CHAPTER 3

PRELIMINARY STUDIES AND REPRODUCIBILITY

3.1 Introduction

This preliminary study included some basic investigations on the sigmoidal nature of the water vapour sorption isotherms of wood and the property of sorption hysteresis between the adsorption and desorption loops of the isotherm. Determining the equilibrium moisture content (EMC) of wood at different given relative humidities (RH) is a means of evaluating the sorption properties of wood. The gravimetric method is a suitable way to determine the EMC by conditioning the wood samples over different saturated salt solutions at a constant temperature to attain a desired RH, however this method is difficult to use for kinetic studies. More recently, a dynamic vapour sorption (DVS) technique has been introduced to investigate the sorption properties of different natural fibres and wood. Sorption isotherm curves for various wood species were studied for their hygroscopicity and sorption hysteresis values. Further analysis with the Hailwood-Horrobin (H-H) model revealed the different types of water (water of hydration and dissolution water) in the wood cell wall. A comparison between the magnitude of water of hydration in the cell wall from the H-H model (by converting the percentage moisture content into moles of water molecules per gram of dry cell wall mass) with a theoretical cell wall OH content which can be calculated from the macromolecular composition method (Rowell 1980). Five wood species were selected for this phase of the study, which comprised two tropical hardwoods which are currently being promoted as potential plantation species in Malaysia (Rushdan *et al.* 2007), two temperate softwoods which are widely planted in the UK and New Zealand and Accoya (acetylated radiata pine). In this preliminary study, the reproducibility of the data

obtained using the DVS apparatus was established. The reliability and reproducibility of the PEK model and curve-fitting software are also investigated in this chapter.

3.2 Materials and Methods

3.2.1 Sample preparations

Four wood species *Acacia mangium*, *Endospermum malaccense*, Sitka spruce (*Picea sitchensis*), radiata pine (*Pinus radiata*) and one commercially modified wood, namely Accoya (radiata pine chemically modified by acetic anhydride by Titanwood based at Arnhem in the Netherlands) were used in this study. Kiln dried wood of *A. mangium* and *E. malaccense* were obtained from the Forest Research Institute Malaysia (FRIM) (Selangor, Malaysia) while Sitka spruce wood was sourced locally (Scotland, United Kingdom). Radiata pine and Accoya were supplied by Titanwood. The wood samples (20 x 20 x 175 mm (tangential x radial x longitudinal) were chipped and ground with an analytical mill model A11 Basic (IKA® Werke GmbH and Co.KG, Germany) into fine particles/flour, which were passed through a BS410-1:2000 mesh sieve no. 20 (0.841 mm sieve opening). These fine particles were used throughout this preliminary study.

3.2.2 Sample morphology

The morphology of the wood particles was characterised using a Hitachi S-4800 Ultra-High Resolution Field Emission Scanning Electron Microscope (SEM). The specimens were affixed on SEM stubs with double sided tape and coated with carbon as the conductive material. An accelerating voltage of 3 kV (for the lignocellulosic material) was used for the observation of the samples under SEM.
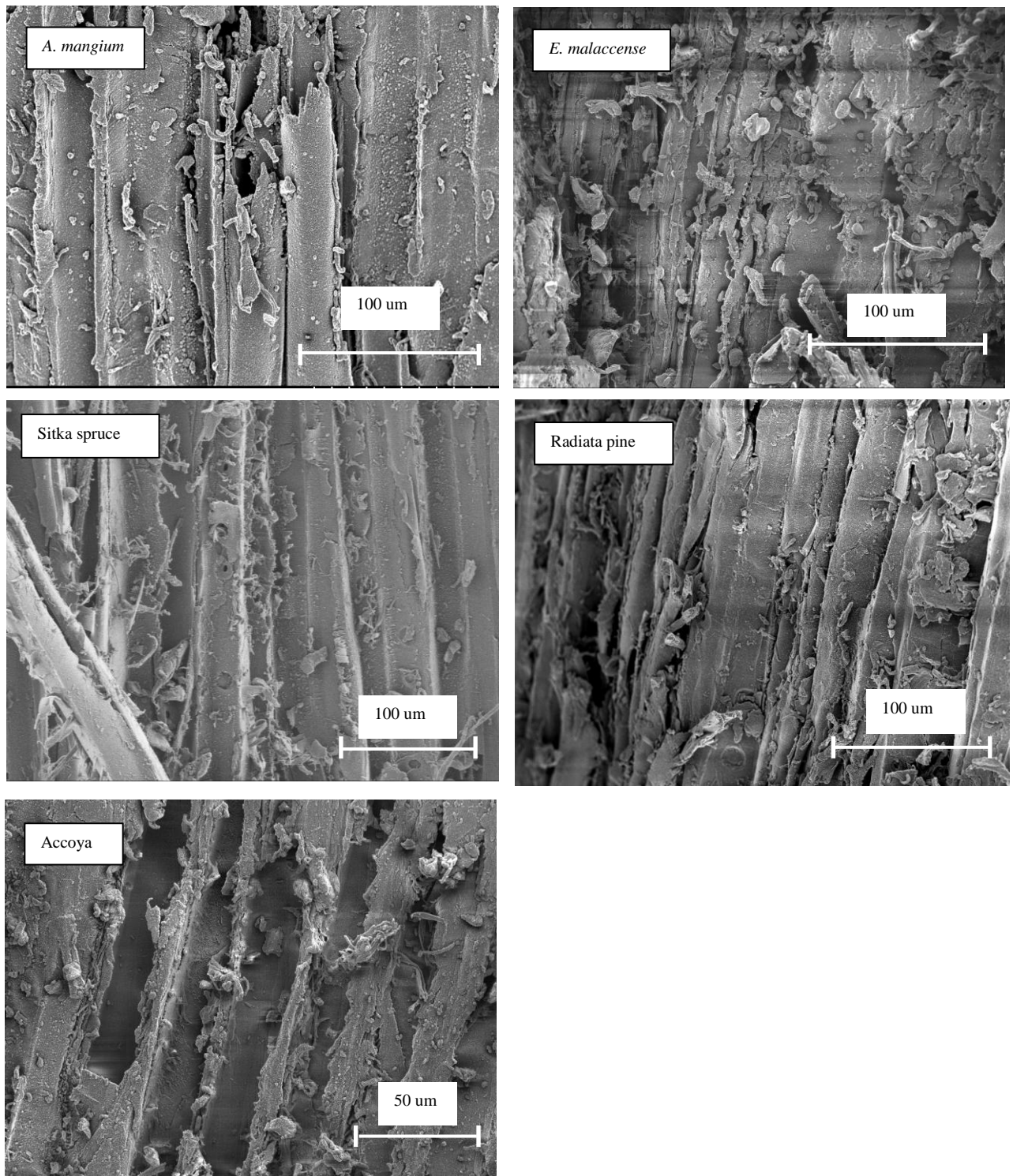
Figure 3.1 The morphological characteristics of *A. mangium* (300x), *E. malaccense* (1100x), Sitka spruce (350x), radiata pine (400x) and Accoya (600x).

Although the wood materials were in the form of fine particles, the cell wall structure as observed in the SEM with high magnification was still essentially intact (Figure 3.1). This study is performed on the water vapour sorption of bundles of wood cell walls.

