STUDY OF THE DIFFUSION BEHAVIOR OF NATURAL FIBERS

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Abstract

Owing to their good mechanical properties, natural fibers could replace glass fibers for reinforcing material composites. The main disadvantage of the natural fibers is their hydrophilic nature. Therefore, the ageing of composite materials made with such fibers can be critical since the diffusion of water molecules could lead to a premature degradation. The aim of this work is to understand the diffusion phenomenon in vegetal fibers. Indeed, the diffusive behavior of four kind of natural fibers: hemp, jute, flax and sisal were investigated. In practice, the samples of fibers were submitted to hygro-thermal ageing either in total water immersion at room temperature or in an environmental chamber at 80 % relative humidity and 23°C. Periodic gravimetric measurements were achieved on the specimens in order to follow their absorption kinetics. Various predictive models were used to simulate experimental curves.

1 Introduction

Plant fibers already used in textile could act as reinforcement in material composites. This kind of natural fibers is a suitable alternative to glass fibers for reinforcing polymeric matrix. They are light, abundant and renewable. Moreover, they exhibit higher specific mechanical properties than glass fibers [1]. However, one particularity of these fibers is their hydrophilic behavior because of hydrogen bonding in their structure [2]. Therefore, the ageing of composite materials made with these fibers can be critical since the diffusion of water molecules could lead to a premature degradation and a loss of their mechanical properties [3]. To prevent this phenomenon, fiber surface properties could be modified by chemical treatments in order to promote adhesion [1,4]. A lot of investigations have been done in this sense but few people have explored the diffusion phenomenon inside these fibers to understand their mechanism of moisture absorption [5]. It is the topic of the present work. By doing gravimetric measurement on natural fibers and using predictive models we want to understand the diffusive behavior of four kind of natural fibers. Experimentally, the samples of fibers were submitted to hygro-thermal ageing either in total water immersion at room temperature or in an environmental chamber at 80 % relative humidity and 23°C. Periodic gravimetric measurements were achieved on the specimens in order to study the weight gain as a function of the time.

2 Materials and methods

2.1 Materials

Fibers studied in this work are hemp, flax, jute and sisal. Among plant fibers these one present the best mechanical properties to replace glass fiber (figure 1). Flax, hemp and jute are extracted from the stem of the plant and sisal is extracted from the leaf. Plant fibers have a multi-scale structure (figure 2). Here, the samples are bundles of fibers. The bundles are made of unit fibers linked by a middle lamella. According to Morvan et al. [6] this wall is principally made by pectin which is responsible of the hygroscopic behavior of the fiber. The unit fiber is a composite material with a hemicellulose matrix reinforced by cellulose [7]. Hydroxyl bonding in cellulose and hemicellulose lead also to moisture absorption in fibers [8].

fiber	Density (g/cm^3)	Specific stress ($MPa*cm^3/g$)	Specific Young Modulus ($GPa*cm^3/g$)
Flax	1.4-1.55	238-1000	34-76
Hemp	1.4-1.5	214-1264	24-50
Jute	1.3-1.46	286-650	7-22
E-Glass	2.55	941	29

Figure 1. Mechanical properties of different fibers [9,10,11]

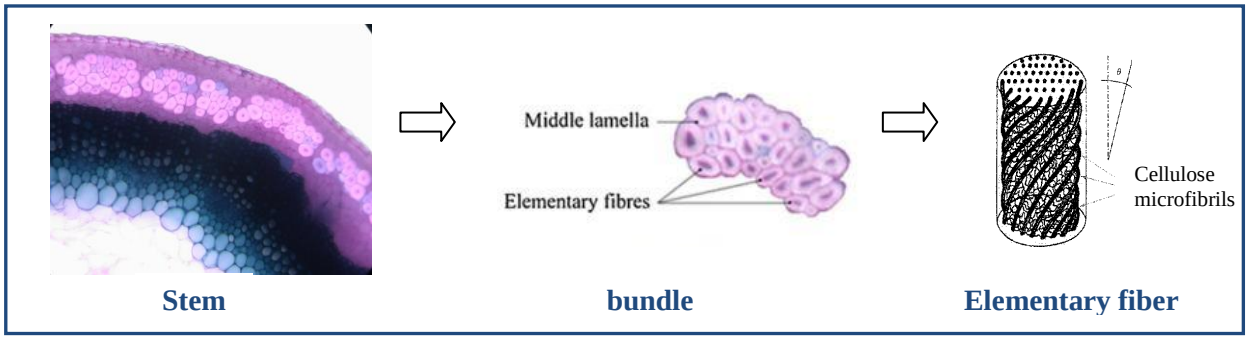

Figure 2. Multi-scale structure of the flax fiber [6,7]

