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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?

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Abstract In a previous article, the sorption kinetics' properties of a range of natural fibres were reported. Analysis of the sorption kinetics was made using the parallel exponential kinetics (PEK) model, and it was argued that the rate limiting step of the sorption process was determined by substrate swelling rather than being diffusion limited. The PEK model divides the sorption kinetics curve into two first-order kinetics processes (fast and slow) but there is as yet no generally accepted explanation of what these two processes represent. In this article, the PEK parameters for sorption have been further evaluated in terms of two Kelvin–Voigt elements arranged in series. The force constant in the spring of each Kelvin–Voigt elements determines the equilibrium moisture content for each of the processes, whereas the viscosity of the dashpot is represented by the time constant for each process. Determination of interfibrillar matrix modulus using the Kelvin–Voigt model gives values that are in line with what would be predicted, giving credence to this interpretation of the sorption kinetics. Possible interpretations of the fast and slow kinetics processes are discussed.

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Introduction

In a previous article [1], the sorption behaviour of a range of natural fibres cotton (*Gossypium barbadense*), flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), jute (*Corchorus capsularis*), sisal (*Agave sisalana*) and Whatman Grade No. 4 cellulose filter paper was reported upon. The sorption kinetics behaviour was determined by the use of a dynamic vapour sorption apparatus and the resulting kinetic curves were analysed using the parallel exponential kinetics (PEK) model. The PEK model has a double exponential form (Eq. 1):

$$\mathrm{MC} = \mathrm{MC}_0 + \mathrm{MC}_1[1 - \exp(-t/t_1)] + \mathrm{MC}_2[1 - \exp(-t/t_2)] \qquad (1)$$

where MC is the moisture content at time t of exposure of the sample to a constant relative humidity (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 $\{\mathrm{MC}_1[1 - \exp(-t/t_1)]\}$ and a slow $\{\mathrm{MC}_2[1 - \exp(-t/t_2)]\}$ 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. In the previous article published in this journal, it was argued that the sorption kinetics was determined by the rate of swelling of the cellular matrix [1]. The objective of this article is to further develop this interpretation of the PEK model. It is well known that the time-dependent mechanical properties of the cell wall of wood are appropriately described by viscoelastic models composed of Kelvin–Voigt and Maxwellian elements [2]. In papers submitted elsewhere, the sorption kinetics of wood flour has been interpreted using Kelvin–Voigt elements and values for both the modulus and viscosity of the intermicrofibrillar matrix of the wood cell wall have been derived which appear reasonable [3, 4]. This interpretation is herein extended to the sorption behaviour of plant fibres.

The fast and slow components of the PEK equation have a mathematical form that is identical with that describing the dynamic response of a Kelvin–Voigt element when subjected to an instantaneous stress increase (σ_0):

$$\varepsilon = (\sigma_0/E)[1 - \exp(-t/\varphi)] \tag{2}$$

where ε is the strain at time t, E is the elastic modulus and φ is a time constant which is defined as the ratio η/E, where η is the viscosity [5]. In the case of a plant fibre subjected to a change in RH, there is a change in the swelling pressure (Π—equivalent to σ_0) exerted within the cell wall when the atmospheric water vapour pressure is raised from an initial value p_i to a final value p_f given in Eq. 3 [6]:

$$\Pi = -(\rho/M)RT \cdot \ln(p_\mathrm{i}/p_\mathrm{f}) \tag{3}$$

where ρ is the density and M is the molecular weight of water, R is the gas constant and T is the isotherm temperature in kelvin. In the model described herein, the strain of the system is assumed to be equivalent to the volume change of the cell wall as a result of water vapour adsorption or desorption. This volume change is further assumed to be linearly related to the change in the mass fraction of the water present in the cell wall. The appropriate mechanical analogue comprises of two Kelvin–Voigt elements arranged in series (Fig. 1) with E_1, E_2 being the moduli associated with the fast and slow processes, respectively, and η_1 and η_2 being the equivalent matrix viscosities. It should be noted that although the first-order kinetics is also displayed by Maxwellian elements, only the use of Kelvin–Voigt elements is appropriate since there is no permanent change in cell wall volume as a result of water vapour adsorption or desorption.

Materials and methods

The natural agrofibres, such as cotton (*G. barbadense*), flax (*L. usitatissimum*), hemp (*C. sativa*) and jute (*C. capsularis*), were supplied by the BioComposites Centre, Bangor, Gwynedd, UK. Sisal (*A. sisalana*) was supplied by CSIR Materials Science and Manufacturing, Nonwovens and Composites Group, Port Elizabeth, South Africa. Filter paper (Whatman Grade No. 4) purchased from Fisher Scientific UK Ltd. (Leicestershire, UK) was used as a 'pure' cellulosic fibre reference (referred to as 'filpa' in this context). All the fibres were used as-received. A full description of the experimental procedure for determining the sorption kinetics and the analysis of the kinetics curves has been given in [1].

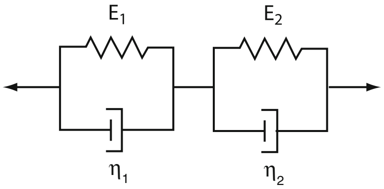


Fig. 1 The two Kelvin–Voigt elements in series related to the fast (E_1, η_1) and slow (E_2, η_2) sorption processes

