Study of Water Sorption in Modified Flax Fibers

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ABSTRACT: Because of their good mechanical properties and low density, natural fibers are more and more considered as reinforcement in composite materials. To improve the adhesion between the polymer matrix and natural fibers and to reduce the water sorption, helium cold plasma and autoclave treatments have been performed on flax fibers. The effect of these treatments on water sorption has been investigated by means of a gravimetric static equilibrium method (IGA). Water sorption isotherms have been deduced from kinetic data. Specific mathematical models have been tested to predict the water sorption isotherms of the treated flax fibers. The Park model based on the three sorption modes: Langmuir, Henry's law, and clustering, was successfully used to simulate the experimental sorption data. The results show no significant effect after plasma treatment while an increase of moisture resistance has been observed after autoclave treatment. This effect of autoclave treatment is interpreted in terms of modifications of cell-wall structure. In a kinetic point of view, for the untreated and treated flax fibers, the variation of the diffusion coefficient with water concentration is in agreement with the three sorption modes of the Park model. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4281–4289, 2006

Key words: water sorption kinetics; flax fibers; isotherm sorption; plasma; autoclave; clustering; Park model

INTRODUCTION

The ecological concern has resulted in a renewed interest in natural polymeric materials. Natural fibers, such as flax, hemp, sisal, and jute, are interesting, environmentally friendly alternative to the use of glass fibers as reinforcement in polymer based engineering composites.[1,2] These fibers are renewable, nonabrasive, and can be incinerated for energy recovery since they possess a good calorific power. Moreover, these fibers give less concern with health and safety during handling of fiber products. They also exhibit excellent mechanical properties, low density, and low cost. This excellent price-performance ratio at low weight, in combination with the environmentally friendly character, is very important for the acceptance of natural fibers in large volume engineering markets, such as automotive,[3] aeronautic, and building industries. However, natural fibers present some disadvantages: high-moisture sorption, poor dimensional stability, low-thermal resistance, anisotropic fiber resistance, and variability.[4]

One difficulty that has prevented the use of natural fibers is the lack of good adhesion with polymeric matrices. In particular, the great moisture sorption of natural fibers adversely affects adhesion with hydrophobic matrix, leading to premature ageing by degradation and loss of strength. To prevent this phenomenon, surface fiber has been modified to promote adhesion.[5]

In this study, two different treatments have been performed on flax fibers: (1) an autoclave treatment to increase moisture resistance, (2) a Helium (He) glow discharge low-pressure plasma treatment to improve adhesion with a thermoset matrix, such as unsaturated polyester resin.[6] In contrast to chemical treatments like acetylation, the He cold plasma technique is an original method, which allows surface modification of fibers without affecting the bulk properties. In addition, no solvent is used, and the duration times of treatment are short, and the temperature never exceeds 120°C.

The aim of the present work is to investigate the flax fibers behavior toward water molecules, by means of gravimetric measurements. The effects of treatments have been analyzed from kinetic results and the deduced water sorption isotherms. To interpret sorption isotherms, different models have been tested. The best fitting model has been used to estimate the mean cluster size (MCS) of water.

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THEORY

Sorption models

The relationship between water activity a_w and the equilibrium moisture content M at constant temperature is described by sorption isotherm. M is defined by the ratio of the difference between wet and dry mass to mass dry matter:

$$M = \frac{M_{w(\mathrm{eq})} - M_d}{M_d} \tag{1}$$

Water activity (a_w) is defined as the ratio of the vapor pressure of water in equilibrium with the material to the saturated vapor pressure of pure water at the same temperature.

$$a_w = \frac{P}{P_{sat}} \tag{2}$$

Sorption models are useful for predicting water sorption properties of cellulosic materials, giving some information concerning the sorption mode and possible interactions between water molecules and cellulosic fibers.[7] Although several mathematical models exist to describe water sorption isotherms of cellulosic materials,[8] they are limited in the fitting of the experimental data for the whole range of water activities and for all types of cellulosic materials. Labuza[9] attributed this fact to different mechanisms of water association with cellulosic matrix in different water activity regions.

The Ferro-Fontan model[10] allows to well predict sorption isotherm in 90% of cellulosic products.

Peleg[11] suggests a four parameter model, which can be used for both sigmoidal and nonsigmoidal isotherms.

The Smith model[12] is convenient for sorption isotherms of biological materials, such as starch.

Henderson[13] proposes a semiempirical model for the equilibrium moisture of cereal grains.

