1   **Title:** Applicability condition of time-temperature superposition principle (TTSP) to a multi-phase
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3
4   **Author:** Takato Nakano
5
6   **Affiliation:** Laboratory of Biomaterials Design, Division of Forest and Biomaterials Science, Graduate
7   School of Agriculture, Kyoto University
8
9   **address:** Kita-shirakawa, Kyoto, 606-8502 Japan.
10
11   **e-mail:** tnakano@kais.kyoto-u.ac.jp
12
13   **phone:** +81-75-753-6234
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19   **Abstract**

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21   The applicability condition of the time–temperature superposition principle (TTSP) to a multi-phase

22   system is analytically discussed assuming a mixture law. It was concluded that the TTSP does not

23   hold for a multi-phase system in general but does hold for a multi-component system in which some

24   components have the same temperature dependence and the others have no temperature dependence.

25   On the basis of the results, the application of the TTSP to plant materials such as wood and bamboo

26   was examined using a mixture law and a stretched-exponential function having a characteristic

27   relaxation time τ_0 and a stretching parameter β. Wood can be treated as a multi-phase system

28   consisting of a framework (f) and matrix (m). In this case, it was expected that the TTSP holds for the

29   matrix in the shorter time region $t << \tau_{0f}$ under $T < T_{gf}$, while the TTSP holds for the framework in

30   the longer time region $t >> \tau_{0m}$ under $T > T_{gm}$, where t and T_g is a measurement time and the

31   glass transition temperature, respectively

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34   **Keywords:** time-temperature superposition principle, relaxation, multi-phase, wood

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Introduction

In this work, the applicability of the time–temperature superposition principle (TTSP) to a multi-phase system is analytically discussed. The TTSP is applicable only under limited conditions (Fesko and Tschoegl, 1971; Nakano, 1995; Tschoegl et al., 2002). According to Tschoegl (2002), the TTSP definitely does not apply to multi-phase materials such as graft copolymers, hybrid materials, and some other systems. In this study, we analytically identified both applicable and non-applicable conditions and applied the TTSP to plant materials considered as multi-phase systems.

The TTSP has been widely applied. However, most of the studies have not strictly considered thermorheological simplicity. In order for the TTSP to be applicable, two requirements must be satisfied: curves measured at different temperatures can be superimposed, and all system responses are equally dependent on temperature. It should be noted that just a smooth curve established by superimposing curves at different temperatures does not validate the TTSP.

Fesko and Tschoegl (1971) found that the TTSP does not hold for multi-phase systems and that the shift factor is time-dependent. Kaplan and Tschoegl (1974) applied the TTSP to two-phase polyblends and concluded that the master curve could not be constructed using just one shift factor. Tschoegl et al. (1999) reviewed the effect of temperature and pressure on the mechanical properties of polymeric materials and again pointed out limitations of the TTSP. Nakano (1995) also reported non-applicability of the TTSP to wood when viewed as a multi-phase system. Nevertheless, rigorous application of the TTSP for multi-phase systems is highly desirable because it would enable the prediction of relaxation properties over longer and shorter time intervals and at lower and higher frequencies.

The relaxation behavior of wood has been examined extensively. Samarasinghe et al. (1994) reported that the relaxation curve obtained over a long time interval agreed with a master curve derived from curves at various temperatures. Bond et al. (1997) reported that the TTSP holds for creep in compression and tension for yellow poplar, Douglas fir, and southern pine. Irvin (1980) and Salmén (1984) reported that the Williams–Landel–Ferry (WLF) equation held for isolated lignin and *in situ* lignin, respectively. Stephen et al. (1987) claimed that the TTSP should be restricted to the amorphous components of wood. Dlouhá et al. (2009) examined five wood species and did not definitively conclude that the TTSP was applicable. In an analytical study, Nakano (1995) indicated that the TTSP was not applicable for wood as a multi-phase system. The TTSP has also been applied to various multi-phase systems (e.g., Simon and Ploehin, 1999; Brostow and D'Souza, 1999; Akinay et al., 2002; Macaúbas and Demarquette, 2002; Barbero and Julius, 2003; Tajvidi et al., 2005; Liu et al., 2009; Barbero and Ford, 2004; Nakada et al., 2011).

