS + WR	Adsorption	0.1257	1.843	0.9799	0.1349	0.9988
	Desorption	0.1131	2.735	0.9357	0.2247	0.9986

moisture content shows the importance of sorption of the primary water compared to binding water molecules to the secondary sites. The paper treatment with starch resulted in a distinct increase of m_{GDW} to 0.137 kg/kg in the adsorption phase. It was due to the higher hydrophilicity of starch as compared to cellulose. The application of starch modified with silanes usually reduced m_{GDW} compared to paper coated with unmodified starch. The only exception was paper coated with starch modified with TEOS, which caused an additional increase of m_{GDW}.

The ratio of water molecules bound to the primary sites and converted into the secondary ones (w) was analyzed for the adsorption mode only as it refers to water gain. The w parameter was much lower than 1 for all analyzed treatment options. It can be concluded from the results presented in Table 4 that statistically, less than every fifth water molecule bound to the primary sorption site was converted into the secondary site. However, the improvement of paper hygroscopicity should be analyzed for the combined values of the parameters m_{GDW} and w. It is evident from the results in Table 4 that the best improvement should be expected for the treatment with starch modified with WR. It is consistent with the results presented in Fig. 1d. The reported values of the kinetic constant related to sorption on the primary sites (K_{GDW}) were consistently higher than those of the kinetic constant related to sorption on the secondary sites (k_{GDW}). It indicates that water molecules directly sorbed on active sorption sites were more strongly attached to the material than the molecules of secondary water.

Furmaniak et al. (2011) proposed a simplified classification of sorption isotherms based on the fitted GDW model. The type I isotherms with only primary sorption sites occurring in a sorbent were identified for the w parameter being equal or close to zero. However, the last alternative condition seems to be not clearly specified. It is of special importance in light of the values of the w parameter obtained in the present study, i.e. ranging from as small value as 0.13 to the highest of only 0.25. The type II isotherms were originally classified by Furmaniak et al. (2011) for $w > 0$ and $K_{GDW} > 1$, while the type III ones for $w > 0$ and $K_{GDW} < 1$. When strictly applying the listed conditions, the sorption isotherms obtained in the present study were classified as type II. However, the reservations specified on the proposed classification derived from the GDW model induced us to perform more analysis on the sorption isotherms classification.

3.3 The Yanniotis and Blahovec (Y-B) model

The estimated coefficients of the Yanniotis and Blahovec model are depicted in Table 5. Unfortunately, the mathematical structure of the model did not allow for direct coefficient analysis. Therefore, the model was only used for classifying sorption isotherms. The additional parameters D_{10}, R_{fi} and X_4 were calculated for each isotherm. The obtained values of D_{10} and X_4 were always positive, while the values of R_{fi} were always negative. Therefore, all sorption isotherms were classified as type IIb, i.e., sigmoid more to the solution-like (Table 5). It supports our earlier statements that the Langmuir mechanism is significant during water sorption in the analyzed materials but not the only one. The secondary water bonding has to be accounted for as the sorption mechanism and regarded almost equivalent to the previous one.

3.4 Sorption hysteresis

The sorption isotherms obtained for all treatment options were used for quantifying sorption hysteresis. The set of descriptors defined by Majka et al. (2016) was used. The descriptors consisted of sorption hysteresis loop (H), the maximum difference of equilibrium moisture content for desorption and adsorption (ΔEMC), and corresponding relative humidity (RH). The estimated descriptors of hysteresis are presented in Table 6. The applied treatment options

