JOURNAL OF MATERIALS SCIENCE 25 (1990) 4036–4041

Superposition properties of relaxation or retardation spectra

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The time–temperature superposition principle is widely used to construct a master curve from individual curves of mechanical or electrical properties, measured as a function of time or frequency and at different temperatures. This principle, however, is not applied, in general, to the distribution functions of retardation or relaxation times that characterize the micromechanisms associated to a polymeric system.

A detailed treatment of the superposition properties of the spectra is considered and some typical distribution functions, presented in the literature, are analysed to show the conditions that must be fulfilled according to the time–temperature superposition principle.

1. Introduction

The behaviour of a viscoelastic material is usually described in terms of the micromechanisms that govern the different molecular processes. These micromechanisms are characterized by their relaxation times and by the distribution functions, usually called spectra, that give the probability of having a molecular response associated to each characteristic time, τ. Moreover, for certain kinds of polymers (dilute solutions, linear polymers with narrow molecular weight distribution, undilutes amorphous polymers, etc.) the micromechanisms are represented by physical models, as the ones given by Rouse [1], Ferry *et al.* [2], Zimm [3], Osaki [4], Chompff and Duiser [5], Edwards [6], Ziabicki [7], among others. The behaviour of polymers cannot be generally explained, however, in terms of known physical models, so that, the time or frequency dependence of the mechanical properties (stress relaxation, creep and dynamic tests) is a helpful tool for the characterization of the micromechanisms controlling the viscoelastic properties. The experimental methods, however, can normally cover only three or four decades of time or frequency, while ten to fifteen decades are needed to reflect the variety of molecular motions in polymeric systems. In fact, the spectra provide useful information about the polymer properties only if the viscoelastic functions are measured over many decades.

A very useful tool in this respect is the time–temperature superposition principle (TTSP) which provides a much larger effective range of time or frequency by making measurements of the viscoelastic functions at different temperatures. According to this principle, a given property measured for short times must be identical with one measured for longer times at lower temperature, except that the curves are shifted parallel to the horizontal axis, matching to a master curve. Then, from the master curve it is possible to obtain the distribution function of all the characteristic times involved in the relaxation process.

On the other hand, if single curves are measured over a great period of time at each temperature, then, the respective individual distribution functions can be calculated. This procedure has been used by Sommer [8] for data obtained in polyvinyl chloride (PVC), where experimental curves extending over near nine decades in time or frequency were obtained, at each temperature. Furthermore, the author has constructed master relaxation or retardation spectra by applying the time–temperature superposition to the spectra obtained at each temperature. No demonstration of the validity of this procedure was given.

It is the purpose of this paper to show that if the individual spectra verify the TTSP then, the individual distribution functions also have a translation parallel to the abscissa such that the matching of the segments leads to a master curve. Finally, some typical distribution functions are analysed to determine the temperature dependence of the parameters according to the scaling conditions imposed by the TTSP.

2. Theory

2.1. Theoretical background

When a transient or dynamic test is performed, the modulus or compliance, F, can be measured as a function of the time, t, or the frequency, $\nu = \omega/2\pi$, for different temperatures. Hence, F is a function that can be written as

$$F = F(x, z) \qquad (1)$$

on defining the variables $x = \ln t$ (or $x = -\ln \omega$) for transient (or dynamic) measurements and using the

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0022-2461/90 $03.00 + .12

variable z for the temperature. Any modulus (or compliance) can be expressed as [9, (Ch. 3)]

$$F(x, z) = C + \int_{-\infty}^{\infty} D(u, z)\, g(x, u)\, \mathrm{d}u \qquad (2)$$

where $D(u, z)$ is the relaxation (or retardation) spectrum, $g(x, u)$ is the time (or frequency) dependence of a Maxwell (or Voigt) element, C is the equilibrium modulus, G_e, (or the glassy compliance J_g) and the characteristic time, τ, is expressed in terms of the variable $u = \ln \tau$. For example, if F is the storage compliance, J' (t, T), Equation 2 can be written as [9, (Ch. 3)].

