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The dynamic water vapour sorption behaviour of natural fibres and kinetic analysis using the parallel exponential kinetics model

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Abstract Hygroscopic behaviour is an inherent characteristic of natural fibres which can influence their applications as textile fabrics and composite reinforcements. In this study, the water vapour sorption kinetic properties of cotton, filter paper, flax, hemp, jute, and sisal fibres were determined using a dynamic vapour sorption apparatus and the results were analyzed by use of a parallel exponential kinetics (PEK) model. With all of the fibres tested, the magnitude of the sorption hysteresis observed varied, but it was always greatest at the higher end of the hygroscopic range. Flax and sisal fibres displayed the lowest and highest total hysteresis, respectively. The PEK model, which is comprised of fast and slow sorption components, exhibited hysteresis in terms of mass for both processes between the adsorption and desorption isotherm. The hysteresis derived from the slow sorption process was less than from the fast process for all tested fibres. The fast processes for cotton and filter paper dominated the isotherm process; however, the hemp and sisal fibres displayed a dominant slow process in the isotherm run. The characteristic time for the fast sorption process did not vary between adsorption and desorption, except at the top end of the hygroscopic range. The characteristic time for the slow process was invariably larger for the desorption process. The physical interpretation of the PEK model is discussed.

Introduction

Natural fibres are extensively used in the textile industries for fabric making and are also used as fillers or reinforcements in composite materials. These fibres can be classified according to where in the plant they originate: leaf such as sisal, banana, palm, pineapple; seed such as cotton; bast such as jute, hemp, flax; fruit such as coir, oil palm, kapok; grass such as bamboo, bagasse; and stalk such as straw [1]. The fibres most commonly used are from the bast and leaf, and are mainly produced in Asia, Africa, and America.

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Natural fibres are hygroscopic materials because their cell walls contain abundant water sorption sites (hydroxyl groups) and because they can swell to accommodate the sorbed water in the cell wall. In the textile industry, fabrics made from natural fibres vary in their ability to absorb perspiration, transport moisture, and adjust the relative humidity (RH) in the clothing microclimate. The sorption behaviour of garments is closely related to the perception of comfort [2–5]. Used as fillers or reinforcements in polymer matrix composites, these renewable and biodegradable natural fibres can offer the resulting composites many claimed advantages due to high specific strength, ease of disposal, and potentially reduced environmental impact [6]. These hydrophilic fibres can be blended well with many thermoset matrices, but they are much less compatible with non-polar thermoplastics thereby resulting in insufficient interfacial adhesion [7, 8]. Although encapsulation of natural fibres by polymer matrices can decelerate the rate of water sorption compared with natural fibres alone, long-term outdoor exposure can also produce severe warping, mould growth, fungal decay, and strength loss [9–15]. These issues are mostly associated with the moisture adsorbed by the hygroscopic natural fibres and subsequently entrapped by the polymer matrix. Consequently, it is of importance to understand the moisture sorption behaviour of various natural fibres, thereby predicting the properties of materials containing them. Finally, there is considerable interest in using natural materials in the built environment, impelled by initiatives such as the UK Government's aspiration to have zero carbon homes being built in the UK by 2016. Natural fibres possess advantages in this respect, not only because they contain sequestered atmospheric carbon dioxide, but also because their hygroscopic behaviour can be advantageously exploited in moderating climatic extremes in the interior environment of buildings.

The interaction of water vapour with a natural fibre involves a dynamic exchange of water molecules between the atmospheric water vapour and water molecules located within the cell wall internal nanopores [16–18]. The water sorption behaviour of natural fibres is complicated due to the complex internal geometry of the cell wall and also the continuous nano-structural changes associated with the dynamic behaviour of the cell wall macromolecular components. Determining the equilibrium moisture content (EMC) of natural fibres by the gravimetric method at a given RH invariably uses saturated salt solutions as a means of evaluating the sorption properties of fibres [19–21]. More recently, a dynamic vapour sorption (DVS) technique has been used to investigate the sorption properties of different natural or regenerated cellulosic materials [22–26]. This DVS technique yields highly reproducible data and can provide accurate isotherms over a wide RH range and at different pre-set isotherm temperatures [22].

The ability of this technique to gather 'real time' data additionally allows for the analysis of the sorption kinetic behaviour of natural fibres. Previous attempts to model sorption kinetic processes have invariably utilized Fick's law on the assumption that the rate limiting step is a diffusion process, which is likely to be true for samples where the volume to surface ratio is high. But in studies of cell wall sorption processes, where single fibres or fibre bundles are used, the kinetics may not be diffusion limited and indeed it has been shown unequivocally that the sorption kinetics fits a so-called parallel exponential kinetics (PEK) model for natural fibres, regenerated cellulose fibres, microcrystalline cellulose, and some foodstuffs [26–35]. However, whilst it has been established that the PEK model is applicable, there is as yet no definitive explanation as to what the model may represent in terms of the physical behaviour of the cell wall undergoing sorption.

We have already reported on the isotherm sorption properties of cotton, flax, hemp, jute fibres using a DVS apparatus under conditions of equilibrium [22]. The DVS kinetic behaviour of flax fibre has also been presented recently [27]. In this study, for the first time a comparative study of the DVS kinetic behaviour of a wide range of natural fibres is presented and discussed. The sorption kinetics were analyzed by fitting the dynamic moisture content data using a PEK model; the fast and slow sorption processes and their separate hysteresis behaviour was also calculated and compared with those from experimental isotherms. A discussion of the physical interpretation of the PEK model is also presented.

Materials and methods

Natural fibres

The natural agrofibres, cotton (*Gossypium barbadense*), flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), and jute (*Corchorus capsularis*), were supplied courtesy of the BioComposites centre, Bangor, Gwynedd, UK. Sisal (*Agave 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) and was used as a 'pure' cellulosic fibre reference (referred to as "filpa" in the context). All the fibres were used in an as-supplied state.