The application of the TTSP requires that all relaxation processes depend equally on

88   temperature. This requirement has not been rigorously considered in the literature. Thus, the validity

89   of the TTSP must be strictly considered before applying it to a multi-phase system. In some cases,

90   authors have pointed out the non-applicability of the TTSP to multi-phase systems but did not suggest

91   conditions that might make it applicable.

92   In this work, the applicability of the TTSP to a multi-phase system has been formulated

93   using a mixture law. The analytical conditions for applicability are discussed. The

94   stretched-exponential function has been applied to analysis of wood as a multi-phase system.

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97   **Results and discussion**

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99   **Time–temperature superposition principle (TTSP)**

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101   The TTSP implies that time or frequency is equivalent to temperature. That is, time or

102   frequency at temperature T_1 is related to that at temperature T_0 by the following equations:

103
$$t(T_1) = \frac{t(T_0)}{a_T} \, , \tag{1}$$

104
$$\omega(T_1) = \omega(T_0)a_T \, , \tag{2}$$

105   where $t(T_0)$ and $t(T_1)$ are times and $\omega(T_1)$ and $\omega(T_0)$ are frequencies at temperatures T_0 and

106   T_1. These relationships make it possible to establish a curve ("master curve") as a function of the

107   logarithm of the time or frequency by superimposing the curves measured at various temperatures.

108   Rouse theory predicts the TTSP and indicates that it should be applied to the glass transition and

109   rubbery regions where relaxation processes relate to the free volume. Application of the TTSP to

110   polymers in the glassy state and to crystalline polymers has been reported (Faucher, 1959;

111   Nagamatsu and Yoshitomi, 1959; Yoshitomi et al., 1958). The authors reported different mechanisms

112   having different temperature dependencies. It should be stressed that equations (1) and (2) imply that

113   all relaxation processes depend equally upon temperature.

114   Time at temperature T_1, $t(T_1)$, is reduced to that at temperature T_0, $t(T_0)$, using equations

115   (1) and (2). Figure 1 shows how a relaxation curve measured at temperature T_1 can be superimposed

116   on one measured at temperature T_0 using a small vertical shift.

117   Using equations (1) and (2), we have

118
$$E(t/a_T, T_0) = \frac{T_0\rho_0}{T\rho} E(t, T_1) \, , \tag{3}$$

119
$$E'(\omega a_T, T_0) = \frac{T_0\rho_0}{T\rho} E'(\omega, T_1) \, , \tag{4}$$

120
$$E''(\omega a_T, T_0) = \frac{T_0 \rho_0}{T\rho} E''(\omega, T_1) , \tag{5}$$

121 where $E(t,T)$, $E'(\omega,T)$, and $E''(\omega,T)$ are the relaxation modulus, storage modulus, and loss modulus

122 at temperature T. The factor $T_0\rho_0/T\rho$ is related to thermal expansion and is almost unity.

123 Equations (3) to (5) show that two curves can be superimposed on a logarithmic scale by shifting on

124 the basis of $\ln a_T$. Similar equations can also be derived for viscosity, static compliance, and dynamic

125 compliance.

126 　　　　Equations (1) and (2) require that all relaxation processes depend equally on temperature. A

127 smooth curve established by superimposing curves at different temperatures does not necessarily

128 validate the TTSP and is rheologically nonsensical if the above requirement does not hold. The TTSP

129 implies equivalence between time and temperature but not superimposition of curves simply by

130 shifting.

131 　　　　The applicability of the TTSP to multi-phase systems for stress relaxation processes is

132 discussed below. A thermal correction factor $T_0\rho_0/T\rho = 1$ is used to simplify the analysis. The same

133 analysis should be valid for dynamic behavior.

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136 **Applicability of the TTSP to a multi-phase system**

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138 　　　　Fesco and Tschoegl (1971) theoretically examined the application of the TTSP to a

139 thermorheologically complex system and found that the shift factor was a function of both

140 temperature and time. Subsequently, Kaplan and Tschoegl (1974) derived the master curve for a

141 two-phase system using the master curve of each component and Takayanagi's mixture law. They

142 estimated the time dependence of the shift factor using the distance between the obtained master

143 curve of each component and an experimental curve. Their results showed that the master curve

144 cannot be established from relaxation curves at various temperatures simply by shifting on a

145 logarithmic scale. Here, we analytically determine the conditions of applicability of the TTSP for a

146 multi-phase system by extending the work of Kaplan and Tschoegl (1974).

