

The water vapour sorption kinetics of Sitka spruce at different temperatures analysed using the parallel exponential kinetics model

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Abstract

In this study the water vapour sorption of Sitka spruce (*Picea sitchensis* (Bongard) Carr.) was measured using a Dynamic Vapour Sorption (DVS) apparatus and then analysed using the parallel exponential kinetics (PEK) model. The water vapour sorption rate of wood quickly increased when the relative humidity was changed. With the elapse of time, the sorption rate gradually decreased within any specific relative humidity range. The sorption hysteresis of wood reduced with increasing isotherm temperature. The equilibrium moisture contents obtained from DVS measurements were comparable to these derived from PEK model in the full relative humidity range. The PEK model deconvolutes the sorption kinetics curve into two exponential kinetics processes (fast and slow) which have characteristic times and moisture contents associated with them. The slow adsorption and desorption processes exhibited important differences in their characteristic times, although hysteresis in the moisture contents was found to be variably distributed between the fast and slow processes depending on isotherm temperature.

1 Introduction

Wood is a hygroscopic material because the cell walls contain abundant water sorption sites (hydroxyl groups). Most of the wood properties concerning utilization, such as dimensional instability and fungal decay, are closely related to the wood's water sorption behaviour (Hon 2001). The interaction of water with cellulosic materials involves a dynamic proton exchange on the cellulose internal pore surfaces (Carles and Scallan 1972). The water sorption behaviour of cellulosic and lignocellulosic materials is complicated due to the complex internal geometry of the cell wall and also the continuous structural change resulting from cell wall dimensional variation. It has been demonstrated that the water vapour sorption behaviour of both natural fibres (Kohler *et al.* 2003, Hill *et al.* 2010a), regenerated cellulose fibres (Okubayashi *et al.* 2004, 2005a, 2005b), microcrystalline cellulose (Kachrimanis 2006) and some foodstuffs (Madamba *et al.* 1996, Rahman *et al.* 1998, Tang *et al.* 2008) can be accurately described using the parallel exponential kinetics (PEK) model (Equation 1).

$$MC = MC_0 + MC_1[1 - \exp(-t/t_1)] + MC_2[1 - \exp(-t/t_2)] \quad (1)$$

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where MC is the moisture content at time (t) of exposure of the sample to a constant RH, MC_0 is the moisture content of the sample at time zero. The sorption kinetic curve is composed of two exponential terms which represent a fast [$MC_1(1-e^{-t/t_1})$] and a slow [$MC_2(1-e^{-t/t_2})$] process having characteristic times of t_1 and t_2 , respectively. The terms MC_1 and MC_2 are the moisture contents at infinite time associated with the fast and slow processes, respectively. There has been speculation as to what physical phenomena the two processes represent and there is no clear view on this at the present time. The sorption kinetics can thus be deconvoluted into two first order kinetic processes with the reciprocals of the characteristic times giving the rate constants. The main objective of this study was to establish the sorption kinetics of Sitka spruce wood by fitting the moisture content data attained from the Dynamic Vapour Sorption apparatus. The sorption kinetics was evaluated using a parallel exponential kinetics model (PEK model).

2 Kinetic curve fitting to the data

Each kinetic curve was obtained by plotting percentage mass gain against time, with time zero corresponding to the point at which a relative humidity step change occurs.

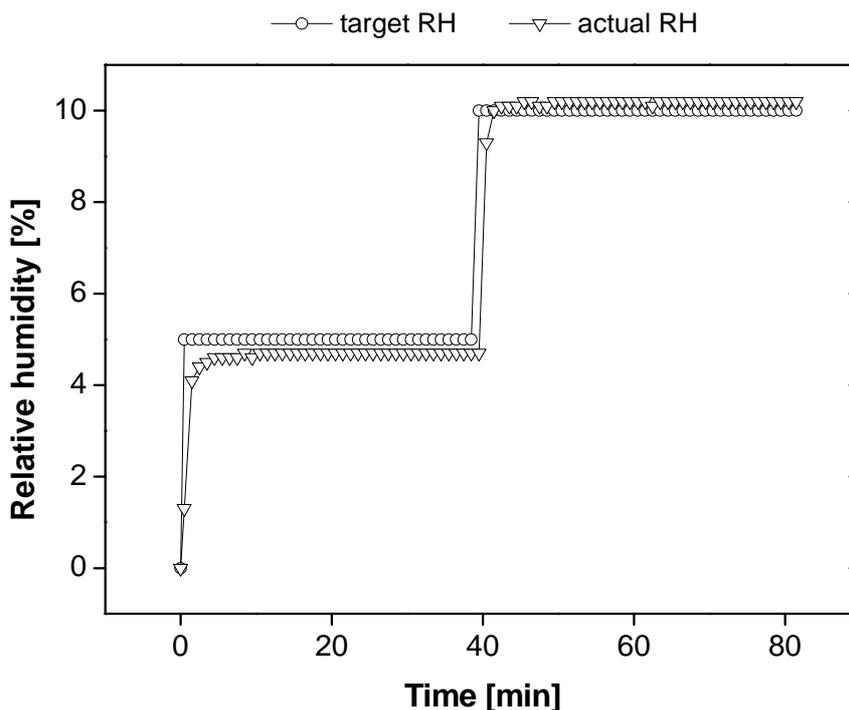


Figure 1: Typical changes of target relative humidity and actual relative humidity in the sample chamber during sorption process. The target relative humidity changed from 0 to 5% and subsequently 5 to 10%. Wood sample was tested at 35 °C.