Determination of dynamic water vapour sorption

Sorption isotherms of natural fibres were determined using a DVS Intrinsic apparatus (DVS, Surface Measurement Systems Ltd, London, United Kingdom) as previously reported [22]. The natural fibre was cut with a pair of scissors to short pieces measuring approximately 5 mm long and placed in a conical steel wire gauze (sample holder) which was hung in the thermostatically controlled cabinet where the pre-set RH was increased from 0 to 95% in steps of 5% in a pre-programmed sequence, before decreasing to 0% RH in the reverse order. The mass of fibres was strictly set at 5 mg in order to remove any effect of fibre mass on the sorption kinetics between the different types of fibres. The sorption processes were run at a constant temperature of 25 ±0.1 °C over the full RH range. The instrument maintained a constant target RH until the rate of sample moisture content change (dm/dt) was less than 0.002% per minute over a 10 min period. This pseudo-equilibrium condition had been previously established as giving moisture content data within 0.1% of the EMC [22]. The running time, isotherm temperature, target RH, actual RH, and sample weight were recorded throughout the isotherm run. We have previously found that the EMCs in the fibre replicates obtained with DVS apparatus are highly reproducible in the RH range of 0–80% and exhibit only minor variation in the RH range of 80–95% [22]. Accordingly, in this study only one measurement is reported for each type of natural fibre.

Kinetic analysis using PEK model

The experimental moisture content data obtained at each target RH using the DVS apparatus were curve-fitted using OriginPro 8.0 software (OriginLab Corporation, USA) to the function 'expassoc' which has a double exponential form (Eq. 1):

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

where MC is the moisture content 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 $[\mathrm{MC}_1(1 - e^{-t/t_1})]$ and a slow $[\mathrm{MC}_2(1 - e^{-t/t_2})]$ 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. The experimental data of dynamic moisture content at each RH level was curve-fitted ($R^2 > 0.99$) and the parameters of MC_0, MC_1, MC_2, t_1, and t_2 obtained as described in detail previously [22, 24, 25, 27–29]. Utilizing these given parameters, the fitted curve can be deconvoluted according to Eq. 1 into a fast process associated with moisture content (MC_1) and a slow process associated with moisture content (MC_2) at infinite time t (Fig. 1). It must be noted that the RH does not change instantaneously in the apparatus and that accordingly the first few (normally two) data points corresponding to this period of RH change must be removed from the fitting process. This has been discussed in some detail by Hill et al. [24, 27].

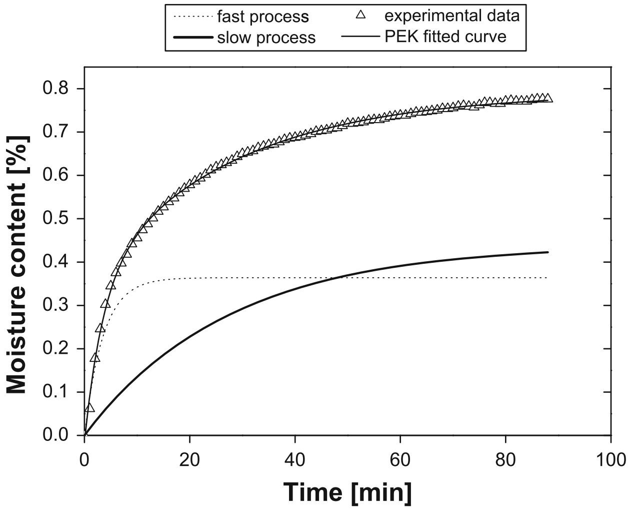

Fig. 1 Example of PEK curve fitting to experimental adsorption data (*open triangles*) of hemp fibre at 65% target RH, the fitted curves (*lines*) showing the slow and fast parallel exponential kinetic processes, and the sum of fast and slow processes

Results and discussion

Sorption dynamics of natural fibres

The response of the moisture content of a fibre sample to a change in RH in the sample chamber produced an asymptotic curve when plotted as moisture content against time, approaching the EMC after infinite time of exposure at a given RH (Fig. 2). The moisture content of the fibre gradually increased in the adsorption process or decreased

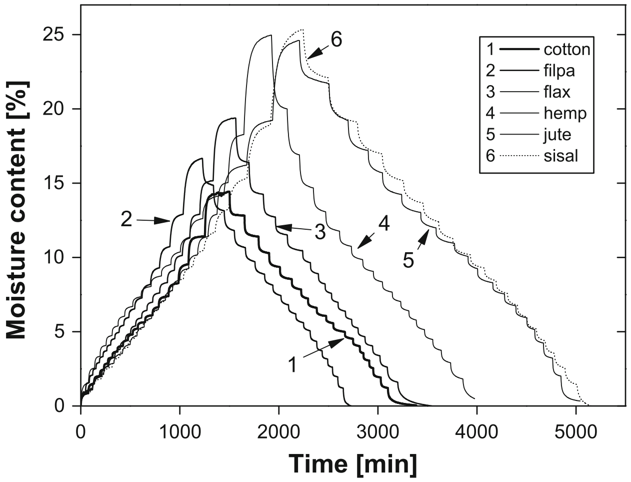

Fig. 2 Changes in moisture content of natural fibres with the variable RH levels over the time profile during isotherm runs

