

1 **Analysis of stress relaxation on the basis of isolated relaxation spectrum for wet wood**

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16 ***Keywords:***

17 stress relaxation

18 relaxation spectrum

19 spectrum isolation

20 wet wood

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23 **Abstract**

24 In this study, we investigated the relaxation properties of wet wood based on spectra
25 isolated from the whole wood relaxation spectrum, calculated using Alfrey's approximation at
26 temperatures ranging from 25 to 85°C. Three relaxation processes were identified, I, II, and III, in
27 the order of low to high temperature and these were attributed to local molecular motions of
28 hemicellulose, lignin, and cellulose, respectively. Processes I and II (but not III) depended on
29 temperature and the apparent activation energy, which was calculated from the temperature
30 dependence of their relaxation time and was approximately 85 kJ/mol (20 kcal/mol) for both
31 processes. The peak positions and intensity of the isolated relaxation spectra indicated that the
32 molecular motion of the relaxation processes in the temperature range studied represent not whole
33 molecular motion, but rather local molecular motion of the hemicellulose and lignin matrix. This
34 study also demonstrated that the isolation procedure using a Gaussian function can be used to
35 analyze the relaxation process of wood.

37 Introduction

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39 The aim of this paper is to analyze relaxation properties of wood on the basis of the new
40 method that spectra of wood components are isolated from the whole relaxation spectrum of wood
41 at each temperature. The method has never been tried for wood and woody materials to our
42 knowledge.

43 Many reports have examined the relaxation properties of wood, as described in Yamada et
44 al.'s (1985) review of previous measurement conditions and analytical methods, as well as both
45 static and dynamic methods. However, it has been difficult to discuss relaxation spectrum for wood,
46 because the relaxation spectrum is not obtained over a wide time range due to the uncertainty
47 regarding the validity of the time-temperature superposition principle (TTSP) for the whole wood.
48 Several studies have suggested that this principle does not hold perfectly, regardless of wet or dry
49 wood (Yamada, 1962; Urakami and Nakato, 1966; Hushitani, 1968; Sawabe, 1974; Hirai et al.,
50 1981; Nakano and Nakamura, 1986). On the other hand, the principle has been reported to hold for
51 water-saturated milled wood lignin (Irvin, 1980), for wood and isolated wood components with
52 various moisture contents (Irvin, 1980), and for in situ lignin under wet conditions (Salmén, 1984).
53 Kelley et al. (1987) also reported a similar result. Additionally, Bond et al. (1997) reported that the
54 TTSP was valid under limited conditions or wood species.

55 The TTSP is the principle of equivalence of time and temperature effects. On the basis of
56 the principle, data obtained at each temperature over time or frequency scale are shifted into
57 superposition along logarithmic scale time or frequency axis. The amount of shift $\log a_T$ is referred
58 to "shift factor". The TTSP requires that all relaxation mechanism depend equally on temperature.
59 Thus, it does not apply multi-phase materials such as hybrid materials, crystalline polymers and so
60 on, because in general each phase for them has different temperature dependence.

61 Fesco and Tschoegl (1971) clarified analytically that the shift factor depends on the
62 temperature and frequency for the application of the TTSP to a multi-component system. This
63 implies that the TTSP does not hold in a multi-component system, especially one consisting of
64 different temperature/frequency-dependent components. Considering the results of past reports,
65 the cellulose in wood, especially crystalline cellulose, may negate the principle. Furthermore, for
66 wood, the validity of the principle cannot be verified solely by a smooth master curve. Because the
67 relaxation curves for wood are generally flat under various conditions, so that they can be
68 apparently superposed in many cases if shifted along a logarithmic time axis. As well known, wood
69 is a multi-component system, consisting of cellulose, hemicellulose, and lignin, which differ from
70 one another in chemical structure and physical properties. Thus, an amorphous matrix with
71 hemicellulose and lignin should differ from crystalline cellulose in terms of relaxation behavior and
72 its temperature dependence.

