JOURNAL OF MATERIALS SCIENCE 25 (1990) 3671–3676

Longitudinal shrinkage–moisture relations in softwood

D. G. HUNT
Department of Mechanical Engineering Design and Manufacture, South Bank Polytechnic, Borough Road, London SE1 0AA, UK

Data have been presented on the axial dimensional changes of wood under zero load, both in equilibrium and non-equilibrium humidity conditions. The results support the idea of differing energy levels of moisture bonding, and suggest the division of sorbed moisture into two components: the first is a high-energy moisture that is associated with dimensional changes and shows very little hysteresis, and the second is a lower-energy moisture that is not associated with dimensional changes and shows considerable hysteresis. Diffusion of the first moisture component obeys Fick's laws with a concentration-dependent diffusion coefficient, whilst the hysteresis and the very slow approach to equilibrium of the second component makes the application of Fick's laws difficult or impossible. The addition of the two effects in diffusion measurements based on mass change alone could explain the difficulties normally encountered in the analysis of moisture diffusion in wood. No statistically significant effect of stress on the diffusion coefficient could be detected. Some results on very thin pieces show a strain reversal during the approach to moisture equilibrium, as predicted by some previous workers and attributed to the relaxation of internal stresses.

1. Introduction

Despite much previous research there are some unexplained aspects of the longitudinal movement of wood. Longitudinal movement, although small in comparsion with radial and tangential movements, is important because it takes place over much larger dimensions and therefore can have an important bearing on bowing and other distortions. Its direction also coincides with the usual direction of maximum loading, and the resulting elastic and creep strains act in the same direction. The magnitude of the longitudinal movements under zero load also correlates with susceptibility to mechano-sorptive creep [1].

The experimental results presented in this paper were the by-products of research on mechano-sorptive creep. Because they have been made using modern high-precision equipment, and it is some years since the comprehensive measurements were made by Meylan [2], it was felt to be worth presenting them in the hope that they would contribute to a deeper understanding of shrinkage–moisture relations. The relatively high precision of these results also allowed methods of data analysis that would not be appropriate with less precise results. Whilst the results of the analysis may not agree fully with present knowledge of wood structure, they were felt to provide a new viewpoint.

A comprehensive analysis of the subject was made by Cave [3]. He proposed a model based on the molecular structure of wood, using the stiffness and swelling characteristics of the main constituents lignin, hemicellulose and cellulose. This model allowed both the stiffness and swelling characteristics of the wood to be calculated and to be compared with experimental measurements. He showed that in the case of longitudinal movement, although there was no external stress, the differential movements of the various constituents resulted in internal stress within the material. Experimental evidence suggested that the material was free of internal stress in the neighbourhood of fibre saturation (30% moisture content). He also divided the sorbed moisture into a high-energy or bound fraction, and a low-energy or relatively free fraction. He suggested that it is the high-energy moisture that, by altering the degree of cross-linking in the matrix, is responsible for swelling stresses in the cell wall and therefore for the swelling and shrinkage behaviour. This accounted for the non-linear swelling.

Cave's model was based on the very careful movement measurements made by Meylan [2] in which he studied swelling and shrinkage between 0% and 30% moisture for a large range of microfibrillar angles in *Pinus radiata.* His measurements showed considerable hysteresis between swelling and shrinkage, i.e. the dimensions were always greater during sorption than during desorption for any given moisture content. Meylan also measured movements in the radial and tangential directions but obtained basically linear effects and found that he could not measure sufficiently accurately to draw any conclusions on whether or not hysteresis occurred.

The division of sorbed water into various components had been previously proposed by Kollmann [4] in which he suggested, on the basis of the analysis of the sorption isotherm, that the sorbed water could

0022–2461/90 $03.00 + .12

be divided into three groups. These were monolayer adsorption at low humidities, multilayer adsorption starting at intermediate humidities, and relatively free capillary water which predominates at higher humidities.

