# Stress relaxation of wood treated with the formaldehyde in bending and in torsion during adsorption of water vapor.*

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**Summary** Measurements of stress relaxation in bending and in torsion during adsorption of water vapor were carried out on Hinoki wood (*Chamaecyparis obtusa* ENDL.) treated with formaldehyde to varying extent.

The results obtained are as follows:

(1) It was found that the stress relaxation behaviors of the treated wood in bending and torsion during adsorption were the same as those of the untreated one, although the values were different (Figs.3 and 4).

(2) The linear relation between the total amount of stress relaxation induced by moisture in torsion and the total swelling from dryness to saturation of moisture was recognized (Fig.6).

(3) The tendency between the fractional change of relaxation rigidity N(t) and that of moisture content R(t), calculated by Eqs. (1) and (2) shown in the previous paper,[10] was very similar, but the values of N(t) were always greater than those of R(t). However, the difference between them reduced as the antiswelling efficiency increased (Fig.7).

(4) The stress relaxation curves observed were compared with the theoretical ones calculated by making use of Eq.(11) obtained on the basis of the assumption that the breaking rate of hydrogen bonds between adjacent chain molecules in the amorphous regions controlled the rate of stress relaxation (Figs.8 and 9). From these results, it was evident that the stress relaxation during adsorption of water vapor was affected by the internal stresses due to the moisture gradients.

## Introduction

It is well known that the creep and the stress relaxation in wood become considerably greater when the moisture content decreases and increases while the specimen is under a constant load or deformation than when it remains constant. To elucidate this behavior, many researches have been carried out by various investigators from different points of view. For example, it has been shown by Christensen,[1] Armstrong and Christensen,[2] Armstrong and Kingston,[3] and Suzuki[4] that there is a large increase in deflection of small beams of wood under constant bending load when exposed to moist conditions. Using the technique similar to those of Armstrong & Christensen,[2] Hearmon & Paton[5] investigated on the creep behavior of wood

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with changing moisture content at controlled temperatures, and it was found that the additional deflection was shown to be dependent on applied load, moisture content, and temperature. Okusa and Hayashi⁶⁾ observed the shrinkage and the swelling of wood under the compressive stress, and it was found that the wood under the stress shrinks more and swells less than when stress free. The stress relaxation under the non-equilibrium state of moisture was measured by Takemura and Fukuyama et al,⁷⁾ Takemura,⁸⁾ Sadoh and Urakami,⁹⁾ and Urakami and Fukuyama.¹⁰⁾

It has been assumed that abnormally large deformation and relaxation as mentioned above results from either the enhanced plasticity or the effect of the internal stresses due to the moisture gradients, or both. The effect of the internal stress due to the moisture gradients on the creep was denied by Christensen,¹⁾ who found that the anomalous increase in deflection under stress during adsorption or desorption of water vapor appears even in creep tests carried out by working with very small beams (1~2 mm thick) in the absence of air without the moisture gradients. Takemura,⁸⁾ Hearmon and Paton,⁵⁾ and Okusa and Hayashi⁶⁾ have revealed the possibility of the occurrence of permanent deformation due to stresses lower than that of the proportional limit shown in stress-strain diagramms.

As already reported,¹⁰⁾ we found that the stress relaxation in bending and in torsion during adsorption of water vapor were greater than those under the equilibrium state of moisture, but the behaviors in bending and in torsion were different; relaxation rigidity G(t) during adsorption decreased simply with time, but relaxation modulus E(t) in the same process decreased rapidly in the early stage of adsorption, and then increased slightly. Especially it was found that in the case of torsion, the tendency between the fractional change of stress relaxation N(t) and that of moisture content R(t) with time was similar, but the values of N(t) were always greater than those of R(t). Furthermore, we reported that the stress relaxation of wood treated with polyethylene glycol during adsorption of water vapor in bending was expressed as the curve that decreased simply with varying moisture content,¹¹⁾ although no dimensional change occurs.⁹⁾

Higgins¹²⁾ observed the distribution of moisture content within the laminated paper sheets (the total thickness: 0.01 inch) during drying, and recognized that there exist the moisture gradients within such thinner paper sheet. Similar results were observed by Fujita et al¹³⁾ as indicated in the previous paper.¹⁰⁾

From these facts, it seems that the influence of the internal stresses developed during moisture content changes on the rheological properties is not necessarily negligible.

The purpose of this study is to observe phenomenally the behaviors of the stress relaxation of wood treated with formaldehyde to varying extent under the equilibrium state of moisture (moisture content: ca. 2.3 percent) and the non-equilibrium state of moisture (moisture content change corresponding to relative humidity from dryness to saturation of moisture) in both bending and torsion, to find the relationship between the change of moisture content and relaxation of stress in the process of adsorption, and to ascertain the effect of the internal stesses due to the moisture gradients on the relaxation behaviors.

In order to vary the degrees of the internal stresses developing accompanying moisture content change, the formaldehyde treatment was used in this experiment.

## Experimental

Material used in this experiment was Hinoki wood (*Chamaecyparis obtusa* ENDL.). All of the specimens used were prepared from an air-dried block of heartwood and closely matched, being continuous and including almost the same number of growth ring. The average density and the annual ring width in air-dry state were 0.43g/cm$^3$ and 4.5 mm, respectively. The nominal dimensions of specimens in torsion were 6.0 (L) × 1.0(R) × 0.1(T) cm (excluding the portions grasped by the clamps), and in the case of bending, it was 11.0(R) × 1.0(L) × 0.1(T) cm with a span of 8.0 cm.

