CHAPTER 6

SORPTION KINETICS INTERPRETATION USING A VISCOELASTICITY MODEL

6.1 Introduction

This chapter discusses a possible interpretation of the PEK model by using a mechanical explanation of the kinetics. In Section 2.10 it was noted that the sorption kinetics with small wood samples cannot be described by using Fickian models, although this has largely been ignored in the wood science literature. It was also noted with a swelling material, that the kinetics may be limited by the swelling rate of the material. The type of behaviour observed depends upon the rate limiting step, a bottleneck of the process. If the rate of relaxation is slow compared with the rate of diffusion then the process is relaxation limited. If the rate of relaxation is fast compared to the rate of diffusion, then the process is diffusion limited. With PEK kinetics a Fickian model cannot be used and here a model based upon the idea of matrix relaxation being the rate limiting step is used. The data for this study is identical with that used in Chapter 5. In addition, a further study has been done with constant 5% RH steps at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 and 95% RH for adsorption and in the reverse sequence for the desorption process at five temperatures (20, 25, 30, 35 and 38 °C).

6.2 Background in analysing sorption kinetics data using the Kelvin-Voigt model

The form of the fast and slow component of the PEK equation is identical with that describing the dynamic response of a Kelvin-Voigt (K-V) viscoelastic element when subjected to an instantaneous stress increase (σ_0):

$$\varepsilon_i = (\sigma_0 / E_i)[1 - \exp(-t/\varphi_i)] \qquad \textbf{(6.1)}$$

Where ε_i is the strain at time t, E is the elastic modulus and φ is a time constant which is defined as the ratio η_i/E_i, where η_i is the viscosity (Barnes *et al.* 1989). The subscript i refers to the fast or slow component. In the present case, there is a change in atmospheric relative humidity (RH) which leads to a response in the wood cell wall with a resultant increase in moisture content. The presence of water molecules within the matrix of the wood cell wall exerts a swelling pressure within the substrate, leading to a proportionate increase in volume. The swelling pressure (Π which is here equivalent to σ_0) that is exerted on an elastic gel when the surrounding water vapour pressure (p) is raised from an initial value p_i to final value p_f is given by the following equation (Krabbenhoft and Damkilde 2004):

$$\Pi = -(\rho/M)RT.\ln(p_i/p_f) \qquad \textbf{(6.2)}$$

Where ρ is the density of water (1000 kg m^{-3}) and M is the molecular weight of water (18 x 10^{-3} kg mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the isotherm temperature in kelvin (K).

The sorption kinetic parameters were used as input into Equation 6.1, with the swelling pressure associated with each measured RH incremental step calculated according to Equation 6.2. The moisture content (MC) at infinite time (equilibrium condition) is given for the fast and slow processes respectively by the following expression:

$$MC_1 = \Pi / E_1;\ MC_2 = \Pi / E_2 \quad \textbf{(6.3)}$$

In the present situation, the strain of the system as described in the K-V model is taken to be proportional to the volume change of the matrix as a result of water vapour adsorption or desorption (Equation 6.1). This volume change is assumed to be linearly related to the change in the mass fraction of the water (MC) in the inter-microfibril matrix. Given that the sorption kinetics is accurately described by the PEK model, the correct viscoelasticity description is given by the consideration of two K-V elements in series (Figure 6.1).

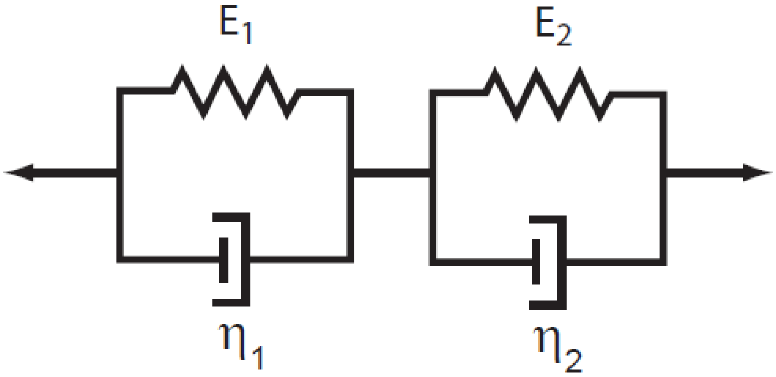

Figure 6.1 The PEK sorption kinetics is interpreted as two K-V elements in series representing the viscoelastic behaviour of the inter-microfibril matrix.

It should be noted that Maxwellian elements also display the same kinetic behaviour as that shown in Equation 6.1, but since there is no permanent deformation (i.e. creep) during sorption process, the acceptable description is one invoking K-V elements only. While the equilibrium moisture content associated with the two processes is determined by the swelling pressure and stiffness (Π/E) of the matrix, the rate of the adsorption process is determined by the matrix stiffness and viscosity (E/η), as shown earlier. Similar considerations apply during the desorption process, except that a decrease in atmospheric RH results in a reduction in swelling pressure and hence moisture content.

6.3 Results and Discussion

6.3.1 Interpretation using the Kelvin-Voigt (K-V) viscoelasticity model

The force constant in the spring of the K-V elements determines the equilibrium moisture content for each of the processes, whereas the viscosity of the dashpot is related to the time constant for each process. Through use of the K-V model the modulus (E) and the viscosity (η) of the fast and slow processes were calculated based on the PEK parameters from the sorption kinetics data. These properties, which are related to the micromechanical behaviour within the wood cell wall at a molecular level, can be determined using this method, if the assumptions are correct. This is due to an internal stress is being applied by the sorbed water molecules, unlike conventional mechanical tests where an externally applied stress is used. The PEK model with fast and slow processes with their characteristic times (φ) and MC was used to calculate the modulus (E) and viscosity (η) of the matrix in the wood cell wall. E_1 and η_1 are associated with fast process, whereas E_2 and η_2 are associated with slow process.

6.3.1.1 Tropical hardwood species

The results are shown in Figure 6.2, 6.3, 6.4 and 6.5 where the elastic modulus and viscosity data is separated into adsorption and desorption plots for each of the wood species. All the six tropical hardwoods show no significant differences related to species in E_1, E_2, η_1 and η_2 values throughout the hygroscopic range.