Results and discussion

The magnitudes of the moisture contents associated with the fast (MC_1) and slow (MC_2) sorption processes under adsorption and desorption conditions are shown in Fig. 2. It should be noted that, in this and all other figures in this article, the RH values are the user-set values and refer to the final RH for adsorption and the initial RH for desorption. It was previously described that the determination of these parameters does involve some error and this needs to be taken account of when analysing the data [1]. The distribution of water between the fast and slow sorption processes is approximately equal with most of the fibres studied, except at the extreme ends of the hygroscopic range. In all cases, the fast process has a higher allocation of water (MC_1) during the later adsorption steps, although the point where this occurs varies with the fibre type studied. Similarly, during the initial desorption step (from 95% RH) there is a greater loss of water allocated to the fast rather than the slow process. It was also noted in [1] that the sorption hysteresis effect was almost entirely attributable to the differences in the moisture content increment (during adsorption) and decrement (desorption) occurring at the highest end of the hygroscopic range. This represents the lower change in moisture content that occurs when the desorption curve 'scans' across the region between the adsorption and desorption boundary curves [1]. The behaviour noted with the various fibres in this study can broadly be divided into those where the change in moisture content is mostly due to the differences between the fast sorption processes (cotton, filpa, jute, sisal) and where it is primarily due to differences in the slow sorption processes (hemp and flax). The reasons for this variation in behaviour are not known at the present time. Kohler et al. [7] attributed the fast and slow processes to the related sorption sites and noted that with flax fibres there was less water desorbed from slow sites than had been adsorbed, as shown in Fig. 2. This was interpreted as water that had been adsorbed at the slow sites subsequently being stored at newly generated fast sites and this was termed 'extra water'. However, interpretation of the kinetics data in terms of matrix relaxation processes does