If the sorbed moisture can be divided into two or more groups, of which only one is responsible for expansion and shrinkage, this suggests two things: (1) that moisture-diffusion measurements based on mass changes alone would be confusing, because there could be two different diffusion coefficients acting simultaneously, and (2) that a quasi-diffusion coefficient, based on dimensional change rather than mass change, could cast some light on the diffusion of the higher-energy moisture which Cave [3] said was responsible for dimensional changes alone. Whilst this approach to moisture-diffusion measurements might be controversial, it was felt that the results obtained in this present study are sufficiently interesting to be worth presenting.

In the literature there is considerable disagreement regarding the diffusion of moisture vapour in wood. The normal starting point of diffusion theory is Fick's laws, of which the second can be written as

$$\partial C/\partial t \quad = \quad \partial/\partial x(D\partial C/\partial x)$$

where D is the diffusion coefficient, t the time, for unidirectional diffusion in which the diffusion coefficient varies from point to point [5]. This assumes that the driving force for diffusion is the concentration gradient; but it is now generally agreed that in wood the driving force for diffusion is the vapour-pressure gradient [6]. Many previously published results were reviewed by Walker [7] who emphasized the very wide variation in published results for diffusion rates, based on weight changes alone.

Recently published work [8] showed that by a suitable load and moisture regime a piece of wood can be taken to a limiting state of creep under a tensile bending or compressive load, so that further time or moisture cycling will not increase the deformation under the given load. In the limiting state, under a tensile load, the rate of expansion and shrinkage with moisture change was found to be lower than in the stress-free state. Conversely, with compression the movement rate was higher. The ability to obtain a creep limit gives another opportunity to study the effect on moisture-diffusion rates, by basing the moisture changes on strain rather than on mass. This was previously studied in a more traditional manner on beech [9]. The subject is of interest because the expected effects of stress on moisture-diffusion rates and sorption equilibrium have sometimes been suggested as contributing factors in mechano-sorptive creep.

The scope of this paper is as follows.

1. Further study has been made of movement hysteresis, both with respect to equilibrium moisture content and to the relative vapour pressure, or relative humidity.
2. Movement in non-equilibrium states of moisture change has been studied, both for small and larger pieces.
3. Quasi-diffusion rate measurements, based on dimensional changes, have been made in "limiting creep states" under zero load and in tension and compression. A limiting creep state means here that the strain–moisture content graph forms a closed loop over one complete humidity cycle.

2. Materials and techniques

All of the results described here were obtained from Scots pine (*Pinus sylvestris*). The pieces had cross-sections 8 mm (radial) by 3.2 mm (tangential), or 3.2 mm (radial) by 0.5 mm (tangential). The pieces were carefully prepared to avoid any surface damage, and the samples were observed for any evidence of reaction wood.

Testing was done at 23.5° C in a precisely controlled environmental chamber that has been described previously [10]. Measurements of movement were made directly with super linear variable capacitance (SLVC) transducers. Tensile, bending and compression loading was done on machines that have been described in the literature [8, 10, 11].

3. Results

3.1. Zero-load dimensions in equilibrium moisture conditions

The longitudinal strain – equilibrium moisture content loop over a complete humidity cycle between 30% and 93% r.h. is shown as the solid line in Fig. 1. For each point the relative humidity was kept constant sufficiently long to achieve the equilibrium dimensions. This loop agrees qualitatively with the results of Meylan [2]. Also in Fig. 1 are shown two strain–moisture paths taken when the moisture cycle is foreshortened. These were also measured in equilibrium conditions, and explain why a complete humidity cycle always forms a closed loop on a strain–moisture graph, regardless of the extent of the cycle. This is because, on reversal of the direction of the humidity change, the equilibrium strain–moisture

