

CHAPTER 5

SORPTION KINETICS STUDIES USING THE PEK MODEL

5.1 Introduction

This chapter reports on the investigation of the sorption kinetics of the same six tropical hardwoods and the thermally modified wood, which were investigated in Chapter 4. The kinetic curves were analysed using the parallel exponential kinetics (PEK) model that was previously discussed in Section 2.10. The PEK model has only recently been used in sorption kinetics studies with wood and as yet there is no satisfactory explanation for why this type of kinetics is observed with small wood and plant fibre samples. With the PEK model, the sorption kinetics is composed of two exponential terms which represent fast and slow processes, with their own characteristic times and moisture contents. In this study, a comparison was made between the PEK model and the H-H model which was undertaken to see if there is any relation between the PEK model with fast and slow processes and the formation of water of hydration and water of dissolution, as described in the H-H model. This type of model is based upon the concept of different types of water in the cell wall displaying different sorption behaviour. This was done to see if the two kinetic processes could be associated with sorption sites, as is claimed in the literature.

5.2 Material and Methods

5.2.1 Sample preparations

The same material, as studied in Section 4.1.1.1 and 4.1.1.2, was used in this investigation. The adsorption behaviour of wood at each RH was analysed by fitting the experimental data by means of the H-H model that has been introduced previously in Chapter 4 (Section 4.2.2.1 and 4.2.2.2). The analysis of the PEK model of the

adsorption and desorption curves of the specimens were performed with the nonlinear curve fitting function ‘ExpAssoc’ (exponential associate), (see Equation 2.29) using Origin 6.1 software (Origin Lab. Corporation United States of America).

5.2.2 Analysis of sorption kinetics data with the PEK model

Each kinetic curve was obtained by plotting percentage mass gain/loss against time, with time zero corresponding to the point at which a RH step change occurs (Figure 4.1). However, a change of RH from i.e. 10 to 15% 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. This has been explained in Section 3.3.1. During this period, the MC of the sample is not moving towards a static equilibrium point, which consequently affects the kinetics curve for the first minute or so (Figure 4.2). The PEK parameters for the MC changes in MC_1 , MC_2 , t_1 and t_2 were obtained from the DVS data at each RH interval. The fast process has a related characteristic time t_1 and moisture content at infinite time MC_1 and the slow process is related to the values t_2 and MC_2 as stated below (Equation 2.29).

$$MC = MC_o + MC_1[1 - \exp(-t/t_1)] + MC_2[1 - \exp(-t/t_2)] \quad (2.29)$$

However, except for the first adsorption step, the moisture content at time zero (MC_o) will have a finite value and this has to be included in the curve fit. There are two methods for doing this. Either the experimental value for MC_o from the previous RH step can be used as an input parameter, or the curve fitting software can find its own value by iteration. In practice, it was found by trial and error that the second approach gave more accurate curve fits and minimised the possibility of the software iterating to a

local, rather than a true minimum. To be consistent, this method was adopted for the first adsorption step also. It is to be appreciated that this leads to errors in determination of both the MC values and the characteristic times.

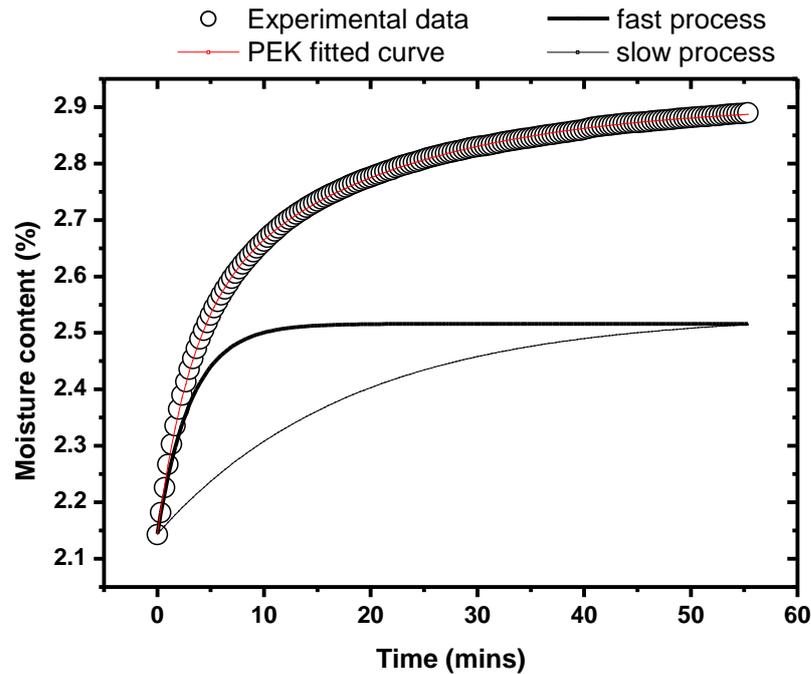


Figure 5.1 Example of a curve fit for *A. mangium* at 25 °C (adsorption of 10-15% RH) showing the slow and fast exponential kinetic processes data points (open circles) and the lines (PEK fitted curve).

Throughout the experiment at each target RH, the PEK curves gave excellent fits with the experimental data ($R^2 > 0.999$) (Figure 5.2). However, it is emphasised that this should not be taken as proof that the fitting function is necessarily the correct one. What is being tested in this thesis is the applicability of the PEK model and whether it has any value in interpreting cell wall sorption kinetic behaviour. In Figure 5.2a, a curve fit to the raw experimental data is presented. However, despite a high value of R^2 (0.9994),

the fit is not acceptable because the data includes the ‘induction curve’ which arises because the RH has not yet stabilised. Table 5.1 (in bold-two data points removed) and Figure 5.2c shows the best value and the smallest error for the PEK parameters when two of the data points were removed, resulting in a new acceptable fit. A detailed interpretation of the results sensitivity of fits is described in Section 5.2.3. A high R^2 value does not prove that the fitting function is correct.

It has to be realised that the curve fitting is to some extent a compromise that does involve some errors in the determination of the values of MC_1 , MC_2 and to a much lesser extent t_1 and t_2 . There are two factors leading to possible inaccuracy relating to the evaluation of the parameters MC_1 and MC_2 :

- (a) Allowing the value of MC_o to be identified by the software. The reasons for this are to minimize the probability of encountering local minima and to obtain much more accurate values of t_1 and t_2 .
- (b) The rapidly changing RH at the initial stages of the sorption process necessitating removal of some of the early data points.

Although errors do vary from fit to fit, typically these were no greater than 10% of the values of MC_2 and characteristic times (20% for MC_1), except in exceptional cases. It is important to note that considerable care is needed to avoid the software iterating to a local minimum even with such a high quality data set as provided by the DVS. Compromised data sets (where for example, there is a temporary drift in the MC values) do not give satisfactory fits.

Table 5.1 PEK parameters from nonlinear curve fitting with Origin 6.1 with number of point that had been removed for the best fitting for *A. mangium* at 25 °C (actual RH = 4.1 to 9.0%)

No. of data points removed	PEK parameters										
	MC_o		MC_1		t_1		MC_2		t_2		R^2
	value	error	value	error	value	Error	value	error	value	error	
0	2.07522	0.00247	0.46758	0.00852	3.72953	0.08392	0.37003	0.00704	20.55324	0.70883	0.99944
1	2.10512	0.00155	0.41639	0.00464	3.33801	0.04915	0.38645	0.00397	18.91828	0.32766	0.99977
2	2.14423	0.00132	0.37201	0.00368	3.15303	0.04275	0.38968	0.00318	18.26474	0.24718	0.99983
3	2.18938	0.00132	0.33525	0.00374	3.17539	0.04812	0.38152	0.00321	18.33693	0.25873	0.99981
4	2.23424	0.0012	0.3057	0.00366	3.32949	0.05219	0.3677	0.00311	18.81989	0.27236	0.99982

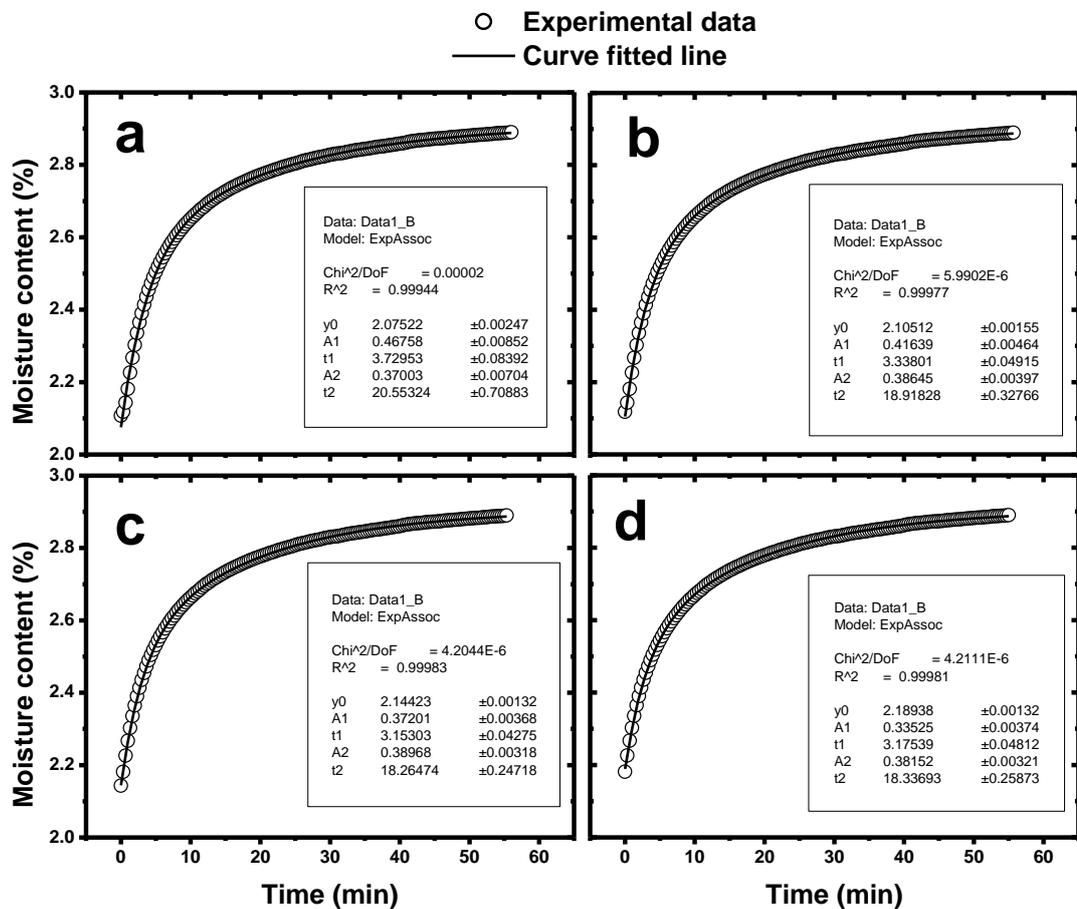


Figure 5.2 Non-linear curve fit to adsorption data (25 °C) for *A. mangium* exposed to a change in RH from 4.1 to 9.0%. Inclusion of all the data points compromises the curve fit and results in inaccurate values of the characteristic times of the fast (t_1) and slow (t_2) adsorption process. (a) none, (b) first, (c) second, (d) third data points have been removed resulting in a better curve fit, but now the moisture content values MC_1 and MC_2 are less accurate.

