J Wood Sci (2007) 53:187–191
DOI 10.1007/s10086-006-0858-4

ORIGINAL ARTICLE

Wenbo Zhang · Morihiko Tokumoto · Takashi Takeda

Effects of temperature on mechano-sorptive creep of delignified wood

Received: June 14, 2006 / Accepted: September 27, 2006 / Published online: March 4, 2007

Abstract The effects of temperature on mechano-sorptive (MS) creep of delignified hinoki wood (*Chamaecyparis obtusa* Endl.) were investigated using longitudinal (L) and radial (R) specimens during adsorption and desorption over the temperature range of 20°–80°C. The results were compared with those of stepwise delignified specimens tested at a constant temperature of 20°C. It was found that the effects of temperature on the MS creep of delignified specimens are more remarkable than for untreated specimens. The tendencies of increasing MS creep with temperature, delignification, and their combination were observed. The increase in MS creep for L specimens was relatively small and almost equal in both adsorption and desorption processes, while for R specimens the MS creep was small in desorption, but significantly different in adsorption. In addition, good correlation was observed between the MS coefficient (K) and instantaneous compliance (J_0). The increase in MS creep occurs as a result of temperature increase or decrease in lignin content, or their interacting effects. However, in the case of desorption for R specimens, the increase of MS creep was unexpectedly small due to a remarkably increased J_0.

Key words Adsorption and desorption · Lignin content · Mechano-sorptive creep · Instantaneous compliance

Introduction

In our previous studies,[1,2] the effects of delignifying treatments on mechano-sorptive (MS) creep of wood were investigated by using small longitudinal (L) and radial (R) specimens. The results showed that the effects of delignification are more extensive for R specimens than for L specimens. The occurrences of MS creep in adsorption are larger than that in desorption for delignified R specimens, while those for delignified L specimens are comparatively small or almost equal in both adsorption and desorption. Furthermore, the effects for both R and L specimens in strongly delignified treatment are more easily distinguished.

Wood, as a polymer shows a softening or transition temperature in its rheological behavior over a certain temperature range.[3–5] Many researchers[6–8] studied the temperature effect on the MS creep of wood. Wu and Milota[9] reported that tensile and compressive creep strains under constant moisture reach maximum values between 65.6° and 82.2°C, which is explained using the concept of the glass transition temperature of wood. Tokumoto et al.[10] investigated the effect of temperature on the bending creep of wood during adsorption and desorption, and concluded that the effect of temperature is remarkable during adsorption, but is minor during desorption. These results suggest that the effect of temperature on MS creep is analogous to that of delignification to some degree.

Thus, it is considered that either an increase in temperature or a decrease in lignin content softens or weakens the rigidity of matrix components (i.e., hemicellulose and lignin) in wood, and that factors affecting MS creep of wood include not only the change in moisture content but also temperature and extractive content, which interact in some manner to accelerate the creep of wood.

Lignin, one of the main components of wood cell walls, is less hygroscopic and its mechanical properties are less sensitive to moisture than other hydrophilic polysaccharides.[11,12] The prime function of lignin is to protect the hydrophilic cellulose and hemicelluloses. However, how lignin influences the mechanical properties of wood is still uncertain.

The dominant mechanism of MS creep is generally considered to be related to the behavior of the amorphous region of wood polymers; thus, effects of temperature on MS creep should not be ignored. It is likely that both heating and delignification weaken the matrix of cell walls in the same way.

W. Zhang · M. Tokumoto (✉) · T. Takeda
Faculty of Agriculture, Shinshu University, 8304 Minamiminowa
Nagano 399-4598, Japan
Tel. +81-265-77-1509; Fax +81-265-72-5259
e-mail address: mortoku@shinshu-u.ac.jp

Part of this report was presented at the 15th Annual Meeting of the Chubu Branch of the Japan Wood Research Society in Fukui, October 2005

The purpose of this study was to clarify the effect of temperature on MS creep of untreated and delignified wood. The difference between temperature effect and delignification is discussed.

