

Modelling of Hydric Behaviour of Textiles

A. Marolleau, F. Salaun, D. Dupont, H. Gidik, S. Ducept.

Abstract—The goal of this study is to analyze the hydric behaviour of textiles which can impact significantly the comfort of the wearer. Indeed, fabrics can be adapted for different climate if hydric and thermal behaviors are known. In this study, fabrics are only submitted to hydric variations. Sorption and desorption isotherms obtained from the dynamic vapour sorption apparatus (DVS) are fitted with the parallel exponential kinetics (PEK), the Hailwood-Horrobin (HH) and the Brunauer-Emmett-Teller (BET) models. One of the major finding is the relationship existing between PEK and HH models. During slow and fast processes, the sorption of water molecules on the polymer can be in monolayer and multilayer form. According to the BET model, moisture regain, a physical property of textiles, show a linear correlation with the total amount of water taken in monolayer. This study provides potential information of the end uses of these fabrics according to the selected activity level.

Keywords—Comfort, hydric properties, modelling, underwear.

I. INTRODUCTION

HYDRIC behavior of textile is a major concern for Engineering and scientific researchers, designers, developers, and manufacturers. It influences the comfort of the wearer. Different materials are studied with the PEK model like wood [1]-[3], natural fibers like flax, jute and hemp [4]-[6], cellulosic fibers [7], regenerated cellulose fibers [8], [9], microcrystalline cellulose [10] and wool fibers [11]. Water vapour sorption and desorption processes of fibers are difficult to explain with the PEK model. Indeed, a lot of suppositions are made about the shape of curves obtained. These hypotheses are hard to confirm. Sorption and desorption of water vapour with the PEK model is studied only for fibers or mixtures with a high hygroscopic degree. Blend of synthetic fibers are not commonly studied in the literature. In this study, hydric behavior of synthetic fabrics has been investigated with DVS apparatus. Isotherm is fitted with the PEK model but also with other models like the HH model [4], [12], [15] and the BET model [9], [16], [17].

II. MATERIALS AND METHODS

A. Materials

Fabrics tested are underwear composed of fibers sensible of

A. Marolleau is with ENSAIT, 2 Allée Louise et Victor Champier, 59100 Roubaix, France (e-mail: adeline.marolleau@ensait.fr).

F. Salaun, is with ENSAIT and University of Lille 1, Cité scientifique, 59650 Villeneuve d'Ascq, France (e-mail: fabien.salaun@ensait.fr).

D. Dupont is with University of Lille 1 and HEI-Yncrea, 13 rue de Toul, 59100 Lille, France (e-mail: daniel.dupont@yncrea.fr).

H. Gidik is with HEI-Yncrea and University of Lille 1 (e-mail: hayriye.gidik@yncrea.fr).

S. Ducept is with Damart, 160 boulevard de fourmies, 59100 Roubaix (sducpet@damart.com)

moisture. Table I gives information about these samples.

B. Methods

1. Dynamic Vapor Sorption

The dynamic vapor sorption measures the water vapour sorption/desorption of a textile material by weighing successively with an electrical balance (SMS Ultrabalance TM) at $\pm 0.1 \mu\text{g}$. Approximately 12 mg of material is tested and placed onto a sample holder. Samples are initially dried for 600 minutes under a continuous flow of dry air at $35 \pm 0.1 \text{ }^\circ\text{C}$ to get closer to the skin temperature. Textile samples are subjected to humidity varying from 0 to 98% Relative Humidity (RH) in sorption and it is the same in desorption. The sample is held at each moisture level for 120 minutes and data is taken every 20 seconds. Two tests are carried out by samples in order to ensure the reproducibility of results.

TABLE I
DESCRIPTION OF TEST SAMPLES

Sample code	Fabric design	Fabric weight (kg.m ⁻²)	Thickness (mm)	Density (kg.m ⁻³)	Moisture regain (%)
A	1×1 interlock	0.204±0.002	1.31±0.03	165±4	1.75
B	1×1 interlock	0.156±0.004	1.22±0.08	128±6	5.18
C	1×1 interlock	0.157±0.002	1.09±0.06	143±4	3.36

2. Modelling

(a) PEK Model

The PEK model is applicable to DVS results for a relaxation-limited diffusion situation where the rate of diffusion is faster than the rate of relaxation. (1) gives the expression of this model [1], [18].

