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A review

Transient moisture effects in materials

J. Z. WANG*, D. A. DILLARD*, F. A. KAMKE‡
*Departments of *Engineering Science and Mechanics and ‡Forest Products,*
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

The paper reviews transient moisture effects in various materials with emphasis on their viscoelastic properties and durability. The first part of the review is dedicated to the phenomenological aspects of the effects in materials such as whole wood, plywood, particleboard, fibreboard, paper, natural and synthetic fibres and composite materials. Creep, creep recovery, dynamic response and failure as influenced by various transient moisture conditions are discussed in relation to the materials system, the extent and rate of moisture change, loading modes, temperature levels, specimen sizes, type of solvent and preventive measures. The second part is devoted to the discussion of mechanistic models. Explanations of the phenomenon from a molecular and materials standpoint are assessed, compared and discussed in depth so that one can gain deeper insight into the phenomenon as discussed in the first part. The main mechanisms discussed include: (i) hydrogen bonding, (ii) slip planes and (iii) crystallite slippage and rotation.

1. Introduction

Numerous studies have shown that transient moisture conditions have additional effects on the mechanical properties of hygroscopic materials over any constant moisture condition. The interaction of moisture sorption processes and mechanical properties is referred to as the mechano-sorptive phenomenon. This phenomenon has been a research topic for more than 30 years since Armstrong and Kingston [1] and Mackay and Downes [2] first discovered this phenomenon in wood materials and wool fibres. As a result of these studies, a large body of literature has accumulated in this area. A detailed review on these published papers reveals that the materials studied included wood, wood-based products, natural fibres, synthetic fibres and composite materials. The studied properties included creep, delayed failure, dynamic mechanical moduli and dimensional stability.

Relative humidity (RH) and temperature variations may result in moisture changes in materials. A variety of factors influence the level of humidity, for example the time of the day; the season of the year; precipitation; location changes for long distance moving structures; and elevation changes for flying vehicles. There are many structures and materials which could experience humidity changes, such as: airplane wings and fuselage; bridge structures; exposed beams in restaurant kitchens, boiler rooms, and cooling towers; roofing decks; fruit packs; paper during unwinding and converting operations or paper-based packaging; and books in long-term storage in places without relative humidity control equipment. The effects of transient moisture conditions in materials are frequently dramatic, complex, and difficult to interpret. Yet, in a very practical sense, these effects are so influential that they cannot be ignored. Transient moisture effects could affect the long-term performance of materials in many ways and the effects could cause concern to a variety of industries. For example, in wood and wood-based panels, transient moisture conditions have been found to increase creep and reduce creep rupture life substantially, thus degrading their stability and durability. In the transportation industry, apple packs have been found to distort severely after being unloaded from the refrigerated holds on to the wharf and stored under relatively light load. In the textile industry, transient moisture conditions may result in excessive dimensional instability or wrinkles in textile products. In the paper industry, surface wrinkles and baggy edges were found in rolls of paper formed during unwinding and converting operations or due to the difference in the producer's packing environment and the customer's unpacking environment. In homes, the warping and delaminating of decorative paper from walls is a more domestic example.

The purpose of this review is to bring together the existing knowledge on this common subject and highlight the fundamentals of the phenomenon. The review is grouped into two parts. Section 2 below is focused on the phenomenological aspect of the behaviour. The experimental results from many researchers have been related and discussed so that a coherent picture of the phenomenon may be appreciated. Section 3 is focused on the mechanistic aspect. Fundamentals of the phenomenon and proposed mechanisms are discussed so that one can gain a deeper insight into the phenomenon.

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2. Phenomenological aspects

2.1. Behaviour of solid wood

One of the first reports indicating the interaction between moisture sorption and creep behaviour of wood was published in 1960 by two Australian researchers, Armstrong and Kingston [1]. Their results showed that even though the relative creep (creep expressed as percentage of the initial elastic deformation) of wood materials was not affected by constant moisture content, it was increased to a large extent by moisture sorption processes. For example, as shown in Fig. 1, the relative creep of wood allowed to dry while under load was about three times that occurring in wood maintained at a constant moisture condition. Later, Grossman [3] termed this the mechano-sorptive phenomenon.

Studies have shown that both softwoods and hardwoods exhibit mechano-sorptive phenomenon. A relative comprehensive but non-exhaustive list of studied species may include: among softwood species, klinki pine (*Araucaria klinkii* Lauterb) [4, 5], hoop pine (*Araucaria cunninghamii* Ait) [6, 7], radiata pine (*Pinus radiata* D. Don) [6], bunya pine (*Araucaria bidwillii*) [8], ponderosa pine (*Pinus ponderosa*) and Scots pine (*Pinus sylvestris*) [9–11], yellow poplar (*Liriodendron tulipifera* L.) [12], and Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) [13–15]; among hardwood species, beech (*Fagus sylvatica*) [11, 16–20], alpine ash (*Eucalyptus gigantea* Hook. f.), mountain ash (*Eucalyptus regnans* F. Muell) and blackbutt (*Eucalyptus pilularis* Sm.) [6], buna (*Fagus crenata* Blume) [21], redwood (*Sequoia sempervirens*) [22], and messmate stringybark (*Eucalyptus obliqua*) [23, 24]. Among the properties studied, most tests were performed to examine the creep behaviour of the materials under transient moisture conditions. Experimental results showed that all of these species exhibited mechano-sorptive phenomenon. While detailed comparison may reveal quantitative differences which may be associated with the structural differences among species, there are no qualitative differences between these species. Therefore, the primary effect may be at a microscopic level which is common to all wood species.

The phenomenon is exhibited under both absorption and desorption* conditions. Whether the material is allowed to absorb or desorb moisture, the creep levels are higher than those at any constant moisture content [6, 8]. However, as indicated in Fig. 1, a desorption process has a larger effect on relative creep than an absorption process [6, 8, 12].

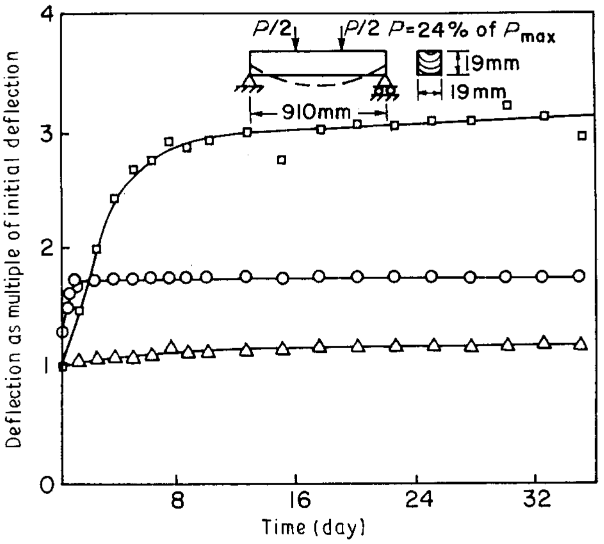

Figure 1 Relative creep for alpine ash beams under various moisture conditions (after Armstrong and Kingston [6]): (□) desorption, (○) absorption, (△) constant moisture conditions. Creep measured at midpoint of the beam; $T = 25\,^{\circ}C$.

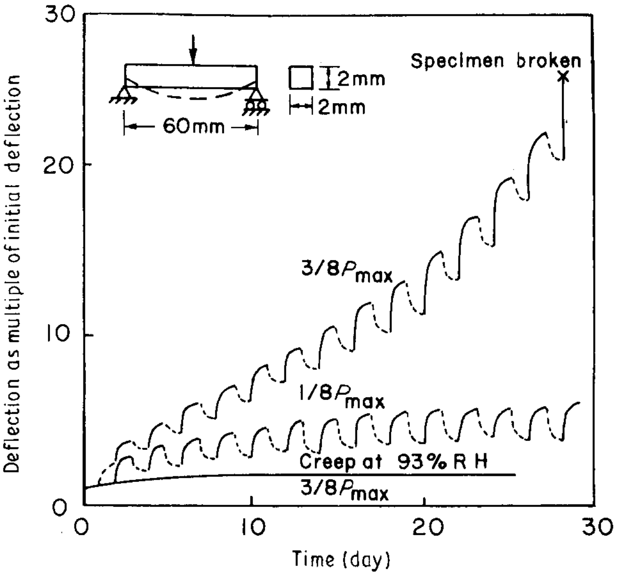

Figure 2 The effects of cyclic moisture conditions on the creep levels of wood beams (after Hearmon and Patton [16]): (- - -) wetting cycle (93% RH), (—) drying cycle. Creep measured at midpoint of the beam.

