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The recovery of mechano-sorptive creep strains

K. M. Entwistle · A. Zadoroshnyj

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Abstract Mechano-sorptive strain was generated in strips of rectangular section stressed in torsion with the humidity cycled between 38% and 84%. After a number of humidity cycles the specimen was unloaded, the applied stress was reversed and further humidity cycles were imposed. All the initial strain was recovered and reversed strain was developed. Tests were carried out at two maximum shear stress levels, 1.12 MPa and 5.05 MPa. After seven humidity cycles at the higher stress a large mechano-sorptive strain of about 0.06 was developed, which was nearly nine times the initial elastic strain. During the development of this strain no significant change of the shear modulus occurred, from which it is concluded that the large MS strain produces no permanent change of the features of the cell wall structure that determine the shear modulus. There are close parallels between the mechanism generating the MS strains and that responsible for the large plastic strains reported by Keckes et al. in wet compression wood loaded in tension. In both cases it is suggested that the shear strains arise from the breaking and reforming of hydrogen bonds between parallel polymer chains.

K. M. Entwistle (✉) · A. Zadoroshnyj
Materials Science Centre, School of Materials, University of Manchester, Grosvenor Street, Manchester M1 7HS, UK
e-mail: ken.entwistle@manchester.ac.uk

K. M. Entwistle
Department of Mechanical Engineering, University of Canterbury, Christchurch, New Zealand

Introduction

Early reports of mechano-sorptive creep were by Armstrong and Kingston [1]. They measured creep of beams under four point bending and found that a beam that was loaded whilst the wood was drying showed twice the creep deflection of a beam that was loaded at constant moisture content. Later, work by Hearmon and Paton [2] found that a simply supported beam of beech loaded to 1/8 of the maximum load showed a creep strain of 5 times the elastic strain after 14 humidity cycles between 53% and 93%. A similar beam loaded to 3/8 of the maximum load developed a creep strain 25 times the elastic strain after 14 similar humidity cycles. The specimen fractured immediately thereafter. Navi et al. [3, 4] have proposed that the mechano-sorptive strain is generated by slip between polymer chains that are cross-linked by hydrogen bonds. The bonds are broken and reform after a shear displacement. Entwistle [5] has made measurements of mechano-sorptive strains in bending and torsion and has deduced that the magnitude of the strain is determined by the shear stress component along the cellulose/matrix interface. If the short hemicellulose chains are oriented parallel to the cellulose micro-fibrils then shear stress parallel to that interface will also be directed along the interface between adjacent hemicellulose chains and will generate slip between them. A striking feature of mechano-sorptive creep is the very large shear strains that it can develop without apparently causing any change of the structure of the wood. That aspect of the effect is further examined in this article. In what follows mechano-sorptive will be abbreviated to MS.

There must be a close relationship between the deformation process that causes MS creep and that which generates large permanent (plastic) strains. Keckes et al. [6] have reported that tensile loads produce permanent strain of at least 20% in *Picea abies* compression wood with a micro-fibril angle of 45°. It is significant that with this micro-fibril angle, tension will produce the maximum shear stress along the direction of these micro-fibrils. They ascribe the strain to shear between parallel polymer chains due to breaking and reforming of hydrogen bonds. At the end of a large strain of this kind the original structure is judged to be preserved because there is no change of specimen stiffness. These significant observations on tensile plastic strain are returned to the discussion in which parallels are drawn to the mechanism that generates MS strains.

The article presents measurements of MS strains in *Pinus radiata* specimens strained in torsion. Moisture-induced swelling produces no torsional shear strain if spiral grain does not exist. In contrast measurements in bending and tension always include a contribution from either axial or lateral swelling which is added to the MS strain and must be subtracted from the measured strain. In torsion it is easy to give the specimen freedom to accommodate any moisture-induced change its axial length without generating any constraint that would impose stresses that would interfere with the creep process. Also in torsion it is possible to make a smooth transition from forward to reverse straining, a facility which is deployed in the work now described.