73 Therefore, we examine the new method that spectra of wood components are isolated from
74 the whole relaxation spectrum of wood at each temperature and then their temperature
75 dependence is examined. This method can be applied regardless of validity of the TTSP and allow
76 us to describe the molecular dynamics of wood components in detail according to the temperature
77 dependence of the relaxation time dispersion and the intensity, *i.e.*, the shape change and shift
78 along the time axis of a relaxation spectrum obtained at a certain temperature.

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81 **Experimental**

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83 Sample and measurement
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85 Yezo spruce (*Picea jezoensis* Carr.) with dimensions of 90 (R) × 1.5 (L) × 8 (T) mm was
86 prepared as a sample, where L, R, and T represent measurements in longitudinal, radial, and
87 tangential directions, respectively. The specimens were kept at room temperature overnight after
88 being injected with distilled water under vacuum.

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91 Stress relaxation measurement

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93 For stress-relaxation measurements at various temperatures, wet samples were subjected
94 to a three-point bending test with a center-concentrated load in a water bath with a heater. **Load**
95 **signal under constant deformation** were detected by load cell at a constant logarithmic time interval
96 $\Delta \ln[t/s] = 0.1$, except immediately after the start of measurement, when the interval was
97 approximately $\Delta \ln[t/s] > 0.1$ due to the ability to receive the signal. The detected signal was
98 converted from analog to digital using an A/D converter and then treated with a home-made
99 program on a microcomputer.

100 The span was 70 mm. The load was applied to a radial-tangential (RT) face of a sample was
101 less than 30% of the proportional limit load under the wet condition (*i.e.*, 1.0 to 2.0 mm deflection,
102 depending on the measurement temperature). Measurements were carried out in a water bath at a
103 fixed temperature from 25 to 85°C for approximately 17 h. Two or three samples were measured
104 under the same condition to confirm reproducibility; however, no statistical analyses were
105 performed. The relaxation modulus in the bending mode was calculated by

$$106 \quad E(t) = P(t)l^3 / 4ab^3d \quad (1)$$

107 where $P(t)$ represents the detected load as a time function, l is the span, and a , b , and d are the
108 width, thickness, and deflection of a sample, respectively.

109 The relaxation spectrum $H(\ln\tau)$ was calculated from the relaxation modulus as a time
110 function using Alfrey's approximation equation (Alfrey, 1945), given as

$$111 \quad H(\ln\tau) = dE(t)/d\ln t \Big|_{t=\tau} \quad (2)$$

112 which can be obtained from the following relaxation modulus based on linear viscoelastic theory:

$$113 \quad E(t) = E(\infty) + \int_{-\infty}^{\infty} H(\ln\tau) \exp[-t/\tau] d\ln\tau \quad (3)$$

114 by approximating the exponential function $\exp[-t/\tau]$ to the step function, where $E(\infty)$ represents
115 the equilibrium relaxation modulus, and t and τ are measurement time and relaxation time,
116 respectively.

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119 Isolation of relaxation spectrum

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121 Spectra of wood components were isolated from the whole relaxation spectrum of wood at
122 each temperature using the PeakFit (SeaSolve Software, Inc.) software for peak isolation. The
123 software has three methods for peak isolation: a residuals method, a second derivative method, and
124 a de-convolution method. We used the residuals method after preliminary trials, because the others
125 detected many virtual hidden peaks due to the lack of smooth curves of experimental data.
126 Considering previous reports about the relaxation behavior of wood, we assumed that the target
127 component curves were Gaussian and consisted of two or three components. Both the whole and
128 isolated curves were obtained by the first trial run after inputting the number of peaks. The curve
129 obtained on the display screen was roughly fitted to an experimental curve by manually changing
130 the width and height of the component Gaussian curves. Then, the parameters of the component
131 curves were computed to have the least difference in area between the empirical and simulated
132 curves. The best fit results were obtained under the two-component condition for all relaxation
133 curves.