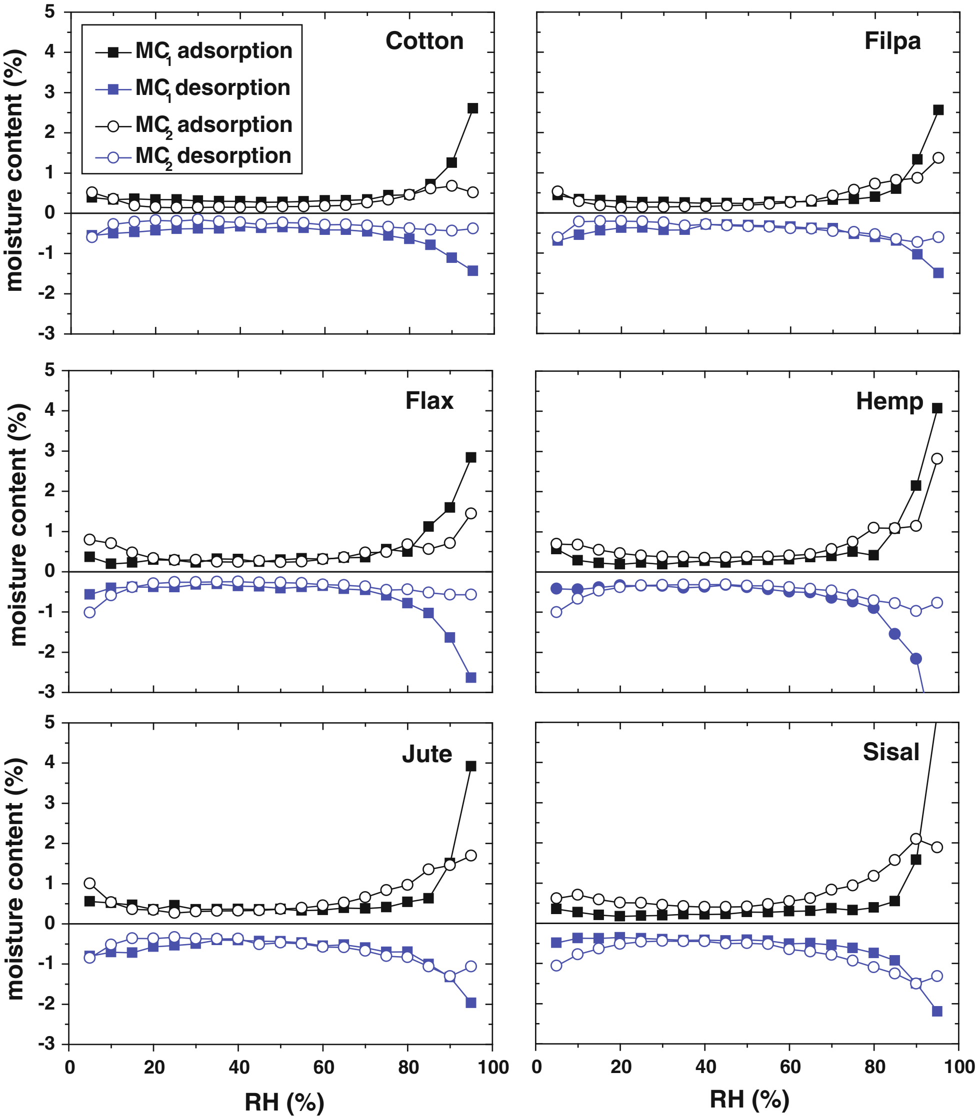


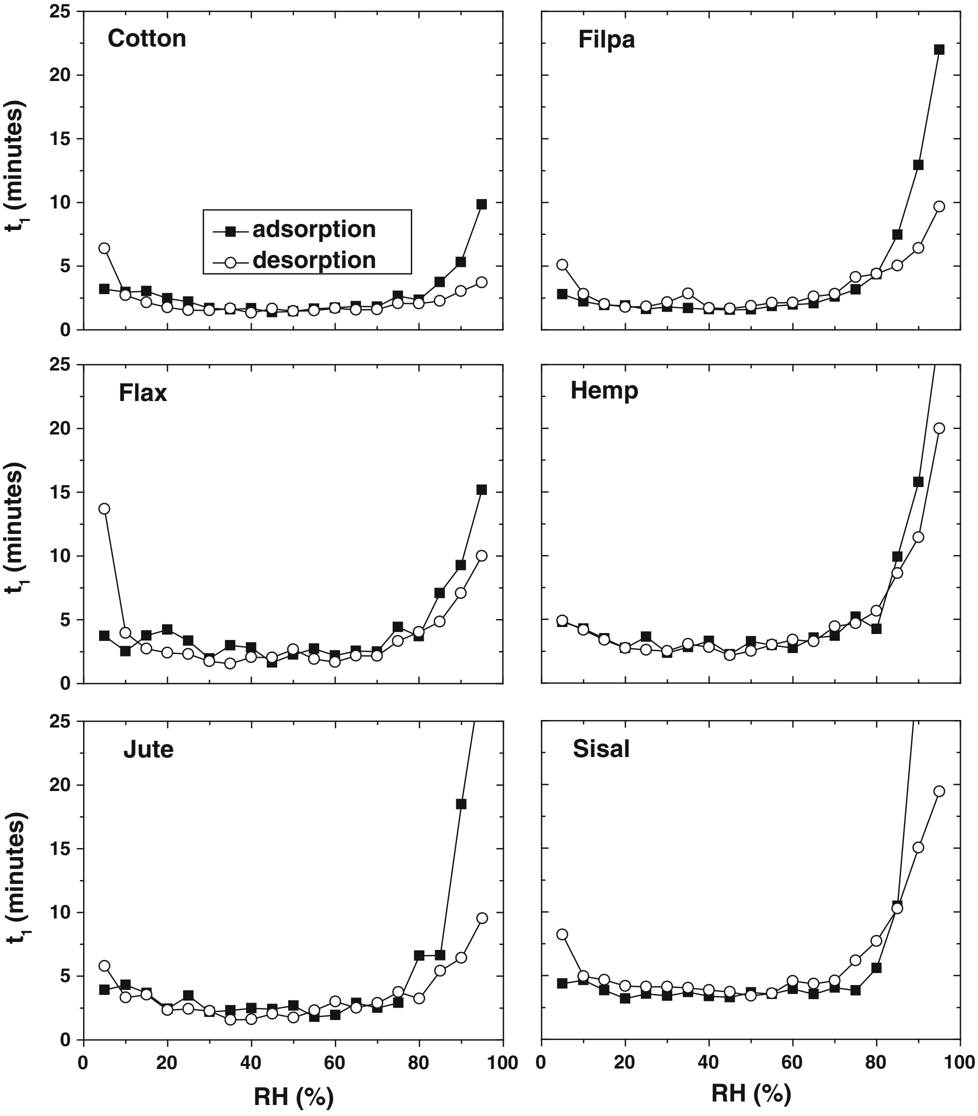
Fig. 2 Differences in moisture content at infinite time of exposure with RH for the fast (MC_1) and slow (MC_2) adsorption and desorption processes (final RH for adsorption and initial RH for desorption)

not require the sorbed water to be assigned to specific sites and there is therefore no significance in the presence of this ‘extra water’ at the top end of the hygroscopic range.

Variations in characteristic times with RH for the different fibres are shown in Fig. 3 (fast process) and Fig. 4 (slow process). Clear differences are observed when comparing the characteristic times linked to adsorption and desorption. With t_1 (fast process) the values for adsorption and desorption are comparable, except at the top end of the hygroscopic range where the characteristic times associated with adsorption are higher and at the lower end where t_1 for desorption is greater (hemp excepted). This is contrasted by the behaviour exhibited by the slow process characteristic times (t_2) where the t_2 values are higher throughout the hygroscopic range except when approaching 95% RH. This indicates that the hysteresis effect is more closely associated with the slow sorption kinetics process.

By applying the sorption kinetic parameters to the Kelvin–Voigt model representing the viscoelastic response of the cell wall matrix, it is possible to derive values for the matrix modulus and viscosity. This has been done for the matrix modulus associated with the fast process (E_1) and slow process (E_2) and these data are presented in Figs. 5 and 6, respectively. Values for the fast and slow moduli are of the order of 10 to 30 GPa at the low cell wall moisture contents associated with the bottom end of the hygroscopic range. These moduli decrease to very low values at the higher RH range, as would be predicted for a matrix that is being plasticized by the presence of water. Important differences are noted between the adsorption and desorption moduli throughout the hygroscopic range tested. At lower

Fig. 3 Variation in the characteristic time for the fast adsorption and desorption processes versus RH



RH values (the RH range varying between fibres) the E_1 moduli for adsorption are higher than those for desorption. With the E_2 moduli only cotton and filpa exhibit higher modulus values for adsorption, with the other fibres essentially showing no differences except at the lowest RH range.

These modulus values at low RH are comparable with tensile modulus properties reported in the literature for these fibres [8]. However, flax and hemp have much higher literature tensile modulus values than cotton and sisal, which is not reflected in the results obtained herein. Given that the expansion and contraction of the cell wall takes place within the intermicrofibrillar matrix, it seems reasonable to assume that the modulus values obtained are dominated by those associated with the matrix polymers, e.g. pectin, hemicellulose, lignin. Unfortunately, there is little in the way of direct measurement of the mechanical properties of these substances reported in the scientific literature.

Salmén [9] has discussed the subject of wood polymer elastic constants at some length. Although elastic modulus values for isolated lignin and hemicellulose have been determined, there is no reason to suppose that this is a true measure of their behaviour within the cell wall. Salmén considers that hemicelluloses may have a maximum modulus value in the dry cell wall of around 2 GPa, falling to 20 MPa under moist conditions and that lignin may exhibit a maximum modulus of about 2 GPa under both moist and dry conditions. A dry modulus value for isolated xylan of 8 GPa has been reported [10] but as already noted this is unlikely to be representative of behaviour within the cell wall. Values for isolated, dry, isotropic lignin have been reported from 4 to 7 GPa [11, 12] but the same considerations apply. Assuming that these reported values are

