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A New Kinetic Model for Water Sorption Isotherms of Cellulosic Materials

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Summary: Some natural fibres like flax, hemp and others show excellent mechanical properties which make them a promising choice for the reinforcement of polymers. For natural fibre reinforced composites, hydrophilicity is a problem with respect to dimensional changes, fibre to matrix adhesion and long term stability. The interaction of differently prepared and modified fibres with water vapour has been investigated by dynamic vapour sorption. It has been found that the sorption and desorption kinetics of cellulosic fibres can be excellently fitted by assuming two parallel, independent first order processes. This empirical model, defined here as the "Parallel Exponential Kinetics" model (PEK-model), reveals two distinct mechanisms with slow and fast exchange of water vapour respectively, related to different sorption sites. The specific sorption mechanisms are represented by individual sorption-desorption isotherms as components of the total isotherms. The results suggest a relation to the differing types of amorphous regions in the fibres and/or to the different states of "bound" or "free" water, discussed for hydrophilic materials. The PEK-model proved to be consistently applicable for sorption and desorption over the whole humidity range, and also for all tested cellulose fibres. It is especially useful for a clearer distinction of different fibre types or modifications and can be successfully used for an extended fibre characterization.

Keywords: Cellulose; fibres; isotherms; kinetic model; water sorption

Introduction

The high tensile strength of several natural fibres can be effectively utilised for polymer reinforcement. Composites with fibres such as flax, hemp, sisal and others are increasingly applied in the car industry, mainly for interior parts, but exterior components are already being produced as well. The hydrophilic nature of the cellulosic fibres presents a major problem for many applications. Water uptake and release result in dimensional changes affect the fibre-matrix adhesion and reduce the mechanical strength of the composites. The hydrophilicity depends on the fibre type and preparation and can be considerably influenced by surface modifications. The quantitative sorption and desorption behaviour is therefore an important characteristic of the fibres.

Natural cellulose fibres have a complex composite structure.[1,2] The basic unit is the elementary fibril, composed of interlinked cellulose macromolecules. The macromolecules are to a great part closely packed, forming oriented, crystalline segments, but pass also through less oriented amorphous regions. The elementary fibrils are arranged into microfibrils, macrofibrils and finally fibril bundles which make up the different layers of the cell wall, illustrated in a simplified scheme in Figure 1.

The total structure is to a great part crystalline. Amorphous regions exist within the fibrils, but primarily between the fibrils

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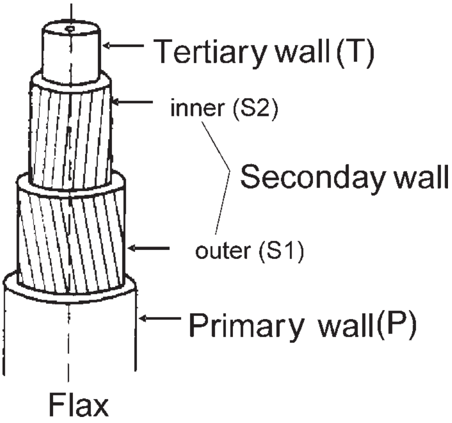

Figure 1.
A simplified model of a flax fibre showing the layered structure. The fibrils in the different layers are oriented with different microfibrillar angles.

and bundles, which are imbedded in a non-fibrous matrix consisting of hemicellulose, pectin and lignin as the main constituents. A schematic model of the structure is given in Figure 2.

Water can penetrate into the amorphous parts only. The areas between the fibrils and bundles are supposed to be more accessible to water molecules than the free volume of the disordered cellulose molecules inside the fibrils.