2.2 Characterization

Fibers were analyzed by FTIR spectroscopy and Scanning Electronic Microscopy in order to identify and compare their composition and study their structure.

2.3 Gravimetric experiments

Each specimen was immersed in distilled water at room temperature during 11 days until saturation is reached. Then they are placed in a desiccators with saturated salt (RH = 7.5 %) at room temperature and they are weighted periodically. Data were read to 0.01 mg in a precision balance. The initial weight of the saturated bulk specimens, M_0, was also measured. The moisture content (M_w) is calculated at several times and is expressed in terms of percentage as follows in order to obtain desorption curves for each fiber:

$$M_W(\%) = \frac{M(t) - M_0}{M_0} \quad (1)$$

The specimens were aged, with the same protocol, in a climatic chamber with RH=80%. Sorption and desorption kinetics have been followed.

The diameter of each bundle was determinate by microscopy using picture analysis software. The diameter is not constant along the fibers [10]. We measured diameter in 6 points on a 3 cm long sample and the average value was considered. Figure 3 shows the variation of the diameter along each kind of fiber. Finally, fibers have been assumed to be assimilated as a complete cylinder of radius r very small compared to the length.

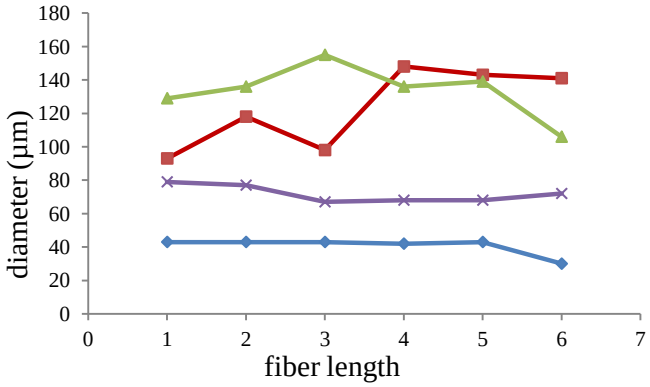

Figure 3. Variation of the diameter along fibers

3 Results

3.1 Characterization

3.1.1 FTIR Spectroscopy

The chemical structure of the components of hemp, jute, flax and sisal fibers was analyzed using FTIR-ATR (Fourier Transformed InfraRed spectroscopy- Attenuated Total Reflectance).The interesting peaks have been identified in figure 4. The four fibers have the same footprint. The large absorption band between 3600 cm^{-1} and 3100 cm^{-1} is the characteristic O-H stretching vibration and hydrogen bond of the hydroxyl group. This band and the other one at 1675 cm^{-1} testify the presence of water in the samples [12]. The two peaks at 2935 cm^{-1} and 2862 cm^{-1} correspond to C-H stretching vibration from CH and CH_2 and the absorbance at 1758 cm^{-1} is the characteristic for the C=O stretching vibration of ester groups. These three lasts peaks show the presence of hemicellulose. Finally, the peak group circled on the figure 4 is the footprint of cellulose [13].