When moisture content is allowed to change between absorption and desorption in a cyclic manner, the creep level accumulates over the moisture cycles. Fig. 2 is a typical example of the cyclic moisture effect on creep [16]. Detailed observations of the creep during a cyclic moisture process reveal three aspects of the effect [5, 6, 16, 17]. First, during any desorption steps, the creep level increases. Secondly, during an absorption step, at moisture levels reached for the first time since the load was applied (the first wetting cycle in Fig. 2), the creep level increases. And thirdly, during a moisture absorption step at levels reached for the second and the subsequent steps since the load was applied, the creep level decreases. However, the recovery in the absorption step is less than the increase in the desorption step and, therefore, the resultant creep level continues to increase over moisture cycles. Hoffmeyer and Davidson [25] have examined the amplitude of oscillation of the mechano-sorptive creep under cyclic moisture conditions from the results of several researchers [16, 17, 26]. As indicated in Fig. 3

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* The term *absorption* in this paper refers to the event that moisture or solvents diffuse into a solid, while the term *desorption* refers to the event that moisture or solvents diffuse out of a solid.

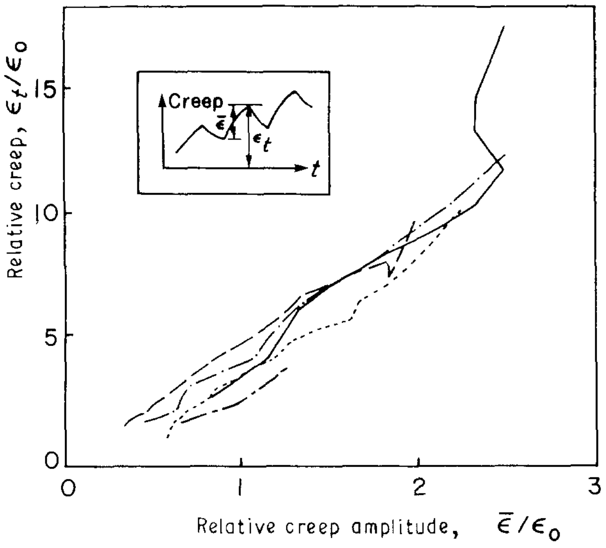

Figure 3 Relative creep level against relative creep oscillation amplitude (after Hoffmeyer and Davidson [25]): ε_t = creep strain at time t, ε_0 = creep strain at $t = 0$, $\bar{\varepsilon}$ = amplitude of creep oscillation.

[25], when the amplitude was plotted against total creep, a fairly linear relationship was found.

Mechano-sorption could lead to delayed failures in shorter times and at lower load levels than for specimens held at constant moisture conditions. The results of Hearmon and Paton [16], as indicated in Fig. 2, showed that beech beams (2 mm × 2 mm × 60 mm) failed at 3/8 of the static strength after only 14 moisture cycles, which corresponded to about a 28-day time duration. However, when maintained at high constant moisture content and under the same load level, a specimen of the same material crept only 1/12 of the failure strain and showed no evidence of future failure. Armstrong and Kingston [6] also noticed minute compression failures in their mechano-sorption specimens (12.5 mm × 38 mm × 102 mm). However, they reported that no failure was observed on specimens 10 mm × 10 mm × 102 mm under a tension loading mode in mechano-sorptive experiments. Humphries and Schniewind [13] have studied the behaviour of Douglas-fir columns (6.4 mm × 9.5 mm × 280 mm) under cyclic relative humidities. Creep levels of specimens under cyclic moisture conditions (RH between 35 and 87%) were about two orders of magnitude higher than those of the specimens kept at highest constant moisture condition (RH ≅ 87%). Of the 34 specimens tested under cyclic moisture conditions, five failed in less than 3 days, 10 failed after 3 but less than 14 days, and 19 specimens had not failed after 14 days, when the tests were discontinued. Schniewind [15] and Schniewind and Lyon [14] have studied the creep-rupture life of Douglas-fir beams (10 mm × 10 mm × 200 mm and 50.8 mm × 50.8 mm × 1016 mm, respectively) under cyclic moisture conditions. Their results showed that the mean creep-rupture life under cyclic moisture conditions could be less than that under constant moisture conditions by an order of magnitude. Among the eighteen specimens tested by Schniewind and Lyon [14], about half of the specimens failed when the relative humidity was high and the other half of the specimens failed when the relative humidity was low. Therefore, it seems that the surface conditions at the moment of failure were not an important factor.

Under certain conditions, there may be a process of exhaustion of available deformation in repeated moisture cycles. Hunt and Shelton [10, 27] have investigated the possibility of obtaining a stable-state creep during a cyclic moisture process. They found that a stable state could be produced by loading Scots pine beams at a higher load level and at a high humidity level, making one absorption–desorption cycle, and then reducing the load followed by another absorption–desorption cycle. Thereafter, any subsequent moisture cycles caused the creep to follow a loop on a moisture content versus creep strain curve. In the tests when the creep strains were measured, the load levels were kept below 10% of the rupture load. The results are shown in Fig. 4 [27]. Moreover, if the creep loops under tension and compression in Fig. 4 are corrected by the loop under zero load, the resulting loops will appear more closed and the shapes of the loops for tension, compression, and bending will resemble each other as shown in Fig. 5 [27]. It needs to be noted that relatively low stress levels may be necessary in obtaining a stable-state creep under cyclic moisture conditions.

The mechano-sorptive creep rate is dependent on the rate of change in moisture content. Armstrong and Kingston [6] measured the creep of alpine ash and blackbutt under a bending load at different desorption rates. Fig. 6 shows the results obtained on alpine ash specimens. The results showed that the rate of change in creep was related to the rate of change in moisture content. Especially, as shown in curve B, the creep rate closely followed the rate of moisture changes. Christensen [5] tested small klinki pine specimens

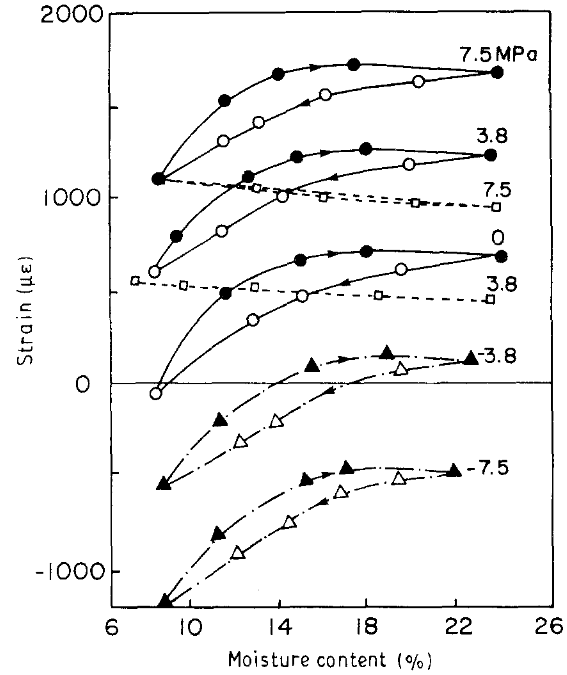

Figure 4 Creep strain against moisture loops at various stresses (MPa) (after Hunt and Shelton [27]): (○) tension, (□) bending, (△) compression; (●, ▲) creep under absorption, (○, △) creep under desorption.

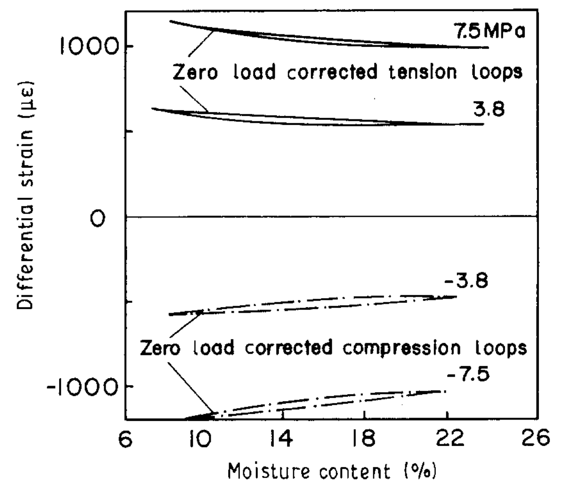

Figure 5 Zero-load corrected creep strain against moisture loops (after Hunt and Shelton [27]). Curves were obtained by subtracting the deformation due to moisture-induced swelling (at $\sigma = 0$) in Fig. 4 from the creep deformations in Fig. 4 at $\sigma = \pm 7.5$ and ± 3.8 MPa.