However, a change of RH from (for example) 10 to 20% does not occur instantaneously in the instrument and there is a finite time during which the RH

is moving from one stable value to the next (Fig. 1). During this period, the moisture content of the sample is not moving towards a static equilibrium point, which consequently affects the kinetics curve for the first minute or so. The data from the kinetics curves were fitted to Equation 1, using the function 'expassoc' in Origin software (Originlab, Northampton, MA, USA). Since the first few data points in this curve are associated with the sample moisture content under conditions of changing relative humidity, the characteristic times for any fit including these curves will not be representative of the material properties and they are consequently removed from the fit. However, as more data points are excluded from the curve fitting process, the values for the mass changes for the fast and slow kinetics process become less accurate. In practice, with data being collected every 20 seconds, removal of the first three data points was sufficient to obtain good quality curve fits.

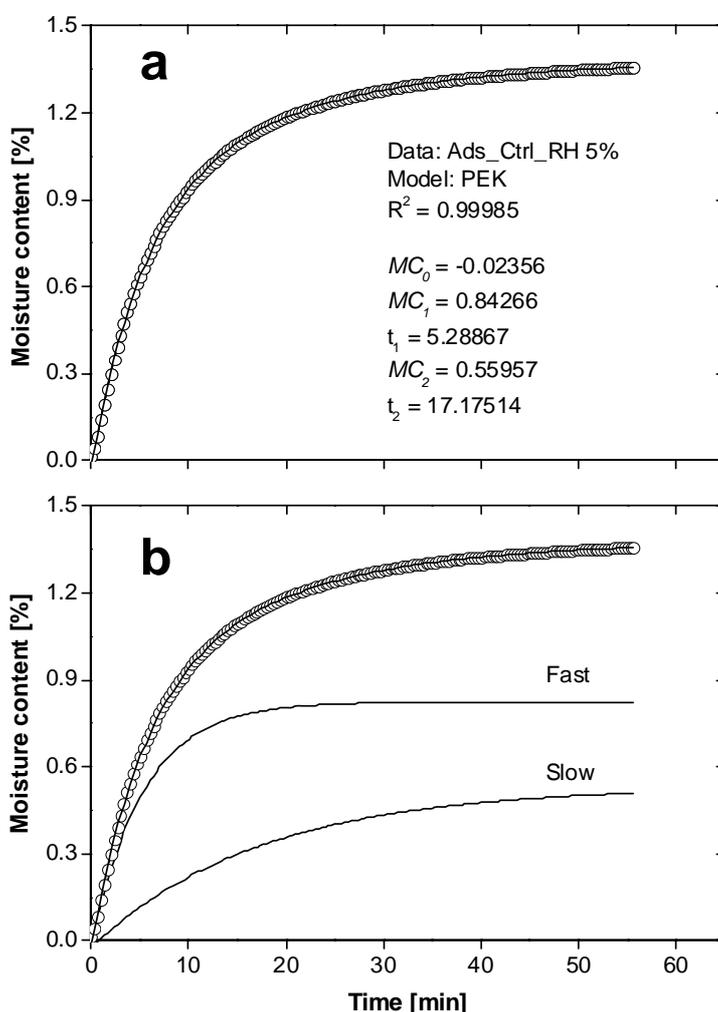


Figure 2: Example of PEK fit to experimental adsorption data (open circles) of wood sample at 5% target relative humidity (a) and the fitted curves (lines) showing the slow and fast parallel exponential kinetic processes (b).

A representative example is presented in Figure 2a for a kinetic curve fit of the experimental data measured at the RH level of 5% for Sitka spruce using the

PEK model, which showed an excellent fit to the experimental data of wood ($R^2 > 0.99$). The fit parameters were given automatically by the software. Typically, the fitted curve can be deconvoluted into a fast process ($MC_1[1 - \exp(-t/t_1)]$) associated with moisture content (MC_1) and a slow process ($+ MC_2[1 - \exp(-t/t_2)]$) associated with moisture content (MC_2) at infinite time t according to Equation 1 (Figure 2b). The fast kinetic process has been proposed to be related to the fast moisture sorption at the sites of 'external' surfaces and 'amorphous' regions, while the slow kinetic process has been related to sorption onto the 'inner' surfaces and 'crystallites' (Morton and Hearle 1997, Okubayashi *et al.* 2004). The slow process has been described as a rate limiting step associated with the cell wall swelling process (Hill *et al.* 2010b,c). However, it is not yet known for certain what these two processes represent in terms of physical phenomena taking place within the cell wall. The sorption isotherm obtained from the PEK fitting was created by summing the cumulative moisture contents associated with the fast and slow kinetic processes and the moisture content at time zero ($MC_0 + MC_1 + MC_2$) in the adsorption and desorption runs.