Table 5 Estimated coefficients of the Y-B model

Treatment option	Sorption phase	a_1	b_1	a_2	b_2	R^2	D_{10}	R_{fi}	X_4
Control	Adsorption	4.16	80.07	10.26	79.32	0.9997	33.93	-23.16	0.05
	Desorption	3.87	77.59	10.11	76.70	0.9987	34.71	-21.48	0.06
WS	Adsorption	3.86	73.38	9.23	73.10	0.9991	30.11	-25.43	0.02
	Desorption	4.56	116.22	7.14	116.17	0.9985	25.65	-88.40	0.00
WS + MTMOS	Adsorption	3.60	52.80	10.25	50.57	0.9995	25.48	-11.38	0.16
	Desorption	3.21	55.38	9.39	53.14	0.9994	27.30	-12.71	0.18
WS + TEOS	Adsorption	4.30	81.17	7.59	81.17	0.9985	22.48	-48.32	0.00
	Desorption	3.28	55.87	8.48	54.54	0.9991	24.82	-17.01	0.11
WS + NOTES	Adsorption	3.65	70.36	9.93	70.25	0.9996	32.53	-21.12	0.01
	Desorption	4.06	71.34	6.19	70.93	0.9988	14.95	-61.34	0.04
WS + WR	Adsorption	3.08	52.51	11.29	47.98	0.9988	30.19	-7.19	0.32
	Desorption	3.43	56.46	9.38	52.82	0.9986	26.49	-11.58	0.28

Table 6 Sorption hysteresis loop (*H*), the maximum difference of equilibrium moisture content for desorption and adsorption (ΔEMC), and corresponding relative humidity (RH)

Treatment option	*H* (arb. units)	Δ*EMC* (kg/kg)	*RH* (–)
Control	0.0097	0.023	0.88
WS	0.0103	0.025	0.89
WS + MTMOS	0.0102	0.021	0.88
WS + TEOS	0.0105	0.024	0.89
WS + NOTES	0.0090	0.018	0.82
WS + WR	0.0101	0.020	0.87

had no significant influence on sorption hysteresis. It was clearly resulting from the values of all descriptors of sorption hysteresis.

3.5 Hygroscopic properties vs. hydrophobization

The observed increase of equilibrium moisture content of paper treated with starch modified with MTMS, TEOS, and NOTES was contrary to the findings reported for the interaction with liquid water (Nowak et al. 2022). It was reported that the application of the coatings caused a significant improvement in the static water contact angle (WCA). The values of the WCA recorded by Nowak et al. (2022) started from non-measurable ones for untreated paper (control material), with some improvement for starch-treated paper (contact angle approx. 50°), up to a significant increase over 115° for paper treated with starch modified with MTMS. However, not all options of the paper treatment were equally effective, e.g., a coating made of starch modified with TEOS and NOTES revealed less significant improvement of the angle than unmodified starch. The differences in the properties of paper properties were explained by the starch network's silane distribution. MTMS molecules were characterized by short side chains (i.e., methyl groups) and relatively easily fixed within the starch structure. In contrast, silanes having longer side chains (e.g., NOTES) primarily covered starch surfaces. The Penetration Dynamics Analysis supported the findings, and the recommendation was made that the paper coating with starch modified with MTMS can be considered an effective method for improving the properties related to the interaction of paper with liquid water.

Table 7 Static water contact angle of coated paper

Treatment option	WCA (°)
Control	Not measurable
WS	52 ± 1.6*
WS + MTMOS	112 ± 3.9*
WS + TEOS	99 ± 4.2*
WS + NOTES	108 ± 5.4*
WS + WR	125 ± 3.8

*Results reported by Nowak et al. (2022)

A different relation was observed for paper coated with starch modified with WR (Table 7). It was the only treatment option causing the reduction in the equilibrium moisture content of the paper sheets. Moreover, the measured static water contact angle was the highest among all studied treatment options and equal to 125°. It clearly shows that the paper treatment with starch modified with WR ensured the best hydrophobization of the material and improved the hygroscopic properties. Similar results on the effectiveness of fluorosilane coating were reported by Szubert et al. (2019), where high hydrophobic properties of surface treated wood were presented (WCA > 120°). The disparate characteristics obtained for the interaction of coated paper with moist air are presumably related to mechanisms blocking active sorption sites within the paper and/or starch.