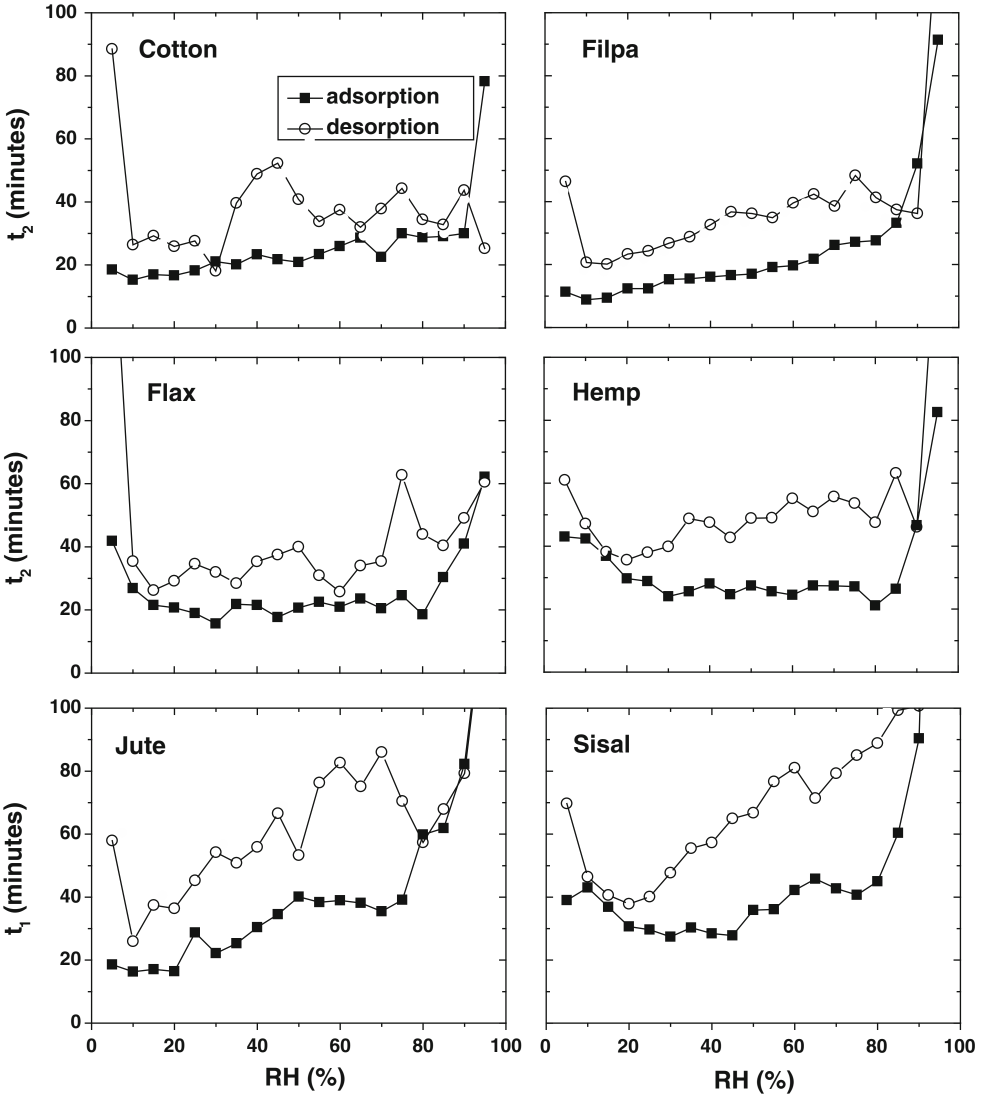


Fig. 4 Variation in the characteristic time for the fast adsorption and desorption processes versus RH

representative, it is apparent that the modulus values calculated using the Kelvin–Voigt model in this study for the dry cell wall are considerably higher at low cell wall MC. This implies that the moduli also have a contribution from the deformation of the cell wall microfibrils. Although Salmén quotes axial microfibrillar modulus values of 134 GPa, the off-axis modulus is given as 27.2 GPa, but is not affected by moisture [8]. Thus, the dry modulus values calculated using the Kelvin–Voigt model in this study appear to be of the order expected given contributions both from the matrix and microfibrils, but in this case why should the microfibrillar contribution decrease at higher cell wall MC? The explanation may lie in consideration of the geometry of the microfibrils within the cell wall. For example, it has been demonstrated with jute fibres that water adsorption and desorption result in a rotation of the fibre about the long axis as well as an increase in cell wall volume [13]. This indicates that the distortion of the microfibrils occurring as a result of cell wall volume changes does not involve a simple off-axis bending motion. It may be that verification of the applicability of the Kelvin–Voigt interpretation of the sorption kinetics could be obtained by nano-indentation methods. The authors of this study are not aware of any such studies with plant fibres, but there have been investigations of the properties of the wood cell wall. Nanoindentation methods have given values for the modulus of the order 13–21 GPa for the cell wall of spruce [14–16] comparable with the low MC modulus values reported herein.

Differences in behaviour between fibres are also found when the matrix viscosities are examined for the fast process, as shown in Fig. 7 (η_1) and slow process as illustrated in Fig. 8 (η_2). Cotton and filpa show very little difference in η_1 values between adsorption and desorption, whereas with the other fibres η_1 values for adsorption exceed those