Materials and methods

Specimens

The wood species used in the study was hinoki (*Chamaecyparis obtusa* Endl.). Two types of small rectangular specimens were used: longitudinal (L) specimens (R × T × L: 10 × 3 × 120 mm) and radial (R) specimens (R × T × L: 120 × 3 × 10 mm). These two types of specimens were successively cut from each wood block. Specimens were selected according to Young's modulus.

Delignifying treatment

The delignifying treatment was conducted with acidified sodium chlorite solution, i.e., the sodium chlorite method.[13] After being immersed in this solution under reduced pressure for 12 h at room temperature, specimens were subsequently immersed in the solution for 40 h at a constant temperature of 40°C. Thereafter, specimens were washed in running water for 5 days and were dried in air. The same treatment was repeated twice. After the delignifying treatment, specimens with a lignin content of about 15.4% and 12.4% in L and R specimens, respectively, were conditioned for 2 h at a temperature of 80°C and relative humidity (RH) of 98%. Then specimens were dried slowly and were conditioned at 20°C and 40% RH. Untreated specimens were also used as controls.

Bending creep test

Bending creep tests were carried out in a chamber in which both temperature and humidity could be controlled. Deflections were measured using a digital reading microscope (accuracy of measurement: 0.01 mm). The load was applied at the center of a beam with a span of 100 mm. Bending loads were nearly one third of proportional limits at the low end of the prescribed RH ranges where creep experiments were carried out. Matched specimens closely placed with the creep specimens were used for measurement of moisture content (MC) change. Experimental results were the average of three specimens under each condition.

Test conditions

Bending creep tests during adsorption (A) and desorption (D) processes were carried out at four different temperatures (20°, 40°, 60°, and 80°C). The ranges of RH at each temperature were as follows: 20°C/40%–94% RH, 40°C/40%–94% RH, 60°C/55%–94% RH, and 80°C/61%–97% RH. Before the creep test, specimens were allowed to equilibrate sufficiently at the prescribed RHs. After loading, the creep deflection measured within the initial 1 min was termed as instantaneous compliance (J_0); thereafter, MC was kept constant for 1 h and then creep deflection during adsorption or desorption process was measured over 12 h.

Results and discussion

The curves of creep versus MC for untreated wood during adsorption and desorption are shown in Fig. 1. For L specimens, the bending creep increased with increasing temperature during both adsorption and desorption. For R specimens, the increases in MS creep with increasing temperature are significant during adsorption, but were small during desorption. For both L and R specimens, however, the increases in bending creep from 60° to 80°C are remarkable during both adsorption and desorption. These remarkable changes are caused by the softening of the matrix of cell walls, which becomes significant with water sorption.[3–5]

The increasing tendencies of MS creep in Fig. 1 are in agreement with the previous study.[10] The tendencies are also similar to that of MS creep with delignifying treatments;[1,2] that is, the increases in MS creep with increasing temperature are relatively small and equivalent during both adsorption and desorption for L specimens, while increases