The hydrophilic behaviour of cellulose fibres is best characterised by sorption/desorption isotherms. Like many other hydrophilic materials, the isotherms are of type II in the IUPAC classification.[3] Desorption occurs with a characteristic hysteresis over the whole humidity range from 0–95% relative humidity (r.h.). Various theories are available for the evaluation of sorption isotherms. For type II isotherms, the Brunauer-Emmet-Teller (BET) model is most common, but it is limited to the lower range of partial pressures below 30%. A novel and very powerful description of isotherms has been presented by Adolphs and Setzer.[4–7] This new thermodynamic approach describes the isotherms over the whole range and proves to be extremely useful for the evaluation of our experimental and calculated isotherms. The most relevant quantities with respect to our considerations are: 1. The Excess Surface Work (ESW) defined as

$$\Phi = n_{ads} \cdot \Delta\mu = \frac{M_\infty}{M_{mol}} \cdot RT \ln\left(\frac{p}{p_0}\right) \qquad (1)$$

where n_{ads} = number of sorbed molecules, $\Delta\mu$ = change in chemical potential, M_∞ = sorbate mass in equilibrium, M_{mol} = molar mass of the sorbate, R = gas constant, T = absolute Temperature and $\left(\frac{p}{p_0}\right) = \left(\frac{r.h.}{100}\right)$ = equilibrium partial pressure of the vapour. 2. The sorbed mass M_{HI} at the ESW-minimum and the corresponding value Φ, i.e. the sorbed mass at that partial pressure

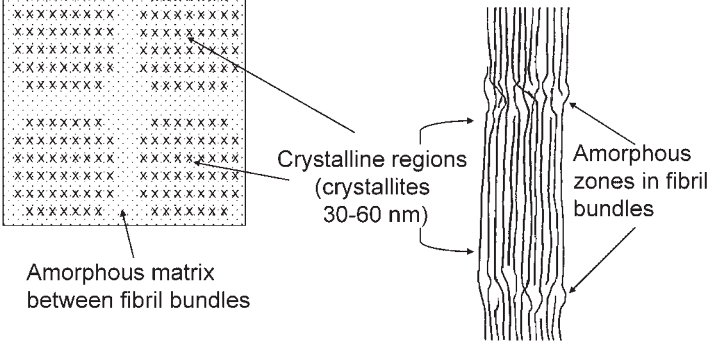

Figure 2.
Model of the composite fibre structure illustrating the arrangement of the fibril bundles and the crystalline and amorphous regions.

where the sorbate undergoes the highest interaction.

Experiments and Results

In order to investigate the sorption and desorption of water vapour, different cellulosic fibres have been chosen. Scutched flax fibres are prepared by mechanically separating the fibres from the stalk ("decortication"), followed by a special mechanical cleaning treatment ("scutching") for removing residual woody particles. Some of the scutched flax fibres have been further treated by steam explosion (STEX).[8] The fibre bundles are first soaked in an alkaline solution at room temperature, then pressurised with saturated steam at about 180 °C for several minutes and finally disintegrated into single fibres by an abrupt pressure release ("explosion"). The main amount of non-fibrous matrix is thereby removed.

The sorption and desorption characteristics of different cellulose fibres have been measured by dynamic vapour sorption, using the gravimetric DVS-1000 system from Surface Measurements Systems, London.

The relative humidity is changed step-by-step and the sorption kinetics is recorded as time dependent mass gain and loss at each individual humidity level. (Figure 3).

The isotherms are obtained by plotting the respective equilibrium mass versus the corresponding level of relative humidity. Isotherms of different cellulose fibres are depicted in Figure 4.

It has been found that the sorption and desorption kinetics on each level of relative humidity can be excellently modelled by assuming two parallel, independent first order processes, defined here as the "Parallel Exponential Kinetics" model (PEK-model).[9]

The model equation for the mass gain is

$$M_t = M_{\infty 1}\left(1 - e^{-\frac{t}{\tau_1}}\right) + M_{\infty 2}\left(1 - e^{-\frac{t}{\tau_2}}\right) \tag{2}$$

where M_t = mass at any time t, M_∞ = mass at equilibrium and τ = time constant i.e. the characteristic time to reach

$$M_t = M_\tau = M_\infty(1 - e^{-1}) = M_\infty\left(1 - \frac{1}{e}\right) \approx 0.6321 \cdot M_\infty \tag{3}$$