In order to set the treating time with formaldehyde vapor, specimens of 3.0(R) × 3.0(T) × 0.5(L) cm in size were used for the swelling measurement. Although the degrees of the formaldehyde treatments in nature should be expressed as the ratio of the reacted OH-groups relative to the total one, conveniently in this experiment the swelling measurement for wood treated with formaldehyde to varying extent was adopted as the index of the degree of treatment. The procedure of the formaldehyde treatment was the same as that by Gotō et al.[14]

Specimens were treated under the following processes:

(1) pretreatment with dry hydrogen chloride for 15 min.
(2) formaldehyde reaction at 95°C for 1, 3, 5, and 7 hours.
(3) the treated specimen were washed in running water for two weeks.
(4) after (3), the specimen were dried at 60°C for 24 hours, and then at 100°C.
(5) the treated specimens were conditioned for two weeks in a desiccator containing calcium chloride.

Also control specimens were treated similarly except for the reaction with formaldehyde and the exposure to hydrogen chloride, and specimens exposed to dry hydrogen chloride alone for 15 min were used for comparison.

The values of swelling and antiswelling efficiency (abbreviated A.E.) were calculated on the basis of the dimensional difference between the dry state and the moisture saturated state. The values of A.E. were obtained by the following equation,

$$\text{A.E.}(\%)=100(\beta_0-\beta_t)/\beta_0\cdots\cdots(1)$$

where $\beta_0$ and $\beta_t$ are the total swelling of the control and the treated specimens, respectively.

The dimensional stability (the radial swelling and A.E.) of the wood treated under each condition is shown in Table 1. From these results, the treating times of 1, 3, and 7 hours, which the appreciable difference is recognized between the values of the total swelling from dryness to saturation of moisture,

Table 1. The radial swelling ($\beta$) and the antiswelling efficiency (A.E.) of Hinoki wood treated with formaldehyde under hydrogen chloride.

| | | | $\beta$ (%) | A.E. (%) |
|---|---|---|---|---|
| formaldehyde treated wood | treating time (hour) | 1 | 1.46 | 36.2 |
| | | 3 | 1.41 | 38.8 |
| | | 5 | 1.33 | 41.9 |
| | | 7 | 1.34 | 41.5 |
| hydrogen chloride treated wood | | | 1.66 | 27.5 |
| untreated wood | | | 2.29 | — |

were adopted.

The apparatus used for the measurements of the stress relaxation in bending and in torsion were essentially similar to those described in the previous paper.⁽¹⁰⁾ In the case of bending, the specimen was supported at the both ends, and a concentrated load was given at the center of span. The measurements of the stress relaxation in bending and torsion were made at a constant temperature of 30°C, and the moisture content of the specimens corresponds to the change of the relative humidities from the lack of water vapor to saturation. The air in the test cabinet was humidified by passing it through the glass bottle containing the humidified agents (silicagel or distilled water).

After the specimen had been enclosed in the cabinet for 2 hours, the constant deformation was given. The given amount of deformation was 0.13 rad/cm in torsion, and 0.06 cm in bending, which correspond to about 50 percent of the proportional limit in air dry.

The measurements of the stress relaxation were made under the equilibrium state of moisture content and in the process of water adsorption. The measurements of the stress relaxation during adsorption were carried out as follows; the specimen was deformed manually by a predetermined amount, and the stress thus produced was allowed to decay under the dry state for a period of time, up to 300 min in bending, and 360 min in torsion. After the rate of stress decay in dry state had decreased sufficiently, the vapor saturated with moisture was introduced, and the subsequent stress relaxation was observed for another 300 min in bending and 360 min in torsion.

Furthermore, in order to ascertain the actual moisture content changes during adsorption of water vapor, the unloaded specimens of matched material were used for checking the moisture content. The adsorption of moisture by specimens was measured by using the torsion balance whose sensitivity is 0.5 mg.

The experimental results shown are the average of five measurements.

## Results and discussion

Table 1 shows the radial swelling and A.E. of specimens treated under the various conditions as mentioned above. Essentially these results are in accordance with those obtained by Gotō et al.⁽¹⁴⁾ From the results in this table, it was found that the longer the treating time, the less the swelling becomes. Assumedly this means that the formaldehyde treatment in the presence of hydrogen chloride as catalyst is effective for the dimensional stability of wood to a high degree through the cross linking reaction, namely the increase of the number of cross linkage between cellulose molecules.

It is of interest in Table 1 that the swelling of the samples exposed to hydrogen chloride alone decreases slightly as compared with that of the control (untreated samples). For the reasons of the decrease in swelling of the hydrogen chloride treated samples, it is thought that the crystallization of the amorphous regions occurs due to the slower hydrolysis of cellulose chains, and as the results the reduction in swelling is given.

Fig.1 shows the stress relaxation in bending for the samples treated with formaldehyde to varying extent, the hydrogen chloride treated one, and the controls under the equilibrium state of moisture (moisture content: ca. 2.3 percent). It is seen from this figure that the instantaneous elastic modulus in bending E(0) tends to increase with increasing the treating time, except for the hydrogen chloride treated samples. Fig.2 illustrates the stress relaxation curves in torsion under the same condition in Fig.1, and also in this case the fact mentioned above is almost true. It is evident from the results in Table 1, Figs. 1 and 2 that the formaldehyde treatments have been carried out desirably, and generally the rate and the amount of stress relaxation (expressed as the difference between the instantaneous elastic modulus and the final one) decrease with increasing the degree of treatment. This may be produced as the results of cross linking.

