

Time, Temperature, and Linear Viscoelasticity

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INTRODUCTION

It is possible to calculate the effects of arbitrary stress or strain histories on linear viscoelastic bodies. A concise statement of the necessary theory is contained in the Boltzmann superposition principle, which, however, requires that other conditions, such as temperature and relative humidity, are kept fixed. The objective of this paper is to provide a generalization of the Boltzmann superposition principle so that an arbitrary thermal history may be included in calculations. This is accomplished by incorporating the time-temperature superposition principle into the theory by utilizing spring and dashpot model concepts. The result for the generalization of these models to continuous relaxation and retardation spectra then becomes evident.

1. MECHANICAL MODELS AND THE TIME-TEMPERATURE SUPERPOSITION PRINCIPLE

Creep, stress relaxation and dynamic measurements on linear viscoelastic materials at different temperatures generally obey the time-temperature superposition principle. In the case of creep or stress relaxation, this principle, in its simplest form,¹⁻³ states that two tests at different temperatures are related by a multiplicative transformation of the time scale. In terms of generalized Voigt or Maxwell spring and dashpot models,⁴ this implies that all viscosities of the dashpot elements in both representations are changed by the same factor as the temperature is changed, but that all spring moduli are independent of temperature.

The spring moduli appearing in both models may, however, be considered temperature-dependent. Assuming the springs to be rubberlike in temperature dependence, the moduli are proportional to temperature and density. Thus, in comparing creep or stress relaxation results at different temperatures, it is customary to correct for this by using so-called reduced moduli⁵ for stress relaxation and creep. The assumed tem-

perature dependence of the springs and of the dashpots are then consistent for the Maxwell and Voigt representations, e.g., the time-temperature shift factor is the same for creep and stress relaxation. This is the form of the time-temperature superposition principle adopted in this paper.

A further refinement⁶ of the time-temperature superposition principle involves recognition that the generalized Voigt model contains an isolated spring, which corresponds to the glassy state and which should be virtually independent of temperature. With this additional assumption, the similarity in the temperature dependence of the mechanical elements in the Maxwell and Voigt representations disappears. For example, if it is assumed⁷ that all moduli of the Maxwell representation are proportional to the temperature and density, then it would follow that the glassy modulus in the corresponding Voigt representation, which is the sum of all moduli in the generalized Maxwell model,⁸ would also be proportional to the absolute temperature and density. Similarly, the existence of a temperature-independent glassy modulus in the Voigt representation implies that a multiplicative temperature dependence for the remaining springs and a second multiplicative temperature dependence for the dashpots will not lead to the same type of behavior for the elements in the equivalent generalized Maxwell model. This follows at once from the general relation between the two representations as given by Gross.⁸

In treating stress relaxation data, a correction for a glassy component of the apparent compliance leads to a similar difficulty. Thus, if a temperature-independent glassy compliance is subtracted from the apparent compliance, the difference has been considered⁹ to be inversely proportional to temperature and density for purposes of time-temperature superposition. While such a glassy compliance is numerically the same in the corresponding Maxwell and Voigt representations, it again happens that the temperature dependence

of the various remaining elements cannot, in general, be similar and multiplicative if the above assumption is made. Indeed, as already discussed, the various moduli in the generalized Maxwell model cannot be proportional to the same temperature dependent factor if there is to be a temperature-independent glassy compliance.

The attempt to justify the time-temperature superposition principle by assigning a specified multiplicative temperature dependence to the elements in the models⁷ thus leads to a lack of symmetry in the temperature behavior of the Voigt and Maxwell model elements when a temperature-independent glassy modulus is made part of the Voigt model. As a simplifying assumption, the spring corresponding to the glassy modulus is here regarded as obeying the same temperature dependence as all remaining springs in order to preserve this symmetry. From the standpoint of making viscoelastic calculations for an arbitrary temperature path, this assumption clearly leads to an insignificant error.