3 Sorption hysteresis

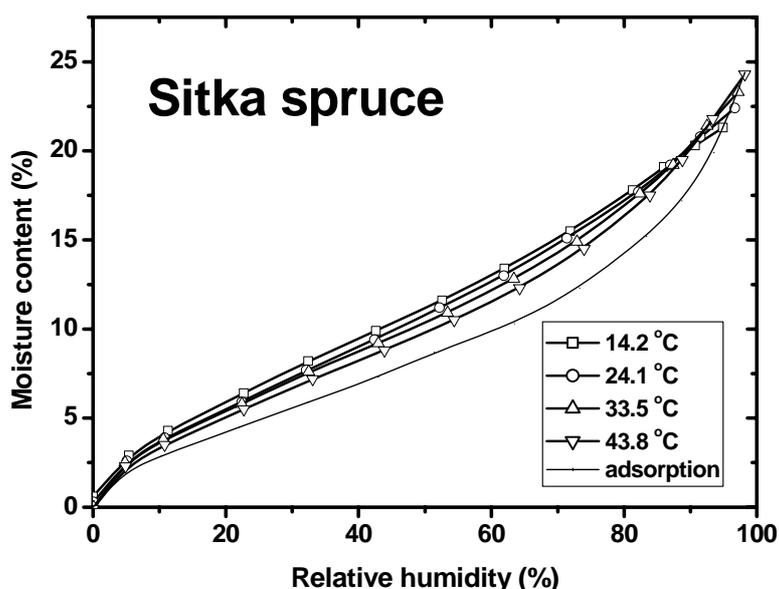


Figure 3: Effects of isotherm temperature on the hysteresis between the desorption and adsorption processes for Sitka spruce.

The sorption hysteresis at different temperatures is shown in Figure 3. The hysteresis exhibited that Sitka spruce decreased significantly as the isotherm temperature was increased, which is behaviour consistent with the description of sorption in a glassy solid (Hill *et al.* 2009). As the isotherm temperature is increased, the size of the hysteresis loop is predicted to decrease until the glass transition temperature of the material is reached, at which point it becomes zero. The glass transition temperature of lignin in the presence of moisture is in

the region of 60 to 90 °C and linear projections of the decrease in hysteresis loops reached zero in this temperature range for Sitka spruce.

A model for sorption hysteresis based upon adsorption and desorption processes on glassy solids below the glass transition temperature has been presented (Hill *et al.* 2009). The model considers the dynamic response of the substrate during the ingress or egress of water molecules into or out of the matrix of a glassy polymer. When water molecules enter the matrix, the structure expands with the creation of molecular sized nanopores to accommodate the water molecules, whereas during desorption, the matrix responds with the collapse of these nanopores as water molecules exit the structure. However, because the process takes place below the T_g of the material, the matrix does not respond instantaneously to the ingress or egress of the water molecules; there is a time lag in the response of the matrix. This process takes place on a molecular time scale, but there will be a connection through to the sorption kinetics observed on macroscopic time scales if the matrix deformation processes are rate determining steps. There are certainly differences observed in the characteristic times observed for the adsorption and desorption processes. The time to obtain equilibrium is always longer for the slow desorption compared to the fast desorption processes, which shows that there is a lack of symmetry between the adsorption and desorption that presumably has its origin in the micromechanical behaviour of the cell wall in the presence of moisture. However, there is no significant difference between the adsorption and desorption characteristic times with the fast kinetic processes, which was also found by Kohler *et al.* (2003). A possible interpretation of this observation is that the fast sorption processes are connected with readily accessible sorption sites in the cell wall internal surface, whereas the slow process is linked to the production of new sites as the cell wall expands or the loss of these sites as the cell wall contracts.

Other studies of water vapour sorption kinetic processes on wood invariably invoke diffusion-based models with varying degrees of success. However, this study has found that the PEK model gave excellent fits to the data in all cases. It has been reported that the swelling of cereal grains in the presence of moisture obeys a PEK model. It is suggested that the rate limiting step in such cases is determined by the rate at which the material can expand to accommodate the cell wall bound water. Further studies are presently underway to examine this possible explanation.

4 Conclusions

This study has shown that water vapour sorption and desorption kinetic behaviour on wood is accurately described by the parallel exponential kinetics (PEK) model. With increasing the temperature, wood exhibited a lower hysteresis in the full RH range. The reduction in hysteresis with temperature can be explained by a model invoking the phenomenon of sorption on a glassy solid below the glass transition temperature.

5 Acknowledgements

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6 References

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