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136 **Results and Discussion**

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138 Relaxation curves and spectra

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140 Figure 1 illustrates typical relaxation curves at various temperatures in our experiment. These
141 curves are similar to the findings reported previously for other wood species, as reviewed by
142 Yamada et al. (1985). The relaxation curves shifted to lower values along the relaxation modulus
143 axis with increasing temperature; the curves show a rapid decrease below 50°C and are relatively

144 flat above 60°C. Additionally, the rapid-decrease region appears to shift to a shorter time along the
145 time axis. These shape changes have been pointed out previously and interpreted as a transition in
146 wood components. However, they have not been shown to represent a single relaxation process
147 isolated from those of all wood components.

148 As noted above, the validity of the TTSP is uncertain for wood, although Yamada (1962)
149 found that the relaxation spectrum obtained from a master curve showed a single broad dispersion
150 assuming the principle. The principle did not hold over the entire time region, but it held partially,
151 especially over a shorter time range, when the data obtained over time intervals of about
152 10 Napierian-logarithmic decades at different temperatures were shifted into superposition along
153 the Napierian-logarithmic time axis. Similarly, several studies have reported that the principle was
154 valid in shorter time regions (Urakami and Nakato, 1966; Hushitani, 1968; Sawabe, 1974; Hirai et
155 al., 1981). This suggests that the principle holds for a matrix with hemicellulose and lignin wood
156 components, as has been found in a number of studies (Irvine, 1980, 1984; Salmén, 1984; Kelley et
157 al., 1987).

158 Considering the above, the relaxation spectra obtained at various temperatures in the
159 current study were calculated using Alfrey's approximation and examined without applying the
160 TTSP (Fig. 2). Asymmetric spectra with clear peaks were obtained in the range of 25–85°C. The
161 peak position of the spectrum shifted to a shorter time along the time axis with an increase in
162 temperature (Fig. 2b), whereas the intensity increased gradually up to 50°C and then rapidly
163 decreased above 55°C (Fig. 2a). The shape of the spectra changed with temperature. As is well-
164 known, the spectrum of dried wood showed little change in shape (*i.e.*, no large peak), unlike wet
165 wood, because dried wood is rigid due to creation of hydrogen bonds in wood substances.

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168 Isolating relaxation spectra of wood as a multi-component system

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170 We found in the above discussion that the relaxation process of a system such as wood,
171 which consists of multiple components with a partial crystalline region, is complex and has no set
172 shape for each part of the relaxation spectrum. The temperature dependence of wood sample
173 cannot necessarily be confirmed because each wood component has different temperature
174 dependence. Thus, it is necessary to isolate the behavior of each component to allow for a detailed
175 understanding.

176 Considering wood to be a material consisting of substances and voids, the modulus of wood
177 is represented by

$$178 \quad E(t) = \theta^m E_S(t), \quad (4)$$

179 where E and E_S represent the moduli of the whole wood and the substance, respectively, θ is the

180 volume fraction of cell wall substance and is equal to the ratio of the whole wood density, ρ to the
 181 density of substance, ρ_S (i.e., $\theta = \rho / \rho_S$), and m is the parameter related to the porous structure
 182 of wood and has values of ab. 1.0, 1.1, and 1.5 for loads along the longitudinal, radial, and
 183 tangential axes, respectively (Ohgama and Yamada, 1971). Equation (4) shows good agreement
 184 with experimental results (Ohgama and Yamada, 1971).

185 Wood cells consist of multiple components, namely cellulose, hemicellulose and lignin, and
 186 thus, the modulus of a wood substance should also be represented by their moduli. Layers in wood
 187 cell wall is parallel to load direction under loading in tension and bending for radial span so that
 188 both S1 and S2 layers mainly support an applied load where wood components are parallel to load
 189 direction (Tang and Hsu, 1973). Thus, assuming that the volume fraction has no time dependence,
 190 $E_S(t)$ in our experiment is approximately represented by

$$191 \quad E_S(t) = \theta_C E_C(t) + \theta_H E_H(t) + \theta_L E_L(t), \quad (5)$$

192 where θ_i ($i = C, H, \text{ and } L$) is volume fraction of wood components, C, H, and L represent cellulose,
 193 hemicellulose, and lignin, respectively, and $\theta_C + \theta_H + \theta_L = 1$.