Table 1 Compositions and cell wall structures of natural fibres

Fibre	Classification	Main compositions (%)			Microfibril angle (°)	Fibre geometry	Reference
		Cellulose	Hemicellulose/pectin	Lignin			
Cotton	Seed	94	6	0	20–34	Single cell	[62–64]
Filpa	Wood	100	0	0	–	Single cell	[64]
Flax	Bast	81	16	3	5–7	Cell bundle	[62–67]
Hemp	Bast	74	19	4	6.2	Cell bundle	[62–64, 68, 69]
Jute	Bast	72	14	13	7–9	Cell bundle	[62–64, 70]
Sisal	Leaf	73	13	11	10–22	Cell bundle	[62, 64, 71, 72]

in the desorption process as a new target RH started, until the moisture content change was less than the defined value (0.002% min^{-1}) for 10 min, and then the RH changed to the next preset value (Fig. 2). The filter paper took the least time to run through the full isotherm sorption process; however, it took the sisal and jute fibres nearly double the time compared to the filter paper to complete the isotherm run (Fig. 2). The total running time for fibres may depend on several factors such as fibre geometrical morphology, chemical compositions, and total mass. In this study the sample mass tested has been set at the same level (5 mg) and so is not a variable in these experiments. The longer running time for sisal and jute may possibly be attributed to their larger diameter of fibre bundles and higher content of lignin, which could slow the diffusion of water molecules into the bundle interior. However, it has been clearly demonstrated here and previously reported [26–34] that the sorption kinetics is not diffusion limited and that any explanation for these differences has to be found elsewhere. In a study of the rate of water vapour sorption into wood single cell walls, Christensen found that the kinetic response was the same irrespective of the cell wall thickness [36].

Cotton fibre is a single cellular botanical entity and the cell often exhibits ribbon-like, twisted, and flattened tube being composed of the interwoven primary wall, helical winding layer and secondary wall with a closely packed parallel microfibril arrangement [37, 38]. Filter paper (Filpa) in this study is made of highly cellulosic wooden pulp. The single fibres in these pieces are arranged randomly in a plane with a thickness of 50 μm. The flax, hemp, jute, and sisal fibres are multi-cellular fibre strand (bundle) containing 10–40 elementary fibres (cells) with a diameter of approximately 100 μm. The architecture of the single cell in these fibres includes a primary and secondary cell wall network microstructure. The cotton and sisal exhibit considerably greater microfibril angles (about 20°) than the other fibres (about 6°). Pectin (above 15%) and lignin (about 3%) constitute the major non-cellulosic composition of flax and hemp fibres; however, the jute and sisal fibres present a similar amount of pectin (hemicelluloses for sisal fibre) and lignin (about 13% each) as summarized in Table 1. A small quantity of wax (around 1%) is distributed in the primary wall of the fibre cells except for filter paper. It is to be appreciated that there are considerable chemical and morphological differences between the fibre types studied making definitive interpretations of the sorption data difficult.

Apart from differences in the sorption rate, there were also differences in the EMC values exhibited by the fibres in the isotherms. At the highest RH (95%) cotton reached an EMC of 14.4%, which was lower than with the other fibres (Fig. 3). This may be explained by the fact that pure cotton is mainly composed of cellulose (about 94% by mass) with a high degree of crystallinity [39]. This results in a lower number of accessible OH groups per unit volume. The low level of inter-microfibrillar matrix material can also limit the cell wall swelling therefore reducing the moisture adsorption amount. The major constituent of the commercial filter paper (filpa) is also cellulose; however, it absorbed slightly more water vapour (16.7%) at 95% RH than the cotton fibres. A possible explanation is that the crystalline segments in filpa fibres are partly destroyed during the preparation of pulp [40–42] resulting in a

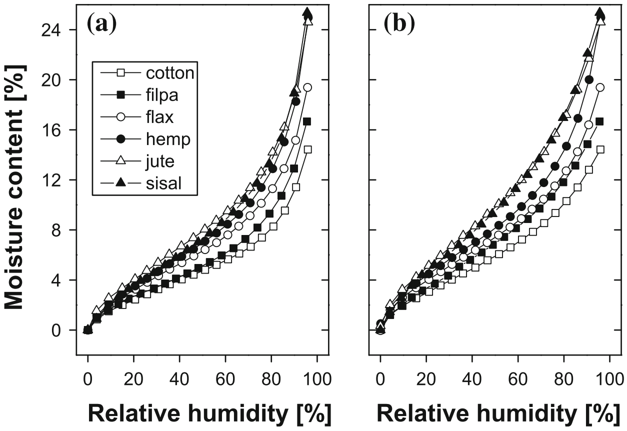

Fig. 3 Equilibrium moisture content of natural fibres in the full set RH range during the adsorption (**a**) and desorption (**b**) processes in the isothermal sorption run

relatively lower crystallinity compared to cotton fibre and hence a higher level of accessible OH and amorphous polymeric content. The EMC exhibited an ascending sequence for flax (19.4%), jute (24.6%), hemp (25.0%), and sisal (25.4%), respectively. All natural fibres in this study showed typical sigmoidal isotherm curves (IUPAC Type II), which is different from the Type III isotherms exhibited by certain polysaccharide films such as high amylase corn starch film, which due to a lack of cross-linking can swell significantly at high RH (above 60%) accordingly resulting in an exponential increase in EMC of 40% or higher at RH values of 85% [43].

Moisture sorption rate of natural fibres

With each step change in RH, there is a response in the material which establishes a new equilibrium condition within a specific time period. Pragmatically, the instrument is programmed to change RH when a pseudo-equilibrium is established (a rate of mass change of lower than 0.002% per minute over a 10 min period). It has been shown previously that this condition provides EMC data within 0.1% of the moisture content at infinite time of exposure (true EMC condition) [24, 25, 27, 28] and this is also demonstrated for the materials in this study in a later part of this paper. Dividing the change in EMC in response to the RH change by the time taken to reach this new EMC gives what is herein termed a ‘sorption rate’.