4 Conclusion

The sorption experiments for untreated and surface treated paper revealed changes in the hygroscopic properties of the studied material. The adsorption and desorption isotherms were constructed and modeled to quantify the hygroscopic properties. The performed analyses on hygroscopic properties led to the following conclusions:

1. The surface treatment with unmodified wheat starch caused an increase in the equilibrium moisture content of paper. It was primarily due to the higher hydrophilicity of starch compared to cellulose. The application of starch modified with methyltrimethoxysilane, tetraethyl orthosilicate, and especially n-octyltriethoxysilane caused an increase in equilibrium moisture content compared to paper treated with unmodified starch. The reported phenomenon was contrary to the effectiveness of the silanes as applied to improving hydrophobic properties. The only silane ensuring improvement of both hydrophobic and hygroscopic properties was 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane. It was probably due to a more effective substitution reaction of silane to hydroxyl groups of polysaccharides. This substitution is perhaps responsible for the efficiency of blocking active sorption sites.
2. The GAB model predicted very low values of the monolayer capacity. It was inconsistent with the literature results on the availability of sorption sites determined with the deuterium exchange method. The consequence of the GAB monolayer capacity was the unrealistic assumption that the majority of absorbed water molecules were linked to the secondary sorption sites. Therefore, the GAB model is not valid for describing water sorption isotherms in the case of untreated and surface treated paper.
3. The maximum content of water bound to the primary sites, as estimated by the GDW model, was always over 0.1 kg/kg. Simultaneously, the ratio of water molecules bound to the primary sites and converted into the secondary ones was usually less than 0.2, i.e., less than every fifth water molecule bound to the primary sorption site was converted into the secondary site. Therefore, one can conclude that water molecules bonding to the primary sites is the dominating mechanism of sorption, and the values of the kinetic constants of the model supported it.
4. Although explaining the dominating mechanism of sorption, a deeper chemical analysis of polysaccharides and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane interaction is necessary to understand the kinetics of the whole of modification process fully.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by JM, WP, ŁC, BM, and WO. The first draft of the manuscript was written by WP and WO, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding This research was funded by National Center for Research and Development, III edition of EEA and Norway grants; The Program “Applied Research in the frame of Norway Grants 2014-2021/POLNOR 2019 (NOR POLNOR/CellMat4ever/0063/2019-00)”.

Data availability The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the University policies.

Declarations

Conflict of interest The authors declare no conflict of interest.

References

Babiak M (2007) Sorption isotherms of wood. In: Perré P (ed) Fundamental of wood drying. Ed. A.R.BO.LOR., Nancy. pp. 67–86

Biricik Y, Sonmez S, Ozden O (2011) Effects of surface sizing with starch on physical strength properties of paper. Asian J Chem 23(7):3151–3154

Camargo JR, Garcia CAO (2011) Effect of silicification on the water sorption properties of microcrystalline cellulose II. Braz J Pharm Sci 47(1):125–135. https://doi.org/10.1590/S1984-82502011000100016

Cunha AG, Freire C, Silvestre A, Neto CP, Gandini A, Belgacem MN, Chaussy D, Beneventi D (2010a) Preparation of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas–solid reaction. J Colloid Interf Sci 344:588–595. https://doi.org/10.1016/j.jcis.2009.12.057

Cunha AG, Freire CS, Silvestre AJ, Neto CP, Gandini A (2010b) Preparation and characterization of novel highly omniphobic cellulose fibers organic–inorganic hybrid materials. Carbohyd Polym 80(4):1048–1056. https://doi.org/10.1016/j.carbpol.2010.01.023

De Vetter L, Van den Bulcke J, Van Acker J (2010) Impact of organosilicon treatments on the wood-water relationship of solid wood.