3.2.3 Determination of dynamic sorption isotherms

Isotherm analyses were performed using a Surface Measurement Systems Ltd. (London, United Kingdom) Dynamic Vapour Sorption Intrinsic (DVS) apparatus. This DVS can accurately determine sorption isotherms at different temperatures (20-40 ^{o}C) and to a range of preset relative humidity (RH) values. It is a well established method for the determination of water vapour sorption isotherms. The DVS apparatus comprises a measurement pan suspended from an ultrabalance/microbalance that is capable of measuring changes in sample mass to a resolution of 1 part in 10 million (i.e. 20±0.000002 mg) with a maximum weight capacity of 150 mg (Figure 3.2). In this study, the wood fine flour prepared as described earlier (ca. 20 mg) was placed onto a cleaned sample pan (a conical steel wire gauze) which was carefully hooked onto the hang down wire connected to the microbalance in a climate controlled chamber (located in a thermostatically controlled cabinet). A constant flow of dry nitrogen gas (200 cm^3 min^{-1}) is mixed into a stream of nitrogen containing water vapour at saturation and this mixed stream passes through the measurement chamber to maintain a set RH. The schedule for the DVS was set to record the sample mass at each of the following RH steps of adsorption at 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90% RH and at a constant temperature of 25 +/- 0.1 ^{o}C and in reverse sequence at 90, 80, 70, 60, 50, 40, 30, 20, 10, 0% RH for the desorption isotherm. The RH schedule was initiated once the rate of change of the initial drying curve rate of mass change reached the set value. The sample

is initially weighed in the atmosphere in the laboratory and consequently contains an unknown amount of moisture (although this can be estimated based upon previous experience). The drying curve determines the dry sample weight. For this reason it is extremely difficult to have exact target samples weights, quite apart from the practical difficulties of preparing such small samples. At this point, the DVS instrument automatically tares the sample mass, so that all subsequent MC values can be accurately calculated as a mass percentage. This sequence of RH steps was subsequently changed in later experiments. Humidity and temperature probes are located in close proximity to the sample, providing direct measurement of these parameters.

The software of the DVS apparatus is user-set to terminate a sorption run and move to the next RH step. The instrument maintained the sample at a constant RH until the rate of change in mass (dm/dt) was less than 0.002% min^{-1} over a 10 min period; a criterion that from previous experiments had been shown to give a sample MC to within less than 0.1% of the equilibrium value at extended time (Hill *et al.* 2010a). The change in weight was recorded and saved every 20 s. The sample mass readings from the microbalance then reveal the vapour adsorption/desorption behaviour of the material. During operation it was found that the temperature and humidity values were very stable (RH +/-0.1%, temperature +/-0.1 ^{o}C) however both the RH and temperature did not always stabilise 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. The running time, isotherm temperature, target RH, actual RH and sample weight were recorded throughout the isotherm run. The weight gains were recorded gravimetrically and EMC was calculated automatically in the DVS using the relation given in Equation 2.1:

$$EMC = [(W_t - W_o)/W_o)] \text{ x } 100 \qquad \qquad \textbf{(3.1)}$$

where W_o is oven dry weight or weight recorded as the measurements taken at 0% RH

and W_t is the weight at each RH step.

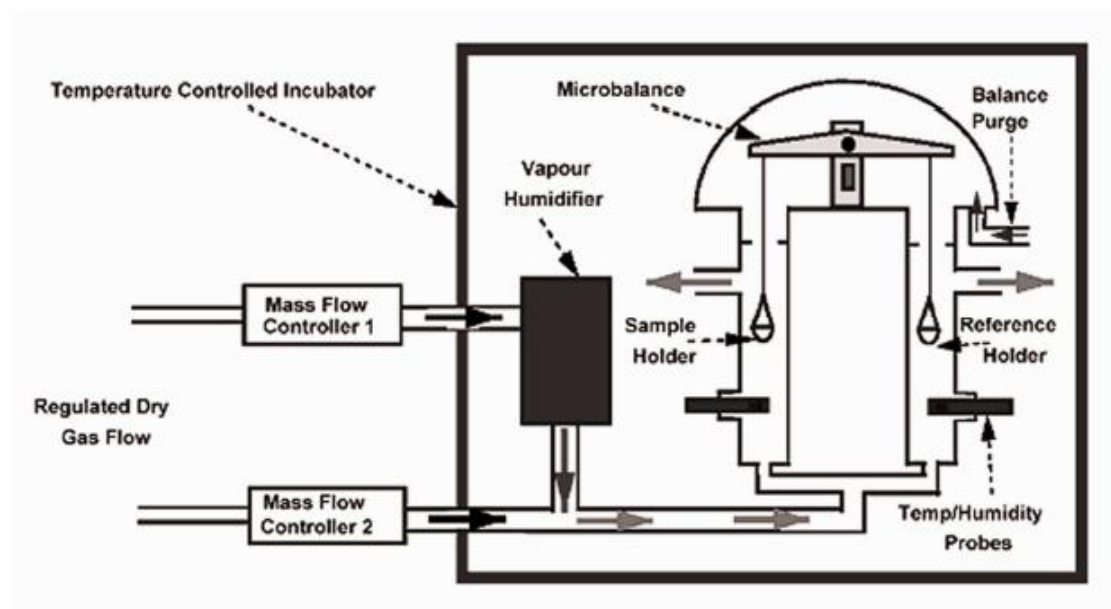**Figure 3.2 A schematic showing the basic working principles of a dynamic vapour sorption (DVS) Intrinsic apparatus (Surface Measurement Systems).**

3.2.4 Reproducibility of DVS Data

Studies on the reproducibility of the data obtained from DVS were performed. This is to ensure the DVS is giving accurate and precise data in operation. A few parameters namely data reproducibility, effect of sample weight and scanning curves were investigated.

3.2.4.1 Effects of data reproducibility

The DVS apparatus used for this study was only able to measure one sample at a time. In order to determine the reproducibility of the sorption data, a sample from *A.*

mangium was subjected to the four consecutive adsorption/desorption cycles instead of one cycle as used in normal testing. The result is shown in Figure 3.3. The sorption curves of the four cycles showed that it was reproducible over most of the RH range studied. The highest standard deviation was in the adsorption isotherm at 80% RH at 0.3%. Therefore the DVS is assumed to be able to give reproducible sorption data for every sample tested and the use of a sample for one test is acceptable. Hill *et al.* (2009) reported that the DVS data from the natural fibres (flax and jute) were reproducible over most of the RH range with slight deviations above 70 % RH.
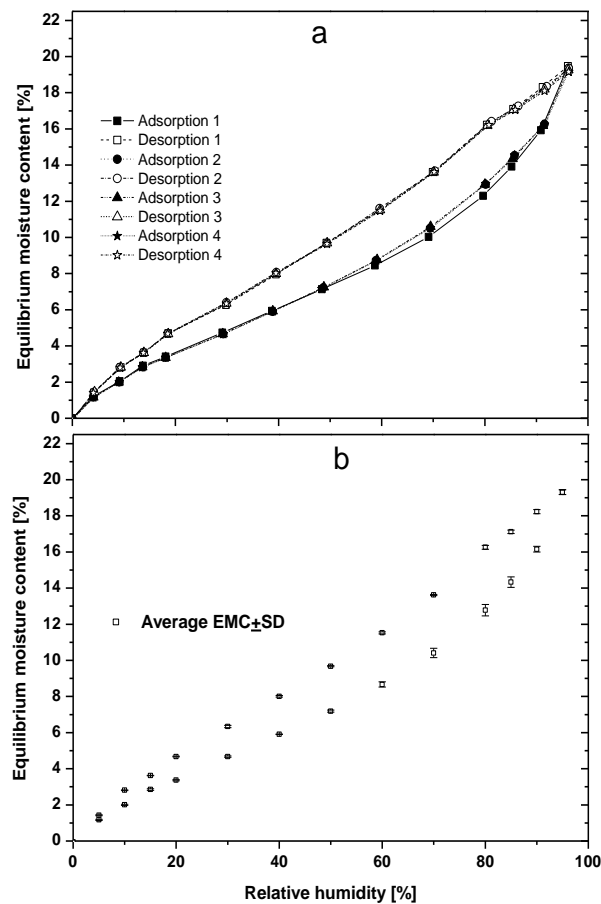

Figure 3.3 Reproducibility of moisture adsorption/desorption of *A. mangium* (a) and average Equilibrium moisture content (EMC)+/-standard deviation (SD) (b) in four cycles at 25 ^{o}C.

3.2.4.2 Effects of sample replicates

This study was to determine the reliability of the data obtained from the DVS with three replicates of *A. mangium* tested at different times. Repeatability of results from the same material and RH of wood fine particles (*A. mangium*) gave highly reproducible measurements whereby the mass changes at different RH coincided with each other (Figure 3.4a), except at the higher RH and the standard deviation is 0.2 % (Figure 3.4a'). The absolute hysteresis also shows very minor variation at higher RH ranges of 80-95% (Figure 3.4b) and the standard deviation is 0.1% (Figure 3.4b'). This variation in results at the higher end of the hygroscopic range has been noted previously (Hill *et al.* 2009).