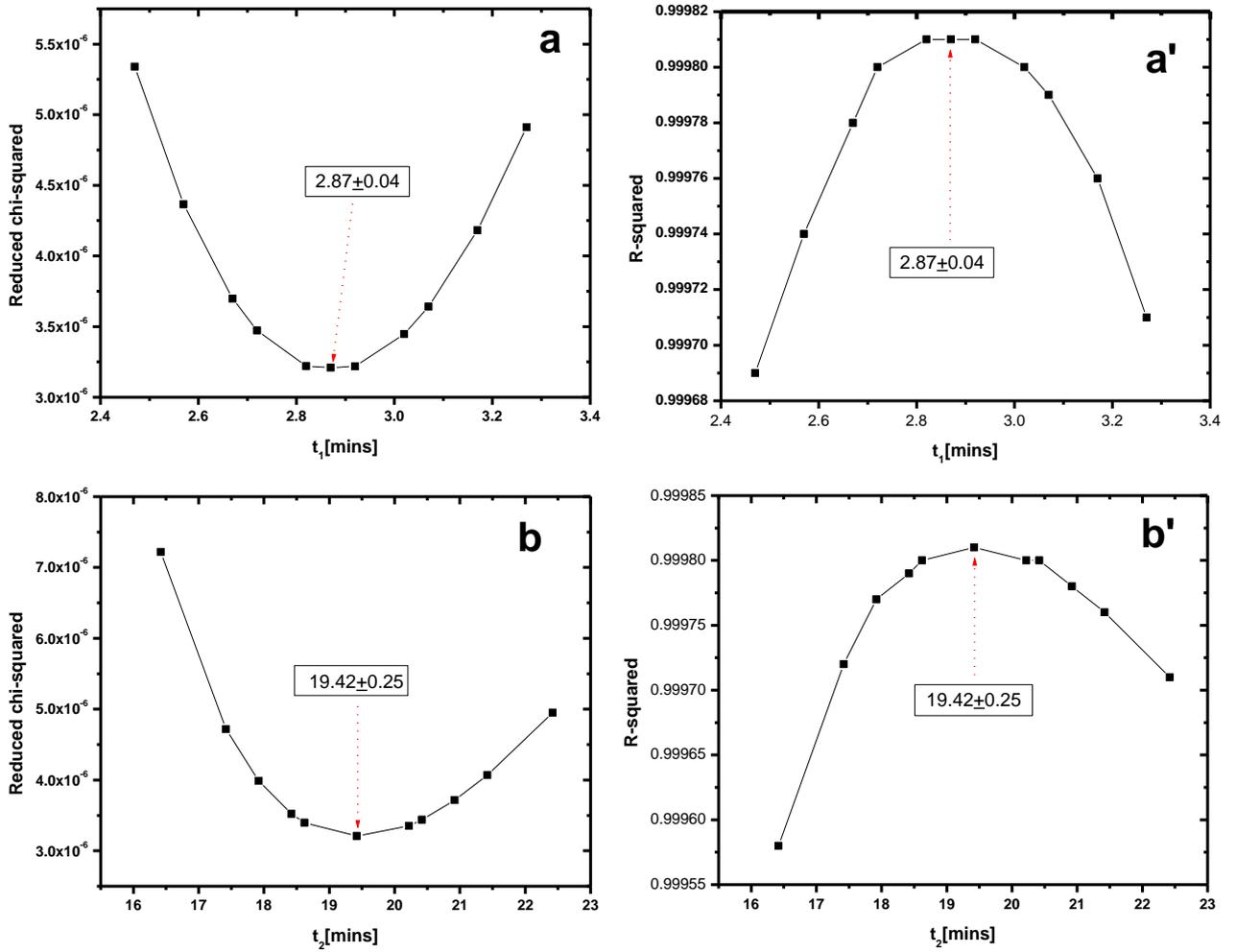


Figure 5.3 Fixing PEK parameters of t_1 (a and a') and t_2 (b and b') with values of reduced chi-squared and R-squared to show the value generated from the PEK model ($t_1 = 2.87 \pm 0.04$ and $t_2 = 19.42 \pm 0.25$) is the best fit of the curve fitting.

5.2.3 Interpreting results of sensitivity of fits

There is a quantitative value that describes how well the model fits the data. The value is defined as reduced chi-squared which is the chi-squared divided by the number of degrees of freedom. The reduced chi-squared is the standard deviation of the residuals, the latter being the vertical distances of the data points from the fitting line. The smaller the value, the better is the fit to the data. The best fit can also be quantified through R-squared (R^2) or coefficient of determination value and it is known as the goodness of fit. A value close to 1 will indicate a good fit. Data generation by the PEK model using the built-in function of 'ExpAssoc' at 0.95 confidence interval has been conducted (Section 5.2.1). *A. mangium* that has been exposed from 13.5 to 17.9% RH produced the smallest reduced chi-squared and the highest R-squared that translated into the best fit of the curve fitting. This best fit was generated at t_1 (2.87 \pm 0.04) and t_2 (19.42 \pm 0.25). If t_1 and t_2 are fixed at other values, larger reduced chi-squared and lower R-squared are produced (Figure 5.3). This study shows that simple visual inspection of the curve fit to the data is worthless and it is essential to rely upon the statistical values reported by the software in order to determine the accuracy of the fit. It is emphasised that even with such high values of R^2 , this cannot be taken as proof that the function used for the fit is correct. Confidence in the fitting values comes about because of many fits to the data being undertaken with different samples and at different RH values. Previous work conducted on flax (and outside of the work discussed in this thesis) also found good agreement with the data reported in the literature. In general, the fitting parameters are in close agreement with one another, although exceptions occur, which must be treated with caution. For example, it was noted that determinations at the lowest and highest RH values sometimes gave anomalous results. The values are not

exact, but indicative and this must be considered when these values are subsequently analysed using the Kelvin-Voigt model.

5.3 Results and Discussion

5.3.1 Fitting of experimental and the PEK model isotherm

The sum of moisture contents associated with the fast and slow processes and moisture content at time zero ($MC_o + MC_1 + MC_2$) obtained from the PEK fitting can be compared with the experimental EMC data as shown in Figure, 5.4 i.e. for two hardwood species (*A. mangium* and *E. malaccense*) and thermally modified wood (TMW). This mathematically fitted isotherm is closely comparable to the experimental isotherm (Figure 5.4), indicating that the EMC values as measured by the instrument are very close to those predicted by the model at infinite exposure time. This gives additional confidence that the set machine parameters are satisfactory and confidence in the curve fitting parameters.

5.3.2 Modelling of the sorption isotherms

As previously noted (Section 2.10), Kohler *et al.* (2003) attributed the fast and slow processes to corresponding sites with no further attempt at interpretation, although it was suggested that this might be related to monolayer and polylayer water formation in the cell wall. The fast process has also been previously assumed to be due to rapid moisture sorption at the sites of external surfaces and amorphous regions within the cell wall matrix, whereas the slow process has been supposed to be due to sorption into inner surfaces and crystallites (Figure 5.5) (Okubayashi *et al.* 2004). One difficulty with models of this type is that they fail to take into account the dimensional changes of the substrate.