147 　　　　Assuming a mixture law that is independent of temperature, a situation that holds for most

148 multi-phase polymers, the relaxation modulus at temperature T of a multi-phase system is

149 represented by

150
$$E^n(t,T) = \sum_i \theta_i E_i{}^n(t,T) , \tag{6}$$

151 where θ_i and E_i are the volume fraction and the relaxation modulus for component i, respectively,

152 and n is the mixture state parameter and $-1 \le n \le 1$.

153   Assuming that the TTSP is valid for each component i, the relationship between moduli at

154 different temperatures T_0 and T_1 is described by equation (7):

155 $$. \quad E_i(t,T_1) = E_i(t/a_{T_i},T_0) . \quad (T_0\rho_0/T\rho = 1), \qquad (7)$$

156 If the temperature dependence of all components is equal, that is $a_{T0} = a_{T1} = \cdots = a_{Ti} = \cdots \equiv a_T$, then

157 the modulus of the entire system is:

158 $$E^n(t,T_1) = \sum_i \theta_i E_i{}^n(t,T_1) = \sum_i \theta_i E_i{}^n(t/a_T,T_0) \qquad (8)$$

159 This equation is equal to $E^n(t/a_T,T_0)$.

160   The above result means that the TTSP holds for a multi-phase system when the TTSP is

161 valid for all components and more they have the same shift factor. This is the simplest case that can be

162 used to validate the TTSP. Our interest is the applicability of the TTSP to a multi-phase system when

163 the temperature dependence of at least one component differs from the others, even though the TTSP

164 is valid for each component.

165   In such a case, when the component that differs from the others is represented by subscript

166 p, equation (8) can be rewritten as

167 $$E^n(t,T_1) = \theta_p E_p{}^n(t/a_{Tp},T_0) + \sum_{i \neq p} \theta_i E_i{}^n(t/a_T,T_0) , \qquad (9)$$

168 where a_{Tp} and a_T are the shift factors of the different component and the others, respectively.

169 Equation (9) means that a curve for T_1 does not superimpose on that for T_0 by the same shift factor

170 because the shift factors a_{Tp} and a_T differ in the first term and the second term on the right-hand

171 side in the equation. This argument is equally valid when more than two components differ from each

172 other and more have shift factors that differ from the others.

173   Equation (9) indicates that curves at different temperatures cannot be superimposed using a

174 common shift factor. However, they can be superimposed using the procedure of Kaplan and Tschoegl

175 (1974). That is, we first establish a master curve for each component using a shift factor for the pure

176 component and then calculate the master curve of the entire system using a mixture law. This

177 procedure is acceptable only when the volume fraction, relaxation properties, and shift factor for each

178 component are known, and the interaction between the components is negligible. That is, equation (9)

179 indicates that superimposition using a single shift factor is impossible for a multi-phase system. The

180 above discussion implies that the TTSP is not valid for a multi-phase system containing components

181 having different temperature dependencies.

182   To date, the applicability of TTSP has been discussed for a multi-phase system in which the

183 components had different temperature dependencies, although the TTSP is not valid for a multi-phase

184 system containing components having different temperature dependencies (Fesco and Tschoegl, 1971;

185 Kaplan and Tschoegl, 1974; Nakano, 1995). Some studies have shown that the TTSP holds completely

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186 or partially for some multi-phase systems, for example polymer liquid crystal and natural products

187 such as wood, respectively. This fact appears to suggest a restrictive condition for applicability to a

188 multi-phase system of TTSP. Thus, we aimed to identify the condition for which the TTSP is valid. We

189 examined a multi-phase system in which some components had slight or no temperature dependence.