3.2.4.3 Effects of sample weight

Samples of weight 10.5, 17.9, 19.5, 38.9 and 76.1 mg of *A. mangium* were tested with a single step adsorption (0 to 50% RH) and desorption (50 to 0% RH) respectively. Results show that different sample weights produced different mass changes. The biggest sample weight has a lower MC and required more time to achieve equilibrium (Figure 3.5a). However, when the sample weight is within 1.0 mg tolerance (sample weight of 20 mg in wet masses), it showed almost the same ratio of mass change over actual RH (Figure 3.5b). This study shows the total running time for wood depends on total mass and the sample mass tested needs to be set at +/- 1 mg to avoid variation. According to SMS company literature this problem can be avoided by the setting of new dm/dt parameters with a sample mass change.
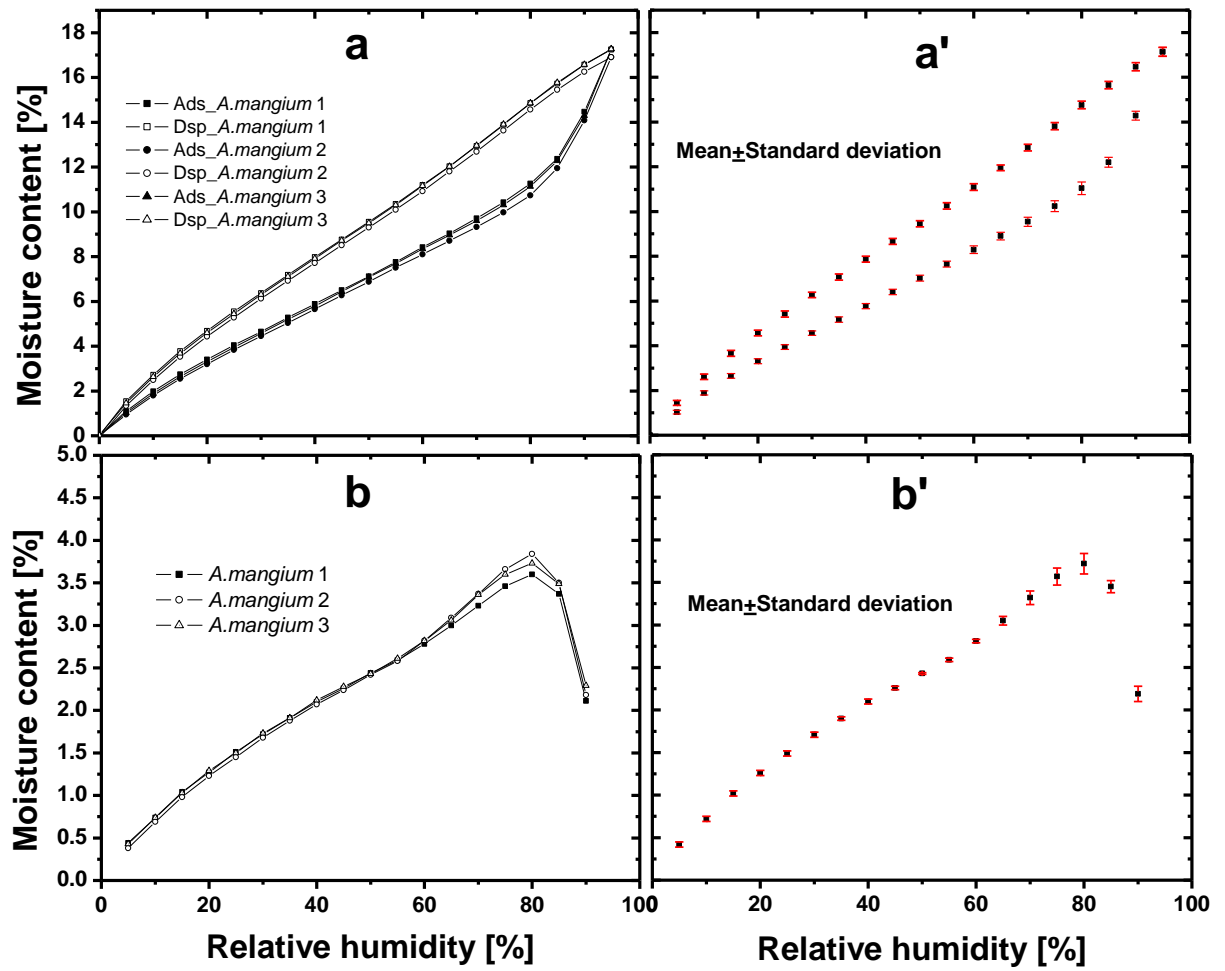
Figure 3.4 Comparisons of the sorption isotherms (a) with the standard deviation (a'), and absolute hysteresis values (b) with the standard deviation (b') for three identical experiments of different samples of *A. mangium* at 25 °C.
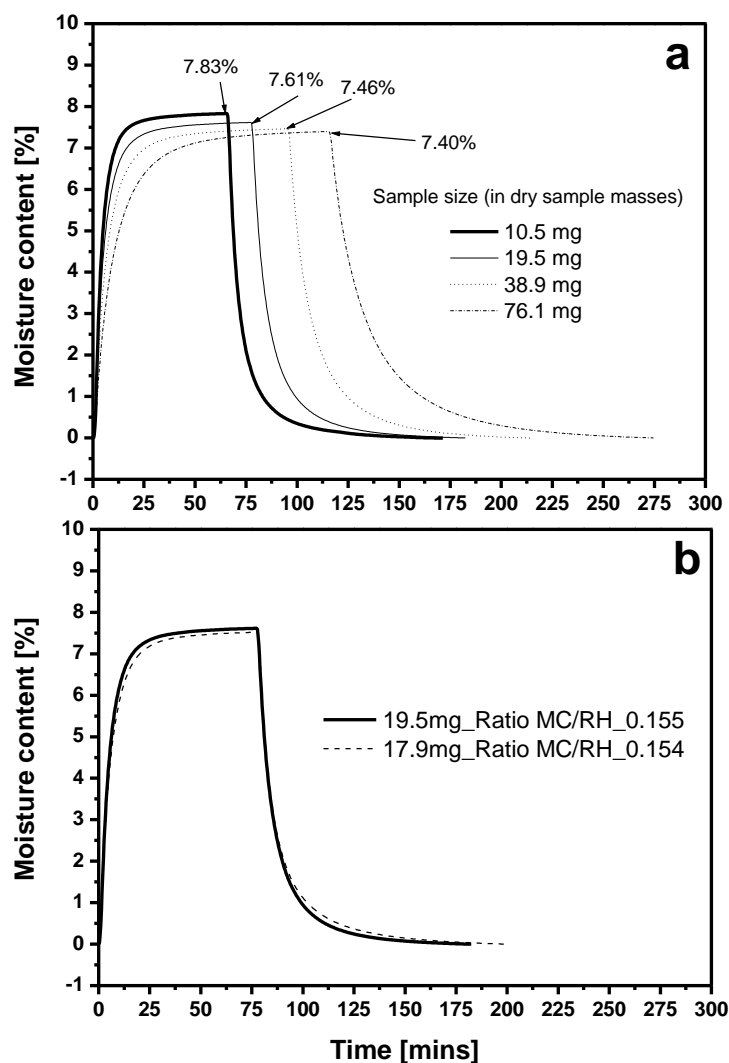
Figure 3.5 MC at different sample size for 0 to 50 and back to 0% RH, (a) 4 different sample weight and (b) sample weight within 1.0 mg tolerance.

In a further check on the reproducibility of the data, the sorption kinetics data used in Figure 3.5b was analysed using the PEK model. The dry sample masses were 17.9, 18.8 and 19.5 mg. The results are shown below in Table 3.1. The results are reproducible within the normally observed +/- 10% variation, with the exception of the sample weighing 20.9 mg, where the t_2 in adsorption and desorption is outside of this

range. This variation has been noted in some curve fits in the data presented elsewhere in the thesis and is more often noted at the bottom and top end of the hygroscopic range. Furthermore, the RH range of 0-50% is much larger that used in the experiments reported in the thesis.