Holzforschung 64(4):463–468. https://doi.org/10.1515/hf.2010.069

Fellers C (2009) The interaction of paper with water vapour. In: Ek M, Gellerstedt G, Henriksson G (eds) Pulp and paper chemistry and technology, vol 4. De Gruyter, Berlin, pp 109–143

Furmaniak S, Terzyk AP, Gauden PA (2007a) The general mechanism of water sorption on foodstuffs—importance of the multitemperature fitting of data and the hierarchy of models. J Food Eng 82(4):528–535. https://doi.org/10.1016/j.jfoodeng.2007.03.012

Furmaniak S, Terzyk AP, Gauden PA, Rychlicki G (2007b) Applicability of the generalised D'Arcy and Watt model to description of water sorption on pineapple and other foodstuffs. J Food Eng 79(2):718–723. https://doi.org/10.1016/j.jfoodeng.2006.02.036

Furmaniak S, Terzyk AP, Gauden PA (2011) Some remarks on the classification of water vapor sorption isotherms and Blahovec and Yanniotis isotherm equation. Dry Technol 29(8):984–991. https://doi.org/10.1080/07373937.2011.566399

Ganicz T, Olejnik K, Rózga-Wijas K, Kurjata J (2020) New method of paper hydrophobization based on starch-cellulose-siloxane interactions. BioResources 15(2):4124–4142. https://doi.org/10.15376/biores.15.2.4124-4142

Ganicz T, Rozga-Wijas K (2021) Siloxane-starch-based hydrophobic coating for multiple recyclable cellulosic materials. Materials 14(17):4977. https://doi.org/10.3390/ma14174977

Hill CA, Farahani MM, Hale MD (2004) The use of organo alkoxysilane coupling agents for wood preservation. Holzforschung 58(3):316–325. https://doi.org/10.1515/HF.2004.049

Holik H (2006) Handbook of paper and board. Wiley-VCH, Weinheim, pp 192–206

Hubbe MA (2007) Paper's resistance to wetting–A review of internal sizing chemicals and their effects. BioResources 2(1):106–145

Kolpak FJ, Weih M, Blackwell J (1978) Mercerization of cellulose: 1. Determination of the structure of mercerized cotton. Polymer 19(2):123–131. https://doi.org/10.1016/0032-3861(78)90027-7

Lewicki PP (1997) The applicability of the GAB model to food water sorption isotherms. Int J Food Sci Technol 32(6):553–557. https://doi.org/10.1111/j.1365-2621.1997.tb02131.x

Majka J, Olek W (2007) Effects of European beech (*Fagus sylvatica* L.) wood steaming on sorption properties and kiln-drying intensity. Folia for Pol B 38:55–65

Majka J, Olek W (2008) Sorption properties of mature and juvenile lime wood (*Tilia* sp.). Folia for Pol B 39:65–75

Majka J, Czajkowski Ł, Olek W (2016) Effects of cyclic changes in relative humidity on the sorption hysteresis of thermally modified spruce wood. BioResources 11(2):5265–5275. https://doi.org/10.15376/biores.11.2.5265-5275

Mohammadzadeh A, Barletta M, Gisario A (2020) Manufacturing of cellulose-based paper: dynamic water absorption before and after fiber modifications with hydrophobic agents. Appl Phys A 126(5):1–11. https://doi.org/10.1007/s00339-020-03577-4

Nakano T (2006) Analysis of the temperature dependence of water sorption for wood on the basis of dual mode theory. J Wood Sci 52(6):490–495. https://doi.org/10.1007/s10086-006-0807-2

Nowak T, Mazela B, Olejnik K, Peplińska B, Perdoch W (2022) Starch-silane structure and its influence on the hydrophobic properties of paper. Molecules 27:3136. https://doi.org/10.3390/molecules27103136

Okano T, Sarko A (1985) Mercerization of cellulose. II. Alkali–cellulose intermediates and a possible mercerization mechanism. J Appl Polymer Sci 30(1):325–332. https://doi.org/10.1002/app.1985.070300128

