CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Introduction

The aim of this work was to further our understanding of the phenomenon of the water sorption of wood. This was driven by a realisation that although many models existed in the wood science literature, there was actually no satisfactory explanation why hysteresis occurred. The work of Hill *et al.* (2009) presented a model suggesting that hysteresis in plant fibres was a result of sorption onto a glassy polymer below the glass transition temperature, which has previously been used as a model in the soil science literature. The aim was to try and further understanding of sorption hysteresis and it was thought that investigating sorption kinetics might provide some useful insights. The PEK model had previously been shown to give highly accurate fits to the experimental data points for sorption processes with plant fibres (e.g. Kohler *et al.* 2003) and it was of interest to find that this was also the case for water sorption and wood. This work showed quite conclusively that the water vapour sorption kinetics was not Fickian in nature and it became apparent that others had also found this, although many workers still persist in using a Fickian analysis of their data. The advantage of using the DVS instrument for conducting sorption studies is the extremely high quality kinetics data that is available, allowing for extremely reliable curve fitting to be performed. Until the advent of such instruments it was much more difficult to obtain data sets for kinetic studies. The ready availability of software that can perform curve fitting is a great benefit, but without a sufficiently accurate data set on which to work it can give false data which appears to be true. This research initially tried to establish to reproducibility of the data before any other studies were undertaken.

8. 2 Preliminary study and reproducibility

The first stage of the work was undertaken to determine the reproducibility and accuracy of the data. The following conclusions were drawn:

a) The data obtained from the DVS apparatus was highly reproducible therefore the use of one sample for one test can be accepted.

b) The amount of sample weight affected both the sorption isotherms and kinetics, and it was therefore extremely important that sample masses did not vary by more than +/-5% between samples.

c) There is some error associated with the curve fitting parameters obtained. This is due to the requirement of removing early data points associated with the regime where the RH is changing. In addition, the curve fitting itself gives data that has some margin of error. Typically this is somewhat less than 10% of the value (20% in the case of MC_1)

The preliminary study showed that there were significant 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. Differing amounts of 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 which is already well known. 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 yielded good fits to the experimental data. When the quantity of water attributed to monolayer formation in the cell wall was calculated, it was 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. It is important to realise that the H-H, along with all other models, is just that a model. The concepts of monolayer/multilayer do not necessarily have any meaning except in the context of the model.

There have been new developments regarding the sorption hysteresis phenomenon in wood which have taken concepts associated with humic soils that consider the importance of matrix stiffness in glassy solids based upon the work of Lu and Pignatello (2002, 2004).

8.3 Sorption properties of wood species and thermally modified wood

In Chapter 3, a study of the effect of different wood species and thermal modification was performed. Thermally modified wood exhibited reduced EMCs at each RH in sorption isotherms. This is the result of the changes in the chemical composition of the wood cell wall caused by thermal degradation. Some of the effects of thermal modification are the increase of relative cellulose content, the loss of hemicelluloses and an increase of the cross-link density of lignin. Modification temperature was found to have a greater influence on EMC than treatment time. The adsorption isotherms were analysed using the H-H model, with excellent fits to the experimental data of six hardwood species and thermally modified wood. Increased stiffness of the cell wall of thermally modified wood appears to be associated with a higher hysteresis ratio. However, when absolute hysteresis is determined the reduced overall EMC masks this effect. This increase in hysteresis ratio (taking account of the loss of hygroscopic materials from the cell wall) is exactly what would be expected according to the model which explains hysteresis on the basis of matrix stiffness.

8.4 Sorption kinetics using PEK model

In Chapter 4, an 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 unsuccessful. It is concluded that interpretation of the PEK model in terms of sites is incorrect. However, this study has clearly shown that the PEK model appears to be a reasonable model for studying cell wall sorption kinetic phenomena. There is sorption hysteresis in the characteristic times and moisture contents between the slow 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. However, as was found later in the work, simply analysing the data in terms of the kinetic parameters of the model is not sufficient to give any meaningful insight. Nonetheless, such an approach does show some promise, provided there is a reasonable physical interpretation undelying the PEK model.

8.5 Sorption kinetics interpretation using a viscoelasticity model

This study has further explored the hypothesis that the sorption kinetics of the cell wall of wood is determined by the micromechanical behaviour of the cell wall matrix polymers. When the data from the parallel exponential kinetics analyses of sorption kinetics experiments were evaluated using a Kelvin-Voigt viscoelasticity model, both modulus and viscosity were found to decrease with increasing relative humidity (and hence cell wall moisture content).

The modulus and viscosity values appear to be reasonable, but confirmation using independent techniques is required. In the study on effect of different isotherm temperatures, only the viscosity associated with the slow sorption process showed any substantial difference between adsorption and desorption, indicating that it is only with the slow sorption process where a link with hysteresis may be found. The existence of a bi-exponential relaxation process is often reported in the polymer science literature, where it is attributed to a two component material, such as a copolymer or side and main chain relaxations. The obvious (too obvious) conclusion to draw here is that the two relaxation processes are related to reinforcement (i.e. microfibril) and matrix (hemicellulose and lignin) relaxation processes, however this cannot possibly be the case if the modulus at low cell wall MC is of the order 10-20 GPa. It is clear that further work needs to be done to determine if the two processes are linked to composition and/or morphology in some way

Finally, it is suggested how hysteresis, which is linked to molecular dynamics occurring in time scales of the order of picoseconds, can be linked to sorption kinetic phenomena which have time constants of the order of minutes. The connection lies with the consideration of nature of cooperative relaxations that have to occur in glassy materials below the glass transition temperature when subjected to an internal stress. It appears that only the slow process of viscosity is associated with matrix relaxations, although this is a very tentative conclusion. It is suggested that further study of kinetic may provide insights into hysteresis.