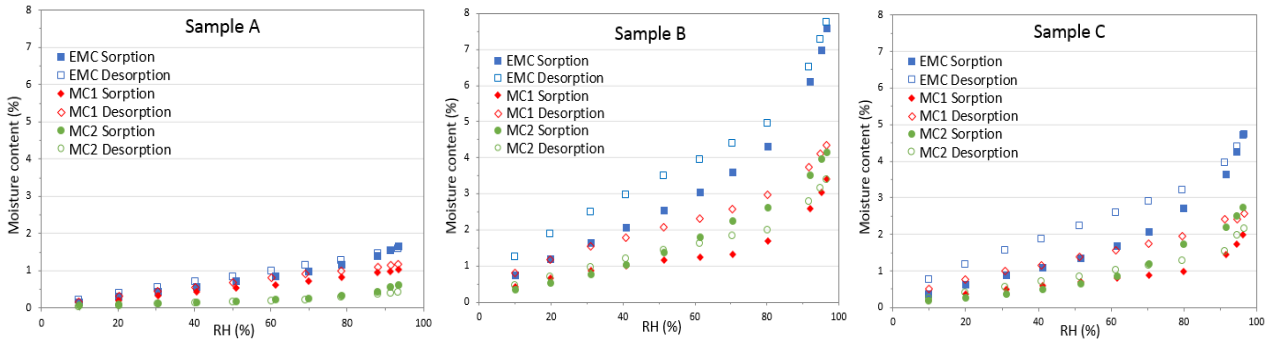
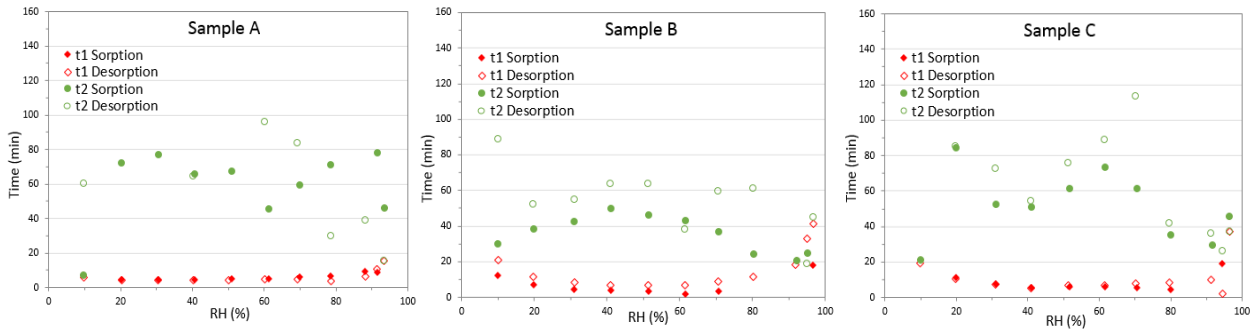
$$MC_{1,\%RH_i} = MC_{1,\%RH_i} \times [1 - e^{-\frac{-t}{t_1}}] + MC_{2,\%RH_i} \times [1 - e^{-\frac{-t}{t_2}}] \quad (1)$$

With MC (%) is the moisture content at time t (min), MC₁ (%) and MC₂ (%) are respectively moisture content at time t₁ (min) and t₂ (min). MC₁ and MC₂ are expressed in (2) and (3). Time t₁ and t₂ are defined in (4) and (5).

$$MC_1 = \frac{\sigma_0}{E_1} \quad (2)$$

$$MC_2 = \frac{\sigma_0}{E_2} \quad (3)$$

$$t_1 = \frac{\eta_1}{E_1} \quad (4)$$


 Fig. 1 Moisture content for EMC, fast (MC₁) and slow (MC₂) sorption and desorption processes

 Fig. 2 Characteristic times for fast (t₁) and slow (t₂) processes

$$t_2 = \frac{\eta_2}{E_2} \quad (5)$$

with E_1 and E_2 elastic modulus of the fast and slow process respectively (GPa), η_1 and η_2 viscosity modulus for fast and slow processes (Tpa.s), and σ_0 is the stress applied (GPa).

