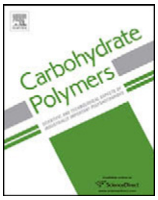
Carbohydrate Polymers 87 (2012) 1817–1821

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Water sorption isotherms of Kraft lignin and its composites

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ARTICLE INFO

Article history:
Received 12 May 2011
Received in revised form 3 October 2011
Accepted 3 October 2011
Available online 8 October 2011

Keywords:
Kraft lignin
Laccase
Chitosan
Polyethylenimine
Composites
Water sorption
BET
GAB

ABSTRACT

The water sorption properties of Kraft lignin before and after treatment with the enzyme laccase, and its composites with branched polyethylenimine and chitosan, respectively, have been studied. The experimental sorption isotherms were obtained by dynamic vapour sorption (DVS) method. The data were analysed using the Brunauer–Emmett–Teller (BET) and Guggenheim–Anderson–de Boer (GAB) models. Monolayer capacity and surface area of the samples were determined by the BET model, showing an increase in these values for the composites. Application of the GAB model over the whole range of humidities (0–95%) gave a perfect correlation between experimental and calculated sorption isotherms using the nonlinear least squares fitting (NLSF).

1. Introduction

Determination of physical properties of natural materials, including composites, is crucial for their further use in different applications. Water plays an extremely important role in nature and in almost all known technologies: food, building materials, pulp and paper, etc. Water uptake by materials has great effect on their mechanical properties and stability. One of the approaches to investigate the surface properties of materials is the measurement of sorption isotherms, which show the relationship between water content of the material and equilibrium humidity. This process of water interaction with different materials has been investigated over the years by many research groups, e.g. for evaluation of hygroscopicity of pharmaceutical solids (Van Campen, Zografi, & Carstensen, 1980) and relationship between surface area and water sorption of microcrystalline cellulose (Zografi, Kontny, Yang, & Brenner, 1984), studying water as a main component in food engineering properties (Lewicki, 1997a, 2004), the effect of temperature on water sorption properties of persimmon skin and pulp (Telis, Gabas, Menegalli, & Telis-Romero, 2000) and sorption properties of cellulose (Chirkova, Andersons, & Andersone, 2004), biodegraded wood (Chirkova, Irbe, Anderson, & Andersone, 2006; Chirkova, Irbe, Andersone, & Andersons, 2009; Irbe et al., 2006), lignin (Chirkova, Andersons, & Irbe, 2007), natural and degradable polymers, including chitosan (Tomczak & Kaminski, 2009). Sorption methods are often used for investigation of microstructures of materials due to the fact that specific characteristics like monolayer capacity and surface area can be determined.

The adsorption of water by wood and its components is mainly associated with the presence of hydroxyl groups on the surface (Hill, Norton, & Newman, 2009). Lignin, cellulose and hemicelluloses are the main components of wood; the two polysaccharides have a very high content of hydroxyls in their structure, while lignin is predominantly aromatic and confers water resistance and mechanical strength to woods. A set of oxidative enzymes is known to be involved in the synthesis as well as degradation of lignin (Boerjan, Ralph, & Baucher, 2003; Hatti-Kaul & Ibrahim, 2012); one of them is laccase (EC 1.10.3.2) that oxidizes phenolic units in lignin in the presence of molecular oxygen and generates the corresponding reactive radicals. Oxidation by laccase is much more efficient in the presence of low molecular weight mediators that are able to diffuse away from the enzyme and can penetrate the lignocellulosic matrix. The enzymatically “activated” lignin and its subunits are more prone for coupling with other molecules (Lund & Ragauskas, 2001).

Recently, dynamic vapour sorption (DVS) method has been introduced to investigate the sorption properties of different natural materials (Hill, Norton, & Newman, 2010; Hill & Xie, 2011; Likos & Lu, 2002; Xie, Hill, Xiao, Mai, & Militz, 2011; Yu, Kappes, Bello-Perez, & Schmidt, 2008). When compared to the classical static method, the DVS technique has the advantages of high data reproducibility with short measurement time, and the requirement of

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doi:10.1016/j.carbpol.2011.10.001

small amounts of samples (typically 10 mg). In addition, isotherms can be accurately determined over a wide range of relative humidities (RH up to 95%).