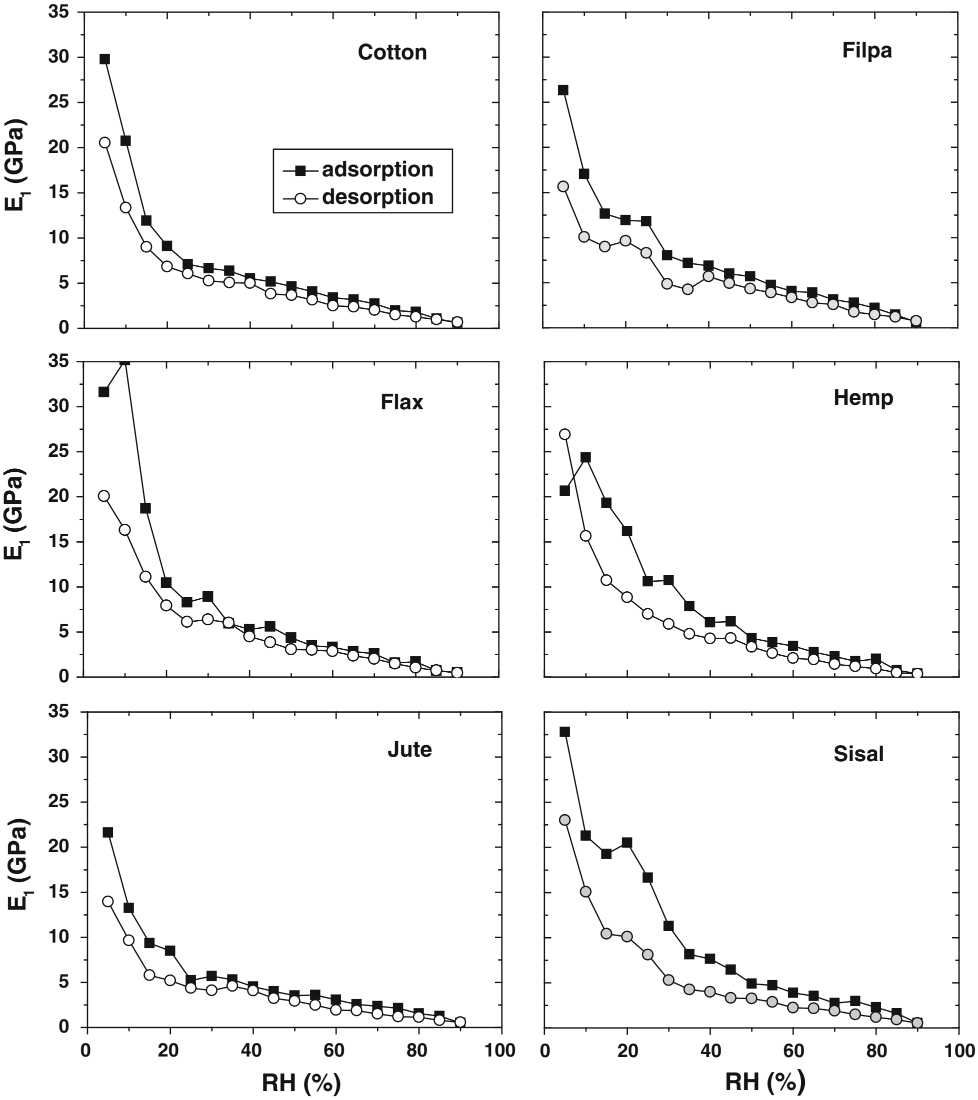


Fig. 5 Variation in the interfibrillar matrix modulus against RH for the fast adsorption and desorption processes

for desorption (Fig. 7). For the viscosities associated with the slow process, the η_2 values are higher for desorption, although there are differences in the behaviour between the fibres studied. Since the fast and slow processes have not been assigned to specific physical properties, it is not at this stage possible to comment upon the significance of such differences. What is clear is that the viscoelastic interpretation does seem to provide an insight into the sorption process and that there are important variations in behaviour that require further study.

The adsorbed water vapour molecules exert a pressure within the cell wall leading to a dimensional change, which is equivalent to the extension of the spring in the Kelvin–Voigt model. This expansion/extension results in an increase in the free energy of the system [17]. Expansion will continue until the free energy of the system is equal to that of the water vapour molecules in the atmosphere. The spring modulus therefore defines the water content of the system at infinite time (MC_1, MC_2).

$$MC_1 = \sigma_0/E_1; \quad MC_2 = \sigma_0/E_2 \tag{4}$$

The rate at which water molecules are adsorbed or desorbed by the system is a function of the viscosity of the dashpot in the model. This viscosity is in turn related to the micro-Brownian motion of the cell wall macromolecular network. The more rapidly the matrix is able to deform, the faster the rate of water ingress or egress into or out of the cell wall. The rate of local deformation is related to the energy barrier associated with the local relaxation process and whether there is sufficient free volume to allow the relaxation process to take place. In glassy solids below the glass transition temperature (T_g) there is insufficient free volume to allow a local relaxation to take place without the cooperative motion of adjacent relaxors (a relaxor is