$$J'(t, T) = J_g + \int_{-\infty}^{\infty} L(\tau, T) \frac{1}{1 + \omega^2\tau^2}\, \mathrm{d}(\ln \tau) \qquad (3)$$

where

$$C = J_g \qquad (4)$$

$$D(u, z) = L(\ln \tau, T) \qquad (5)$$

$$g(x, u) = 1/[1 + e^{-2(x-u)}] \qquad (6)$$

It is clear from Equation 6 that the function g depends not on two independent variables x and u but on a single argument $(x - u)$. The same result is obtained for the other mechanical properties. Then, Equation 2 can be written as

$$F(x, z) = C + \int_{-\infty}^{\infty} D(u, z)\, g(x - u)\, \mathrm{d}u \qquad (7)$$

Now, if the property F is measured as a function of x for two values of the parameter z, that is, z and $z + \Delta z$, according to the TTSP the following equation must be fulfilled for all the values of x [10]

$$F(x + \Delta x, z + \Delta z) = F(x, z) \qquad (8)$$

where the horizontal shift Δx depends only on Δz. Furthermore, it has been demonstrated that if a set of curves $y(x, z)$ satisfies the scaling conditions then, the most general function with translation parallel to the abscissa is given by [11]

$$G(y, x - \xi h(z)) = 0 \qquad (9)$$

where G is an implicit function, $h(z)$ is an arbitrary function that depends only on z and ξ is the slope of the translation path in the $(h(z), x)$ plane, that is,

$$\xi = \Delta x / \Delta h(z) \qquad (10)$$

Moreover, on considering that the increments in x and z, given in Equation 6, are related by the Williams-Landel-Ferry (WLF) equation [12], then [13, 14]

$$h(z) = p + \frac{q}{r + z} \qquad (11)$$

where p, q and r are constants.

2.2. Analysis of the superposition of the spectra

If it is assumed that the distribution function $D(u, z)$ satisfies the TTSP then, the spectrum evaluated at u for a certain temperature z should be the same as the one corresponding to $z + \Delta z$ if it is evaluated at $u + \Delta u$, i.e.,

$$D(u, z) = D(u + \Delta u, z + \Delta z) \qquad (12)$$

where Δu depends only on Δz. Now using Equations 7 and 12, any mechanical property can be written as

$$F(x, z) = C + \int_{-\infty}^{\infty} D(u + \Delta u, z + \Delta z)\, g(x - u)\, \mathrm{d}u \qquad (13)$$

which, on making the change of variable

$$u' = u + \Delta u \qquad (14)$$

can be transformed to

$$F(x, z) = C + \int_{-\infty}^{\infty} D(u', z + \Delta z) g(x + \Delta u - u')\, \mathrm{d}u' \qquad (15)$$

The second member of Equation 15 is the function F evaluated at $x + \Delta u$ for the temperature $z + \Delta z$, so that

$$F(x, z) = F(x + \Delta u, z + \Delta z) \qquad (16)$$

As this last expression is valid for all values of x it has been demonstrated that the function F also satisfies the TTSP. Furthermore, the translation path is the same for both the distribution function $D(u, z)$ and the mechanical property $F(x, z)$, though they correspond to translations of two different variables: the characteristic time $\tau = e^u$ and the time $t = e^x$, respectively.