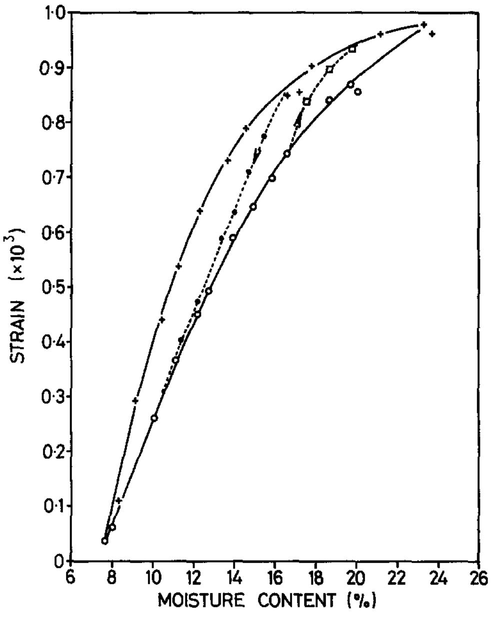

Figure 1 Typical hysteresis loop of zero-load axial equilibrium dimensional changes plotted against moisture content: (+, □) humidifying, (○, ●) dehumidifying, (- - -) paths taken when the moisture cycle is foreshortened.

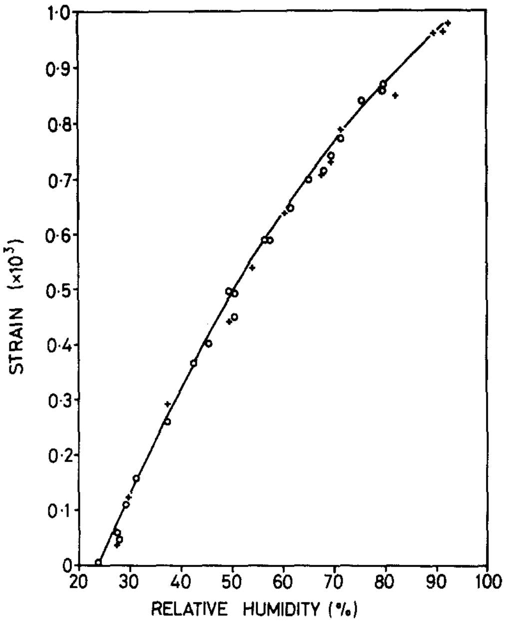

Figure 2 Zero-load axial equilibrium dimensional changes plotted against relative humidity for the same test piece as for the results of Fig. 1: (+) humidifying, (O) dehumidifying.

path rapidly approaches the other side of the loop. The path slope then blends into that of the main loop.

It is interesting to notice in Fig. 2 that the strain–moisture loop has nearly shrunk into a single curve when the zero-load equilibrium strain results for the same test piece are plotted against relative humidity. Data for approximately twenty different tests were examined in the same way and in every case the loop area was reduced by plotting strain against relative humidity. In 70% of the tests the loop area was almost entirely eliminated. Generally those test pieces with larger microfibrillar angles and consequently larger movement coefficients had their strain–moisture loops more effectively shrunk by this method of plotting.

3.2. Longitudinal movements in non-equilibrium moisture states

To investigate the approach to dimensional equilibrium as a function of moisture content, the dimensional changes of 3.2 mm thick pieces were measured at progressive time intervals after step changes in relative humidity of approximately 15%. The relative humidity was maintained constant after the step change in order to reach an approximate equilibrium. The results are shown in Fig. 3 for two different pieces at zero stress. It may be noticed that for each sorption or desorption step the slope of the strain – moisture content curve is steeper at first, but less steep as equilibrium is approached, giving a series of convex outward subsections of the strain–moisture loop. The higher strain loop was for a piece taken from near the centre of the tree with mean growth ring two and with mean microfibrillar angle 29°, whilst the lower loop was for one of mean growth ring eight and a mean microfibrillar angle of 24°.

To investigate this further, a similar experiment was made with thin (0.5 mm by 3.2 mm cross-section) pieces, of which an example is given in Fig. 4 and Table I. It may be noticed that during sorption there is a region of approximately uniform expansion rate as a function of moisture content. This region involves fairly rapid changes with these small test pieces, because the expansion is approximately 50% complete within 1 to 6 min. For the last 23.5 h the moisture content slowly increased with little change in dimensions. This latter moisture increase was small at low humidities but relatively large at high humidities. Table I summarizes the times for 50% change in moisture content and dimensions for each step change in relative humidity. The last column gives the ratios of these half-times, which are seen to be strongly dependent on the humidity level for both sorption and desorption. At higher humidities the dimensional changes were slightly reversed during sorption (i.e. a shrinkage), as can be seen in Fig. 4. During desorption there were similar anomalous effects, and again there appeared to be a slight reversal of movement (i.e. an expansion) during the later stages of the step. An example of both moisture content and strain plotted against the square root of time is shown in Fig. 5, for desorption over the interval 65% to 45% r.h.