However, in general, there is reduction in both modulus and viscosity as the RH increases, in line with what would be predicted arising from the effects of plasticization of the matrix components by sorbed water.

There are differences in modulus and viscosity between adsorption and desorption. E_1 modulus is invariably larger under adsorption compared to desorption conditions, (Figure 6.2), whereas the E_2 adsorption modulus is larger in the lower end of hygroscopic range, but then closely approaches or is lower than the desorption E_2 modulus at higher RH values (Figure 6.3).

Values for the modulus at low cell wall moisture contents are generally of the order of 15 to 25 GPa. In this sorption process, the cell wall modulus values are calculated based on the application of internal force, for which there is no directly comparable data in the literature as noted above.

The viscosity associated with the fast adsorption process η_1 is higher than or closely approaches that associated with the fast desorption process (Figure 6.4). By contrast, the viscosity η_2 associated with the slow process is generally lower than that linked to the slow desorption process (Figure 6.5).

The viscosity of fast and slow processes is significantly different exhibiting values of 5 TPa.s and 25 TPa.s respectively. Increases in MC showed decreases in the value of the viscosity. In adsorption, the parameters η_1 and η_2 also behave differently. The question is whether such values are realistic or not. This is dealt with later in the chapter after the behaviour of thermally modified wood is reported and the effect of varying the isotherm temperatures is also examined.

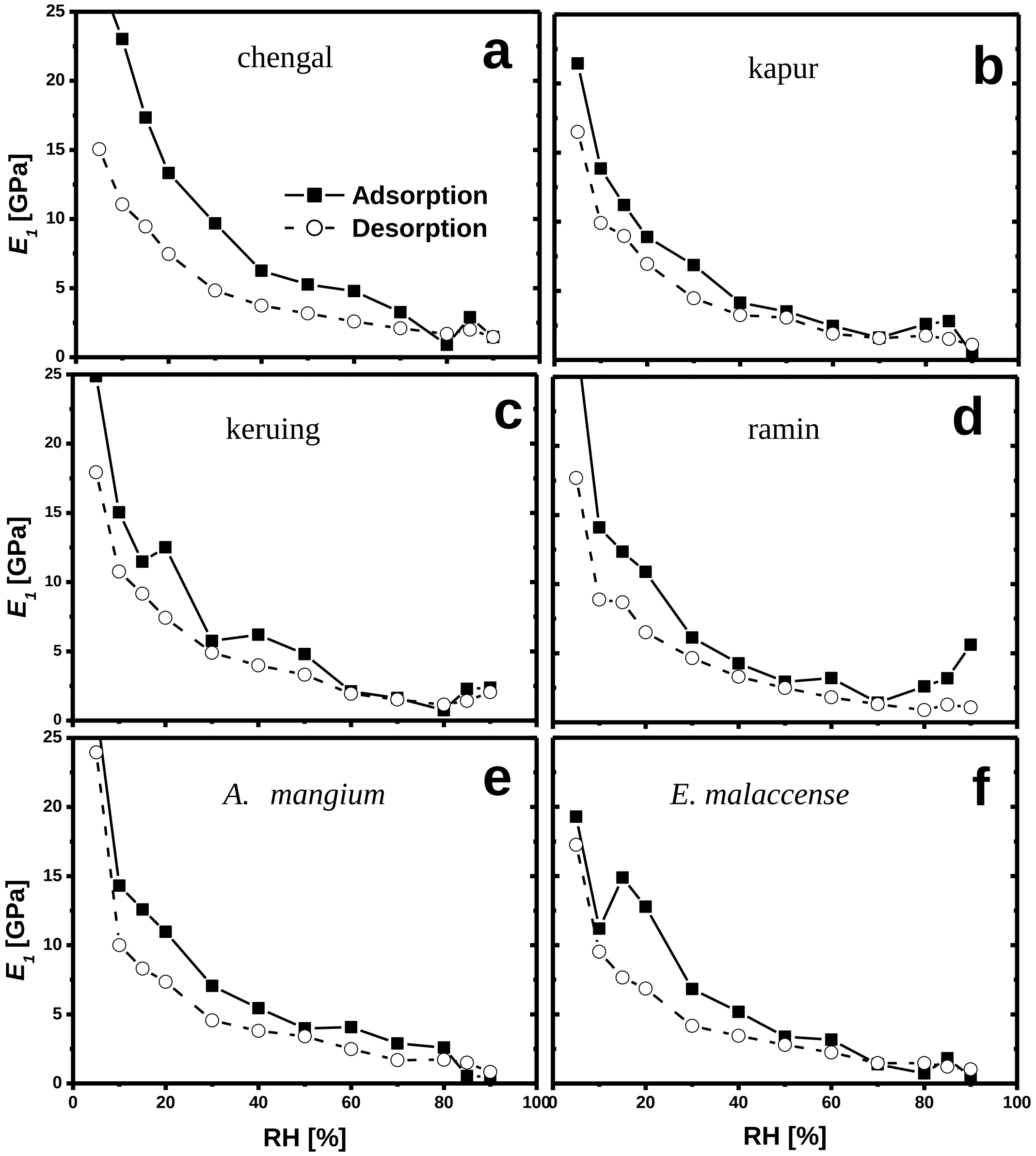

Figure 6.2 Variation in cell wall modulus for the fast sorption kinetic process under conditions of adsorption and desorption on six hardwoods: (a) *Neobalanorcarpus heimii*, (b) *Dryobalanops spp.*, (c) *Dipterocarpus spp.*, (d) *Gonystylus spp.*, (e) *A. mangium* & (f) *E. malaccense.*