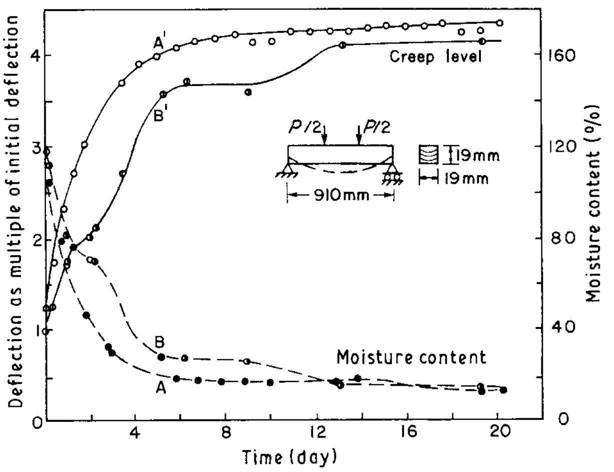

Figure 6 Effect of moisture rates on the creep of wood beams (after Armstrong and Kingston [6]): alpine ash, 8 per group, $T = 40\,^{\circ}\mathrm{C}$, $\sigma = 24\%\ \sigma_{\max}$. A′ and B′ indicate, respectively, the moisture conditions at which the creep curves A and B were obtained. Creep measured at the midpoint of the beam.

(1.5 mm × 1.5 mm × 80 mm) under bending load at different absorption conditions. His results confirmed this rate dependency. The rate dependency suggests that the phenomenon is not directly time-dependent, but moisture rate-dependent.

Even though the creep rate is dependent on the rate of change in moisture content, the creep magnitude is unlikely to be affected by the rate of moisture change but is a function of the total change of moisture content [5, 6, 14, 28]. Schniewind [28] found that the mechano-sorptive creep is related linearly to the extent of moisture change in beech. From the results on alpine ash, Armstrong and Kingston [6] reached the same conclusion. Schniewind and Lyon [14] have shown that the creep rupture life is linearly dependent on the square root of the extent of moisture change.

In the literature, most mechano-sorptive studies were performed on specimens with cross-sectional dimensions of the order of a few millimetres [4, 5, 9–12, 16, 18–21, 27]. Therefore, before the results can be incorporated into design codes, the influence of size effects has to be addressed. The size of a specimen strongly influences its moisture change rate [29], and consequently, within a given period of time, affects the magnitude of moisture change [14]. Armstrong and Christensen [4] compared the creep behaviour of two beams, 1 mm × 1 mm × 60 mm and 20 mm × 20 mm × 900 mm, under cyclic moisture conditions. They concluded that the behaviour of the two specimen sizes was qualitatively similar. However, no numerical comparison was given. Schniewind and Lyon [14] have studied the size effect on the creep rupture life of Douglas-fir specimens. On an average basis, the creep rupture life increased by more than one order of magnitude when the cross-sectional area of specimens increased from 10 mm × 20 mm to 50.8 mm × 50.8 mm. However, the creep rupture life even for the larger specimens was still much less than that recorded at the same load level under constant moisture conditions [14]. Some researchers believe that for large structural members, mechano-sorptive effects may be insignificant. For example, based on the comparison of the trend lines obtained from the results of Schniewind [15] and Schniewind and Lyon [14] with the trend line for tests under constant moisture conditions from Wood [30], Barrett [31] concluded that environmental cycling would have "probably little or no effect on the behaviour of large timbers and glued-laminated members". Before approaching such a conclusion, however, caution needs to be exercised. As reported by Schniewind and Lyon [14] for their large specimens (50.8 mm × 50.8 mm × 1016 mm), the moisture changes actually took place at the outer surface layers, while the moisture content at the inner part occupying 2/3 of the specimen thickness remained relatively constant. Because the outer surface layers of bending specimens carry most of the load, the failure may occur at the surface layers due to moisture changes. As the failure develops, moisture changes could occur at a deeper location around the failed spot, thus resulting in a progressive failure mode. The results of Schniewind and Lyon [14] showed that their specimens indeed failed in this fashion.

The effect of the initial moisture content on mechano-sorptive creep has also been studied [6, 28]. Schniewind [28] reported that, for beech material, the effect was independent of the position of the moisture content at which the test had begun. However, Armstrong and Kingston [6] noted that, for hoop pine specimens, the mechano-sorptive effect increased with increasing initial moisture content for equal moisture increments.

Evidence suggests that mechano-sorptive behaviour may be not present over the entire range of moisture content, there may be a moisture content threshold above which the phenomenon is less pronounced. For example, Armstrong and Kingston [6] reported that for hoop pine specimens with a saturation level of 110% moisture content, moisture change above about 35 to 55% did not affect creep behaviour. It is interesting to note that this moisture threshold is about the same as the fibre saturation point. Above the fibre saturation point, absorbed moisture is mainly present within the wood cells as free water. Below the fibre saturation point, water molecules are primarily contained within the cell walls where they could contribute to the hydrogen bonds between molecular chains or otherwise influence the material.

Even though quantitative differences may be involved, the mechano-sorptive phenomenon was found to be present under all loading modes. For example, Armstrong and Kingston [6] have identified the phenomenon under compression, bending, and tension, Hearmon and Paton [16] have identified the phenomenon under shear, and Humphries and Schniewind [13] under buckling loading. In comparing mechano-sorptive behaviour under bending, compression and tension, Armstrong and Kingston [6] concluded that the phenomenon was most pronounced under compression, and then in descending order, under bending and tension. Ellwood [32] also reported that beech specimens, when drying, showed larger creep in compression than in tension. However, Hunt and Shelton [27] have shown that, for pine materials, bending, compression and tension under low stresses (3.8% and 7.5% of the static strength) give similar results when corrected by the zero-load deformations. Shrinkage, as present in a desorption process, will tend to cause increases in compressive deformation and decreases in tensile deformation. Similarly, swelling, as present in an absorption process, will cause an increase in tensile strain and a decrease in compressive strain. The effects of shrinkage and swelling may, at least partly, contribute to the differences between the creep levels under different loading modes.

Except for a few exclusions, most mechano-sorptive tests were conducted under constant temperature. The effect of temperature during mechano-sorptive processes has been assessed by several researchers [16, 22, 28, 33, 34]. From their results it seems that temperature below about 60 °C does not have appreciable influence on the mechano-sorptive creep level. For example, Hearmon and Paton [16] studied the mechano-sorptive effects on beech at 20, 25, 30 and 40 °C. They reported that temperature did not have much effect on the relative mechano-sorptive creep. Schniewind [28] also reached the same conclusion on beech material. However, influences of temperature have been observed above 60 °C. For most wood materials, this temperature is within the range of glass transition associated with the softening of hemicellulose [35]. Erickson and co-workers [22, 33] measured mechano-sorptive creep under desorption on redwood at 40 and 65 °C. They found that relative creep was several times greater at 65 °C than at 45 °C. Arima [34] has studied the effect of temperature on the recovery behaviour of specimens after mechano-sorptive processes. Initially green wood beams (mountain ash and radiata pine, 15 mm x 15 mm x 600 mm) were clamped in place along tangential and radial directions to produce a fixed deformation, and then were subjected to drying conditions at different temperatures (25, 42, 52, 65 and 80 °C). After about 12 days of clamping, the specimens were released from clamps and their recovery levels were recorded. According to the recovery levels, the results fell into two groups: one was at 25 and 40 °C, and the other was at 65 and 80 °C. The results at 50 °C along the radial direction fell into the former group, while along the tangential direction in the latter group. The latter group recovered to a larger extent. Based on these observations, Arima [34] concluded "it may be considered that some components of wood have begun to change to their softened state between 50 °C and 65 °C".

Even though the scope of this review has been focused on the behaviour of materials under transient moisture conditions, a brief discussion about the effect of transient temperature is relevant at this point. Kitahara and Yukawa [35] have compared creep levels of hinoki bending specimens under transient thermal conditions and constant temperature conditions. As indicated in Fig. 7, test results showed that when the specimens were heated up from either 20, 30 or 40 °C to 50 °C while under a constant load, the creep levels of the specimens were much higher than at constant 50 °C. Moreover, the creep level had an increasing trend when the difference between the two temperature levels increased. However, when the specimens were cooled down from 50 to 40 °C, the creep level of the specimen was lower than those at both 50 and 40 °C. Arima [36] also conducted similar tests on hinoki bending specimens. His results showed that when the temperature was increased from one level (20 °C) to another level (either 40, 50, 60 or 75 °C), the creep levels were higher than the creep levels at either of the constant temperatures. The phenomenon is especially conspicuous when the higher temperature was above 60 °C. Because the equilibrium moisture content or the fibre saturation point decreases as the temperature increases at a given relative humidity [37], the question as to how much the moisture content changes would affect the creep level remains. Schniewind and Lyon [14] have conducted creep rupture tests on Douglas fir specimens under cyclic temperature and moisture conditions. The temperature and relative humidity were cycled sinusoidally

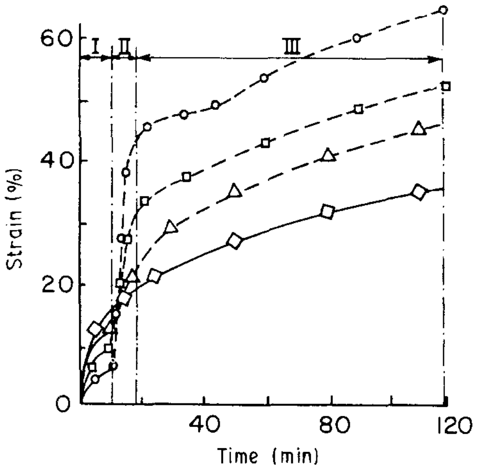

Figure 7 Transient thermal effects in the creep behaviour of wood materials (after Kitahara and Yukawa [35]). Test conditions: (I) constant temperature of (○) 20, (□) 30 and (△) 40 °C; (II) increase of temperature from (○) 20, (□) 30 and (△) 40 °C to 50 °C; (III) constant temperature at 50 °C; (◇) constant temperature of 50 °C throughout.

and 180° out of phase. Their results indicated that temperature cycling has little or no effect on time-to-failure, since the average of time-to-failure is about what would be expected on the basis of the concurrent moisture changes alone.