Two exponential terms composed (1): the first one is expressed with (MC₁, t₁) and the second one expressed with (MC₂, t₂). They represent the fast and slow kinetic processes respectively. The EMC is defined as the sum of MC₁ and MC₂ at each step of RH. These two processes differ by the sorption or desorption sites they used in the cell wall. Water molecules can create a direct or an indirect bond with hydroxyl groups present at the surface of fiber. Direct sorption/desorption of water molecules are possible onto external surface, amorphous regions, and inner surface of voids and crystallites [9]. Indirect moisture sorption/desorption concern additional water molecules which are tied with previous molecules already sorbed. Thus, fast process is associated with easily accessible sites like external surface of fiber and amorphous regions. The slow process concerns sites onto the inner surface and crystallites which are accessible with difficulty [5], [10].

(b) HH Model

The sorption part of the DVS is analyzed by fitting data with the HH model that is mainly used in the literature [3], [4], [12]-[14], [19]. This model analyzed two water vapour molecules sorption processes onto the cell wall (6) monolayer (M_h) and polylayer (M_s). The monolayer sorption concerns the

sorption on the surface of the fabric and in pores with only one layer of water vapour molecules. The polylayer sorption is possible above first layer of water molecules already placed at the surface of the fabric and in pores. It concerns several layer of water vapour molecules piled.

$$M = M_h + M_s = \frac{1800}{W} \times \left(\frac{K_1 \times K_2 \times H}{100 + K_1 \times K_2 \times H} \right) + \frac{1800}{W} \times \left(\frac{K_2 \times H}{100 - K_2 \times H} \right) \quad (6)$$

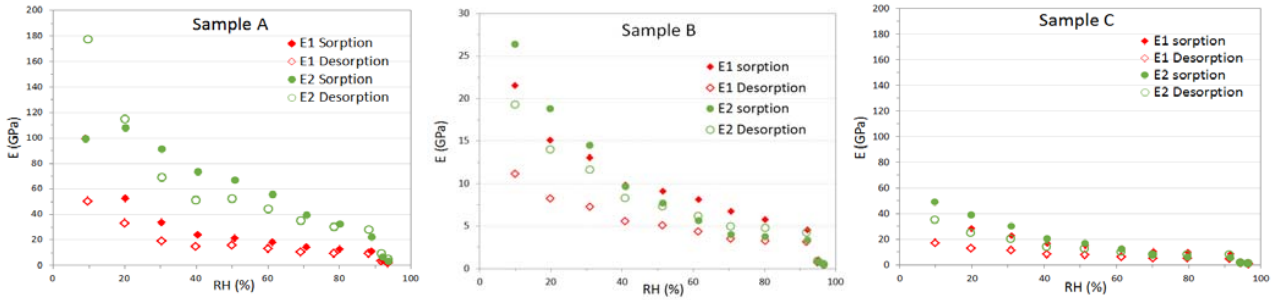
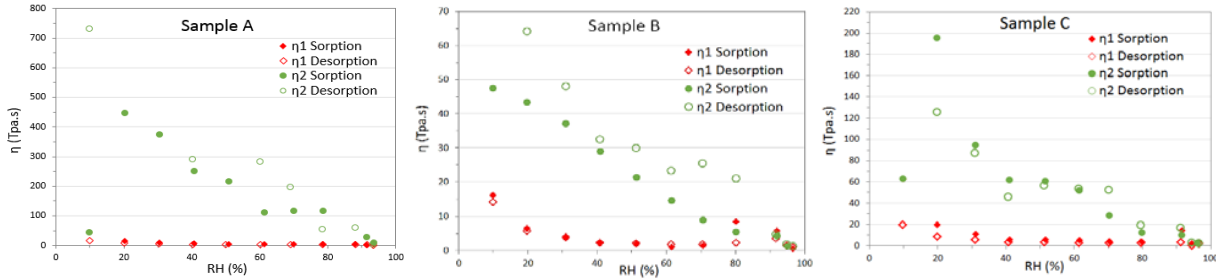
with M is the percentage of moisture content at a given RH, W is the molecular weight of cell wall polymer per sorption site, K_1 is the equilibrium constant of monolayer water formed from dissolved water and cell walls, K_2 is the equilibrium constant between water vapor and dissolved water.