Chirife and Iglesias[14] found that Halsey and Oswin models are also versatile for the description of polysaccharide systems.

The BET II (Brunauer, Emmet, Teller) model, which is a combination of dual mode (Langmuir sorption and Henry law) and Flory-Huggins, is typical of water sorption in hydrophilic materials. Also, in some cases, such as natural fibers, the Flory-Huggins sorption is associated to aggregation phenomena. This is why it is more convenient to consider the Park model. This model[15] corresponds to a multisorption mode, which can be dividing in three steps: (1) Langmuir sorption, (2) Henry's law, and (3) water clustering.

The well-known GAB model based on multilayer and condensed films is considered to be the most versatile model for water sorption in cellulosic materials (GAB model, Guggenheim-Anderson-de Boer[16]).

Only the two latter models correlate clearly parameters to physical characteristics.

All these different models were used to fit our experimental sorption data. The corresponding equations are presented in Table 1, and the appropriate constants were determined by regression analysis.

To evaluate the goodness of the fit of each model, the mean relative percentage deviation modulus (E) was used and which is defined by:

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{|m_i - m_{\mathrm{pi}}|}{m_i} \tag{3}$$

where m_i is the experimental value, m_{pi} is the predicted value, and N is the number of experimental data. The mean relative percentage deviation modulus (E) is widely adopted throughout the literature, with a modulus value below 10% indicative of a good fit practical purposes.[17]

Clustering

For hydrophilic materials, such as flax fibers, the concentration of water in the polymer at high activities becomes large enough to cause relaxation of the preexisting voids, that results in the material's swelling. Zimm and Lundberg[18] and Lundberg[19] have developed a method, which analyses water clustering from the single shape of the experimental isotherm. They have developed, on the bases of statistical mechanics, a method that gives an interpretation of the solution thermodynamic behavior in geometric isotherms. Neglecting the isothermal compressibility of polymer–solvent solution makes the free energy function of the system essentially dependant upon the first derivate of the activity with respect of the volume fraction. The elaborated relation appears as follow:

$$\frac{G_s}{V_s} = -(1 - \Phi_s)\left[\frac{\partial(a_w/\Phi_s)}{\partial a_w}\right]_{p,T} - 1 \tag{4}$$

where G_S is the cluster integral, V_S is the partial molecular volume of the penetrant, Φ_S the volume fraction of the penetrant in the polymer film.

A G_S/V_S value equal to -1 indicates that solvent dissolves into polymer matrix randomly, instead higher values, $G_S/V_S > 1$ means that the concentration of water in the neighborhood of a given water molecule is greater than the average concentration of water molecules in the polymer. The quantity $G_S\Phi_S/V_S$ is the mean number of molecules in excess of the mean concentration of penetrant in the neighborhood of a given penetrant molecule.[20,21]

TABLE I
Sorption Models Used for Fitting Experimental Data

Model	Equation	Characteristics
G.A.B.	$M=M_m\frac{C_G K a_w}{(1-Ka_w)[1+(C_G-1)Ka_w]}$	M_m: Monolayer of absorbed water K: Constant that considers the modified properties of sorbate in the multilayer region C_G: Guggenheim constant
Park	$M = \frac{A_L b_L a_w}{1 + b_L a_w} + k_H a_w + K_a a_w^n$	A_L: Langmuir capacity constant b_L: Langmuir affinity constant k_H: Henry's type solubility coefficient K_a: Equilibrium constant for the clustering reaction n: Mean number of water molecules per cluster
Halsey	$M=\left(\frac{A}{\ln a_w}\right)^{\frac{1}{B}}$	A: Constant B: Parameter that characterizes the type of interaction between vapour and solid
Oswin	$M=A\left(\frac{a_w}{1-a_w}\right)^{B}$	A, B: Constants
Smith	$M=A+[B\log(1-a_w)]$	A, B: Constants
Henderson	$M=\left(-\ln\frac{1-a_w}{A}\right)^{\frac{1}{B}}$	A, B: Constants
Peleg	$M=k_1 a_w^{n1}+k_2 a_w^{n2}$	k_1, k_2, n_1, n_2: Constants $n_1 < 1$ and $n_2 > 1$
Ferro-Fontan	$M = \left(\frac{\alpha}{\ln\frac{\gamma}{a_w}}\right)^{\frac{1}{r}}$	α: Constant that account for the structure of sorbed water γ: Constant r: Constant that entails net isosteric heat with moisture content

Thus, the MCS can be evaluated by:

$$\mathrm{MCS} = 1 + \left[\frac{\Phi_s G_s}{V_s}\right] \tag{5}$$

From similar consideration, Starkweather[22] has proposed another relation to calculate MCS, assuming:

$$\mathrm{MCS} = (1 - \Phi_s)\left(\frac{\partial \ln \Phi_s}{\partial \ln a_w}\right)_{p,T} \tag{6}$$

The water volume fraction Φ_S was obtained from the following relation:

$$\Phi_s = \left(1 + \frac{M_d \rho_s}{(M_{w_{\mathrm{eq}}} - M_d) \odot \rho_p}\right)^{-1} \tag{7}$$

where ρ_S and ρ_p are the density of penetrant and polymer, respectively.

