

A Consideration on Stress Relaxation of Wood Cell Wall*

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Abstract—The experiments on tensile stress relaxation in radial direction for wet Hinoki, Hoonoki, Akamatsu, Keyaki and Shirakashi were carried out at the stress levels of 30 and 80 % and at the temperatures of 20, 35, 50 and 65°C. The relaxation curves of cell wall were estimated and were analyzed by TOBOLSKY-EYRING reaction rate theory. The results were summarized as follows:

(1) The stress relaxation curves of wood and cell wall were almost linear up to ten minutes at all temperatures and stress levels.

(2) Assuming that the stress acting on cell wall decays completely, the values of 73 and 61 kcal/mole as the free energy of activation in the relaxation process were obtained at the stress levels of 30 and 80 % respectively. On the other hand, assuming that the stress acting on cell wall does not relax completely and converges to a definite value, the values of 36 and 32 kcal/mole were obtained at the stress levels of 30 and 80 % respectively. The latter values were comparable to those of cotton plied yarns calculated by FUJITA *et al.*

(3) Considering that the average distance λ is constant, the number of parallel flowing units in a square cm of cross section perpendicular to the stress N was proportional to the stress and was inversely proportional to the temperature. These results show that the arrangement of parallel flowing units becomes better to the direction of the stress applied with increasing stress and with decreasing temperature.

I. Introduction

There are several studies on non-linear viscoelastic behaviors of wood¹⁻⁷⁾. For instance, KUNESH investigated the stress relaxation of yellow poplar at two strain levels above the proportional limit¹⁾. KHUKHRYANSKII studied the stress relaxation and the creep of wood in compression and reported that the relaxation curve of wood in parallel to the grain above the limit of plastic flow σ_{pf} was analogous to that below σ_{pf} , whereas the creep curve above σ_{pf} differed considerably from that below σ_{pf} ²⁾. KING studied short-term creep of wood over wide range of deformation and reported that the creep-stress level relation is characterized by a two-stage relationship consisting of a linear regression up to the threshold of set and a curvilinear regression thereafter³⁾. BACH *et al.*⁵⁾ investigated the creep and the creep recovery at the stresses from 20 to 80 % of strength and showed that the creep compliance are represented by regression equations as functions of moisture content, temperature, stress level, and time. KINGSTON *et al.*^{4,6,7)} studied the bending creep of wood over wide range of deformation and applied TOBOLSKY-EYRING reaction rate theory to the results, and obtained the values of about 30 kcal/mole for the activation free energy.

In this paper, the experiments on stress relaxation of wood were performed at the temperatures of 20 to 65°C and at the stress levels of 30 and 80 %, and the relaxation curves of cell wall were estimated. Furthermore, TOBOLSKY-EYRING reaction rate theory⁸⁾, one of the non-linear viscoelastic theories, was applied to the results.

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II. Experimental

Heartwoods of Hinoki (*Chamaecyparis obtusa* ENDL.), Hoonoki (*Magnolia obovata* THUNB.), Akamatsu (*Pinus densiflora* SIEB. et ZUCC.), Keyaki (*Zelkova serrata* MAKINO) and Shirakashi (*Quercus Myrsinaefolia* BL.) treated for 10 hr. in hot water at 65°C were used as samples for the measurements of tensile strength and stress relaxation. The shape and the dimension of the sample are shown in Fig. 1. Instron type tensile testing instrument (TOM 5000X produced by Shinkoh Ltd.) was used for the measurements of strength and stress relaxation. The tensile stress was applied to the radial direction of the sample. The rate of elongation was 2 mm per min. and the gauge length was 5 cm. The experiments were performed in water at 20, 35, 50 and 65°C. The temperature of the sample was controlled by circulating water through the jacket of the water bath to keep the temperature of the sample constant during the measurement.

The stress relaxation at two initial stresses, 30 and 80 % of the tensile strength, were measured up to 10 min. for two samples and up to 25-200 min. for one sample.

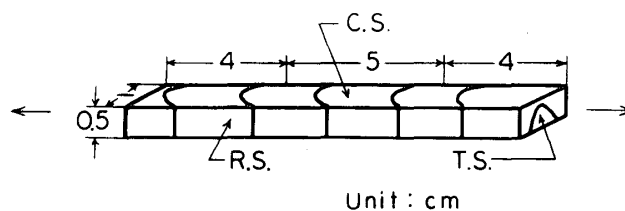


Fig. 1. Shape and dimension of test specimen. R.S., C.S. and T.S. show radial-, cross- and tangential-section, respectively. Arrows show the direction of tension.

III. Results

The tensile strength, the proportional limit and the specific gravity of samples at various temperatures are shown in Table 1. The values of the coefficient of variation for the tensile strength were smaller than 8.4 %. The stress relaxation curves of Hinoki, Hoonoki, Akamatsu, Keyaki and Shirakashi at respective temperatures and stress levels are shown in Figs. 2 to 6, respectively. The stress decreased linearly against the logarithm of time in longer time region.

Table 1. Tensile strength, proportional limit and specific gravity of five species at various temperatures.

| Species | Temp. (°C) | Number | σ_t | | | σ_p/σ_t (%) | Specific gravity |
|----------|------------|--------|-----------------------------|-------------------------------|----------|-------------------------|------------------|
| | | | m. (kg/cm ²) | s.d. (kg/cm ²) | c.v. (%) | | |
| Hinoki | 20 | 5 | 43.8 | 1.4 | 3.2 | 37 | 0.339 |
| | 35 | 5 | 39.4 | 1.4 | 3.6 | 39 | 0.339 |
| | 50 | 5 | 37.3 | 0.8 | 2 | 36 | 0.333 |
| | 65 | 5 | 31.3 | 2.2 | 7.0 | 36 | 0.332 |
| Hoonoki | 20 | 5 | 67.0 | 3.7 | 5.5 | 33 | 0.400 |
| | 35 | 5 | 59.1 | 1.1 | 1.9 | 34 | 0.392 |
| | 50 | 5 | 53.1 | 2.6 | 4.9 | 33 | 0.402 |
| | 65 | 5 | 44.7 | 2.2 | 4.9 | 31 | 0.399 |
| Akamatsu | 20 | 5 | 54.5 | 4.6 | 8.4 | 42 | 0.518 |
| | 35 | 5 | 51.8 | 1.9 | 3.7 | 41 | 0.521 |
| | 50 | 5 | 42.5 | 3.2 | 7.5 | 40 | 0.506 |
| | 65 | 5 | 37.8 | 1.2 | 3.2 | 34 | 0.522 |

| | | | | | | | |
|------------|----|---|------|-----|-----|----|-------|
| Keyaki | 20 | 5 | 108 | 4 | 4 | 28 | 0.586 |
| | 35 | 5 | 90.1 | 1.9 | 2.1 | 29 | 0.575 |
| | 50 | 5 | 79.4 | 3.1 | 3.9 | 24 | 0.588 |
| | 65 | 5 | 62.9 | 2.4 | 3.8 | 22 | 0.584 |
| Shirakashi | 20 | 5 | 119 | 5 | 4 | 26 | 0.678 |
| | 35 | 5 | 95.3 | 4.9 | 5.1 | 26 | 0.673 |
| | 50 | 5 | 84.4 | 3.3 | 3.9 | 23 | 0.674 |
| | 65 | 5 | 64.8 | 2.5 | 3.9 | 24 | 0.671 |

σ_t : Tensile strength, σ_p : Proportional limit,

Specific gravity: Oven-dried weight divided by wet volume,

m.: mean value, s.d.: standard deviation, c.v.: coefficient of variation.