(c) BET Model

The BET model describes only the first part of the sorption isotherm comprise between 0 and 15% HR. This model allows to determine the quantity of water taken in monolayer generally when molecules of water are directly bound with the polymer. The determination of the amount of water took by materials is given by (7) [8], [9], [16].

$$\frac{x}{V \times (1-x)} = \frac{1}{V_m \times C} + \frac{(C-1) \times x}{V_m \times C} \quad (7)$$

with V_m is the moisture regain (%) of the monomolecular layer, x is the partial vapor pressure of water, V is the moisture regain at x , C is a constant defined by (8).

Fig. 3 Elastic modulus for fast (E_1) and slow (E_2) processesFig. 4 Viscosity modulus for fast (η_1) and slow (η_2) processes

$$C = e^{\frac{E_1 - E_L}{RT}} \quad (8)$$

with E_1 is the heat of adsorption on the first layer and E_L on succeeding layers.

III. RESULTS AND DISCUSSION

A. PEK Model

1. Moisture Content

Results from DVS, sorption and desorption isotherms for EMC, fast MC_1 and slow MC_2 processes are presented in Fig. 1. The EMC represents the total moisture took by the fabric during the test. MC_1 and MC_2 are total moisture contents associated respectively with the fast and slow processes. The sample B has the highest moisture regain (Table I) and shows the most important increase of EMC during the sorption isotherm until 7.7% (as shown in Fig. 1). Then, the sample A, with moisture regain of 1.75, presented a rate of moisture content of 1.6% for the EMC and for the sample C; an intermediate value is measured at 4.7%. Thus, the EMC is correlated with the total water vapour sorbed into the fabric at 98%RH.

During the sorption, for the sample A, the fast process (MC_1) is predominant comparing to the slow process (MC_2). Water vapour is taken in high quantity on sites that are easily accessible at external surface of fibers or in amorphous regions (direct or indirect bond). For the sample B, the fast process is more important than the slow process until 41%RH and after it drops below. At the beginning, the water is primarily taken in easily accessible sites of sorption and then water vapour molecules are sorbed onto the inner surface and

crystallites of fabric (direct or indirect bond) which are hard to access.

During desorption, the fast process is more important than the slow one for each sample. It can be explained that more water is desorbed from fast sites than slow sites. Besides, the sorption of water vapour by slow process is always higher than desorption. In contrary, for the fast process, desorption is more important than sorption. Molecules of water vapour are primarily linked on the slow sites. Then, the structure of the matrix changes during the sorption process, so slow sites become more accessible and they are transformed in fast sites during the desorption process. This quantity of water that desorbs by the fast process and misses in the slow process is called “extra water” [7]. This phenomenon is also the reason than the loop of MC_1 and MC_2 for sorption/desorption processes is not closed whereas for the EMC, the moisture content at 98% RH is similar between sorption and desorption process [11], [13].

2. Characteristic Time

The characteristic time is the time necessary for the mass stabilization of fabrics after sorption or desorption of water vapour at each step of RH. Characteristic times for fast (t_1) and slow (t_2) processes are plotted in Fig. 2 for each sample.

For all samples, characteristic times for the fast process are lower than the slow one. This statement is correlated with different works of the literature [2], [5], [18]. Indeed, the sorption or desorption in easily accessible sites take less time than into slow sites which are hard to access. Thus, the fast process is associated with a short characteristic time and the slow process with a long characteristic time. For the fast process, at low and high humidity, characteristic times (t_1) are

higher whereas for middle humidity values are relatively constant. Thus, for RH at extremities, the equilibration process is slowing down [7], [15]. The lack of symmetry between sorption and desorption processes can be caused by the micromechanical behavior of the cell wall in the presence of moisture [5]. Besides, the behavior of characteristic times t_2 are difficult to explain; maybe it is the result of interaction between fiber blends that influence this parameter at different rate of humidity.