190   When the 0th to q^{th} components do not have temperature dependencies, relaxation processes

191 are frozen or completed, and the other components have equal temperature dependencies, the

192 relaxation modulus at T_1 is given by

$$E^n(t,T_1) = \sum_{i=0}^{q} \theta_i E_i{}^n(t,T_1) + \sum_{i>q} \theta_i E_i{}^n(t,T_1) \,. \qquad (10)$$

194 Here, because the 0th to q^{th} components do not have temperature dependencies, the first term of the

195 right-hand side in equation (10) is constant. Thus, equation (10) reduces to

$$E^n(t,T_1) = const. + \sum_{i>q} \theta_i E_i{}^n(t,T_1) \,.$$

197 As the other components have equal temperature dependencies,

$$E^n(t,T_1) = const. + \sum_{i>q} \theta_i E_i{}^n(t/a_T,T_0) \qquad (11)$$

199 This is equal to $E^n(t/a_T,T_0)$. That is, the TTSP is valid.

200   The above discussion shows that, in general, the TTSP holds for a multi-phase system when

201 the TTSP is valid for all components and their shift factors are identical. The TTSP is not valid for a

202 system that contains at least one component having different temperature dependence. Moreover, the

203 TTSP holds for a multi-phase system in which some of the components have no or nearly no

204 temperature dependencies and the others have the same temperature dependence.

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207 Application of TTSP to wood as a multi-phase system

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209 Wood has a complex high-order structure and consists of multiple components, e.g., cellulose,

210 hemicellulose, and lignin. The cell wall of wood contains these three components. Cellulose is a rigid

211 polymer and is the primary component. It is semi-crystalline and constitutes the framework of the cell

212 wall; the cellulose is embedded in a matrix consisting of hemicellulose and lignin. That is, wood is

213 made up of both a framework and matrix having longer and shorter relaxation times. The relaxation

214 process of a multi-phase system with such components thus consists of two processes. Wood and

215 bamboo have characteristic relaxation behaviors, e.g., "mechano-sorptive behaviors" which is the

216 peculiar relaxation behavior under changing moisture content and whose mechanism has not

217 elucidated (Armstrong and Christensen, 1961; Gibson, 1965; Grossman, 1976). The relaxation

218 properties of wood have been examined extensively, and those of bamboo recently, via microstructural

219 analysis (Aoyagi and Nakano, 2009; Tsubaki and Nakano, 2010; Kanzawa et al., 2011).

220   Wood can be regarded as a multi-phase system consisting of a framework (subscript f) and a

221 matrix (subscript m). The temperature dependencies of their relaxation properties are expected to be

222 quite different, that is, $a_{Tm} \neq a_{Tf}$. In general, the TTSP does not hold for wood, according to the above

223 discussion. However, Irvin (1980), Salmén (1984), Stephen et al. (1987), and Laborie (2004) reported

224 that lignin, the main component of the matrix, obeys the WLF equation. The shift factor of the

225 framework is expected to obey the Arrhenius equation because of local contributions to the relaxation

226 of microfibrils (Ferry, 1980). In the following discussion, we examine the applicability of the TTSP to

227 wet wood because in this state, the relaxation properties of a framework and matrix are expected to be

228 very different.

229   Wood is porous biomaterial which consists of vacant space and wood cell substance. Thus,

230 the high-order structure will affect Young's modulus. Its contribution is represented by the front factor

231 in the following equation obtained by using a mixture low (Ohgama and Yamada、1974; Gibson and

232 Ashby, 1997; Nakao and Nakano, 2011):

233
$$E(t) = \Phi(\theta,\xi)E_S(t) , \qquad (12)$$

234 where $\Phi(\theta,\xi)$ is the front factor related to the shape factor ξ and the volume fraction of wood

235 substance θ, and E_S is Young's modulus of the wood substance. Below 100°C, $\Phi(\theta,m)$ is almost

236 independent of time and temperature. Accordingly, $E(t)$ reduces to $E_S(t)$.

237   Reports have stated that the TTSP holds totally or partially for wood, although the above

238 discussion stated that the TTSP generally does not hold for a multi-phase system. We resolve this

239 discrepancy below.

240   In the following discussion, Young's moduli of the wood components are represented by a

241 stretched-exponential function having characteristic relaxation time τ_0 and stretching parameter β.

242 This function is appropriate because relaxation properties are characterized by two parameters. This

243 approach has been applied to the analysis of the effects of water adsorption on the stress relaxation of

244 wood (Nakao and Nakano, 2011). Equivalence between a stretched-exponential function and the

245 formulation by the linear viscoelastic theory has been clarified by Lindsey and Patterson (1987).