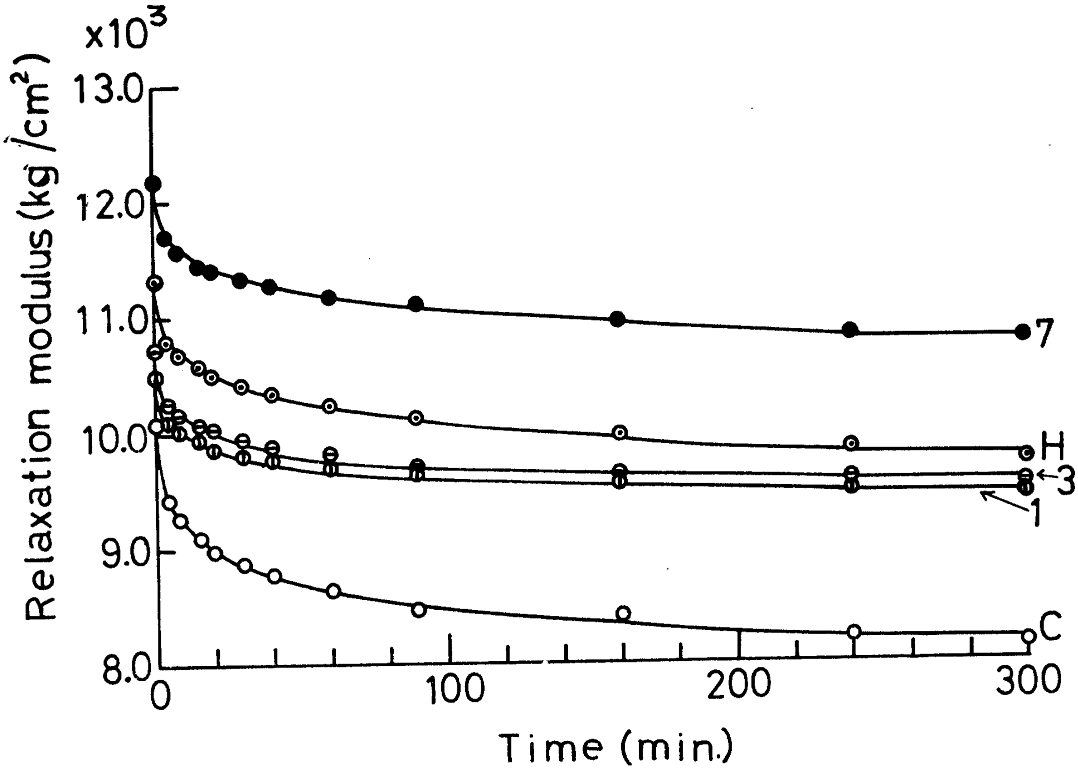

Fig. 1 Stress relaxation curves in bending for Hinoki wood treated with formaldehyde to varying extent at a constant moisture content of about 2.3 percent. The numbers added to the curves indicates the treating time (hour) with formaldehyde vapor, and the symbols of H and C, the treatment by hydrogen chloride alone and the control (untreated), respectively.

Fig.3 shows the stress relaxation curves in bending during adsorption of water vapor after the rate of relaxation became relatively slow and almost zero. The relaxation modulus E(t) after the introduction of wet air were corrected for the progressive swelling of the cross-sectional area of the specimen caused as diffusion of moisture proceeds. It was found clearly in this figure that the relaxation of stress becomes suddenly fast as soon as the specimen is exposed to wet air and then the relaxation modulus E(t) increases as in the previous paper.[10)]

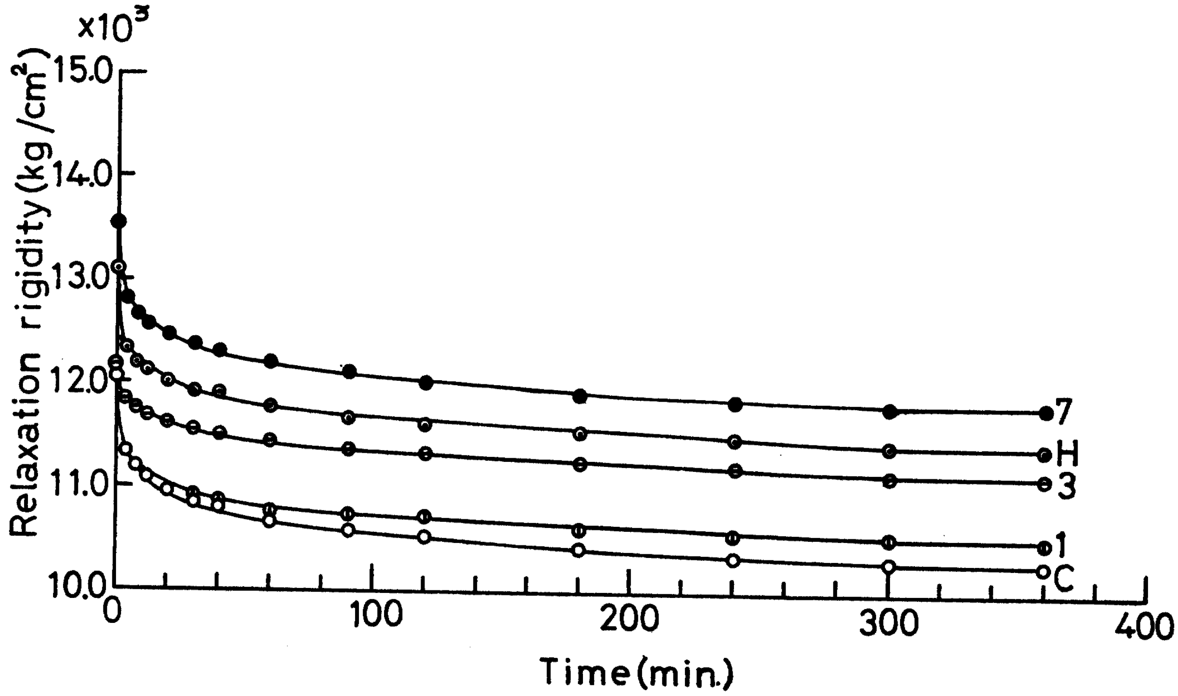

Fig. 2 Stress relaxation curves in torsion for Hinoki wood treated with formaldehyde to varying extent at a constant moisture content of about 2.3 percent. The numbers and the symbols in the figure are the same as shown in Fig. 1.