3. Elastic Modulus

Elastic modulus, produced by a stress applied within the cell wall matrix, is given in Fig. 3 for the fast (E_1) and slow (E_2) processes.

Values of elastic modulus decrease with the increase of RH.

It is caused by the plasticization of the cell wall by sorbed molecules of water [6], [20]-[22]. Indeed, considering water molecules like plasticizers it means that they increase the flexibility of the cell wall by reducing internal hydrogen bonding between polymer chains while increasing molecular space [23]. Indeed, this strong modulus reduction can be representative of an important breaking of hydrogen bond into the matrix at low RH. Elastic modulus (E_1 and E_2) for the sorption are higher than for the desorption process except for the sample A in low humidity with E_2 . The same tendency is found in literature [18], [21], [22]. The sorption of the first molecule of water vapor sorbed can cause more stress into the cell wall than the last water vapour molecule that goes out of the matrix.

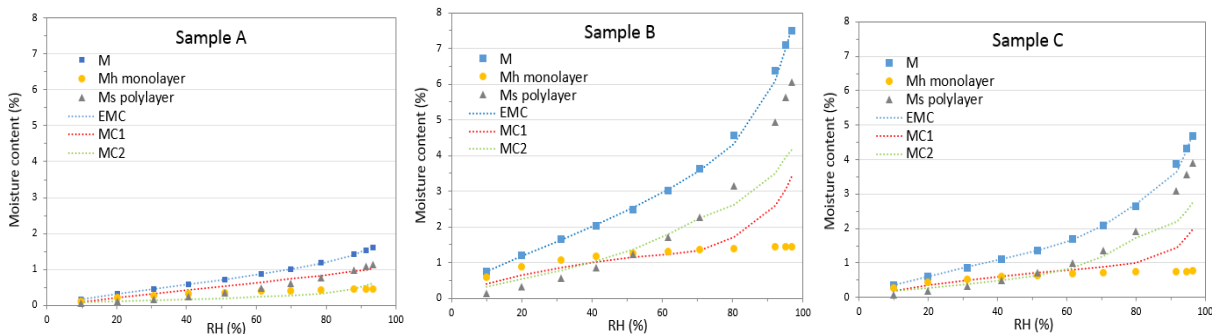


Fig. 5 HH model (M, Mh monolayer, Ms polylayer) and PEK model (EMC, MC₁ and MC₂)