Diffusivity

To interpret kinetic sorption data in terms of rate of water molecules in the fibers, the simplest approach is to consider Fick's laws. By considering a flax fiber as a cylinder of radius with uniform distribution and equal concentrations on both sides, the mass sorbed at time t compared with the mass at equilibrium is given by:

$$\frac{M_t}{M_{\mathrm{eq}}} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{r^2}\right)^{1/2}\left[1 - \frac{\sqrt{\pi}}{4}\left(\frac{Dt}{r^2}\right)^{1/2} - \frac{1}{12}\left(\frac{Dt}{r^2}\right)\right] \tag{8}$$

where M_t is the mass sorbed at time t, and M_{eq} is the mass at equilibrium state.
At short time, when $M_t/M_{\mathrm{eq}} < 0.2$, the analytic solutions is given by:

$$\frac{M_t}{M_{\mathrm{eq}}} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{r^2}\right)^{1/2} \tag{9}$$

The graph of M_t/M_{eq} against $\sqrt{t}$, allows the diffusion coefficient to be calculated from plot of curve.

EXPERIMENTAL

Materials

The flax fibers used in this study are provided by the cooperative "Terre de lin" (Saint-Pierre-Le-Viger, 76740 France). Flax fibers are received in tow form and without chemical treatments. The nonwovens were prepared by a technique called "dry laying" at the "Ecole Industrielle de Rouen" (Rouen, 76000 France). The elaboration and the characteristics of the nonwovens have been already presented in detail in a previous paper.[23]

Plasma treatment

A low-pressure cold plasma treatment was carried out on the fibers. The equipment used has been already presented elsewhere.[24] Briefly, the gas used for this study was helium (Alphagaz 2 He, Air Liquide—-France, purity $>$ 99.99%) and the plasma treatment procedure was as follows: the flax fiber nonwoven was put inside the reactor, then the system was pumped up to a final pressure of 10^{-4} Pa, and the gas was introduced in a controlled flow. In this study, the flax fiber nonwoven was treated in discharge mode, and the plasma conditions were chosen for a treatment time of 5 min and for an incident power $P = 50$ W. These optimal conditions of plasma treatment have been determined from water contact angle.[25]

Autoclave treatment

An autoclave treatment was carried out on the nonwoven of fibers. The upgrading process used for the flax was developed by CERES B.V.[26]

The treatment consists of steaming the flax fiber nonwoven at a temperature above 130°C for a desired period in an autoclave. In our case, three duration times have been chosen: 30, 60, and 90 min. This first step is followed by a drying step at room temperature, then a heating step at 130°C, for 2 h.

Sorption studies

Water uptake from water vapor has been measured by using an electronic microbalance (IGA-002, supplied by Hiden Analytical, Warrington (UK)). After transferring the sample to the measurement reactor, the system is evacuated (10^{-4} Pa) for about 1 day by a turbomolecular pump until a constant weight. The sample environment temperature is controlled by a thermoregulated water bath. Then, vapor pressure is increased in suitable levels up to saturation vapor pressure. At each step, the mass gain is measured as a function of time until an equilibrium state is reached. The water content at equilibrium is used to build the sorption isotherm. More details have been reported elsewhere.[27] In this work, the water sorption measurements have been performed at 25°C.

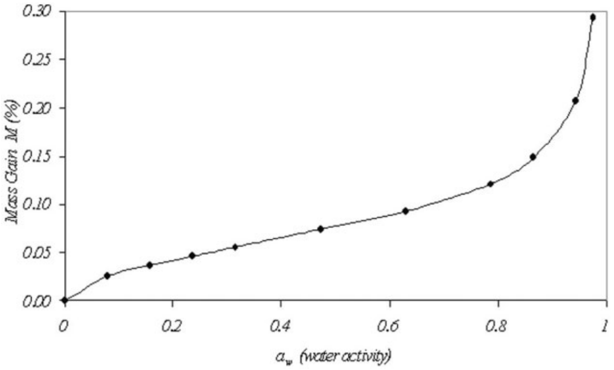


Figure 1 Water sorption isotherms for untreated flax fibers at 25°C.