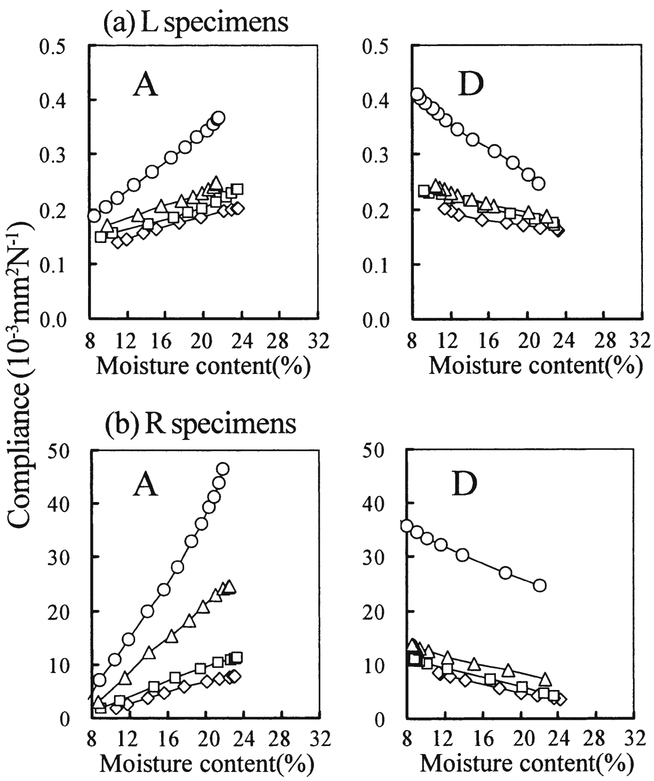

Fig. 1a, b. Effects of temperature on bending creep of a untreated longitudinal (*L*) specimens and b untreated radial (*R*) specimens during adsorption (*A*) and desorption (*D*). *Diamonds*, 20°C; *squares*, 40°C; *triangles*, 60°C; *circles*, 80°C

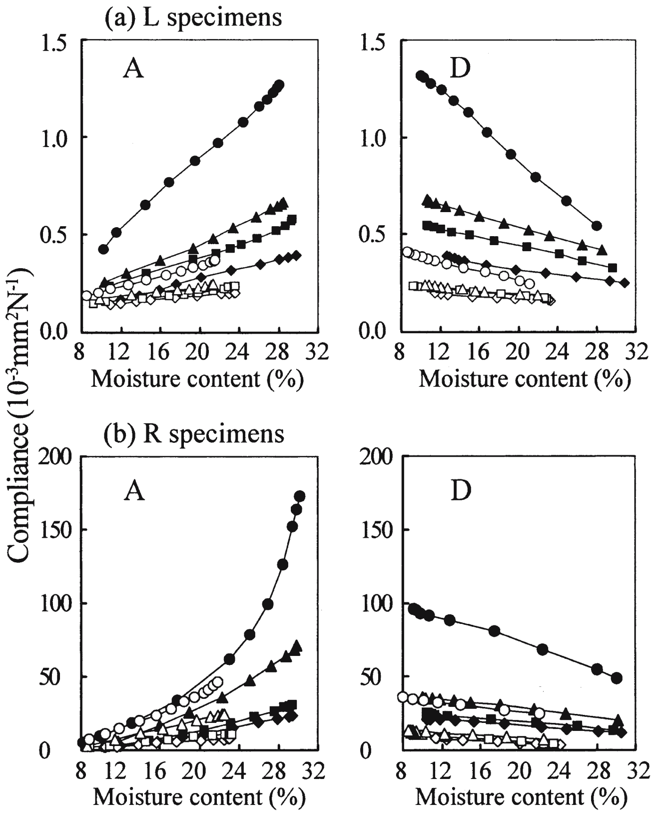

Fig. 2a, b. Effects of temperature on bending creep of **a** delignified longitudinal (*L*) specimens and **b** delignified radial (*R*) specimens during adsorption (*A*) and desorption (*D*). *Diamonds*, 20°C; *squares*, 40°C; *triangles*, 60°C; *circles*, 80°C; *filled symbols*, delignified; *open symbols*, untreated

are remarkable in adsorption and small in desorption for R specimens.

Based on the above results, the rigidity decrease in the matrix components of cell walls is attributed to either an increase in temperature or a decrease in lignin content. Consequently, the increase in MS creep with increasing temperature during both adsorption and desorption is equivalent for L specimens, while for R specimens the MS creep increased remarkably in adsorption and only slightly in desorption.

The effect of temperature on MS creep for delignified specimens is shown in Fig. 2. Creep curves of untreated specimens are also shown in the same figure. The MC changes for delignified specimens during adsorption and desorption processes are 6%–7% larger than that for untreated specimens. This is because the equilibrium moisture contents of delignified specimens are increased after delignification. This indicates a large increase in the number of sorption sites available in the wood substances after delignification.

