The Water Vapor Sorption Behavior of Flax Fibers—Analysis Using the Parallel Exponential Kinetics Model and Determination of the Activation Energies of Sorption

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ABSTRACT: Sorption kinetic data for the interaction of water vapor with flax (*Linum usitatissimum* L.) were analyzed used the parallel exponential kinetics (PEK) model, with excellent fits to the data being obtained. The PEK model is the sum of 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 predominantly associated with the fast process. The kinetics was examined over a range of relative humidity (RH) values and at different temperatures, enabling the determination of activation energies for the adsorption and desorption kinetic processes throughout the hygroscopic range (from 5–95% RH). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2166–2173, 2010

Key words: adsorption; biofibers; activation energy; water vapor; kinetics

INTRODUCTION

Recently, we have reported on the water vapor sorption properties of a range of natural fibers.[1] These data for the adsorption and desorption behavior of the materials were obtained using a dynamic vapor sorption apparatus. The sorption isotherm represents an equilibrium state and is reported in terms of the equilibrium moisture content of the material at different constant relative humidities. The procedure requires that the material in question is maintained in an environment at a constant relative humidity (RH) until the equilibrium state is obtained. Many experiments of this type have been performed over years and it is well established that cellulosic and lignocellulosic materials display characteristic sigmoidal isotherms and hysteresis between the adsorption and desorption branches of the isotherm.[2,3] In the previous article, it was demonstrated that the area enclosed by the hysteresis loop was larger when the plant material had a higher lignin content, and that the area bounded by the hysteresis loop decreased as the temperature at which the isotherm was determined rose. Both of these properties are consistent with a model for hysteresis for adsorption into and desorption from a glassy polymer below the glass transition temperature (T_g).[4–7]

The use of a dynamic vapor sorption apparatus not only allows for the easy and rapid determination of sorption isotherms, but provides an abundance of data reporting on the rate of change of the sample mass over time as the sample adsorbs or desorbs moisture as it approaches equilibrium. These data can be used to examine the kinetics of the adsorption and desorption process, thereby providing further insights into the phenomenon of hysteresis.

This difference between adsorption and desorption cycles would be expected to be reflected in the kinetic processes taking place as the sample attains equilibrium. When the RH is changed, the plant cell wall responds to this by establishing a new equilibrium *MC* value, but this takes a finite time to achieve. It has been found that the so-called 'parallel exponential kinetics' (PEK) model provides exceptionally good fits to adsorption and desorption curves for foodstuffs, pharmaceutical materials, and both natural and regenerated cellulose fibers.[8–14] The PEK equation is a double exponential of the form:

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

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where MC is the moisture content after infinite time of exposure of the sample to a constant RH and 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 and slow 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 of the fast and slow processes giving the corresponding rate constants for those processes ($k_1 = 1/t_1$, $k_2 = 1/t_2$). It is then possible to determine the activation energies associated with the rate determining step of the sorption processes by using the well known Arrhenius relationship [eq. (2)].

$$k = A.\exp(-E_a/RT) \tag{2}$$

where k is the rate constant, A the collision factor, E_a the activation energy, R the universal gas constant, and T the absolute temperature.

Knowledge of the activation energies may in turn be able to provide information regarding the nature of the fast and slow kinetic processes.

Although there have been previous reports of the use of PEKs to model, the sorption and desorption isotherms with plant fibers and with food stuffs, there has been no attempt to determine the activation energies of these processes. However, one report has appeared where activation energies of sorption have been determined for the adsorption of water onto charcoal where, interestingly, the sorption kinetics is accurately described by a simple single exponential function.[15] This observation suggests that the slower kinetic process may be related in some way to the swelling behavior of the cell wall of plant-derived materials.

As noted, although the kinetics for both the adsorption and desorption processes can be deconvoluted into fast and slow processes, it is not known what these processes represent physically. There has also been no study of the effect of temperature upon the kinetic processes with plant-based materials and no previous report of the activation energy of sorption for plant materials. What little evidence exists suggests that the PEK model may be needed when water sorption processes on viscoelastic materials such as the plant cell wall are studied. This investigation was undertaken to increase the understanding of the PEK model when applied to plant-based materials and to provide further insights into the property of hysteresis.