There are differences in sorption rate behaviour at different final RH between the various fibres investigated in this study, as is shown in Fig. 4. Whilst cotton (Fig. 4a) and filter paper (Fig. 4b) are both cellulose-rich substrates, they show quite different behaviour. With the filter paper, the time to establish an equilibrium condition is longer and especially so at the lower and upper end of the hygroscopic range. Jute (Fig. 4e) also exhibits an increase in sorption rate at the lower and upper ends of the RH range. Of the remainder, flax (Fig. 4c), hemp (Fig. 4d), and sisal (Fig. 4f) have an approximately constant sorption rate until the RH reaches 70%, where it then increases.

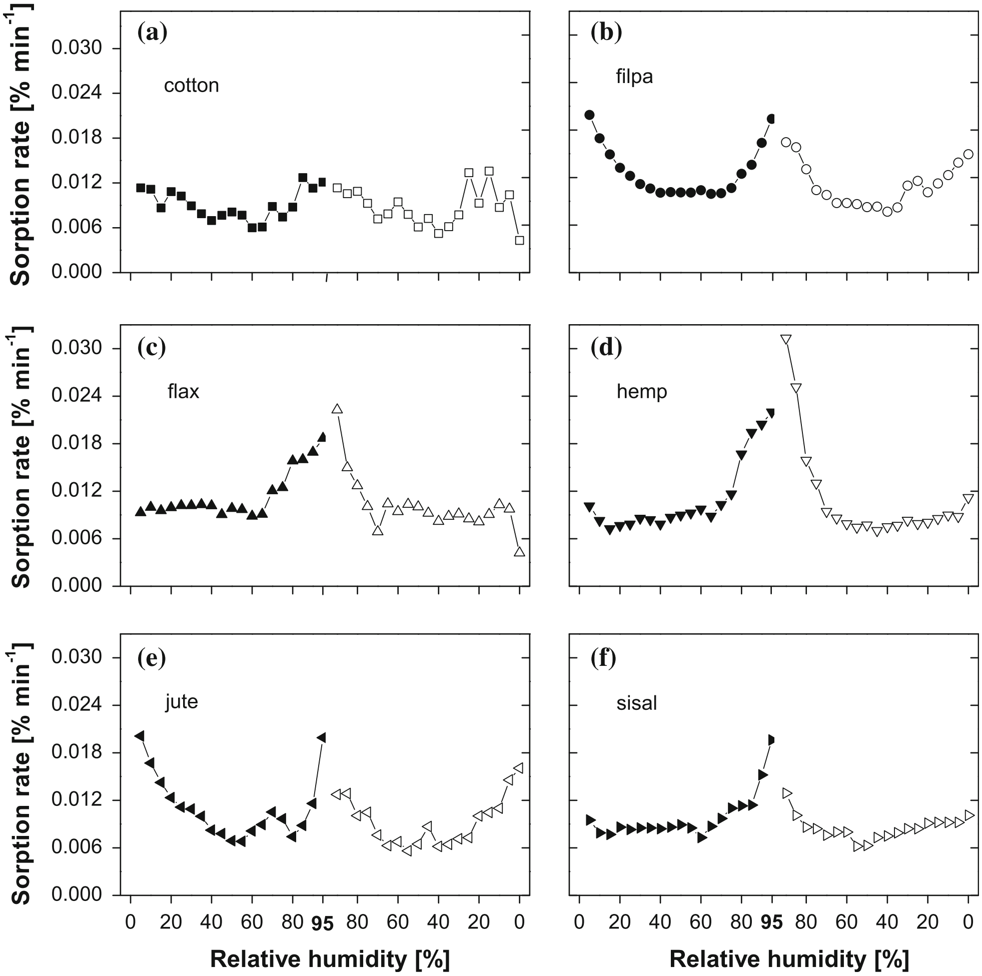

Fig. 4 Average sorption rate within a set RH during the adsorption processes (*solid legends*) and desorption processes (*empty legends*) of cotton (**a**), filpa (**b**), flax (**c**), hemp (**d**), jute (**e**), and sisal (**f**)

Sorption hysteresis of natural fibres

In this study, the sorption hysteresis was analyzed using three means: total hysteresis characterized by the area of isotherm loop, EMC difference through the full RH range by subtracting the EMC in the adsorption isotherm from the EMC in the desorption isotherm at given target RH, and hysteresis coefficient which is a ratio of the EMC for adsorption to that at desorption for any given RH as shown in Eq. 2 [44, 45]:

$$H = \mathrm{EMC_a}/\mathrm{EMC_d} \tag{2}$$

where H is the hysteresis coefficient, $\mathrm{EMC_a}$ is the equilibrium moisture content for adsorption run, and $\mathrm{EMC_d}$ is the equilibrium moisture content for desorption run.

The cotton, flax, and hemp showed similar magnitudes in isotherm loop area (Fig. 5a), suggesting that the total amount of hysteresis exhibited by these fibres is similar, although they exhibited different EMC's through the full RH range (Fig. 3a, b). The loop area of sisal fibre was approximately 60% higher than that of cotton, flax, and hemp (Fig. 5a), which means a higher total sorption hysteresis. Some comment of the differences in the total hysteresis reported in Fig. 5a and b is required. As noted in "Materials and methods" section, it is not possible to obtain an instantaneous change in RH and that there is a transition period during which the RH moves from one set value to the next and this has been fully discussed elsewhere [24–29]. The net result is to introduce an effective 'induction curve' in the mass change kinetic data and these data points must be removed in order to obtain a satisfactory curve fit. The result is that the values for MC_1 and MC_2 are slightly inaccurate and this inaccuracy increases when the cumulative values are calculated. Hence the heights of the columns of Fig. 5b do not correspond with those of Fig. 5a. The partitioning of the water between the fast and slow processes in Fig. 5b is accurate, however.