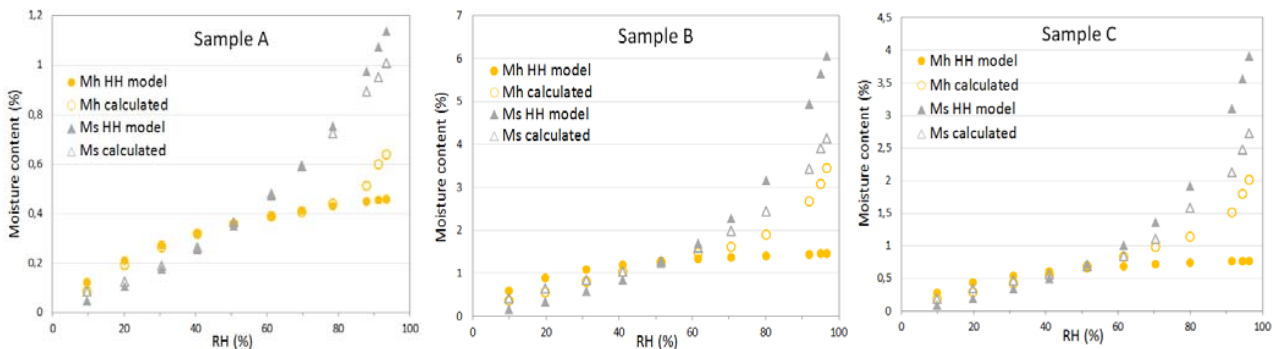


Fig. 6 HH model (M_h monolayer, M_s polylayer) and HH model calculated

For all samples, during desorption, elastic modulus of the slow process is higher than of the fast process. This remark is also available for the sample A during sorption. For the sample B (as shown in Fig. 3), during the sorption, E_2 is higher than E_1 from 0 to 41% RH, after this stage the tendency is reversed. The sample C shows a similar behavior than the fabric B except for the intersection that happen at 61.5% RH. Intersection of sorption curves between E_1 and E_2 are similar of sorption moisture content curves. Besides, a small value of elastic modulus can be associated with a more flexible cell wall structure [21] and by analogy a high value means the rigidity of matrix is important. Indeed, the structure of sample A is more rigid than sample C and B. Fabric B possesses the

more flexible structure with the highest moisture regain.

4. Viscosity Modulus

Viscosity modulus for fast (η_1) and slow (η_2) processes are plotted in Fig. 4. Similar to elastic modulus, the decrease of viscosity is associated with a reduction of the matrix stiffness and a plasticization of the cell wall by water vapour molecules when the RH increases [18]. Viscosity modulus of the slow process is always higher than the fast process [21], [22] for all samples during desorption and only during sorption for the sample A. For the sample B (as shown in Fig. 4), slow process is predominant until 80.2% RH and for the sample C it is the same tendency until 91.6% RH. Intersection points are not

correlated with sorption elastic modulus and moisture content intersection points. Besides, no tendency can be found between the sorption and desorption of each process. Similar to elastic modulus, the sample A shows a high stiffness, followed by samples C and B.

B. HH Model

Different studies have tried to find a relationship between fast and slow kinetic processes (PEK model) and the formation of monolayer and polylayer at various RH (HH model) and concluded there is sometimes no apparent relationship between them [13], [15], [19].

HH model is plotted with the PEK model in the Fig. 5 and parameters calculated from the HH model are given in Table II. The parameter W is the molecular weight of cell wall polymer per sorption site. Thus, when this parameter increases, it means that the cell wall shows a reduction in the number of free hydroxyl groups available for the sorption of water vapour molecules [3]. The sample A possesses the highest value of W and a low rate of moisture regain (Table I) whereas the sample B has the lowest value of W with the highest value of moisture regain. Thus, W is correlated with the moisture regain of samples, a low W means a high capacity for a fabric to sorb water vapour molecules.

TABLE II
PARAMETERS OF HH MODEL

Sample code	A	B	C	K1	K2	W
A	51.177	0.789	0.0076	3.299	0.671	2657.0
B	9.623	0.421	0.0040	6.438	0.803	1035.3
C	21.347	0.686	0.0072	4.855	0.833	1875.2

The parameter M of the HH model has an excellent correlation with the EMC of the PEK model for all samples (as shown in Fig. 5). For the sample A, curves of M_h and M_s cut each other at the point 50.9% RH, for sample B at 51.5% RH and for sample C at 51.6% RH. Besides, MC_1 and MC_2 curves are not following the evolution of M_h and M_s but they are linked all together by (9) and (10).

$$M_h = \left(1 - \frac{\%RH}{100}\right) \times MC_1 + \frac{\%RH}{100} \times MC_2 \quad (9)$$

$$M_s = \frac{\%RH}{100} \times MC_1 + \left(1 - \frac{\%RH}{100}\right) \times MC_2 \quad (10)$$

M_h and M_s , calculated by (9) and (10), are plotted with values obtained directly with the HH model in Fig. 6.

Sample A shows good correlation between values calculated and from HH model except for higher value of RH. For samples B and C, the correlation is good but a difference appears between curves after the intersection point and this gap is more important for M_h calculated. The correlation between (9), (10) and HH model depends of the type of fibers that composed the blend. They demonstrate that the fast and slow processes sorb water at the same time in monolayer and in multilayer.