Traditionally, the results obtained by experimental determination of equilibrium water vapour sorption isotherms are treated by different models. One of these models successfully applied to the interpretation of isotherms obtained for different materials is the classical Brunauer, Emmett and Teller (BET) theory (Brunauer, Emmett, & Teller, 1938). For example, Rawat and Khali (1999) studied the adsorption behaviour of water vapour in lignin using BET theory, while Dalimova and coworkers (Dalimova & Yunusov, 2001; Dalimova & Malikova, 2004) have applied the model to describe the sorption properties of hydrolysed lignin and its derivatives. It is known that this model can be applied for a limited range of relative vapour pressures up to 0.3–0.4. In more recent years the Guggenheim, Anderson and de Boer (GAB) equation has been used by many authors for the description of sorption isotherms over a wider range of RH than BET model could cover (Lewicki, 1997b; Ludwiczak & Mucha, 2010; Mucha & Ludwiczak, 2006; Timmermann, 2003; Timmermann, Chirife, & Iglesias, 2001; Tonon et al., 2009).

In our laboratory, Eucalyptus Kraft lignin treated with laccase mediator system has been used for preparation of composites by reaction with other polymers. The aim of this study was the study of water sorption properties of the lignin and its composites with cationic polymers, chitosan and polyethylenimine, respectively. The equilibrium water sorption isotherms were determined by using the DVS method and the results were evaluated on the basis of BET and GAB models.

2. Materials and methods

2.1. Materials

Eucalyptus Kraft lignin used as a basic component in our experiments was a kind gift from Innventia AB (Sweden). Medium molecular weight chitosan (MW ~75 000 g/mol) was purchased from Fluka BioChemika, Switzerland and branched polyethylenimine PEI (MW ~25 000 g/mol by LS) was from Aldrich, Germany.

Culture supernatant of *Galerina* sp. HC1 was used as a source of crude laccase (Ibrahim, Mendoza, Mamo, & Hatti-Kaul, 2011). The enzyme activity was determined spectrophotometrically at 420 nm by the oxidation of 1 mM 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt (ABTS, Sigma, Germany) at pH 5 and 22 °C.

2.2. Preparation of lignin-chitosan and lignin-PEI composites

Kraft lignin was solubilised in 80 mM sodium hydroxide, chitosan in 1% acetic acid, and the pH of PEI adjusted to 5 by addition of hydrochloric acid. A 20 mL total reaction volume contained the following components: 150 mg Kraft lignin, 150 mg chitosan or PEI, 20 mM Na-acetate buffer pH 5, 0.75 mM ABTS, and 1.5 U of laccase. The reaction mixtures were mixed in round bottom flasks at room temperature for 3 h under proper stirring, and then transferred to 50 mL tubes and centrifuged for 10 min at 2800 × *g*. Supernatants were discarded and precipitates were washed extensively with Millipore quality water to remove residual substances and salts. The remaining material was freeze dried and used for determining the sorption isotherms.

2.3. Dynamic vapour sorption method

The investigation of sorption properties was performed using the dynamic vapour sorption DVS Advantage 1 instrument (Surface Measurement Systems, UK). Each adsorption–desorption experiment took about 5 days during which the running time, target relative humidity (RH), actual RH and sample mass were recorded. The mass of samples used was in the range of 2–5 mg. A typical run started by stabilization of the samples at 0% RH (drying), followed by a gradual increase in RH (10, 20, 30, 40, 50, 60, 70, 80, 90, and 95% RH), and ended by sequential decrease to 0% RH in the reverse order. All steps of sorption measurements were performed at 25 °C. An initial heating step (10 min at 120 °C) was included in some experiments.