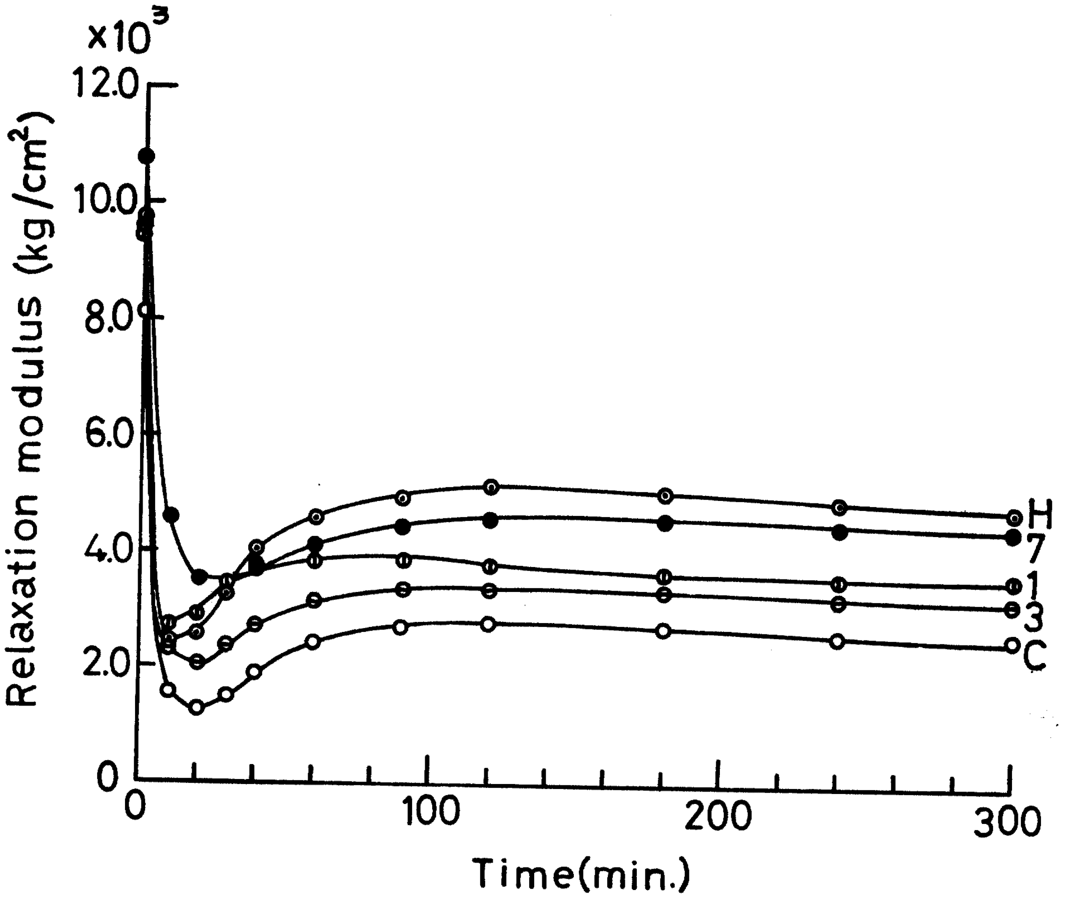

Fig. 3 Stress relaxation curves in bending for Hinoki wood treated with formaldehyde during adsorption of water vapor. The numbers and the symbols in the figure are the same as shown in Fig. 1.

In general, the molecular mechanism for stress relaxation has been classified by Tobolsky and Stein15) into the following five types; (1) chemical reaction; (a) scission, (b) interchange, (2) viscous flow or diffusion, (3) crystallization, (4) release of distortion of molecules and crystals, and (5) orientation of crystals. In the continuous stress relaxation measurement, the stress in sample maintained at a fixed deformation is to decrease simply with time for each of relaxation processes mentioned above. Therefore, it is concluded that the characteristic behavior of stress relaxation in bending during adsorption is caused by other factors, which are the internal stresses resulting from the moisture gradients and the difference of the swelling and the rate of adsorption in the stressed faces (compressive face and tensile face) in the beam. However, it is difficult that the transitions and the magnitudes of the internal stresses on the stress relaxation during adsorption are estimated directly.

Fig. 4 gives the stress relaxation curves in torsion during adsorption, after the stress was allowed to relax under a dry state as in bending, and in this plot zero time was taken at the time of introduction of wet air. In this figure the stress decay becomes suddenly fast as soon as the specimen is exposed to wet air, and approaches a new equilibrium as time goes on.

The ranges and the courses of moisture content changes are shown in Fig.5. Although there are differences between the changes of moisture content in bending and those in torsion, this is not essential, but the problems of the apparatus for air conditioning.