The objective of the research is to develop large MS strains in torsion and to explore the extent to which they can be recovered by humidity cycling at zero torque and by humidity cycling during reversed loading. Evidence of any permanent structural change during this process was sought by periodic measurement of the shear modulus. Measurements are made at two different stress levels. Some measurements are made at the lower stress level of the creep under constant humidity conditions to establish if that creep strain is recoverable by stress reversal.

Material and methods

The torsion straining machine was designed for a specimen 35 × 3 × 1–2 mm. The specimen was fixed at one end and the other end was clamped in a torsion head supported on knife edges and fitted with a 60-mm diameter wheel over which a flexible tape passed. The tape supported two identical scale pans in which weights could be placed to generate either a clockwise or an anti-clockwise torque. The torsion head was mounted on rollers that permitted free movement along the specimen axis so that axial swelling due to changes of moisture content were not constrained. The twist of the specimen was measured by two gold coated mirrors fixed 10 mm apart on the specimen. The mirrors reflected laser light beams on to graduated scales. The whole apparatus was enclosed in a box into which a tray of saturated alkali halide solution could be inserted to provide a controlled relative humidity. The air was gently circulated by a small fan. A relative humidity of about 38% was provided by a saturated solution of sodium iodide and of 84% by potassium chloride. Two *P. radiata* specimens of rectangular section were cut from a single earlywood growth ring. The longer side of the rectangle lay in the radial direction and the shorter side in the transverse direction. The specimen axis lay in the longitudinal direction of the wood cells. The micro-fibril angle was 28° and the density was 0.385 kg/m^3. The spiral grain of the wood was small; reference will be made to its effect later. One specimen was used for a test at a maximum stress of 1.12 MPa and the other for a test at 5.05 MPa.

The shear stress in a twisted strip of rectangular section varies across the section in a complex fashion. The distribution was calculated in the mid 19th century by Saint-Venant. His analysis is summarised by Todhunter and Pearson [7]. If the dimensions of the rectangle are 2b and 2c, where 2b is the longer side, the shear stress and the shear strain are a maximum in the middle of the side 2b. Saint-Venant's analysis gives the value of the maximum shear stress $\tau_{\max}$ and the maximum shear strain $\phi_{\max}$ from the measured twist per unit length θ and the applied torque M,

$$\phi_{\max} = \gamma c \theta$$

where γ is a calculated parameter tabulated by Saint-Venant. It is a function of the parameter

$$P = \frac{b}{c}\sqrt{\frac{G_c}{G_b}}$$

G_c is the modulus for shear over the face lc where l is the longitudinal direction and G_b is the modulus for shear over lb. For the specimen orientation used in the present work,

$$G_c = G_{LT} \text{ and } G_b = G_{LR}$$

it is assumed that

$$\frac{G_{LT}}{G_{LR}} = \frac{1}{1.5}$$

so

$$P = \frac{b}{c}\sqrt{\frac{G_c}{G_b}} = \frac{b}{c}\sqrt{\frac{G_{LT}}{G_{LR}}} = \frac{b}{c}\sqrt{\frac{1}{1.5}} = 0.816\frac{b}{c}$$

The maximum shear stress is

$$\tau_{\max} = \frac{M\gamma}{\beta b c^2}$$

where β is tabulated in the Todhunter reference [7], again as a function of the parameter P.

The elastic shear modulus G_{LR} is the ratio

$$\frac{\tau_{\max}}{\phi_{\max}}.$$

Mechano-sorptive creep measurements at low stress

A MS creep test was carried out on the first *P. radiata* specimen with a cross-section 3.02×1.27 mm. It was subjected to an applied torque of 1.47 Nmm, which gave a maximum shear stress of 1.12 MPa. The test results are shown in Fig. 1. After loading in the anti-clockwise sense, the relative humidity was cycled twice between 40% and 83%, whilst the torque was maintained. The specimen was then left to recover under load for about 73 h at 40% humidity. It is evident that little further strain is generated over that period. After 144 h the specimen was unloaded and immediately exposed to two more humidity cycles. The first cycle produced a large reduction of twist but the second cycle produced little change. The specimen was left unloaded at 38% humidity for a further 89 h during which no further strain developed. At this point about 43% of the MS twist developed in the first loading cycle was recovered. It will be noticed that there are steps in the twist curves at 23, 71, and 167 h. These are clockwise twists caused by slight spiral grain in the specimen. This generates a twist of about 0.002 radians over 10 mm when the humidity is decreased from 84% to 40%.