RESULTS AND DISCUSSION

Sorption isotherms

Water sorption of untreated fibers

The values of mass gain at equilibrium state for each water activity allow to plot the water sorption isotherm. The sorption isotherm curves for untreated flax fibers are represented in Figure 1. The shape of this curve has a sigmoid or S-shape, which correspond to type II classification of Brunauer, Emmett, Teller (1940) into five general types or type IV in the classification of Rogers. This behavior is very typical of cellulosic-based materials[28] and can be generalized to many hydrophilic materials.[29] In particular, the high increase of water sorption for high water activities is usually explained by the formation of water clustering.

Mathematical modeling

The parameters for the sorption models for untreated flax fibers in the increasing order of mean relative percentage deviation modulus E(%) are reported in Table 2. The Ferro-Fontan, G.A.B., Halsey, Smith, and Henderson models failed to adequately describe the experimental data for all materials. For these models, E values are at least equal to 10. Isotherm curves for flax fibers fitting with Ferro-Fontan, G.A.B., Halsey, Smith, and Henderson models are represented in Figure 2(a) .

Examination of the fitting data (R^2, E) indicates that the Park, Oswin, and Peleg models are more convenient and well described the experimental sorption isotherms [Fig. 2(b)]. Park model gives the best fitting in the whole range of water activity.

TABLE II
Sorption Isotherm Model Constants and Regression Coefficient (R^2) Values for Untreated Flax Fibers (constants as defined in Table 1)

Models	Value of constants	R^2	E
Park			
A_L	2.12×10^{-2}	0.999	3.2
b_L	47		
k_H	0.114		
K_a	0.253		
n	18		
Oswin			
A	7.38×10^{-2}	0.999	3.9
B	0.372		
Peleg			
k_1	0.142	0.996	6.1
k_2	0.252		
n_1	0.781		
n_2	20.65		
Ferro-Fontan			
α_f	3.47×10^{-3}	0.994	9.7
γ_f	1.017		
r_f	2.002		
G.A.B.			
M_m	0.036	0.982	10.0
C_G	59.6		
K	0.892		
Smith			
A	2.41×10^{-2}	0.988	11.5
B	−0.156		
Halsey			
A	1.45×10^{-3}	0.990	13.4
B	2.338		
Henderson			
A	19.6	0.971	17.9
B	1.270		

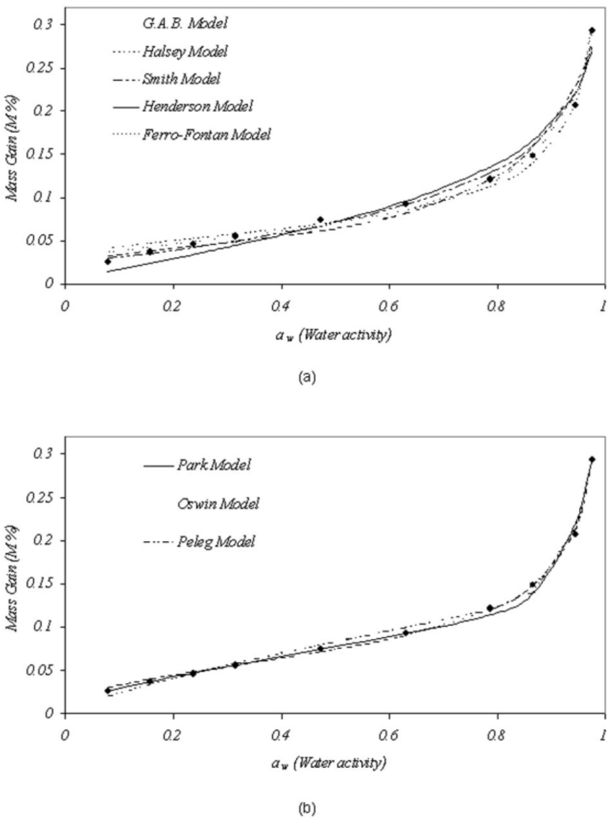
It should be noted that, although the Peleg and Oswin models provide good fitting of sorption data, these semiempirical models give only a mathematical approach without information concerning the sorption mechanisms, while the Park model give a physical approach based on well established sorption modes. This is why in the following only the Park model has been considered.