Gardner *et al.* [18] have studied the effect of solvents other than water on the mechano-sorptive behaviour in beech material. Some solvents such as methanol, ethanol and pyridine were found to cause mechano-sorptive phenomena, while others, such as dioxan, n-propanol and benzene did not produce mechano-sorptive phenomena. The results in Fig. 8 indicate the mechano-sorptive behaviour of a beech specimen when pyridine was used. The difference between these solvents in the ability to produce mechano-sorptive phenomena was found to relate to their polarity, their swelling kinetics, and their own molecular sizes. For example, n-propanol has only about half the swelling power of methanol and ethanol, and also its larger molecular size may hinder n-propanol from entering the material quickly enough to cause the phenomenon. In the case of dioxan, the swelling rate of a beech–dioxan system was found to be very slow, and it has been conjectured that the time window in the experiment might not be long enough to cover the time sufficient for the phenomenon to be observed [18]. Benzene is a non-polar solvent and consequently it does not have any swelling power. Swelling is related to hydrogen bonding. When polar solvents enter a material with hydrogen bonds, the solvent tends to break the original hydrogen bonds and insert between the broken hydrogen bonds to form new bonds, thereby moving the molecular chains further apart. This microscopic process is manifested macroscopically as swelling behaviour. Swelling may be a good indicator of whether a solvent will cause mechano-sorptive phenomena.

When a specimen is unloaded after mechano-sorptive cycling, some recovery may be observed, but it appears that a large permanent deformation will remain. However, the permanent deformation can be reduced by moisture cycling after unloading [4–6, 34, 38]. Experimental results on klinki pine [4, 5], *Eucalyptus gigantea* [4], hoop pine [6], and radiata pine and eucalypt [34, 38] have shown that the absorption steps are much more effective than desorption steps in reducing the permanent deformation. Actually, most recovery occurred during the first absorption step after unloading [4–6], and nearly 100% recovery was obtained after specimens were immersed in water [34, 38]. An example of the influence of the moisture cycling is shown in Fig. 9 [38]. Arima [34, 38] has studied the influence of various parameters on the moisture-cycling-induced recovery. He found that moisture-cycling-induced recovery was not influenced by a delay of two weeks before subjecting specimens to moisture absorption, nor by a temporary increase of moisture content before unloading. However, the temperature during the loading period influenced the recovery to a large extent. For example, when radiata pine was subjected to 80 °C and eucalypt was subjected to 50 °C during a mechano-sorptive process, they lost some of the recovery capacity [34, 38]. This is explained by the formation of a new stable configuration above a critical temperature, namely the glass transition, which reduces the recovery potential during subsequent moisture cycles after unloading [34, 38].

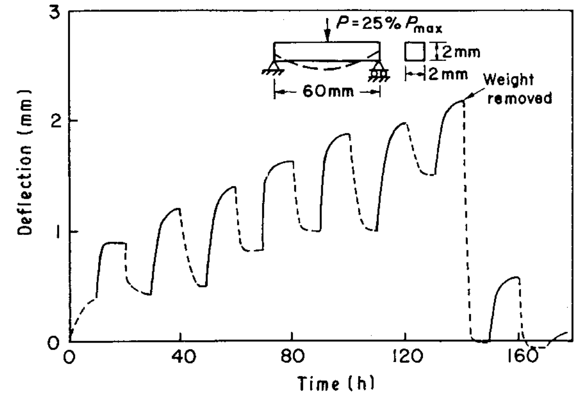

Figure 8 Mechano-sorptive creep of beech wood beams in pyridine environment at room temperature (after Gardner *et al.* [18]): (- - -) absorption cycle, (—) desorption cycle. Creep measured at the midpoint of the beam.

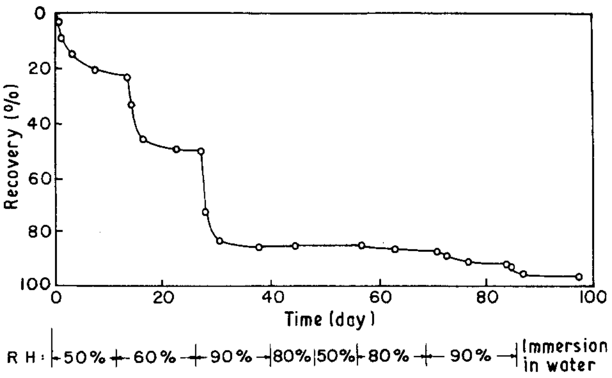

Figure 9 Recovery of mechano-sorptive creep under transient moisture conditions at 25 °C (after Arima and Grossman [38]).

Although the major stream of the research has been along the path of understanding the phenomenon, there have been efforts to find the methods for reducing the effects of the phenomenon. Besides the previously mentioned loading schemes as discovered by Hunt and Shelton [10, 27] in order to produce a stable-state deformation under cyclic moisture conditions, Erickson and Sauer [22] and Erickson *et al.* [33] have found that freezing before kiln-drying (prefreezing) could significantly reduce the amount of mechano-sorptive creep in redwood heartwood. The treatment was especially effective when the temperature was high and the moisture content change was rapid and large.

2.2. Behaviour of wood-based products

Driven by the considerations of economy, conservation of natural forest resources, and tailoring of wood properties to end-uses, wood-based panels such as plywood, particleboard and fibreboard have shown increasing growth in the market. Many grades of these panels are used as load-carrying materials, e.g. in the construction and transportation industries. The

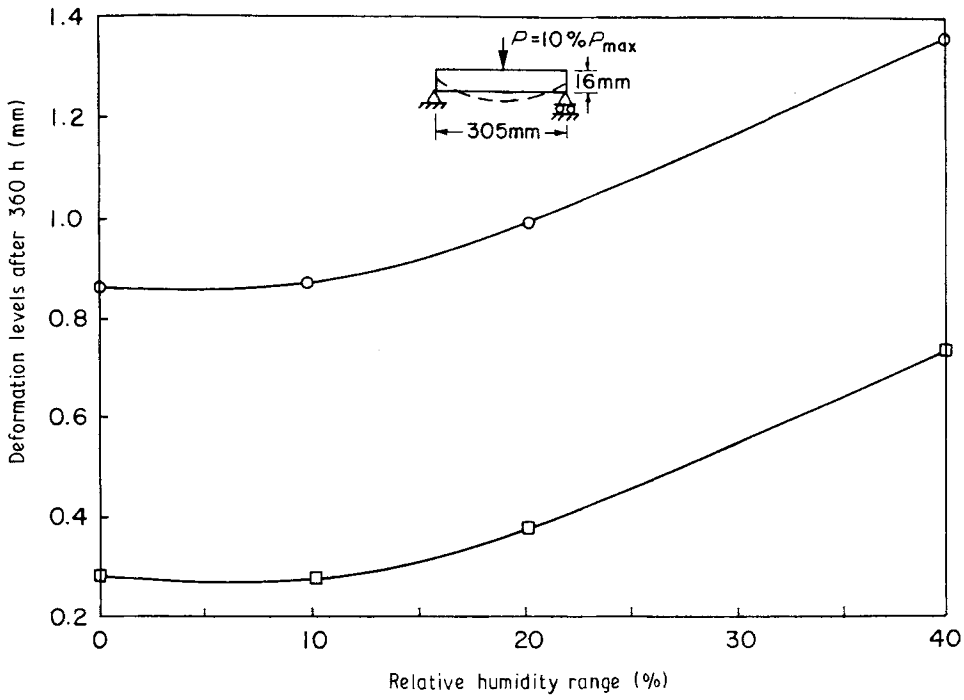

Figure 10 Effects of relative humidity range on the creep level of particleboard (after Haygreen *et al.* [41]): (○) total deformation, (□) creep deformation. Creep measured at the midpoint of the beam; stress = 1.89 MPa, $T = 27\,°\mathrm{C}$, av. RH = 60%.

environment of their application often involves substantial humidity fluctuations. Therefore, the influence of transient moisture conditions must be understood to ensure satisfactory design and performance.