From another point of view, if it is considered that the curves F against x, parametrized by the variable z, satisfy the TTSP then, Equation 8 is fulfilled and, on considering Equation 7, it results

$$\int_{-\infty}^{\infty} D(u, z)\, g(x - u)\, \mathrm{d}u = \int_{-\infty}^{\infty} D(u, z + \Delta z)\, g(x + \Delta x - u)\, \mathrm{d}u \qquad (17)$$

Moreover, on making the change of variable $u' = u - \Delta x$, Equation 16 leads to

$$\int_{-\infty}^{\infty} D(u, z)\, g(x - u)\, \mathrm{d}u = \int_{-\infty}^{\infty} D(u' + \Delta x, z + \Delta z)\, g(x - u')\, \mathrm{d}u' \qquad (18)$$

and rearranging Equation 18 gives

$$\int_{-\infty}^{\infty} [D(u + \Delta x, z + \Delta z) - D(u, z)]\, g(x - u)\, \mathrm{d}u = 0 \qquad (19)$$

Due to the definition of the distribution function, the result given by Equation 19 does not depend on the mechanical property considered since it is valid for different g functions.

As shown in the Appendix, Equation 19 means that the expression included in the brackets must be zero or, which is equivalent,

$$D(u + \Delta x, z + \Delta z) = D(u, z) \qquad (20)$$

leading to the conclusion that the distribution function also satisfies the TTSP, with the same horizontal translation path as the one applied to the curves F against x, for the same increment Δz.