Table 3.1 Results of weight variation in sorption kinetics using PEK model

Sample weight (mg)	Adsorption					Desorption				
	MC_o (%)	t_1 (min)	t_2 (min)	MC_1 (%)	MC_2 (%)	MC_o (%)	t_1 (min)	t_2 (min)	MC_1 (%)	MC_2 (%)
17.9	0.03	4.3	12.6	5.1	2.2	7.5	5.1	23.6	-4.9	-2.6
18.8	0.25	4.3	12.6	5.1	2.1	7.5	5.2	22.7	-4.9	-2.8
19.5	-0.05	4.3	15.7	6.4	1.3	7.6	5.2	19.1	-4.8	-2.8

In a further check of the reproducibility of the curve-fitting parameters, the data is shown for a sample of *A. mangium* which was subjected to four sorption cycles in separate experiments. The data is reproduced below in Table 3.2.

Table 3.2 The *A. mangium* fitting data for the 19.8 mg sample adsorption RH 30-40%

Number of sorption cycles	Adsorption				
	MC_o (%)	t_1 (min)	t_2 (min)	MC_1 (%)	MC_2 (%)
1	4.82	3.31	21.34	0.47	0.65
2	4.75	3.59	23.48	0.54	0.63
3	4.74	3.47	22.37	0.52	0.66
4	4.74	3.72	23.36	0.54	0.64

This shows that the curve fitting procedure and the sorption kinetic data give high levels of reproducibility, within 10%, except in the case of the MC_1 values. Finally, in another examination of the reproducibility, three samples of *A. mangium* of dry weight 18.51, 18.56 and 18.63 mg are shown as an example with the curve fitting

parameters given in Table 3.3. Again, the reproducibility of the data is within 10%, except in the case of the MC_1 values, which are of the order of 20%.

Table 3.3 The *A. mangium* fitting data for the 18.51, 18.56 and 18.63 mg samples adsorption RH 20-25%

Sample weight (mg)	Adsorption				
	MC_o (%)	t_1 (min)	t_2 (min)	MC_1 (%)	MC_2 (%)
18.51	3.23	3.42	25.30	0.23	0.35
18.56	3.32	3.49	25.39	0.27	0.38
18.61	3.44	3.30	25.91	0.28	0.35

3.2.4.4 Scanning curves

A. mangium was subjected to three cycles of adsorption and desorption at three different points (95, 70 and 30% RH) using a 5% RH step and results were highly reproducible. As a result of the experiment three types of scanning curves have been derived which clearly shows the sorption hysteresis phenomenon (Figure 3.6).
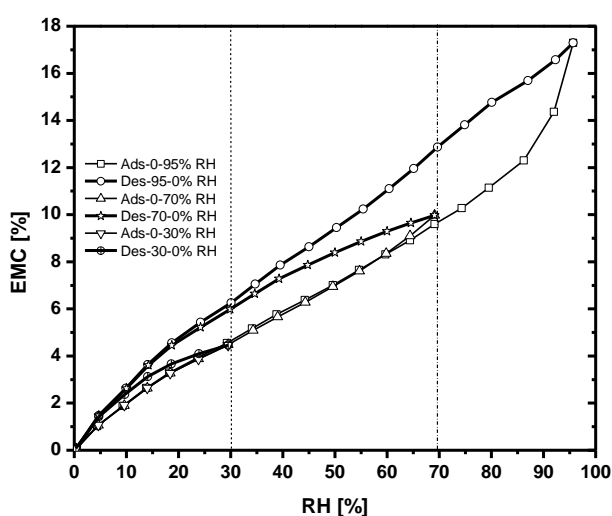

Figure 3.6 Three scanning curves at three points of desorption (95, 70 and 70% RH) for *A. mangium* at 25 ^{o}C.

3.3 RESULTS AND DISCUSSION

3.3.1 General sorption behaviour

The actual RH in the sample chamber did not immediately reach the targeted RH when the testing program changes the RH from one value to the next (Figure 3.7). This resulted in a transition time which can last for a few minutes. In most cases, the actual RH (at equilibrium) was slightly lower than the target RH. Although the actual RH and the set target were not always the same, the instrument RH was nonetheless stable to within +/- 0.1% during a run. The mass response of a wood sample to the changed actual RH produced an asymptotic curve when plotted as moisture content against time approaching the EMC after infinite time of exposure at a given RH (Figure 3.8).

The target RH changes to the next preset value when the moisture content change was less than the defined value ($dm/dt = 0.002\%$ min^{-1}) for 10 minutes. The MC of the wood gradually increased or decreased at the new target RH until the sorption rate reached the defined sorption state, and then the RH changed to the next preset RH and the total running time of the test was determined (Figure 3.8). In Figure 3.8 is shown the differences in EMCs and the total run time of various wood species at a given RH. Sitka spruce shows the highest EMC and followed by radiata pine, *E. malaccense*, *A. mangium* and Accoya, respectively. *E. malaccense*, *A. mangium* and Sitka spruce seem to have the same total running time. The modified wood, Accoya shows the lowest EMC and also in total running time. Although total running time can be used as an approximate guide, other factors will affect this, such as external influences (e.g vibration).
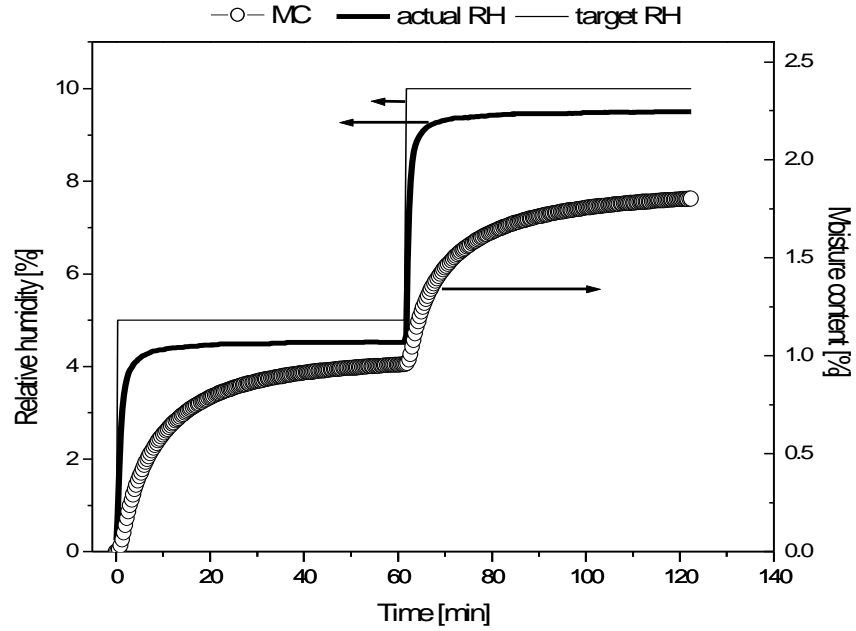
Figure 3.7 Dynamic vapour sorption process of *A. mangium* **at two successive RH levels of 5 and 10% showing the set target RH (thin line) and true RH (bold line) in the test chamber, and MC of** *A. mangium* **obtained under varying moist environment at 25 $^{\circ}$C.**
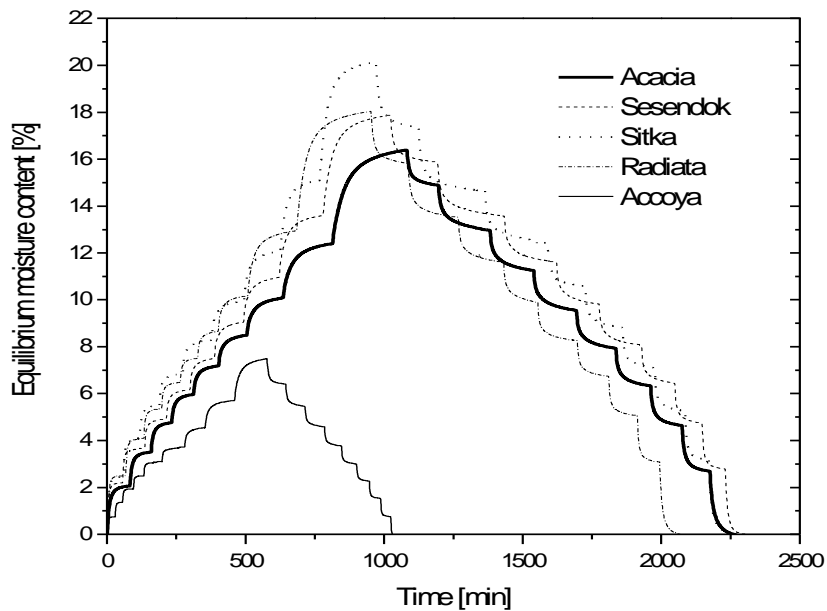