2. GENERALIZED SUPERPOSITION PRINCIPLE: STRESS RELAXATION REPRESENTATION

In this section we consider stress relaxation occurring during an arbitrary temperature path. The treatment is similar to that of Hopkins,¹⁰ except that the moduli are here allowed to be temperature-dependent in the generalized Maxwell model. The generalized Boltzmann superposition principle is then derived. The cases of shear and tensile deformations differ in that for the latter the strain must be corrected for thermal expansion.

Stress Relaxation

Following Gross,⁸ the instantaneous application of a constant shear strain γ_0 at the time $t = 0$ to a linear viscoelastic material under isothermal conditions results in a shear stress $S(t)$ given by

$$S(t) = \gamma_0[\bar{G}_s + \psi(t)] \quad (2.1)$$

Here \bar{G}_s is the static modulus, and the relaxation function, $\psi(t)$, is a monotonic decreasing function of t satisfying $\psi(\infty) = 0$. If the strain is an arbitrary function of time, the Boltzmann superposition principle⁸ is given by:

$$S(t) = \int_0^t \frac{d\gamma(\theta)}{d\theta} [\bar{G}_s + \psi(t - \theta)] d\theta \quad (2.2)$$

where the specimen is considered to be completely relaxed at $t = 0$.

It is customary to represent $\psi(t)$ in terms of the relaxation spectrum $G(\tau)$:

$$\psi(t) = \int_0^\infty G(\tau) e^{-t/\tau} d\tau \quad (2.3)$$

For the generalized Maxwell model,⁴ the spectrum is discrete and

$$\psi(t) = \sum_k \bar{G}_k e^{-t/\bar{\tau}_k} \quad (2.4)$$

Here the relaxation time $\bar{\tau}_k = \bar{\eta}_k/\bar{G}_k$, where $\bar{\eta}_k$ and \bar{G}_k are the viscosity and modulus of the dashpot and spring in the k th Maxwell element. The relaxation function for a discrete spectrum may be made to approach that for a continuous spectrum by increasing the number of elements. It is therefore sufficient to consider the temperature dependence of the discrete elements and to regard the continuous case as a limit.

It is assumed⁷ that the temperature dependence of the elements follows:

$$\left. \begin{aligned} \bar{\tau}_k(T) &= a[T, T_0] \bar{\tau}_k(T_0) \\ \bar{G}_k(T) &= b[T, T_0] \bar{G}_k(T_0) \\ \bar{\eta}_k(T) &= a[T, T_0] b[T, T_0] \bar{\eta}_k(T_0) \end{aligned} \right\} \quad (2.5)$$

Here $a[T, T_0]$ is the time-temperature shift factor with the reference temperature T_0 explicitly introduced, and $b[T, T_0]$ denotes $\rho(T)T/\rho(T_0)T_0$ where ρ is the density. The time-temperature shift factor has also been denoted by a_T ¹¹ and $\kappa(T)$.¹² In deriving the generalized Boltzmann principle it is necessary to use a notation which indicates the reference temperature, T_0 .

For the k th Maxwell element, an imposed constant strain γ_0 is the sum of the separate dashpot and spring strains:

$$\gamma_0 = \gamma(\bar{G}_k, t) + \gamma(\bar{\eta}_k, t) \quad (2.6)$$

These also satisfy⁴:

$$S_k(t) = \bar{G}_k \gamma(\bar{G}_k, t) = \eta_k \frac{d\gamma(\bar{\eta}_k, t)}{dt} \quad (2.7)$$