As seen in Fig. 2, the bending creep of delignified L specimens increases more significantly compared than the untreated L specimens and exhibits an almost linear creep region over the entire MC range. Furthermore, MS creep increases to the same extent in adsorption and desorption. On the other hand, for R specimens, the different influences appear between adsorption and desorption processes. The increase in MS creep with increasing temperature is small in the desorption process, while it is remarkable for adsorption. In adsorption, creep increases moderately until about 24% MC, but increases abruptly over 24% MC. This tendency becomes significant at 80°C, at which the slope of the creep curve over 24% MC is five times larger than the slope below 24% MC. As MC increases, the wetting of wood induces a marked softening of the matrix, although crystalline microfibrils remain unaffected.[3–5] Matrix softening is particularly remarkable in the temperature range of 60°–80°C where part of the matrix components shift from the glassy state to the rubbery state. Accordingly, the softened matrix permits the relative displacement of microfibrils under loading.

The effects of temperature on delignified specimens are qualitatively similar to that of untreated specimens as well as to that of stepwise delignification treatments at 20°C according to the structural direction of wood and direction of moisture change. All results described above show similar effects of temperature and delignification: the increases in MS creep with either increasing temperature or decreasing lignin content are equivalent in both adsorption and desorption for L specimens, while are small in desorption and remarkable for adsorption for R specimens.

Regardless of delignification, delignified and untreated specimens show qualitatively similar effects of temperature on MS creep, but the interacting effect of increasing temperature and delignification was observed for delignified specimens. Delignified specimens used in this experiment contained approximately one third to one half of their original total lignin content. It is hypothesized that when lignin is totally isolated from the matrix of wood, the remaining holocelluloses would probably show MS creep behavior as similar as cellophane,[14] as indicated by significant softening with increasing MC. Due to the similar effects of decrease in lignin content and increase in temperature, it can be assumed that the residual lignin in cell walls functions as a barrier to swelling and heating, while hemicellulose acts a swelling and heating agent.

Relationships between average MS creep coefficients K ($K = \Delta J/\Delta u$) and temperature are shown in Fig. 3. Here, ΔJ and Δu denote the total change of MS creep compliance and moisture content, respectively, during adsorption and desorption processes. K as a constant indicates the increasing tendency of creep.

As can be seen in Fig. 3, K values of the delignified specimens are significantly larger than those of untreated specimens. For L specimens, the increasing tendencies of K with increasing temperature are approximately equal in both adsorption and desorption processes. For R specimens, K values are significantly larger in adsorption than in desorption. For both types of specimens, K increases significantly as temperature increases from 60° to 80°C.

Figure 4 shows the relationships between temperature and the ratio of creep coefficient at temperature T (K_T) to that at 20°C (K_{20}) under all experimental conditions. In adsorption, although the ratios of K_T/K_{20} of R specimens are larger than those of L specimens, the increasing tendencies

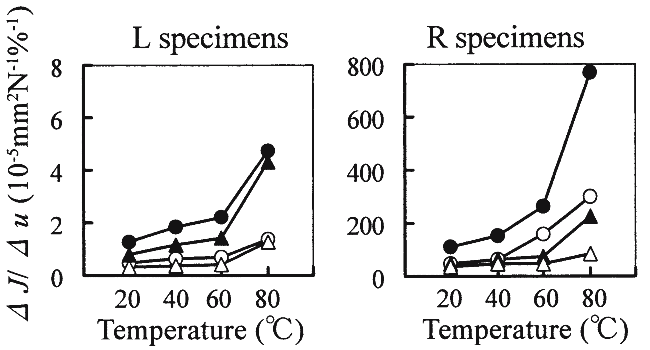

Fig. 3. Effects of temperature on mechano-sorptive (MS) creep coefficients ($K = \Delta J/\Delta u$: the total increase in compliance divided by the size of the moisture change) for longitudinal (L) and radial (R) samples. *Circles*, during adsorption; *triangles*, during desorption; *filled symbols*, delignified; *open symbols*, untreated