194 From equations (4) and (5), the relaxation spectrum using Alfrey's approximation is

$$195 \quad H(\ln \tau) = \theta^m \left[\theta_C \frac{dE_C(t)}{d \ln t} + \theta_H \frac{dE_H(t)}{d \ln t} + \theta_L \frac{dE_L(t)}{d \ln t} \right]. \quad (6)$$

196 Here, by setting $\theta^m \cdot \theta_i = \phi_i$ ($i = C, H, L$) and considering $H(\ln \tau) = dE(t) / d \ln t|_{t=\tau}$

$$197 \quad H(\ln \tau) = \phi_C H_C(\ln \tau) + \phi_H H_H(\ln \tau) + \phi_L H_L(\ln \tau). \quad (7)$$

198 Accordingly, the relaxation spectrum of the whole wood is represented by the sum of the spectra
 199 with the contribution weight of all wood components.

200 Equation (7) suggests that the TTSP does not hold for the whole modulus of wood when the
 201 moduli of wood components differ in their temperature dependence. Because equation (7) implies
 202 that temperature dependence is apparent for the whole wood relaxation spectrum when the
 203 relaxation spectra of wood components differ in temperature dependence. Thus, the molecular
 204 dynamics of wood components cannot be discussed based on the temperature dependence of the
 205 whole wood spectrum. An isolated spectrum allows us to discuss the molecular dynamics of wood
 206 components. The above discussion has already been described in detail by Nakano (1995).

207 **On the basis of the above discussion, we tried to isolate the each relaxation spectrum from**
 208 **the spectrum of the whole wood calculated from the measurements, assuming that the spectrum of**
 209 **the whole wood consists of Gaussian spectra of each relaxation process. Because spectrum of the**
 210 **whole wood shows an asymmetric broad shape with a single peak in the measurement time region**
 211 **as shown in Figure 2.**

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214 Temperature dependence of isolated spectra

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216 The selection of a peak-fit function is important for spectrum isolation. Here, a Gaussian function
217 was selected for the isolation, assuming that the target component curves were Gaussian curves.
218 According to the central-limit theorem, a Gaussian function can be expected for each process, when
219 relaxation dynamics is described by the convolution of the independent single-relaxation mode.
220 Thus, we considered that a Gaussian function would be approximately valid for each relaxation
221 process of wood components, although it might not precisely hold because of complex interactions
222 among wood components. The relaxation curve obtained at each temperature was isolated, with the
223 best isolation being considered to have the least difference between the empirical and simulation
224 data.

225 Figure 3 illustrates typical results at 25°C and 70°C, where each relaxation spectrum
226 consists of two relaxation processes, L and H, in order of increasing temperature. The peak
227 intensity $H_p(\ln[\tau])$, the peak position $\ln[\tau_p]$, and the standard deviation SD were determined for
228 spectra obtained from the relaxation spectrum at each temperature. An isolated spectrum does not
229 necessarily correspond to the same relaxation process at different temperatures and will change
230 with increasing temperature. For example, the relaxation process of spectrum H at 25°C
231 corresponds to spectrum L at 70°C. The assignment can be confirmed based on the temperature
232 dependence of $\ln[\tau_p]$, as shown in Figure 4.