C. BET Model

The amount of water vapour sorbed as a monolayer (V_m) on the material is calculated with the BET model. Results are given in Table III. The sample B has the highest value, the sample A the lowest value and the C shows an intermediate value. A linear correlation exists between the parameter V_m and the moisture regain of samples (as shown in Fig. 7). The coefficient of the slope 4.0994 is maybe representative of the heat of sorption. It is possible to calculate it with the Arrhenius relationship [1], if samples are tested at different temperatures.

TABLE III
PARAMETERS OF BET MODEL

Sample code	V_m (%)
A	0.3876
B	1.2873
C	0.8005

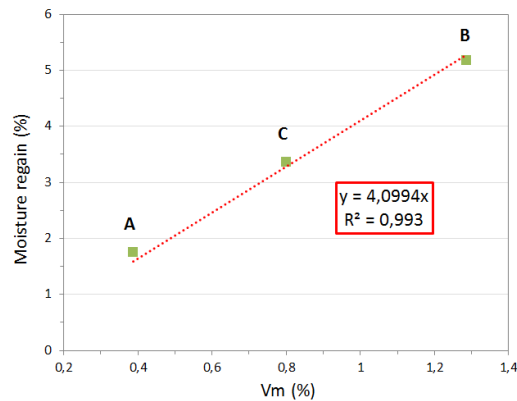


Fig. 7 Linear correlation between V_m and moisture regain

IV. CONCLUSION

This study analyzes only the hydic behavior of textiles by the combination of three models PEK, HH and BET.

The PEK model investigates how water vapour molecules are sorbed in the cell wall. Two processes of sorption/desorption are identified. The fast process concerns sorption of water vapour molecules on easily accessible sites like on external surface of fiber and amorphous regions. Sorption/desorption on inner surface and crystallites sites which are less accessible are representative of the slow process. Besides the fast process is also associated with the diffusion of water vapour into the matrix and the slow process represents the ability of the matrix to relax when water molecules ingress or egress the fabric.

The HH model differentiates the sorption in monolayer or in polylayer. A relationship exists between the PEK and the HH model and it is demonstrated that during fast and slow processes water vapour molecules can be sorbed at the same time in monolayer and in polylayer.

The last model (BET) establishes a relationship between one physical property of the textile, the moisture regain, and the total quantity of water vapour that fabric can sorb in

monolayer.

ACKNOWLEDGMENT

The authors gratefully acknowledge DAMART for their financial support and, ENSAIT and HEI for their technical support.