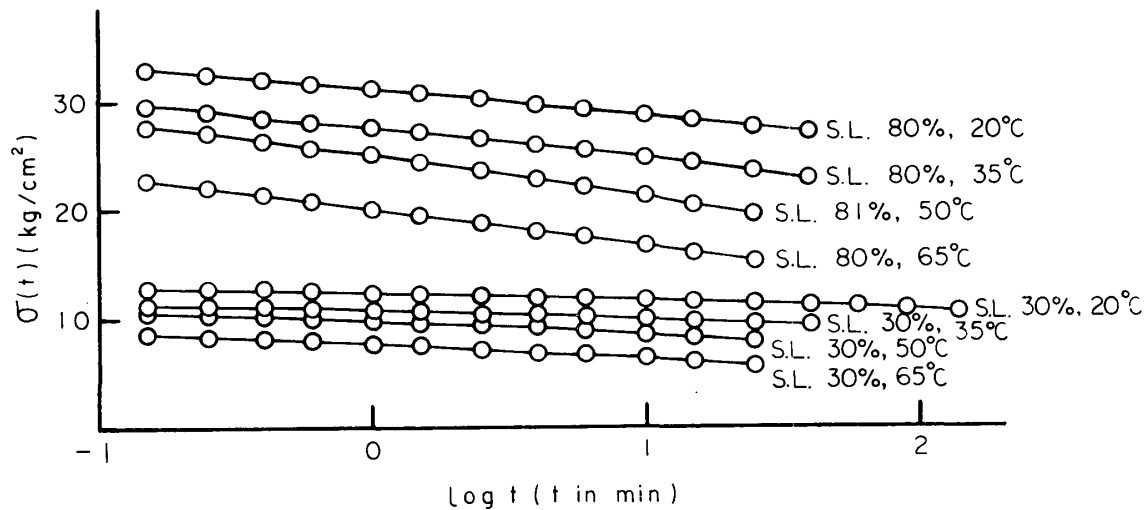


Fig. 2. Stress relaxation curves of Hinoki at respective stress levels and temperatures.

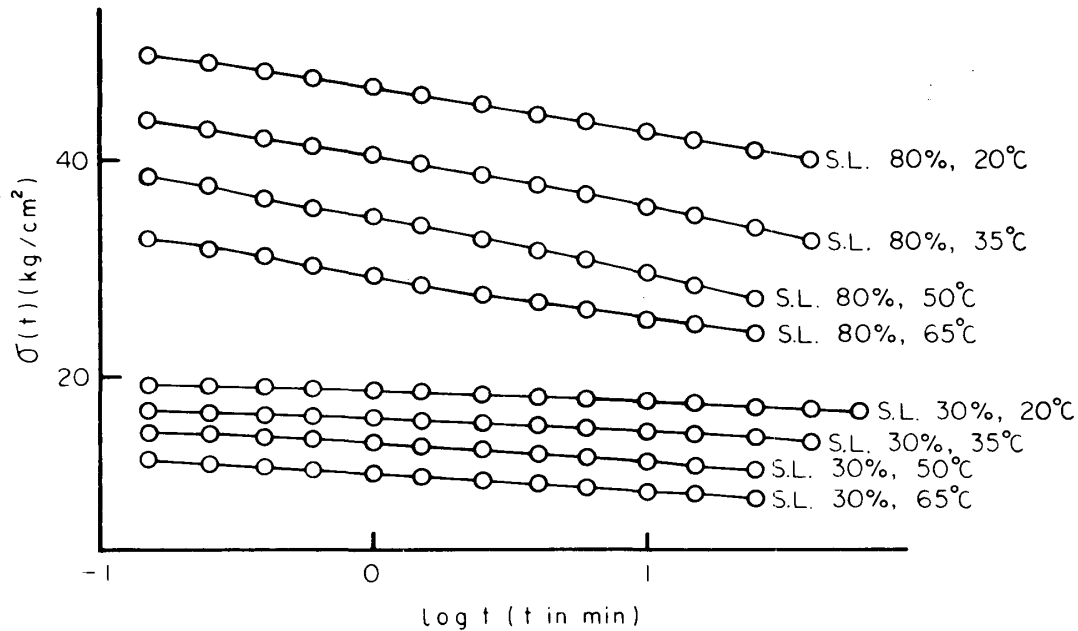


Fig. 3. Stress relaxation curves of Hoonoki at respective stress levels and temperatures.

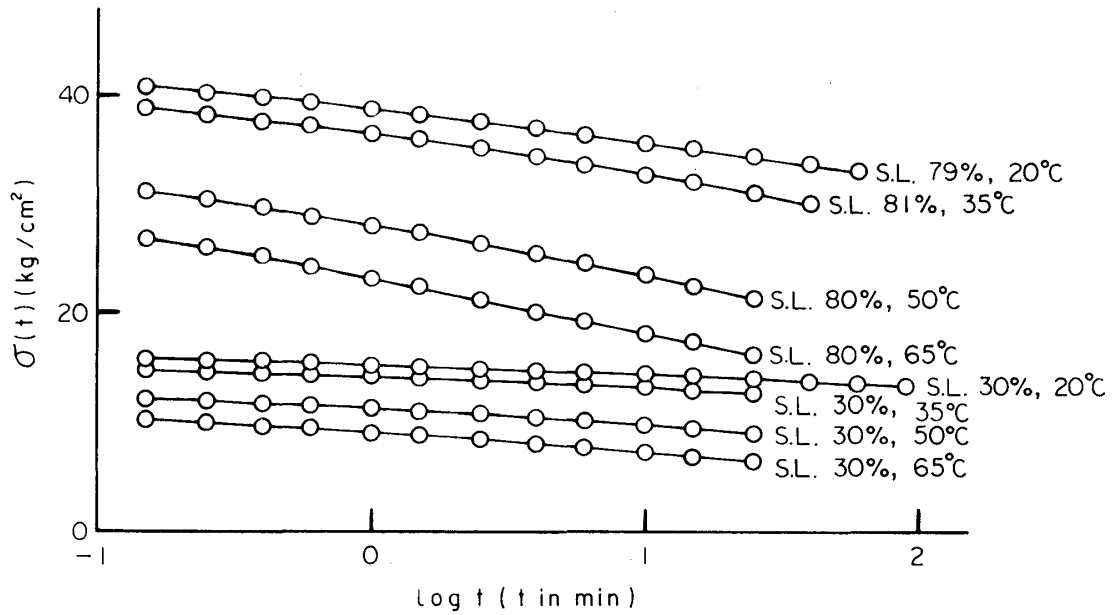


Fig. 4. Stress relaxation curves of Akamatsu at respective stress levels and temperatures.