233 Figure 4 presents the relationship between temperature, T and peak position, $\ln[\tau_p]$ for the
234 confirmed stress relaxation spectra consisting of two relaxation processes. Symbols \circ and \triangle in
235 Figure 4 denote lower and higher peaks of two spectra isolated from the spectrum at each
236 temperature, respectively. In Figure 4, plots of higher peaks at each temperature below 55°C and
237 lower peaks at each temperature above 55°C are on the same straight line, expressed by the symbol
238 II, whereas plots of lower peaks below 55°C and higher peaks above 55°C are on the straight lines
239 expressed by I and III. We concluded from the results in Figure 4 that there are three relaxation
240 processes: process I with lower peaks below 55°C, process II with higher peaks below 55°C and
241 lower peaks above 55°C, and process III with higher peaks above 55°C. Processes I and II showed
242 linearity with a high correlation (Fig. 4). That is, two relaxation processes have a temperature
243 dependence with a high correlation, at least in the temperature range tested. Process III is probably
244 related to restricted molecular motion, such as that in crystalline cellulose chains or nearby
245 cellulose chains. However, process III cannot be precisely confirmed because it appeared just at the
246 tail of the spectrum.

247 The apparent activation energy was calculated for processes I and II from $\ln[\tau_p]$ versus $1/T$,
248 as shown in Figure 5. The relationships for both processes showed a high correlation. The apparent
249 activation energy was nearly equal for both processes, with values of 84.6 kJ/mol for process I and
250 86.3 kJ/mol for process II. Generally, the degree of apparent activation energy corresponds to the

251 local molecular motion of polymers.

252 The apparent activation energy calculated from the temperature dependence of the shift
253 factor without the peak isolation treatment has been reported previously by assuming the TTSP.
254 The temperature dependence of the shift factor corresponds to that of $\ln[\tau_p]$ in this work. Urakami
255 and Nakato (1966) reported 142.3 kJ/mol below 60°C and 27.9 kcal/mol above 50°C for moist hinoki
256 wood. Hushitani (1968) also measured stress relaxation in moist hinoki and reported a range of
257 146.5-372.6 kJ/mol, with the value thought to decrease by delignification or acetylation. Sawabe
258 (1974) reported a value of 92.1 kJ/mol by creep measurement of dried hinoki. Bond et al. (1997)
259 calculated 33.1-125.6 kJ/mol in tension and 41.4-175.8 kJ/mol in compression for various species
260 with various moisture contents. These estimates of apparent activation energy are generally less
261 than 209.3 kJ/mol, but with some scattering that is probably due to the arbitrary setting of the shift
262 factor. Nakano and Nakamura (1986) and Nakano (1994) noted that the apparent activation energy
263 of esterified wood was too low when obtained based on the temperature dependence of the shift
264 factor. They explained that the overall relaxation process consists of multiple relaxation processes
265 and the temperature dependence of the shift factor would relate to those multiple relaxation
266 processes.

267 Not only $\ln[\tau_p]$, but also $H(\ln \tau)_p$ changed with temperature. Figure 6 shows the
268 temperature dependence of $H(\ln \tau)_p$. Process II had a peak near 60°C, whereas processes I and III
269 had no peak. According to Dunell and Tobolsky's (1949) equation, $E'' \propto -dE(t)/d \ln t$, the data in
270 Figure 6 corresponds to the temperature dispersion of the dynamic loss, $E''(T)$. Thus, the peaks
271 $E''(T)$ of the processes would be near 60°C for process I, below 20°C for process II, and above 85°C
272 for process III, if it exists. Figure 7 depicts the temperature dependence of the SDs of the isolated
273 relaxation processes. The SD of process I tended to decrease with temperature, whereas those of
274 processes II and III increased with temperature. This result indicates that the relaxation-time
275 distribution of process I narrows due to increased mobility of molecular motion with increased
276 temperature, and that the distributions for processes II and III broaden due to the creation of
277 molecular motion with longer relaxation times.

278 The temperature dependence of $\ln[\tau_p]$, $H_p(\ln \tau)$, and SD indicates that the whole
279 relaxation process consists of three relaxation processes in the experimental temperature range,
280 and that process II makes the largest contribution. Additionally, the processes below 20°C and
281 above 85°C shown in Figure 2 suggest the existence of the other process.