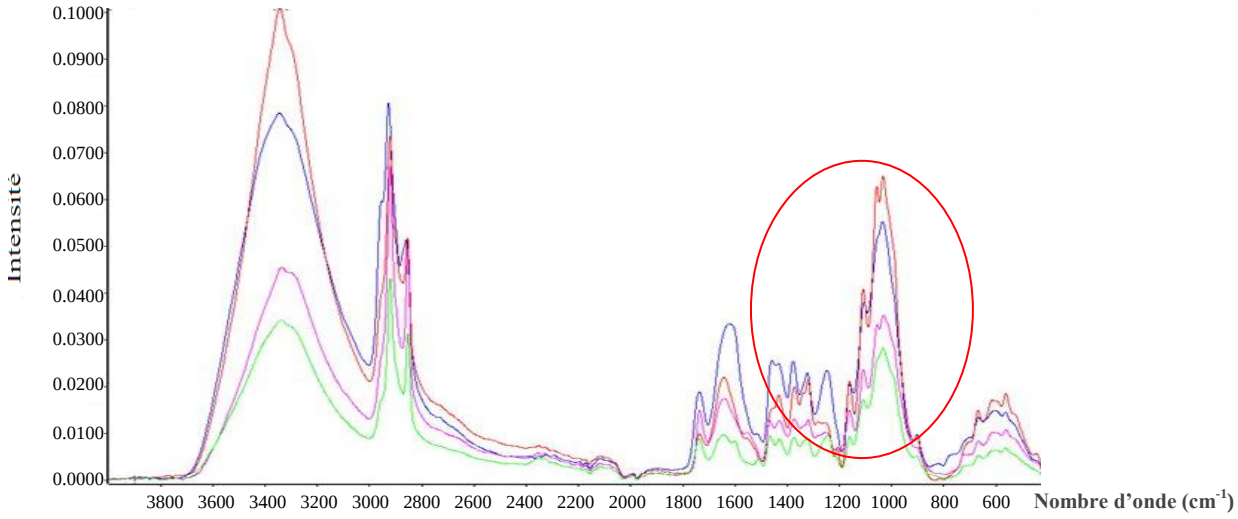

Figure 4. FTIR spectrum of -- flax, -- jute, -- hemp and -- sisal fibers

3.1.2 SEM analysis

SEM observations realized on the four kinds of fibers show the complex structure of the fibers. Pictures of jute and hemp fibers are presented in the figure 5. Elementary fibers are linked together by the middle lamella where moisture sorption is promoted.

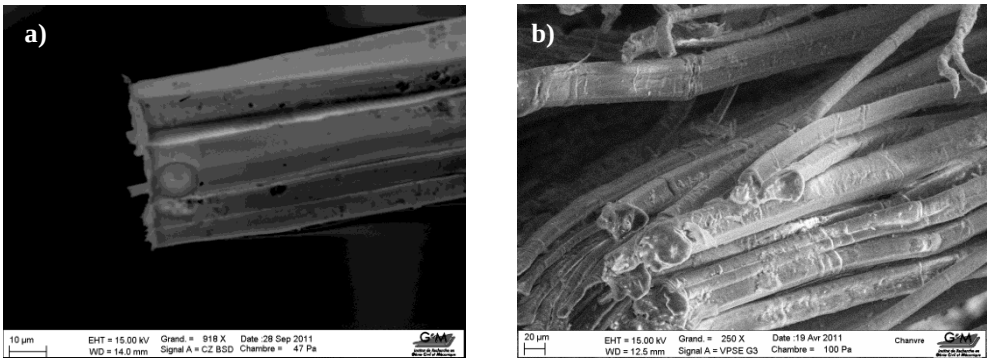

Figure 5. SEM pictures of a) Jute and b) hemp fibers

3.2 Kinetic's diffusion

3.2.1 Experimental results for immersion

The desorption kinetic of the four fibers is represented on the following curve (figure 6). The curves have a sigmoid shape. This particular shape can be the result of a delay time in the establishment of water concentration equilibrium at the fiber surface. Mass gain reaches 153 % for jute in 11 days. This value could be compared to the works of Bessadok et al. [14]. The authors found a mass gain of 140 % for Alfa fibers in immersion.