246   Now, consider wet wood as a two-phase system consisting of a framework and a matrix: the

247 former is cellulose and the latter is hemicellulose plus lignin. Using the stretched-exponential function,

248 Young's moduli of the framework and the matrix are represented by

249
$$E_m(t) = E_m(0)\exp[-(\frac{t}{\tau_{0m}})^{\beta_m}] + E_m(\infty) , \qquad (13)$$

250
$$E_f(t) = E_f(0)\exp[-(\frac{t}{\tau_{0f}})^{\beta_f}] + E_f(\infty) , \qquad (14)$$

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251 where subscripts f and m are the framework and the matrix, respectively, $E_i(0)$ and $E_i(\infty)$

252 $(i = f, m)$ are the instantaneous Young's modulus and the long-time asymptote (equivalent Young's

253 modulus), respectively. Then, according a mixture law, Young's modulus of wood is represented by

$$E_s{}^n(t) = \theta_m E_m{}^n(t) + \theta_f E_f{}^n(t). \tag{15}$$

255 Relaxation properties of both the framework and matrix are expected to differ remarkably under the

256 wet condition. This is because the glass transition temperatures of wet wood components are much

257 more than 100°C, less than room temperature, and about 60°C for cellulose, hemicellulose, and lignin,

258 respectively (Goring, 1963; Irvine, 1980, 1984; Salmén, 1982, 1998), so that T_{gf} and T_{gm} differ from

259 each other.

260   The above discussion concluded that the TTSP holds for a multi-phase system when one

261 phase obeys the relaxation process while the others scarcely contribute to the relaxation. Define

262 category (i) as the condition under which the matrix obeys the relaxation process while the framework

263 scarcely contributes to the relaxation and category (ii) as the opposite condition. For our system,

264   (i) $T < T_{gf}$ and $t \ll \tau_{0f}$

265   (ii) $T > T_{gm}$ and $t \gg \tau_{0m}$

266   Previous work (Irvin, 1980; Salmén, 1984; Stephen et al., 1987) indicated that the TTSP is

267 valid for lignin in the matrix of the cell wall. The matrix consists of hemicellulose and lignin. There are

268 approximately equal amounts of each, although the ratio differs somewhat between hardwoods and

269 softwoods. As mentioned before, the glass transition temperature T_g of hemicellulose is lower than

270 those of the other components and well below room temperature when wet. On the other hand, the

271 T_g of lignin is about 60°C even when wet. Thus, lignin is the phase that obeys the relaxation process

272 of the matrix from room temperature to 100°C, while hemicellulose does not.

273   Now, we consider the condition $t \ll \tau_{0f}$. Considering $t / \tau_{0f} \approx 0$ in the exponential term in

274 equation (11), equation (11) becomes

$$E_f(t) \approx E_f(0) + E_f(\infty) = const. \equiv K_f \tag{16}$$

276 Thus, equation (15) reduces to

277

$$E_s{}^n(t) = \theta_m E_m{}^n(t) + \theta_f K_f{}^n. \tag{17}$$

279 Equation (17) shows that the matrix obeys the relaxation process for wood and the framework does

280 not contribute. The relaxation modulus measured at two temperatures T_0 and T_1 under

281 $T_0 < T_1 \ll T_{gf}$ is represented by

$$E_s{}^n(t, T_0) = \theta_m E_m{}^n(t, T_0) + \theta_f K_f{}^n \tag{18}$$

$$E_s{}^n(t, T_1) = \theta_m E_m{}^n(t, T_1) + \theta_f K_f{}^n \tag{19}$$

284 Now, considering $t(T_1) = t(T_0) / a_{Tm}$ because TTSP is valid for the matrix,

$$E_m(t, T_1) = E_m(t / a_{Tm}, T_0). \tag{20}$$

286   Thus, equation (19) reduces to $E_s{}^n(t, T_1) = \theta_m E_m{}^n(t/a_{Tm}, T_0) + \theta_f K_f{}^n$ .Accordingly,