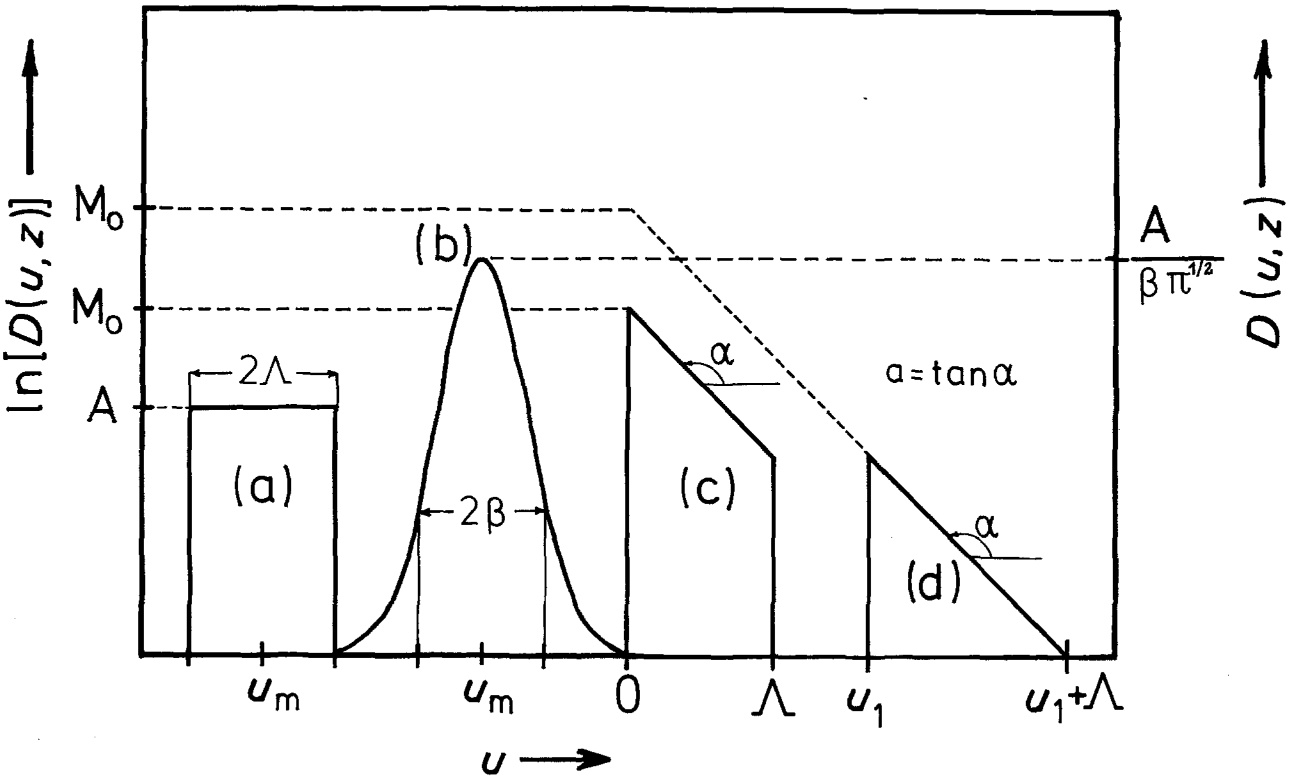

Figure 1 (a) box, (b) lognormal, (c) wedge and (d) ramp distribution functions.

3. Applications

If the spectra measured at different temperatures satisfy the TTSP this means that the corresponding set of curves are related by a translation path parallel to the abscissa. Consequently, as pointed out in Section 2.1, the function D, the abscissa u and the parameter z are related, according to Equation 9, by the implicit function

$$G(D, u - \xi' h(z)) = 0; \quad \xi' = \Delta u/\Delta h(z) \quad (21)$$

An analysis of this equation can only be performed if the spectrum is expressed as an analytical function. The distribution functions for real polymer systems, however, are complex and the functional dependence of D on the characteristic time is not generally known. Nevertheless, Tobolsky and other investigators [15, 16] suggested that the real spectrum can be thought to arise from simpler distributions of relaxation or retardation times. The spectra most commonly used are the box [16, 17], the lognormal [18], the wedge [16, 19] and the ramp [20] distribution functions. All these cases will be considered in detail to show that the time–temperature superposition imposes some restrictions on the parameters of the distribution. The box distribution, shown schematically by curve (*a*) of Fig. 1, will be considered in the first place. This distribution is described by

$$\ln D(u, z) = A(z)\{Y[u - u_m(z) + \Lambda(z)] - Y[u - u_m(z) - \Lambda(z)]\} \quad (22)$$

where $u_m(z)$ is the mean characteristic time of the distribution, $\Lambda(z)$ is the half-width of the distribution and Y is the unitary step function defined by

$$Y(w) = \begin{cases} 0 & \text{for } w < 0 \\ 1 & \text{for } w > 0 \end{cases} \quad (23)$$

Rearranging Equation 23, it follows

$$\ln D(u, z) + A(z)\{Y[u - u_m(z) - \Lambda(z)] - Y[u - u_m(z) + \Lambda(z)]\} = 0 \quad (24)$$

This expression is of the form of Equation 21 if and only if

$$A(z) = A = \text{constant} \quad (25)$$

$$\Lambda(z) = \Lambda = \text{constant} \quad (26)$$

$$h(z) = u_m(z) \quad (27)$$

$$\xi' = 1 \quad (28)$$

Furthermore, on taking into account Equation 10, it follows that

$$\Delta u_m(z) = \Delta x = \Delta u \quad (29)$$

Consequently, the box spectrum measured at different temperatures does not change its form but only translates horizontally with a shift Δu that is a function of Δz.

The second example is provided by the lognormal distribution, shown schematically by curve (*b*) of Fig. 1, which is expressed by

$$D(u, z) = \frac{A(z)}{\beta(z)\sqrt{\pi}} \exp\left[-\left(\frac{u - u_m(z)}{\beta(z)}\right)^2\right] \quad (30)$$

where $u_m(z)$ is the mean characteristic time of the distribution, $A(z)/\beta(z)\sqrt{\pi}$ is the maximum of the spectrum and $\beta(z)$ is the half-width of the spectrum at $D(u, z) = A(z)/\beta(z)\sqrt{\pi}\,e$. Rearranging Equation 30, as for the case of the box distribution, Equation 21 is satisfied if and only if