EXPERIMENTAL

Isotherm analyses were performed using a Dynamic Vapor Sorption apparatus (Surface Measurement Systems, London, UK). This is a very useful means of generating accurate sorption isotherms at different temperatures and using a range of preset RH values. The apparatus contains two measurement pans (sample and reference holders) suspended from the arms of a Cahn ultra sensitive microbalance, capable of measuring changes in sample mass as low as 1 part in 10 million. The instrument has excellent long term stability and no drift in mass values was found when the measurement pans did not contain sample material. The sample and reference holders, that are connected to the microbalance by hanging wires, sit in a climate controlled chamber (located in a thermostatically controlled cabinet) and through which there is a constant flow of nitrogen gas, into which is mixed nitrogen containing a preset amount of water vapor. The instrument was set to record sample mass at each of the following RH steps: 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95%. Three temperature steps were programmed into the apparatus (15, 25, 35°C). The instrument maintained a sample at a constant RH until the weight change per unit time (dm/dt) value reached 0.002% per minute over a 10 min period, a value that from previous long term exposure experiments yielded a sample MC within less that 0.1% of the equilibrium value. Data were gathered every 20 s. It was found that the temperature and humidity values were very stable during the tests (+/− 0.1% RH, +/− 0.1°C), although both the RH and temperature did not stabilize at the preset values and it was necessary to read the actual RH and temperature values at each adsorption and desorption stage from the output data spreadsheets. A full description of the apparatus and the methodology has been reported earlier.[1]

Flax fibers were used in an as-supplied state (supplied courtesy of the BioComposites Centre, Bangor, Gwynedd, UK) and no solvent extraction was employed before use.

Curve fitting of the sorption data—sensitivity analysis

Each kinetic curve is obtained by plotting percentage mass gain against time, with time zero corresponding to the point at which a RH step change occurs. However, a change of RH from (for example) 10–20% does not occur instantaneously in the instrument and there is a finite time, during which the RH is moving from one set value to the next. As a consequence, the moisture content of the sample is not moving towards a stable equilibrium point, which consequently affects the kinetics curve for the first

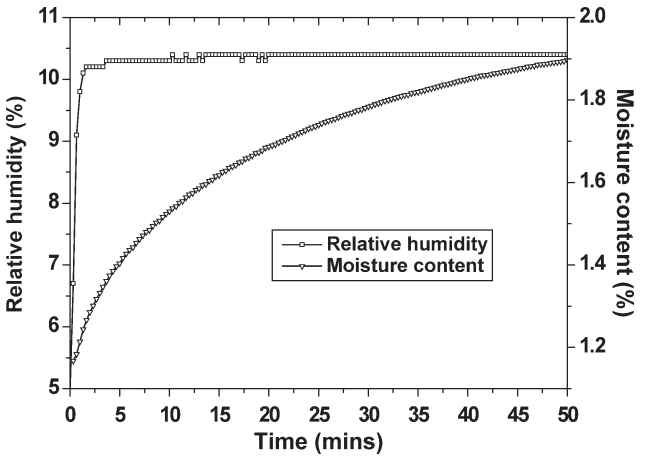

Figure 1 Example kinetics curve for the adsorption of water vapor onto flax fibers at a temperature of 24.4°C and for a programmed relative humidity change of 5–10%.