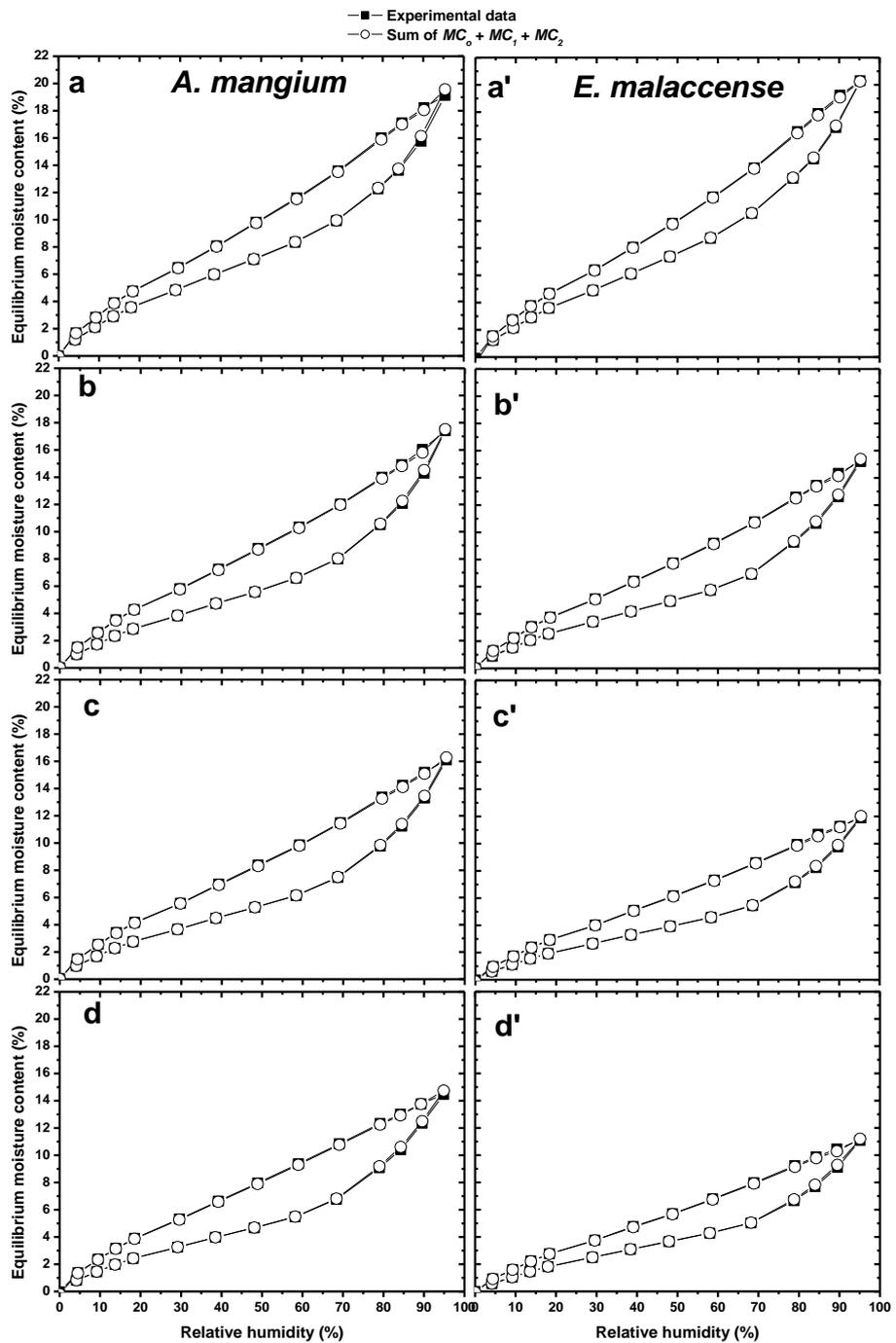


Figure 5.4 Comparison of isotherms derived from experimental data (filled squares) and derived from sums of the cumulative moisture contents of the fast and slow kinetic processes (open circle) for *A. mangium* (a - d) and *E. malaccense* (a' - d'). a/a' untreated wood; b/b' heat treatment 180 °C -1 h; c/c' heat treatment 180 °C-2 h; d/d' heat treatment 180 °C-3 h.

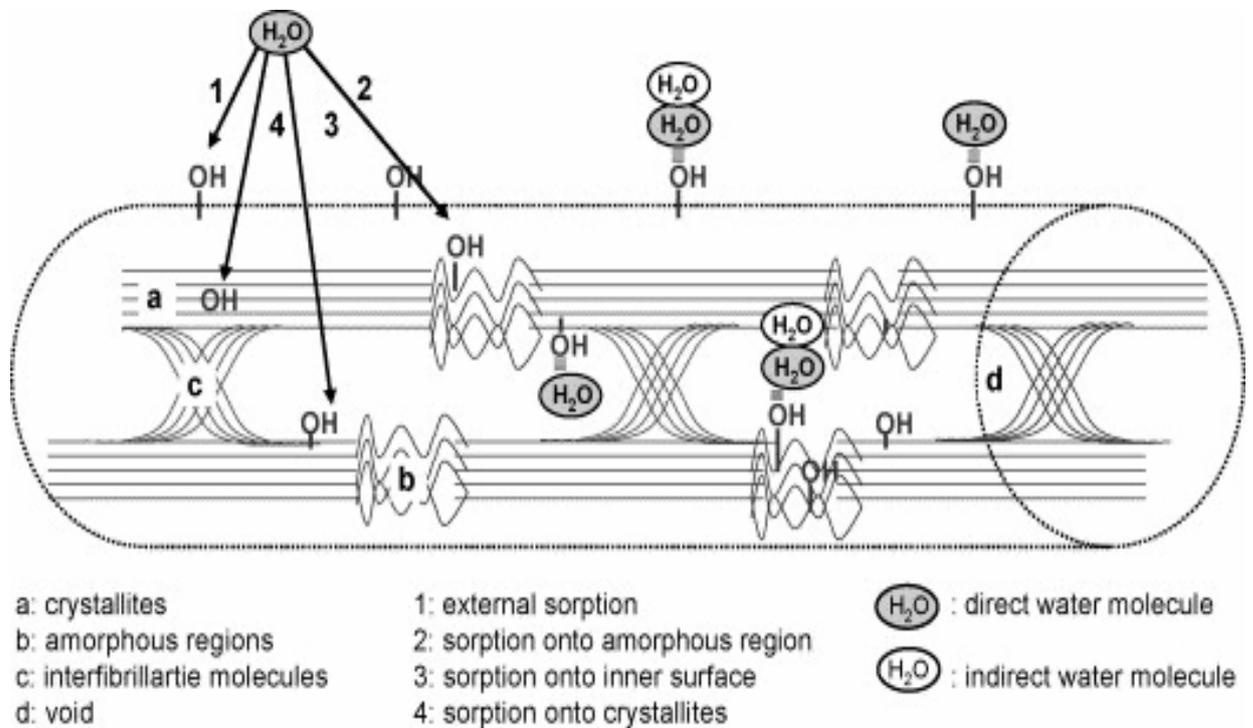


Figure 5.5 A schematic diagram of direct and indirect moisture sorption onto the external surface (1), amorphous regions (2), inner surface of voids (3), and crystallites (4) (Okubayashi *et al.* 2004).

In order to test this hypothesis, a comparison was made between the cumulative mass changes associated with the slow and fast processes at various RH values and the theoretical monolayer and polylayer cell wall water contents calculated from the H-H model. The H-H data and the PEK data were superimposed in order to visualize this hypothetical allocation of fast and slow water.

The result of this analysis is shown in Figure 5.6. From these plots, it can be seen that the fast process (filled squares) and the slow process (open circles) apparently correspond with the monolayer and polylayer components of the adsorption isotherm up to 40% RH in one case, *E. malaccense* (Figure 5.6f), but that above this RH value there is more water associated with the fast process that would be predicted for the monolayer according to H-H model.

In the other five tropical hardwoods, the water associated with the fast process is lower than the monolayer curve at lower RH and much higher at higher RH values. However the slow process (open circles) is higher than the polylayer curve at lower RH values and much lower at higher RH values.

Further investigation with thermally modified wood on two of the hardwoods species, *A. mangium* and *E. malaccense* are shown in Figure 5.7a-d and Figure 5.7a'-d') where the H-H data are compared with those of the PEK MC. From these plots, it is obvious that the behaviour associated with the fast (filled squares) and the slow processes of the two species are different.

With *A. mangium* and thermally modified wood (at different temperatures), there is no close correlation between the mono or polylayer isotherms and the MC associated with the fast and slow processes (Figure 5.7a-d). However, with *E. malaccense* and the thermally modified wood (at different temperature) the slow process appears to correspond with polylayer water formation and the fast process with monolayer water up to a RH of about 40% (Figure 5.7a'-d').

The one exception is *E. malaccense* heated at 180 °C. However, as noted previously, the curve fitting process involves the rejection of some data points which affects the accuracy of determination of MC_1 and MC_2 . These inaccuracies can increase as the values are cumulatively added at each RH step. Nonetheless, it is clear that the

deviation of the cumulative MC values from the monolayer and polylayer sorption curves is considerable and it is not possible to attribute the fast and slow processes to these water types. It will be shown later that interpreting the PEK model in terms of sorption sites or water types is not correct and an alternative model will be presented.

5.3.3 Does the PEK model provide an insight into hysteresis?

The PEK parameters for percentage moisture content mass changes MC_1 and MC_2 were obtained from the DVS data for each RH interval. In order to analyse the effect of the humidity on the moisture sorption behaviour in more detail, the PEK parameters for characteristic times (t_1 and t_2) at each sorption step were plotted against RH for six tropical hardwoods (Figure 5.8 and 5.9) and thermally modified wood (Figure 5.10a-d and 5.11a'-d').

In general, the time to equilibrium was always longer for the slow desorption processes, which shows that there is a lack of symmetry between the adsorption and desorption that most probably has its origin in the micromechanical behaviour of the cell wall in the presence of moisture, as will be explored later in this thesis. In adsorption, from 0 to 50% RH, the t_1 and t_2 values remained almost constant but after approximately 50% RH, both t_1 and t_2 started to increase, indicating that the equilibration process is slowing down. In desorption the same trend is shown.