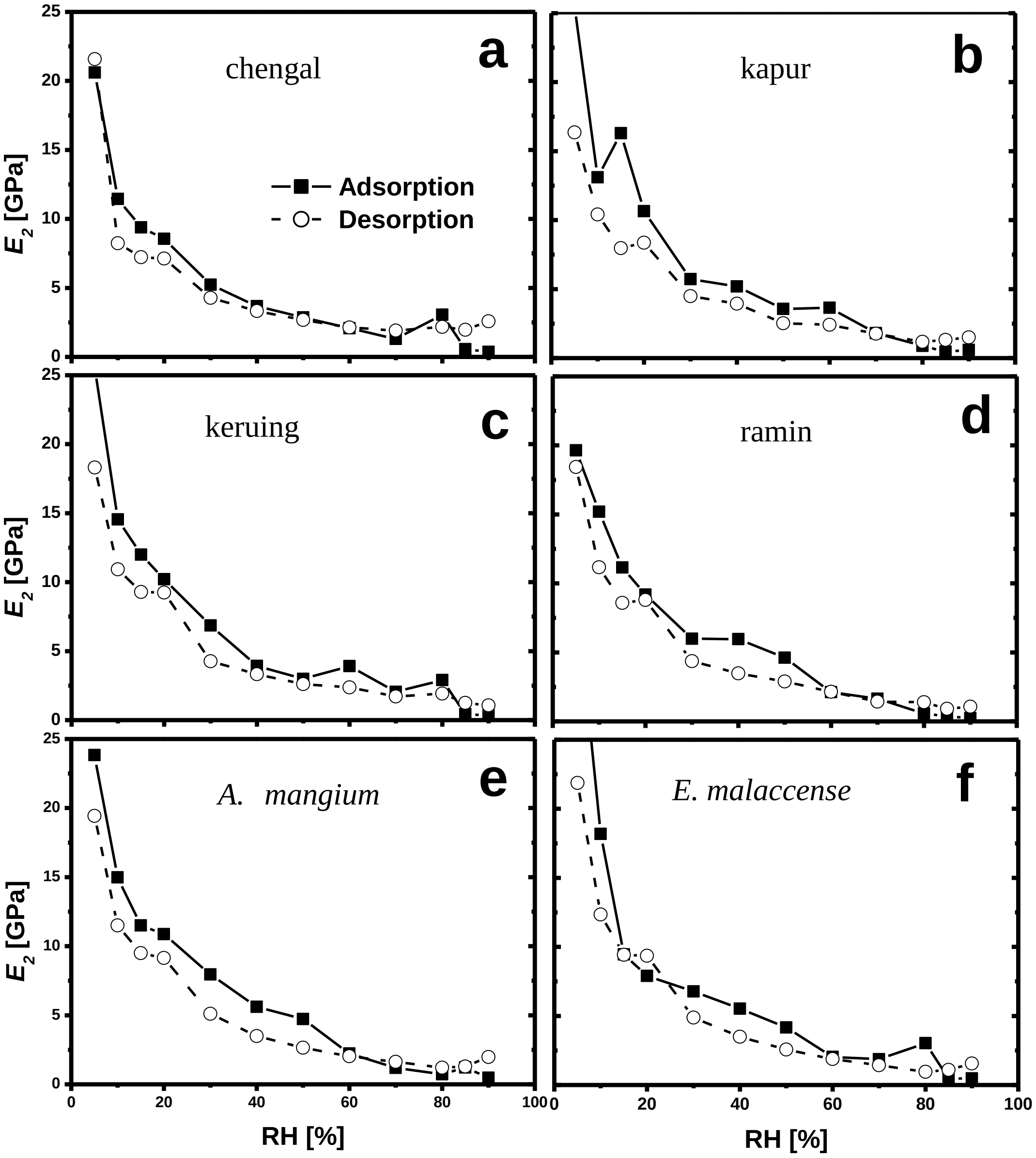

Figure 6.3 Variation in cell wall modulus for the slow sorption kinetic process under conditions of adsorption and desorption on six hardwoods: (a) *Neobalanorcarpus heimii*, (b) *Dryobalanops spp.*, (c) *Dipterocarpus spp.*, (d) *Gonystylus spp.*, (e) *A. mangium* & (f) *E. malaccense.*