Parameters of Park equation

In Figure 3, the theoretical curve obtained with the Park equation for untreated flax fibers has been plotted. The different parameters of the Park equation for untreated flax fibers, treated plasma, and treated autoclave 90 min are given in Table 3. Each parameter has a predominant effect in limited water activity range.[27] Langmuir's terms, A_L (Langmuir capacity constant) and b_L (Langmuir affinity constant) have an influence in the zone I at low water activity ($a_w < 0.1$). Henry's solubility coefficient, k_H, define the slope of the isotherm in zone II ($0.1 < a_w < 0.8$). The last values K_a (equilibrium constant for the clustering reaction) and n (mean number of water molecules per cluster) can be linked to the equilibrium state corresponding to the aggregate formation in zone III ($a_w > 0.8$).

$$n(H_2O) \Leftrightarrow (H_2O)n$$

From this simulation, we can deduce information about the mechanisms of water sorption in flax fibers



(a)

(b)

Figure 2 Experimental results and fits to experimental sorption isotherms for flax native fibers at 25°C. (a) G.A.B., Ferro-Fontan, Halsey, and Henderson equations and (b) Park, Peleg and Oswin equations.

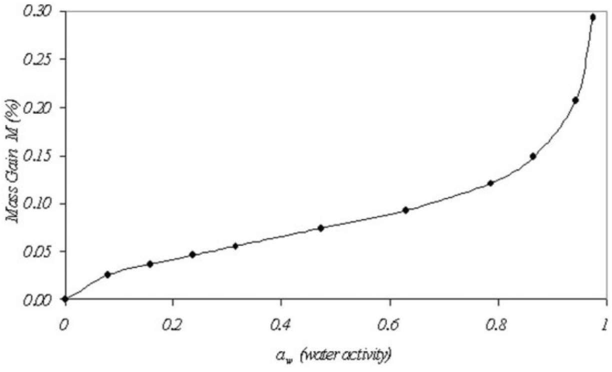


Figure 3. Water sorption isotherms for untreated flax fibers at 25°C (experimental points and calculated curves from Park's equation).

TABLE III
Constants of the Park Model and Regression Coefficient (R^2) Values for the Different Samples

	Constants						
	Langmuir		Henry	Aggregation			
Samples	A_L	b_L	k_H	K_a	n	R^2	E
Untreated flax fibers	2.12×10^{-2}	47	0.114	0.25	18	0.999	3.2
Plasma treated fibers	2.06×10^{-2}	30	0.113	0.19	12	0.999	1.3
Autoclave treated 30 min	1.87×10^{-2}	38	0.097	0.31	15	0.997	3.5
Autoclave treated 60 min	1.83×10^{-2}	38	0.099	0.30	18	0.999	3.7
Autoclave treated 90 min	1.60×10^{-2}	27	0.101	0.50	22	0.996	4.2

and which can be illustrated as follows (Fig. 4): the first sorption (Langmuir's type) occurs in the periphery of fiber bundle where the main components are pectins, rich in galacturonic acid, hence in negative charges.[30] The second sorption (Henry's type) mainly operates in the matrix of the secondary wall where pectic polyanions are also present determining a Donnan free space designated as a micropore structure by Dainty and Hope.[31] The later (aggregate) takes place in the heart of the elementary fibers, named the lumen, but also in the water-free space corresponding to the macropores of cell wall.[31] At this stage of the discussion, it is clear that this illustration is a simple way to explain the different sorption modes. Keeping in mind that flax fiber is a composite structure with high heterogeneous zones so that the sorption mechanisms are obviously more complex to interpret.

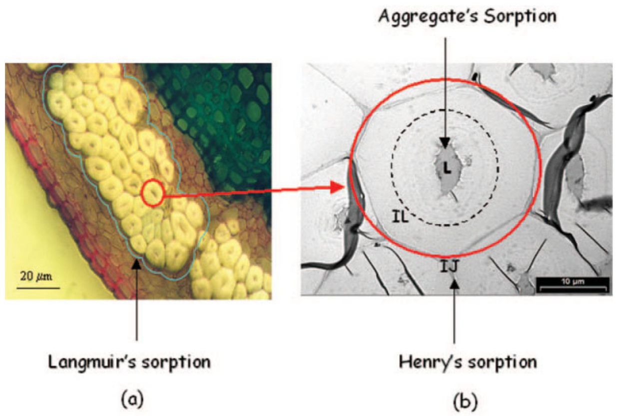


Figure 4 A schematic representation of water sorption mode according to Park's simulation. (a) Light micrograph of hand-cut cross section from flax stem showing the organization of fibers in bundle. The fiber surface consists of negatively charged pectins and corresponds to the main part of Langmuir capacity. (b) Electron micrograph of flax fiber. Intercellular junctions (IJ) as well as internal layer rich in pectins (IL, in dotted line) could account for Henry's sorption. The lumen (L) is the main macropore where water molecules aggregate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mean cluster size