Figure 3.8 Relationship between EMC and sorption time for one sorption cycle *A. mangium*, *E. malaccense*, **Sitka spruce, radiata pine and Accoya at 25 $^{\circ}$C (note the initial decrease in moisture content is due to the drying curve of the sample in the apparatus to determine the dry mass).**

3.3.2 Isotherm plots of different wood species

Individual moisture adsorption/desorption isotherms are shown in Figure 3.9a. All samples exhibited the classic sorption isotherm curves (IUPAC Type II) which is sigmoidal in adsorption and desorption, as observed with other lignocellulosic materials. However, there were considerable differences in the total amount of moisture present in the various wood species at a given RH as well as in the degree of hysteresis exhibited.

The differences in adsorption and desorption behaviour are clearly illustrated when the adsorption isotherm curve (Figure 3.9b) and desorption isotherm curves (Figure 3.9c) were overlaid. Jannot *et al.* (2006) also found differences in EMCs in sorption isotherms for different types of African tropical woods (Afzelia, Ebony, Iroko, Moabi and Obeche) at various RHs.

It should be noted that because samples were desorbing from an EMC below FSP (RH at 90%), the desorption curve was consequently composed of a 'scanning curve' and a 'boundary curve'. The scanning curve means that a few initial data points of EMCs during the desorption process do not coincide with the boundary curve initially but rapidly approaches the boundary curve. Differences between wood species are reliable because the test has been carried out with the same method in the DVS which gave the same scanning curves at various RHs.

At a target RH of 90%, *A. mangium* had a lower EMC than *E. malaccense*, Sitka spruce and radiata pine, with values of 16.2, 17.9, 20.1 and 18.0% respectively (Figure 3.9a). This difference has been attributed as due to variations in chemical composition, crystallinity of cellulose and extractives content (e.g. Wangaard and Grandos 1967).
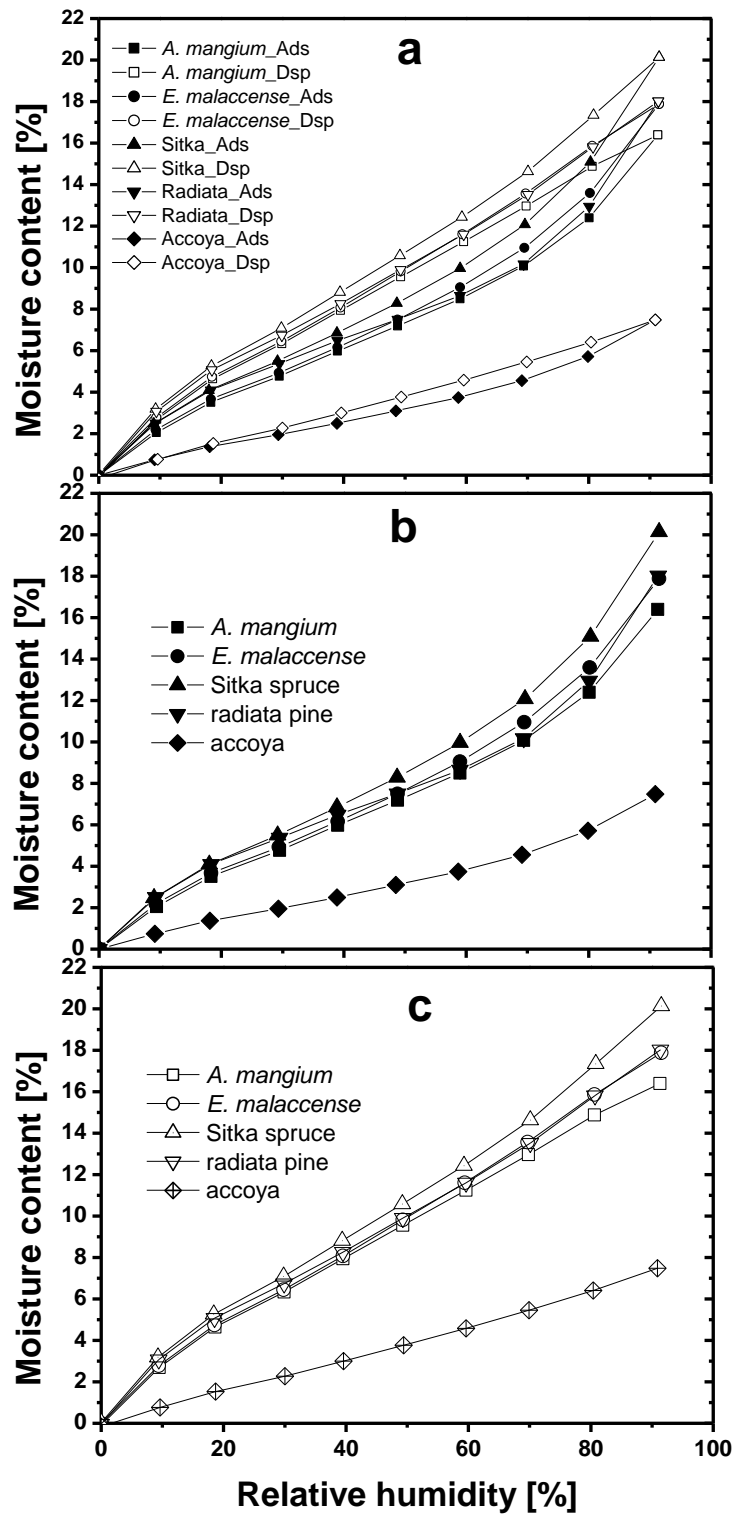
Figure 3.9 Sorption isotherms for for *A. mangium*, *E. malaccense*, Sitka spruce, radiata pine and Accoya: a) isotherms curves, b) adsorption, c) desorption at 25 ^{o}C.
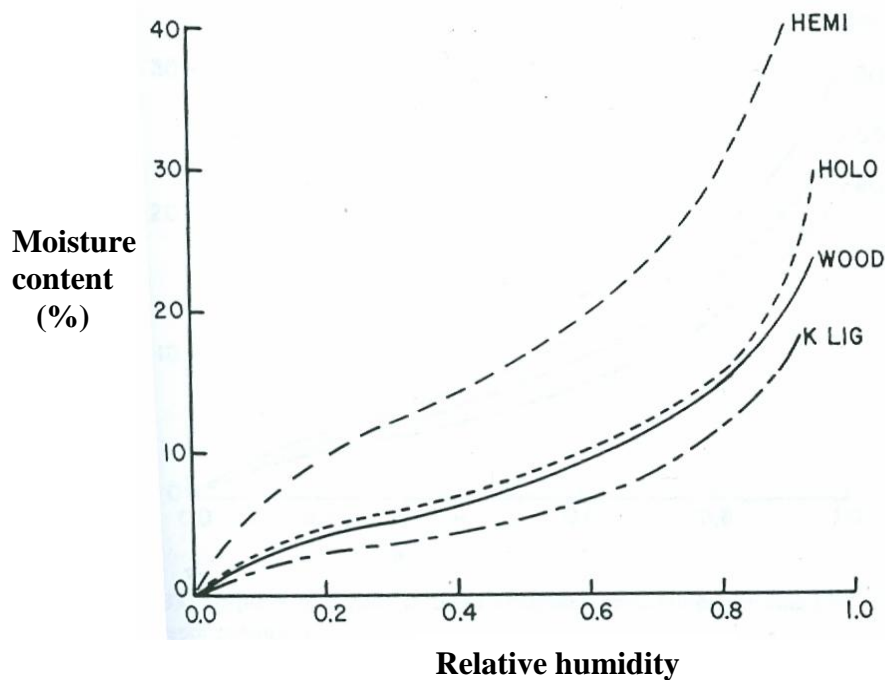
Figure 3.10 Adsorption isotherms for wood hemicellulose (HEMI), holocellulose (HOLO), Klason lignin (K LIG) and gross wood (WOOD) (Christensen and Kelsey 1959).