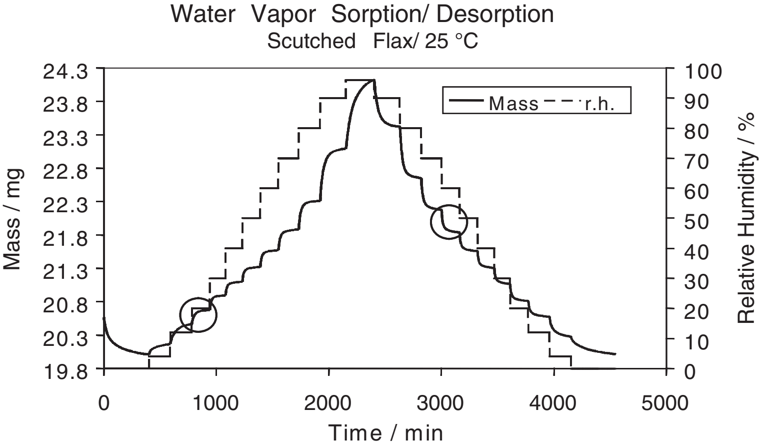

Figure 3.
Example of a sorption experiment. Step-by-step increase of relative humidity and related change of mass. The circles indicate the kinetic curves evaluated in Figure 5 and 6.

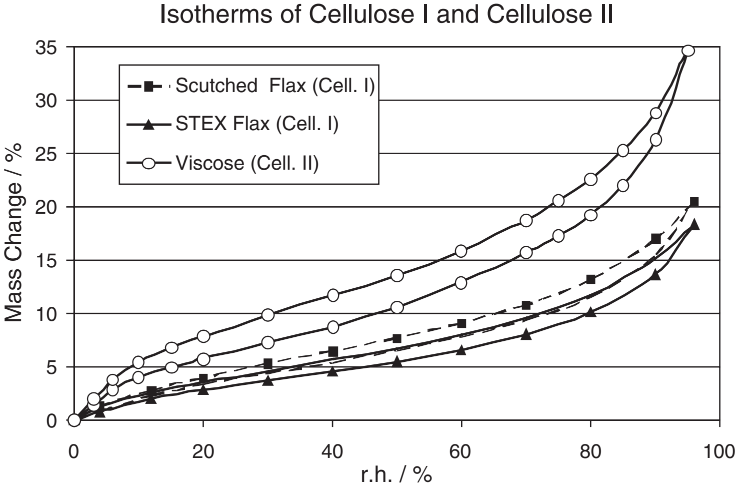

Figure 4.

Typical isotherms of different cellulose fibres. Sorption is represented by the lower and desorption by the upper curve of each cycle. Viscose shows always a significant higher water uptake.

Analogous to equation 2 the mass loss in desorption is

$$M_t = -M_{\infty 1}\left(1 - e^{-\frac{t}{\tau_1}}\right) - M_{\infty 2}\left(1 - e^{-\frac{t}{\tau_2}}\right) \quad (4)$$

The model equations have been used for fitting the experimental mass change curves at each sorption level by nonlinear regression. The fit shows astounding correlation factors of $R^2 > 0.999$ (Figure 5).

The reasonable interpretation of the model is the existence of two distinct sorbent sites, with different accessibilities for water vapour, according to the different characteristic times τ_1, τ_2, and with different sorption capacity given by the equilibrium masses $M_{\infty 1}$, $M_{\infty 2}$. From the constants, partial kinetic curves, attributed to slow and fast sorption/desorption processes, are calculated for both different sorbent sites (Figure 6).

The distinct sorption sites are also described by individual isotherms, as components of the total isotherm, calculated from the equilibrium masses $M_{\infty 1}$ and $M_{\infty 2}$ for sorption and desorption respectively, as shown in Figure 7.

Different from other kinetic models suggested in literature, e.g. Young and Nelson[10] or Breier et al.,[11] which do not correctly describe the experimental isotherms, the PEK-model proved to be consistently applicable for sorption and desorption over the whole humidity range, and also for all cellulose fibre types tested so far.

The results strongly suggest a relation to the differing types of amorphous regions in the fibres and/or to the different states of "bound" or "free" water, discussed for hydrophilic materials.[12–15] More data and additional experiments (e.g. DSC) are necessary to uncover such a connection. Until an independently established correlation has been found, which would considerably support the model, we avoid any bias by defining the two kinetic processes simply as *slow* and *fast,* corresponding to *slow* and *fast* sorption sites.