few minutes. This is shown in Figure 1, where the change in RH and MC for a sample of flax at 24.4°C exposed to a programmed RH change from 5–10% RH is shown, with data being captured every 20 s. The data from this adsorption isotherm was fitted to eq. (1), using the function 'expassoc' in Origin software (Originlab, Northampton, MA). As the first few data points in this curve are associated with a sample moisture content under conditions of changing RH, the characteristic times for any fit including these curves will not be representative of the material. 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. To determine the effect of removing these early data points from the curve fitting process, a sensitivity analysis was undertaken. The results from this analysis are given in Table I. The example given here is for the flax sorption curve given in Figure 1, this shows that the moisture content values associated with the fast (MC_1) and the slow (MC_2) kinetic process decrease as early data points are sequentially excluded from the curve fit, but that the characteristic times for two processes do not vary significantly in this example. It is important to note that the moisture content value at time zero (MC_0) was allowed to vary in the curve fitting routine. Curve fits were also made with the value for MC_0 fixed to the first data point, but it was found that this put to much constraint on the curve fits, resulting in significant differences in the characteristic times when data points were excluded, in some cases. As a consequence of allowing the curve fit routine to select the MC_0 value, there is some variation in MC_1 and MC_2 and this must be considered when the allocations of these moisture contents are made to processes occurring in the cell wall. Similarly, the characteristic times (t_1 and t_2) of the sorption kinetic processes are affected to a lesser extent by the exclusion of successive data points, which does have implications when determining the activation energies of the sorption kinetic processes.

TABLE I
Sensitivity Analysis Showing Variation in the PEK Fitting Parameters as the Initial Data Points are Sequentially Removed from the Fit

MC_0	MC_1	t_1	MC_2	t_2
1.152	0.191	3.578	0.663	27.477
1.170	0.175	3.259	0.659	27.153
1.196	0.158	3.320	0.650	27.213
1.226	0.142	3.741	0.637	27.594

RESULTS AND DISCUSSION

Correspondence of experimental and model isotherm

The software of the DVS apparatus is user set to terminate a sorption run and move to the next RH step, when the relative change in mass per unit time (dm/dt) falls below a predetermined for a period in excess of 10 min. This value of dm/dt is arrived at by trial and error during some preliminary runs. The ability to perform accurate kinetic curve fits allows for the possibility of calculating mass changes at infinite time for each adsorption/desorption stage and this was done for each sorption run. A typical result comparing the experimental with the model sorption isotherm is shown in Figure 2 for flax at 14.1°C. There is a very good correspondence between the experimentally determined and mathematically fitted isotherms, with deviations between the MC values at each RH seldom being more than 0.1%.

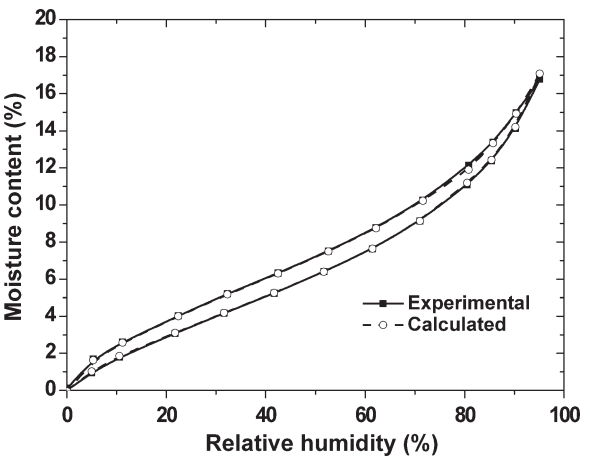

Figure 2 A comparison of the experimental sorption isotherm for flax at a temperature of 14.1°C compared with a calculated isotherm produced from the curve fitting data and based upon the sum of $MC_0 + MC_1 + MC_2$.

Modeling of the sorption isotherms

Kohler et al.[10] suggested that a possible interpretation for the two kinetic components in the sorption isotherm was to ascribe the fast process to sorption on the monolayer sorption sites associated with the cell wall OH groups, whilst the slow process could be attributed to water sorption in the cell wall nanocapillaries (polylayer water). The cell wall nanocapillaries are interconnected voids within the cell wall that are considered to be transient; in that the nanocapillary network will open up when the cell wall adsorbs moisture and collapses when moisture leaves the cell wall. In the collapsed state, the nanocapillaries are held together by hydrogen bonding between adjacent cell wall macromolecules.[15] As adsorption occurs, the cell wall expands due to the presence of water molecules occupying space inside the nanocapillaries. The volume change of plant material has been measured on an environmental scanning microscope and has also been shown to obey the PEK model.[14]