The sorption hysteresis presented as the EMC difference through the full RH range varied with the RH (Fig. 6a). The sorption hysteresis first increased with the RH up to 80%, after which it decreased. In the RH range of 0 to ca. 50% the hysteresis value of hemp was higher than the flax, followed by cotton. Over 50% and up to 80% RH, the hysteresis sequence changed in a descending order of cotton, hemp, and flax fibres (Fig. 6a). The sisal exhibited a significantly higher sorption hysteresis compared with the other five types of fibres over most of the RH range, especially in the high RH range. This further confirms the results of total hysteresis as shown in Fig. 6a. The hysteresis coefficient, which has been used in previous studies [e.g., 46, 47], exhibited a considerable variation ranging from about 0.63 to 0.93, depending upon the type of fibres (Fig. 6b). In previous studies, this hysteresis coefficient supposedly takes account that a material with higher levels of sorption would be expected to exhibit greater hysteresis [47]; however, such hysteresis coefficients for these natural fibres tested in this study did not exhibit any significant correlation with the EMC (Fig. 6a).

The extent of hysteresis can be influenced by the nature and composition of cellulosic materials, relating to their potential for structural and conformational rearrangement, which change the accessibility of sorption sites [48]. Increasing the environmental temperature can also reduce the sorption hysteresis of cellulosic and lignocellulosic materials [22]. In order to further an understanding of the source of sorption hysteresis, the increment/decrement of

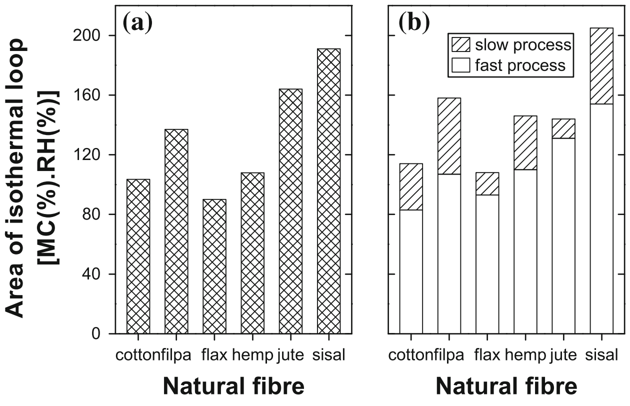

Fig. 5 Mathematical area of the isotherm loop for different fibres, which is calculated by using an empirical 4th order polynomial fitting to the adsorption and desorption isotherm curves, integrating the fitted curves and determining the area difference between the adsorption and desorption isotherm run (**a**) and the area difference of integrated fast and slow process curves which are polynomially fitted with 4th order during the adsorption and desorption runs (**b**)

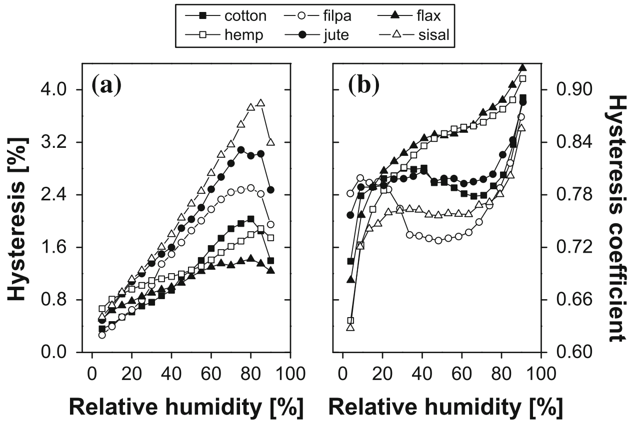

Fig. 6 Sorption hysteresis of natural fibres obtained by subtracting the values of equilibrium moisture contents of the adsorption isotherm by the desorption isotherm at a same RH level (**a**) and hysteresis coefficient which is a ratio of the EMC for adsorption to that at desorption for any given relative humidity (**b**)