3.3. Moisture diffusion rates based on dimensional changes

By plotting dimensional changes against the square root of time, a kind of diffusion coefficient can be determined. This is obviously not a normal diffusion coefficient, although mathematically it can be treated as such. The mean diffusion coefficients, $\bar{D}$, for the

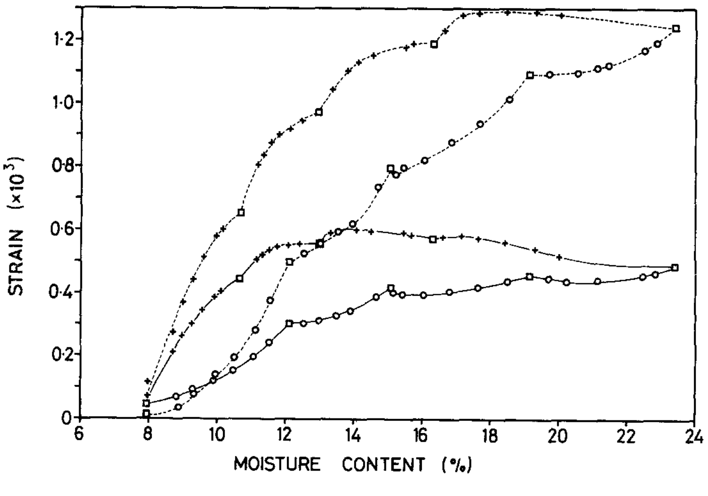

Figure 3 Zero-load axial dimensional changes plotted against moisture content for a series of step changes of r.h., allowing sufficient time to reach equilibrium after each step, using 3.2 mm thick pieces. The higher and lower loops are for test pieces of microfibrillar angles of 29° and 24°, respectively. (□) Equilibrium values; non-equilibrium values, (+) humidifying, (O) dehumidifying.

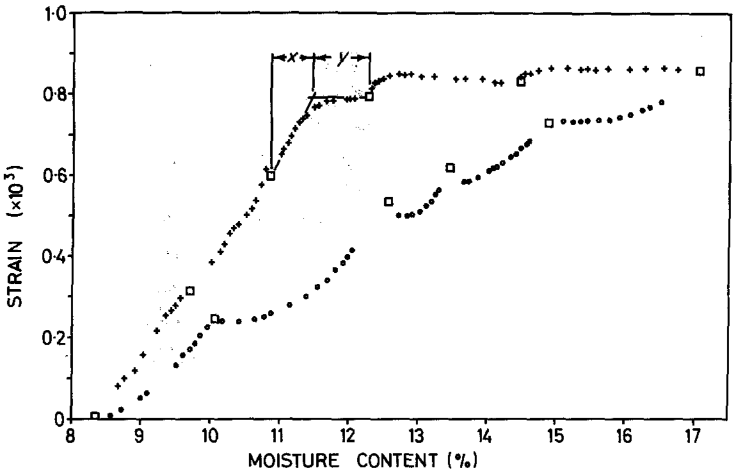

Figure 4 Zero-load axial dimensional changes plotted against moisture content for a series of step change of r.h., allowing sufficient time to reach equilibrium after each step, using 0.5 mm thick pieces. (□) Equilibrium values; non-equilibrium values, (+) humidifying, (○) dehumidifying.

various moisture intervals were calculated [5] using

$$\bar{D} = 0.04919/(t_{1/2}/L^2)$$

where $t_{1/2}$ is the time for 50% equilibrium change and L is the thickness. Fig. 6 shows a plot of the natural logarithm of the mean sorption diffusion coefficient, $\bar{D}_s$, against the mean relative vapour pressure, p/p_0 for various sorption intervals which, despite a considerable scatter, allows the determination of an approximate expression relating $\bar{D}_s$ to p/p_0 of

$$\bar{D}_s = D_0 \exp(ap/p_0)$$

This agrees qualitatively with the results of Kawai *et al.* [12] and Christensen and Kelsey [13]. The results of Fig. 6 were analysed to give $\bar{D}_s = 0.19 \exp(2.46\, p/p_0)\,\mathrm{mm^2\,h^{-1}}$ with a root mean square error of $0.1\,\mathrm{mm^2\,h^{-1}}$.