To understand the physical phenomena that may be associated with the fast and slow kinetic processes, the Hailwood–Horrobin (HH) model was used to deconvolute the adsorption isotherm into a monolayer and multilayer component. A full description of the HH model has appeared recently.[1] Example plots showing the HH monolayer and multilayer isotherms and the cumulative cell wall water content for the fast and slow kinetic processes at different relative humidities are shown in Figure 3. With flax, the water content associated with the fast kinetic process follows the multilayer sorption isotherm line up to about 50% RH at the two higher temperatures (24.4 and 34.1°C) but after this, the fast process water content is lower than the calculated multilayer sorption isotherm. With the slow sorption process meanwhile, the data and monolayer sorption line coincide until about 50% RH, but thereafter the water content associated with the slow sorption process is greater than the monolayer water isotherm line. At the lower temperature (14.1°C) the same behavior is observed, but the departure from the HH calculated isotherms occurs at a lower RH (near 20%). It can also be seen from these plots that the slow kinetics process becomes less dominant as the temperature increases. The results are consistent with the fast process being associated with the monolayer water formation and the slow process with polylayer water in the cell wall at the lower end of the hygroscopic range.

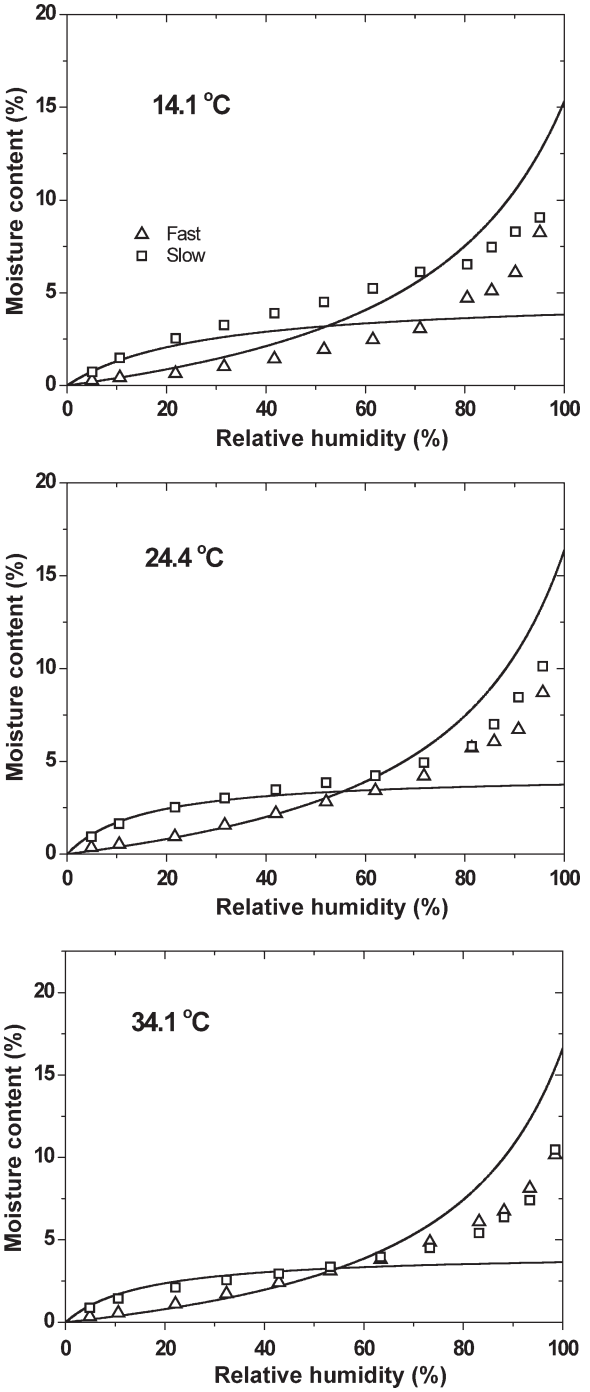

Figure 3 A comparison of the cumulative moisture contents associated with the fast and slow adsorption kinetics processes on flax fibers compared with the multilayer and monolayer curves calculated using the Hailwood and Horrobin model at different temperatures.