Now if the total amount of stress relaxation (the difference between the initial relaxation rigidity G(0) and the final one G(∞)) is plotted against the swelling in the radial direction from dryness to saturation of moisture, the relationship between

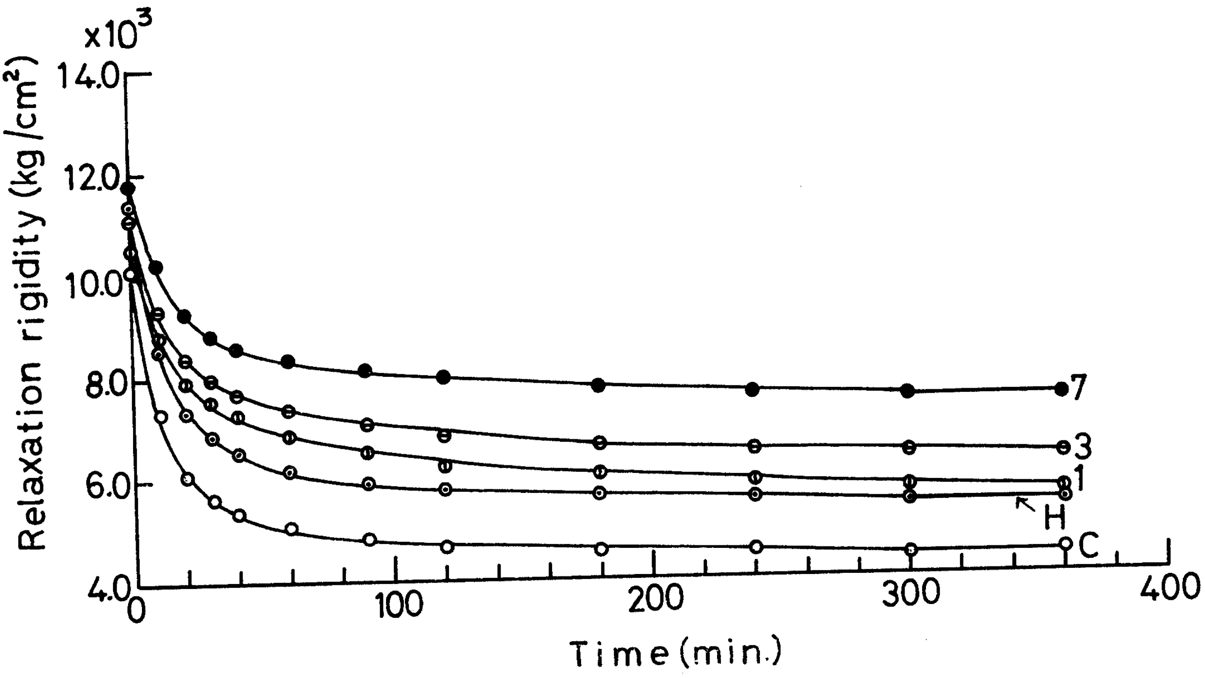

Fig. 4 stress relaxation curves in torsion for Hinoki wood treated with formaldehyde during adsorption of water vapor. The numbers and the symbols in the figure are the same as shown in Fig. 1.

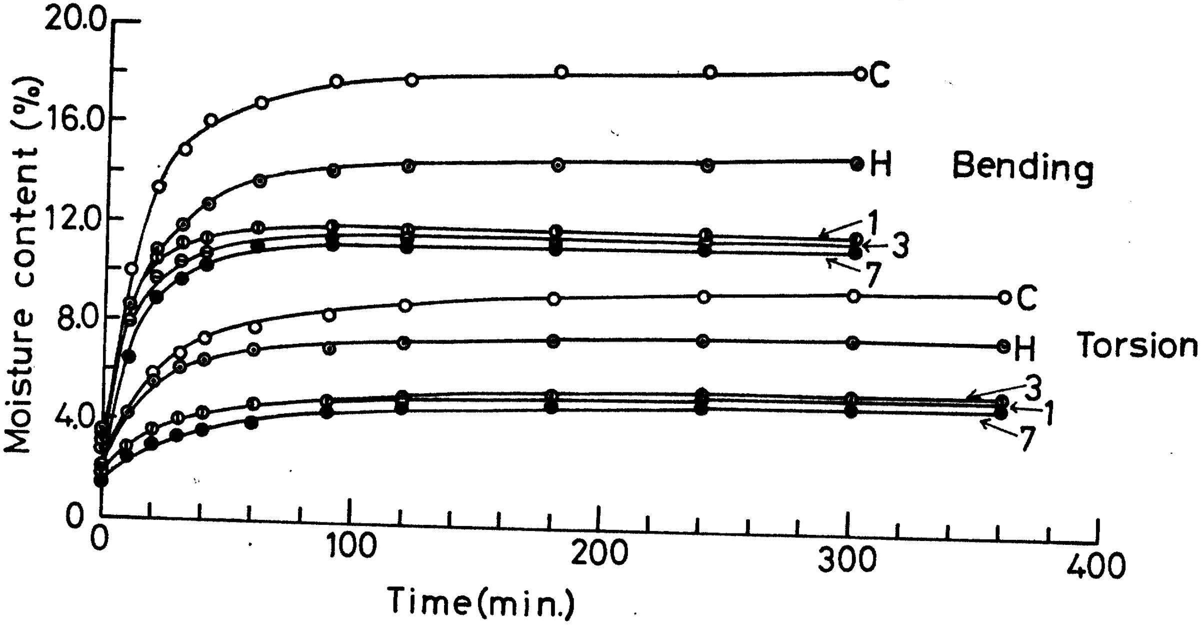

Fig. 5 Moisture content changes of the formaldehyde-treated wood for the stress relaxation tests in bending and in torsion. The numbers and the symbols in the figure are the same as shown in Fig. 1.