Regarding the curves for flax, it seems intriguing that the slow desorption does not reach 0 and the fast desorption shows even negative values. A closer evaluation of the component isotherms in the higher humidity range reveals a change in the binding of water. From Figure 8 it can be seen that, by shifting the slow desorption curve down, it

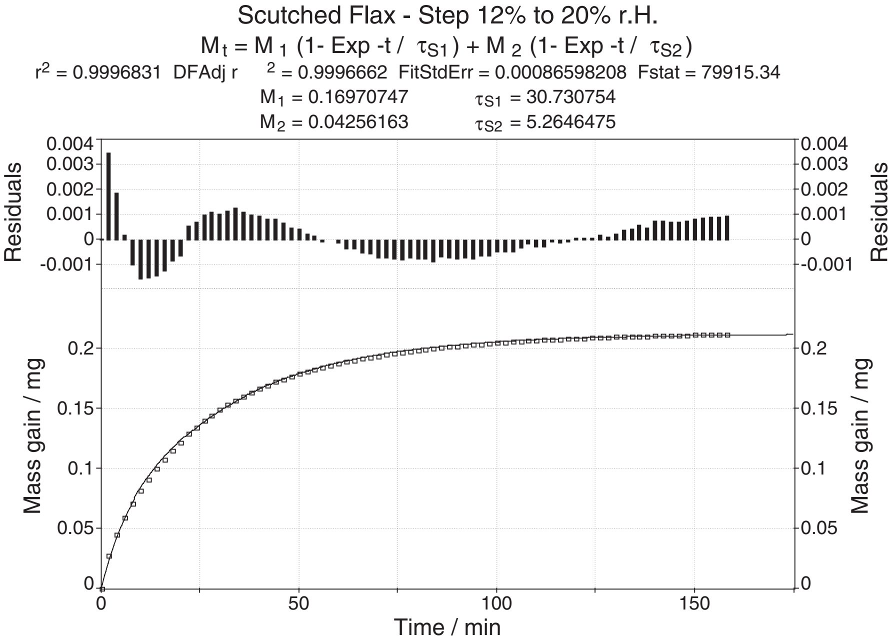

Figure 5.
Example of a nonlinear regression fit of the experimentally measured sorption values.

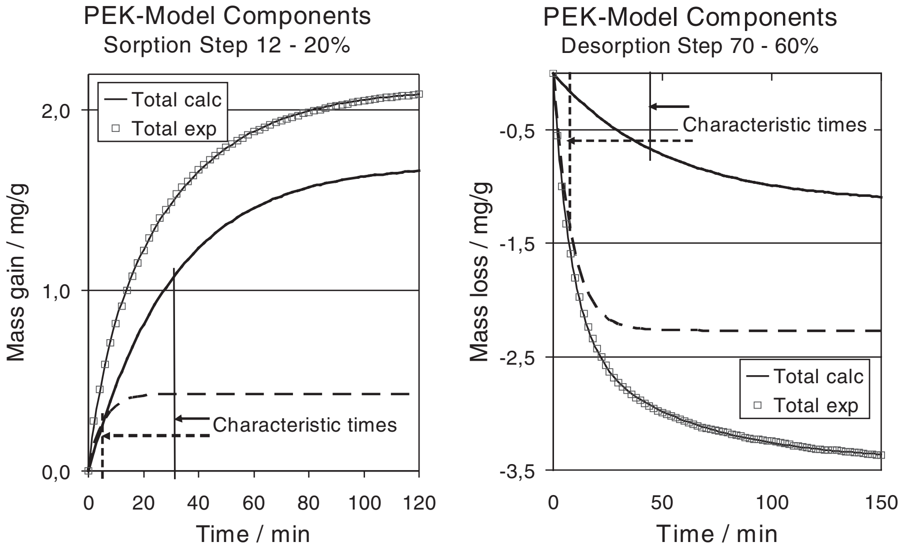

Figure 6.
Two experimental kinetic curves (□) (circles in Figure 3) are shown here for sorption (left) and desorption (right). The constants obtained from fitting the model equations 1 and 2 have been used to calculate the two partial sorption curves for the fast and slow process respectively.