The determination of the MCS is deduced from the Park model, which seems to be the best model to describe our experimental sorption. Considering the key parameters of this model, A_L, b_L, k_H, K_a, and n, MCS could be expressed as follow:

$$\mathrm{MCS}_{\mathrm{park}} = \frac{\rho^2}{M^3(1+\rho/M)^2}\left(K_H a_w + \frac{A_L b_L a_w}{(1+B_L a_w)^2} + K_a \boldsymbol{\pi} a_w^n\right) \quad (10)$$

The plots of $\mathrm{MCS}_{\mathrm{Park}}$ versus activity for all different samples are represented in Figure 5. The calculated values of MCS are strongly affected by the exactness of the used model. The shape of the curve for water activity lower than 0.8 is a general shape obtained with dual-mode sorption. This is the combination of two sorption modes: some water molecules are sorbed randomly in the polymer with no specific interaction (Henry's law) and others are sorbed in specific sites or in porous structure (Langmuir's site). For the low water activities ($a_w < 0.1$), the Langmuir's sorption is predominant, and when the associated sites are saturated, the Henry's sorption takes place. Then, for higher water activities ($a_w > 0.8$), the water clustering appears.

The interpretation of clustering phenomena by Zimm–Lundberg theory is relatively complex. Some authors[32] emphasize the fact that the assumption of the additivity of the water and polymer specific volumes. This is the case with natural fibers having a high quantity of microvoids. The consequence is an error in the volume fraction Φ_S of water. The authors conclude that the average size of the solvate cluster in materials determined by Zimm–Lundberg method should be considered only as a first approximation.

Effect of plasma treatment on water sorption

Isotherm curves for untreated and plasma-treated flax fibers are presented in Figure 6(a). The fact that these

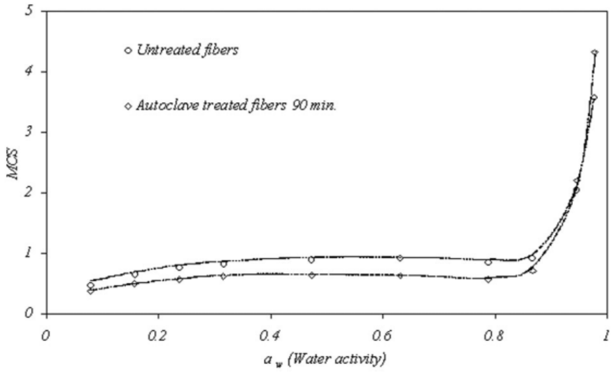


Figure 5 Variation of MCS calculated from Park's equation versus water activity for untreated flax fibers and autoclave treated 90 min.

curves merge together indicates that plasma treatment does not modify the final amount of water molecules able to be absorbed by flax fibers in all water activity range.

Helium plasma treatment is known to bring radicals at the surface of the materials. Measurements of water contact angle on fibers tended to show an increase of the hydrophilic character of the fibers.[25] These radicals lead to crosslinking reactions on the surface, by creating double bonds and in the same fine give functionalities by forming peroxides with dioxygen from ambient air. Then, crosslinking reactions at the surface may reduce the water sorption of the fibers. Thus, the combination of these two antagonist phenomena may explain the same water content of untreated and plasma-treated flax fibers, keeping in mind that cold plasma treatment should not affect the heart of the materials.

Effect of autoclave treatment on water sorption

Isotherm curves for untreated and autoclave-treated flax fibers for 30, 60, and 90 min are presented in Figure 6(b). Autoclave-treated fibers exhibit some differences compared to untreated fibers. In the activity range $0 < a_w < 0.8$, the moisture content in autoclave-treated fiber is lower, including effects on both Langmuir and Henry parameters. The effect of autoclave decreasing both the capacity A_L and constant of Langmuir b_L appeared similar, whatever the time of treatment. Preliminary experiments indicate a degradation of about half of the pectic polymers present at the fiber surface leading to a significant decrease of its negative charge density and consequently of A_L. Besides, the constant of Henry k_H decreased more importantly with the treatment time, showing that more layers inside the secondary wall were affected. We suggest that a part of pectins present in the secondary wall were progressively degraded and, similarly as at the fiber surface, the reduction of their negative charge number lead to a decrease of the free space of Donnan.