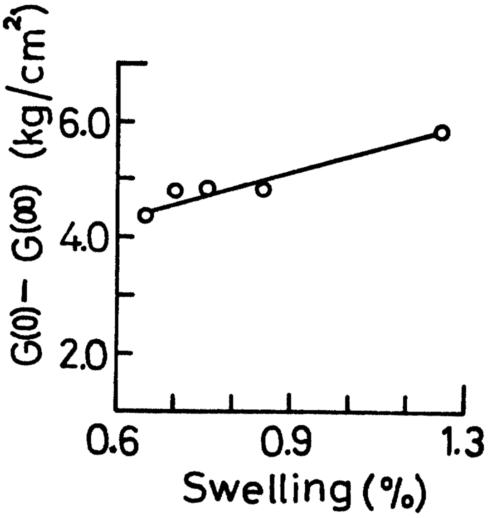

Fig. 6 The relationship between the total amount of stress relaxation induced by moisture adsorption and the total swelling from the dryness to the saturation of moisture. The symbols of G(0) and G(∞) in this figure indicate the initial and the final relaxation rigidity, respectively.

both is approximately linear as shown in Fig.6, and the amounts of relaxation $G(0) - G(\infty)$ increase with increasing the swelling. This, of course, is related to the amounts of moisture adsorbed. Consequently, it was decided to compared with the rates of stress relaxation on a fractional basis, i.e., taking the final moisture induced relaxation for a given moisture content change as unity and expressing intermediate relaxations as a fraction of this, because of the variations in the magnitude of the moisture induced relaxation under various treatment conditions. The results are shown in Fig.7. As is seen in this figure, although the curves of the moisture change and the stress relaxation on a fractional basis are very similar, the values of both do not coincide, and the former is always less than the latter for each of the treatment conditions. From this result, the relaxation of stress accompanying adsorption appears to be faster than the corresponding moisture content change. Thus, the discrepancy of $N(t)$ and $R(t)$ by Eqs.(1) and (2) given in the previous paper,[10] would seem to be due to the remarkable decrease of the cohesion between cellulose molecular chains and internal stresses arising from the moisture gradients.

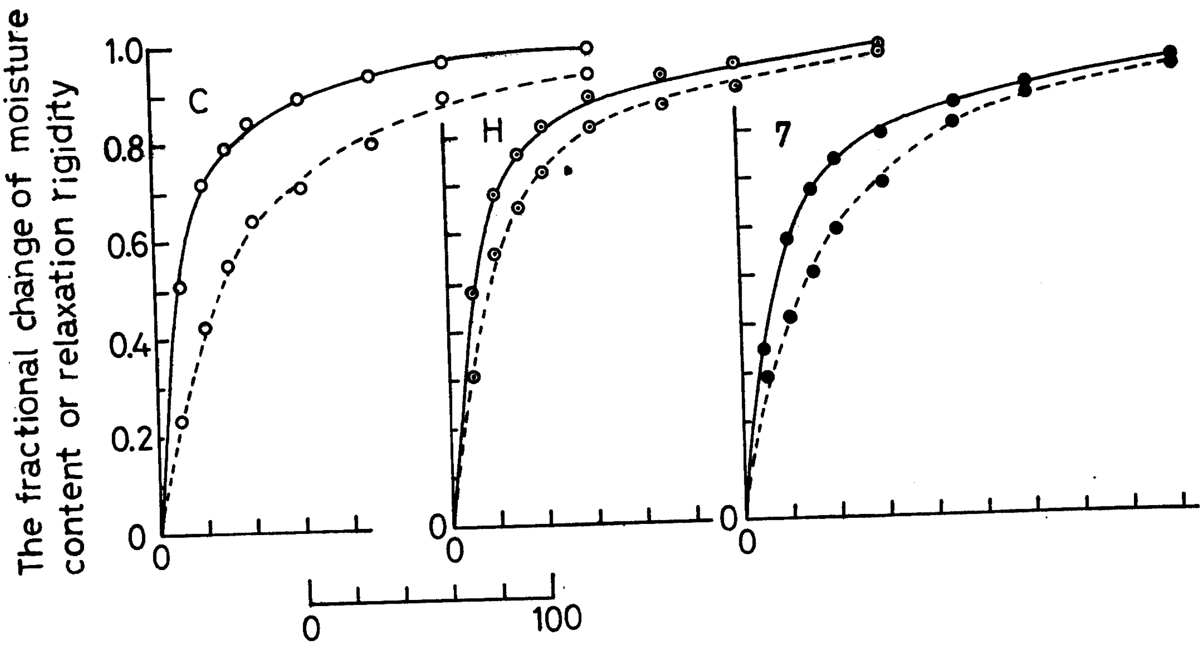

Fig. 7 Comparisons of the fractional change of moisture content (the dotted line) and relaxation rigidity (the solid line), obtained by equations (1) and (2) in the previous paper.[10] The number and the symbols in this figure are the same as in Fig. 1.

Now when the water molecules break the hydrogen bond, which links the adjacent hydroxyl groups in the amorphous regions, the reaction is assumed to go by the following scheme:

$$\text{water molecules} + \text{hydroxyl groups linked with hydrogen bonding} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{broken bonds}$$

(free hydroxyl groups) + hydroxyl groups

satisfied by water molecules·········(2)

where $k_1$ and $k_2$ are the rates of the forward and reverse reactions, respectively. In the case where controls the rate of stress relaxation, it is possible to make assumption that the reverse reaction occurs in such a manner that the hydrogen bonds are formed in stress-free positions only and therefore do not affect the stress decay. This reaction follows the first order one, and it can be expressed mathematically by

$$-d(B_t - B_f)/dt = k(B_t - B_f), \cdots\cdots\cdots (3)$$

where $B_t$ is the total number of the hydrogen bonds linking between adjacent chain molecules remaining unbroken at time t, $B_f$ is the number of these bonds not available for scission, and k is the rate of the forward reaction considering the initial vapor pressure to be constant. When the total number of hydrogen bonds at $t=0$ is $B_0$, integrating Eq. (3) under this condition,

$$B_t = (B_0 - B_f)\exp(-kt) + B_f. \cdots\cdots\cdots (4)$$

In order to relate the rate of the bond scission to the rate of stress relaxation, the additional assumption must be made that the relaxation modulus E(t) and the relaxation rigidity G(t) at the time t are proportional to the number of the bonds remaining unbroken:

for example, in the case of relaxation modulus E(t),

$E(t) \propto B_t$.········(5)