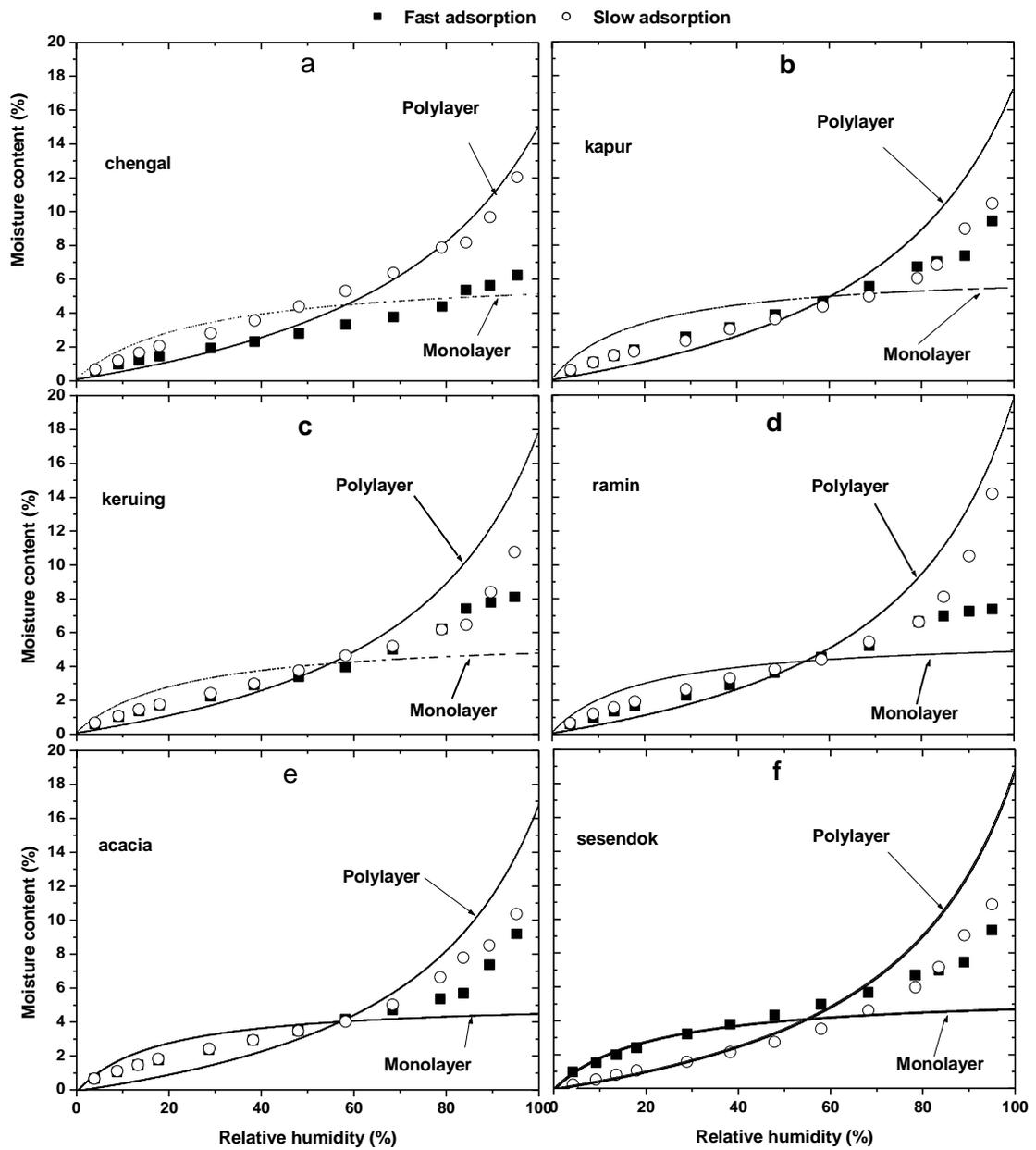


Figure 5.6 A comparison of the cumulative MCs associated with the PEK model fast and slow processes on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* and (f) *E. malaccense* compared with the polylayer and monolayer curves calculated using the H-H model.

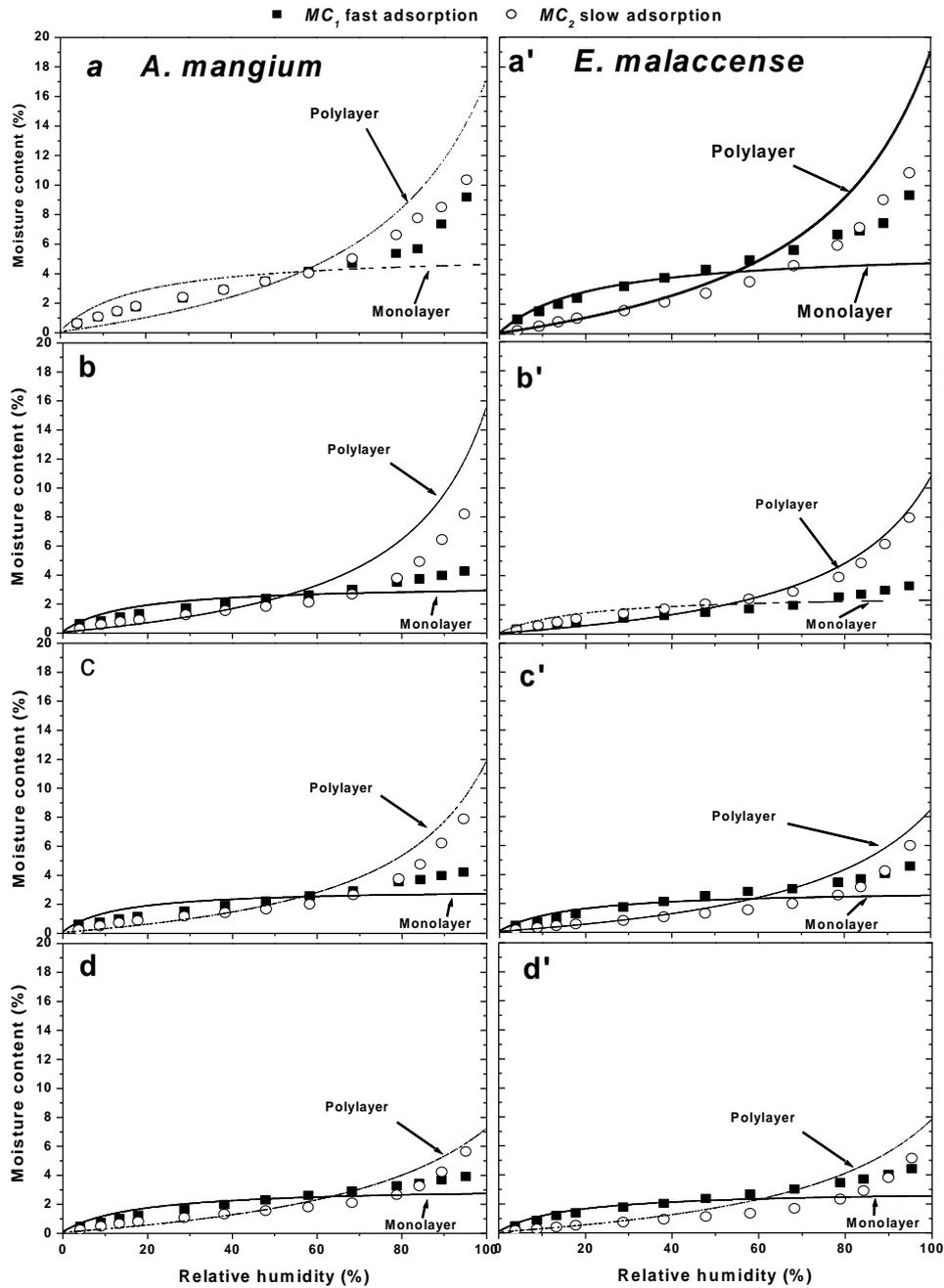


Figure 5.7 A comparison of the cumulative MCs in plots versus the RH. The data are associated with the PEK model in terms of fast (MC_1) and (MC_2) slow processes for *A.mangium* (a - d) and *E.malaccense* (a' – d'). For comparison, the polylayer and monolayer curves calculated by the H-H model are included. a/a' unmodified wood; b/b' thermal modification 180 °C-3 h; c/c' thermal modification 200 °C-3 h; d/d' thermal modification 220 °C-3 h.

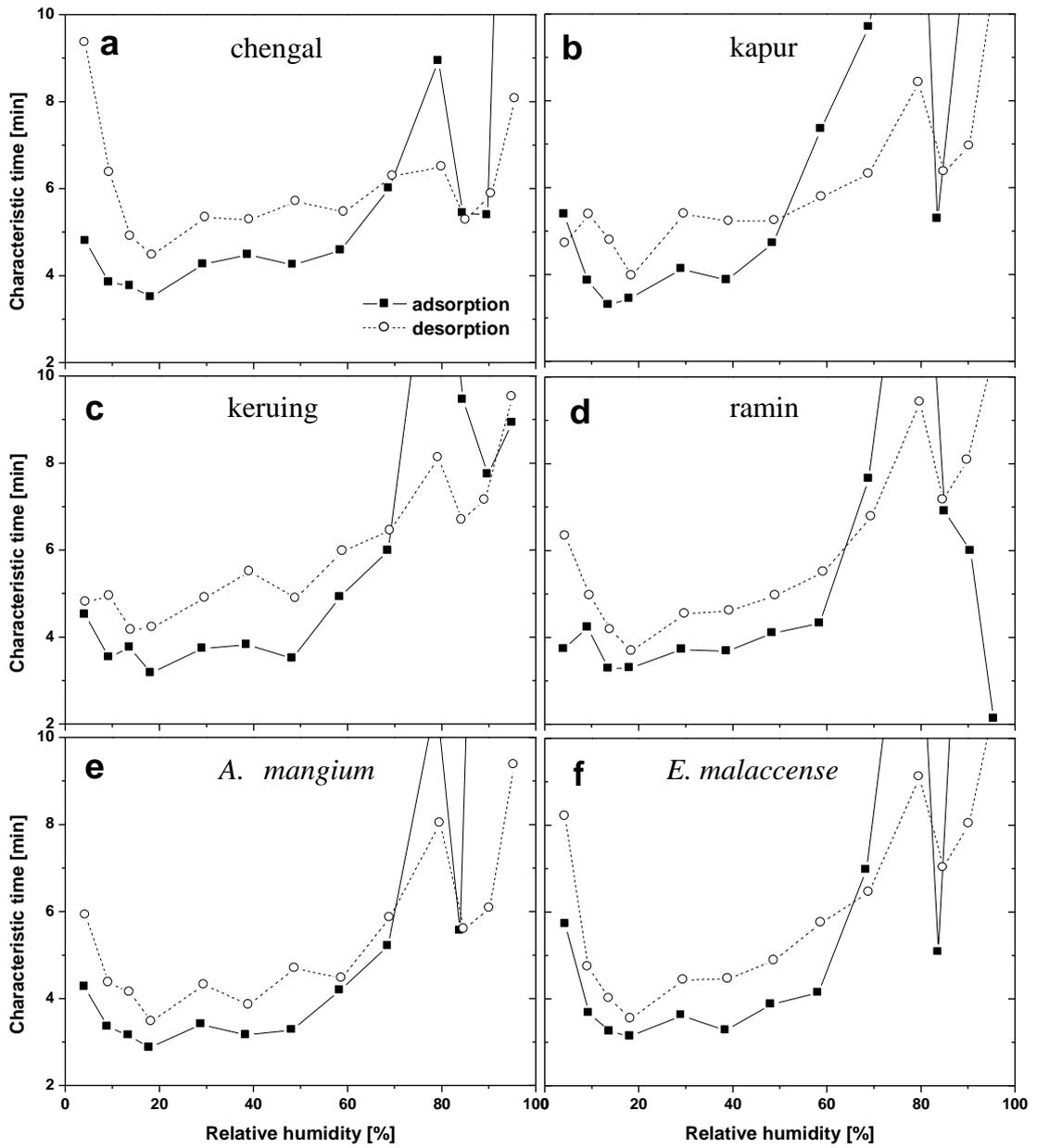


Figure 5.8 Variation of characteristic times with change in RH for the fast t_1 exponential kinetic processes for adsorption and desorption on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* and (f) *E. malaccense*.