Here $S_k(t)$ is the stress developed by the k th Maxwell element, and \bar{G}_k and $\bar{\eta}_k$ are regarded as functions of time, since the temperature is allowed to vary with time. From eqs. (2.6) and (2.7) it follows that:

$$d \ln S_k(t)/dt + 1/\bar{\tau}_k = d \ln \bar{G}_k/dt \quad (2.8)$$

This has the solution:

$$S_k(t) = \gamma_0 \bar{G}_k(t) \exp \left\{ - \int_0^t dt' / \bar{\tau}_k(t') \right\} \quad (2.9)$$

which satisfies the initial condition $S_k(0) = \gamma_0 \times \bar{G}_k(0)$. Introducing the temperature explicitly

using the first two relations in eq. (2.5), and summing over all elements, we have

$$S = \gamma_0 b[T(t), T_0] \left\{ \bar{G}_s(T_0) + \sum_k \bar{G}_k(T_0) \exp[-w/\bar{\tau}_k(T_0)] \right\} \quad (2.10)$$

where, following the notation of Hopkins,¹⁰ we have let

$$w = \int_0^t dt' / a[T(t'), T_0] \quad (2.11)$$

and T_0 is the temperature at $t = 0$. For a continuous spectrum we may write generally:

$$S(t) = \gamma_0 b[T(t), T_0] \{ \bar{G}_s(T_0) + \psi[T_0, w] \} \quad (2.12)$$

Here the notation $\psi[T_0, w]$ is used to indicate that the relaxation function ψ is taken at the initial temperature, T_0 . This result is the same as that of Hopkins,¹⁰ with the additional correction for the temperature dependence of the moduli which appears in the factor b .

Generalized Superposition Principle

Let a shear strain γ be applied starting at zero time, and let γ be a function of time. During a given increment of time, say between the times θ and $\theta + d\theta$, we may regard an infinitesimal strain $d\gamma(\theta)$ as being applied to the system. This infinitesimal strain results in an infinitesimal stress dS which decays with the further passage of time, according to eq. (2.12), so that at some later time t the stress resulting from $d\gamma(\theta)$ is:

$$dS(t) = d\gamma(\theta) b[T(t), T(\theta)] \{ \bar{G}_s[T(\theta)] + \psi \left\{ T(\theta), \int_0^t dt' / a[T(t'), T(\theta)] \right\} \} \quad (2.13)$$

For a sequence of such infinitesimal strain applications, the resulting infinitesimal stresses at time t are assumed to be additive, so that the total stress at time t is:

$$S(t) = \int_0^t \frac{d\gamma(\theta)}{d\theta} b[T(t), T(\theta)] \times \left(\bar{G}_s[T(\theta)] + \psi \left\{ T(\theta), \int_0^t dt' / a[T(t'), T(\theta)] \right\} \right) d\theta \quad (2.14)$$

where $d\gamma(\theta)$ has been replaced by $[d\gamma(\theta)/d\theta]d\theta$.

This can be simplified further by considering the discrete case eq. (2.4). Thus let

$$\psi \left\{ T[\theta], \int_0^t dt' / a[T(t'), T(\theta)] \right\} = \sum_k \bar{G}_k(T(\theta)) \times \exp \left\{ - \int_0^t \frac{dt'}{a[T(t'), T(\theta)] / \bar{\tau}_k(T(\theta))} \right\} \quad (2.15)$$

From eq. (2.5) the relation

$$a[T(t'), T(\theta)] = a[T(t'), T_0] / a[T(\theta), T_0] \quad (2.16)$$

is readily established. Hence it follows that the right-hand side of eq. (2.15) equals:

$$b[T(\theta), T_0] \sum_k \bar{G}_k(T_0) \exp \left\{ - \int_0^t \frac{dt'}{a[T(t'), T_0] / \bar{\tau}_k(T_0)} \right\} \quad (2.17)$$

Hence, in general,

$$\begin{aligned} \psi \left\{ T(\theta), \int_0^t dt' / a[T(t'), T(\theta)] \right\} \\ = b[T(\theta), T_0] \psi \left\{ T_0, \int_0^t dt' / a[T(t'), T_0] \right\} \\ = b[T(\theta), T_0] \psi[T_0, w(t) - w(\theta)] \end{aligned} \quad (2.18)$$

Inserting eq. (2.18) into eq. (2.14) and using the relation for b corresponding to eq. (2.16), we obtain, finally,

$$S(t) / b[T(t), T_0] = \int_0^t \frac{d\gamma(\theta)}{d\theta} \{ \bar{G}_s(T_0) + \psi[T_0, w(t) - w(\theta)] \} d\theta \quad (2.19)$$