Similarly at t=0

$E(0) \propto B_0$,········(6)

and at $t=\infty$

$E(\infty) \propto B_\infty$.········(7)

Then, combining Eqs.(4), (5), (6), and (7), and dividing by E(0), Eq.(4) becomes

$$\frac{E(t)}{E(0)}=\left\{1-\frac{E(\infty)}{E(0)}\right\}\exp(-kt)+\frac{E(\infty)}{E(0)}\cdot\text{········(8)}$$

Eq.(8) can be furthermore rewritten as follows:

$$\frac{E(0)-E(t)}{E(0)-E(\infty)}=1-\exp(-kt).\text{········(9)}$$

The following expression for moisture content changes is obtained, in which the rate of reaction k is equal to that of the stress relaxation.

$$\frac{M(t)-M(0)}{M(\infty)-M(0)}=1-\exp(-kt)\text{········(10)}$$

where M(0), M(∞), and M(t) are the moisture content at the time t=0, equilibrium, and t after the introduction of wet air, respectively.

Substituting Eq.(10) into Eq.(9), there results

$$E(t)=E(0)-\frac{M(t)-M(0)}{M(\infty)-M(0)}\left\{E(0)-E(\infty)\right\}.\text{········(11)}$$

From this equation, the stress relaxation curves during adsorption without the effect of the internal stresses due to the moisture gradients etc., may be evaluated with the change of moisture content.

The stress relaxation curves obtained by Eq.(11) (represented by the solid line) and the observed curves (represented by the dotted line) are shown in Fig.8

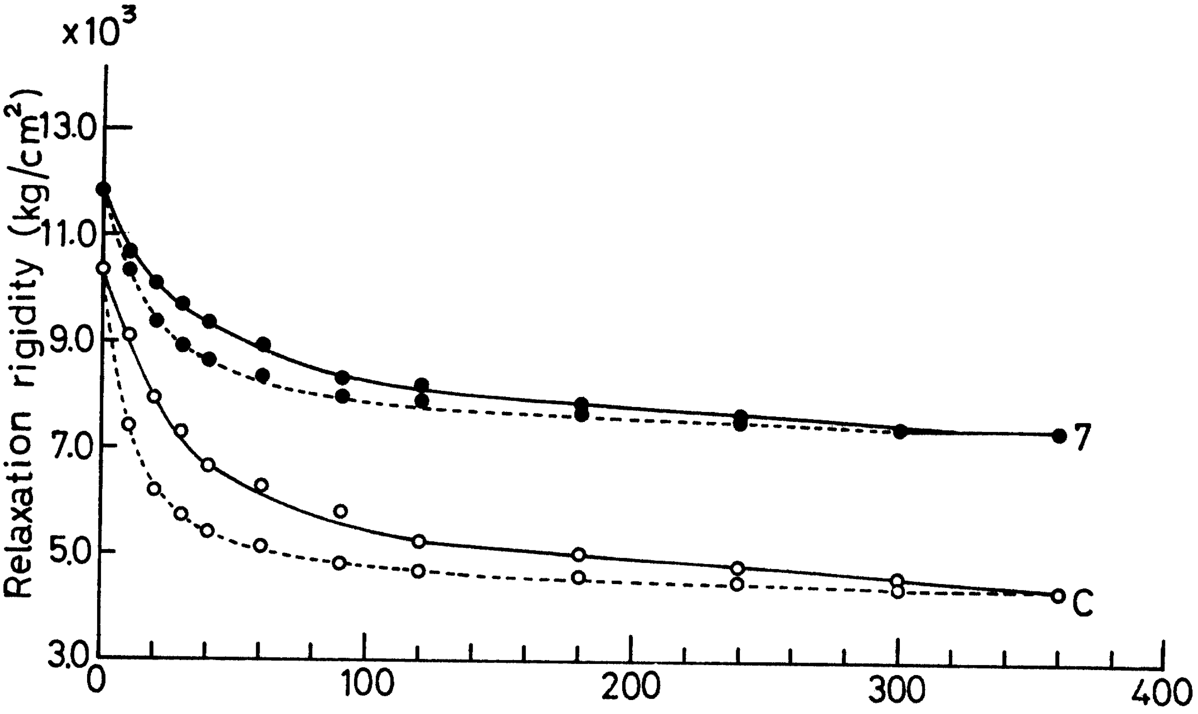

Fig. 8 The relationship between the observed stress relaxation curves in torsion (the dotted line) and those obtained by equation (12) (the solid line). The number and the symbol are the same as shown in Fig. 1.