Hysteresis effect of the fast and slow kinetic components

With flax, the cell wall moisture contents associated with the fast kinetic component exhibited hysteresis between the adsorption and desorption cycle, whereas there was a lower hysteresis observed with the slow process over much of the RH range (Fig. 4). In the upper part of the hygroscopic range the moisture content associated with the slow process was greater for the adsorption cycle, whereas for the fast process the associated moisture content was lower

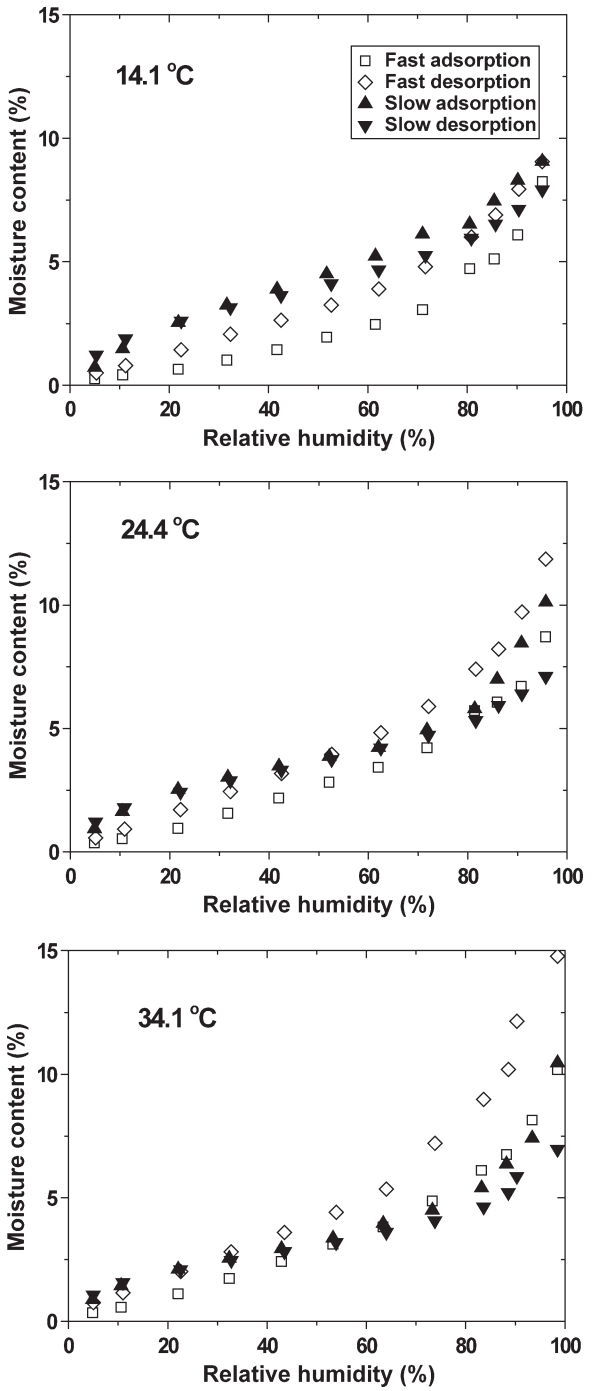

Figure 4 A comparison of the cumulative moisture contents associated with the fast and slow adsorption and desorption kinetics processes on flax fibers at different temperatures.

throughout the adsorption part of the isotherm. Kohler et al.[10] reported on the hysteresis between moisture contents at infinite time associated with the fast and slow components of the sorption isotherm of flax, finding that the hysteresis effect was not associated with one process only. They did note the discrepancy in the MC associated with the slow adsorption and desorption process at the higher RH levels, which was attributed to the presence of 'extra water'. However, they did not attribute this extra water to any physical effect. This extra water is manifested as an upturn in the MC curve at higher RH and can be clearly seen in these plots in differences between slow adsorption and slow desorption water in Figure 4. The reason why this occurs is not known, but it may be associated with capillary condensation processes at these high levels of RH. Other points to note are the generally open nature of the hysteresis loops in most of the graphs and that hysteresis is predominantly associated with fast kinetic process.