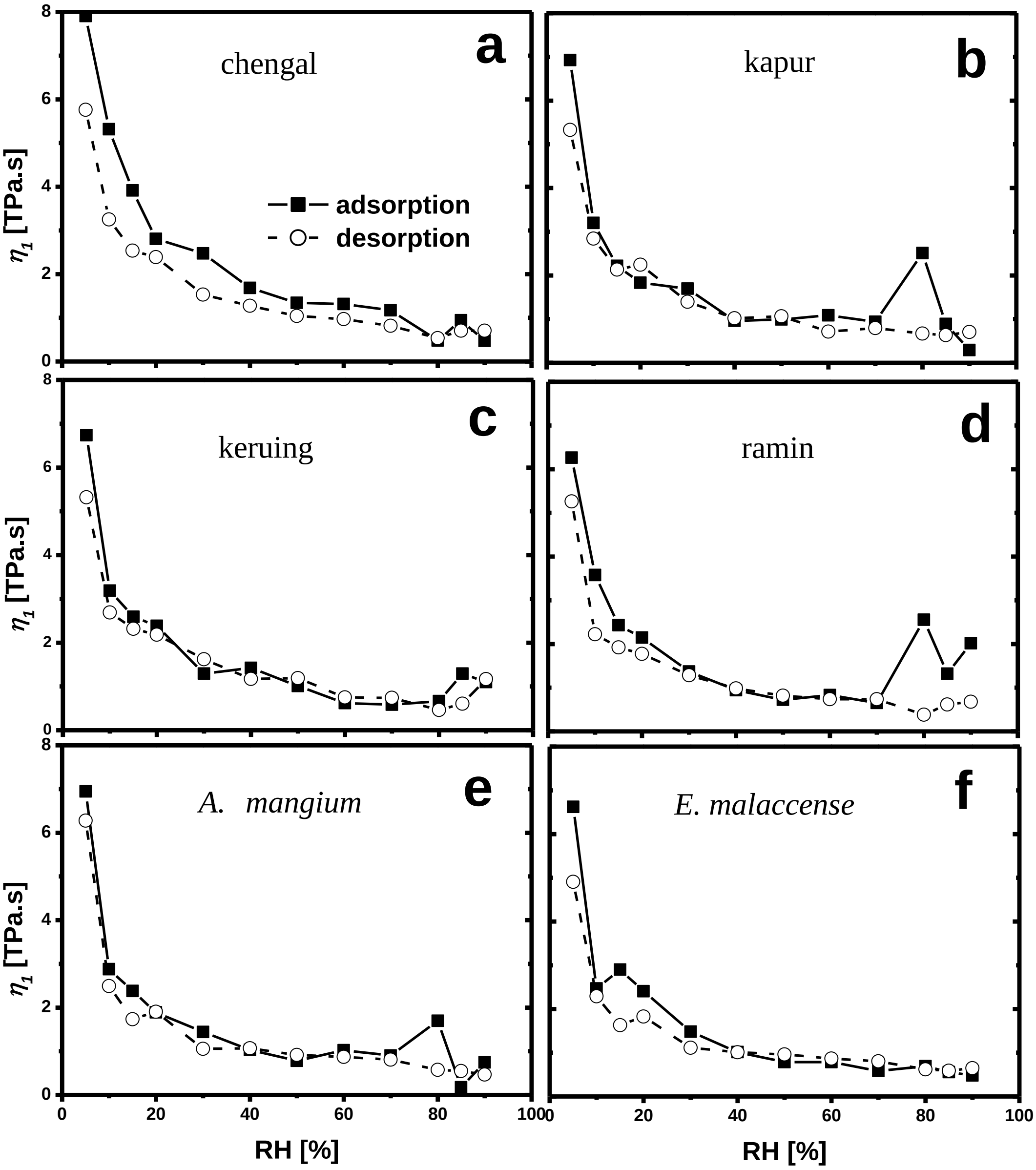

Figure 6.4 Variation in cell wall viscosity for the fast sorption kinetic process under conditions of adsorption and desorption on six hardwoods: (a) *Neobalanorcarpus heimii,* (b) *Dryobalanops spp.,* (c) *Dipterocarpus spp.,* (d) *Gonystylus spp.,* (e) *A. mangium* & (f) *E. malaccense.*

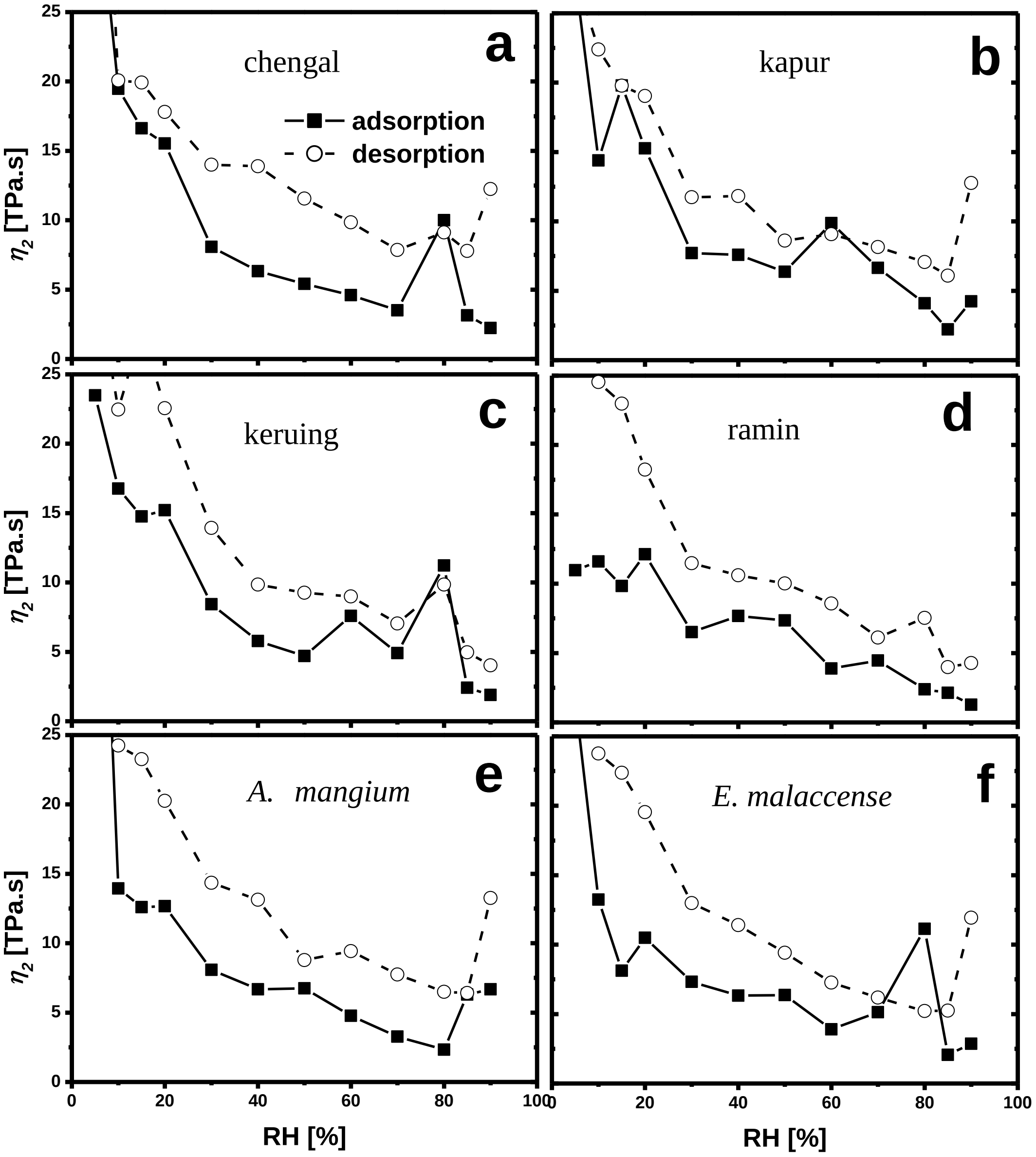

Figure 6.5 Variation in cell wall viscosity for the slow sorption kinetic process under conditions of adsorption and desorption on six hardwoods: (a) *Neobalanorcarpus heimii*, (b) *Dryobalanops spp.*, (c) *Dipterocarpus spp.*, (d) *Gonystylus spp.*, (e) *A. mangium* & (f) *E. malaccense.*

6.3.1.2 Thermally modified wood

Results were determined for the fast and slow processes for thermally modified *A. mangium* and *E. malaccense*. The results for this are shown in Figures 6.6-6.7, where the modulus and viscosity data are separated into adsorption and desorption plots for each wood species (Control and TMW at 220 ^{o}C for 3 h).