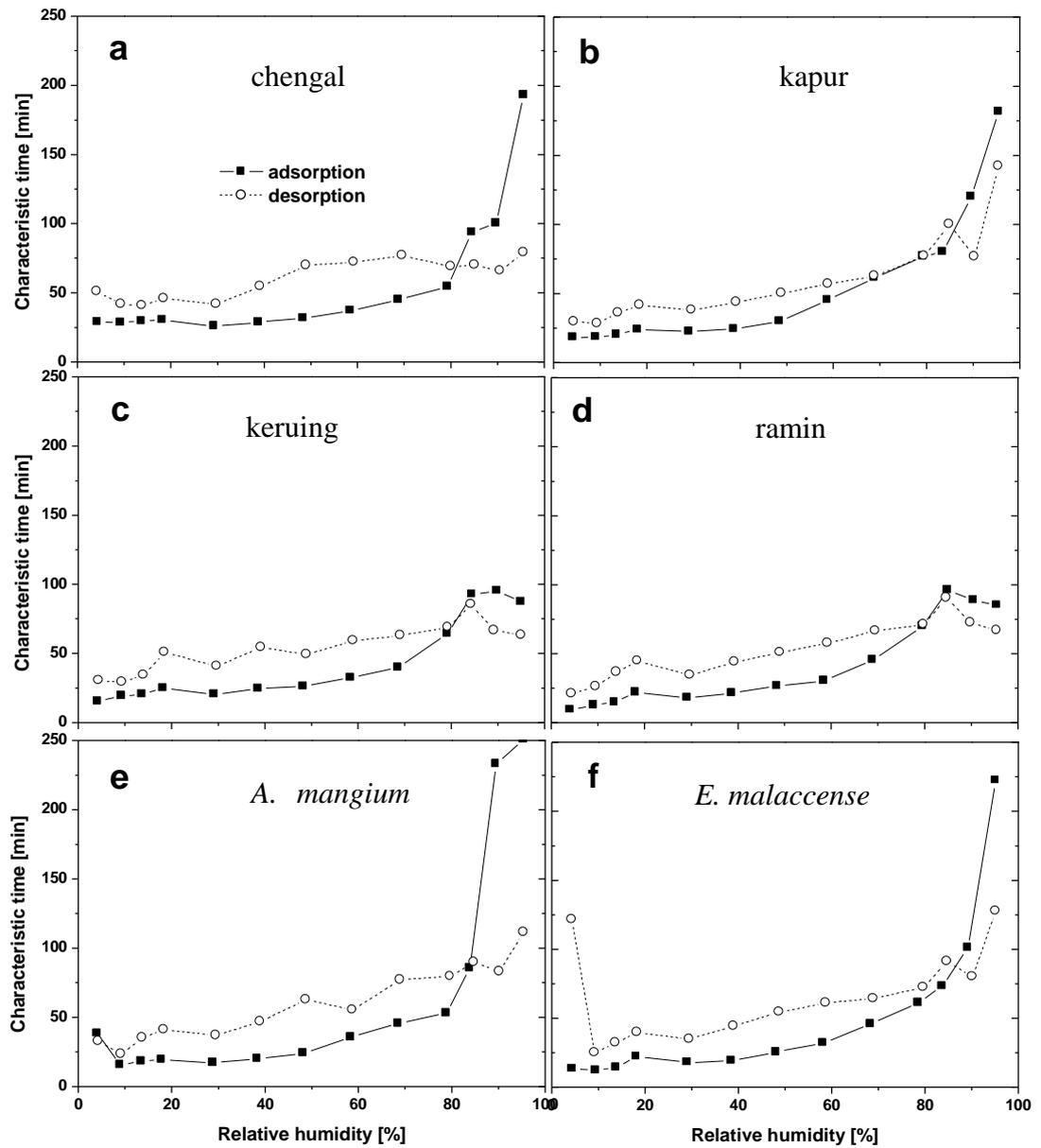


Figure 5.9 Variation of characteristic times with change in RH for the slow t_2 exponential kinetic processes for adsorption and desorption on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* & (f) *E. malaccense*.

An important observation is the difference in the characteristic times; the slow adsorption and desorption process has a big difference (between 10-40 mins) whereas there are small differences in the characteristic times of the fast process under adsorption and desorption conditions (between 0.5-5 mins). After 80% RH, the characteristic time increases greatly in all the hardwoods studied, especially during adsorption. At the moment, no physical interpretation can be made with respect to this high RH range. Other factors, such as capillary condensation may be becoming significant in this range. At 0% RH, during desorption, *E. malaccense* has the highest equilibration time compared to the other tropical hardwood species. The anomalous behaviour found at the high end of the RH range has already been noted.

Referring now to the characteristic times associated with the adsorption and desorption processes for thermally modified wood. The characteristic times for desorption for both the fast and slow processes are greater than those for adsorption over much of the RH range, as noted with the unmodified tropical hardwoods. However, with the slow process characteristic times, the point at which the adsorption t_2 exceeds the desorption t_2 occurs at higher RH values as the thermal modification becomes severe (Figure 5.11). This difference in behaviour in terms of characteristic times between adsorption and desorption is striking. There is clearly a difference between adsorption and desorption in both the kinetic and equilibrium behaviour. The obvious question is then, are these two phenomena related in some way? This idea will be further considered as the thesis progresses.

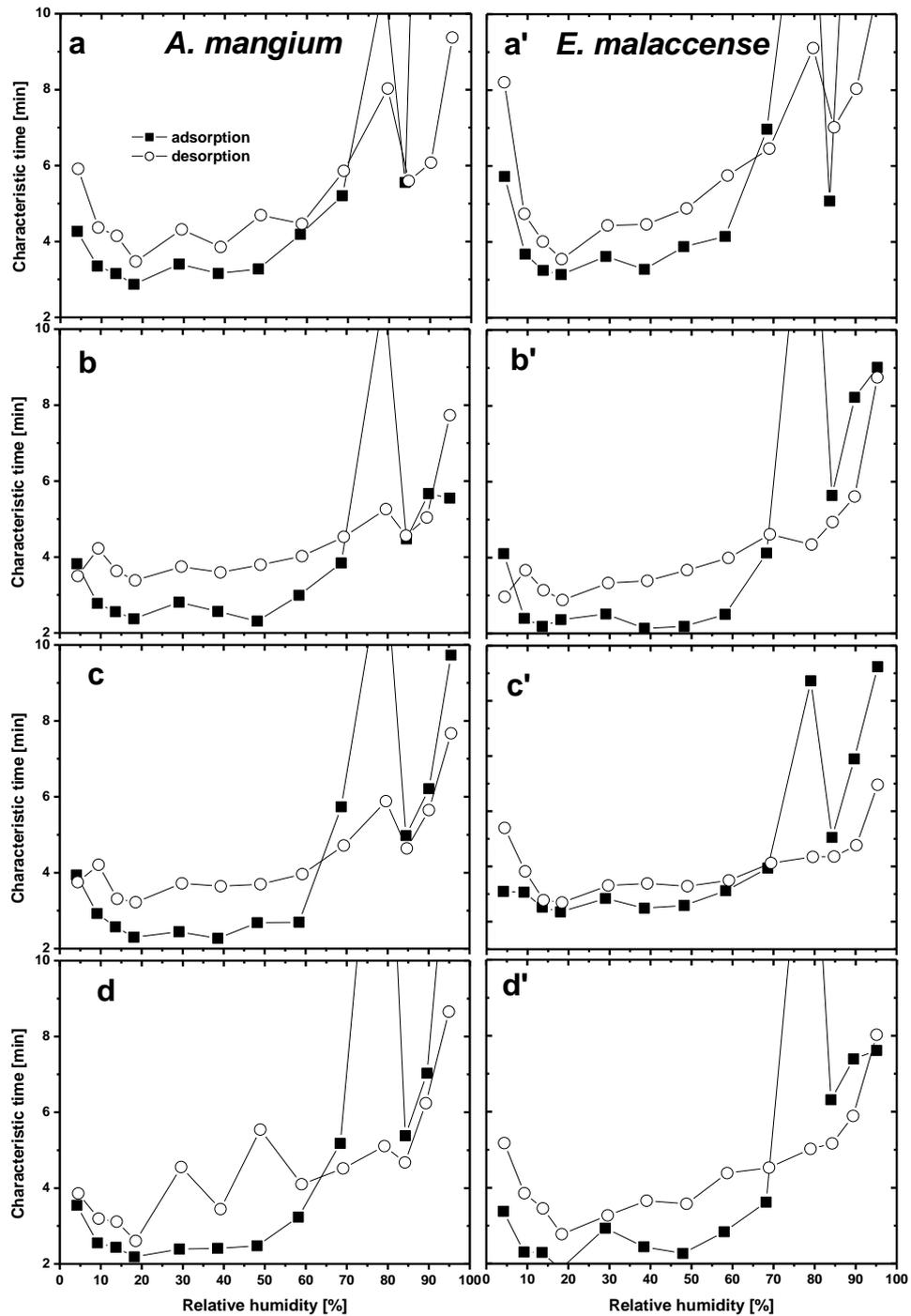


Figure 5.10 Variation of characteristic times with change in RH for the fast t_1 exponential kinetic processes for adsorption and desorption for *A.mangium* (a - d) and *E.malaccense* (a' - d'). a/a' unmodified wood; b/b' thermal modification 180°C-3 h; c/c' thermal modification 200°C-3 h; d/d' thermal modification 220°C-3 h.