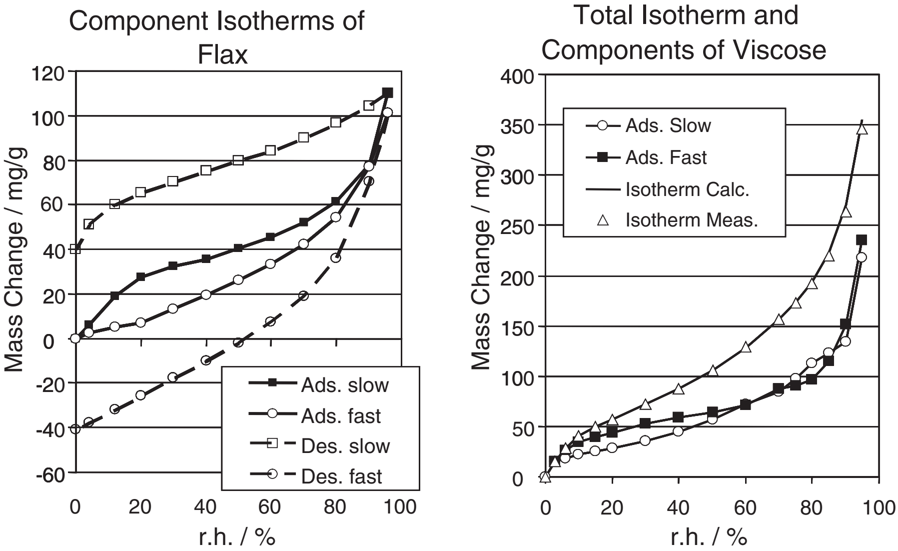

Figure 7.
The component isotherms, calculated from the fitted model equations, exemplify the *slow* and *fast* contributions to the sorption and desorption characteristics of scutched flax (left) and also the total sorption isotherm and its components for Viscose (right). The considerably higher water uptake of viscose is a well known fact in textile finishing.

coincides with the fast sorption between 0 and 70% r.h.

Obviously, at higher humidity, the slow sorption process has transported more water (denoted "extra water") to slow sites than is later desorbed slowly. Adding the difference to the fast desorbing water exactly compensates the negative values of the fast component isotherm. The fast release of this extra water from the initially less accessible sites is an indication for the swelling of the fibres.

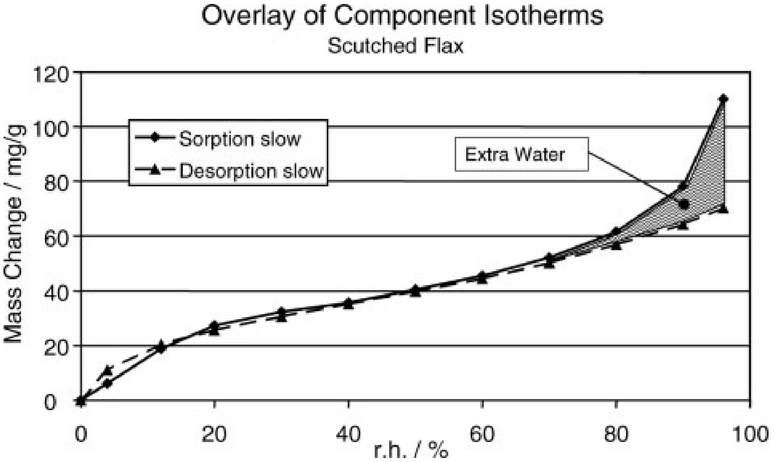

Figure 8.
Congruence of the slow sorption and desorption isotherms in the humidity range below 70%. The excess water in slow sorption at higher humidity ("extra water") is desorbed in the fast process.

The PEK-model turned out to be especially effective in combination with the thermodynamic description of isotherms by the excess surface work method. By example, this is clearly demonstrated for the isotherms of modified flax. The surface of steam exploded flax fibres has been treated with different amounts of silane, in order to reduce the total water uptake of the fibres. The dried fibres contained 1.5% and 3% silane. From the total isotherms in Figure 9 it can be seen that the total water sorption is indeed less compared to the untreated fibres shown in Figure 4. But the isotherms of the silane treated fibres are very similar within the range of experimental error.