After discovery of mechano-sorptive phenomenon in whole wood, a number of papers has emerged addressing the transient moisture effects in particleboards [39–45], fibreboards [40, 44–47] and plywood [41, 43–45]. Not surprisingly, these studies show that mechano-sorption effects are also present in wood-based panels, and are even more pronounced than in whole wood [39, 40, 44, 45]. Also in contrast with whole wood, relative creep was found to increase with increasing equilibrium moisture content [39, 40].

As in whole wood, the mechano-sorptive phenomenon is present under absorption, desorption and cyclic moisture conditions [39, 40, 42–47]. Contrary to the experience with whole wood [6], however, Sauer and Haygreen [46] in studying wet and dry process hardboards of aspen, and Bryan and Schniewind [39] in studying urea- and phenolic-bonded particleboards of Douglas fir, found that absorption conditions had greater effects than desorption conditions. On the other hand, in studying urea-bonded particleboards of radiata pine and standard and tempered hardboard of eucalypt, Armstrong and Grossman [40] demonstrated that desorption plays a larger role than absorption in increasing creep levels under cyclic moisture conditions. The discrepancy may be explained through the direct effect of constant-moisture effects on creep. If the constant-moisture effect is not negligible in creep, the deformations arising with changes in moisture content could be overtaken.

Haygreen *et al.* [41] studied the effect of the extent of moisture changes on mechano-sorptive creep levels of particleboards under cyclic moisture conditions Their data have been reprocessed and are shown in Fig. 10. As indicated in the graph, the creep deformations increased as the range of moisture content increased.

Mechano-sorptive phenomenon in wood-based panels were also studied under different loading modes. Hunt [42] tested mechano-sorptive effects under tension and compression. His results showed that after 21 days under cyclic moisture conditions the creep levels were about three times higher than those under constant moisture conditions. Martensson [48] and Martensson and Thelandersson [49] investigated the creep behaviour of hardboards under tensile, compressive and bending loads. They concluded that mechano-sorptive effects were most pronounced in bending, less in compression, and least in tension.

Generally speaking, the creep compliance of wood-based panels in an increasing order is in the following sequence: plywood, particleboards, and hardboards. Haygreen *et al.* [41] have studied the creep behaviour of particleboards and plywood under absorption conditions and found that creep levels of particleboard specimens were as much as two to three times those of plywood specimens. Armstrong and Grossman [40] have studied the creep behaviour of particleboards and hardboards under cyclic moisture conditions. They found that the creep deflection of hardboards (made of eucalypt species of medium and high density) are higher than those of particleboards (made of radiata pine). However, limited data suggest that when the ratios of mechano-sorptive creep level to constant moisture level are compared, the picture might be different. Reprocessed data from the experiment of Haygreen *et al.* [41] on plywood and particleboards suggests that the ratio may be even higher

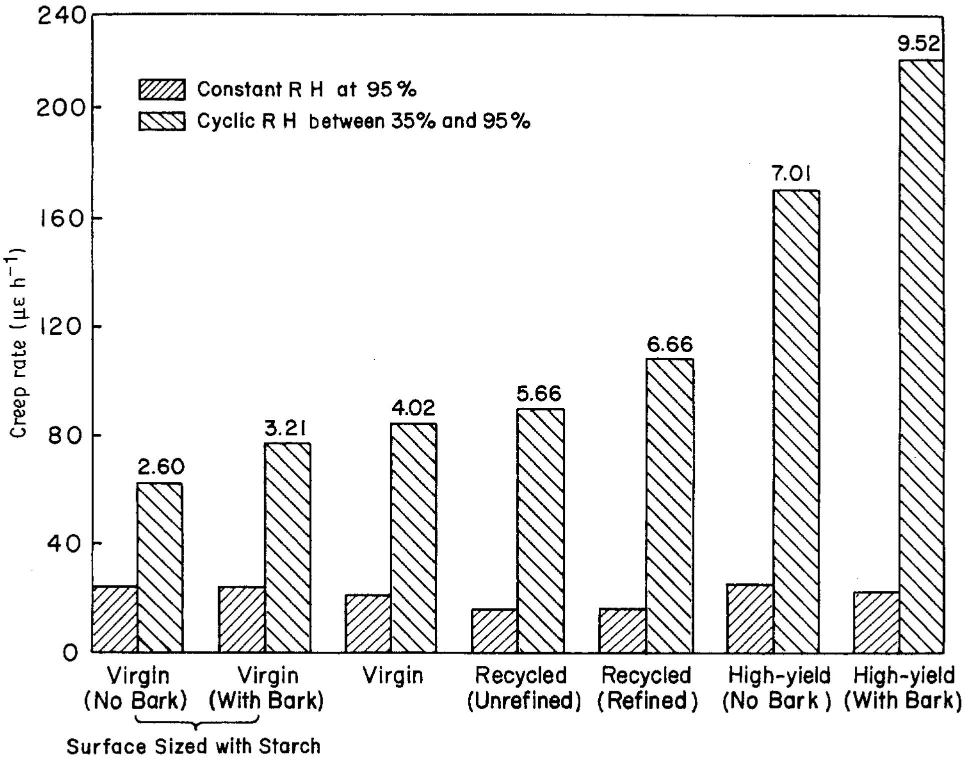

Figure 11 Effects of material constituents on the mechano-sorptive behaviour of A-flute corrugated fibreboard (after Byrd and Koning [47]). $T = 23\,^{\circ}\mathrm{C}$, $\sigma = 25\%\ \sigma_{\max}$; numbers on top of bars indicate the creep rate ratio.

for plywood than for particleboards. The data from Sauer and Haygreen [46] on wet- and dry-process hardboard show parallel results.

The processing methods in making the wood-based panels or the treatment on the panels could also influence the creep deflection levels. For example, Sauer and Haygreen [46] found that dry-process hardboard exhibited a higher creep level than wet-process hardboard. Armstrong and Grossman [40] found that the tempering treatment on hardboard could reduce the mechano-sorptive creep level. Byrd and Koning [47] found that surface-sizing treatment with starch on corrugated fibreboards could reduce the mechano-sorptive creep level. The influence of these factors may be through their influence on the moisture absorption capacity or rate.

The constituent materials of the boards may affect the extent of the mechano-sorptive creep. Byrd and Koning [47] have investigated the compressive mechano-sorptive creep behaviour of fibreboards with different constituents or proportion of constituents. Their results have been reprocessed and are shown in Fig. 11. From the results we may see that the bark content and a high yield of pulp could cause an increase in the mechano-sorptive creep rate. Several interesting points may be drawn from the graph:

(i) the yield of fibre content has a greater effect on the mechano-sorptive creep than the content of bark;

(ii) factors affecting mechano-sorptive creep may not affect the creep behaviour under constant moisture condition as much;

(iii) the characteristic in (ii) resulted in the fact that higher mechano-sorptive creep rate had a higher creep rate ratio (the ratio of creep rate under transient moisture condition to that under constant moisture condition); and

(iv) a higher creep rate under constant moisture condition does not necessarily mean a higher mechano-sorptive creep rate.

McNatt and Hunt [43] have studied the creep behaviour of flakeboards and plywood specimens under cyclic moisture conditions. Their results indicate that the mechano-sorptive creep level of oak flakeboard is higher than that of aspen flakeboard, and that of Douglas fir plywood is higher than that of southern pine plywood.

Results from some researchers suggest that the binders used in bonding the constituents do not significantly affect the mechano-sorptive behaviour [41, 50]. The results of Haygreen *et al.* [41] indicated that the mechano-sorptive creep of urea- and phenolic-bonded particleboards were very similar both qualitatively and quantitatively. The results of Gressel [50] also indicated that even though different binders could affect the equilibrium moisture content in particleboards, they do not cause different creep rates. However, Byrd [51] has shown that different adhesives could result in different levels of compressive mechano-sorptive creep in corrugated fibreboard.

Byrd [52] has studied the cyclic moisture effects on tensile and compressive creep of kraft paper handsheets. As indicated in Fig. 12, when papersheets were subjected to cyclic relative humidity from 35 to 90%, the creep level was 4.6 to 9 times higher than that when the papersheet was subjected to a constant 90% RH. Under compressive load, the creep obeyed a linear relationship in the time domain. As a result of this increased creep rate, the creep rupture time under cyclic moisture conditions was much less than that under constant moisture conditions [53].