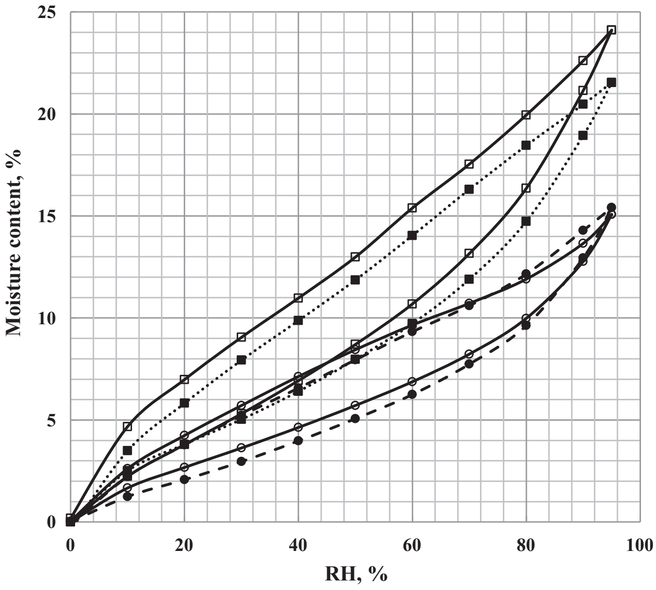

Fig. 1. Experimental sorption isotherms of (○) L, (●) LL, (□) LLP, and (■) LLC (without a pre-heating step).

3. Results and discussion

Sorption–desorption isotherms were obtained for 4 different samples: L-Eucalyptus Kraft lignin, LL-lignin treated with laccase-mediator system (LMS), LLP-composite of laccase treated lignin with polyethylenimine (PEI), and LLC-composite of laccase treated lignin with chitosan. The initial water content in the samples was calculated from the drying step of each experiment as *w*/*w*%: L 35.92%, LL 1.03%, LLP 2.26%, and LLC 5.06%.

First measurements were performed on samples without any pre-heating. Experimental sorption isotherms plotted as moisture content (%) against relative humidity (RH in %) are presented in Fig. 1. All obtained isotherms show the sigmoidal shape, which is typical for wood-derived materials, and are in good agreement with the published data for different types of lignin and its derivatives (Chirkova, Andersons, & Irbe, 2007; Dalimova & Yunusov, 2001; Dalimova & Malikova, 2004; Rawat & Khali, 1999; Reina, Domínguez, & Heredia, 2001). The decrease in the sorption ability of LL can be caused by the fact that the laccase probably utilises primarily less ordered part of lignin and the appearance of the reactive radicals can promote the crosslinking. The composites exhibited higher water uptake in comparison with the untreated and LMS treated lignin (L and LL) at all humidities, which may be attributed to the increase in their hydrophilic content provided by chitosan/PEI. The water sorption–desorption behaviour of pure PEI and chitosan was investigated in separate experiments. For pure PEI it was not possible to reach equilibrium at any humidity with the applied method. The water uptake was extremely high over the whole range of RH. For the pure chitosan the obtained values (e.g. at 95% RH, 27% moisture content) were in good agreement with the published results (Gocho, Shimizu, Tanioka, Chou, & Nakajima, 2000; Ludwiczak & Mucha, 2010; Mucha & Ludwiczak, 2006). All

Table 1
Surface characteristics for investigated samples (BET).

Sample	W_m, g/g	S, m^2/g	C	E_1, kJ/mol	E_1-E_{EV}, kJ/mol	Θ
L	0.034	121	7.21	48.94	4.94	0.27
L, 120 °C	0.034	122	5.93	44.1	0.1	0.29
LL	0.031	111	4.92	39.49	−4.51	0.31
LL, 120 °C	0.035	127	8.21	52.17	8.17	0.26
LLP	0.052	186	5.83	43.68	−0.32	0.29
LLP, 120 °C	0.046	167	7.10	48.57	4.57	0.27
LLC	0.044	160	9.15	54.85	10.85	0.25
LLC, 120 °C	0.046	166	8.69	53.57	9.57	0.25

materials tested showed a sorption hysteresis presenting a maximum at 60–70% RH. The desorption isotherm curves displayed quasi-linear behaviour for the composites LLP and LLC.