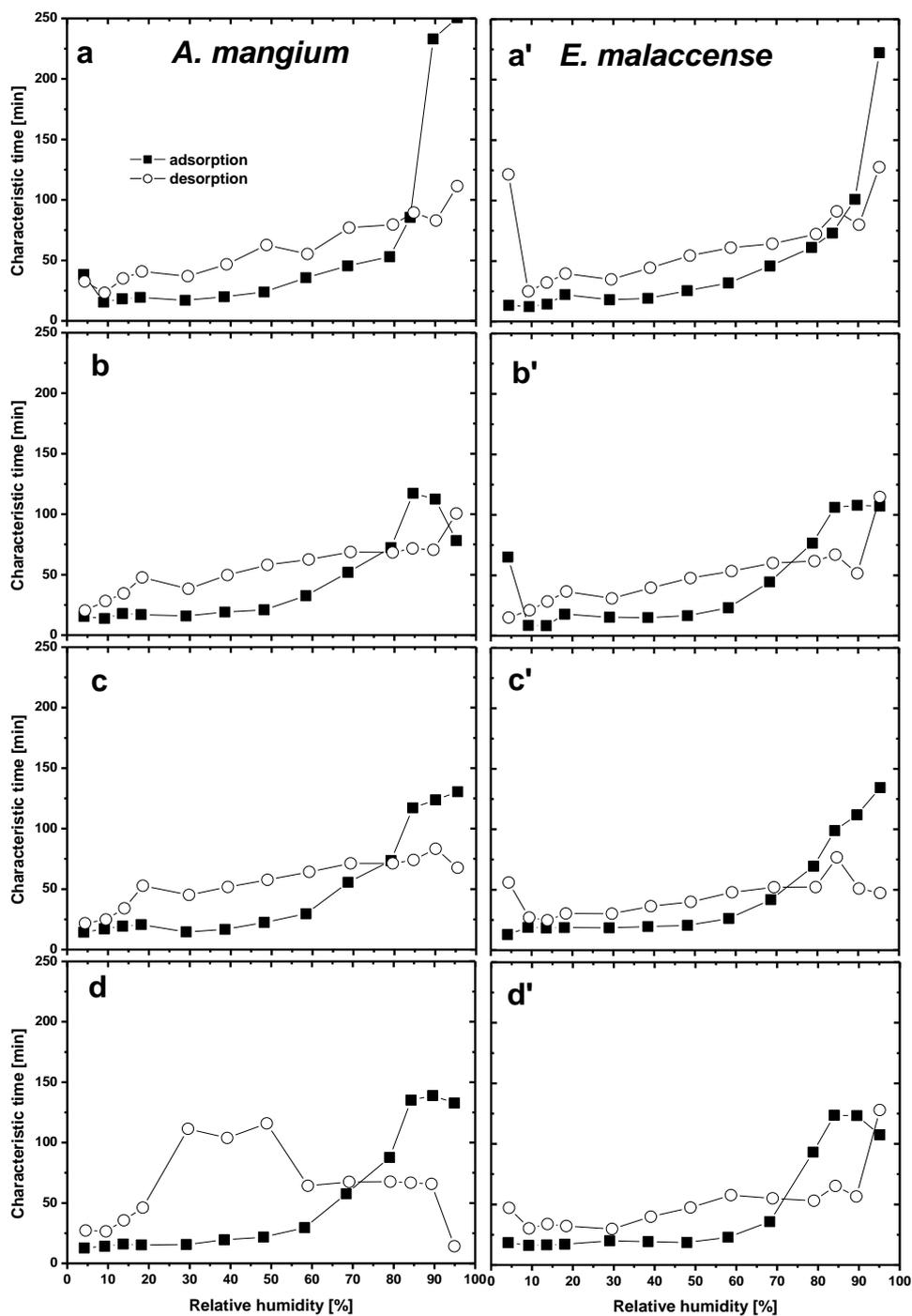


Figure 5.11 Variation of characteristic times with change in RH for the slow t_2 exponential kinetic processes for adsorption and desorption for *A.mangium* (a - d) and *E.malaccense* (a' - d'). a/a' unmodified wood; b/b' thermal modification 180°C -3 h; c/c' thermal modification 200°C-3 h; d/d' thermal modification 220°C-3 h.

5.3.4 Hysteresis effect of the fast and slow kinetic mass components

The PEK model gives the MC values for the fast and slow kinetics processes after an infinite time of exposure for a range of RH values, and these can be cumulatively added together (subtracted in the case of desorption) for each subsequent RH step in the isotherm to produce pseudo-isotherm plots, such as those for the tropical hardwoods (Figure 5.12 and 5.13) and thermally modified wood (Figure 5.14a-d and 5.15a'-d'). In this case the adsorption process data was obtained at the end of the pre-set RH and the desorption process data taken at the beginning of the pre-set RH. Through this method the cell wall MC associated with the slow and fast kinetics show absolute hysteresis between desorption and adsorption at the same target RH. It can be seen that the different tropical hardwoods species show different sorption hysteresis behaviour in both fast and slow kinetic processes.

N. heimii, *Gonystylus* spp. and *A. mangium* exhibit larger hysteresis in the fast process (Figure 5.12) compared to the slow process (Figure 5.13); *E. malaccense*, *Dryobalanops* spp. and *Dipterocarpus* spp. have similar levels of hysteresis in both the slow and fast kinetic process. In the fast kinetic process, there are two types of hysteresis; open-loop (*N. heimii*, *Dipterocarpus* spp., *Gonystylus* spp. and *E. malaccense*) and closed-loop (*Dryobalanops* spp. and *A. mangium*). However, in the slow kinetic process all the hardwoods showed the closed-loop hysteresis and in the upper range of hygroscopic range the MC adsorption was greater than MC for desorption (Figure 5.13). *A. mangium* and *E. malaccense* have a bigger magnitude of hysteresis in the slow kinetic process compared with *Dipterocarpus* spp., *Dryobalanops* spp., *Gonystylus* spp. and *N. heimii*.

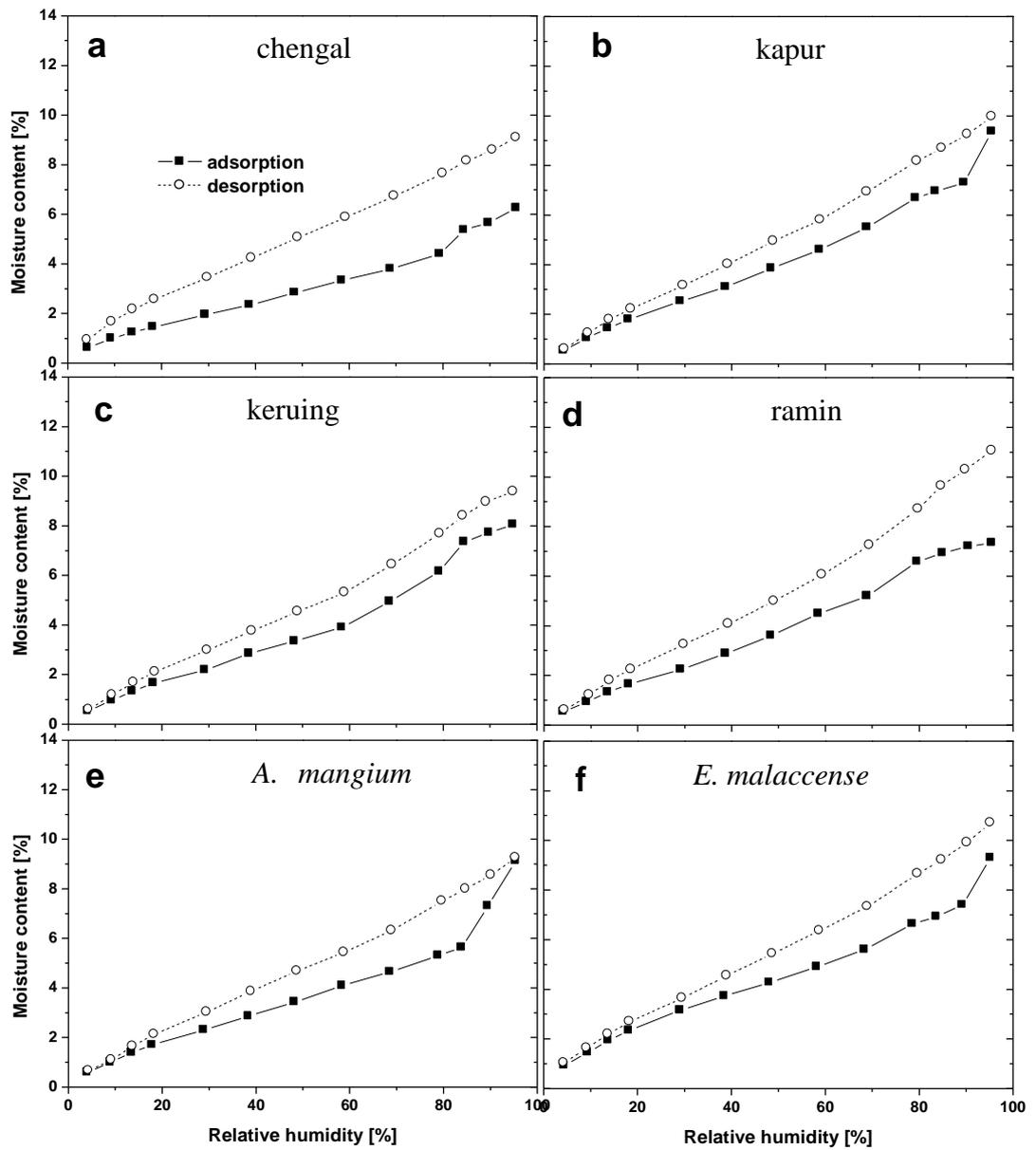


Figure 5.12 A comparison of the cumulative moisture contents associated with the fast adsorption and desorption kinetics processes on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* & (f) *E. malaccense*.