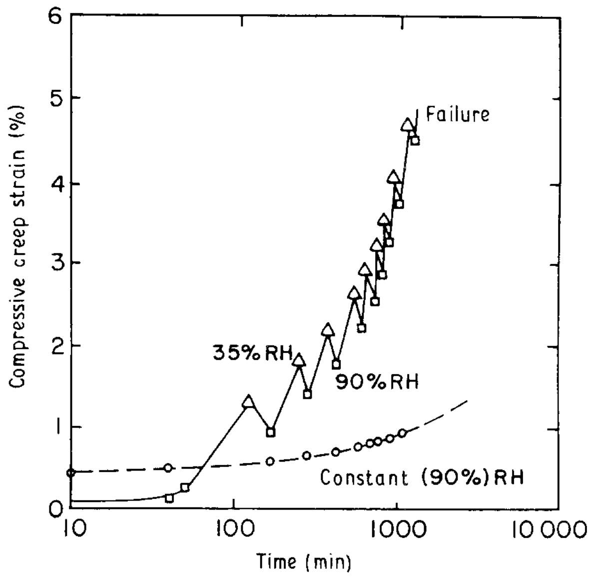

Figure 12 Mechano-sorptive phenomenon in C-flute corrugated paperboard under compression (after Byrd [53]). $T = 27\,^{\circ}\mathrm{C}$, $\sigma = 57\%\ \sigma_{\max}$.

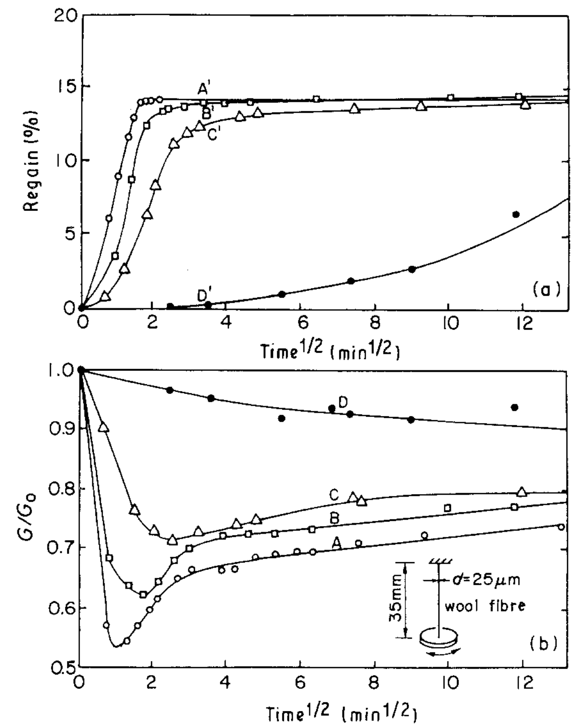

Figure 13 (a, b) Transient moisture effects in the dynamic modulus of wool fibre (after Mackay and Downes [2]). 0–61% RH; curves A′, B′, C′ and D′ indicate, respectively, the moisture conditions under which the rigidity curves A, B, C and D were obtained.

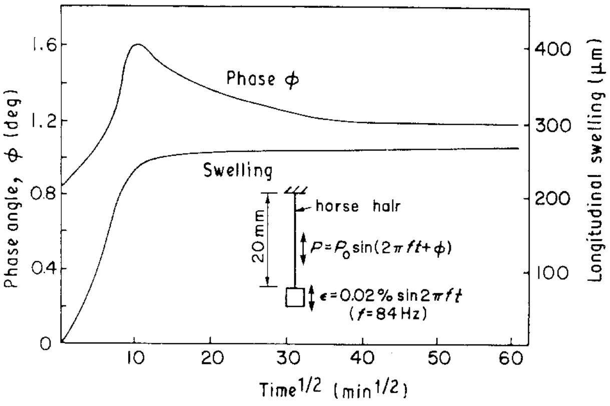

Figure 14 Swelling behaviour and phase angle of a horse hair as influenced by an absorption condition (after Danilatos and Feughelman [58]).

2.3. Behaviour of natural fibres

Natural fibres such as wool and cotton fibres are mainly used in the garment industry. The wrinkling behaviour of garments under transient conditions, such as washing and drying, is an important factor in influencing their appearance. Natural fibres are also used in ropes, where rigidity and strength under transient moisture conditions are important.

Mackay and Downes [2] measured the effect of sorption processes on the dynamic rigidity modulus of wool fibres. Their results showed that, when a large increase was made in the relative humidity surrounding a wool fibre, its dynamic torsional rigidity was found to pass through a minimum value considerably less than the final equilibrium value. The more abrupt the increase in relative humidity, the more pronounced was the effect. Furthermore, the recovery from the minimum to the equilibrium value of rigidity takes a much longer time than the time to reach moisture equilibrium. This phenomenon is shown in Fig. 13. Nordon [54] confirmed this finding by a more detailed study. He concluded that any changes in the relative humidity surrounding the fibre first led to a reduction and then led to a partial recovery of the rigidity. The effect was most pronounced at the higher humidities. Jentzen [55] performed creep tests under a drying environment on holocellulose pulp fibres made from longleaf pine. The diameter of the fibres was about 10 μm. A fibre was taken out from water immersion and then subjected to a tensile creep test. He found that while the surface of the fibre was still covered by water droplets, no appreciable deformation was apparent. However, at the instant when the water droplets disappeared and the fibre began to dry, a sudden increase in deformation was observed.

Test results indicated that cotton fabrics wrinkled more during moisture changes than at moisture equilibrium. If the fabrics, however, are treated with a process known as wet crosslinking, the sensitivity of wrinkling during transient moisture conditions could be reduced [56]. Shishoo [57] has measured the creep behaviour of dry wool fibres in a steam environment. Samples were subjected to the action of steam before loading. It was found that pre-steaming from 0 to 60 s markedly influenced the subsequent creep in steam, and maxima in creep were obtained at a pre-steaming time of ca. 30 s (fibre diameter 47 μm). Danilatos and Feughelman [58] have studied the dynamic damping behaviour of wool fibres and horse hair during moisture absorption processes. They found that, as indicated in Fig. 14, the damping reached a maximum at the point in time when the swelling of the fibre reached an equilibrium plateau. This phenomenon parallels others and confirms the general picture that during sorption the molecular structure of keratin fibres have a maximum mobility. Feughelman [59] has noted that, in relaxation tests on wool fibres, as indicated in

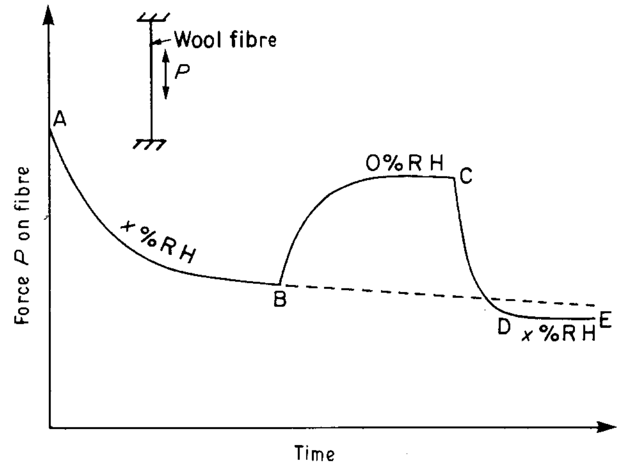

Figure 15 Transient moisture effects in the relaxation behaviour of a wool fibre (after Feughelman [59]): (A–B) constant moisture conditions at x% RH ($0 \leqslant x \leqslant 80$); (B–C) desorption conditions induced by change from x to 0% RH; (C–D) absorption conditions induced by change from 0 to x% RH; (D–E) constant moisture conditions at x% RH.

Fig. 15, the force had an additional decrease over constant x% RH ($x > 0$) after a moisture cycle from x to 0% RH and then back to x% RH. The additional decrease reached a maximum when x was about 40. When x was about 80, the phenomenon disappeared [59].

2.4. Behaviour of synthetic fibres

Along the line of studying the transient moisture effects in composite materials, Wang and co-workers [60–62] have studied the mechano-sorptive creep behaviour of aramid fibres (Kevlar 29, Kevlar 49 and Kevlar 149 fibres). The creep of single fibres was measured under constant temperature at 60 °C under both cyclic and constant moisture conditions. For comparison, and to reduce the effect of fibre variability, the same fibre was used under both constant and cyclic moisture conditions. An approximately straight line results when the creep strain for these fibres is plotted in semi-log coordinates as shown in Fig. 16. If the ratio of the slope under cyclic moisture conditions to that under constant moisture conditions is taken as an indicator of the degree of mechano-sorptive effect, the trend of the data suggests that the mechano-sorptive effect is most pronounced in Kevlar 29 fibres, and least pronounced in Kevlar 149 fibres.