$$A(z) = A = \text{constant} \quad (31)$$

$$\beta(z) = \beta = \text{constant} \quad (32)$$

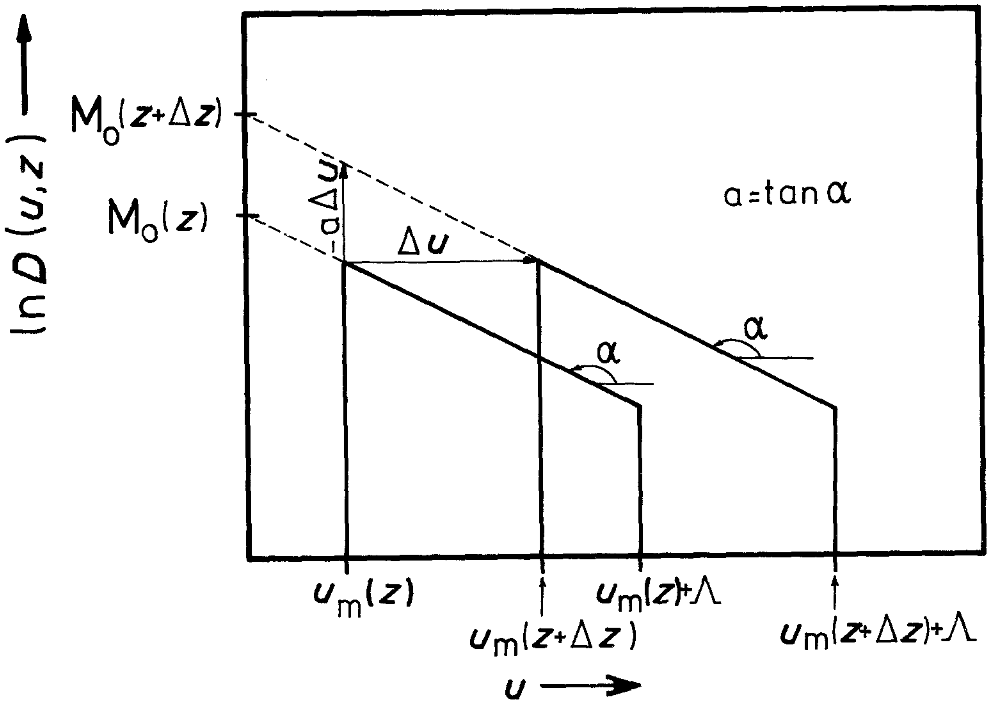

Figure 2 Schematic representation of the conditions imposed by the TTSP on the wedge spectrum.

showing that the lognormal spectrum does not change its shape when it is measured at different temperatures. Furthermore, $\xi' = 1$ and $h(z) = u_m(z)$ just as for the box distribution function, pointing out the analogy between these two spectra.

The third example corresponds to the wedge spectrum, represented schematically by curve (*c*) of Fig. 1, and described by the following expression

$$\ln D(u, z) = [M_0(z) + a(z)u]\,\{Y(u - u_l(z)) - Y(u - u_l - \Lambda(z))\} \qquad (33)$$

where $a(z)$ is the slope of the wedge that begins at $u_l(z)$ and ends at $u_l + \Lambda(z)$, that is, $\Lambda(z)$ is the width of the spectrum. $M_0(z)$ is the value of $D(u, z)$ for $u = 0$. Now, Equation 33 can be written in the implicit form given by Equation 21 if and only if

$$a(z) = a = \text{constant} \qquad (34)$$

$$\Lambda(z) = \Lambda = \text{constant} \qquad (35)$$

and

$$M_0(z) = M - au_l(z) \qquad (36)$$

where M is a constant. In this case, according to Equation 21, $h(z) = u_l(z)$ and $\xi' = 1$. Then, from Equation 10 it follows that $\Delta u_l = \Lambda u$ and from Equation 36, $\Delta M_0 = -a\Delta u$. Consequently, if two spectra that satisfy the TTSP are measured at the temperatures z and $z + \Delta z$ and, one of them is wedge the other will be also wedge with the same width and slope, and, will begin at $u_l + \Delta u$ with an intercept