The effect of chemical composition has been shown by Christensen and Kelsey (1959) for the differences of adsorption curves for holocellulose, hemicellulose and lignin of *Eucalyptus regnans* (Figure 3.10). But in this context it is important to note that it is very unlikely that the isolated polymers behave in the same way as they do in the cell wall.

There was a slightly higher cellulose and extractive content in *A. mangium* which has the lowest EMC compared to other wood species (Table 3.4). The higher content of cellulose means that the wood has more crystalline OH groups (ca. 60% crystalline content in cellulose according to Fengel and Wegener (1984, 1989) which

are inaccessible to water molecules (Christensen and Kelsey 1959, Christiansen and Giertz 1966). Barkas (1949), Stamm (1964), Skaar (1972) and Siau (1994) have stated that only amorphous polysaccharides can adsorb water molecules, but this seems at odds with the results of Christensen and Kelsey (1959), who show that lignin also absorbs moisture (Figure 3.10).

Table 3.4   Chemical composition (wt %) of *E. malaccense*, *A. mangium*, Sitka spruce and radiata pine.

Wood species	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
A. mangium[1]	50.3[1]	27.2[1]	23.5[1]	9.6[5]
E. malaccense [2]	42.2[2]	29.4[2]	26.3[2]	2.4[5]
Sitka spruce[3]	40.0[3]	31.0[3]	28.0[3]	2.1[6]
Radiata pine[4]	45.3[4]	23[4]	26.8[4]	4.3[7]

References: [1]Rushdan *et al.* (2007), [2]Mohd.Nor (1991), [3]Fengel (1989), [4]Araque *et al.* (2008), [5]Table 3.1, [6]Caron (2010), [7]Semple and Evans (2000)

The sorption behaviour of wood is also affected by extractives (Wangaard and Granados 1967, Choong and Achmadi 1991, Nzoku and Kamdem 2004, Hernandez 2007) which showed that the extracted wood exhibited higher EMCs than the unextracted wood at higher RH. A number of scientists have also indicated that wood species with high extractive contents show low EMCs (Nearn 1955, Spalt 1958, Stamm 1964). In this study, Sitka spruce with a slightly higher amorphous polysaccharide and lignin content showed the highest EMC. However, simply invoking chemical composition (in terms of OH content) as the sole determinant in controlling EMC is not sufficient. It has been shown that with natural fibres, coir with a high lignin content (and hence low OH to C ratio compared to polysaccharides) nonetheless exhibits high EMC levels compared to fibres with lower lignin contents (Hill *et al.* 2009). The explanation

here appears to be related to the ability of the cell wall matrix to deform in the presence of sorbed water. This idea will be further developed in this thesis.

The unmodified woods *A. mangium*, *E. malaccense,* Sitka spruce (*Picea sitchensis*) and radiata pine (*Pinus radiata*) exhibited higher EMCs on adsorption and desorption compared with Accoya or acetylated wood (Figure 3.9a). The unmodified woods also had larger hysteresis loops compared with Accoya (Figure 3.11). The absolute hysteresis values (by subtraction method) of the wood species seem to be similar at lower RH but after 50% RH they started to be variable. At 70% RH, radiata pine had the highest hysteresis followed by *A. mangium*, *E. malaccense*, Sitka spruce and Accoya at 3.3, 2.9, 2.6, 2.6 and 0.9% respectively.

In Figure 3.12 is shown the hysteresis ratio (normalised values) (Equation 2.25 in Chapter 2) of all the wood species. There is no difference in absolute hysteresis value between 0 to 50% RH, however when the absolute values have been normalised, the difference can be clearly seen. *A. mangium* has the highest hysteresis ratio value of approximately 33% and maintains the value between 0 to 50% RH and after 50% RH the hysteresis ratio value starts decreasing to 17%. Most of the wood species show the same trend, however, the hysteresis ratio of radiata pine is lower than that of the other species studied at the lower RH but exceeds that of *A. mangium* at 60% RH. It is apparently that the hysteresis ratio value of Accoya is the lowest for the whole range of RH compared to other wood species.
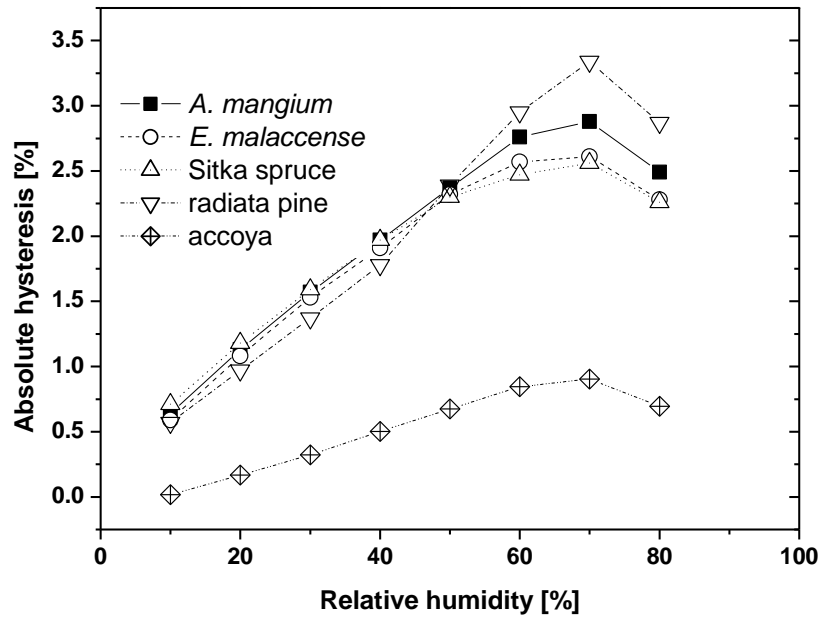
Figure 3.11   Absolute hysteresis between adsorption and desorption curves (obtained by subtraction of EMCs) at different values of RH.
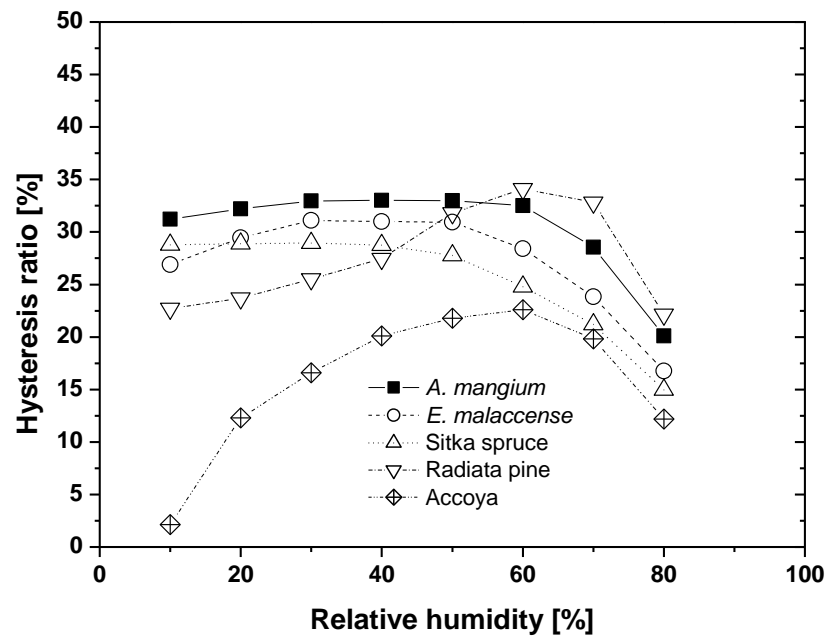

Figure 3.12 Hysteresis ratio of *A. mangium*, *E. malaccense*, Sitka spruce, radiata pine and accoya   at different values of RH.