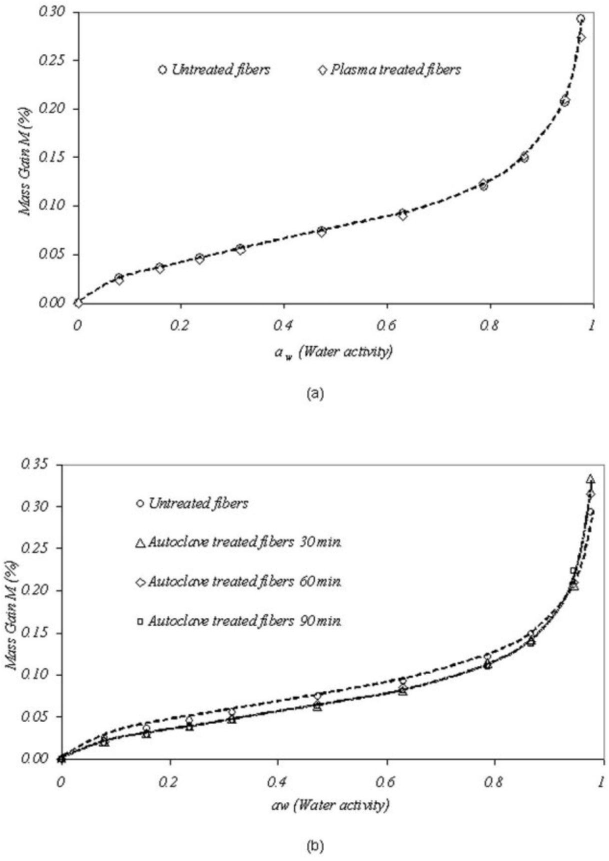
Alternatively, and according to Stamboulis and Baillie,[26] during autoclave treatment, the pectins, hemicellulose, and lignin are depolymerized into lower molecular aldehyde and phenolic functionalities, which are combined by the subsequent curing reaction into a water resistant resin, and that keeps the cellulose microfibrils together.

For $a_w > 0.8$, the moisture content for the treated fibers becomes higher, compared to the untreated ones. The constant of aggregation K_a increased with the autoclave treatment time. This indicates an effect on the size of macropores and lumen, possibly due to the hydrolysis of long side-chains of pectins that have been shown to be present in the secondary wall of fibers[33,34] or to the separation of hydrogen bonds between the cellulose microfibrils and the hemicellulose polysaccharides, which act as interface with the matrix.

Sorption kinetics

Sorption kinetics for untreated fibers

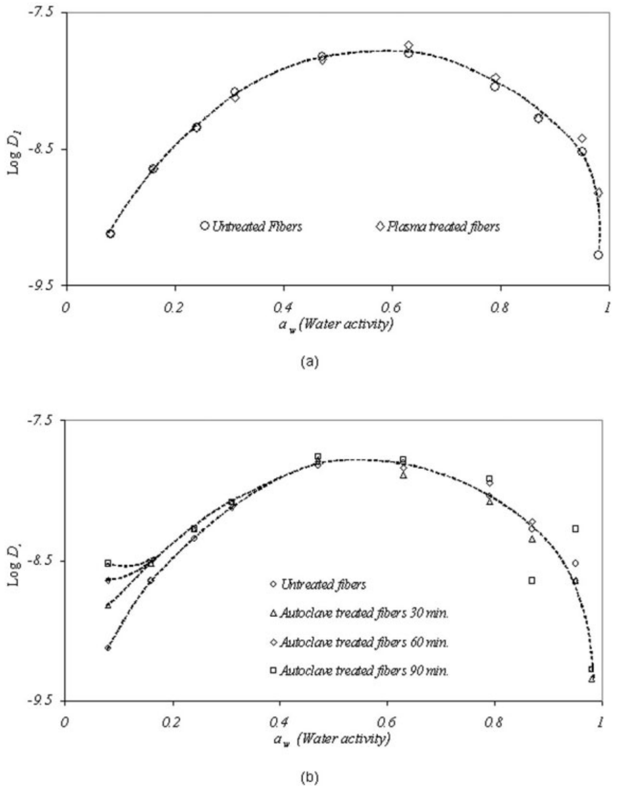
The variation of the water diffusion coefficient D [calculated from eq. (9)] versus water activity is presented



(a)

(b)

Figure 6 Water sorption isotherms at 25°C for: (a) untreated flax and plasma-treated fibers and (b) untreated and autoclave-treated flax fibers (30, 60, and 90 min).