2.5. Behaviour of Kevlar composite material

The experimental results from dynamic mechanical tests and bending creep tests indicate that under transient moisture conditions, Kevlar composite material will exhibit mechano-sorptive phenomenon [60–62]. As indicated in Fig. 17, when a Kevlar 49–Fiberite 7714 epoxy specimen saturated with moisture was undergoing a desorption process, its relative creep bending deformation (creep deformation normalized by the elastic deformation) was higher than that of a similar specimen kept at the saturation state throughout the test. In a dynamic mechanical test, a specimen saturated with moisture was allowed to undergo desorption processes by introducing dry air into the test chamber, and relatively constant moisture conditions without the introduction of the dry air. As indicated in Fig. 18 when the specimen was under desorption conditions, the storage modulus decreased and the value of tan δ increased significantly. These results clearly suggest that during desorption conditions, the stiffness of the material will reduce while the damping behaviour will increase. Although the actual creep levels may be considered small (in comparison with the static strain at break), a need is shown for a better understanding of why and to what degree moisture changes may influence the behaviour of composite structures.

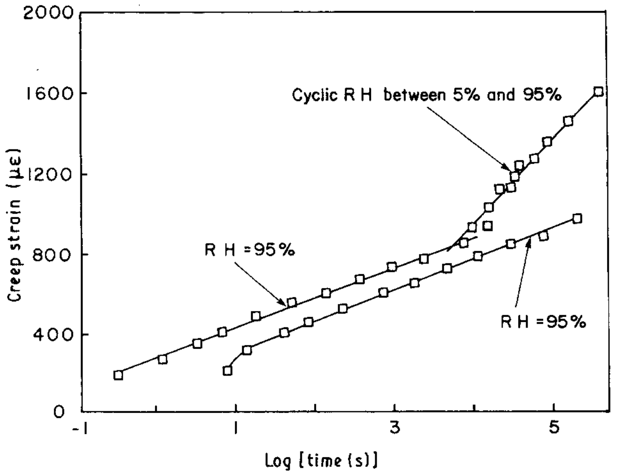

Figure 16 Typical example of the mechano-sorptive behaviour in a single Kevlar 49 aramid fibre (after Wang *et al.* [60]): (□) experimental data, (—) fitted line. $T = 60$ °C.

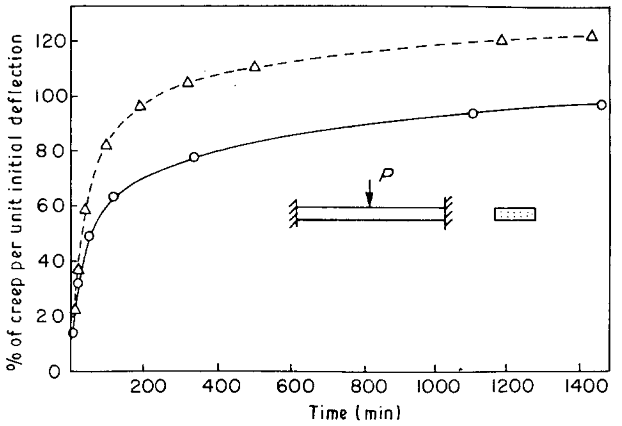

Figure 17 Desorption effects in the bending creep of a composite coupon with Kevlar 49 fibre reinforcement (after Wang *et al.* [60]): (△) desorption condition, (○) constant moisture condition. Creep measured at the midpoint of the beam; $T = 60$ °C.

3. Mechanistic aspects

In order to model and predict the phenomenon rigorously, a comprehensive understanding about the cause of the mechano-sorption effect is necessary. Although the topic has been the subject of numerous investigations for over 30 years, a fully satisfactory explanation

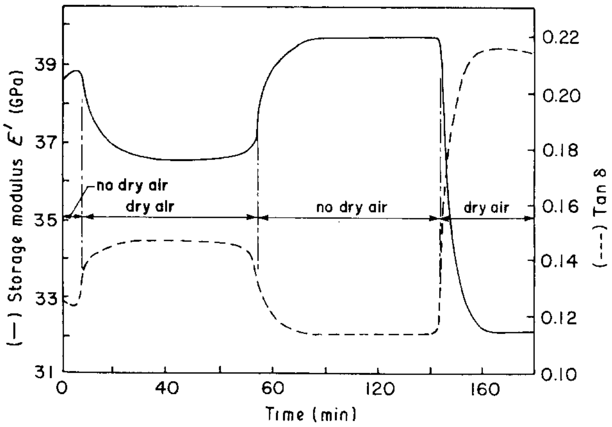

Figure 18 Transient moisture effects in the dynamic properties of a composite coupon with Kevlar 49 fibre reinforcement (after Wang *et al.* [60]). Constant temperature 60 °C; 8-layer 0° wet composite coupon; peak-to-peak amplitude 0.30 mm.

of the phenomenon has not been advanced. Nevertheless, several mechanisms have been proposed. These mechanisms are mainly based on the argument of hydrogen bonding, molecular mobility, and internal stress gradient due to the presence of a moisture gradient.

3.1. Hydrogen bond mechanism

Gibson [17] proposed that the mechano-sorptive phenomenon is caused by the continual making and breaking of hydrogen bonds due to the change in moisture content. During the temporary disruption of the hydrogen bonds, a stress bias will favour additional deformation. This explanation is based on the consideration that adjacent cellulose chains in wood materials are held together by hydrogen bonds with a strength of 5–8 kcal mol^{-1} (21–33 kJ mol^{-1}). The bonds are formed between the hydrogen atoms of hydroxyl groups and suitably situated oxygen atoms in an adjacent chain. The hydrogen bonds play an important role in determining the mechanical properties, such as stiffness and strength, of wood materials. When water molecules are absorbed into the material, some water molecules, being small and polar, may disrupt the original bonds and bridge in between to form new hydrogen bonds. Similarly, when water molecules are desorbed from the material, some of the water molecules which acted as bridges between the molecular chains will leave the sites and cause a temporary breakage of the hydrogen bonds.

A logical development of the hydrogen-bond explanation would be that if other polar solvents are used, mechano-sorptive effects would be manifested also. Gardner *et al.* [18] have found that, besides water, methanol, ethanol and pyridine also cause mechano-sorption effects in beech wood material. However, besides the polarity, the effects of solvents may also depend on such factors as molecular size and the swelling kinetics of the solvents [18].

Armstrong [8] has questioned the hydrogen-bond mechanism based on his constant moisture flux experiment. In this experiment, a constant flux of moisture was produced by imposing different humidity levels on the inside and outside of a hollow bunya pine specimen. The results of the experiment indicated that the relative creeps, determined for wood under compressive load parallel to the grain, were similar in wood subjected to constant moisture flux conditions and to constant moisture conditions without moisture flux [8]. However, a constant moisture flux may not cause hydrogen bond change. Under a constant moisture flux condition, the number of water molecules will be the same at any time within any infinitesimal volume of the wood material. In order to have disruption of hydrogen bonds, in the context of the hydrogen-bond mechanism, the number of water molecules must change to induce the disruption. The movement of water molecules inside the material could be accomplished through the movement of free water molecules. Because the free water molecules are not associated with the wood molecular chains, their movement would not cause any change in the hydrogen bonds. Actually, when water molecules are in equilibrium inside the material, there is a constant rate of exchange of water molecules between free and bound water. So the equilibrium is actually a rate equilibrium or dynamic equilibrium. Only when this equilibrium of exchange is upset, say, by a change in external environment, is a statistical disruption of hydrogen bonds possible. Therefore, the mechanism may more accurately be considered as a disturbance in the exchange rates between the breaking and reforming of hydrogen bonds between the wood molecules. In this sense, the mechano-sorption mechanism may be treated as a special form of a chemical reaction.

Although the breaking and remaking of hydrogen bonds during transient moisture conditions may provide a general explanation of the mechano-sorptive phenomenon, it does not furnish a detailed explanation for the quantitative differences between different materials or under different conditions. Therefore, to explain the phenomenon to a full extent and to provide analytical models, the incorporation of material structure in the mechanism is necessary.

3.2. Slip plane mechanism

Based on SEM microscopic observations, Hoffmeyer and Davidson [25] have proposed a "slip zone" model to explain the mechano-sorptive phenomenon in wood under compression and bending. Polarized microscopy revealed zones of minute failures as distinct planes extending through the S2 layer of the cell wall. The angle between the slip plane and the longitudinal axis of the cell wall is typically of the order of 60°. The number of slip planes is known to be a function of stress level, moisture content and duration of load. To relate the formation of slip planes to the mechano-sorptive creep, Hoffmeyer and Davidson hypothesized that the changes of the elastic, viscoelastic and plastic properties of wood are proportional to the number of slip planes, and the number of slip planes is proportional to the amount of moisture change.

Because slip planes only form under compression and bending and at relatively high stress levels, this model is insufficient to explain the mechano-sorptive phenomenon under tension and at low stress levels. However, it is possible that different mechanisms prevail under tension and under compression and bending, or at low stresses versus moderate stresses and high stresses.