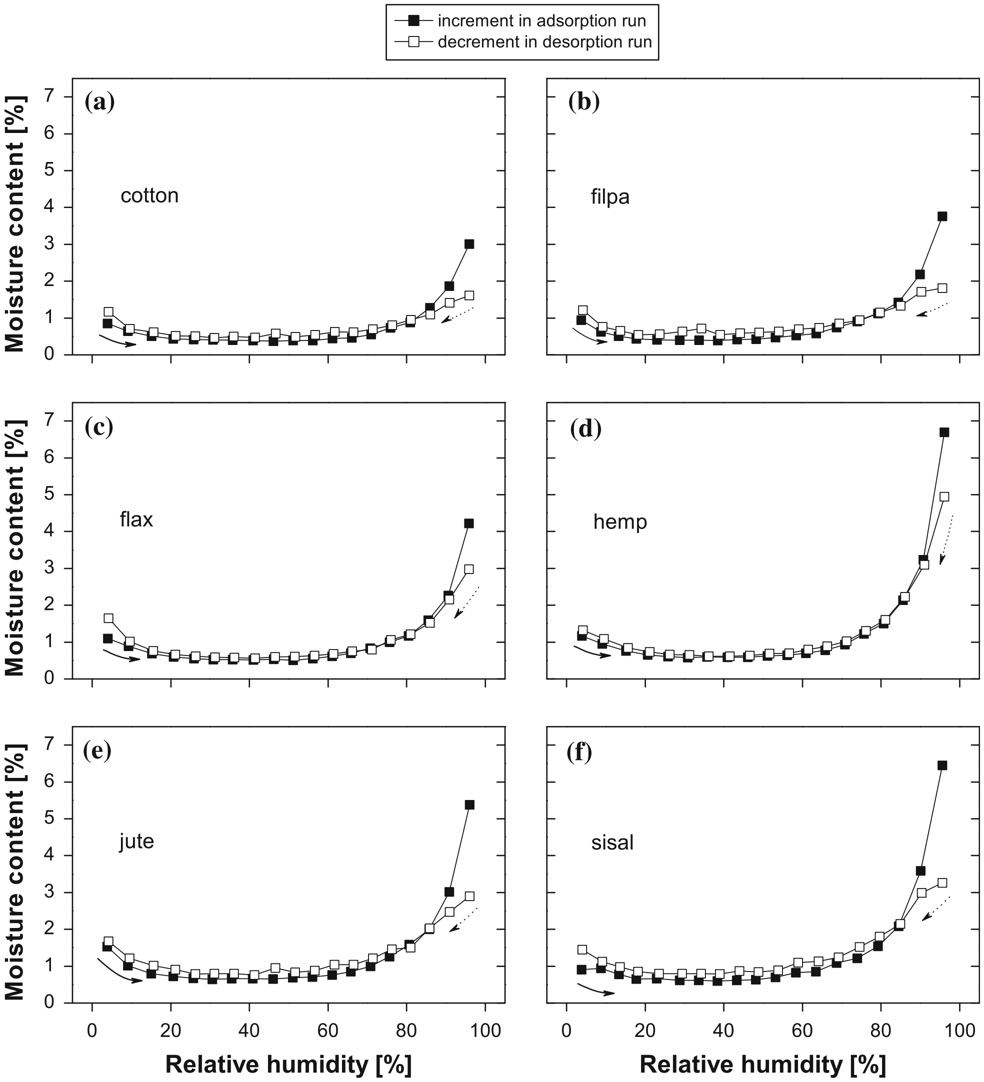

Fig. 7 Moisture increment within a set RH in the adsorption run (*solid arrow direction*, RH from 5 to 95%) and moisture decrement in the desorption run (*dot arrow direction*, RH from 95 to 5%) of cotton (**a**), filter paper (**b**), flax (**c**), hemp (**d**), jute (**e**), and sisal (**f**)

moisture content at a given RH in the adsorption and desorption run were plotted in Fig. 7a–f.

It is notable that at a specific RH, the MC decrement in the desorption isotherm was slightly greater than the MC increment in the adsorption isotherm in the RH range of 5–85%. Only at the RH levels of 90 and 95% were the MC increments significantly higher than the MC decrements, especially at the 95% RH level. In the desorption run from 95 to 90%, the MC does not decrease as much as it gains from 90 to 95%. This 'residual' MC is stored in the fibre cell wall acting as a reservoir and is subsequently released gradually in the desorption run. The hysteresis of the natural fibres in the isotherm run thus primarily resulted from the difference in MC increment and decrement resulting from the change in RH from 95 to 90%. Comparison of the difference between the MC increment and decrement at the 95% RH level with the total hysteresis (Fig. 5a) also showed that the greater difference corresponded to a higher total hysteresis. It is, however, wrong to interpret the origin of sorption hysteresis solely to any changes occurring at the top end of the hygroscopic range. It is well established that hysteresis is displayed when desorbing from any RH, with the desorption line initially scanning across the space occupied by the hysteresis loop until it reaches the desorption boundary curve [49, 50]. This type of behaviour with scanning curves running through the space delineated by the boundary adsorption and desorption curves is a characteristic feature of the independent domain theory for explaining hysteresis phenomena [51–54] and this theory has recently been applied to the study of the hysteresis associated with the sorption of water vapour into wood [49, 50]. It is central to the independent domain theory that each of the domains is able to display bistable behaviour for hysteresis to be observed. A suitable model that provides a basis for these domains to exist in two possible states has been developed for explaining hysteresis in humic soils [55–57] and glassy polymers [58] and this theory has recently been applied to cellulosic and lignocellulosic materials [27, 29]. This 'dual mode' model considers the response of a glassy solid below the glass transition temperature to the ingress or egress of sorbate molecules under adsorption or desorption conditions. The structure of plant fibres is one of crystalline microfibrils embedded within an amorphous matrix. Adsorption of water vapour into the fibre wall results in the creation of nanopores between the microfibrils and within the matrix substances. The nature of the matrix substances varies, depending on the fibre type (Table 1). In the dual mode model description, the creation of nanopores in response to the incoming sorbate molecules is inelastic on the time scale of molecular diffusion. This time lag in the response of the matrix to incoming or exiting molecules means that the creation of nanopores is delayed during the adsorption process and their collapse is delayed during the desorption process. Hence adsorption and desorption are occurring in different physical environments. This is a molecular scale process taking place on a molecular scale time-frame. The dual mode behaviour is only exhibited if the isotherm temperature is below the glass transition temperature of the matrix. One consequence is that as the isotherm temperature is increased, the area bounded by the hysteresis loop decreases, as has been observed experimentally [22]. The presence of an amorphous cross-linked glassy polymer such as lignin in the cell wall matrix would also be expected to result in an increase in the area bounded by the hysteresis loop, as has also been shown experimentally herein and elsewhere [22]. The question then arises, that if the hysteresis property is related to matrix stiffness in the cell wall, is this also reflected in the sorption kinetic behaviour?