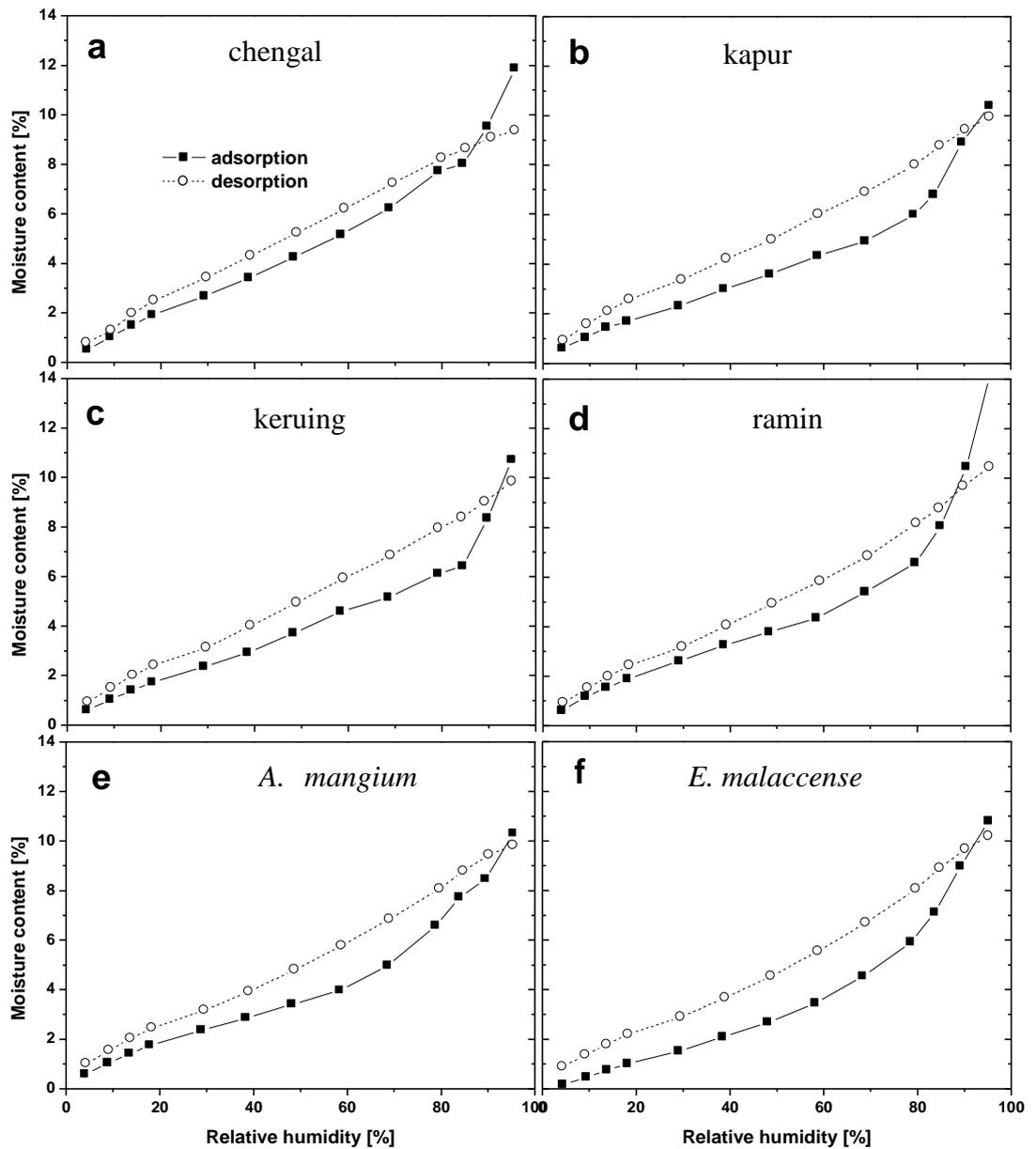


Figure 5.13 A comparison of the cumulative moisture contents associated with the slow adsorption and desorption kinetics processes on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* and (f) *E. malaccense*.

Kohler *et al.* (2003) reported on the hysteresis between the PEK derived MCs of desorption and adsorption processes at infinite time associated with the fast and slow components of flax, noting that the hysteresis effect was associated with both process. They did mention the similar observation in the MC associated with the slow adsorption and desorption process at the higher RH levels, which was attributed to the presence of what they called ‘extra water’ (Figure 5.14). However, this ‘extra water’ was not attributed with any physical meaning. It is manifested as an upturn in the MC₂ curve at higher RH. Kohler *et al.* (2003) supposed that water was somehow transferred between ‘fast sites’ and ‘slow sites’. It will be shown later that it is not necessary to use the troublesome idea of sorption sites when explaining PEK behaviour.

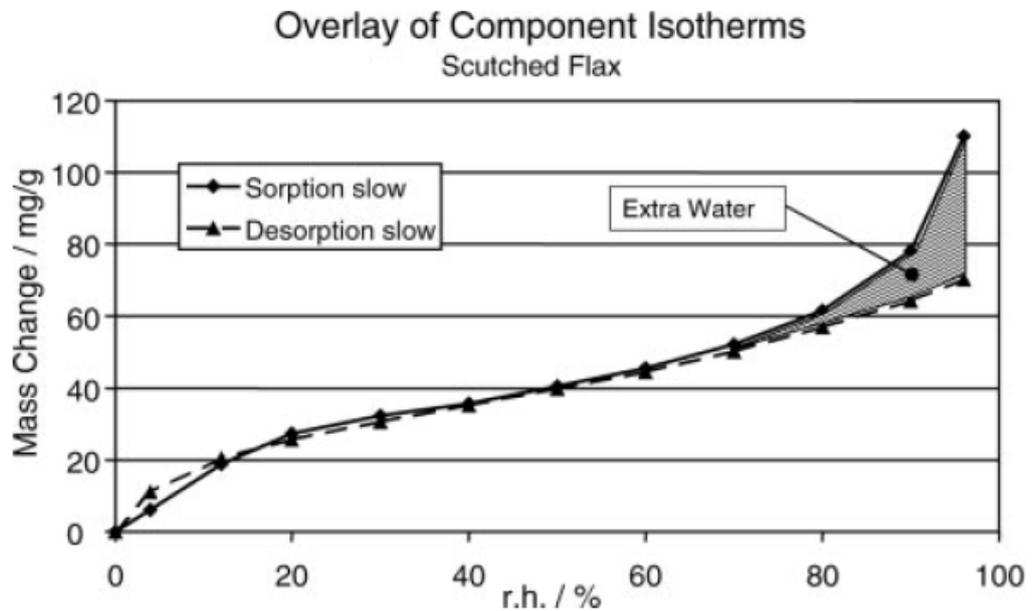


Figure 5.14 Congruence of the slow sorption and desorption isotherms suggesting the existence of ‘extra water’ (Kohler *et al.* 2003).

As noted in Section 3.3.1, 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 discussed. 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. This means there will be some uncertainty when assigning MC’s to the fast and slow processes accurately.

Thermal modification reduces the cumulative moisture contents MC_1 (fast process) (Figure 5.15) and MC_2 (slow process) (Figure 5.16). The higher the modification temperature resulted the lower the cumulative moisture content (MC_1 and MC_2). However, it is clear that the fast process pseudo-isotherms invariably form an open hysteresis loop, whilst with the slow process the loops are closed. Furthermore, with the slow process, the cumulative MC of the adsorption process exceeds that of the desorption process at the highest RH. This is particularly noticeable with the thermally modified wood (Figure 5.16).

This behaviour, where the adsorption of slow process MC exceeds desorption the of slow process MC has been found in flax, hemp jute and sisal, but not for cellulose-rich materials, such as cotton or filter paper (Figure 5.17) (Xie *et al.* 2011). This behaviour has been found to be reproducible, giving some confidence in the curve fitting procedure.

If cellulose-rich substrates do not show this behaviour, can it therefore be linked to matrix relaxation processes in some way? If this is correct and if hysteresis is also linked to matrix relaxation, then does this suggest a link between the two phenomena?