287
$$E_s{}^n(t, T_1) = E_s{}^n(t/a_{Tm}, T_0) \tag{21}$$

288   This equation implies that the TTSP is applicable for wood.

289   When the framework follows the relaxation process after the relaxation process of the matrix

290   is complete, that is, under the condition $t \gg \tau_{0m}$,

291
$$E_m(t) \approx E_m(\infty) = const \equiv K_m . \tag{22}$$

292   Thus,

293
$$E_s{}^n(t) = \theta_m K_m{}^n + \theta_f E_f{}^n(t) \tag{23}$$

294   Accordingly,

295
$$E_s{}^n(t, T_1) = E_s{}^n(t/a_{Tf}, T_0) \tag{24}$$

296   Equation (24) also shows the validity of the TTSP.

297   It is clear from the above discussion that the TTSP holds for wood as a multi-phase system if

298   condition (i) or (ii) is satisfied, in other words, in a limited temperature region or time period. The

299   same discussion is also valid for dynamic behavior. Moreover, even if the TTSP is not valid for the

300   framework, the TTSP is applicable for wood under the conditions $T_0 < T_1 \ll T_{gf}$ and $t \ll \tau_{0f}$. This is

301   because wood consists of components having very different relaxation properties. This result supports

302   reports stating that the TTSP is partially valid. It should be noted that the above discussion has not

303   been applied to materials made of similar components.

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305

306   **Conclusion**

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308   The applicability of the TTSP to multi-phase systems was analytically discussed assuming a mixture

309   law. It was concluded that the TTSP does not hold for multi-phase systems in general but does hold for

310   the two-phase system when both components have the same temperature dependence and when both

311   have no temperature dependence. The applicability of the TTSP to wet wood was examined using a

312   mixture law and a stretched-exponential function having characteristic relaxation time τ_0 and

313   stretching parameter β . Wood can be considered as a multi-phase system made up of a framework (f)

314   and a matrix (m); at less than 100°C, the framework (microfibrils) is rigid while the matrix

315   (hemicelluloses and lignin) is flexible, because their glass transition temperatures T_{gf} and T_{gm}

316   under wet condition are much more than 100°C and near or less than 60°C, respectively. As a result,

317   the TTSP holds for the matrix in the shorter time region $t \ll \tau_{0f}$ under $T < T_{gf}$, while the TTSP

318   holds for the framework in the longer time region $t \gg \tau_{0m}$ under $T > T_{gm}$.

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412 **Caption**

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415 Fig. 1. Shift of the relaxation modulus along a logarithmic time axis and correction along a logarithmic

416 vertical axis for the application of the time–temperature superposition principle (TTSP).

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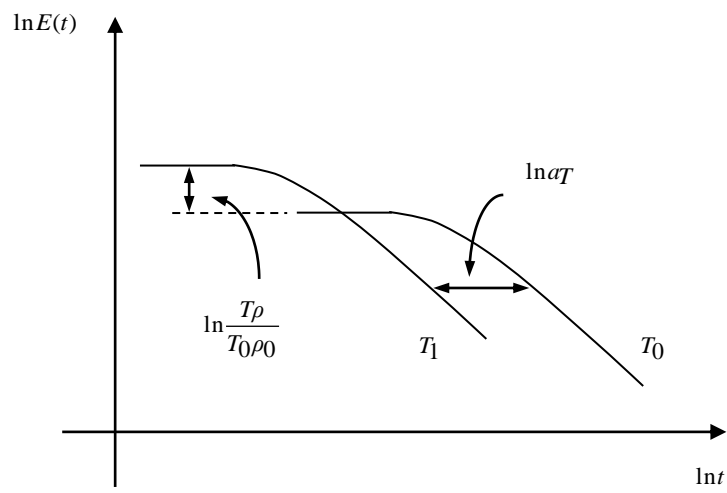462

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467   Fig. 1. Shift of the relaxation modulus along a logarithmic time axis and correction along a logarithmic

468   vertical axis for the application of the time–temperature superposition principle (TTSP).

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The figure shows a plot with vertical axis labeled $\ln E(t)$ and horizontal axis labeled $\ln t$. Two relaxation curves are shown, labeled T_1 and T_0. The vertical correction is labeled $\ln\frac{T\rho}{T_0\rho_0}$ and the horizontal shift is labeled $\ln a_T$.