3.3.3 Hailwood-Horrobin fitting to the experimental data

A full description of the H-H theory was given in Section 2.5. The values of A, B, C and coefficient of determination (R^2) for the second order polynomial fit to the data points for the plot of H/M versus H, for Sitka spruce is shown in Figure 3.13 based on Equation 2.18:

$$\frac{H}{M} = A + BH - CH^2$$

where H is relative humidity and M is the moisture content. The adsorption behaviour of wood at each RH can be analysed by fitting the experimental data with the H-H model based on Equation 1.15:

$$M = M_h + M_s = \frac{1800}{W}\left(\frac{K_1 K_2 H}{100 + K_1 K_2 H}\right) + \frac{1800}{W}\left(\frac{K_2 H}{100 - K_2 H}\right)$$

where M is the EMC at a given relative humidity (H), M_h is the moisture content from water of hydration or monolayer sorption, M_s is the moisture content due to dissolution water or polylayer sorption, K_1 is the equilibrium constant of the monolayer water formed from dissolved water and cell walls, K_2 is the equilibrium constant between water vapour and dissolved water, and W is the molecular weight of cell wall polymer per mole of water sorption sites.
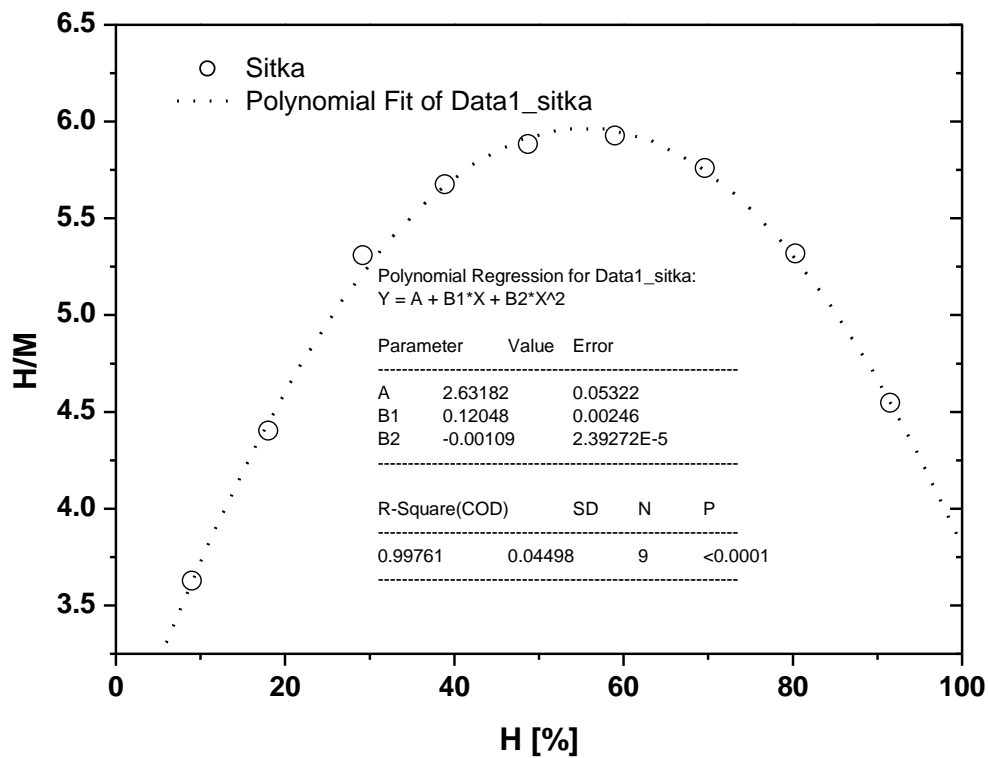
Figure 3.13 Sitka spruce plot of H/M against H, in order to obtain A, B, C and R^2 values (note that the values are direct output from the software and should not be taken to indicate that this level of confidence can be realistically expected from the fit).

In Table 3.5 is shown the values of A, B, C, K_1, K_2 and W of the woods studied. Accoya has a lower value of K_1 compared with untreated wood species. A low K_1 implies a decrease in the activity of hydrated wood with respect to both the activities of dry wood and dissolved water. It means Accoya has less accessibility for monolayer water, through the presence of bulking chemical inside the cell wall micropores. The K_2 value is comparable for treated and untreated wood which shows the activity of dissolved water in the cell wall. In this H-H fitting, W or the molecular weight per sorption site for different species showed differences, with Accoya having the highest value at 673.7 with the lowest EMC at 9.6% and the four wood species being comparable to each other. The increase of W is taken as evidence for a decrease in the

number of active sorption sites. Acetylation reduces the number of active sites by chemical substitution of hydroxyl groups by acetyl groups. Therefore an increase in W with acetylation is what would be predicted (Popper and Bariska 1972). However, in a previous study (Hill and Papadopoulos 2003, Hill 2008) it was shown that the increase in W was related to weight percentage gain with all anhydrides studied and was actually independent of OH substitution. The physical reality of the parameters obtained by H-H fitting may hence be questioned.

Table 3.5   **Fitted and physical constants calculated from the H-H model in adsorption isotherm**

Wood species	A	B	C	R^2	K_1	K_2	W
A. mangium	3.43	0.12	0.0011	0.99	5.94	0.73	312.0
E. malaccense	3.16	0.12	0.0011	0.99	6.17	0.76	310.4
Sitka spruce	2.63	0.12	0.0011	0.99	6.92	0.77	290.2
Radiata Pine	2.19	0.15	0.0013	0.97	10.12	0.77	338.5
Accoya	10.22	0.22	0.0022	0.99	3.95	0.74	673.7

Table 3.6 Values for monolayer (Mh) and polylayer (Ms) water derived from Hailwood-Horrobin fits projected to 100% relative humidity.

Wood species	Mh (%)	Ms (%)	Mh + Ms (%)
A. mangium	4.7	15.5	20.1
E. malaccense	4.8	18.5	23.3
Sitka spruce	5.2	21.2	26.54
Radiata pine	4.7	17.9	22.6
Accoya	2.0	7.6	9.6

The fitted curve using the H-H model coincided well with experimental EMC values of *E. malaccense*, Sitka spruce and Accoya (Figure 3.14 (b, c, e)]. The sigmoidal adsorption isotherm curve of the water content was deconvoluted into water of