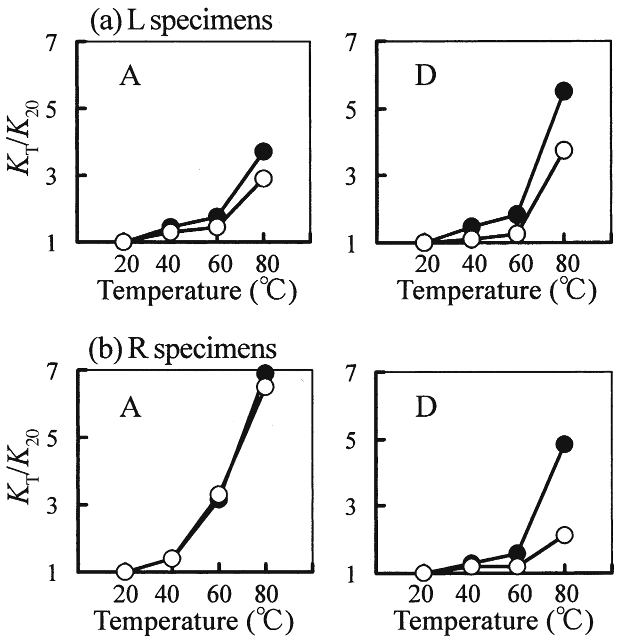

Fig. 4a, b. Relationship between K_T/K_{20} and temperature for **a** longitudinal (L) samples and **b** radial (R) samples during adsorption (A) and desorption (D). K_T/K_{20} denotes the ratio of K at the temperature considered to that at 20°C. *Filled symbols*, delignified; *open symbols*, untreated

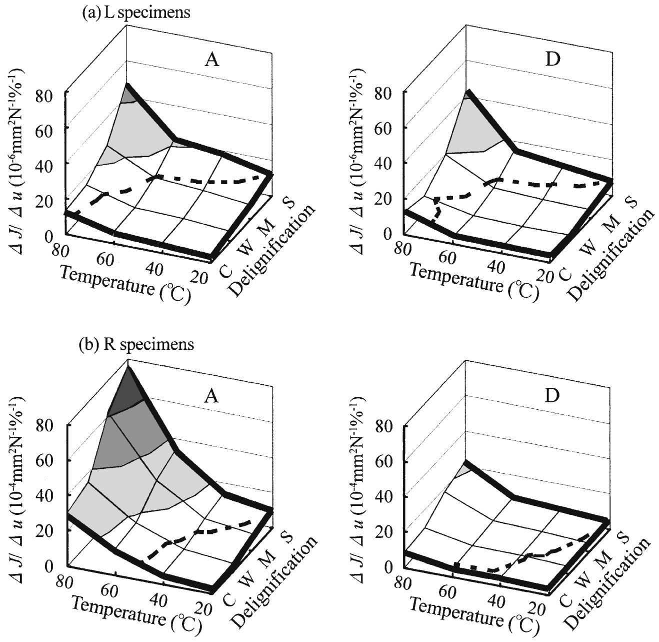

Fig. 5a, b. Variation of $\Delta J/\Delta u$ with temperature and the degrees of delignification for **a** longitudinal (L) samples and **b** radial (R) samples for adsorption (A) and desorption (D). C, Control; W, delignifying treatment for 10h; M, delignifying treatment for 30h; S, two delignifying treatments for 30h each

with increasing temperature are similar for both delignified and untreated specimens. On the other hand, in desorption, the ratios of K_T/K_{20} of delignified specimens are larger than those of untreated L and R specimens. Judging from the ratio of K to the values at 20°C, the effect of temperature on MS creep is almost equal for both delignified and untreated specimens in adsorption, while it is larger for delignified specimens than untreated specimens in desorption.