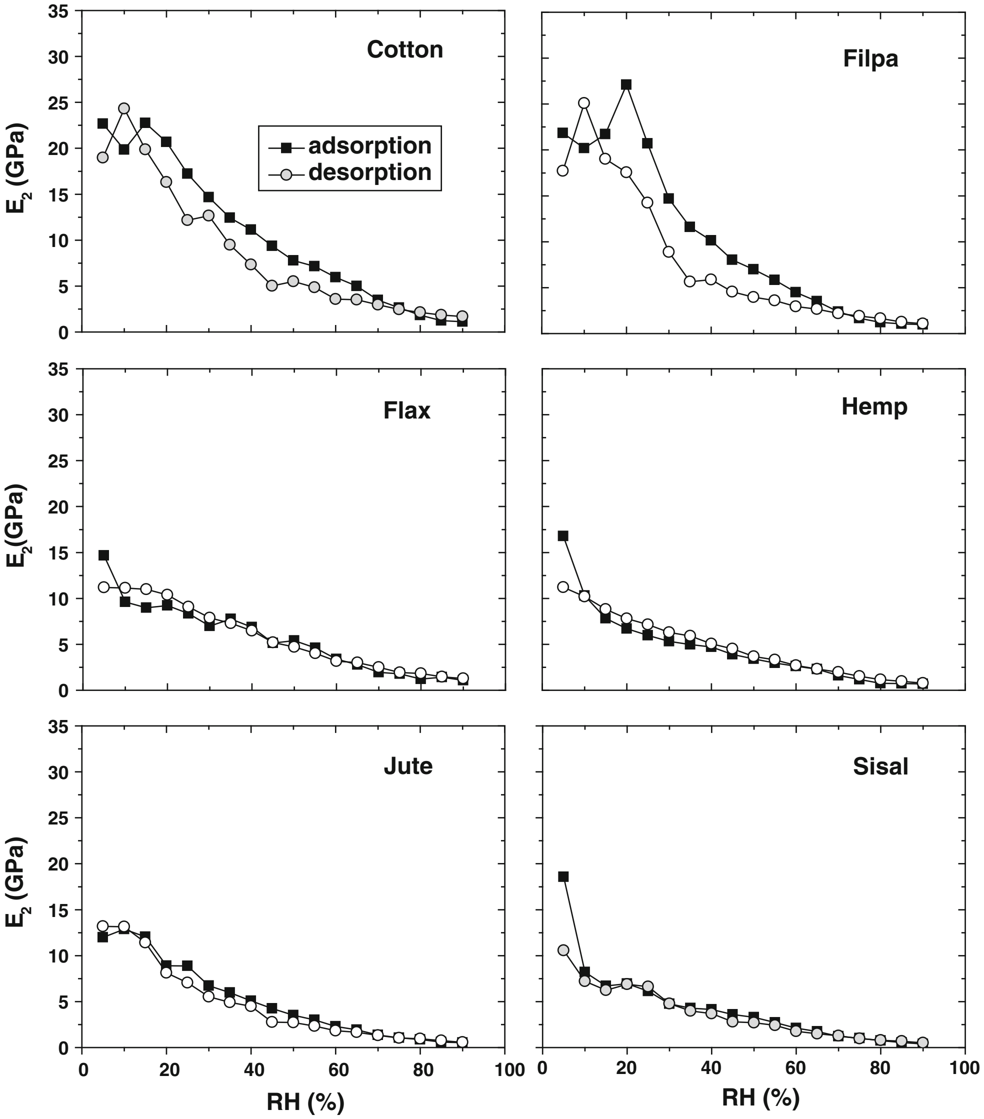


Fig. 6 Variation in the interfibrillar matrix modulus against RH for the slow adsorption and desorption processes

defined as the smallest molecular segment of relaxation in each polymeric unit). This gives rise to the concept of cooperative domains within the matrix [17–19]. As the glass transition temperature is approached, the domain size decreases until T_g is reached. At this point, the domain contains only one relaxor and there is sufficient free volume to allow for relaxation without the cooperation of neighbours.

It has previously been argued that an appropriate model describing sorption hysteresis in plant fibres and wood is related to the matrix response during adsorption/desorption [20]. In essence, the model describes the creation of nanopores in the matrix during the adsorption step and the collapse of these nanopores during desorption [21–24]. However, below the T_g of the matrix, the matrix is unable to respond instantaneously to the ingress or egress of water molecules because of the structural rigidity of the matrix. This results in an increased nanopore volume in the matrix during desorption compared to the adsorption process, leading to an increased affinity for the water molecules. The time scale of the nanopore formation/annihilation processes is molecular (i.e. of the order of 10^{-10} s). By invoking the concept of cooperative relaxation in polymer systems below T_g, Matsuoka [17] is able to show that relaxation times of the order of minutes can be observed as the size of the cooperative domain increases (i.e. as the temperature decreases). This suggests that there should be a link between the hysteresis effect and the relaxation times observed in the sorption process. Larger values of the sorption characteristic time should presumably be found in