Activation energies associated with the fast and slow kinetic components

The reciprocal of the characteristic times for the two kinetic processes represents a rate constant for that process. The rate constants for the two processes at different temperatures can then be used to determine activation energies for these processes by using the well known Arrhenius relationship. The results obtained are given in Figure 5. The relative accuracy of the data is indicated by including standard deviations in the plots of activation energy against RH. The accuracy of the fits was compromised by a number of factors. The temperature range, over which the kinetic data was obtained was within the operating range of the instrument (between 10°C to 40°C). There are also errors associated with the determination of t_1 and t_2, which have been mentioned already. Finally, as the gradient of the Arrhenius plot approaches zero, the scatter of the rate constant data can result in very high errors. Nonetheless, although the experiment was suboptimal, some useful and indicative data was obtained and this is the first report of sorption kinetics activation energies for plant material. A number of remarks can be made about the data presented, where the errors are low enough to place confidence in the activation energies obtained. In the case of Figure 5(a–d) there is a clear trend towards lower activation energies at higher RH values. The data set is rather limited and further studies are necessary before definitive conclusions can be drawn, but some tentative statements can be made based upon this study.

In Figure 5(d) (slow desorption process), the activation energy associated with the final desorption step is over 50 kJ $mol^{-1,}$ much higher than those found for the other processes, which have values of 30–40 kJ mol^{-1} at lower RH values. With the exception of the final desorption step of Figure 5(d), the magnitude of the activation energy for the sorption process at lower cell wall moisture content is of the same order as the energy of the hydrogen bond, indicating the important role of hydrogen bond