The specimen was then loaded in the opposite (clockwise) sense and immediately exposed to two humidity cycles. It was then left under load at 38% humidity for 70 h. The total reversed MS twist generated by unloading and then loading in the revered sense is 0.0498 radians over 10 mm. This is very close to the forward MS twist of 0.0475 radians over 10 mm generated by the first loading cycle. So at this point in the test almost all of the initial strain had been recovered. After 480 h the specimen was unloaded and two humidity cycles caused some of the reversed strain to be recovered.

The first loading cycle produced a MS strain that is four times the elastic deformation. Humidity cycling following unloading and then reversed loading causes most of this strain to be recovered. So during this test the wood matrix is subjected to the imposition and removal of large strains. Measurements of the shear modulus were made to establish if the imposed strains caused any irreversible change of structure. The data are listed in Table 1.

Sample standard deviation 0.0031 GPa. Figures in parentheses are the points on the time scale in Fig. 1 where the shear modulus was measured. All the shear modulus measurements were made at a relative humidity of 38%.

These data indicate that the MS strains produced no permanent change in the features of the cell wall structure that determine the shear modulus.

Mechano-sorptive measurements at higher stress

A MS test was carried out at a higher stress on the second specimen to explore the possibility that the higher strains

Table 1 Values of the shear modulus G_{LR} measured at indicated points in the MS test of Fig. 1

Measurement point		Elastic twist/unit length	Shear modulus G_{LR} (GPa)
Initial loading	(0)	0.001199	0.74_5
Unloading	(143.8)	0.001194	0.74_8
Reversed loading	(310.8)	0.001190	0.75_1
Unloading	(480)	0.001188	0.75_2

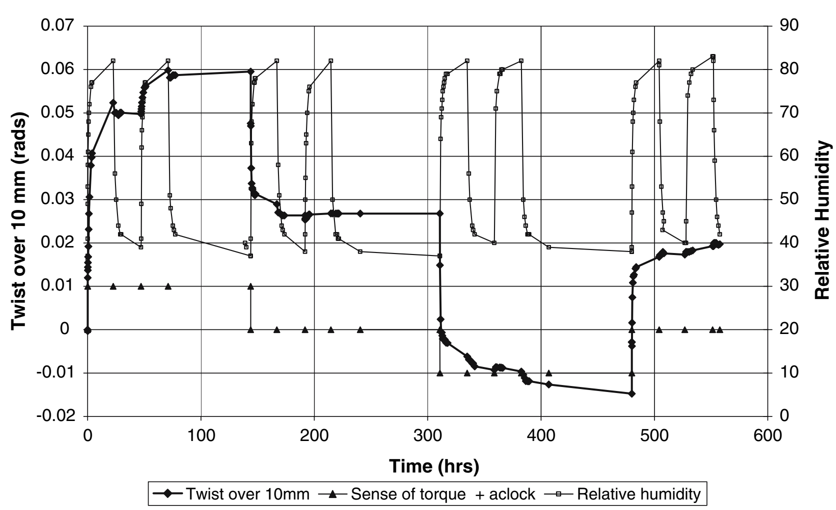

Fig. 1 Mechano-sorptive test on a *pinus radiata* strip 3.02×1.27 mm stressed in torsion with a torque of 1.47 Nmm producing a maximum shear stress of 1.12 MPa. The specimen twist, in radians, arising from a sequence of changes of loading and of relative humidity are indicated. The triangles show the sense of the applied torque. Referring to the left-hand scale, 0.01 is an anti-clockwise torque, 0 is zero torque and –0.01 is a clockwise torque