REFERENCES

- [1] C. A. Hill, B.A. Keating, Z. Jalaludin, E. Mahrtdt, "A rheological description of the water vapour sorption kinetics behaviour of wood invoking a model using a canonical assembly of Kelvin-Voigt elements and a possible link with sorption hysteresis", *Holzforschung*, 2012, 66, 35-47.
- [2] C.-M. Popescu, C. Hill, S. Curling, G. Ormondroyd, Y. Xie, "The water vapour sorption behaviour of acetylated birch wood: how acetylation affects the sorption isotherm and accessible hydroxyl content" *Journal of Materials Science*, 2014, 49.
- [3] Y. Xie, C.A Hill, Z. Xiao, Z. Jalaludin, H. Militz, C. Mai, "Water vapor sorption kinetics of wood modified with glutaraldehyde", *Journal of applied polymer science*, 2010, 117, 1674-1682.
- [4] C.A. Hill, A. Norton, G. Newman, "The water vapor sorption behavior of natural fibers", *Journal of Applied Polymer Science*, 2009, 112, 1524-1537.
- [5] C.A. Hill, A. Norton, G. Newman, "The water vapor sorption behavior of flax fibers—Analysis using the parallel exponential kinetics model and determination of the activation energies of sorption", *Journal of applied polymer science*, 2010, 116, 2166-2173.
- [6] C.A. Hill, Y. Xie, "The dynamic water vapour sorption properties of natural fibres and viscoelastic behaviour of the cell wall: is there a link between sorption kinetics and hysteresis ?", *Journal of materials science*, 2011, 46, 3738-3748.
- [7] R. Kohler, R. Dück, B. Ausperger, R. Alex, "A numeric model for the kinetics of water vapor sorption on cellulosic reinforcement fibers", *Composite Interfaces*, 2003, 10, 255-276.
- [8] S. Okubayashi, U.J. Griesser, T. Bechtold, "Moisture sorption/desorption behavior of various manmade cellulosic fibers", *Journal of applied polymer science*, 2005, 97, 1621-1625.
- [9] S. Okubayashi, U.J. Griesser, T. Bechtold, "A kinetic study of moisture sorption and desorption on lyocell fibers", *Carbohydrate Polymers*, 2004, 58, 293-299.
- [10] K. Kachrimanis, M. Noisternig, U. Griesser, S. Malamataris, "Dynamic moisture sorption and desorption of standard and silicified microcrystalline cellulose", *European journal of pharmaceutics and biopharmaceutics*, 2006, 64, 307-315.
- [11] G.A. Ormondroyd, S.F. Curling, E. Mansour, C.A. Hill, "The water vapour sorption characteristics and kinetics of different wool types", *The Journal of The Textile Institute*, 2017, 108, 1198-1210.
- [12] Ö. Ceylan, F. Goubet, K. Clerck, "Dynamic moisture sorption behavior of cotton fibers with natural brown pigments", *Cellulose*, 2014, 21.
- [13] C.A. Hill, A.J. Norton, G. Newman, "The water vapour sorption properties of Sitka spruce determined using a dynamic vapour sorption apparatus", *Wood Science and Technology*, 2010, 44, 497-514.
- [14] Z. Jalaludin, C.A. Hill, H.W. Samsi, H. Husain, Y. Xie, "Analysis of water vapour sorption of oleo-thermal modified wood of *Acacia mangium* and *Endospermum malaccense* by a parallel exponential kinetics model and according to the Hailwood-Horrobin model", *Holzforschung*, 2010, 64, 763-770.
- [15] J. Zaihan, C. Hill, S. Curling, W. Hashim, H. Hamdan, "The kinetics of water vapour sorption: analysis using parallel exponential kinetics model on six Malaysian hardwoods", *Journal of Tropical Forest Science*, 2010, 107-117.
- [16] B. Siroka, M. Noisternig, U.J. Griesser, T. Bechtold, "Characterization of cellulosic fibers and fabrics by sorption/desorption", *Carbohydrate research*, 2008, 343, 2194-2199.
- [17] R.M. Syamaladevi, S.S. Sablani, J. Tang, J. Powers, B.G. Swanson, "Water sorption and glass transition temperatures in red raspberry (*Rubus idaeus*)", *Thermochimica Acta*, 2010, 503, 90-96.
- [18] C.A. Hill, J. Moore, Z. Jalaludin, M. Leveneu, E. Mahrtdt, "Influence of earlywood/latewood and ring position upon water vapour sorption properties of Sitka spruce", *International Wood Products Journal*, 2011, 2, 12-19.
- [19] J. Zaihan, C. Hill, S. Curling, W. Hashim, H. Hamdan, "Moisture adsorption isotherms of *Acacia mangium* and *Endospermum malaccense* using dynamic vapour sorption", *Journal of Tropical Forest Science*, JSTOR, 2009, 277-285.
- [20] Y. Xie, C.A. Hill, Z. Jalaludin, D. Sun, "The water vapour sorption behaviour of three celluloses: analysis using parallel exponential kinetics and interpretation using the Kelvin-Voigt viscoelastic model", *Cellulose*, 2011, 18, 517-530.
- [21] C.-M. Popescu, C.A. Hill, "The water vapour adsorption--desorption behaviour of naturally aged *Tilia cordata* Mill. Wood", *Polymer degradation and stability*, 2013, 98, 1804-1813.
- [22] C.A. Hill, J. Ramsay, B. Keating, K. Laine, L. Rautkari, M. Hughes, B. Constant, "The water vapour sorption properties of thermally modified and densified wood", *Journal of Materials Science*, 2012, 47, 3191-3197.
- [23] S. Mali, L. Sakanaka, F. Yamashita, M. Grossmann, "Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect", *Carbohydrate Polymers*, 2005, 60, 283-289.