hydration or monolayer (Mh) and dissolution water or polylayer (Ms) water. The monolayer water dominates at the initial stage when RH values are below 20%. However, the polylayer water became dominant when above the RH of ca. 55%. The total water above 80% RH was slightly overestimated in the case of *A. mangium* and radiata pine (Figure 3.14a, d). Values for Mh, Ms and total water (Mh + Ms), giving a crude estimate of FSP or projected FSP (p-FSP) at 100% RH are given in Table 3.6. With a value of 20.1%, *A. mangium* had the lowest p-FSP compared with the three wood species *E. malaccense* (23.3%), Sitka spruce (26.6%) and radiata pine (22.6%) respectively. The use of the term p-FSP is to distinguish this parameter from FSP values obtained by other methods (such as solute exclusion) which do not give the same results (Stamm 1964, 1971, Hill 2008). It should be noted that the projection method can produce spurious data, especially when the isotherm is rising sharply towards the higher end of the hygroscopic range (Stamm 1971, Hill 2006). Nonetheless the use of such a method provides a convenient indication of differences in sorption behaviour between species. If it is assumed that each water molecule in the monolayer is associated with a primary sorption site (OH group), then it is possible to determine the accessible OH group content of the wood. The number of OH groups per unit mass of dry wood can be calculated on the basis of an estimate of the number of OH groups associated with each of the cell wall polymeric constituents, as described in Section 2.7 (Rowell 1980). For the cellulose component, only 40% of the OH content is considered in the calculation as 60% of the groups are assumed to be in the crystalline region and thereby inaccessible. The values of the total OH concentration for each species are shown in Table 3.7.
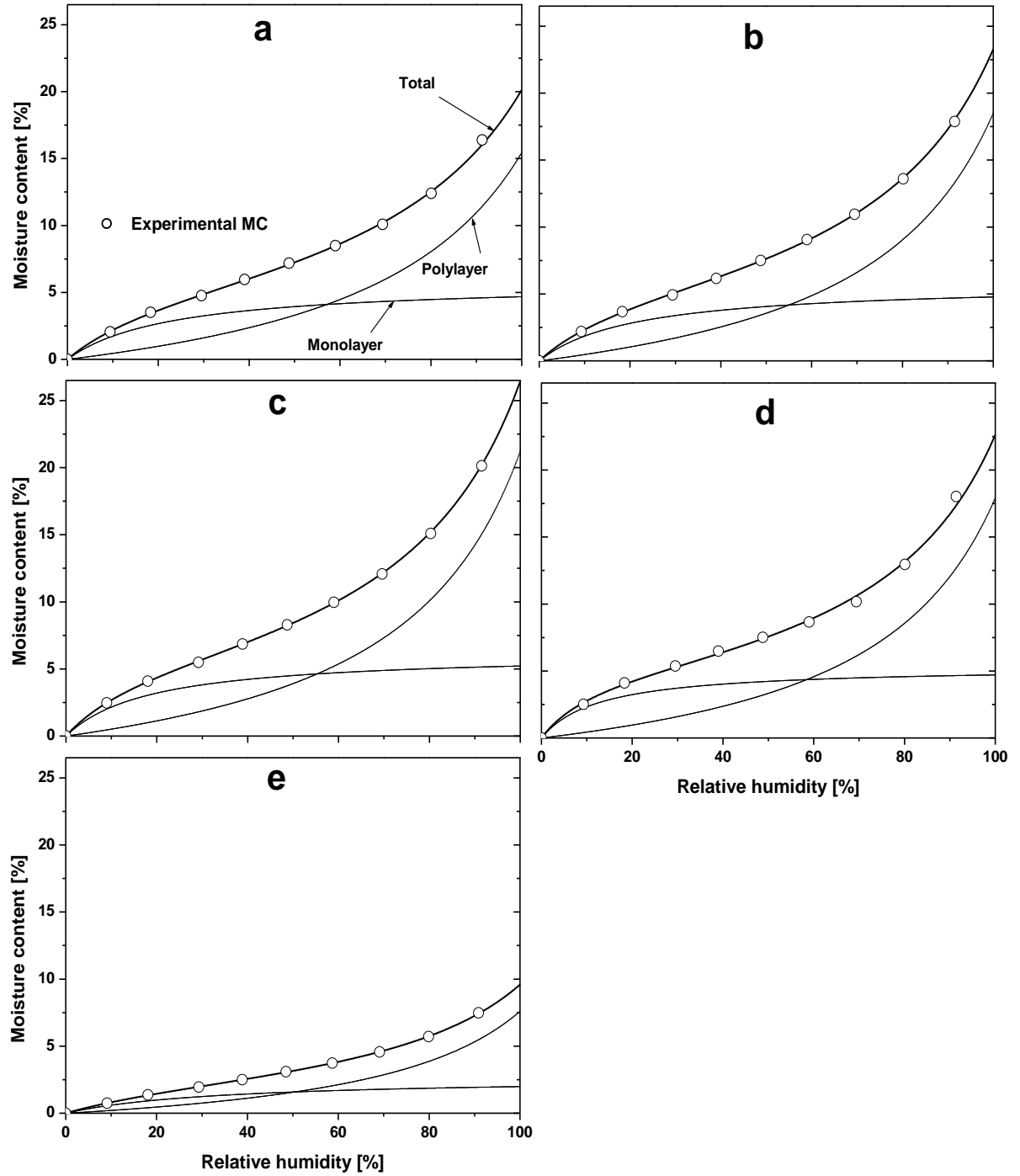
Figure 3.14 **Monolayer, polylayer calculated using the Hailwood-Horrobin model, and the sum of monolayer and polylayer water (total) in adsorption isotherm through the relative humidity run compared with the experimental moisture content of (a)** *A. mangium***, (b)** *E. malaccense***, (c) Sitka spruce, (d) radiata pine and (e) Accoya.**

Comparison of the number of accessible OH groups associated with the monolayer as determined by the H-H theory did not correspond with that determined using Rowell's method (Rowell 1980) for any of the samples. Also the W values did not correspond to the accessibility of the OH groups. Based on the H-H model, the monolayer water sorption at 100% RH for all four species divided by the water molecular weight showed OH concentrations between 2.6 to 2.9 mmoles g^{-1}. On the other hand, with Rowell's method the OH concentrations were calculated as 8.7 to 9.7 mmoles g^{-1}. This ratio of 3 to 1 implies that each water molecule in the monolayer is associated with three primary sorption sites. This is comparable to previous studies that have been observed by Hill *et al.* (2010a), White and Eyring (1947) and Papadopoulos and Hill (2003) with Sitka spruce, cotton and Corsican pine, respectively. Even if it is accepted that the theoretical estimation of the OH content will involve some errors, it is clear that there is large difference between the OH content calculated from the cell wall composition and that calculated from the H-H monolayer content. This is assuming that the concepts such as monolayer have any physical meaning in the complex internal geometry of the cell wall.

Furthermore, the results suggest that OH concentration cannot be reliably determined from the monolayer water sorption only and also indicates that the assumption of one water molecule per sorption site in the monolayer is not correct. Previous studies have used wood exposed to deuterated water in order to estimate the accessible OH content. Results show that various species have different OH contents, e.g. 8.0 and 6.9 mmoles g^{-1} for black spruce and white birch respectively (Sumi *et al.* 1964) and 3.3 mmoles g^{-1} for Japanese cypress (Taniguchi *et al.* 1978). Further investigations using deuterium exchange may be a useful method to determine the accessibility of OH content. Similar considerations apply when a surface area is

reported based upon a BET analysis, where again the concept of a monolayer may not have any physical meaning.

Table 3.7 Estimation of OH concentration (in mmoles per gram) of dry cell wall substance from monolayer water content at 100% RH obtained from the Hailwood-Horrobin fits

Wood species	H-H monolayer OH concentration	H-H molecular weight	Totally accessible calculated OH concentration	OH concentration (60% crystalline cellulose)
A. mangium	2.6	312.0	15.2	9.6
E.malaccense	2.7	310.4	14.2	9.5
Sitka spruce	2.9	290.2	14.2	9.7
Radiata pine	2.6	338.5	13.7	8.7

3.4 Conclusions

The data obtained from the DVS apparatus tested with wood fine particles was highly reproducible. Sample weight was found to affect the sorption isotherms and kinetics and it is necessary to use closely comparable sample masses to ensure reproducibility (+/- 1.0 mg for a 20 mg sample). This study has shown that there are differences in the adsorption/desorption behaviour between the two tropical Malaysian hardwoods, two temperate softwoods and Accoya. Variation in macromolecular chemical composition especially a high content of extractives affected the sorption properties. Amorphous polysaccharides in wood such as hemicelluloses and lignin also affected the sorption behaviour. Between the unmodified woods, *A. mangium* showed the lowest hygroscopicity. Accoya exhibited the lowest level of hysteresis compared with the rest of the samples tested. Hysteresis was reduced for samples which showed lower sorption, even when hysteresis ratio was used as a measure. Analysis of the adsorption isotherms using the Hailwood-Horrobin model has yielded good fits to the

experimental data. When the quantity of water attributed to monolayer formation in the cell wall is calculated, it is found that each sorbed water molecule was apparently associated with three cell wall OH groups or primary sorption sites. This does not mean to say that each water molecule is in direct contact with these OH groups. Further evaluation on sorption isotherms with different types of wood and thermal modification wood will be further discussed in the following chapter.