might produce some permanent structural change. The specimen cross-section was 2.05 × 2.94 mm. The larger value of the section dimension 2c (2.05 mm) compared to that of the first specimen (1.27 mm) permitted higher stresses to be developed with reasonable specimen twists. The test comprised two loading cycles, one with an anti-clockwise torque and the other with a clockwise torque. The results are plotted in Figs. 2 and 3. The two cycles comprised one continuous run.

The results of the first loading cycle are shown in Fig. 2. At the beginning of this test the specimen was equilibrated at 44% relative humidity and then subjected to an anti-clockwise torque of 14.7 Nmm. This gave a maximum shear stress of 5.05 MPa. The specimen, whilst under this load, was subjected to seven humidity cycles between 44% and 88% over a period of 480 h.

This produced a MS twist corresponding to a maximum shear strain of 0.0696. This is 8.8 times the initial elastic twist. The MS shear strain is 11.5 times that generated by the first loading cycle in the previous lower stress test.

The specimen was then unloaded at 44% relative humidity and left for 24 h with no humidity change, during which only a small amount of recovery took place.

The specimen was next loaded on the reverse (clockwise) sense with a torque of 14.7 Nmm. It was then exposed to five humidity cycles between 44% and 88%. A large MS strain of 0.1221 followed. This represents the recovery of all the MS strain of 0.0696 generated in the first loading cycle and a reverse MS strain of 0.0525. The data for this second loading cycle are plotted in Fig. 3. After 908 h the specimen was unloaded and immediately loaded in the clockwise sense. During two humidity cycles a large MS strain recovery of 0.1074 occurred.

Evidence of any permanent change of structure generated by these large MS strains was sought by making periodic measurements of the shear modulus G_{LR} from the

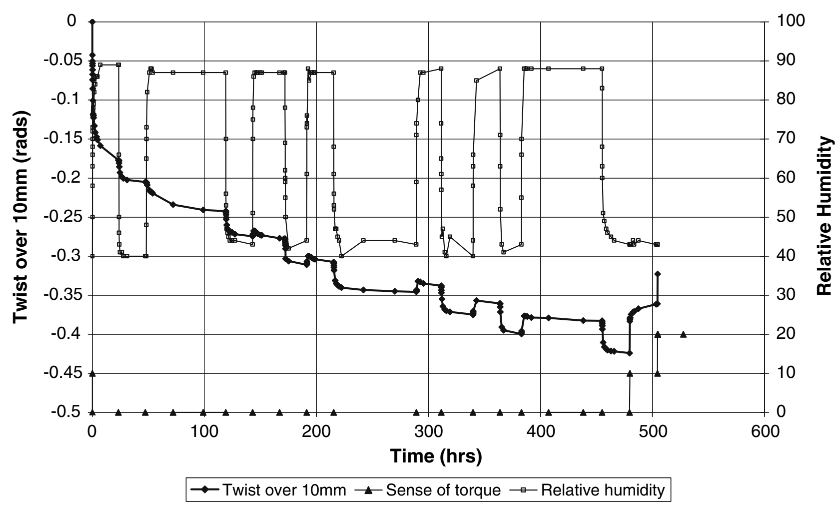

Fig. 2 The first mechano-sorptive test cycle on a *Pinus radiata* strip 2.94 × 2.05 mm stressed in torsion with a torque of 14.7 Nmm producing a maximum shear stress of 5.05 MPa. The effect of changes of humidity and of applied load on the torsional twist, in radians, of the specimen are indicated. The open triangles show the sense of the applied torque. Referring to the left-hand scale, –0.4 is an anti-clockwise torque, –0.45 is zero torque and –0.5 is a clockwise torque