The variation in matrix modulus related to the fast kinetic process (E_1) is presented in Figure 6.6a (*A. mangium*, Control and TMW) and Figure 6.7a (*E. malaccense*, Control and TMW). Values for the modulus at low cell wall moisture contents are generally of the order; (a) *A. mangium* (18-23 GPa for control, 24-26 GPa for TMW), (b) *E. malaccense* (11-17 GPa for control, 24-26 GPa for TMW). It is very clearly seen that the E_1 modulus values and their absolute hysteresis of TMW are greater than the control for both wood species. This behaviour is what would be expected, since it is known that the thermal modification increases the stiffness of wood (Hill 2006).

Similar results are obtained when the modulus associated with the slow sorption kinetic processes (E_2) is examined, as seen in Figure 6.6b (*A. mangium*, Control and TMW*)* and Figure 6.7b (*E. malaccense*, Control and TMW). In the case of E_2, at the lower MC the E_2 values (between 20-50 GPa) are higher than those for E_1 for both wood species. As with E_1, the E_2 modulus decreases to very low values at the upper end of the hygroscopic range. The E_2 modulus for the adsorption process show a greater value for TMW than the control at the various ranges of RH, again in agreement with predictions.

The increase of stiffness as a result of thermal modification on the wood species can be attributed due to a number of effects, (a) There is a substantial loss of hemicelluloses, resulting in a reduction of overall OH groups and some conversion to reactive compounds such as furfural may occur leading to potential cross-linking reactions, (b) Lignin can become more cross-linked, resulting in a restraining effect upon cell wall expansion and (c) There may be an increase in cellulose crystalline content resulting in a reduction of accessible OH groups (Hill 2006). However, it should be noted that although this model does give apparently sensible results, the reduced moisture content of the cell wall may also be attributed to a reduction in accessible OH content. Further work is necessary to study this idea.

There is no relationship noted when the viscosity associated with the fast sorption process (η_1) is determined, as shown in Figure 6.6c (TWM-*A. mangium*) and Figure 6.7c (TMW–*E. malaccense*). There is also a decrease in viscosity with increasing cell wall moisture content. The viscosity associated with the slow sorption process (η_2) decreases as the cell wall MC reaches higher values. The values of η_2 for desorption in general exceed those for adsorption (Figure 6.6d and Figure 6.7d). It is also apparent that the viscosities associated with the slow process are greater for TMW compared with unmodified wood. Why should thermal modification have little effect upon the fast relaxation process but such a substantial effect upon the slow relaxation process where the viscosity determinations are concerned? Do these two relaxation process refer to specific components within the cell wall? It is well established that thermal modification has dramatic effects upon the matrix substances, but leaves the microfibrils essentially unchanged, unless the modification is severe (Hill 2006). The obvious (tentative) conclusion to draw at this stage is that the slow process is related to relaxation of the matrix whereas the fast process is related to relaxation of the microfibrils. A similar model has been introduced into the literature recently (Nakao and Nakano 2011). However, it is noted that the moduli of both fast and slow processes are of the order of 20 GPa at low moisture content. This means that if the mechanical model is correct that both processes must have contributions from matrix and microfibrils. It is much more likely that the processes are not coupled in such a simplistic way with the cell wall components.

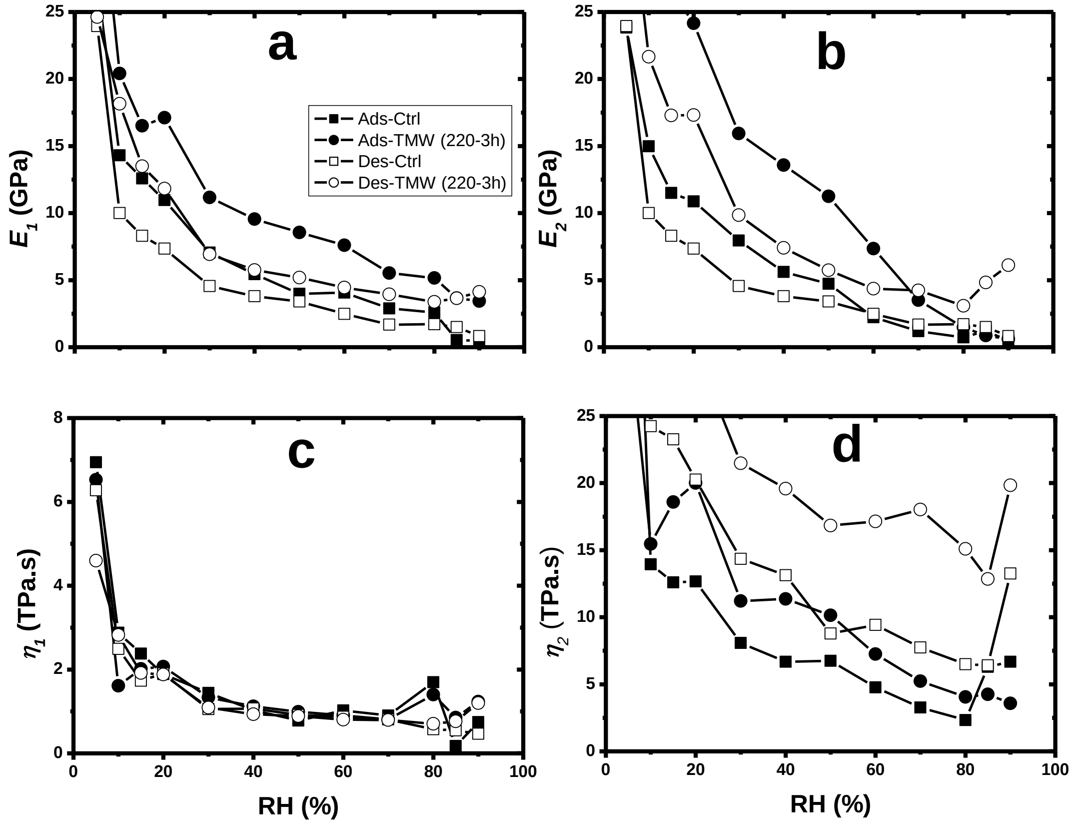

Figure 6.6 The relationship between the modulus and the viscosities; associated with the fast process E_1 (a) and η_1 (b) and slow process E_2 (c) and η_2 (d) with RH for *A. mangium*. For comparison under conditions of adsorption and desorption, control (Ctrl) and thermally modified wood (TMW) at 220 ^{o}C-3h.