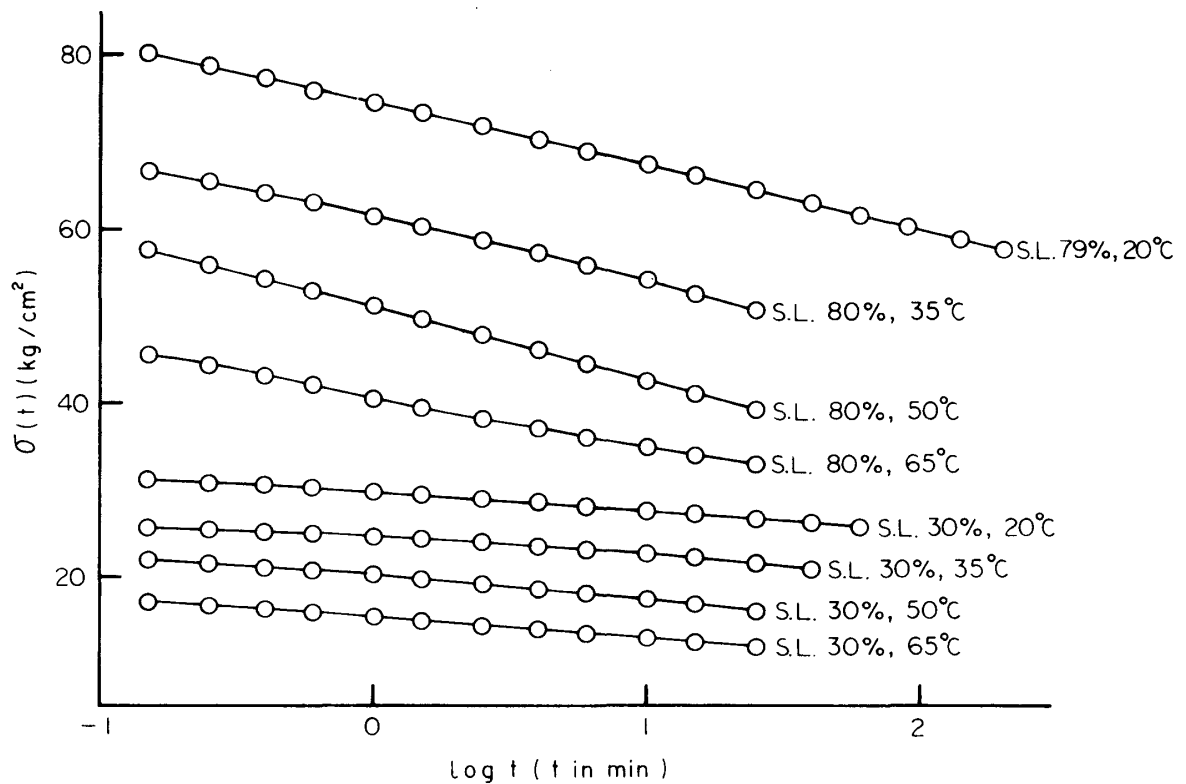


Fig. 5. Stress relaxation curves of Keyaki at respective stress levels and temperatures.

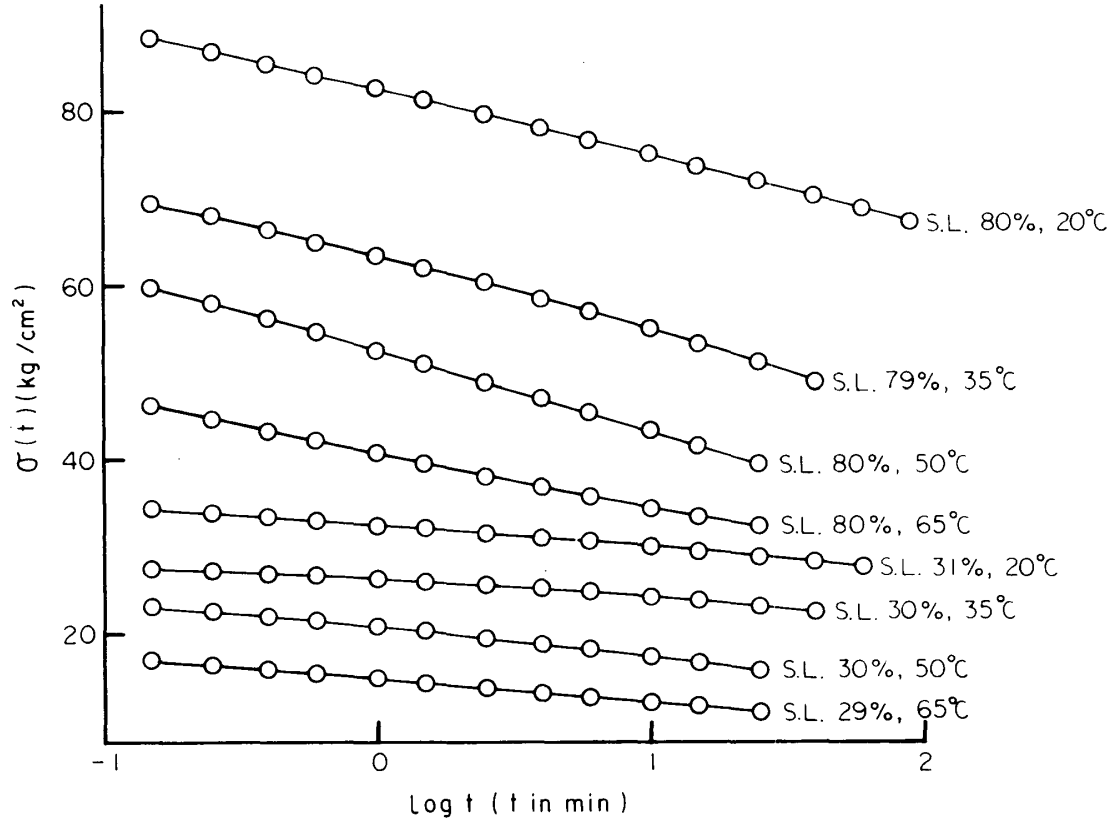


Fig. 6. Stress relaxation curves of Shirakashi at respective stress levels and temperatures.

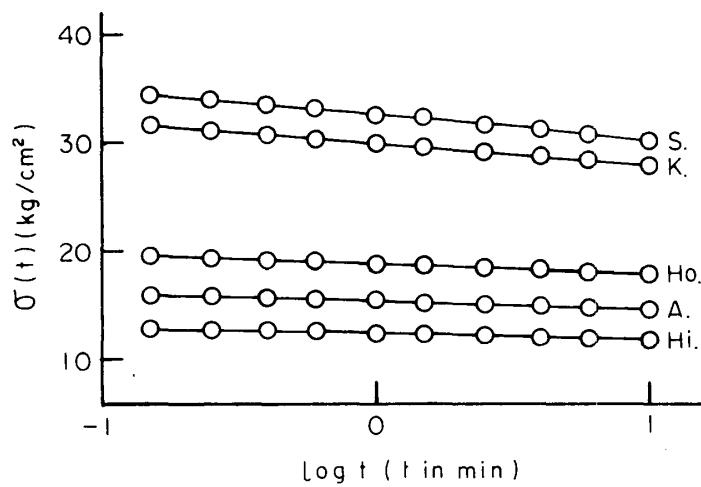


Fig. 7. Stress relaxation curves of five species at 20°C and at stress level of 30%. Hi., Hinoki; Ho., Hoonoki; A., Akamatsu; K., Keyaki; S., Shirakashi.

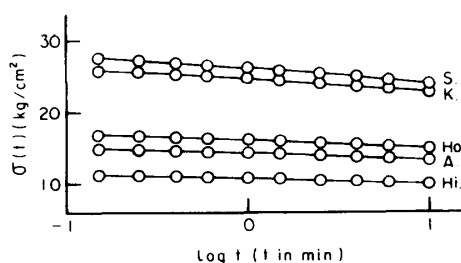


Fig. 8. Stress relaxation curves of five species at 35°C and at stress level of 30%. Symbols are same as those in Fig. 7.