3.4. Effects of stress on diffusion

Because wood is such a variable material, it is better to compare diffusion rates on the same piece with and without stress rather than to rely on the matching of test pieces. Accordingly, a series of measurements was made such as those shown in Fig. 6, but in which the test pieces had been taken to a limiting state of creep in either tension or compression. Any resulting changes in the apparent diffusion coefficient were sufficiently small to be well within the root mean square error of $0.1\,\mathrm{mm^2\,h^{-1}}$ quoted above. This showed that, if stress affects the diffusion rate, the effect on the rate is only small. Detailed results are therefore not presented here.

4. Discussion

4.1. Anomalous equilibrium and non-equilibrium strain measurements

In an attempt to interpret the data presented above, the results quoted by Christensen [14] should also be considered. The latter's relevant results may be summarized as (a) below a limiting thickness the sorption rate was independent of material thickness, (b) for moisture increments of a given size the sorption rate was markedly lower at higher initial moisture contents, whereas the diffusion coefficient is known to be greater at higher moisture contents, and (c) for the same final moisture content, large moisture increments were completed much faster than smaller ones. His explanation postulated that the rate of sorption was limited by relatively slow molecular rearrangements within the swelling substance; and that the speed of rearrangement depended on the swelling pressure, because the rate of sorption was found to be related empirically to log p_f/p_i where p_i and p_f are the initial and final vapour pressures, respectively. This results in the concept of a history-dependent diffusion coefficient. A second concept that should be considered is that of moisture bonding involving differing energy levels, as postulated by Kollmann [4] and by Cave [3].

Bearing these concepts and Christensen's results in mind, the interpretation of the results of Figs 1 to 5 leads to the following three conclusions.

1. There is strong evidence of two different forms of moisture bonding. For ease of visualization, this could be imagined as two different types of moisture; and for this discussion, they are labelled types I and II.

TABLE I Half-times for sorption or desorption of 0.5 mm pieces

r.h. range (%)	Sorption (S) or desorpn. (D)	Half-time moisture (h)	Half-time dimensions (h)	Ratio, $t_{1/2}$ moist./$t_{1/2}$ dimens.
34–42	S	0.0433	0.0416	1.0
42–52	S	0.258	0.1076	2.4
47–66	S	0.372	0.052	7.2
66–78	S	0.734	0.028	26.2
78–90	S	0.769	0.0119	64.6
89–78	D	0.250	0.0167	15.0
78–67	D	0.221	0.0181	12.2
67–55	D	0.314	0.0217	14.5
55–45	D	0.127	0.0339	3.7
46–30	D	0.578	0.160	3.6

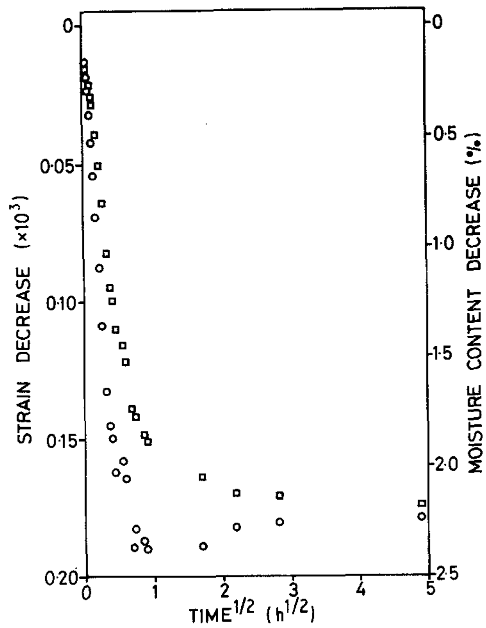

Figure 5 Zero-load axial dimensional and moisture-content changes with square root of time of 0.5 mm thick pieces for a step reduction in the relative humidity from 65 to 45%. (○) Dimensions, (□) moisture.