If we regard a and b as known functions, then we may let w be the independent variable, in which case eq. (2.19) becomes

$$S(w) / b[T(w), T_0] = \int_0^w \frac{d\gamma(w')}{dw'} \{ \bar{G}_s(T_0) + \psi[T_0, w - w'] \} dw' \quad (2.20)$$

The result admits of a very simple interpretation. If we call $w(t)$ the equivalent time¹⁰ and $\sigma(w) = S(w) / b[T(w), T_0]$ the equivalent stress, the result of an arbitrary shear strain application during any temperature path gives the equivalent stress as a function of equivalent time, just as if the experiment were performed under isothermal conditions where the temperature has the value T_0 . Equation (2.20) is also an integral equation for strain as a function of equivalent time where the equivalent stress is applied in an arbitrary manner. Therefore, a similar superposition statement holds with respect to the creep representation, and we shall show this independently later.

Tensile Behavior: Thermal Expansion Effects

Shear viscosities and moduli may be converted to approximate tensile values by multiplying by 3. Thus, all that has been said about shear holds for tensile deformation, with the exception that the

observed tensile strain e must be corrected for thermal expansion. With reference to eq. (2.20) it is clear that the superposition principle takes the form

$$F(w)/b[T(w), T_0] = 3 \int_0^w \frac{d[e - \alpha(T(w') - T_0)]}{dw'} \{ \bar{G}_s(T_0) + \psi[T_0, w - w'] \} dw' \quad (2.21)$$

where F is the tensile stress and α is the linear thermal expansion coefficient. The result of a tensile stress relaxation experiment in which the value of e is fixed is thus not simply analyzed for nonisothermal conditions unless the thermal expansion is truly negligible.

3. GENERALIZED SUPERPOSITION PRINCIPLE: CREEP REPRESENTATION

In this section we first consider creep occurring during an arbitrary temperature path. This leads to a generalized superposition principle in the same way as for stress relaxation. Thermal expansion effects again complicate the tensile case.

Creep

The application of an instantaneous constant shear stress S_0 to a linear viscoelastic material under isothermal conditions results⁸ in a shear strain $\gamma(t)$ given by:

$$\gamma(t) = S_0 [J_g + t/\eta_0 + \varphi(t)] \quad (3.1)$$

Here J_g is the glassy compliance, η_0 is the viscosity of the irrecoverable part of the deformation, and $\varphi(t)$ is the creep function which satisfies $\varphi(0) = 0$. The isothermal Boltzmann superposition principle⁸ for creep is

$$\gamma(t) = \int_0^t \frac{dS(\theta)}{d\theta} [J_g + (t - \theta)/\eta_0 + \varphi(t - \theta)] d\theta \quad (3.2)$$

For a discrete⁴ retardation spectrum (generalized Voigt model), the creep function is

$$\varphi(t) = \sum_k (1/G_k)(1 - e^{-t/\tau_k}) \quad (3.3)$$

where $\tau_k = \eta_k/G_k$, and η_k and G_k are the viscosity and modulus of the spring and dashpot of the k th Voigt element.

Consider the application of a constant shear stress S_0 at $t = 0$, and let the temperature vary according to an arbitrary path. The spring corresponding to J_g will have the strain $\gamma(J_g, t) =$

$S_0 J_g(t)$ while the single dashpot η_0 develops a strain given by

$$\gamma(\eta_0, t) = S_0 \int_0^t dt'/\eta_0(t') \quad (3.4)$$

The strain $\gamma_k(t)$ of the k th Voigt element satisfies⁴

$$S_0 = G_k(t)\gamma_k(t) + \eta_k(t)d\gamma_k(t)/dt \quad (3.5)$$

The solution of this equation satisfying the initial condition $\gamma_k(0) = 0$ is

$$\gamma_k(t) = S_0 \int_0^t \exp \left\{ - \int_{t'}^t dt''/\tau_k(t'') \right\} dt'/\eta_k(t') \quad (3.6)$$