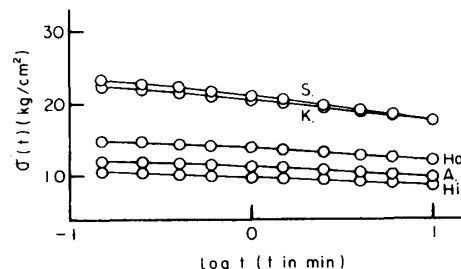


Fig. 9. Stress relaxation curves of five species at 50°C and at stress level of 30%. Symbols are same as those in Fig. 7.

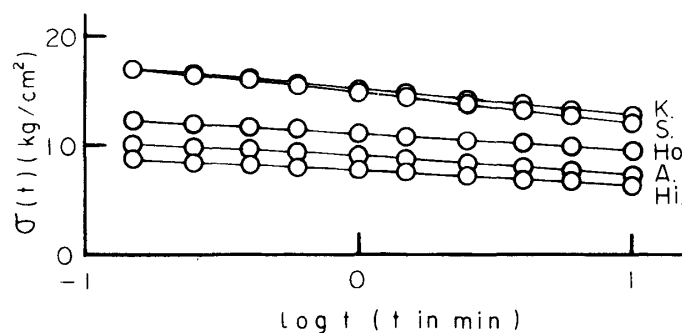


Fig. 10. Stress relaxation curves of five species at 65°C and at stress level of 30%. Symbols are same as those in Fig. 7.

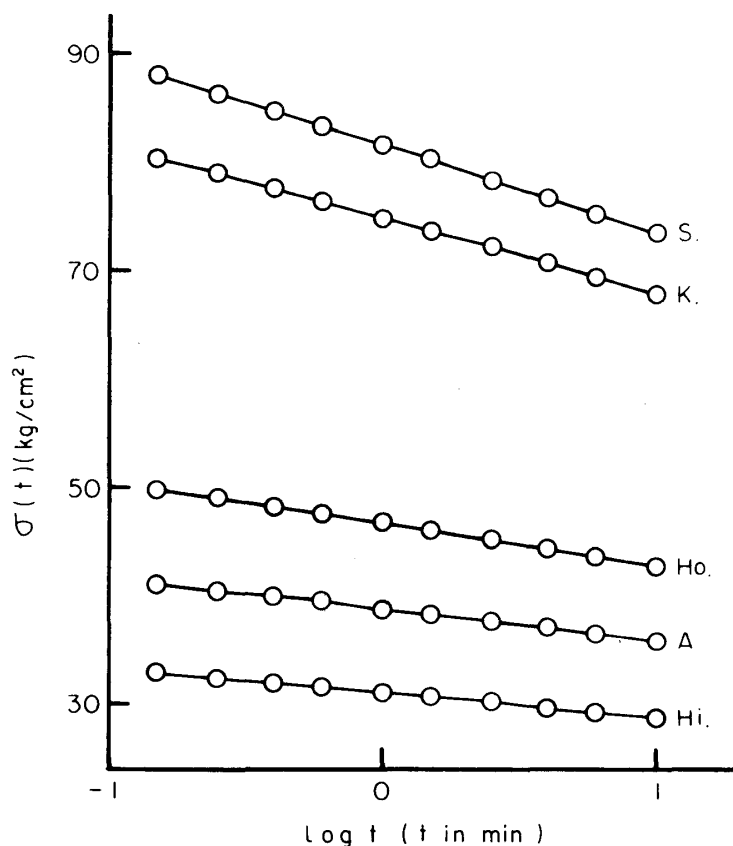


Fig. 11. Stress relaxation curves of five species at 20°C and at stress level of 80%. Symbols are same as those in Fig. 7.

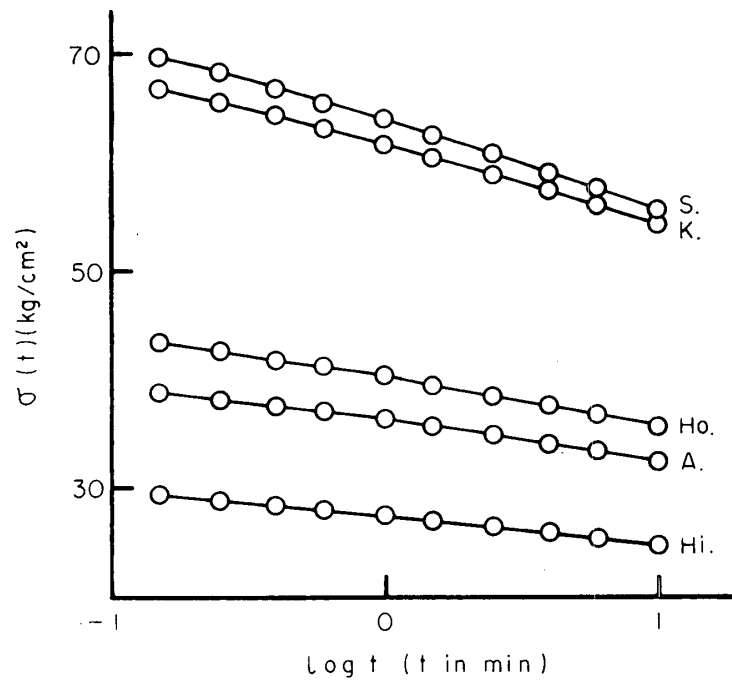


Fig. 12. Stress relaxation curves of five species at 35°C and at stress level of 80%. Symbols are same as those in Fig. 7.

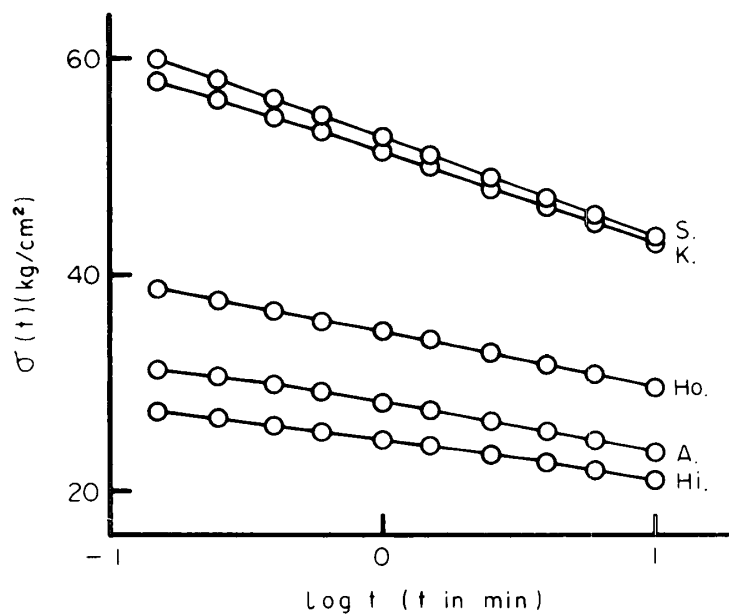


Fig. 13. Stress relaxation curves of five species at 50°C and at stress level of 80%. Symbols are same as those in Fig. 7.