2. The characteristics of type I are:

(a) it is strongly associated with longitudinal dimensional changes;

(b) there is little or no hysteresis with respect to the direction of relative humidity changes;

(c) it is more important at lower relative humidities than at high ones; and

(d) its apparent diffusion coefficient obeys Fick's law but is concentration-dependent.

3. The characteristics of type II are:

(a) it has little or no relation to longitudinal dimensional changes,

(b) there is strong hysteresis with respect to relative humidity, especially at high humidities, where a real equilibrium may never by reached at all (e.g. [15]),

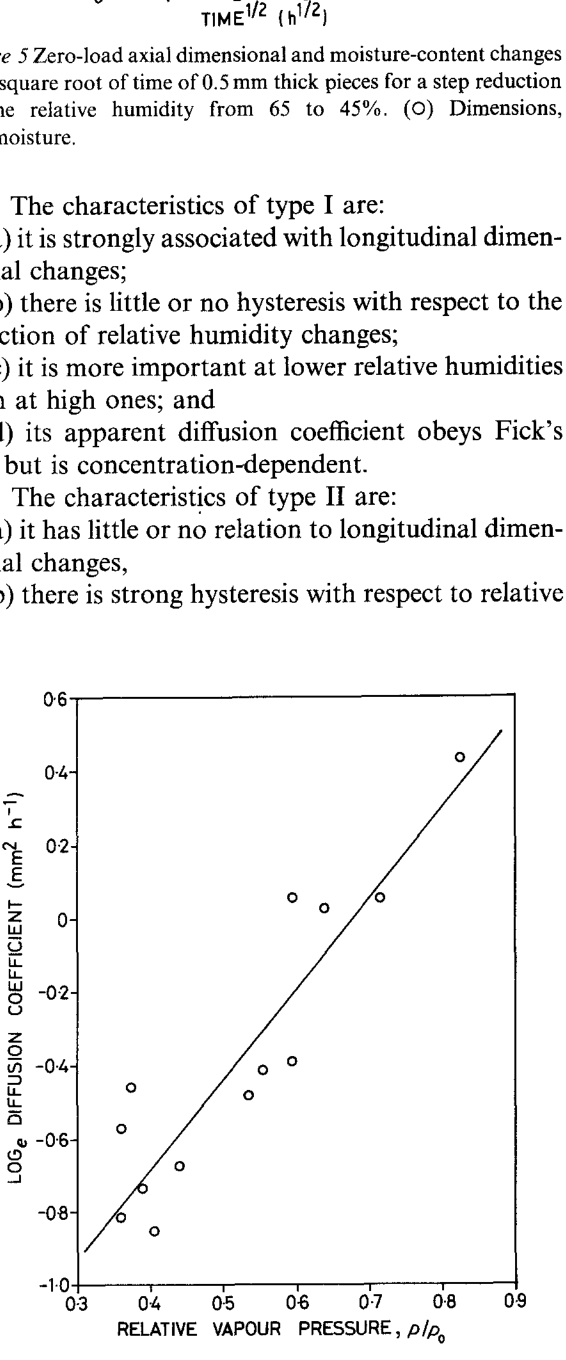

Figure 6 Mean quasi-diffusion coefficient based on dimensional changes, for sorption over small relative vapour pressure intervals plotted against mean relative vapour pressure at zero stress.

(c) it is more important at high relative humidities, and

(d) because of the strong hysteresis, diffusion theory cannot be applied.