On the other hand, calculation of the component isotherms using the PEK-model and evaluation of the component isotherms by the ESW-method reveals clear differences as illustrated in Figure 10.

In a very recent work on water sorption in flax fibres, Gouanvé et al.[16] compare different models for sorption equilibrium by numerical fitting them to the experimental isotherms. The Park model is chosen as the best fit, providing a convincing description of the sorption equilibrium by a combination of three sorption modes. In addition, the authors use sorption kinetics for the calculation of diffusion coefficients supporting their interpretation.

Different from fitting an equilibrium model to the isotherms, the PEK-approach uses the sorption kinetics to calculate component isotherms, which add up to the complete isotherm. The τ_1 and τ_2 (see equations 2–4) are the inverse of kinetic rate constants and are certainly related to diffusion coefficients, which can be calculated from the kinetic curves as well. The dependence of the sorption rate on the relative humidity has been presented in ref.[9]. Whereas the characteristic times of the fast sorption process are independent from the humidity level, the sorption rate of slow process is substantially reduced below 30% and above 70% of relative humidity, similar to the trend of the diffusion coefficients described by Gouanvé et al.[16]

Conclusion

The PEK-model has been advantageously used to evaluate and compare the water sorption behaviour of different cellulosic fibres. Although it is an empirical model based on numerical fitting of the kinetic curves, it allows for reasonable interpretations related to the fibre structure. The combination of the PEK model with the ESW-description of sorption isotherms is especially effective for detecting differences not observed by considering the overall

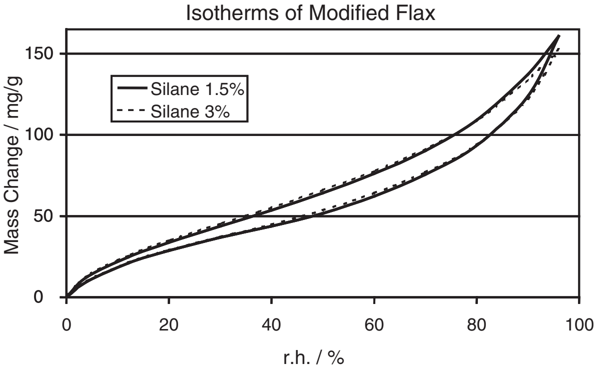

Figure 9.
The total sorption and desorption isotherms of silane-treated fibres are almost identical and therefore not useful for discriminating the different samples. (The experimental points have been omitted in order to clearly show the coincidence).

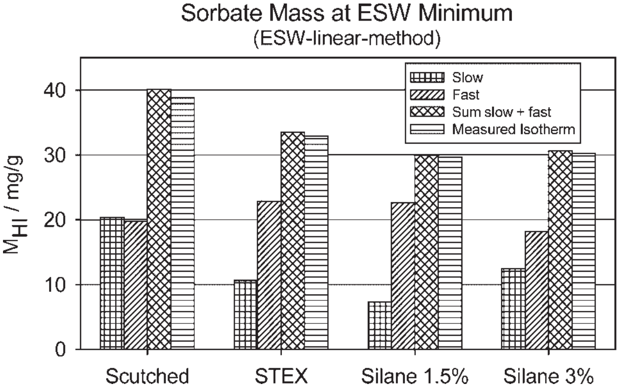

Figure 10.

Comparison of the mass of sorbate with highest interaction M_{HI} for differently treated flax fibres, determined with the ESW-method from the total isotherms, and from the component isotherms obtained with PEK-model. Each component sums up to the total mass at ESW minimum. Only the components reveal the existing differences of the silane treated probes. Obviously, in the fibres with the higher silane content, more water is stored at the slow sites and less at the fast sites, i.e. the water is less mobile.

isotherms. Comparing the results of the PEK-approach, including diffusion coefficients, with the reported model of Gouanvé et al. should contribute to an improved interpretation of sorption data.

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