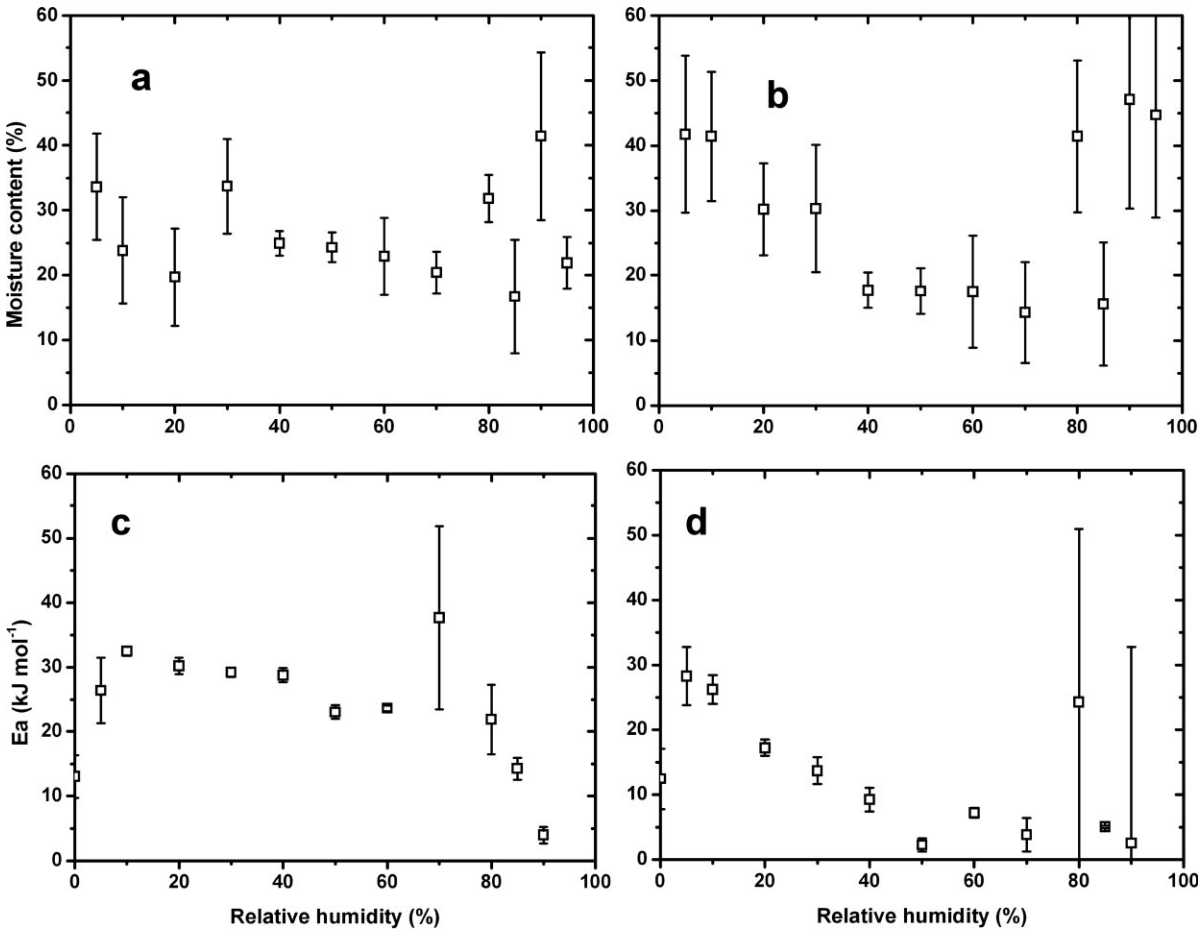

Figure 5 Activation energies for the fast adsorption (a), slow adsorption (b), fast desorption (c), and slow desorption (d) kinetics processes for flax at different relative humidities.

breaking and creation during the sorption process. The reduction in activation energy at higher RH values may be due to the presence of a much higher proportion of water in the cell wall microcapillaries that is not immediately associated with the macromolecular OH content. This results in a much reduced energy barrier to transport processes within the cell wall, indicating that the diffusion processes are no longer rate limited by hydrogen bond breaking or formation processes. Only one other study of the activation energy for the sorption of water vapor has been reported in the literature and this is for adsorption onto and desorption from carbon. The sorption kinetics was accurately described in this case as a single exponential process.[16] The results from the reported study of water on carbon gave activation energies no higher than 40 kJ mol^{-1}, reducing at higher RH values, but also at lower RH values in addition (the latter result not being found in the work reported herein. The data obtained in the experiments on plant material give activation energies comparable with this, the only known other study investigating the activation energies associated with the sorption kinetics. An increase in activation energy was attributed to an increase in the resistance of diffusion through pores in the substrate, and a subsequent reduction in E_a to the complete filling of these pores by water molecules, thereby facilitating transport. A similar mechanism is proposed here, except that any energy barrier to diffusion in the cell wall is here attributed to a rate determining step involving hydrogen bond formation/breaking. The bond breaking process occurring during the opening up of the nanocapillaries has also been referred to as the 'zipper' model.[17]

Hysteresis and the PEK model

In a previous article a model for sorption hysteresis based upon adsorption and desorption processes on glassy solids below the glass transition temperature was presented.[1] 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 nanocapillaries to accommodate the water molecules, whereas during desorption, the