Fig. 2 provides evidence for statements 2a and b because, provided that equilibrium at a given relative humidity is reached, the dimensions are almost independent of relative-humidity history. Figs 1 to 3 support statement 3b because the horizontal spacing between the sorption and desorption curves is greater at higher moisture contents than at lower ones. Figs 3, 4 and Table I support statements 2c and 3c because it can be seen that, especially for the thinner pieces, the dimensional changes take place quite quickly, and these are followed by much slower changes in moisture content with little or no further dimensional change. If the results of Fig. 4 are separated into the sloping and the horizontal components such as is indicated by the dimensions x and y, the values in Table II result. The dimension x can be postulated to be associated with moisture bonding type I, and y with type II.

Support for statement 2d comes from Fig. 6. Given the results of Fig. 4 and Table I, especially at high humidities, and the results of previous workers [15], statement 3d is self evident. It can be argued that this could explain many of the difficulties experienced by previous researchers in determining the diffusion coefficient of water vapour in wood when basing their measurements on mass sorbed or desorbed.

If it can be assumed that there are at least two forms of moisture bonding, it would be useful if they could be quantified. This was attempted by Kollmann [4] on the basis of a statistical and microstructural approach. He then used curve fitting to obtain the actual parameters. His curves for a softwood are shown in Fig. 7. The equation for sorption was $u_1 = 0.113\phi^{0.54}$, for submicroscopic capillary condensation was $u_2 = 0.192e^{-1/2(2.7\phi-3.7)^2}$ and for microscopic capillary condensation was $u_3 = 0.09e^{-1/2(20.5\phi-21.5)^2}$, where ϕ is the relative vapour pressure. He made no allowance for hysteresis.

To quantify the separate moisture components of these data it was assumed that

(a) only two forms of moisture bonding should be

TABLE II Moisture content changes associated with u_{I} and u_{II} (dimensions x and y in Fig. 4)

r.h. range (%)	Moisture content, x (u_{I}) (%)	Moisture content, y (u_{II}) (%)	y/x
34–42	0.87	0.10	0.11
42–52	0.94	0.77	0.82
47–66	0.62	1.44	2.32
66–78	0.08	2.02	25.25
78–90	0.30	5.78	19.27
89–78	0.55	3.00	5.45
78–67	0.66	2.01	3.05
67–55	0.65	1.75	2.69
55–45	0.60	1.25	2.08
46–30	1.08	1.47	1.36

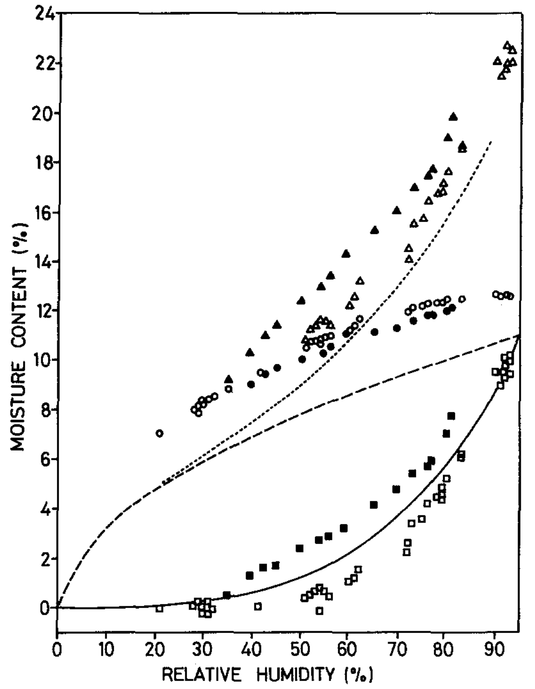

Figure 7 Separation of total equilibrium moisture values (△▲) ($u_{\rm I}$ + $u_{\rm II}$) into (○●) $u_{\rm I}$, corresponding to axial dimensional changes and (□■) $u_{\rm II}$, independent of axial dimensional changes, for cycling between extremes of 30% and 93% r.h. (△, ○, □) Humidifying, (▲, ●, ■) dehumidifying. Lines represent Kollmann's values [4]: (– – –) $u_{\rm I}$, (——) $u_2 + u_3$, (· · · ·) $u_1 + u_2 + u_3$.

considered: $u_{\rm I}$ and $u_{\rm II}$, both of which are zero at zero relative humidity,

(b) $u_{\rm I}$ correlates linearly with the axial dimensional changes, and

(c) at 30% r.h. $u_{\rm II}$ is approximately zero (following Kollmann's analysis).