282 The glass transition temperature, T_g , of wood components, which indicates the molecular
283 motion of a polymer, has also been examined by many researchers. Goring (1963), in a study using
284 a thermo-mechanical apparatus, reported that the T_g values of cellulose, hemicellulose, and lignin
285 were in the ranges 222–250°C, 54–142°C, and 77–128°C, respectively. Salmén and Back (1977)
286 examined the effects of water on the T_g of cellulose on the basis of Kaelbe's equation (1971). They

287 also reported that the Tg of hemicellulose decreased to below room temperature with water
288 adsorption, whereas that of lignin was not influenced by water adsorption and remained constant
289 at 115°C (Back and Salmén, 1982). Causins (1976, 1978) and Irvine (1980, 1984) found that the Tg
290 values of hemicellulose and lignin depended on the water content, and that Tg of milled wood lignin
291 (MWL) was 45°C and higher than that of moist hemicellulose. Salmen (1984) found the major
292 transition between 20–140°C related to the glass transition of the in situ lignin. Kelley et al. (1987)
293 reported Tg values for lignin and hemicellulose of 60°C and -10°C, respectively, by measurement of
294 wood with 30% moisture content using DSC and a viscoelastic apparatus.

295 These reports suggest that Tg values of hemicellulose, lignin, and cellulose are below room
296 temperature, 60°C, and above 100°C under wet conditions, respectively. Thus, processes I, II, and
297 III in this work appear to be due to the molecular motions of hemicellulose, lignin, and cellulose,
298 respectively.

299 As mentioned above, the apparatus activation energy in processes I and II was about
300 85 kJ/mol (20 kcal/mol). This value was obtained from the isolated spectrum, meaning that it was
301 obtained from components apart from the rigid microfibrils, at least. Considering that the
302 activation energy of main chains is generally more than 400 kJ/mol (100 kcal/mol), the molecular
303 motion corresponding to our values should not be assigned to the molecular motion of main chains.
304 Rather, these values may be more appropriately assigned to local molecular motion; that is, to the
305 local mode in which their molecular motion is restricted by the other components due to
306 interactions among the components. This suggests, as pointed out by Salmén and Olsson (1998),
307 that under moist conditions, wood components without cellulose exist in a matrix with strong
308 interaction between components that causes only local mode relaxation.

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311 **Conclusions**

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313 Spectra isolated from the whole wood spectrum have been discussed to examine relaxation behavior
314 based on the relaxation spectrum of moist wood. The asymmetric shape of the relaxation spectrum
315 of moist wood and its temperature dependence indicate the involvement of multiple relaxation
316 processes. Spectra isolated from the whole spectrum were attributed to the molecular motions of
317 hemicellulose, lignin, and cellulose, referred to as processes I, II, and III, respectively. The
318 apparatus activation energy, calculated from the temperature dependence of spectral peaks of
319 processes I and II (but not process III), was about 85 kJ/mol (20 kcal/mol). Thus, processes I and II
320 appear to relate to the local mode relaxation process. This shows that wood components without
321 cellulose under moist conditions exist in a matrix under conditions of strong interactions between
322 components that causes only local mode relaxation. The above discussion also demonstrates the

323 effectiveness of the isolation procedure using a Gaussian function for the analysis of wood
324 relaxation processes.
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380

381 **Captions**

382

383 Fig. 1. Typical relaxation curves for wet wood at various temperatures.

384

385 Fig. 2. Relaxation spectra and their relative ones at various temperatures using Alfrey's
386 approximation for wet wood.

387

388 Fig. 3. Typical examples of isolated relaxation spectra at 25°C and 70°C. L and H indicate lower and
389 higher spectra, respectively.

390

391 Fig. 4. Relaxation time at the peak versus temperature. Symbols ○ and △ indicate lower and
392 higher peaks of spectra isolated from the spectrum at each temperature, respectively; I, II, and III
393 indicate the relaxation processes.