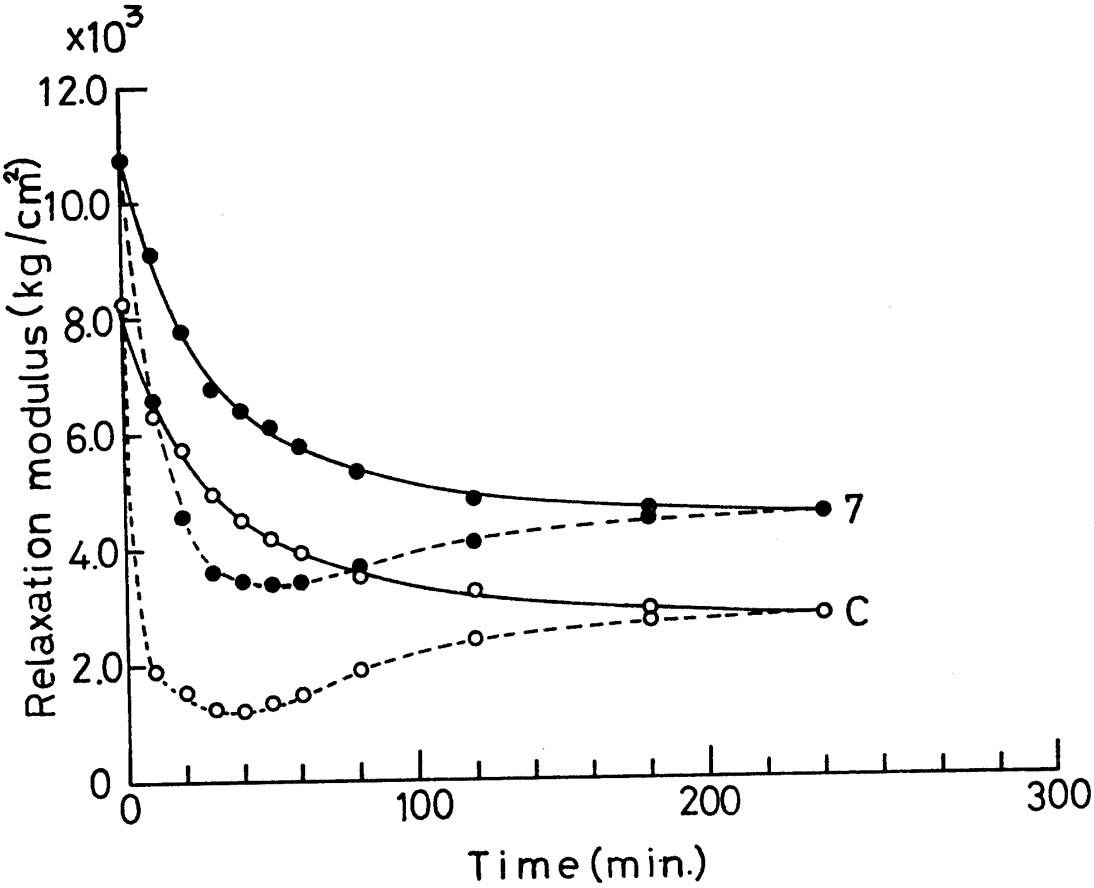

Fig. 9 The relationship between the observed stress relaxation curves in bending (the dotted line) and those obtained by equation (12) (the solid line). The number and the symbol are the same as shown in Fig. 1.

for torsion, and in Fig.9 for bending. From these figures, it is found that the difference between both curves (the solid and the dotted lines) becomes less with decreasing the swelling by water adsorption, and especially in torsion the curve obtained by Eq. (11) almost coincides with the observed one under the treating time of 7 hours, as compared with the control. Similar tendency is recognized in bending. Thus, even in the case of torsion, in which the distribution of the shearing stress within specimen is not uniform, but is symmetrical to the axis of torsion, the measured stress relxation curves become lower than the theoretical ones on the basis of the assumption mentioned above, as if the effects of the internal stresses due to the moisture gradients on the stress relaxation do not exist at the initial and final stages of adsorption. Accordingly, the effects are unable to deny, and the difference between both curves should be taken as the index of the effects of the internal stresses arising from the moisture gradients on the stress relaxation. It is assumed that the characteristic behaviors of the stress relaxation in bending are based on the following reasons; (1) the difference of swelling between the surface layer and interior layer of beam, (2) that of the relaxation behavior under compressive and tensile stresses, and (3) the effects of the resultant of the internal stresses due to the moisture gradients and bending stresses corresponding to the external force. To solve these problems quantitatively, the following must be known: (1) the distribution of moisture content, (2) the distribution of modulus of elasticity in bending perpendicular to the grain (radial direction) through the depth of beam, (3) the stress relaxation under compressive and tensile stresses, (4) the amounts of moisture adsorbed under stresses, and (5) the coefficient of moisture swelling. It is difficult to measure for some of them. Therefore, at present it is impossible to explain these phenomena quantitatively. However, since the total amounts of relaxation in torsion are related linearly to the those total swelling, and the observed values of the stress relaxation are always lower than obtained by Eq.(11) in either of bending and torsion, and the difference between both curves decreases with decreasing the swelling from dryness to saturation of moisture, it is concluded that the remarkable relaxation of stress during adsorption and the characteristic behavior of relaxation in bending are caused mainly by the internal stresses due to the moisture gradients.

The exact explanationd for this problem will be left over for deliberation later.

## Acknowledgement

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**要旨**：吸湿過程における木材の応力緩和挙動に及ぼす水分傾斜に基づく内部応力の影響を検討するために，種々の程度にホルマール化処理を施したヒノキ材 (Table 1) について曲げと捩りの応力緩和を測定した。

得られた主な結果を要約すると次のとおりである。

(1) 曲げと捩りのいずれの場合にも，ホルマール化処理を施した材と未処理材の吸湿にともなう応力緩和挙動は非常によく類似しているが，緩和弾性率や剛性率の値には差がある (Figs.3と4)。

(2) 捩りの場合，乾燥状態から飽湿状態まで吸湿させたときの全緩和量と全膨潤率との間には直線関係が認められた (Fig.6)。

(3) 前報10) で示した式 (1) と (2) を用いて求めた緩和剛性率の変化割合 N(t) と含水率のそれ R(t) との比較から，両曲線の傾向は非常によく類似しているが，値はつねに N(t) の方が R(t) よりも大なること，ならびに，両曲線間の差は抗膨潤能 (A.E.) が大なるほど少なくなることなどを見出した (Fig.7)。

(4) 非晶領域にある隣接鎖状分子間の水素結合の切断速度が吸湿過程の応力緩和速度を支配するという仮定に基づいて得られた式(12)から推定した応力緩和曲線と実測した緩和曲線との比較から，吸湿過程における応力の緩和は水分傾斜に基づく内部応力に影響されていることを明らかにした。

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