$$M_0(z + \Delta z) = M_0(z) - a\Delta u \qquad (37)$$

These conditions are illustrated schematically in Fig. 2. Finally, the ramp distribution function, illustrated schematically by curve (*d*) of Fig. 1, will be considered as a fourth example. This spectrum does not require a new analysis since it is only a particular case of the wedge function treated above, when

$$\Lambda(z) = [-M_0(z)/a] - u_l(z) \qquad (38)$$

Then, all the conditions given for the wedge function must also be fulfilled in this case and, according to Equation 37, it follows that $\Delta\Lambda = 0$, that is, the ramp spectrum only translates keeping its shape.

The Rouse theory will be considered as an application of the ramp distribution function. In fact, it has been shown that the discrete characteristic times determined by this theory can be expressed in terms of a continuous spectrum defined by [8, (Ch. 9)]

$$\ln D(u, z) = [(C - a\ln z) + au]\,\{Y(u - u_l(z) - Y(u - u_l(z) - \Lambda)\} \qquad (39)$$

with

$$C = \ln\left\{\frac{1}{\pi}\left[\frac{3}{2}nk(\eta - \eta_s)\right]^{-a}\right\} \qquad (40)$$

where n is the number of molecules per cubic centimeter, k is Boltzmann constant, η is the viscosity of the polymer, η_s is the viscosity of the solvent (for dilute solutions), a is the slope of the spectrum, $u_l = \ln \tau_{min}$ and $\Lambda = \ln(\tau_{max}/\tau_{min})$ is the width of the spectrum. The minimum, τ_{min}, and maximum, τ_{max}, characteristic times are determined by Rouse theory [8, (Ch. 9)]. Moreover, since the spectrum associated to this molecular theory satisfies Equation 21, then Equations 34 to 37 are fulfilled. In fact, the slope, a, is a constant, being its value -0.5 for the relaxation spectrum and 0.5 for the retardation distribution function. Moreover, from Equations 36 and 39

$$M_0(z) = C - a\ln z = M - au_l(z) \qquad (41)$$

Finally, since [9, (p. 189)]

$$\tau_{min} = 150\,(\eta - \eta_s)/\pi^2 N^2 nkT \qquad (42)$$

where N is the number of monomers in the polymer chain, and, on combining Equations 40 to 42 it is easy to show that

$$nz = nT = \text{constant} = K \tag{43}$$

and

$$h(z) = \ln(150/\pi^2 N^2 Kk) + \ln(\eta - \eta_s) \tag{44}$$

On taking into account that $\zeta' = 1$, Equation 44 leads to

$$\Delta u = \Delta h(z) = \Delta \ln(\eta - \eta_s) \tag{45}$$

Furthermore, if $(\eta - \eta_s)$ depends on temperature according to the expression

$$\eta - \eta_s = \eta_0 \exp[H_\infty / k(T - T_0)] \tag{46}$$

where η_0 is a constant, H_∞ is the activation enthalpy when T tends to infinity and T_0 is an empirical constant, it can be shown that $h(z)$ of Equation 44 is of the form of Equation 11 and Equation 46 can be written as [14, 21]

$$\Delta u = -C_1(T_r)\{(T - T_r)/[C_2(T_r) + T - T_r]\} \tag{47}$$

where

$$C_1(T_r) = H_\infty / k(T_r - T_0)2.303 \tag{48}$$

$$C_2(T_r) = T_r - T_0 \tag{49}$$

T_r is the reference temperature and C_1, C_2 are the constants of WLF equation. In other words, if the spectrum is described by the Rouse theory and the increments in u and T, needed to form the spectrum of the master curve, are related by WLF equation, then, $\eta - \eta_s$ should depend on temperature according to Equation 46.

It should be pointed out, finally, that the considerations made in the paper can be applied also if reduced variables and spectra are used.