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395 Fig. 5. Relationships between the relaxation time $\ln[\tau_p]$ at the peak of the relaxation spectrum and
396 $1/T$.

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398 Fig. 6. Relationship between the peak intensity of the relaxation spectrum and temperature.

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400 Fig. 7. Relationship between the standard deviation of the relaxation spectrum and temperature.

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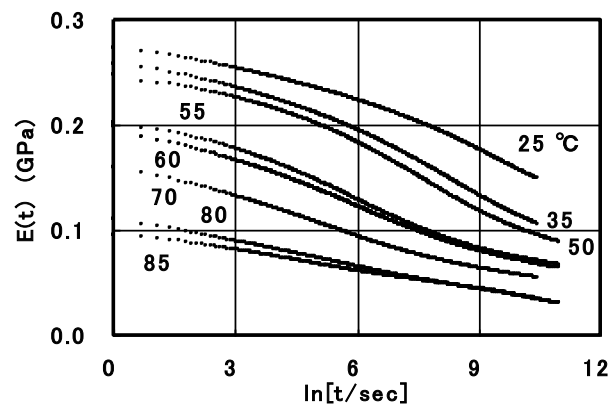


Fig.1. Typical relaxation curves for wet wood at various temperatures.

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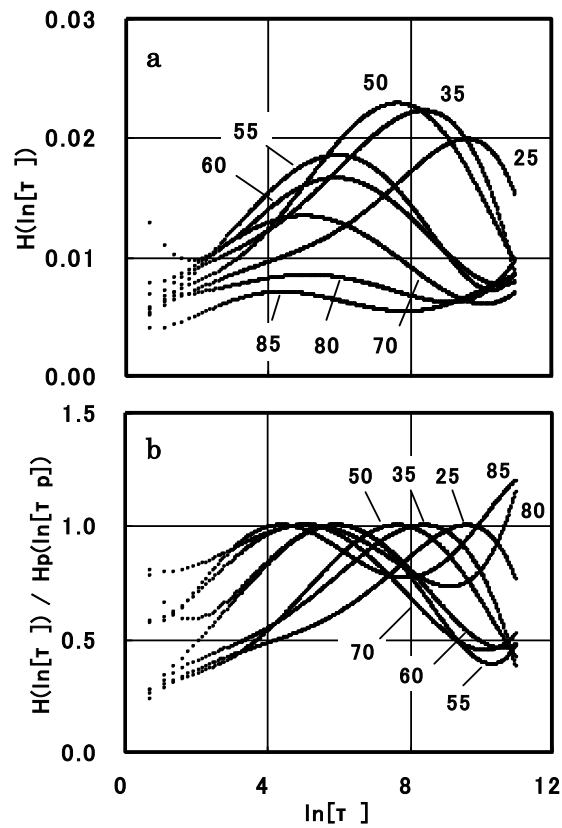


Fig.2. Relaxation spectra and their relative ones at various temperatures using Alfrey's approximation for wet wood.

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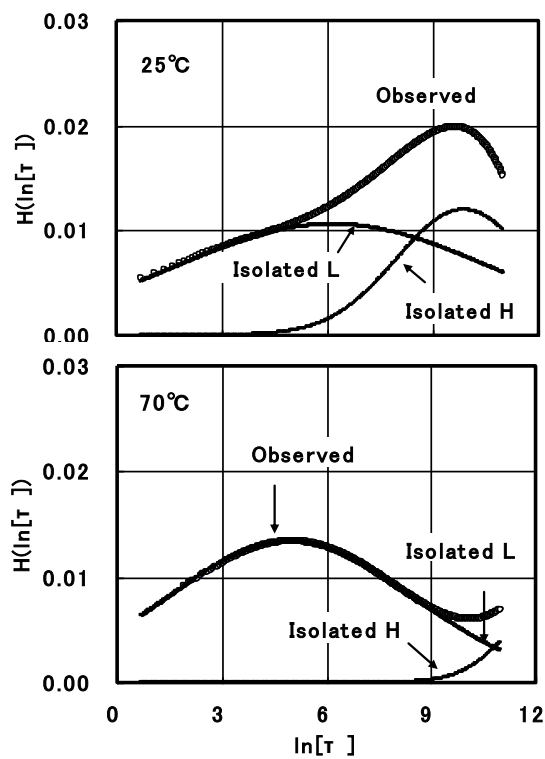