Kinetic analysis using the PEK model

The moisture content associated with fast kinetic process has been proposed to be related to the fast moisture sorption at the sites of the readily accessible internal surfaces and 'amorphous' regions, while the slow kinetic process has been related to sorption onto the 'inner' surfaces and 'crystallites' [59, 60]. This hypothesis has been tested and reported upon previously and it is concluded that there is little evidence supporting this idea [22, 24, 25, 27–29]. It is known that the swelling behaviour of foodstuffs also obeys a PEK model [33–35] suggesting that the sorption kinetics is rate limited by the ability of the cell wall matrix to deform in response to the ingress or egress of water molecules. Krabbenhoft and Dankilde [61] whilst noting the general failure of Fickian diffusion models when applied to dynamic substrates such as wood, consider that the swelling of the material is a crucial factor affecting the sorption kinetic behaviour. When water vapour is adsorbed into a plant cell wall, the sorbed water molecules exert an internal pressure on the interfibrillar elastic gel matrix. The volume change of this matrix material is a result of the swelling pressure exerted by the adsorbed water molecules and the resistance to that swelling pressure offered by the matrix. During the initial stages of adsorption, the matrix is in a dry state and the rate of diffusion is dependent upon the rate of hydrogen bond breaking within the matrix, as is suggested by recent studies of the activation energy of sorption for flax [27] and Sitka spruce [29]. The rate of matrix deformation limits the kinetics if this is the rate limiting step, however, if matrix deformation is rapid then Fickian diffusion would be the limiting factor. The PEK model accurately fits the sorption data, indicating that matrix deformation is indeed the rate limiting process. Given that this is the case, the question then arises as to what the fast and slow exponential kinetics processes represent in terms of matrix deformation. This problem is currently being addressed by the development of a model to describe this behaviour and which will be reported upon in due course.

The correspondence of the experimental with the mathematically generated isotherm is shown in Fig. 8. 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 ($\mathrm{EMC} = \mathrm{MC}_0 + \mathrm{MC}_1 + \mathrm{MC}_2$) in the adsorption and desorption runs. This fitted isotherm was closely comparable to the experimental isotherm loop for natural fibres (Fig. 8a–f), indicating that the EMC values as measured by the instrument are very close to those predicted by the model at infinite exposure time.

Since the isotherm can be generated by summation of the fast and slow moisture content components, it then becomes possible to generate pseudo-isotherm curves based upon the cumulative summation of MC_1 or MC_2 values (Fig. 9). By so doing, it is possible to provide information to the following questions: (a) Is there any difference between the fast and slow processes throughout the sorption isotherm range? (b) Does hysteresis exist for both the fast or slow processes between the desorption and adsorption isotherm? In some cases, closed loop isotherms are not found, which can in part be related to the inaccuracies associated with determination of the MC_1 and MC_2 values, as discussed earlier. However, there are also differences due to the allocations of MC_1 and MC_2 between the adsorption and desorption isotherms, which is particularly noticeable with flax (Fig. 9c) and hemp (Fig. 9d). In the case of flax and hemp there virtually no difference in the MC_2 values between the adsorption and desorption

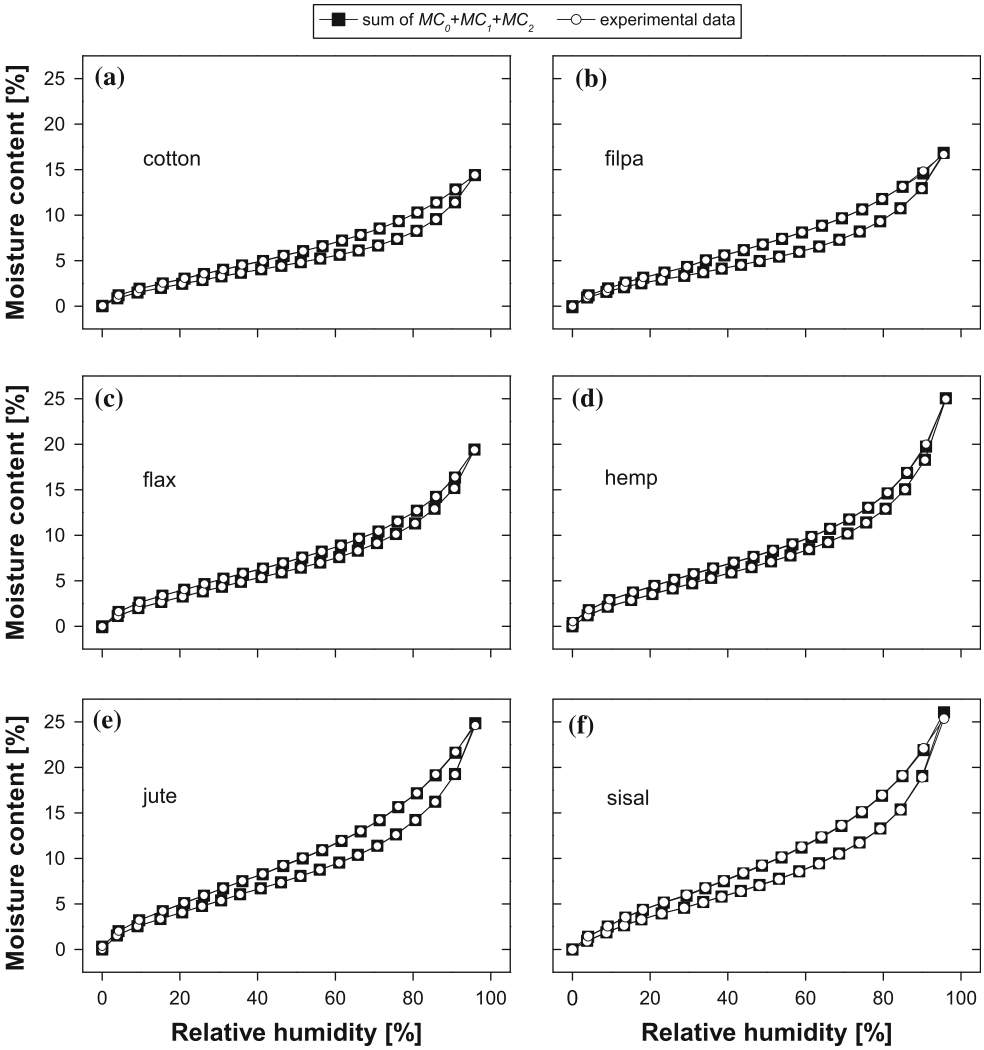

Fig. 8 Comparison of sorption isotherm loops derived from experimental data and derived from sums of MC_0, MC_1, and MC_2 obtained from curve fitting using PEK model for cotton (**a**), filter paper (**b**), flax (**c**), hemp (**d**), jute (**e**), and sisal (**f**), respectively

loops until higher RH values. Where the MC_2 values diverge at the upper end of the hygroscopic range this then results in an open isotherm loop in the MC_1 values. With the other fibres, there is some hysteresis in the MC_2 values, with a resultant closed (or nearly so) MC_1 isotherm. In all cases the majority of the hysteresis associated with the mass values is with the fast sorption process. Mathematically derived areas revealing the hysteresis of the fast and/or the slow processes in the sorption run of natural fibres were illustrated in Fig. 5b, showing clearly that the hysteresis in the fast sorption process was significantly greater than this in the slow process.