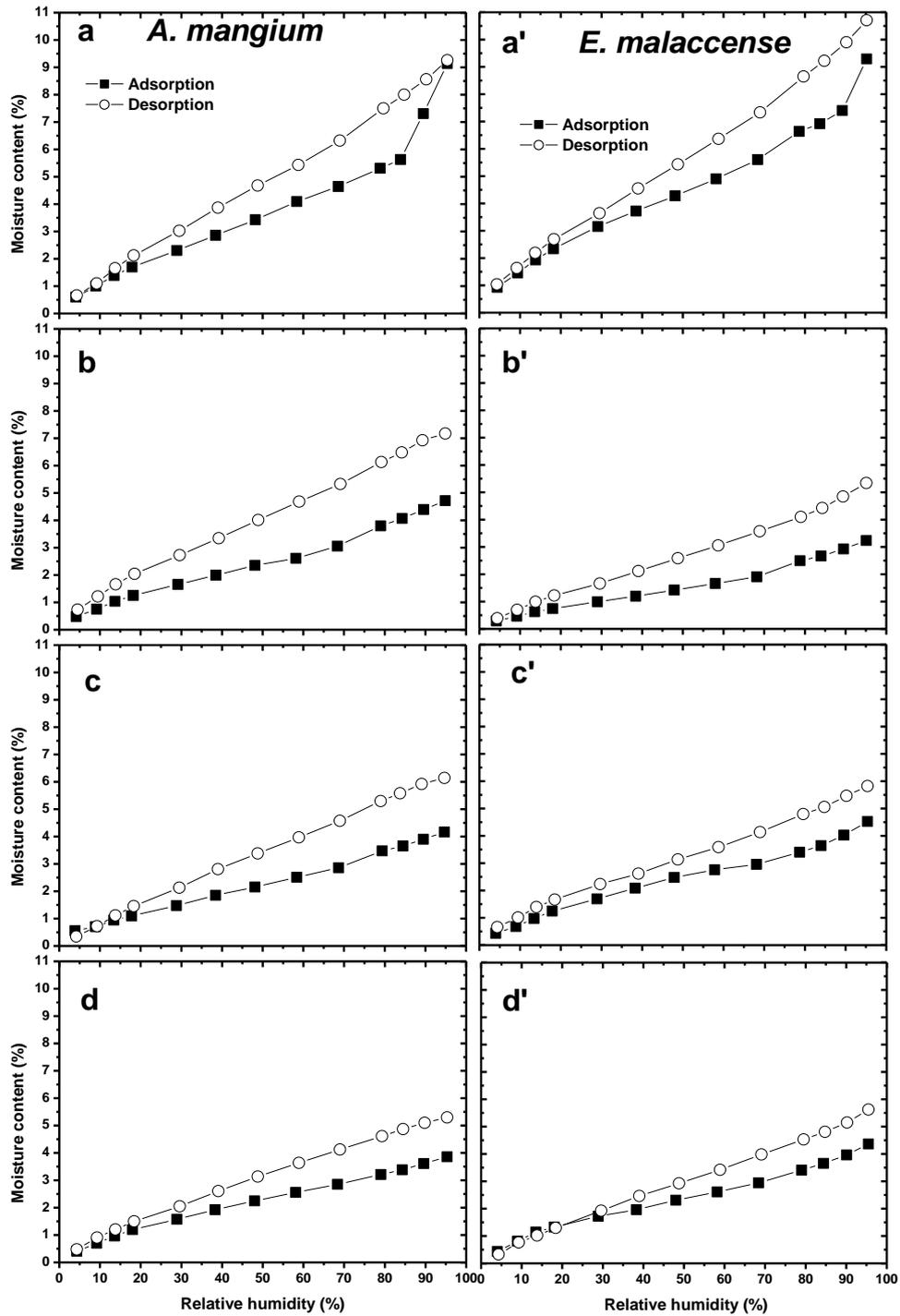


Figure 5.15 Plots of cumulative moisture contents associated with the fast (MC_I) exponential kinetic processes versus the RH for *A. mangium* (a - d) and *E. malaccense* (a' - d'). a/a' unmodified wood; b/b' thermal modification 180°C-3 h; c/c' thermal modification 200°C-3 h; d/d' thermal modification 220°C-3 h.

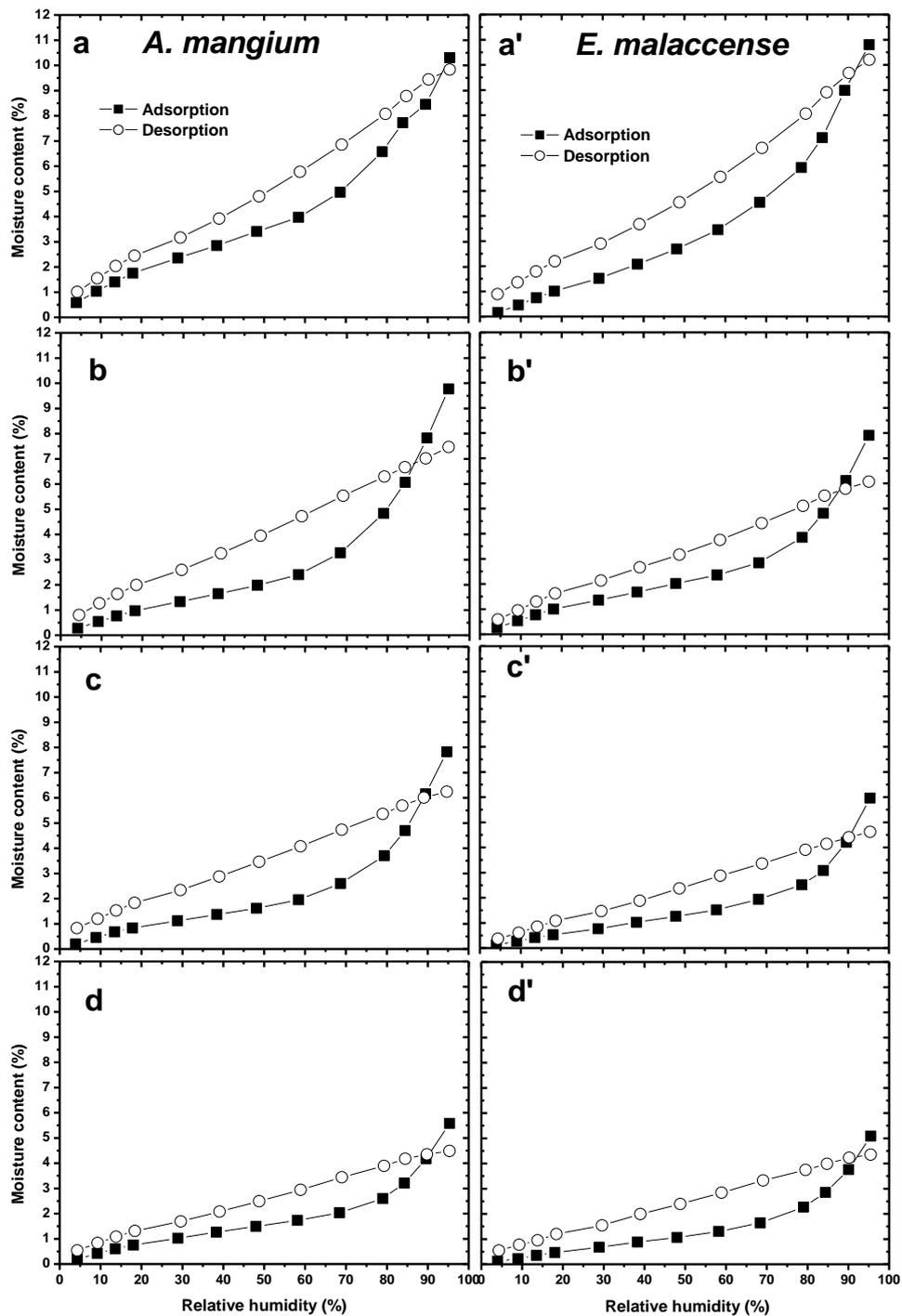


Figure 5.16 Plots of cumulative moisture contents associated with the slow (MC_2) exponential kinetic processes versus the RH for *A. mangium* (a - d) and *E. malaccense* (a' - d'). a/a' unmodified wood; b/b' thermal modification 180°C -3 h; c/c' thermal modification 200°C-3 h; d/d' thermal modification 220°C-3 h.

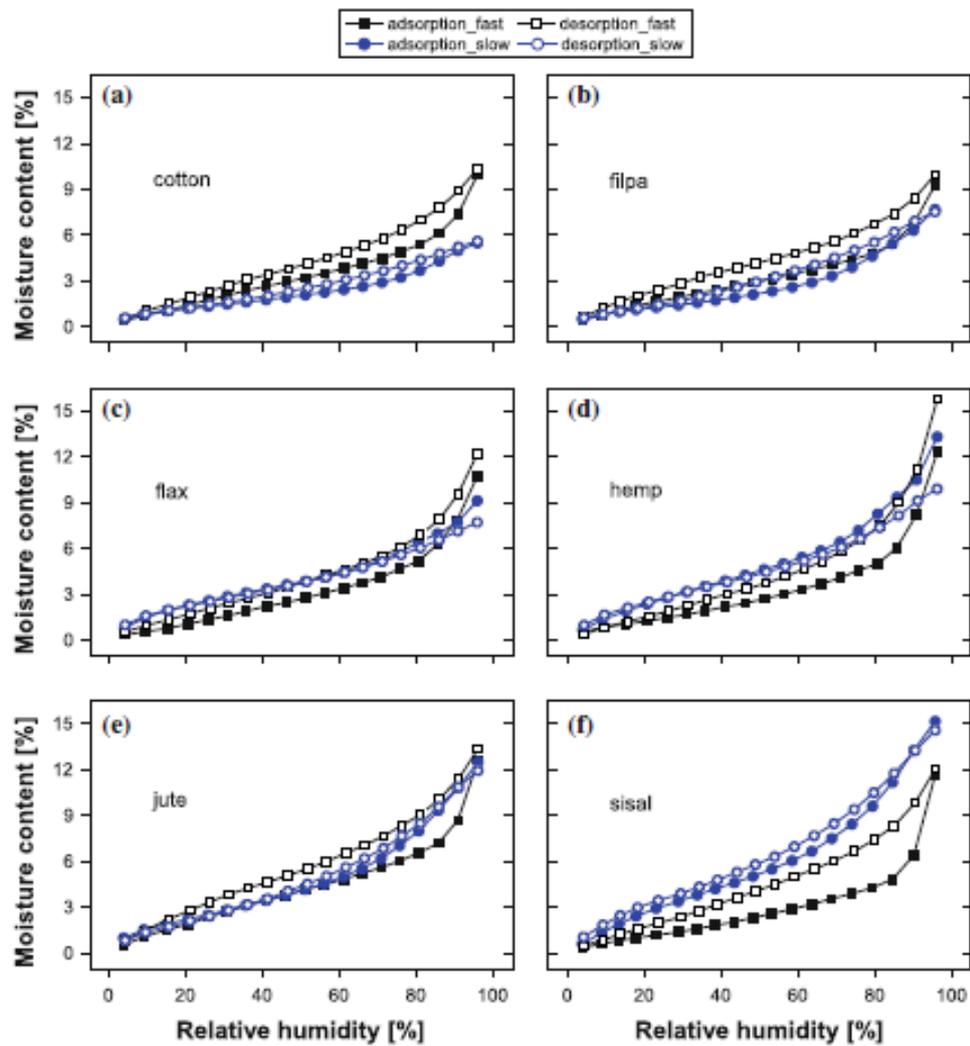


Figure 5.17 Cumulative moisture content associated with the fast (MC_1) and slow (MC_2) exponential kinetics processes in water vapour adsorption and desorption runs for cotton (a), filter paper (b), flax (c), hemp (d), jute (e), and sisal (f), respectively (Xie *et al.* 2011).

5.4 Conclusion

Analysis of sorption kinetics was conducted using the parallel exponential kinetics model, with excellent fits to the experimental data obtained. Attempts to correlate the fast and slow sorption moisture contents with monolayer and polylayer water were generally unsuccessful. It is concluded that interpretation of the PEK model in terms of sites is unlikely to be correct. However, this study has clearly shown that the PEK model is an appropriate method for studying cell wall sorption phenomena. There is sorption hysteresis in the characteristic times and moisture contents between the adsorption and desorption process in both fast and slow processes of all hardwood species and thermally modified wood. The difference in the behaviour with the pseudo-isotherms of cumulative PEK MCs is also interesting. Different types of behaviour are also found with different wood species and also depending upon sample modification. The next chapter considers a possible interpretation of the PEK model based upon matrix relaxation processes.