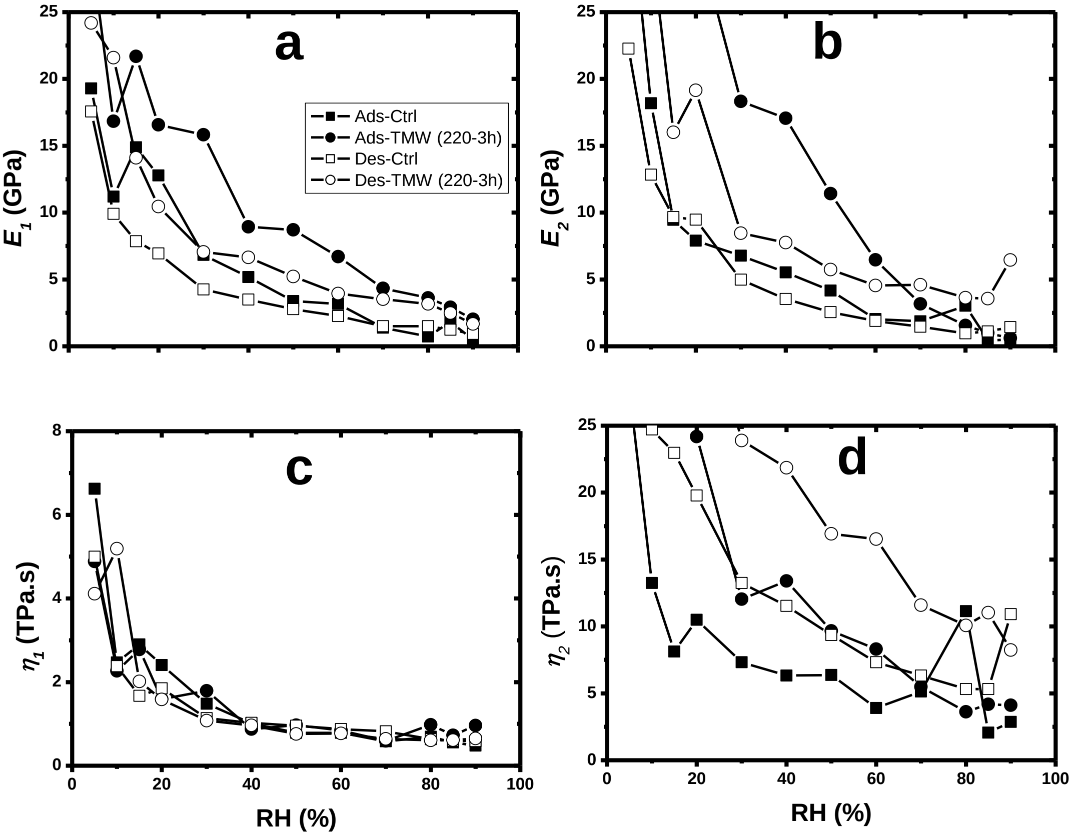

Figure 6.7 The relationship between the modulus and the viscosities; associated with the fast process E_1 (a) and η_1 (b) and slow process E_2 (c) and η_2 (d) with RH for *E. malaccense*. For comparison under conditions of adsorption and desorption, control (Ctrl) and thermally modified wood (TMW) at 220 ^{o}C-3h.

6.3.1.3 Effect on variation of the isotherm temperature

The effect of varying the isotherm temperature upon the viscoelastic properties is examined in this section.There was no difference noted between the two wood species in this study for the evaluated results for matrix modulus and viscosities (fast and slow processes) (Figure 6.8 and 6.9). However, there is a temperature effect noted when the modulus and viscosity associated with the fast and slow sorption processes are determined for both wood species. Figure 6.8 shows there is a decrease in modulus with increase in isotherm temperature, which can be explained as being due to an increase in matrix mobility (plasticization) as the temperature increases. However, in case of E_2, the difference between adsorption and desorption can be observed only specifically at lower RH. This might be associated to the effect of the thermal motion of the cell wall macromolecules at higher temperature on the deformation of the matrix wood cell wall.

Interestingly, there is no substantial difference between adsorption and desorption with the modulus and viscosity associated with the fast process (Figure 6.8a-a' and Figure 6.9a-a'). It was only with the slow process (E_2 modulus and the η_2 viscosity) where differences were clearly noted between values for adsorption and desorption, suggesting that the hysteresis phenomenon is only associated with the slow sorption process.

One particularly striking observation that has arisen from these studies is related to the differences in the viscosity linked to fast and slow processes:

(a) The viscosity associated with the fast sorption process does not change under conditions of adsorption and desorption.

(b) In complete contrast, the viscosity associated with the slow process does change under desorption compared to adsorption conditions.

Does this then provide any insight into the origins of the fast and slow process? Based upon the data presented herein, as noted with the results with thermally modified wood, the moduli of both fast and slow of the same order of 20 GPa and it is not possible to conclude that the fast process is related to relaxation events associated with the microfibrils, whereas the slow process is related to matrix relaxation. However, double relaxation processes in the polymer literature are commonly interpreted as bi-component models.