(a)

(b)

Figure 7 Variation of the water diffusion coefficient D versus water activity at 25°C for the water sorption in flax fibers: (a) untreated and plasma treated, (b) untreated and autoclave treated.

in Figure 7(a). A high dependency of D with the water concentration can be observed. Indeed, the value of D lower at low water activities increases until a maximum is reached then decreases for higher activities. This variation is apparently in good agreement with the Park sorption mode. The increase of D can be explained by the double sorption mode, dual mode: the first water molecules sorbed in Langmuir's sites are partially or totally stopped and next the Henry's adsorption becomes predominant, so that water diffusivity increases due to the further molecular mobility. This effect is probably more pronounced with the swelling effect of the fibers. The decrease of D observed at higher activities is described by Rouse[35] and would correspond to the aggregate of water molecules.

Influence of treatments

The variations of the water diffusion coefficient D versus water activity for flax fibers before and after plasma or autoclave treatments are presented in Figure 7. In a general point of view, the variation of D does not seem to affect by plasma treatment [Fig. 7(a)] or autoclave treatment [Fig. 7(b)]. However, it is interesting to observe significant differences in the D values at very low water activity ($a_w < 0.1$) between the untreated and autoclave-treated fibers. Indeed, as shown in Figure 7(b), for low-water concentration, an increase of water diffusivity with the duration of autoclave treatment can be observed. This tendency can be easily interpreted by the restructuring of fibers components after autoclave treatment. In other words and as mentioned previously, the reduction of Langmuir's sites, which retain water molecules due to the hydrophilic charged sites, allows in the competitive dual mode sorption that Henry sorption becomes earlier predominant. In that way, the water mobility is increased.

CONCLUSIONS

Water vapor sorption isotherms of flax fibers, untreated and treated (plasma or autoclave), have been investigated from water sorption kinetics and by using a microgravimetric technique. Among the various sorption models tested, Park model is the most convenient model allowing a good fitting of data from physical parameters. From that, three sorption modes have been considered: Langmuir and Henry sorption (dual-mode) and water clustering. In this latter case, it was possible to determine the MCS.

The He plasma treatment used in this study does not seems to modify the final amount of water molecules able to be absorbed by flax fibers, while with autoclave treatment, the moisture content decreases, compared to the native fibers, in the activity range inferior to 0.8.

Thus, in contrast to He plasma treatment, autoclave treatment modify not only the surface but also the core of the fibers, leading to an increase of moisture resistance. In a kinetic point of view, when the driving force is still low (at low water activity), an increase of the water diffusivity appears with the duration of autoclave treatment. This increasing is directly linked to the pectins removal, which occurs during the autoclave treatment; these pectins act as hydrophilic charged sites and allow specific interactions with water molecules, and so reduce mobility of water molecules. Thus, it was possible to correlate the structure properties of fibers to the sorption parameters. In that way, water molecules act as a probe inside the matter at a molecular scale. To have a better fundamental approach, our next work will be to better characterize the effect of autoclave and plasma treatments on chemical composition and structure flax fibers. From that, it will be interesting to refine the water sorption of fibers in the low range of water activity especially in the Langmuir zone.

Finally, in terms of application, it will be envisaged to study the water sorption properties of composite films based on flax fibers untreated and treated (plasma and autoclave).

NOMENCLATURE

A	constant (dimensionless)
$\mathrm{a_w}$	water activity
B	constant (dimensionless)
b_L	Langmuir affinity constant
C	BET model parameter (dimensionless)
C_G	GAB model parameter (dimensionless)
E	mean relative deviation modulus (%)
K	GAB model parameter (dimensionless)
K_a	equilibrium constant for the clustering reaction
k_H	Henry's type solubility coefficient
k_1, k_2	equation parameters (dimensionless)
M	equilibrium moisture content (g water/g dry solids)
M_d	mass of wet matter (g)
M_m	monolayer moisture content
M_w	mass of dry matter (g)
m_i	experimental value
m_{pi}	predicted value
N	number of experimental data
n	mean number of water molecules per cluster
n_1, n_2	equation parameters (dimensionless)
r	equation parameter (dimensionless)
α	equation parameter (dimensionless)
γ	equation parameter (dimensionless)
θ	equation parameter (dimensionless)

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