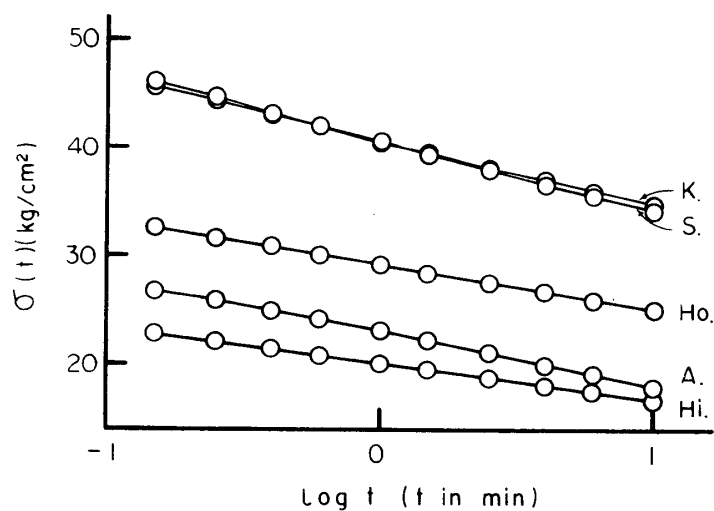


Fig. 14. Stress relaxation curves of five species at 65°C and at stress level of 80%. Symbols are same as those in Fig. 7.

Table 2. Specific gravity and error of initial strain for stress relaxation test of five species at various temperatures and at stress levels of 30 and 80%.

| Stress level m. (%) | Temp. (°C) | Species | Number | Specific gravity m. | Error ($t=10$ min.) m. (%) |
|------------------------|------------|---------|--------|------------------------|--------------------------------|
| 30 | 20 | Hi. | 3 | 0.337 | 2 |
| 30 | 20 | Ho. | 3 | 0.400 | 4 |
| 30 | 20 | A. | 3 | 0.528 | 4 |
| 31 | 20 | K. | 3 | 0.585 | 2 |
| 31 | 20 | S. | 3 | 0.678 | 4 |
| 30 | 35 | Hi. | 3 | 0.335 | 3 |
| 30 | 35 | Ho. | 3 | 0.398 | 4 |
| 30 | 35 | A. | 3 | 0.529 | 5 |
| 30 | 35 | K. | 3 | 0.590 | 5 |
| 30 | 35 | S. | 3 | 0.672 | 8 |
| 30 | 50 | Hi. | 3 | 0.344 | 4 |
| 30 | 50 | Ho. | 3 | 0.398 | 5 |
| 30 | 50 | A. | 3 | 0.520 | 7 |
| 30 | 50 | K. | 3 | 0.579 | 7 |
| 30 | 50 | S. | 3 | 0.666 | 10 |
| 30 | 65 | Hi. | 3 | 0.334 | 4 |
| 30 | 65 | Ho. | 3 | 0.400 | 5 |
| 30 | 65 | A. | 3 | 0.522 | 8 |
| 30 | 65 | K. | 3 | 0.575 | 6 |
| 29 | 65 | S. | 3 | 0.667 | 8 |
| 80 | 20 | Hi. | 3 | 0.338 | 1 |
| 80 | 20 | Ho. | 3 | 0.392 | 2 |
| 80 | 20 | A. | 3 | 0.535 | 2 |
| 80 | 20 | K. | 3 | 0.590 | 2 |
| 80 | 20 | S. | 3 | 0.673 | 4 |

| | | | | | |
|----|----|-----|---|-------|---|
| 80 | 35 | Hi. | 3 | 0.339 | 1 |
| 79 | 35 | Ho. | 3 | 0.391 | 2 |
| 80 | 35 | A. | 3 | 0.510 | 2 |
| 80 | 35 | K. | 3 | 0.579 | 3 |
| 79 | 35 | S. | 3 | 0.670 | 4 |
| 80 | 50 | Hi. | 3 | 0.334 | 1 |
| 80 | 50 | Ho. | 3 | 0.401 | 2 |
| 81 | 50 | A. | 3 | 0.487 | 3 |
| 80 | 50 | K. | 3 | 0.576 | 2 |
| 80 | 50 | S. | 3 | 0.667 | 3 |
| 80 | 65 | Hi. | 3 | 0.335 | 4 |
| 80 | 65 | Ho. | 3 | 0.400 | 1 |
| 80 | 65 | A. | 3 | 0.532 | 3 |
| 80 | 65 | K. | 3 | 0.576 | 1 |
| 80 | 65 | S. | 3 | 0.671 | 2 |

Hi. : Hinoki, Ho. : Hoonoki, A. : Akamatsu, K. : Keyaki, S. : Shirakashi,
 Specific gravity: Oven-dried weight divided by wet volume,
 m. : mean value, Error: Error of initial strain at 10 min.

The relaxation curves for five species shown by the average value are illustrated in Figs. 7 to 14. The curves were almost linear up to 10 min. at all temperatures and stress levels. The error of the initial strain resulted from strain recovery in load cells during the stress relaxation of wood is given in Table 2. The error was in the range of 2 to 10 % at the stress level of 30 % and in 1 to 4 % at the stress level of 80 %.

In order to apply TOBOLSKY-EYRING reaction rate theory to the results, the stress acting on cell wall should be calculated. It is reported that the relationship between relaxation modulus $E(t)$ and specific gravity ρ is represented by the following equation⁹⁾.

$$\log E(t) = n \log \rho + C(t), \quad (1)$$

where n and $C(t)$ are constants at given time. As the relaxation modulus is defined as a ratio of stress $\sigma(t)$ to initial strain ϵ_0 , the following relation can be derived.

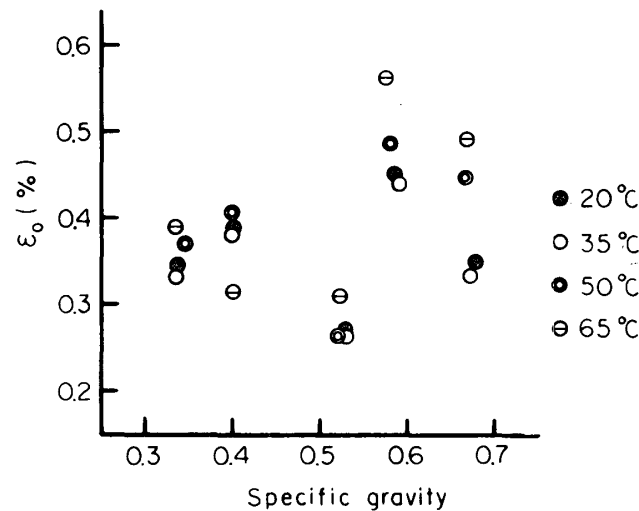


Fig. 15. Relation between strain at stress level of 30% and specific gravity at various temperatures.