Olek W, Majka J, Czajkowski Ł (2013) Sorption isotherms of thermally modified wood. Holzforschung 67(2):183–191. https://doi.org/10.1515/hf-2011-0260

Peleg M (2020) Models of sigmoid equilibrium moisture sorption isotherms with and without the monolayer hypothesis. Food Eng Rev 12(1):1–13. https://doi.org/10.1007/s12393-019-09207-x

Ratajczak I, Wichłacz-Szentner K, Mazela B, Hochmańska P, Rissmann I (2010) Silicon compounds as additives improving coating performance: fixation of silicon compounds with cellulose. Eur J Wood Prod 68(4):483–486. https://doi.org/10.1007/s00107-010-0420-3

Rodríguez-Fabià S, Torstensen J, Johansson L, Syverud K (2022) Hydrophobization of lignocellulosic materials part II: chemical modification. Cellulose 29(17):8957–8995. https://doi.org/10.1007/s10570-022-04824-y

Sèbe G, Brook MA (2001) Hydrophobization of wood surfaces: covalent grafting of silicone polymers. Wood Sci Technol 35(3):269–282. https://doi.org/10.1007/s002260100091

SIST PN-EN ISO 5267-1:2000/AC:2003 Pulps—determination of drainability—part 1: Schopper-Riegler method (ISO 5267-1:1999/Cor.1:2001)

Siuda J, Perdoch W, Mazela B, Zborowska M (2019) Catalyzed reaction of cellulose and lignin with methyltrimethoxysilane—FT-IR, 13C NMR and 29Si NMR Studies. Materials 12:2006. https://doi.org/10.3390/ma12122006

Skaar C (1988) Wood-water relations. Springer-Verlag, Berlin

Szubert K, Dutkiewicz A, Dutkiewicz M, Maciejewski H (2019) Wood protective coatings based on fluorocarbosilane. Cellulose 26(18):9853–9861. https://doi.org/10.1007/s10570-019-02737-x

Taylor JR (1997) An introduction to error analysis. The study of uncertainties in physical measurements, 2nd edn. University Science Books, Sausalito

Thybring EE, Boardman CR, Zelinka SL, Glass SV (2021) Common sorption isotherm models are not physically valid for water in wood. Colloid Surface A 627:127214. https://doi.org/10.1016/j.colsurfa.2021.127214

Timmermann EO (2003) Multilayer sorption parameters: BET or GAB values? Colloid Surface A 220(1–3):235–260. https://doi.org/10.1016/S0927-7757(03)00059-1

Tshabalala MA, Gangstad JE (2003) Accelerated weathering of wood surfaces coated with multifunctional alkoxysilanes by sol-gel deposition. J Coating Technol 75:37–43. https://doi.org/10.1007/BF02730098

Väisänen S, Pönni R, Hämäläinen A, Vuorinen T (2018) Quantification of accessible hydroxyl groups in cellulosic pulps by dynamic vapor sorption with deuterium exchange. Cellulose 25(12):6923–6934. https://doi.org/10.1007/s10570-018-2064-0

Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Silane coupling agents used for natural fiber/polymer composites: a review. Compos Part A 41(7):806–819. https://doi.org/10.1016/j.compositesa.2010.03.005

Yanniotis S, Blahovec J (2009) Model analysis of sorption isotherms. LWT Food Sci Technol 42(10):1688–1695. https://doi.org/10.1016/j.lwt.2009.05.010

Zelinka SL, Glass SV, Thybring EE (2018) Myth versus reality: do parabolic sorption isotherm models reflect actual wood-water thermodynamics? Wood Sci Technol 52(6):1701–1706. https://doi.org/10.1007/s00226-018-1035-9

Zelinka SL, Glass SV, Thybring EE (2020) Evaluation of previous measurements of water vapor sorption in wood at multiple temperatures. Wood Sci Technol 54(4):769–786. https://doi.org/10.1007/s00226-020-01195-0