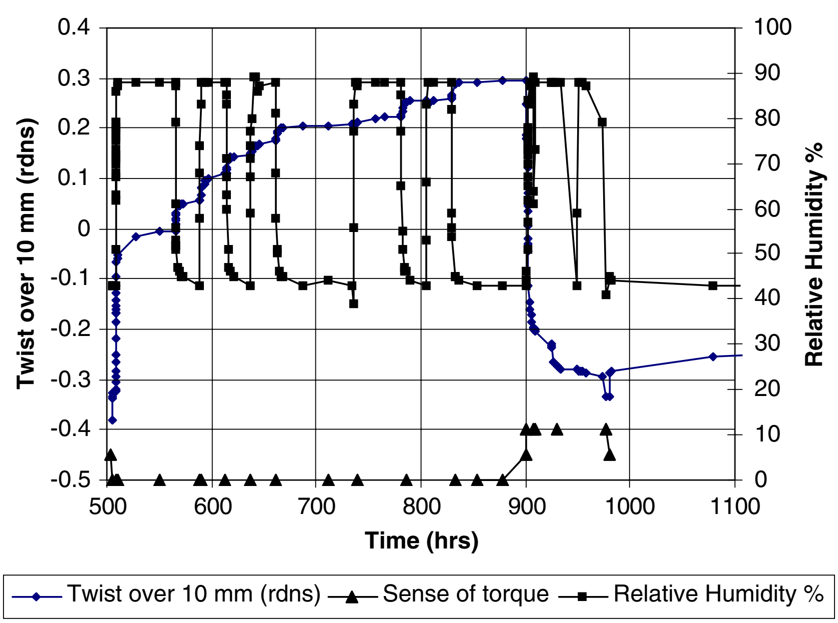

Fig. 3 Data for the second mechano-sorptive test cycle. It is a direct continuation of the cycle in Fig. 2. The test conditions are identical to those in Fig. 2 except that the sense of the applied stress is reversed

Table 2 Values of the shear modulus G_{LR} measured at indicated points in the MS test of Figs. 2 and 3

Measurement point		Twist/ unit length	Shear modulus G_{LR} (GPa)
Initial loading	(0)	0.00426	0.64_7
Unloading at end of first cycle	(479.6)	0.00440	0.62_5
Loading at beginning of second cycle	(504.7)	0.00422	0.65_2
Unloading at end of test	(981.1)	0.00451	0.61_0

elastic twist either on loading or on unloading. The data are listed in Table 2.

Sample standard deviation 0.019 GPa. Figures in parenthesis are the values on the time scales in Figs. 2 and 3 at which the shear modulus was measured. All the shear modulus measurements were made at a relative humidity of 44%.

Having regard to the very large MS strains involved, the small variation of the measured shear modulus justifies the conclusion that little permanent change of the structural features that define the shear modulus has been generated even by these large strains. The structural feature that most sensitively affects the elastic constants is the micro-fibril angle. The significant modulus in this work is G_{LR}. Astley et al. [8] have calculated that for a micro-fibril angle around 30° a 5° increase of MFA causes a 7% increase of G_{LR}. The sample standard deviation for the data in Table 2 is about 3% of the average modulus 0.633 GPa. These data suggest that the range of micro-fibril angle for the specimen in the four conditions listed in Table 2 is below 5°. It is possible using laminate theory to calculate the relationship between the shear modulus and the orientation of the applied stress axes for a homogeneously stressed body. The inhomogeneous elastic strain in the twisted strip of rectangular section makes such a calculation complex.

Creep at constant humidity

Creep occurs under load at constant humidity and this will contribute to the total strain measured during an MS test. Measurements were made to establish the order of this constant humidity component and also to find out if the strain was recoverable.