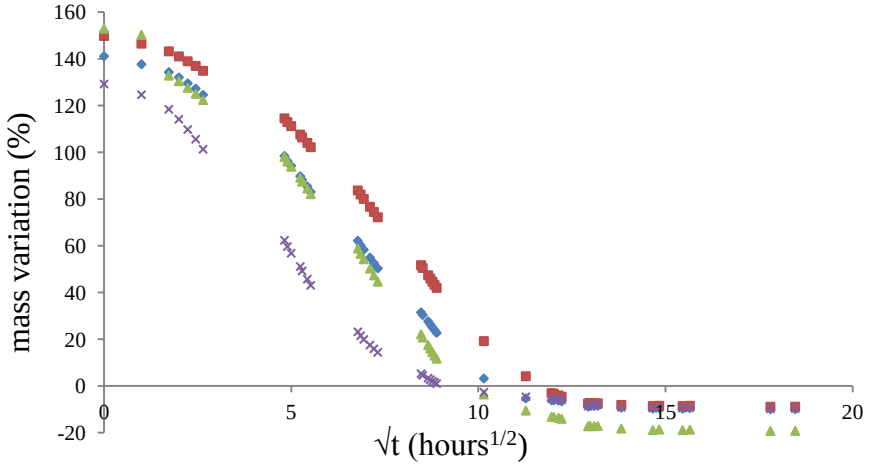

Figure 6. Desorption curves of natural fibers (** flax, ** hemp, ** sisal, ** jute)

3.2.1.1 Fick's law

Initially, the experimental data are fitted with the traditional Fickian diffusion model [15]. This is the most common model used for the diffusion of humidity in the materials. The model is consistent on the so-called free volume theory [16].

Considering a long circular cylinder in which diffusion is everywhere radial (one dimensional case), the moisture concentration C is then a function of radius *r* and time *t*, and the diffusion equation is written as follow [17]:

$$\frac{\partial C}{\partial t} = D\left(\frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2}\right) \tag{2}$$

where D is the diffusion coefficient.

Indeed, the integration of the analytical solution of Eq. (2), over the cylinder radius r yields the following expression of moisture uptake:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D\alpha_n^2 t) \tag{3}$$

where $J_0(x)$ is the first kind Bessel function of order zero. Indeed the values of α_n are the roots of the first species of Bessel's function at order 0.

The Fickian diffusion coefficients for each fiber were obtained using Eq. (3). They are shown in Table 1. These data were then used in conjunction with the saturation mass uptake values (M_∞) and Eq. (3) to obtain a predicted uptake curve. These predicted results are shown in figure 7. From these figures, it can be seen that the Fickian diffusion model with constant diffusion coefficient failed to fully reproduce the experimental uptake curves in all cases.

3.2.1.2 Dual stage Fick's law

Then, a dual stage moisture transport model is proposed to simulate the observed uptake characteristics of the bundles [18]. W.K. Loh et al. developed a dual stage uptake model consisting of two Fickian diffusion models in parallel. Both the Fickian diffusion models use Eq. (4) with separate diffusion coefficient (D_1 and D_2) and saturation levels ($M_{\infty 1}$ and $M_{\infty 2}$), respectively. The sum of each saturation level gives the total saturation.

$$M_t = M_{\infty 1}\left(1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n{}^2} \exp(-D_1 \alpha_n{}^2 t)\right) + M_{\infty 2}\left(1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n{}^2} \exp(-D_2 \alpha_n{}^2 t)\right) \tag{4}$$

$$M_{\infty 1} + M_{\infty 2} = M_\infty \tag{5}$$

The diffusion parameters from these best fitting processes are listed in Table 1. However this model, also failed to fully reproduce the experimental uptake curves in all cases.

3.2.1.3 Langmuir law or two-phase model of Carter and Kibler

This model was developed 35 years ago by Carter and Kibler [19]. This model is based on the Langmuir theory of adsorption on surface. In this model, the moisture absorption can be explained quantitatively by assuming that absorbed moisture consists of mobile and bound phases. Molecules of the mobile phase diffuse with a concentration and stress independent diffusion coefficient D_γ, and are absorbed (become bound) with a probability per unit time γ at certain site (for example: voids within the polymer, hydrogen bonding and heterogeneous morphology). Molecules are emitted from the bound phase, thereby becoming mobile, with a probability per unit time β.