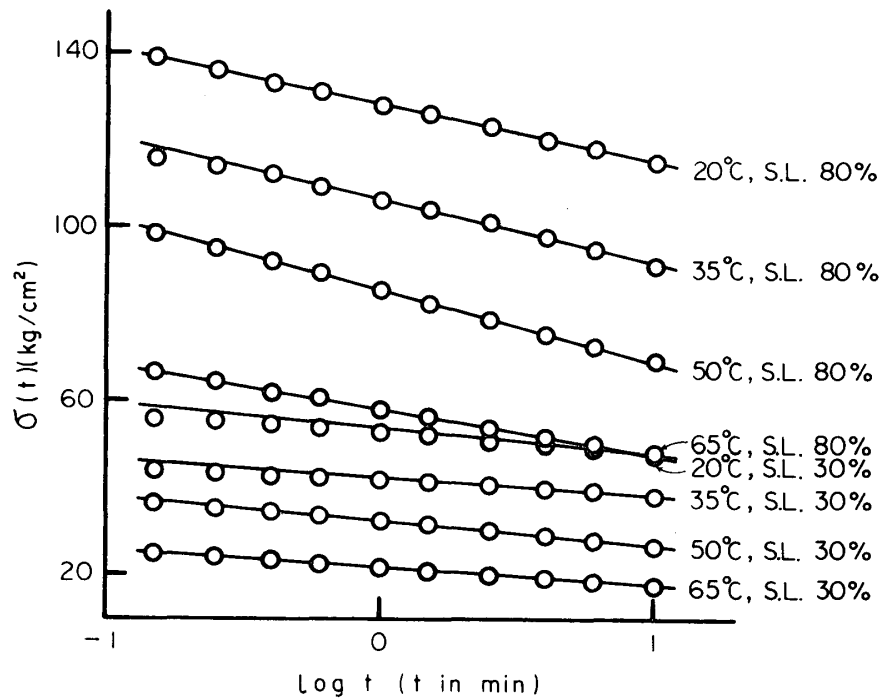


Fig. 16. Stress relaxation curves of cell wall at respective stress levels and temperatures.

$$\log \sigma(t) = n \log \rho + (C(t) + \log \varepsilon_0). \quad (2)$$

Here, as shown in Fig. 15, $\log \varepsilon_0$ which is a function of specific gravity ρ can be considered constant. From the experimental results, the regression lines for $\log \sigma(t)$ vs. $\log \rho$ curves were calculated by the method of least squares. The correlation coefficients were in the range of 0.712 to 0.891. The value of the stress acting on cell wall $\sigma(t)$ was calculated by substituting 1.05 as the specific gravity of cell wall in wet condition¹⁰⁾ into the regression lines. The stress relaxation curves of cell wall calculated in this manner are shown in Fig. 16. The curves were linear for first 10 min. at all temperatures and stress levels. From the figure, it is obvious that linear part of the curve shifts to shorter time region as temperature and stress level increase.

Incidentally, the tensile strength of cell wall in the transverse direction calculated from the initial stresses were 193, 156, 136 and 94.3 kg/cm² at 20, 35, 50 and 65°C, respectively.

IV. Discussion

The relaxation curves of cell wall can be represented schematically as Fig. 17A. At the

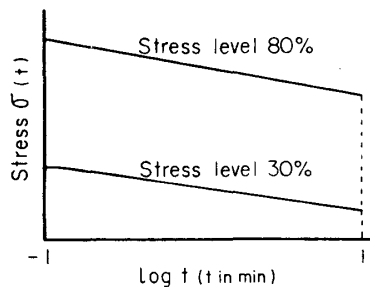


Fig. 17A. Schematic stress relaxation curves of cell wall.

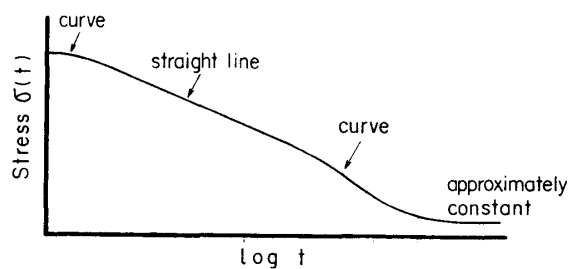


Fig. 17B. Schematic stress relaxation curve of wood.

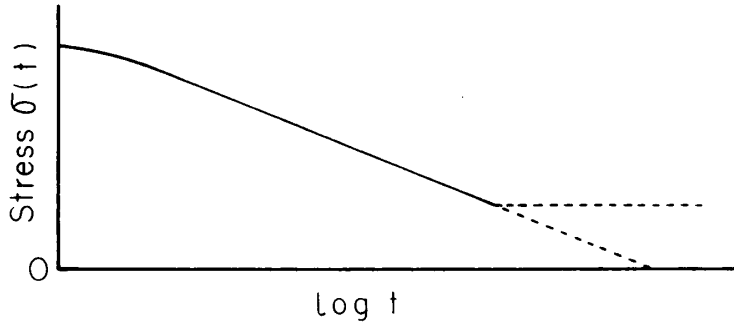


Fig. 17C. Schematic stress relaxation curve of cell wall.


 Fig. 18. Mechanical model for cell wall when stress relaxes completely. G is elastic modulus and η is viscosity.

stress level of 30 % a curve is concave to the time axis at first and then is followed by a straight line, whereas at 80 % a curve is a straight line from the beginning. Furthermore, the relaxation curves of wood^{11,12,13)} can be represented schematically as Fig. 17B. However, it is still in a question whether the stress decays completely or not in longer time region. From these, it may be considered that the relaxation curve of cell wall is curvilinear at first and then followed by a straight line and finally converges to a finite value or relaxes linearly as shown in Fig. 17C.

Now, the authors shall analyze the relaxation curves of cell wall by TOBOLSKY-EYRING reaction rate theory⁸⁾. If the stress relaxes completely, the process of stress relaxation can be represented by the mechanical model as shown in Fig. 18 in which the dash pot has EYRING's viscosity. The authors shall assume that the observed stress decay is mainly due to the slippage of cellulose chains caused by breaking of secondary bonds and that the stress decay due to segmental motion cannot be observed since it is accomplished very rapidly or the stress acting on segment is small. Furthermore, the authors shall assume that the primary bonds in a cellulose chain are not broken within the time range measured. Then, the equation of motion for the relaxation of secondary network units is given as

$$\frac{d\gamma}{dt} = \frac{1}{G} \cdot \frac{d\sigma}{dt} + A \sinh B\sigma, \quad (3)$$

where $d\gamma/dt$ is the rate of strain, $d\sigma/dt$ is the rate of stress, and G is the elastic modulus of secondary network units. A and B are defined as

$$A = 2n\lambda \frac{kT}{h} \exp(-\Delta F^\ddagger/RT), \quad (4)$$

$$B = \frac{\lambda}{2NkT}, \quad (5)$$

where n the number of flowing units per centimeter in the direction of stress in series, N the number of parallel flowing units in a square cm of cross section perpendicular to the stress, λ the average distance projected in the direction of stress between equilibrium positions of each flowing unit in the relaxation process, ΔF^\ddagger the free energy of activation per one mole for movement of each flowing unit from one equilibrium position to the next, k BOLTZMANN's constant, h PLANK's constant, R the gas constant, and T the absolute temperature. As $d\gamma/dt=0$ in the case of stress relaxation,

$$\tanh(B\sigma/2) = \tanh(B\sigma^0/2) \exp(-ABGt), \quad (6)$$

where σ^0 is the initial stress. If $B\sigma/2 \gg 1$, $\sigma^0 > \sigma$ and $ABGt \ll 1$, the next approximate equation is obtained.

$$\sigma = -\frac{2.303}{B} \log \frac{ABG}{2} - \frac{2.303}{B} \log t. \quad (7)$$

The slope and the intercept of σ vs. $\log t$ curve are given by $-\frac{2.303}{B}$ and $-\frac{2.303}{B} \log \frac{ABG}{2}$ respectively. In Fig. 19¹⁴⁾, σ/σ^0 is plotted against $\log ABGt$ for various values of the parameter

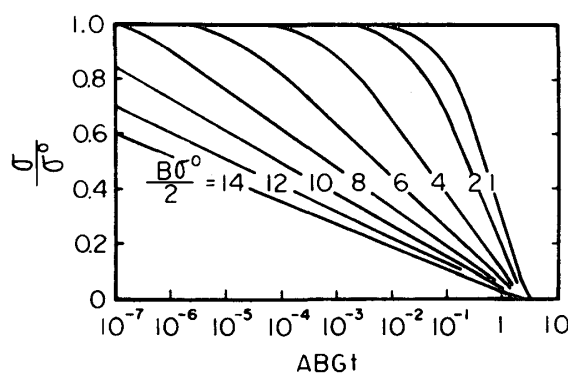


Fig. 19. Hyperbolic tangent decay curves for values of $B\sigma^0/2$.