Figure 5 shows the average MS creep coefficients K as a function of temperature and degrees of delignification in a comparison of the temperature effects with the delignification effects. Figure 5 shows contour maps of K, in which heavy and thin lines are drawn based on the measured and estimated values, respectively. The data showing the relationship between K and degree of delignification (C, W, M, and S) at a temperature of 20°C are taken from previous reports.[1,2] Here, lignin contents corresponding to the degree of delignification C, W, M, and S are about 30.1%, 26.1%, 20.2%, and 15.4% in L specimens, and about 31.7%, 24.9%, 16.3%, and 12.4% in R specimens. The values of K for the degrees of delignification W and M at a temperature higher than 20°C are estimated based on the relationship between K and the degree of delignification at 20°C. Also, the broken lines denote contour lines of K corresponding to the values of delignified specimens at 20°C. From this contour line, the K values at 20°C for specimen S in the L and R directions correspond to the values in the temperature ranges of 70°–80°C and 50°–60°C, respectively. It is obvious that the temperature ranges of L specimens are higher than those of R specimens. Figure 5b shows in the case of desorption for R specimens a peculiar moderately increasing tendency of MS creep with increasing temperature or decreasing lignin content compared with all other cases.

Figure 6 shows the relationships between average MS creep coefficients (K) and instantaneous compliances (J_0). J_0 presents instantaneous compliance at the low end of the MC interval for adsorption or at the high end of the MC interval for desorption. Under all the experimental conditions, there exist good correlations between K and J_0. Therefore, it is clear that increase in MS creep is in proportion to the increase in J_0. This is a result of the increase in temperature or the decrease in lignin content, or, furthermore, the cumulative effects of temperature and delignification. It is noteworthy that the increases in the MS creep for R specimens in desorption are unexpectedly small in contrast to remarkably increased J_0.

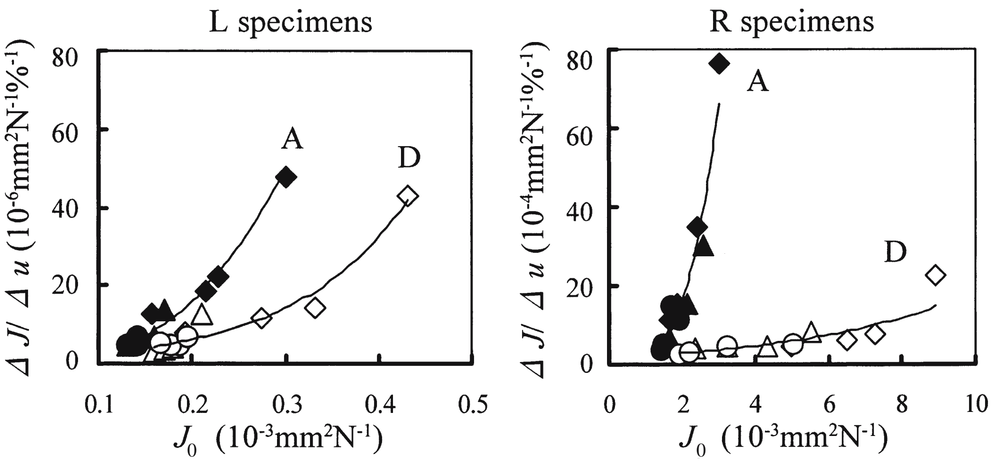

Fig. 6. Relationships between $\Delta J/\Delta u$ and J_0 for longitudinal (*left*) and radial (*right*) samples. J_0 is the value at the low end of the moisture content (MC) interval for adsorption (*A*) and at the high end of the MC interval for desorption (*D*). *Diamonds*, delignified; *triangles*, untreated; *circles*, stepwise delignified

MS creep for L specimens increased equivalently during both adsorption and desorption as J_0 increases. However, the increases in MS creep for R specimens are significantly different between adsorption and desorption, which is a point worthy of further investigation.