The characteristic time of fibres in the fast process (t_1) was comparable between the adsorption and desorption processes in most of RH range (not shown here), which is consistent with the previous findings [26, 29]. Generally, the characteristic time of the slow process (t_2) in the adsorption run was shorter than in the desorption run. Thus, whilst the sorbed water can be allocated in terms of mass between the fast and slow process for both adsorption and desorption, it is only the slow process characteristic time that changes under conditions of adsorption and desorption. This has been universally observed with all analyses of water vapour sorption kinetics based upon the PEK model.

Conclusions

The different natural fibres exhibited variable dynamic water vapour sorption behaviour. The maximum sorption rate at a given RH appeared at the initial stage and the average sorption rate increased with increasing RH. Sisal and flax exhibited the highest and lowest hysteresis, respectively. The PEK model can be used to accurately fit

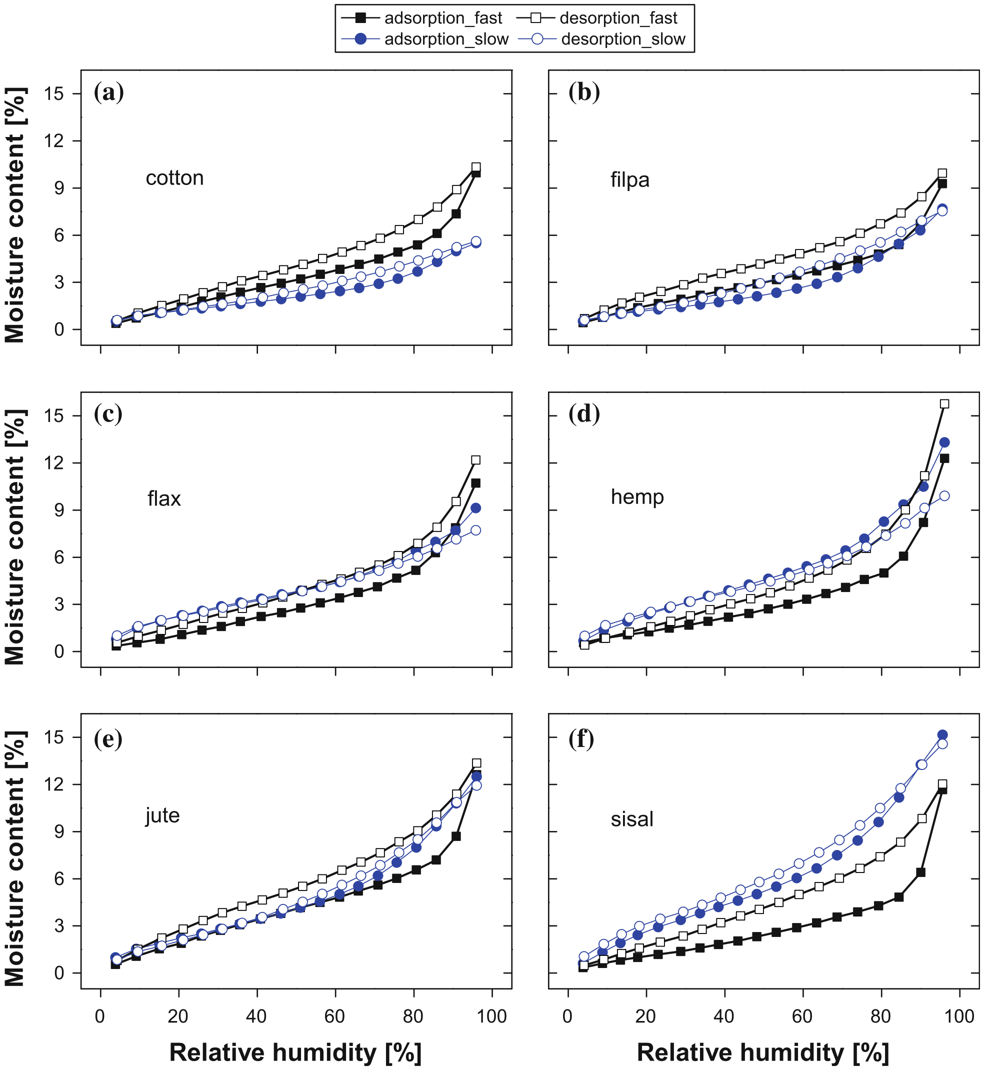

Fig. 9 Cumulative moisture contents associated with the fast (MC_1) and slow (MC_2) exponential kinetic processes in the water vapour adsorption and desorption runs for cotton (**a**), filter paper (**b**), flax (**c**), hemp (**d**), jute (**e**), and sisal (**f**), respectively

the experimental measurements. The sorption kinetics resulted from curve fitting showed that both the fast and slow processes in the fibre cell wall exhibited hysteresis between the adsorption and desorption isotherm. The reason for the differences in the allocation of moisture to the fast and slow processes is not understood at present. It is suggested that the PEK kinetics is related to the swelling behaviour of the cell wall under conditions of adsorption and desorption.

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