Fig.3. Typical examples of isolated relaxation spectra at 25°C and 70°C. L and H indicate lower and higher spectra, respectively.

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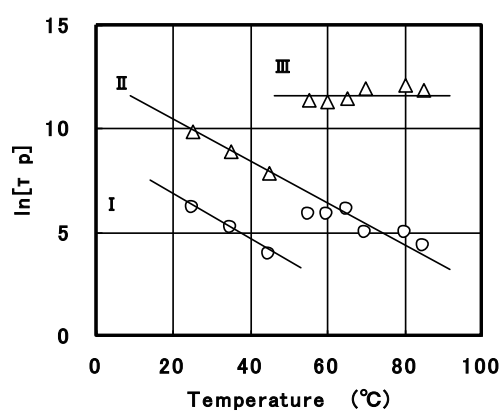


Fig.4. Relaxation time at the peak versus temperature. Symbols ○ and △ indicate lower and higher peaks of spectra isolated from the spectrum at each temperature, respectively; I, II, and III indicate the relaxation processes.

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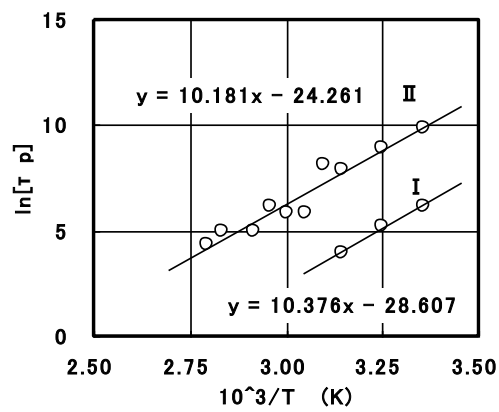


Fig.5. Relationships between the relaxation time $\ln[\tau p]$ at the peak of the relaxation spectrum and $1/T$.

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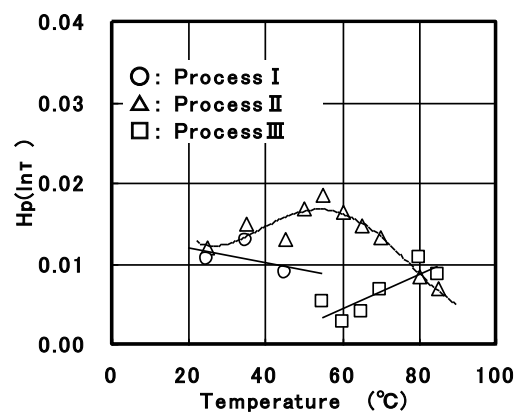


Fig.6. Relationship between the peak intensity of the relaxation spectrum and temperature.

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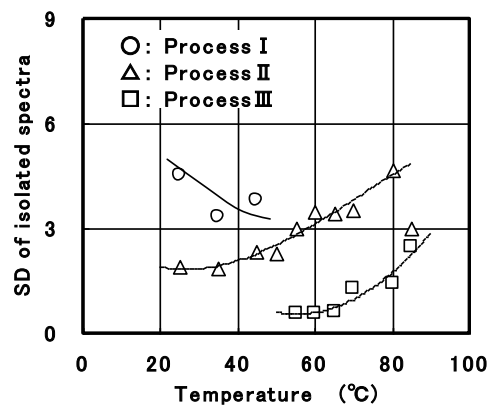


Fig.7. Relationship between the standard deviation of the relaxation spectrum and temperature.