For the behavior of the generalized Voigt model as a whole, we then have:

$$\gamma(t) = S_0 \left[J_g(t) + \int_0^t dt'/\eta_0(t') + \int_0^t dt' \sum_k \frac{1}{\eta_k(t')} \times \exp \left\{ - \int_{t'}^t dt''/\tau_k(t'') \right\} \right] \quad (3.7)$$

Through eqs. (2.5) the temperature may be introduced explicitly, which gives:

$$\begin{aligned} \gamma(t)/S_0 &= J_g(T_0)/b[T(t), T_0] \\ &+ [1/\eta_0(T_0)] \int_0^t dt'/a[T(t'), T_0] b[T(t'), T_0] \\ &+ \int_0^t \{ dt'/a[T(t'), T_0] b[T(t'), T_0] \} \sum_k [1/\eta_k(T_0)] \\ &\times \exp \left\{ - \int_{t'}^t \frac{dt''}{a[T(t''), T_0]} / \tau_k(T_0) \right\} \end{aligned} \quad (3.8)$$

From eq. (3.3) we find that, for isothermal conditions,

$$\varphi'(t) = \sum_k \frac{e^{-t/\tau_k}}{\eta_k} \equiv \chi(t) \quad (3.9)$$

where $\chi(t)$ may be defined¹ as the recollection function. Thus, $\chi(t)$ corresponds to the summation in eq. (3.8), so that, in general:

$$\begin{aligned} \gamma(t)/S_0 &= J_g(T_0)/b[T(t), T_0] \\ &+ [1/\eta_0(T_0)] \int_0^t dt'/a[T(t'), T_0] b[T(t'), T_0] \\ &+ \int_0^t \chi \{ T_0, \int_{t'}^t dt''/a[T(t''), T_0] \} dt'/a[T(t'), T_0] \\ &\times b[T(t'), T_0] \end{aligned} \quad (3.10)$$

Thus, for the case of creep, the nonisothermal result is not as simple as for stress relaxation. This is because, in the case of creep, it is the stress, not the apparent stress, that is held constant, as will become clear in the next section. It should be noted that if the temperature dependence of the moduli were neglected,¹⁰ the above difficulties would not appear.

Generalized Superposition Principle

Consider the application of an arbitrary stress $S(t)$ commencing at $t = 0$. During the time interval θ to $\theta + d\theta$, the stress $dS(\theta)$ is applied resulting in the strain $d\gamma(t)$ at some later time t , which is obtained from eq. (3.10). Assuming the validity of superimposing all such infinitesimal strains, we obtain:

$$\begin{aligned} \gamma(t) = & \int_0^t \frac{dS(\theta)}{d\theta} \left(J_\sigma[T(\theta)]/b[T(t), T(\theta)] \right. \\ & + \{1/\eta_0[T(\theta)]\} \int_0^t dt' / a[T(t'), T(\theta)] b[T(t'), T(\theta)] \\ & + \int_0^t \chi \left\{ T(\theta), \int_{t'}^t dt'' / a[T(t''), T(\theta)] \right\} dt' / \\ & \left. a[T(t'), T(\theta)] b[T(t'), T(\theta)] \right) d\theta \quad (3.11) \end{aligned}$$

By considering χ for the discrete case of eq. (3.9) and using the relations (2.5), this can be rewritten as:

$$\begin{aligned} \gamma(t) = & \int_0^t \frac{dS(\theta)}{d\theta} \left(J_\sigma(T_0)/b[T(t), T_0] \right. \\ & + [1/\eta_0(T_0)] \int_0^t dt' / a[T(t'), T_0] b[T(t'), T_0] \\ & + \int_0^t \chi \left\{ T_0, \int_{t'}^t dt'' / a[T(t''), T_0] \right\} dt' / \\ & \left. a[T(t'), T_0] b[T(t'), T_0] \right) d\theta \quad (3.12) \end{aligned}$$