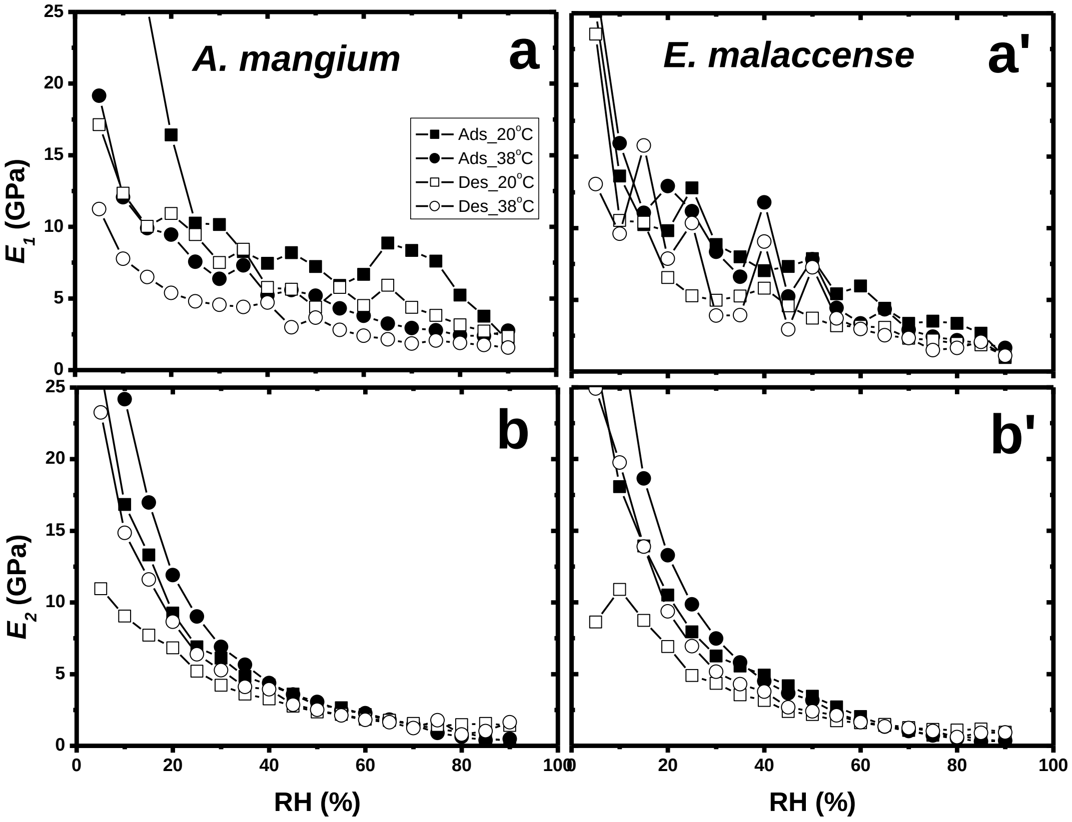

Figure 6.8 The relationship between the modulus associated with the fast (E_1) and slow (E_2) sorption processes and relative humidity for two isotherm temperatures (20 and 38 °C) for *A. mangium* (a-b) and *E. malaccense* (a'-b') under adsorption and desorption conditions.

6.3.1.4 Comparison of the K-V viscoelasticity model with related studies

There is no report in the literature where the cell wall modulus and viscosity have been determined by the application of an internal force, as is occurring with these sorption experiments. However, the calculated modulus values appear to be reasonable given that Salmén (2001) reports the modulus of dry hemicellulose as 2 GPa (reducing to 40 MPa at high moisture content) and that for wet or dry lignin as 2 GPa; an off-axis modulus of 20 GPa is quoted for the microfibril. Nanoindentation methods have given values for the modulus of the order 13 to 21 GPa for the cell wall of spruce (Wimmer *et al.* 1997, Gindl and Gupta 2002, Gindl and Schöberl 2004).

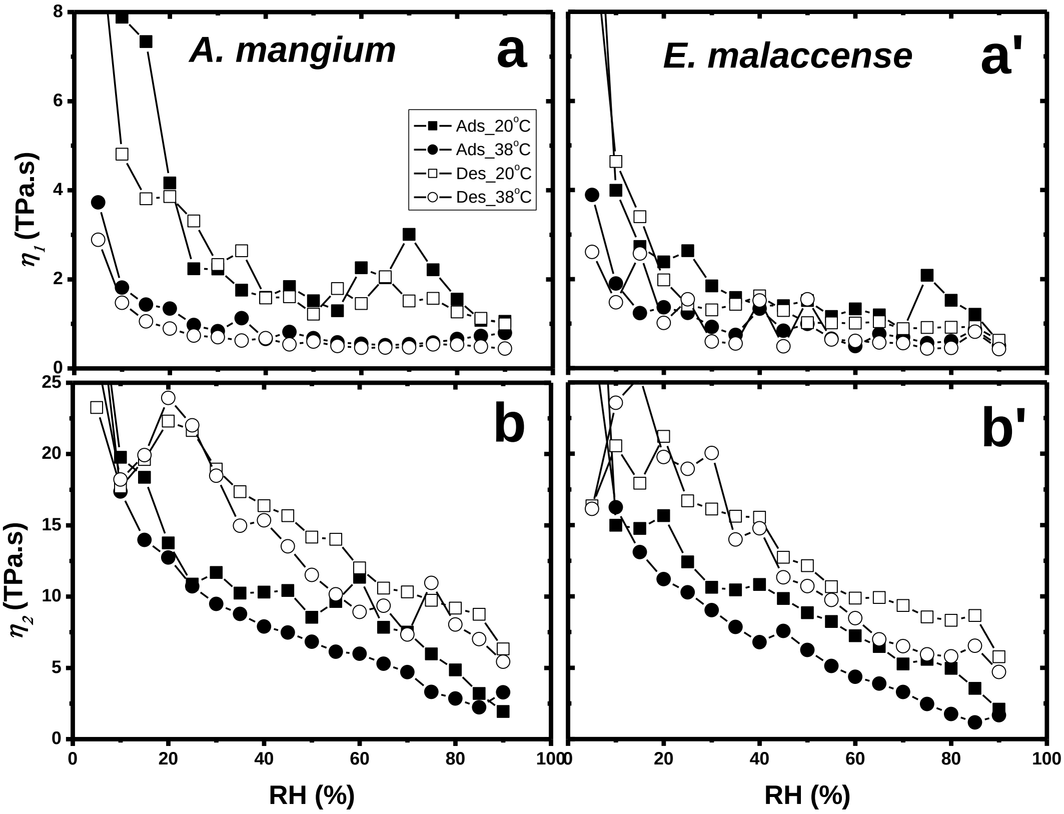

Figure 6.9 The relationship between the viscosities associated with the fast (η_1) and slow (η_2) sorption processes and relative humidity for two isotherm temperatures (20 and 38 ^{o}C) for *A. mangium* (a-b) and *E. malaccense* (a'-b') under adsorption and desorption conditions.