$B\sigma^0$ according to equation 6. The value of B was calculated from the slope a of the linear portion in the relaxation curve of cell wall, and the value of the intercept k' was evaluated from the stress at 1 min. in the straight line. These results are shown in Table 3. Furthermore, B is plotted against the absolute temperature T in Fig. 20. Since the value of B can be considered

Table 3. Values of molecular constants.

| Stress level % | Temp. °C | a kg/cm ² | B | | k' kg/cm ² | $B\sigma^0/2$ | $B\sigma(t)/2$ ($t=10$ min.) | $ABGt$ ($t=600$ sec.) |
|----------------|----------|---------------------------|---------------------|--|----------------------------|---------------|----------------------------------|---------------------------|
| | | | cm ² /kg | $\times 10^{-7}$ cm ² /dynes | | | | |
| 30 | 20 | - 5.8 | 0.40 | 4.1 | 53.5 | 12 | 9.5 | 9.6×10^{-7} |
| | 35 | - 4.2 | 0.55 | 5.6 | 42.4 | 13 | 11 | 1.2×10^{-7} |
| | 50 | - 5.7 | 0.40 | 4.1 | 32.3 | 8.0 | 5.5 | 3.0×10^{-3} |
| | 65 | - 4.0 | 0.58 | 5.9 | 21.6 | 8.0 | 5.0 | 3.0×10^{-3} |
| 80 | 20 | -13 | 0.18 | 1.8 | 128 | 14 | 11 | 1.2×10^{-7} |
| | 35 | -14.6 | 0.158 | 1.61 | 106 | 10 | 7.0 | 4.8×10^{-5} |
| | 50 | -16.7 | 0.138 | 1.41 | 85.3 | 7.6 | 5.0 | 7.8×10^{-3} |
| | 65 | -10.4 | 0.221 | 2.25 | 57.9 | 8.4 | 5.5 | 3.0×10^{-3} |

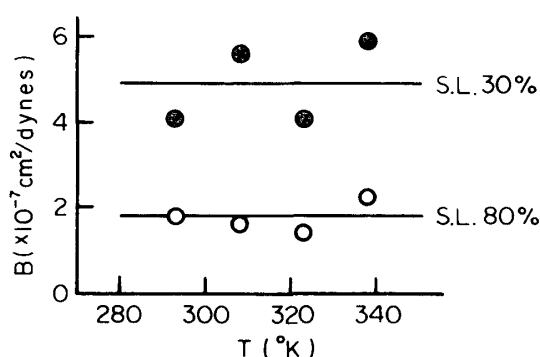


Fig. 20. Relation between the constant B and the absolute temperature T at two stress levels.

constant at each stress level independently of temperature, its average value \bar{B} was used as the value of B at each stress level. As $B = \lambda/2NkT$, if λ is unchanged regardless of both temperature and initial stress, N increases with increasing stress level when the temperature is fixed and decreases with increasing temperature when the stress level is fixed. The increase of N , which is the number of parallel flowing units in a square cm of cross section perpendicular to the stress, shows that the arrangement of parallel flowing units becomes better to the direction of the stress. The intercept k' is given by

$$k' = -\frac{2.303}{\bar{B}} \log \frac{ABG}{2}. \quad (8)$$

Substituting $\frac{n\lambda^2 \exp(-\Delta F^\ddagger/RT)}{Nh}$ into AB in equation 8 and using \bar{B} in stead of B , the following equation is derived.

$$k'\bar{B} + 2.303 \log G = -2.303 \log \frac{n\lambda^2}{2Nh} + \frac{\Delta F^\ddagger}{RT}. \quad (9)$$

Where, both $k'\bar{B}$ and $\log G$ are functions of temperature. Assuming that n is proportional to $1/T$, $n\lambda^2/2Nh$ can be considered constant since N is proportional to $1/T$. The value of ΔF^\ddagger which is the free energy of activation per one mole for movement of each flowing unit can be calculated from the slope of the straight line obtained by plotting the value of $k'\bar{B} + 2.303 \log G$ against $1/T^{15}$.

As it is considered that the relationship between stress and strain is linear at the stress level of 30 %, the elastic modulus of secondary network units G was calculated by the following equation.

$$G = \frac{\sigma^0}{\epsilon_0}, \quad (10)$$

where σ^0 is the initial stress acting on secondary network units in cell wall and corresponds to the total initial stress of cell wall, and ϵ_0 is the initial strain of secondary network units and equivalent to that of cell wall. The relation between the strain and the specific gravity at the

Table 4. Values of ϵ_0 , σ^0 and G .

| Stress level (%) | Temp. (°C) | ϵ_0 (%) | σ^0 (kg/cm ²) | G ($\times 10^4$ kg/cm ²) |
|------------------|------------|------------------|----------------------------------|--|
| 30 | 20 | 0.362 | 59.4 | 1.64 |
| | 35 | 0.351 | 45.8 | 1.30 |
| | 50 | 0.396 | 39.8 | 1.01 |
| | 65 | 0.414 | 28.3 | 0.684 |

Table 5. Molecular constants for stress relaxation of cell wall.

| Stress level (%) | Temp. (°C) | G ($\times 10^{10}$ dynes/cm ²) | \bar{B} ($\times 10^{-7}$ cm ² /dynes) | $k'\bar{B} + 2.303 \log G$ | $1/T$ ($\times 10^{-3}$ 1/°K) | ΔF^\ddagger (kcal./mole) |
|------------------|------------|--|--|----------------------------|--------------------------------|----------------------------------|
| 30 | 20 | 1.61 | 4.9 | 49.5 | 3.41 | 72.8 |
| | 35 | 1.28 | | 43.3 | 3.25 | |
| | 50 | 0.991 | | 39.0 | 3.10 | |
| | 65 | 0.671 | | 32.6 | 2.96 | |
| 80 | 20 | 1.61 | 1.8 | 46.5 | 3.41 | 60.8 |
| | 35 | 1.28 | | 42.3 | 3.25 | |
| | 50 | 0.991 | | 38.0 | 3.10 | |
| | 65 | 0.671 | | 32.6 | 2.96 | |

stress level of 30 % is shown in Fig. 15. Since the value of ϵ_0 can be considered constant at each temperature independently of specific gravity, the average value of five wood species was used as ϵ_0 . The values of ϵ_0 and G are shown in Table 4. The value of G decreased with increasing temperature. The values of $k'\bar{B} + 2.303 \log G$ calculated are shown in Table 5, and they are plotted against $1/T$ in Fig. 21. The values of the correlation coefficients of the regression lines in Fig. 21 were 0.997 and 0.996 at the stress levels of 30 and 80 % respectively. The values of ΔF^\ddagger calculated from the slope of these lines were 72.8 and 60.8 kcal/mole at the stress levels of 30 and 80 % respectively. Assuming that the flow is caused by breaking of the secondary bonds, it may be considered that the stress relaxation of cell wall is due to the slippage of the cellulose chains in the amorphous region caused by the breaking of hydrogen bonds. Moreover, since it is reported that the value of potential energy for hydrogen bond is about 6 kcal/mole¹⁶⁾, it may be considered that about ten hydrogen bonds are broken simultaneously and rather large part of a cellulose chain moves during the stress relaxation.