The common increasing tendencies of MS creep caused by temperature, delignification, or their combination occurs through various mechanisms, such as softening of the wood cell wall matrix by rising temperature, loosening of the matrix and increasing hygroscopicity by delignification, or their interaction. More detailed investigation toward clarifying these mechanisms is under way.

Conclusions

Based on the above results and discussion, the following conclusions can be drawn:

1. For untreated specimens, the increases in MS creep with increasing temperature for longitudinal specimens are relatively small and almost equal in both adsorption and desorption processes, while for radial specimens the increases in MS creep are small in desorption, but significantly different in adsorption. These increasing tendencies with temperature are similar to that of stepwise delignified specimens according to either structural direction or direction of moisture change.
2. The effects of temperature on MS creep of delignified specimens are more remarkable than those on untreated specimens, and the tendencies of increasing MS creep are qualitatively similar to those of untreated specimens according to either structural direction or direction of moisture change.
3. There are good correlations between K values and instantaneous compliances (J_0).

It is obvious that the increases in MS creep under all the experimental conditions are in proportion to the increases of J_0, which results from increase in temperature or decrease in lignin content, or, furthermore, the interacting effects of temperature and delignification. However, the increases in MS creep for radial specimens in desorption are unexpectedly small due to the remarkably increased J_0.

Acknowledgments The authors thank Dr. Meng Gong, Research Scientist, University of New Brunswick, Wood Science and Technology Center, for his kind assistance in reviewing this manuscript.

References

1. Zhang W, Tokumoto M, Takeda T, Yasue K (2006) Effects of delignifying treatments on mechano-sorptive creep of wood I: instantaneous and total compliance of radial specimens (in Japanese). Mokuzai Gakkaishi 52:19–28
2. Zhang W, Tokumoto M, Takeda T, Yasue K (2006) Effects of delignifying treatments on mechano-sorptive creep of wood III: MS creep of longitudinal specimens (in Japanese). Mokuzai Gakkaishi 52:206–214
3. Goring DAI (1963) Thermal softening of lignin, hemicellulose and cellulose. Pulp Pap Mag Can 64:517–527
4. Takahashi N (1968) Studies on hot pressing and drying process in the production of fibreboard III: softening of fibre components in hot pressing of fibre mat. Mokuzai Gakkaishi 14:75–79
5. Hillis WE, Rozsa AN (1978) The softening temperature of wood. Holzforschung 32:68–73
6. Davidson RW (1962) The influence of temperature on creep in wood. Forest Prod J 12:377–381
7. Hisada T (1981) Creep and set behaviour of wood related to kiln drying V: effect of temperature on creep of wood during drying (in Japanese). Mokuzai Gakkaishi 27:381–389
8. Hanhijarvi A (2000) Deformation properties of Finnish spruce and pine wood in tangential and radial directions in association to high temperature drying III: experimental results under drying conditions (mechano-sorptive creep). Holz Roh Werkst 58:63–71
9. Wu Q, Milota MR (1995) Rheological behavior of Douglas-fir perpendicular to the grain at elevated temperatures. Wood Fiber Sci 27:285–295
10. Tokumoto M, Takeda T, Nakano T (1996) Effect of temperature on bending creep of wood during moisture adsorption (in Japanese). J Soc Mater Sci Jpn 45:376–380
11. Cousins WJ (1976) Elastic modulus of lignin as related to moisture content. Wood Sci Technol 10:9–17
12. Cousins WJ (1978) Young's modulus of hemicellulose as related to moisture content. Wood Sci Technol 12:161–167
13. Wise LE, Murphy M, D'Addieco AA (1946) Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. Paper Trade 122:35–43
14. Tokumoto M, Sawada K (2001) Tensile creep of cellophane during adsorption and desorption (in Japanese). Abstracts of the 51st Annual Meeting of the Japan Wood Research Society, April 2–4, Tokyo, Japan, p 55