The magnitudes of E_2 also exhibit a range of values that appear reasonable. Although a decrease in modulus with increasing cell wall moisture content is a well known phenomenon, such low values are not observed when external loads are applied.

One study of the creep behaviour of macroscopic spruce samples quoting viscosity values as high as 10^{13}-10^{14} Pa.s (Lagaňa *et al.* 2008), which is one to two orders of magnitude higher than the values calculated from the sorption kinetics data. However, the type of behaviour is quite different, since, there is no external applied load and creep effects are absent in the sorption experiments. Therefore, it is not possible to verify whether the viscosity values calculated using this method is correct. A method of independent verification is required.

All the literature values have been obtained by applying an external force to the materials and they may not be directly comparable with the results obtained herein, which are obtained as a result of the application of an internal stress (the swelling pressure). Given that the sorption processes take place within the matrix region between the microfibrils, it is reasonable to suppose that the matrix properties will dominate the behaviour at the upper end of the hygroscopic range. Where external stresses are applied, the mechanical properties of the microfibrils would be more dominant in this region.

There are also interesting differences in behaviour between adsorption and desorption data which may be used to provide some insight into the nature of sorption hysteresis. It is not clear at the present time what the physical interpretation of the fast and slow processes is; however bi-exponential relaxation processes in polymers are invariably associated with two component systems, copolymers, or side and main chain relaxation (Meng *et al.* 1996, Barry and Soane 1996, Buffeteau *et al.* 1996, Usha and Ramasamy 1999, Spontak and Vratsanos 2000). At this time, it is not possible to assign the fast and slow processes to specific relaxation events. However, it is important to note that this type of behaviour is not solely restricted to sorption kinetics with wood and appears to be widely found where substrate dimensional change is associated with sorption. Further work is needed in order to examine whether this tentative hypothesis has any validity using well-characterised model materials e.g. cross-linked poly(vinyl alcohol).

6.3.2 Matrix stiffness and viscosity in water vapour sorption

The adsorbed water vapour molecules exert a pressure within the cell wall leading to dimensional change which has been explained in Chapter 2 (section 2.2). This expansion/extension associated with a higher MC result in an increase in the free energy of the polymer system (Matsuoka 1992). Expansion will continue until the free energy of the system is equal to the free energy of the water vapour molecules in the atmosphere. The spring modulus therefore defines the MC of the system at infinite time (MC_1, MC_2). The rate at which water molecules are adsorbed or desorbed by the system is a function of the viscosity of the dashpot in the model. This viscosity is in turn related to the micro-Brownian motion of the cell wall macromolecular network. The more rapidly the matrix is able to deform, the faster the rate of water ingress or egress into or out of the cell wall.

The adsorption and desorption of water molecules into and out the cell wall is associated with dimensional change. At the molecular level this is related to the micromechanical deformations of the matrix polymers.

The rate of local deformation is related to the energy barrier associated with the local relaxation process and whether there is sufficient free volume to allow the relaxation process to take place. In glassy solids below the *Tg* there is insufficient free volume to allow a local relaxation to take place without the cooperative motion of adjacent relaxors (a relaxor is defined as the smallest molecular segment of relaxation in each polymeric unit). This gives rise to the concept of cooperative domains within the matrix (Figure 6.10) (Matsuoka 1992, Matsuoka and Hale 1997, Bartolotta *et al.* 2010). The viscosity is therefore associated with molecular rearrangement.

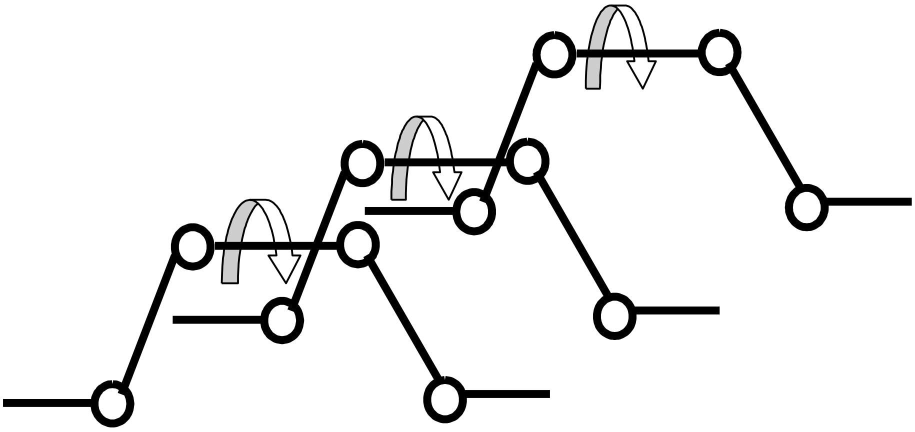

Figure 6.10 Cooperative domains within the matrix, where relaxation exists with the cooperation of neighbouring molecule.

As the *Tg* is approached, the domain size decreases until *Tg* is reached. At this point the domain contains only one relaxor and there is sufficient free volume to allow for relaxation without the cooperation of neighbours. Relaxation is then essentially instantaneous or at least only dependent upon the energy barrier associated with the change in conformation. The time scales involved in these molecular processes are of the order of 10^{-10} s (single event), yet differences in the time constants of the slow kinetic process are of order of minutes with multiple simultaneous relaxation (Matsuoka 1992).

6.4 Conclusions

This study has explored the possibility 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 are evaluated using a Kelvin-Voigt viscoelasticity model, it is possible to obtain values for cell wall matrix modulus and viscosity. Both modulus and viscosity decrease with increasing relative humidity (and hence cell wall moisture content) in all kind of wood (six hardwood species, thermally modified wood, different isotherms temperature).

The modulus and viscosity values appear to be reasonable, but confirmation using nanoindentation or other suitable techniques is required. In the study on the effect of different isotherm temperatures, whilst the modulus changes between adsorption and desorption, only the viscosity associated with the slow sorption process shows 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. 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. This appears to be an interesting line of enquiry for further research.