The effect of sample pre-heating on the sorption properties was investigated (Fig. 2). The untreated lignin (a) and composite with chitosan (d) did not show significant changes in values of moisture content or the character of sorption–desorption curves after pre-heating. On the other hand, enzymatically treated lignin (b) and the composite with PEI (c) were more affected by the heat treatment. Sorption–desorption values are increased for LL, especially at high humidities, and decreased for LLP, however with a less pronounced impact. This can be due to the formation of additional bonds between the Kraft lignin and PEI as a result of the heat treatment, hence reducing the number of available binding sites for water.

All obtained experimental sorption isotherms were treated according to the BET and GAB models. The state of water molecules in the second and higher layers are the same in both models, but different from that in the liquid state. The GAB model introduced an additional parameter K, which is the measure of the difference of free enthalpy (standard chemical potential) of the sorbate molecules that occur in layers above monolayer and in a pure liquid (Timmermann, 2003). This improves the range of applicability for GAB model in comparison with BET. For the water activity range $0.1 \le p/p_0 \le 0.4$, BET theory was applied using the following equation:

$$\frac{1}{W[(p_0/p)-1]} = \frac{1}{W_mC} + \frac{(C-1)}{W_mC}\left(\frac{p}{p_0}\right), \tag{1}$$

where W is the experimental equilibrium water content of the sample, p and p_0 are the equilibrium and the saturation pressure of water at the temperature of adsorption, respectively; W_m is the monolayer capacity and C is the BET constant, which is given by:

$$C = \exp\left(\frac{E_1 - E_{EV}}{RT}\right), \tag{2}$$

Here, E_1 is the heat of adsorption for the first layer, and E_{EV} is the heat of evaporation of pure water at a given temperature, R is the molar gas constant and T is the temperature for sorption measurements. The plots of $1/W[(p_0/p)-1]$ versus p/p_0 yield are straight lines with slope s and intercept i, which are equal to:

$$S = \frac{C-1}{W_mC} \quad \text{and} \quad i = \frac{1}{W_mC}. \tag{3}$$

The specific surface area (S) for investigated samples was calculated according to following equation:

$$S = \frac{W_mNaA}{M}, \tag{4}$$

where W_m is monolayer capacity, N_a is Avogadro's number, A is cross-sectional area of adsorbate; for water 10.8 Å^2, Livingston (1949) and M is molecular weight for water. The results for BET calculations (regression coefficients were better than 0.994 for all samples) are given in Table 1, which shows that both W_m and S are higher for the composites in comparison with untreated and treated lignin, reflecting the real coupling or interaction occurring between lignin and its partner molecules. The lowest values correspond to treated lignin, LL, and the highest ones to the composite with PEI, LLP (Table 1) and are in the same range as that reported by Chirkova et al. (2007), W_m (0.047–0.180 g/g) and S (78–170 m^2/g), for lignins obtained by different isolation methods. Except for LLP, the pre-heating step increased the surface area of the samples; in other words, a material can have higher chances of interactions, which is a desirable property in many applications. In Eq. (2), the difference (E_1-E_{EV}) refers to the heat of adsorption; this parameter quantifies the energy of interaction between the surface of samples and the first monolayer of adsorbed water molecules. It is known that when adsorption occurs to cover the surface with a monolayer, the fraction of surface, Θ, not covered by any molecule is dependent on the BET constant (C) values and given by the formula:

$$\Theta = \frac{\sqrt{C}-1}{C-1} \tag{5}$$

The above mentioned characteristics are also presented in Table 1. Higher values of (E_1-E_{EV}) indicate stronger forces of hydration between sample surface and water molecules in comparison to the interactions between water molecules in a gas and liquid state. The composite LLC with chitosan shows the highest interaction energy (9.57 and 10.85 kJ/mol) followed by pre-heated LL sample (8.17 kJ/mol). Three samples, L (with pre-heating), LL and LLP (without pre-heating) showed the negative or close to zero values for (E_1-E_{EV}), which is an indication of very energetically weak water binding capacity (Likos & Lu, 2002). Values for Θ are an additional evidence for this observation.