8.6 Activation energy, entropy and Gibbs free energy

It was possible to obtain values for the activation energy, entropy and Gibbs free energy of sorption throughout the hygroscopic range using the time constants associated

with sorption kinetics data according to the parallel exponential kinetics (PEK) model. The trend in behaviour of the activation energy (Ea) with relative humidity (RH) gave mixed results. In some cases, the Ea was found to decrease from a value approximately of 40 kJ mol^{-1} towards effectively zero at the highest RH levels. This type of behaviour is thought to represent hydrogen bond breaking being the rate-limiting step at low cell wall moisture contents, but with this barrier being removed at high cell wall moisture contents. However, this type of behaviour was not always observed and in order to gain a better insight into the sorption process it was necessary to also determine the activation entropy of the process.

The values for activation entropy were found to always be negative for both adsorption and desorption conditions for both wood species. This kind of phenomenon can be explained as being due to the rate determining step for dynamic sorption processes being associated with molecular rearrangements within the cell wall matrix. Although the opening up of micropores in the matrix requires the breaking of hydrogen bonds, it is also necessary that the matrix relaxes. Macromolecular relaxation in the cell wall matrix to allow for the transport of water molecules requires cooperative behaviour between adjacent molecular segments when the isotherm is determined below the glass transition temperature of the substrate. This type of behaviour is a non-random, low probability process and consequently gives rise to the large negative entropy values. Due to the narrow temperature range available with the DVS intrinsic apparatus the data quality was variable, even though five temperatures were used to determine the rate constants. Further work is needed in this very promising area using a much wider temperature range. It is also necessary to make determinations of both the sorption isotherms and sorption kinetics up to and beyond the glass transition temperature of the matrix.

Evaluation of the Gibbs free energy of activation (ΔGa) revealed some very clear trends in behaviour as RH is increased. The ΔGa values for the slow process were higher than those associated with the fast sorption process. Similarly ΔGa values for desorption were invariably higher than those for adsorption, except at the higher end of the hygroscopic range. Whilst ΔGa for the fast process initially decreased and then increased as RH rose, the ΔGa values for the slow process increased throughout the hygroscopic range. The reasons for this behaviour with respect to ΔGa are not understood at the present time. It is however clear that a full understanding requires the determination of entropy and Gibbs free energy of activation as well as activation energy.

This study has revealed some completely new findings in sorption isotherms, hysteresis and sorption kinetics of the wood cell wall. The relationship between sorption kinetics, wood micromechanics, matrix polymer relaxation, activation energy and molecular rearrangement can create new interesting research at the molecular level of the wood cell wall. Additionally, the science being developed here has far wider application and is likely to be of use for all such studies of swelling gel-like systems.

8.7 Future work

This work represents the start of a much more comprehensive investigation into the sorption properties of wood and other swelling materials. Application of the PEK model to the sorption data is a new science and there remains a large amount of experimental work to perform. The model attributing sorption hysteresis to molecular relaxation processes of the glassy matrix below Tg is new to the wood science area even though it is very well established in the polymer physics community. It will no doubt be some time before this model finds acceptance and many future kinetic analyses will

continue to use Fickian-based models. However, the applicability of a relaxation based model appears to be correct for smaller wood samples. The question that then arises is at what point does the sorption kinetic behaviour change from relaxation limited to diffusion limited – or does it change at all? This requires an in-depth study with samples of different geometries and masses. Such an experiment cannot be performed on a DVS Intrinsic and requires the much more expensive DVS Advantage.

The sorption kinetics behaviour is affected by changes to the substrate, such a thermal modification. It has also been found that there is variation within the tree, although these affects are subtle. What is now required is a much more in-depth study of well-characterised material to help with interpretations of the data. This should certainly include natural material, but it is extremely difficult to change only one variable at a time with natural materials. For this reason, such studies should also include the use of model compounds. Some work was actually performed as part of this PhD looking at hydrogels with different levels of crosslinking, but unfortunately this investigation was compromised because the hydrogel underwent a recrystallization event during the adsorption process. Such studies will help in determining what the fast and slow relaxation processes are related to in the material.

This study has also investigated the activation energies and entropies associated with the sorption process. Only when these are combined to calculate the Gibbs free energy of activation does a pattern in behaviour begin to emerge. The problem at this stage is that there does not seem to be any simple interpretation of what the behaviour in Gibbs free energy represents. Further experimental work with well-characterised materials will help in this respect, but it will also be necessary to perform theoretical studies.

Interpretation of the sorption kinetics in terms of the PEK model provides characteristic time data which it is suggested here is related to polymeric relaxation processes within the cell wall. It would be useful to seek and independent means of verification of this by using molecular relaxation experiments, such as nuclear magnetic resonance.

By interpreting the PEK data in terms of two-series K-V elements, values of cell wall modulus and viscosity have been obtained. The values appear to be realistic, but independent verification is required. Time-dependent nanoindentation studies may go some way towards providing such verification.

This study has shown that the PEK model may be used to analyse sorption kinetics and that interpretation using the Kelvin-Voigt model yields mechanical values that do not seem to be wildly inaccurate. Values for the activation energies, entropies and Gibbs free energy of sorption that are obtained by this method also appear to be reasonable. This indicates that further studies using this approach may be of value.