This expression is equivalent to:

$$\begin{aligned} \gamma(w) = & \int_0^w \frac{d\sigma(w')}{dw'} \{ J_\sigma(T_0) + (w - w')/\eta_0(T_0) \\ & + \varphi[T_0, w - w'] \} dw' \quad (3.13) \end{aligned}$$

where w is equivalent time and σ is equivalent stress. The equivalence of eqs. (3.12) and (3.13) follows when both integrals are integrated by parts taking $S(0) = 0$.

Just as for the case of stress relaxation, the generalized Boltzmann principle is equivalent to the isothermal case, provided σ and w are used instead of S and t , respectively. It is clear from eq. (3.13) that the nonisothermal creep experiment does not obey a simple expression [which is given by eq. (3.10)], since it is S , not σ , that is fixed.

Tensile Behavior: Thermal Expansion Effects

The extension to the tensile case is similar to the case of stress relaxation. It follows at once that

$$\begin{aligned} e(w) - \alpha(T(w) - T_0) \\ = \frac{1}{3} \int_0^w \frac{d\sigma(w')}{dw'} \{ J_\sigma(T_0) \\ + (w - w')/\eta_0(T_0) + \varphi[T_0, w - w'] \} dw' \quad (3.14) \end{aligned}$$

4. DISCUSSION

In the case of shear, it will be seen that the result of any isothermal experiment may be extended to nonisothermal conditions by replacing the stress by σ and time by w , provided the initial temperature is the same as that of the isothermal experiment. In the case of tensile experiments, the strain e must also be replaced by ϵ where

$$\epsilon = e - \alpha(T(w) - T_0) \quad (4.1)$$

The preceding discussion is not limited to varying just the temperature. Thus, Fujita and Kishimoto have shown¹³ that variation of the plasticizer content is similar in effect to the variation of temperature. Thus a and b may be considered as functions of plasticizer content instead of temperature, or even as functions of both. In any case, the formal relations and conclusions with regard to superposition are the same, the only change being in the form of the time dependence of a and b .

In the case of stress relaxation, two experiments following different temperature paths are simply related. From eq. (2.12), we see that if the equivalent stresses σ_1 and σ_2 are equal at times t_1 and t_2 , respectively, in the two experiments following temperature paths $T_1(t)$ and $T_2(t)$, then $w_1 = w_2$ or

$$\int_0^{t_1} dt' / a[T_1(t')T_0] = \int_0^{t_2} dt' / a[T_2(t), T_0] \quad (4.2)$$

By differentiation it follows that:

$$\frac{dt_2}{dt_1} = a[T_2(t_2), T_1(t_1)] \quad (4.3)$$

Hence, by plotting t_2 against t_1 at the same equivalent stress levels, the shift factor a is readily found. The factor b is simply $\rho(T)T/\rho(T_0)T_0$ so that the interpretation is simple. However, in the case of creep, the analogous treatment¹⁰ is not possible unless b is assumed to be unity. For stress relaxation in tension, the relations (4.2)

and (4.3) do not apply unless thermal expansion effects are negligible.

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Synopsis

Linear viscoelastic bodies satisfy the Boltzmann superposition principle which permits the calculation of the effect of arbitrary stress or strain history in terms of creep or stress relaxation parameters, respectively. In such calculations, the temperature is not considered as an independent variable; rather, the temperature must be constant, and the stress relaxation and creep parameters used are for the given temperature. By assuming the validity of the time-temperature superposition principle, it is shown how an arbitrary thermal history may be included. By employing spring-dashpot model methods, Boltzmann's principle is generalized, leading to the concepts of equivalent stress $\sigma(t)$ and equivalent time $w(t)$, the latter concept having also been introduced for creep and stress relaxation by Hopkins. These quantities are defined by

$$\sigma(t) = \rho(0)T(0)S(t)/\rho(t)T(t), \quad w(t) = \int_0^t dt'/a[T(t'), T(0)]$$

where t = time, ρ = density, T = temperature, and $a[T(t'), T(0)]$ is the time-temperature shift factor between temperatures $T(0)$ and $T(t')$. In terms of the equivalent stress and equivalent time, Boltzmann's principle for shear remains the same as for the isothermal case with stress relaxation or creep parameters at the initial temperature, $T(0)$. In the case of tensile experiments, the observed strain must be corrected for thermal expansion.