For the complete range of water activities, we also applied the GAB model. A non-linear least squares fitting (NLSF) from the "Origin7.0 Data Analysis" software was used to find the parameters for the GAB equation:

$$W = \frac{W_{GAB}C_{GAB}K_{GAB}a_w}{(1-K_{GAB}a_w)(1-K_{GAB}a_w+C_{GAB}K_{GAB}a_w)} \tag{6}$$

where W is the moisture content of the material on a dry basis, C_{GAB} is the Guggenheim constant related to heat of sorption, a_w is the water activity (equal to relative p/p_0 for BET model), K_{GAB} is the constant related to multilayer molecular properties and W_{GAB} is the moisture content of monolayer similar to W_m in a BET theory The graphical presentation of Origin fitting procedure is presented for

Table 2
GAB fitting parameters for experimental sorption isotherms.

Sample	W_{GAB}, g/g	K	C_{GAB}
L, no heat	0.043	0.767	6.63
L, 120 °C	0.046	0.742	5.20
LL, no heat	0.040	0.796	4.34
LL, 120 °C	0.037	0.866	10.28
LLP, no heat	0.075	0.752	4.24
LLP, 120 °C	0.066	0.755	5.04
LLC, no heat	0.063	0.763	5.72
LLC, 120 °C	0.066	0.764	5.40

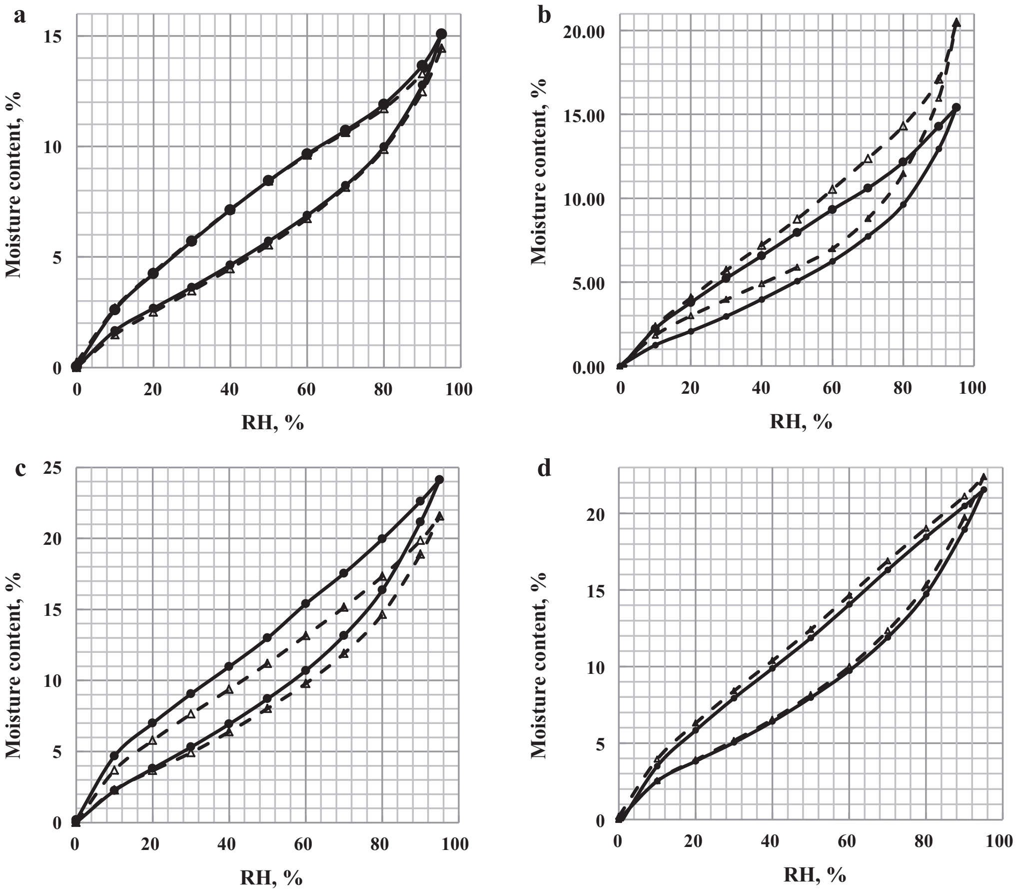

Fig. 2. Effect of initial heating on water sorption isotherms for (a) L, (b) LL, (c) LLP and (d) LLC. The results from pre-heated samples are shown as dashed lines. The solid curves are for the unheated samples (same data as in Fig. 1).