Figure 4 shows the twist in the same specimen used for the tests in Figs. 1–4, which was equilibrated at 38% relative humidity and subjected to the following loading sequence. The specimen was loaded in the anti-clockwise sense to a maximum stress of 1.12 MPa and left to creep at constant stress and humidity for 216 h. It was then unloaded and left to recover at zero stress for 100 h. It was then loaded in the clockwise sense to the same stress level, allowed to creep for 210 h, was unloaded and recovered for 72 h at zero stress. The creep strain over the first 216 h was 1/4 of the elastic strain and about 7% of the MS strain in Fig. 1 and less than 1% of the maximum MS strain in Fig. 3. The striking feature of Fig. 4 is that the creep strain almost completely recovers after unloading. At the end of the two loading cycles the original specimen dimensions are completely recovered.

A similar test was carried out at a relative humidity of 84%. The data are plotted in Fig. 5. The constant humidity

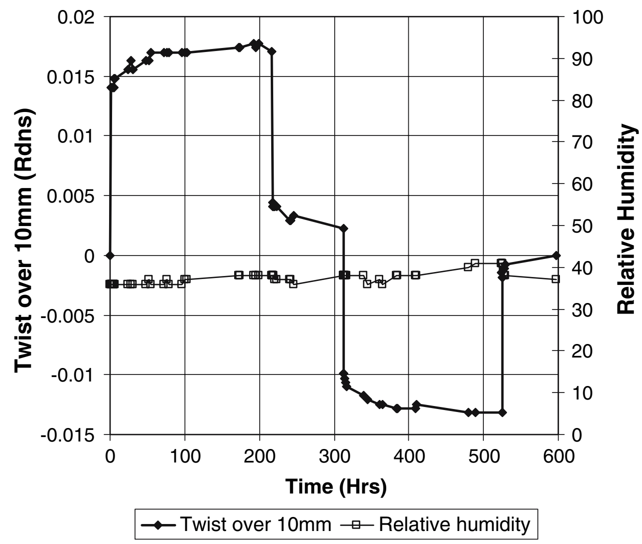

Fig. 4 Creep test at a constant humidity of 38% on the same specimen that features in Fig. 1. An anti-clockwise torque of 1.47 Nmm is followed by unloading and then a clockwise torque of 1.47 Nmm was applied

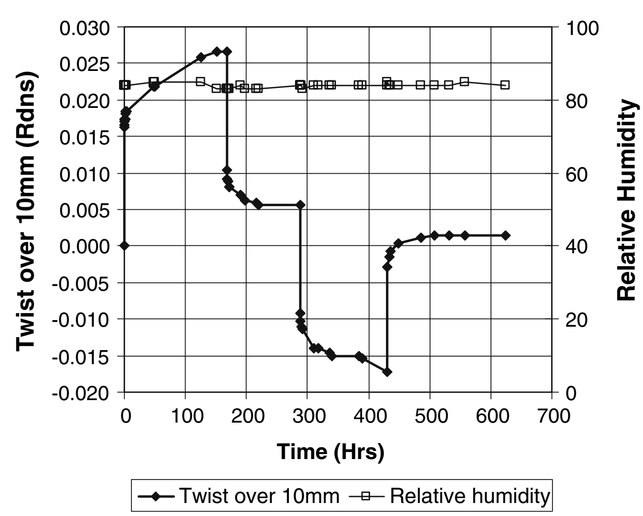

Fig. 5 Creep test under the same conditions as in Fig. 5, but with a constant relative humidity of 84%

creep over the first 168 h is 60% of the elastic strain and 20% of the MS strain in Fig. 1 and 2.6% of the maximum MS strain in Fig. 3. At the end of the two loading cycles the original specimen dimensions are retrieved.

Discussion

These measurements reveal that within the cell walls there exists a deformation mechanism that generates large shear strains that are recoverable.