The analysis was tried on a number of different test pieces, of which an example is shown in Fig. 7. The strain, ε, at various equilibrium moisture contents, u, was measured both humidifying and dehumidifying. Based on the assumptions above, the slope in the 7% to 9% moisture content range was measured as 0.634 moisture per strain (dimensionless). Zero strain, based on the starting dimension of the test, coincided with 8% moisture, as indicated in Fig. 7. The assumptions quoted above allowed calculation of $u_{\rm I}$ as $u_{\rm I} = (8 + 6340\varepsilon)$ % moisture and $u_{\rm II} = u - u_{\rm I}$. These values were then plotted as shown in Fig. 7. It can be seen that they follow the same trends as those developed on a theoretical basis by Kollmann [4].

4.2. Diffusion measurements

It is evident that the measurement of axial strain as a guide to diffusion rates cannot be considered as an alternative to the measurement of mass; rather as a complementary measurement. There are two difficulties with the use of strain:

1. During sorption the equilibrium axial strain starts to decrease at high moisture contents in some samples of smaller microfibril angles (for example, see Fig. 3).
2. During both sorption and desorption the non-equilibrium axial strain can change direction as equilibrium is approached (for example, see Figs 4 and 5).

The first difficulty makes it impossible to obtain a sorption diffusion coefficient at high moisture contents, based on the strain of pieces of low microfibril angle. The second difficulty causes serious errors in diffusion coefficients at higher moisture contents.

The observed reversal of strain may possibly be attributed to the relaxation of internal stresses with a simultaneous slow rearrangement of molecular bonds, thus reducing the total energy of the system. Such rearrangements have been discussed in detail by previous workers such as Boyd [16] in his lenticular trellis theory, and by Struik [17] in his theory of physical ageing.

5. Conclusion

Some accurate strain measurements, under equilibrium and non-equilibrium conditions, have been presented; together with some suggestions for methods of their analysis. The analysis methods are mainly numerical, and with the present state of knowledge cannot be firmly based on structural effects within the material. It is nevertheless hoped that a slightly different approach to moisture sorption analysis will provide a further step towards the understanding of wood-moisture relations.

Acknowledgements

The author thanks the UK Science and Engineering Research Council and European Commission for support for this research.

References

1. D. HUNT and C. SHELTON, *J. Mater. Sci.* **22** (1987) 313.
2. B. MEYLAN, *Wood Sci. Technol.* **6** (1972) 293.
3. I. CAVE, *ibid.* **12** (1978).
4. F. KOLLMANN, *Forsch. Gebiete Ingenieurw.* **29** (1963) 33.
5. J. CRANK and G. PARK, "Diffusion in Polymers" (Academic Press, London, 1968).
6. G. BRAMHALL, *Wood Sci.* **12** (1979) 3.
7. I. WALKER, *New Zealand J. Sci.* **20** (1977) 3.
8. D. HUNT and C. SHELTON, *Wood Sci. Technol.* **22** (1988) 199.
9. D. HUNT, *J. Mater. Sci.* **19** (1984) 1456.
10. D. HUNT and M. DARLINGTON, *Polymer* **19** (1978) 977.
11. D. HUNT, *J. Mater. Sci.* **21** (1986).
12. S. KAWAI, K. NAKATO and T. SADOH, *Memoirs Coll. Agr. Kyoto Univ.* **115** (1979).
13. G. CHRISTENSEN and K. KELSEY, *Holz Roh-Werkstoff* **17** (1959) 178.
14. G. CHRISTENSEN, *Nature* **213** (1967) 782.
15. H. HERGT and G. CHRISTENSEN, *J. Appl. Polym. Sci.* **9** (1965) 2345.
16. J. BOYD, in "New Perspectives in Wood Anatomy", edited by P. Baas (Nijhoff and Junk, The Hague, 1982) pp. 171-222.
17. L. STRUIK, *Chim. Indust.* **58** (1976) 549.

Received 2 February
and accepted 26 September 1989