3.3. Crystallite rotation and slippage mechanism

Ericksen [63] has proposed crystallite rotation theory to explain the creep of aromatic fibres under constant moisture conditions. Combining his concept with the concept of the hydrogen-bond mechanism, in an attempt to explain the mechano-sorptive phenomenon in aramid fibres, Wang and Dillard [60] have advanced the so-called "crystallite rotation and slippage mechanism". The crystallites and molecular chains in the fibre are collectively called flow units. Flow units are assumed to orient at an angle relative to the fibre axis. The connections at interfaces between the flow units are mainly due to hydrogen bonds. During a sorption process, water molecules will break the hydrogen bonds, causing a temporary disruption of the hydrogen bonds. When the hydrogen bonds are temporarily disrupted at the interfaces, the flow units may slip relative to each other and, at the same time, crystallites may rotate toward the loading direction, thus causing an increase in deformation. Based on this mechanism, a recent analysis yielded the following conclusions: the mechano-sorptive creep level will increase as the initial crystallite angles and the crystallite lengths increase, and compressive loading will result in a higher mechano-sorptive level than tensile loading.

The crystallite rotation mechanism may also explain the dynamic modulus change in a sorption process as observed by Mackay *et al.* [2]. In a test to measure dynamic rigidity and damping under transient moisture conditions, the dynamic rigidity will drop due to the breakage of hydrogen bonds, and the damping will increase due to the friction between the crystallites. However, when moisture reaches its equilibrium condition, the modulus of rigidity will increase as the result of more oriented crystallites and re-established hydrogen bonds between the crystallites, and, for the same reason, the damping will decrease.

Crystallite rotation has been identified in fibres during processes of deformation. In testing holocellulose pulp fibres, Jentzen [55] found that the crystallite angles of the fibres decreased during tensile creep tests under drying conditions. He also found that the decrease in crystallite angles caused increases in Young's modulus and tensile strength. Northolt [64] and Northolt and Van Aartsen [65] have studied the change in crystallite angles of aramid fibres due to deformation. They tested PPTA fibres and found that the crystallite angles decreased as a result of tensile deformation. Ericksen [63] measured the Young's modulus of PPTA fibres after creep elongation and found that the Young's modulus increased. Berkeley and Kerr, Rebenfeld and Preston *et al.* had similar results indicating decreases in the fibre crystallite angles after deformation [55].

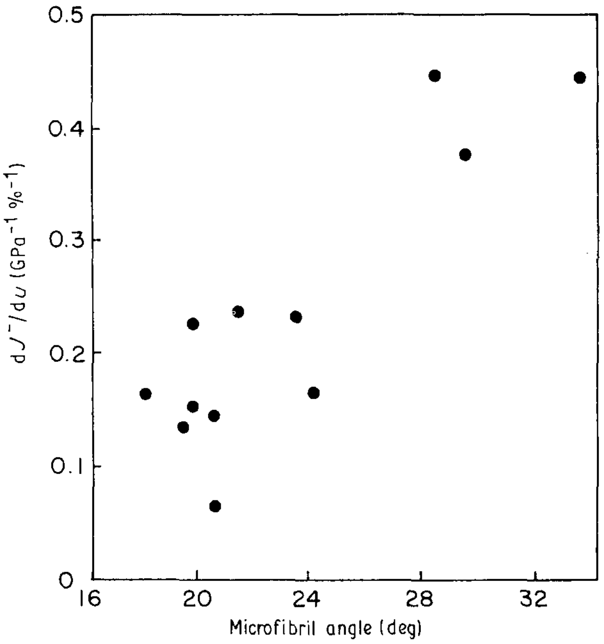

Figure 19 Effect of microfibril angle on the mechano-sorptive bending creep of wood material (after Hunt [9]): J^- = creep compliance during desorption (GPa^{-1}), u = moisture content (%). Ponderosa pine, $T = 23.5\,^\circ$C.

Even though the crystallite rotation and slippage mechanism is proposed to explain the mechano-sorptive phenomenon in crystalline or semi-crystalline fibres, the concept could also be used when other micro-elements, such as fibrils, have a tendency to rotate under transient moisture conditions. For example, there is evidence suggesting that a similar mechanism could prevail in wood materials. Hunt [9] has correlated the mechano-sorptive effect with the microfibrillar angles of the S2 layer in wood materials. He showed that, under tension and bending, the mechano-sorptive effects increase with increasing microfibril angles. Some typical results are shown in Fig. 19. In wood materials, microfibrils are laterally connected together through hydrogen bonds and van der Waals forces. The microfibrils generally have an orientation with respect to the longitudinal axis. For example, in the S2 layer the microfibrils are in a right-hand spiral with an orientation of around 20°. When the water content changes, moisture will constantly break the hydrogen bonds, thus resulting in fewer connections between microfibrils, and therefore may cause shear deformation between the microfibrils along their interfaces. At the same time, the microfibrils may rotate toward the load direction. It is this rotation that may give an additional deformation during transient moisture processes. The greater the initial microfibril angle, the greater will be the potential for rotation.

3.4. Other mechanisms

In explaining the behaviour of wool fibres in a transient moisture environment, Mackay and Downes [2] proposed that the temporary reduction and the later recovery in rigidity modulus are due to the transient stresses produced as a result of differential swelling during the penetration of the water front into the fibre, and that these stresses cause temporary rupture of bonds which contributes to the drop of rigidity. Nordon [54] suggested that there are two competing factors in influencing the observed behaviour. The rigidity is decreased during a sorption process when hydrogen bonds between molecular chains are broken and one or more water molecules are inserted between the chains, forming much weaker and more flexible links between molecular chains. The other process responsible for the increase of rigidity is time-dependent and is more effective in the later stage of the experiment. It was assumed that for each equilibrium moisture content there is a corresponding molecular configuration in the lowest free energy state. In this state, the rigidity is a maximum. When this state is upset by moisture sorption, molecular chains will reorient themselves to constitute a new energy state so that the condition of a minimum free energy for the system can be satisfied. However, the sorption rate is much faster than the rate at which the molecular chains reorient themselves, so one first observes a reduction in rigidity followed by a slower recovery after the moisture equilibrium has been attained [54].

In studying the mechano-sorptive behaviour of wood materials, Mukudai and Yata [66–68] proposed that slippage between the S1 and S2 layers of the secondary wall results in a redistribution of stress. Since each cell-wall layer has different molecular orientations and chemical makeup, each layer will exhibit a different viscoelastic response and swelling characteristics. Van de Put [69, 70] has employed molecular deformation kinetics to describe the mechano-sorptive behaviour in wood. Accelerated deformation is caused by an increase of "holes" (apparent free volume), called flow units, which allow an increase of molecular mobility. The flow of the polymer is then analogous to a quasi-first-order chemical reaction.

4. Summary

Compared to constant moisture conditions, changes in moisture content accelerate creep [6, 8, 12, 16, 40, 52, 55, 57, 60], creep recovery [4–6, 34, 38], and relaxation processes [59], cause reductions in creep rupture life [14–16, 53] and dynamic modulus [2, 54, 57] and increases in damping [58], and influence the wrinkle behaviour of fabrics [57, 58].

The influences of moisture changes in materials behaviour have been found to be present in wood [1–28, 30–34], wood-based panels [39–51], paper [52–53], natural fibres [54, 55, 57–59, 66], fabrics [56], high-strength synthetic fibres and composite materials [60–62]. It is interesting to note that all of these materials contain hydrogen bonds on a molecular level. Another common characteristic of these materials is that they all possess anisotropic responses to moisture effects such as swelling strains along different material directions. While their common molecular structure may relate to the origin of the phenomenon, it is also important, however, to note that there are quantitative differences in the mechano-sorptive behaviour among different materials which may be explained through the differences in their material structures.

For a given material system, factors which may directly influence mechano-sorptive effects are the direction of moisture changes [6, 8, 12], the history of moisture changes [5, 6, 10, 16, 17, 27, 41, 57], the rate of moisture changes [5, 6], and the magnitude of moisture changes [5, 6, 14, 28, 41, 54]. The factors which may indirectly, or to a second-order degree, influence the mechano-sorptive phenomenon are the temperature levels [16, 22, 28, 33, 34], specimen dimensions [14, 15, 31], and loading modes [6, 13, 16, 42, 48, 49]. The influences of temperature levels and specimen dimensions may result, at least partly, from their influences on the moisture rate and magnitude of moisture changes, while the loading modes may be related to the responses of materials to moisture effects along different material directions.

Recent trends of study on mechano-sorptive behaviour appear to be oriented towards searching for theoretical explanations to the phenomenon [25, 60], and practical assessment of parametric influences [9, 10, 20, 27, 43, 44, 45]. On the theoretical aspects, emphasis has been placed on the incorporation of material structures into the phenomenon. On the practical aspects, focal points are on the design levels such as more practical environmental factors, effects in larger members, temperature levels, etc.

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