Analytical solution for the case of an initially dry slab of thickness 2δ exposed to a constant moisture environment on both side at t = 0 is:

$$M_t = M_\infty \left[\frac{\beta}{\gamma+\beta} e^{-\gamma t} \left(1 - \frac{8}{\pi^2} \sum_{p=1}^{\infty} \frac{e^{-kp^2 t}}{p^2}\right) + \frac{\beta}{\gamma+\beta}\left(e^{-\beta t} - e^{-\gamma t}\right) + \left(1 - e^{-\beta t}\right) \right] \quad (6)$$

with:

$$k = \frac{\pi^2 D\gamma}{(2\delta)^2} \text{ and } 2\gamma, 2\beta << k$$

where, D is a (constant) coefficient of diffusion, n represents the number of mobile molecules (per unit volume) having a probability γ (s^{-1}) to become bound whereas N stands for the number of bound molecules having a probability β (s^{-1}) to become mobile.

As can be seen from figure 7, the model originally developed by Carter and Kibler describes very well the kinetics of water uptake in these natural fibers in condition of immersion. Diffusion parameters are presented in Table 1.

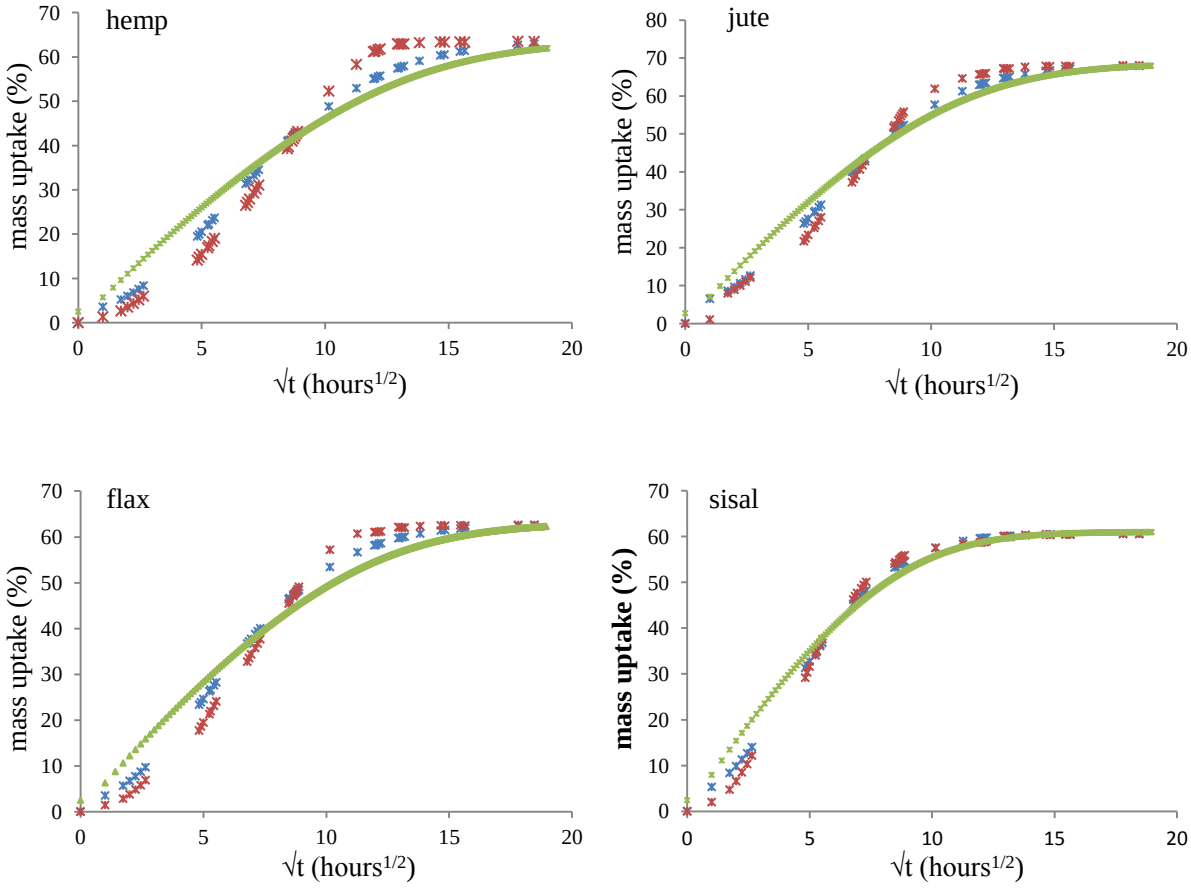

Figure 7. Results for diffusion in immersion (** experimental results, ** Langmuir simulation, -- Fick simulation)