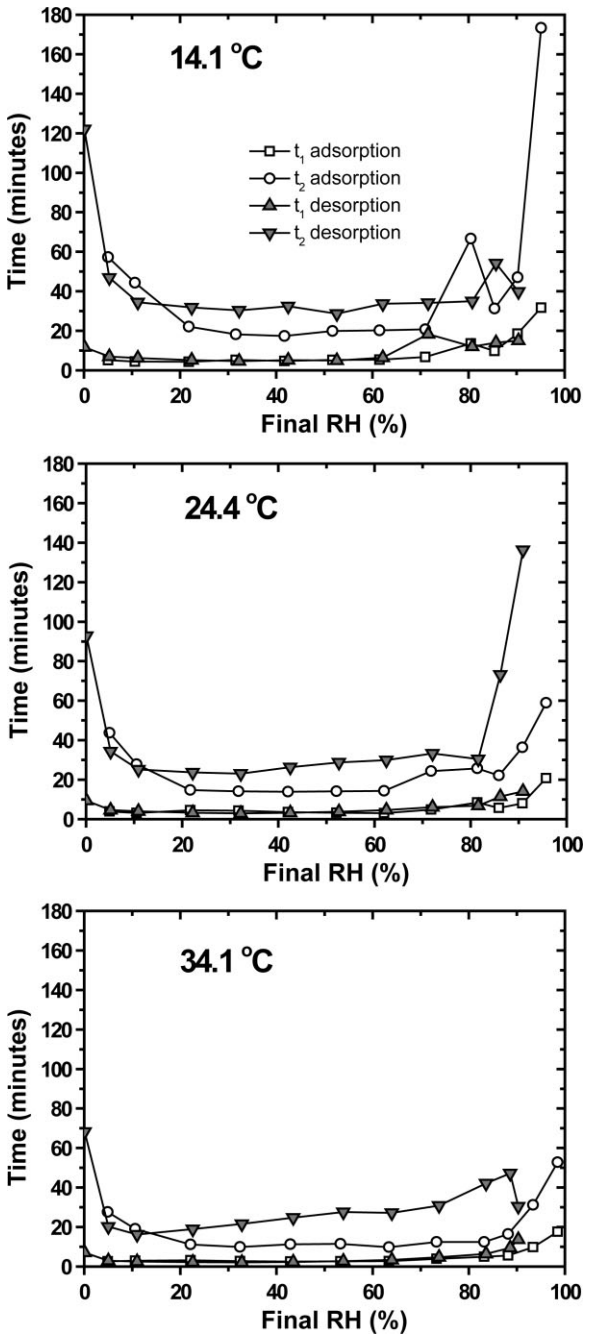

Figure 6 Plots showing the variation in characteristic times for the fast and slow processes for flax at different temperatures.

matrix responds with the collapse of these nanocapillaries 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 if it is the rate limiting step, there will be a connection through to the sorption kinetics observed on macroscopic time scales. There are certainly differences observed in the characteristic times observed for the adsorption and desorption processes, as is shown in Figure 6 for flax at different temperatures.

The characteristic time is invariably longer for the slow desorption compared with the slow adsorption processes, which shows that there is a lack of symmetry between the adsorption and desorption that presumably has its origin in the micromechanical behavior of the cell wall in the presence of moisture. There is however, no significant difference between the adsorption and desorption characteristic times with the fast kinetic processes with any of the species studied, which was also found by Kohler et al.[10] 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. If this is the explanation, then it is interesting to note that the hysteresis effect in terms of the allocation of moisture contents at equilibrium is more closely associated with the fast kinetic process rather than the slow process.

CONCLUSIONS

The adsorption of water vapor into and desorption out of the cell wall of flax fibers has been shown to be accurately described by the PEKs model. Activation energies have been determined for the fast and slow adsorption and desorption processes, which are of the order of the hydrogen bond at low cell wall moisture contents (the final desorption step of the slow process being an exception). With the exception of the slow adsorption process there is a clear reducing trend in the activation energy as the cell wall moisture content increases. Such behavior is consistent with a model in which cell wall nanocapillaries are held shut by hydrogen bonding, with these H-bonding networks decoupling in the presence of adsorbed moisture. The fast adsorption process appears to correlate with the formation of monolayer water in the cell wall at lower RH values. Hysteresis between the moisture contents is found predominantly in the fast sorption process, whereas only the characteristic times of the slow process exhibit differences between adsorption and desorption.

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