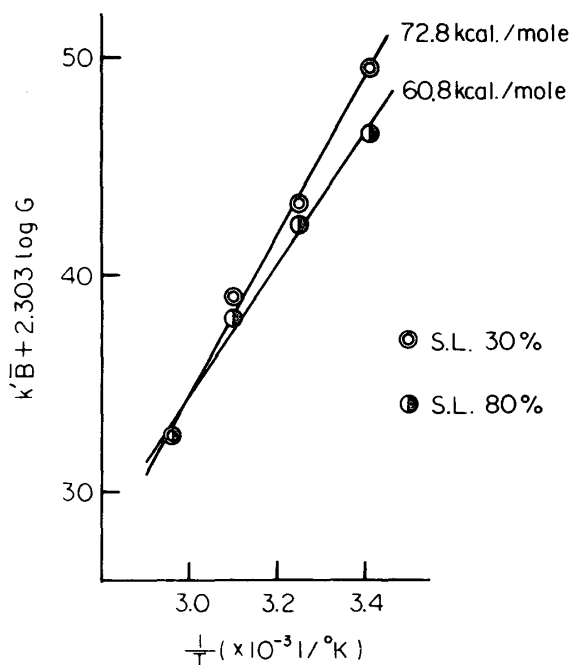


Fig. 21. Evaluation of the free energy of activation ΔF^\ddagger for stress relaxation at two stress levels.

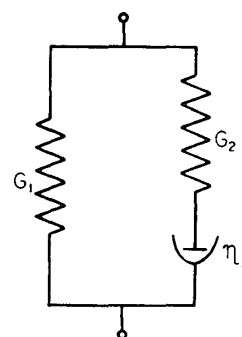


Fig. 22. Mechanical model for cell wall when stress does not relax completely. G_1 and G_2 are elastic moduli, and η_2 is viscosity.

On the other hand, assuming that the stress acting on cell wall does not relax completely and converges to a definite value, the process of stress relaxation can be represented by the mechanical model shown in Fig. 22. In the mechanical model, G_2 and η_2 are the elastic modulus and the viscosity concerned with secondary network units, and G_1 is the elastic modulus concerned with primary network units. Moreover, the authors shall assume that primary cross bonds among cellulose chains and primary bonds in a cellulose chain are not broken. Then, the following equations are obtained

$$i) \quad \frac{d\gamma}{dt} = \frac{1}{G_1} \frac{d\sigma_1}{dt}, \quad (11)$$

primary network units,

$$\text{ii) } \frac{d\gamma}{dt} = \frac{1}{G_2} \frac{d\sigma_2}{dt} + A_2 \sinh B_2 \sigma_2, \quad (12)$$

secondary network units,

where σ_1 and σ_2 are the stresses acting on primary and secondary network units respectively, and

$$A_2 = 2n_2 \lambda_2 \frac{kT}{h} \exp(-\Delta F_2^\ddagger / RT), \quad (13)$$

$$B_2 = \frac{\lambda_2}{2N_2 kT}. \quad (14)$$

Here, the total stress σ is given by $\sigma_1 + \sigma_2$.

If the elastic moduli G_1 and G_2 depend on temperature similarly, the value of σ_2^0/σ_1^0 becomes constant independently of temperature and stress level, where σ_1^0 and σ_2^0 are the initial stresses acting on primary and secondary network units respectively. As it is considered that the ratio σ_2^1/σ_1^0 is approximately equal to σ_2^0/σ_1^0 , where σ_1^0 and σ_2^1 are the stresses at 1 min. acting on primary and secondary network units respectively, so σ_2^1/σ_1^0 can be considered constant regardless of temperature and stress level. The authors shall now analyze the stress relaxation curve of cell wall by assuming that σ_2^1/σ_1^0 is unity. Since k' is the intercept at 1 min., σ_2^1 is equivalent to $k'/2$. By using equation 7, σ_2 vs. $\log t$ curve was analyzed and the results obtained are shown in Table 6 and Fig. 23. The values of the slope and B_2 are equivalent to a and B in Table 3 respectively, and the value of \bar{B}_2 , the average of B_2 , is equivalent to \bar{B} in Table 5. The values

Table 6. Values of molecular constants for stress relaxation of cell wall.

| Stress level (%) | Temp. (°C) | $k'/2$ (kg/cm ²) | $B_2 \sigma_2^0/2$ | $B_2 \sigma_2(t)/2$ (t=10 min.) | $A_2 B_2 G_2 t$ (t=600 sec.) | $G_2 (\times 10^9)$ dynes/cm ² | $(k'/2) \bar{B}_2 + 2.303 \log G_2$ | ΔF_2^\ddagger (kcal./mole) |
|------------------|------------|------------------------------|--------------------|---------------------------------|------------------------------|---|-------------------------------------|------------------------------------|
| 30 | 20 | 26.8 | 6.5 | 4.2 | 3.0×10^{-2} | 8.84 | 35.9 | 36 |
| | 35 | 21.2 | 7.0 | 4.7 | 1.2×10^{-2} | 6.88 | 32.7 | |
| | 50 | 16.2 | 4.7 | 2.1 | 1.9 | 5.85 | 30.5 | |
| | 65 | 10.8 | 5.0 | 2.0 | 2.4 | 4.15 | 27.2 | |
| 80 | 20 | 64.0 | 7.5 | 4.6 | 1.6×10^{-2} | 8.84 | 34.9 | 32 |
| | 35 | 53.0 | 6.0 | 3.0 | 3.0×10^{-1} | 6.88 | 32.7 | |
| | 50 | 42.7 | 4.6 | 1.8 | 3.0 | 5.85 | 30.0 | |
| | 65 | 29.0 | 5.0 | 2.1 | 1.9 | 4.15 | 27.2 | |

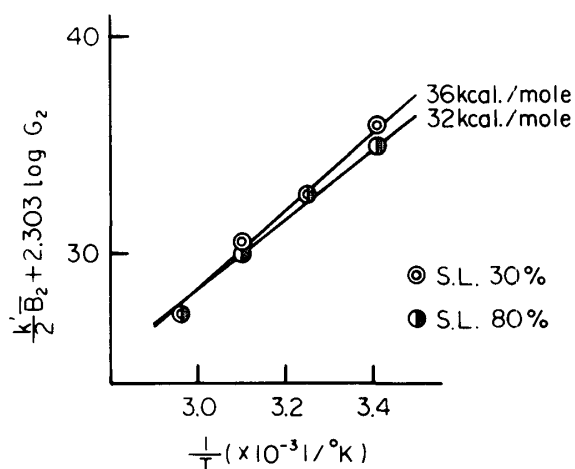


Fig. 23. Evaluation of the free energy of activation ΔF_2^\ddagger for stress relaxation at two stress levels.

of the free energy of activation ΔF_2^\ddagger calculated in this manner were 36 and 32 kcal/mole at the stress levels of 30 and 80 % respectively. These values were comparable to that of cotton plied yarns reported by FUJITA *et al.*¹⁵⁾ Considering that the stress relaxation process of cell wall is similar to that of cotton, it may be concluded that the stress acting on cell wall does not decay completely and converges to a definite value.

As reported previously¹²⁾, the stress relaxation curve measured up to 10^4 min. and the master relaxation curve of wet Buna do not decay completely and converge to a definite value which is equivalent to about 30 to 40 % of the stress at 1 min.

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