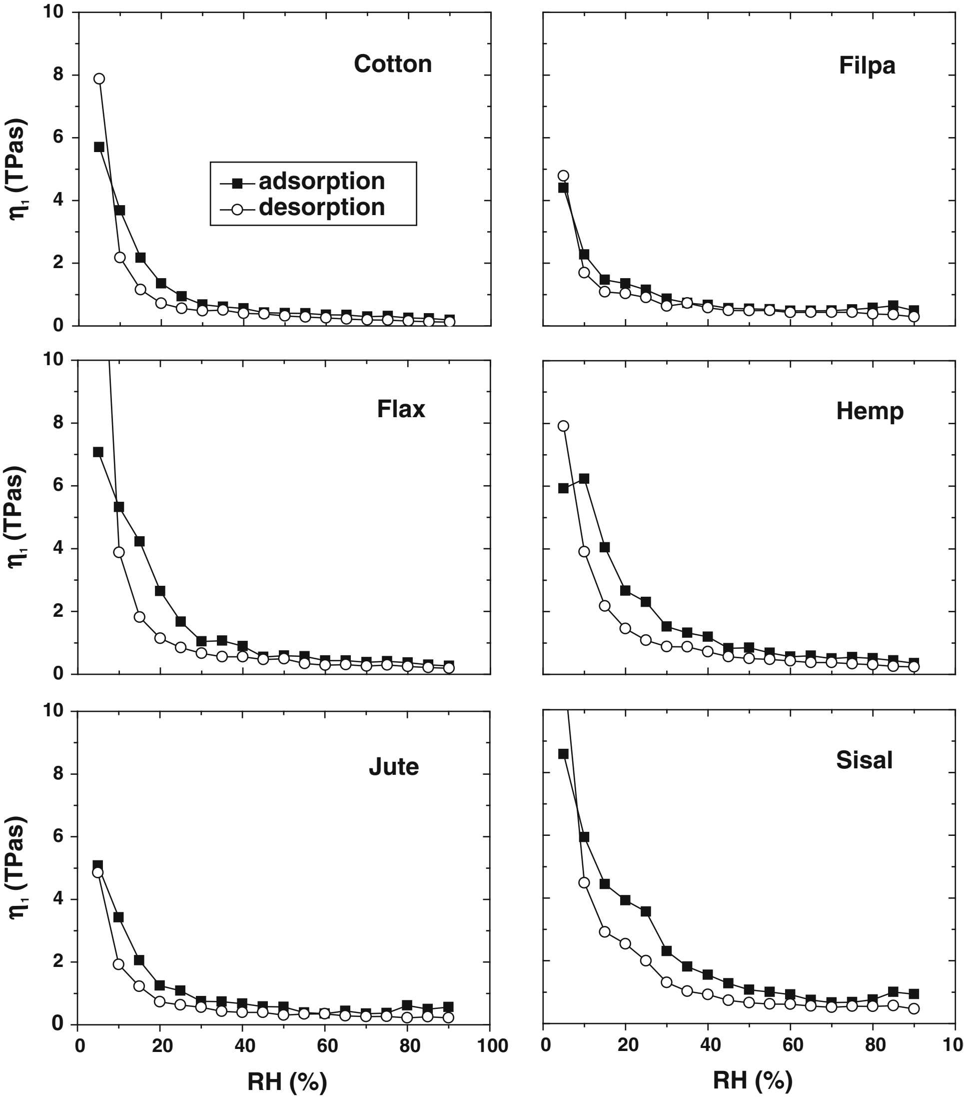


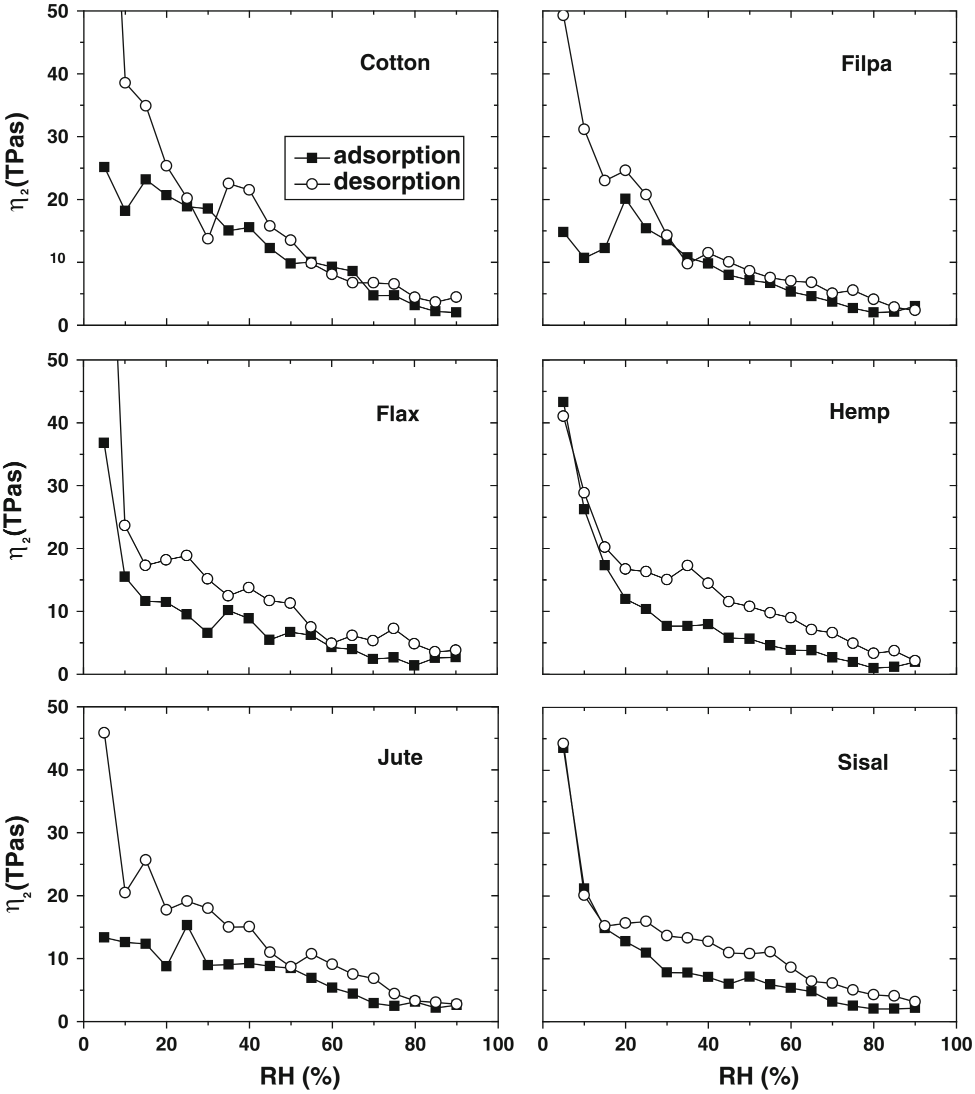
Fig. 7 Variation in the interfibrillar matrix viscosity against RH for the fast adsorption and desorption processes

samples exhibiting greater hysteresis. Both sisal and jute exhibit higher t_2 values for adsorption and desorption compared with the other fibres and also exhibit a larger hysteresis [1]; however, filpa, which shows greater hysteresis than hemp, does not exhibit higher t_2 values. It is apparent that the characteristic time data are not amenable to such a simplistic interpretation. However, with the sorption phenomena, the characteristic time values are dependent not only upon matrix relaxation processes (i.e. a viscous component), but also upon the change in cell wall MC (i.e. matrix stiffness).

There are certainly differences in both matrix modulus and viscosity with fibre type, as can be seen from Figs. 7 and 8, but which can be seen much more clearly in Fig. 9 (modulus) and Fig. 10 (viscosity) where the data for the different fibre types are overlaid (note the change in scale). Although there is no clear variation related to cell wall composition [1] for the E_1 modulus, this is not the case with E_2 modulus where both cotton and filpa exhibit higher values compared with the other fibre types throughout the hygroscopic range. This may be an indication that the slow sorption process is more susceptible to changes in cell wall composition than the fast process. Regarding viscosity (Fig. 10), the fast process η_1 values of sisal and hemp are higher than all other fibre types below 50% RH, but under desorption conditions the values for filpa are higher than hemp above 50% RH. Given the hysteresis properties noted for these fibres previously [1], this may indicate a link between cell wall matrix processes and hysteresis. There are also differences in η_2 values for the different fibre types but they do not form any discernable pattern.

Does the Kelvin–Voigt interpretation of the sorption kinetics behaviour provide any insight into the nature of the

Fig. 8 Variation in the interfibrillar matrix viscosity against RH for the slow adsorption and desorption processes



fast and slow sorption processes? Bi-exponential relaxation processes in polymers are invariably associated with two component systems, such as copolymers, or with side and main chain relaxations [25–31]. One potential interpretation is to assign the two processes to matrix relaxation and microfibril relaxation, but this is probably being simplistic. At this time, it is not possible to assign the fast and slow processes to specific relaxation events. However, it is important to note that this type of sorption behaviour is not solely restricted to sorption kinetics with plant fibres and appears to be widely found where substrate dimensional change is associated with sorption. The apparent universality of this behaviour with materials of widely differing chemical compositions suggests that an explanation relying on two specific matrix components is unlikely to be applicable. Investigation is ongoing to explore this phenomenon further.