		HEMP	JUTE	FLAX	SISAL
Fick	D (m^2/s)	$4.00\ 10^{-12}$	$1.12\ 10^{-11}$	$1.19\ 10^{-11}$	$2.14\ 10^{-11}$
Dual Stage Fick	D1 (m^2/s)	$5.29\ 10^{-13}$	$2.33\ 10^{-13}$	$2.11\ 10^{-12}$	$4.00\ 10^{-12}$
	D2 (m^2/s)	$5.80\ 10^{-13}$	$2.30\ 10^{-13}$	$2.11\ 10^{-11}$	$4.38\ 10^{-13}$
Langmuir	Dγ (m^2/s)	$5.6\ 10^{-12}$	$5.9\ 10^{-12}$	$6.8\ 10^{-12}$	$9.1\ 10^{-12}$
	β (s^{-1})	$4.25\ 10^{-6}$	$4.95\ 10^{-6}$	$5.75\ 10^{-6}$	$8.25\ 10^{-6}$

Table 1. Diffusion parameters for each model

3.2.2 Experimental results for vapor environment

Absorption kinetics for fibers aged in environmental chamber with RH = 80% are presented in figure 8. The curve is representative of a Fickian diffusion. Parameters are calculated by using Eq. (3) and they are presented in Table 2. Mass gain is 10 times less important than for immersion conditions. Saturation is reached in 8 hours.

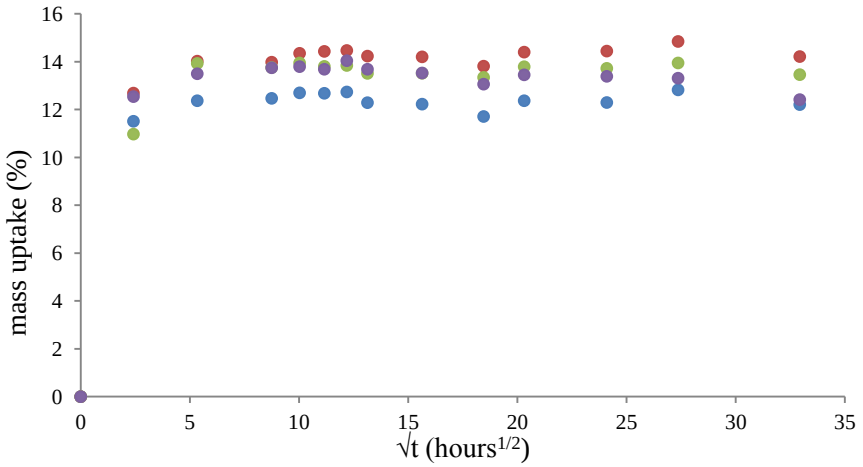

Figure 8. Absorption kinetics of natural fibers in hygrothermal conditions: RH = 80 %, T = 23°C (•• Hemp, •• Jute, •• Flax, •• Sisal)

	HEMP	JUTE	FLAX	SISAL
D (m^2/s)	$2.27\ 10^{-10}$	$4.02\ 10^{-10}$	$2.00\ 10^{-10}$	$1.17\ 10^{-10}$

Table 2. Fickian parameters for fibers ageing in hygro-thermal conditions RH = 80 %, T = 23°C

4 Conclusion

Natural fibers exposed to moisture in immersion or vapor humidity conditions don't exhibit the same diffusive behavior. Langmuir theory actually describes very well diffusion inside fibers immerged in liquid water whereas the same fibers follow a Fickian diffusion in the case when they are exposed to vapor during relative humidity ageing. The mass gain in immersion is ten times more important than in an environment at 80% relative humidity. This gap can be explained by the specimen's geometry. Free volume in such fibers is important and liquid water could be trapped inside pores. In vapor conditions it is possible that some water molecules remain in a gaseous state within the void parts of the samples. Then gaseous water could be released easily and the mass gain is less important.

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