Résumé

Les corps linéaires viscoélastiques satisfont au principe de superposition de Boltzmann qui permet le calcul de l'effet d'une force arbitraire du d' une tension antérieure en termes de paramètres de contraction et relaxation respectivement. Dans de tels calculs, la température n'est pas considérée comme une variable indépendante; plutôt, la température doit être constante et les paramètres de tension-relaxation et contraction sont pour une température donnée. Si l'on considère le principe de superposition temps-température comme valide, on peut voir comment on peut développer une théorie thermique arbitraire. En employant les méthodes de modèles amortisseurs le principe de Boltzmann se trouve généralisé, ce qui conduit aux concepts de force équivalente $\sigma(t)$ et de temps équivalent $w(t)$, ce dernier concept ayant aussi été introduit pour la contraction, la tension-relaxation par Hopkins. Ces quantités sont définies par:

$$\sigma(t) = \rho(0)T(0)S(t)/\rho(t)T(t), \quad w(t) = \int_0^t dt'/a[T(t'), T(0)]$$

où t est le temps, ρ = la densité, T = la température et $a[T(t'), T(0)]$ est le facteur temps-température variable entre les températures $T(0)$ et $T(t')$. En termes de force équivalente et de temps équivalent, le principe de Boltzmann pour le cisaillement reste le même que dans le cas isothermique avec des paramètres tension-relaxation et contraction à la température initiale $T(0)$. Dans le cas d'expériences sous tension la force observée doit être corrigée pour l'expansion thermique.

Zusammenfassung

Linear viskoelastische Körper gehorchen dem Boltzmannschen Superpositionsprinzip, das die Berechnung des Einflusses einer willkürlichen Folge von Spannungen oder Verformungen als Funktion von Kriech- oder Spannungsrelaxationsparametern gestattet. Bei solchen Berechnungen wird die Temperatur nicht als unabhängige Variable betrachtet; vielmehr muss die Temperatur konstant sein und die verwendeten Spannungsrelaxations- und Kriechparameter gelten für die gegebene Temperatur. Unter Annahme der Gültigkeit des Prinzips der Zeit-Temperatursuperposition wird gezeigt, wie eine willkürliche thermische Zustandsfolge aufzulösen ist. Durch Anwendung von Methoden, die auf dem Feder-Reibungselementmodell beruhen, wird das Prinzip von Boltzmann verallgemeinert und führt zu dem Konzept einer Äquivalentenspannung $\sigma(t)$ und einer Äquivalentzeit $w(t)$, wobei die letztere auch schon von Hopkins für die Kriech- und Spannungsrelaxation eingeführt wurde. Diese Größen werden durch

$$\sigma(t) = \rho(0)T(0)S(t)/\rho(t)T(t), \quad w(t) = \int_0^t dt'/a[T(t'), T(0)]$$

definiert, wo t = Zeit, ρ = Dichte, T = Temperatur und $a[T(t'), T(0)]$ der Faktor der Zeit-Temperaturverschiebung zwischen den Temperaturen $T(0)$ und $T(t')$ ist. Als Funktion der Äquivalentenspannung und der Äquivalentzeit bleibt das Boltzmannsche Prinzip für den Schub das gleiche wie für den isothermen Fall mit Spannungsrelaxations- oder Kriechparametern bei der Ausgangstemperatur $T(0)$. Bei Dehnungsversuchen muss an der beobachteten Verformung eine Korrektur für die thermische Ausdehnung angebracht werden.

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