Conclusions

This study has shown that interpretation of the sorption kinetics data for water sorption with various plant fibres yields values for cell wall modulus that are credible and which decrease with cell wall moisture content as would be predicted. Given that the values are dominated by matrix properties, it is not surprising that the modulus values decrease much more rapidly with cell wall moisture content than those derived from mechanical measurements by externally applied stresses. In addition, the values obtained at low cell wall moisture content appear to indicate that the cell wall microfibrils influence the sorption kinetic behaviour at least in the lower part of the hygroscopic range. Values for cell wall viscosity show similar behaviour although there is no appropriate data in the literature with which to compare. A link between the sorption kinetic

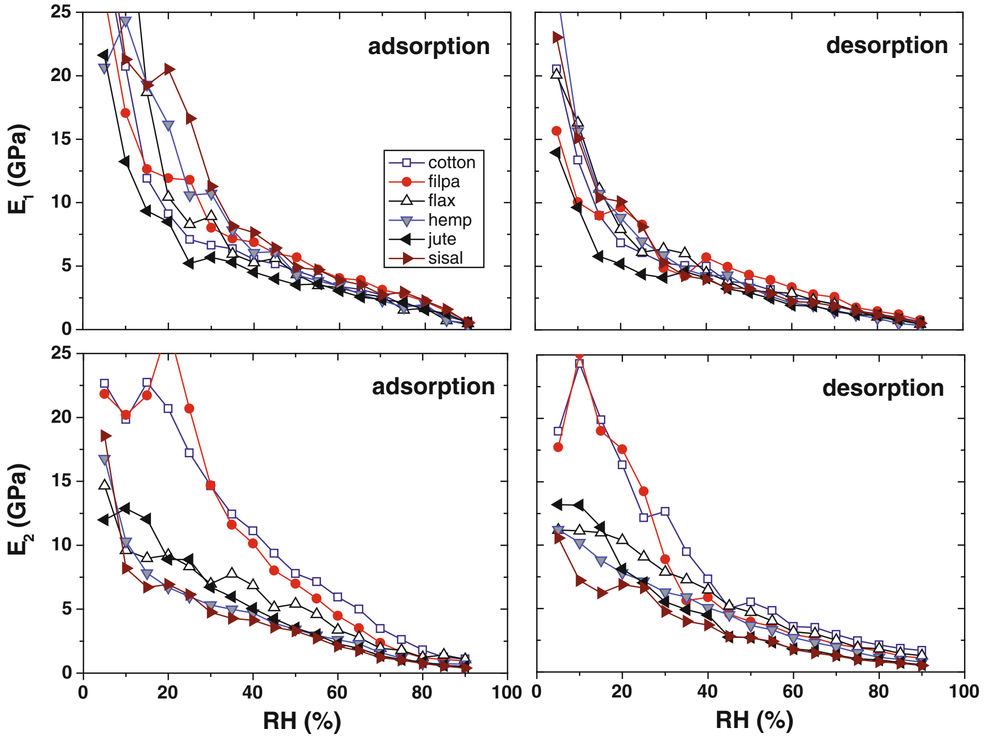


Fig. 9 Variation in the interfibrillar matrix modulus against RH for the two adsorption and desorption processes showing comparisons between the different fibre types

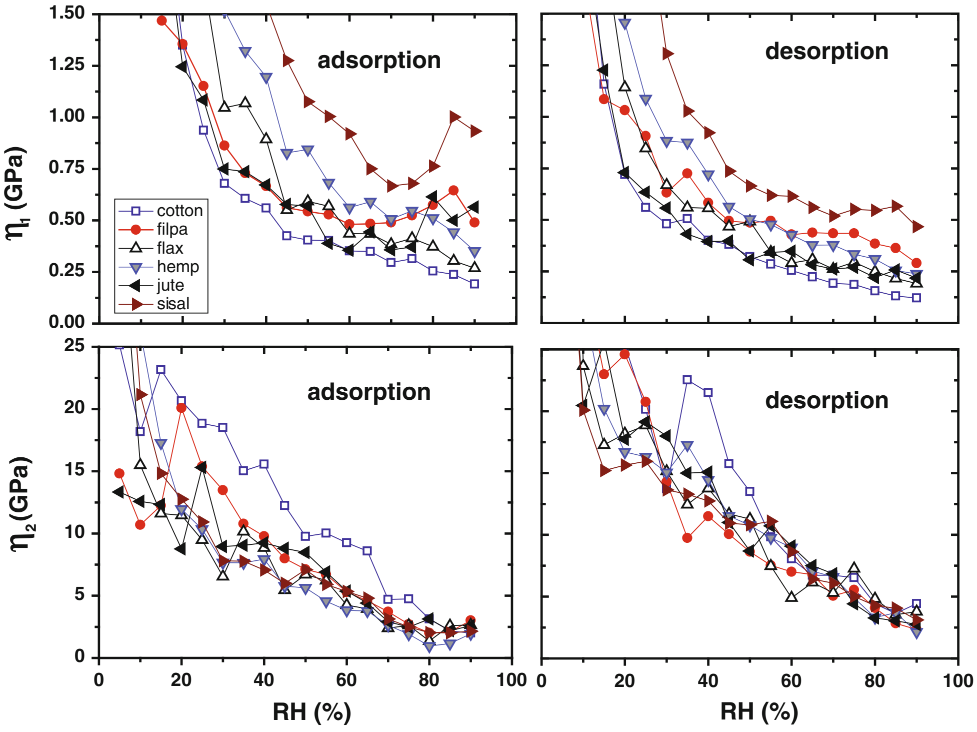


Fig. 10 Variation in the interfibrillar matrix viscosity against RH for the two adsorption and desorption processes showing comparisons between the different fibre types

behaviour and hysteresis properties is suggested, although this is not simply interpreted by referring to the characteristic times for the sorption process.

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