There is a kinship between these measured MS strains and the strains observed by Keckes et al. [6] in wood cell walls stressed beyond the elastic limit. They carried out tensile tests on wet compression wood specimens of *P. abies* with a micro-fibril angle of about 45°. Tensile elongations with strains up to 0.20 were generated. They observed, by periodic tensile unloading, that the stiffness of the specimen over this range of strain did not change. They concluded from this that the plastic strain did not produce any significant damage to the matrix. Continuous measurements of micro-fibril angle were made during straining. The observed reduction of micro-fibril angle was consistent with the cellulose micro-fibrils being substantially unchanged in length and their rotation could be used to estimate the magnitude of the plastic strain. In principle this strain could arise either from relative sliding between contiguous walls over the middle lamella or by shear in the hemicellulose/lignin matrix. A careful tensile test on a single cell wall reproduced all the behaviour of the intact tissue proving that the permanent strain was generated in the cell wall matrix. The proposed mechanism that causes this strain is the following. The short hemicellulose polymer chains lie parallel to each other and to the cellulose/matrix interfaces. They are laterally bonded to their neighbour or to the cellulose chains by hydrogen bonds. A shear stress directed along the chains will break the hydrogen bonds and produce slip along the chain length. At the end of such a slip displacement the bonds will reform in the new location and retrieve an identical structure to that existing initially. They call this the “Velcro Effect”.

The MS strains measured in the present investigation are of the same order as those observed during tensile plastic straining. The maximum tensile strain reported by Keckes et al. [6] was about 0.2. The maximum shear strain associated with this tensile strain is twice the associated change of micro-fibril angle. This was about 12° so the shear strain was $2*\tan(12°) = 0.42$. The maximum MS shear strain measured in the present work was 0.07, which is large but significantly smaller than the tensile plastic strains. However it can be deduced from the measurements of Hearmon and Paton [2] that if the MS test of Fig. 3 had been extended to more humidity cycles a significantly larger MS strain would have been developed. Keckes et al. conclude that the large plastic strain produces no permanent structural damage; this implies that correspondingly even larger MS strains than the 0.07 measured herein would generate no permanent structural change.

It is asserted that the MS strain mechanism and the plastic strain mechanism are identical. The MS strains arise from the shear slip between laterally hydrogen bonded polymer chains. The slip involves stress directed relocation of hydrogen bonds as they form in arrangements different from those that would be adopted in the unstressed state. Further slip arises when the humidity decreases in the stressed specimen, but this is smaller than that generated by a humidity increase. When hydrogen bonds are removed from the cell wall by a reduction in the ambient humidity it must be presumed that the remaining bonds are left in an unstable state. They will then redistribute themselves into the new equilibrium state and the strain associated with the resulting bond shifts will generate the mechano-sorptive strain. It is evident that, by a judicious choice of combinations of humidity cycling, recovery at zero load and with reverse loading, large MS strains can be recovered and the original specimen dimensions retrieved. The large MS strains produce no permanent change of cell wall structure. The partial recovery of MS strain during humidity cycling at zero torque must be driven by some internal stress generated by the previous strain history. Maybe the hydrogen bonds are driven together by stress, in the manner of dislocations piling up on metallic slip planes, and spread out again to produce a reversed strain when the stress is removed. This reverse strain appears to eliminate the reverse stress before the original strain is completely recovered. The creep strains developed at constant stress and humidity are presumably produced be hydrogen bond breaking also. These strains are much smaller than the MS strains, they do not need humidity cycling to develop and they are completely recovered after unloading. Presumably the forward stressing develops internal stresses that drive the reverse recovery when the applied stress is removed. In this regard the wood appears to have a retentive memory. The constant humidity creep strains are in general shown to be a small part of the total measured strain.

It is a remarkable feature of the mechano-sorptive effect that such large and recoverable strains can be generated. The relative displacement of adjacent parallel polymer chains necessary to produce the measured shear strain of 0.06 can be very roughly estimated in the following way. Assume that the separation between hemicellulose chains is similar to that for cellulose, which is about 0.7 nm. If slip occurs, for example, on planes separated by 10 inter-chain distances then to produce a macroscopic shear strain of 0.06 the slip distance over each slip plane will be

$10 \times 0.7 \times 0.06 = 0.42\,\mathrm{mm}.$

This is not unrealistic.

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