two samples in Fig. 3. GAB model shows perfect fit for all experimentally obtained sorption isotherms through total humidity range. The regression coefficients obtained were all close to unity. The results for GAB parameters are given in Table 2. It is known that the monolayer capacity obtained by GAB model is always higher than the one obtained by BET (Timmermann et al., 2001), which is true according to our data (Tables 1 and 2). The energy constant *C* by BET is known to be higher than the *C* from the GAB model. Only one sample, LL, pre-heated at 120 °C, showed unusual behaviour: *C* by BET model (8.21 kJ/mol) was lower than C_{GAB} (10.28 kJ/mol), and monolayer capacity was almost the same for both models (0.035 g/g for BET and 0.037 g/g for GAB). The parameter *K* varied between 0.742 (L) and 0.866 (LL, pre-heated at 120 °C) indicating a less organized state of water in the GAB layers that follow the first

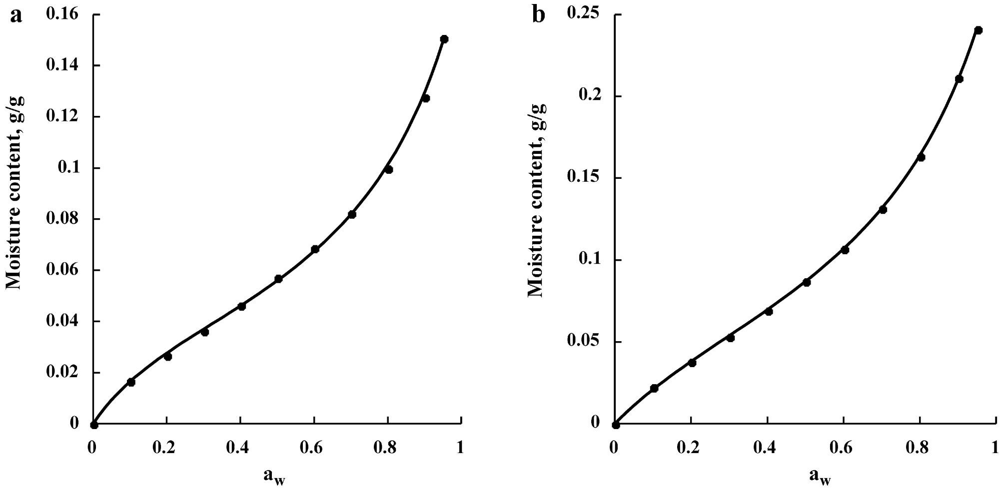

Fig. 3. Fit of water sorption data for (a) L and (b) LLP to the GAB equation. The full lines represent the calculated values while the dotted lines are experimental values (both without pre-heating the samples).

layer than in the pure liquid water state (Timmermann et al., 2001, 2003).

4. Conclusions

The DVS method was successfully applied for experimental determinations of equilibrium sorption–desorption isotherms of Kraft lignin and lignin-based composites. This study has shown a significant difference in the adsorption–desorption behaviour of Kraft lignin after treatment with laccase mediator system and modification with different polymers. The enzymatic treatment of Kraft lignin drastically changes the surface properties of the sample, thus highlighting the efficiency of the enzyme treatment in modifying the surface of the natural polymer. The enzymatically modified lignin and the composite with PEI were most affected by temperature in comparison with original lignin and composite with chitosan. The BET and GAB models were successfully applied to the treatment of experimental data and determination of significant parameters. The surface areas were much higher for composites in comparison with untreated and laccase treated lignin samples, which can render them attractive for different applications such as in lignin based adhesives.

Acknowledgments

The authors are grateful to Mistra (The Swedish Foundation of Strategic Environmental Research) for financial support. Innventia AB (Stockholm) is thanked for providing us with Kraft lignin.

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