4. Conclusions

It has been demonstrated that if the curves that describe the time or frequency dependence of the mechanical properties at different temperatures obey the time–temperature superposition, then, the corresponding individual distribution functions can also be matched to form a master spectrum, and, vice versa. The increments in time or frequency at each temperature needed to form the master curve, coincide with the increments in the corresponding retardation or relaxation times needed to form the master spectrum. Finally, some applications to typical spectra presented in the literature have been given, to show how the time–temperature superposition imposes some restrictions on the parameters of the distribution.

Acknowledgements

This work was supported in part by the "Proyecto Multinacional de Investigación y Desarrollo en Materiales" OAS-CNEA and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Appendix

The normalized viscoelastic functions for a single element (Maxwell or Voigt) can be written as

$$g_G(x - u) = \exp[-\exp(x - u)] \tag{A1}$$

$$g_{G'} = \exp[3(x - u)]/2\cosh(x - u) \tag{A2}$$

$$g_{G''}(x - u) = 1/2\cosh(x - u) \tag{A3}$$

$$\begin{aligned} g_J(x - u) &= 1 - \exp[-\exp(x - u)] \\ &= 1 - g_G(x - u) \end{aligned} \tag{A4}$$

$$\begin{aligned} g_{J'}(x - u) &= \exp(x - u)/2\cosh(x - u) \\ &= \exp[-2(x - u)]g_{G'}(x - u) \end{aligned} \tag{A5}$$

$$g_{J''}(x - u) = 1/2\cosh(x - u) = g_{G''}(x - u) \tag{A6}$$

where the subscripts indicate the respective viscoelastic property. Now, g being one of the functions given in Equations A1 to A6, let us consider a function, f, which does not depend on g, such that

$$\int_{-\infty}^{\infty} f(u)g(u)\,\mathrm{d}u = 0 \tag{A7}$$

The function f must fulfill certain conditions. In fact, it is known that any arbitrary function can be expressed as a sum of an even function and an odd function, as for example

$$f_e + f_o = f$$

where

$$f_e = [f(u) + f(-u)]/2 \tag{A8}$$

and

$$f_o = [f(u) - f(-u)]/2 \tag{A9}$$

The subscripts o and e indicate odd and even, respectively. A similar analysis can be made for the function g. Then, Equation A7 can be written as

$$\int_{-\infty}^{\infty} [f_e(u)g_o(u) + f_o(u)g_e(u)]\,\mathrm{d}u + \int_{-\infty}^{\infty} [f_e(u)g_e(u) + f_o(u)g_o(u)]\,\mathrm{d}u = 0 \tag{A10}$$

The integrand of the first term is an odd function so that the first integral is zero; consequently, the second integral is also zero but, since the integrand is an even function the only possibility is the trivial solution, that is,

$$f_e(u)g_e(u) + f_o(u)g_o(u) = 0 \tag{A11}$$

which means that $f \cdot g$ is an odd function. Hence, if $g_o = 0$, that is, if g is an even function, f must be an odd function in order to satisfy Equation A7. The normalized viscoelastic functions, given by Equations A1 to A6, however, do not possess a definite parity, which means that $g_o \neq 0$. Then, Equation A11 can be expressed as

$$f_o(u) = -[g_e(u)/g_o(u)]f_e(u) \tag{A12}$$

leading to

$$f = f_e\{1 - [g_e(u)/g_o(u)]\} \tag{A13}$$

Furthermore, on taking into account Equation A13 and the definition of g_e and g_o in terms of g it follows that

$$f = 2f_e/[1 - g(u)/g(-u)] \qquad (A14)$$

Since f does not depend on the viscoelastic functions, Equation A14 means that either f_e is zero or $g(u)/g(-u)$ is the same for all the functions given by Equations A1 to A6. The last possibility does not apply, as shown by the two examples that follows: On considering Equation A5, it is easy to show that

$$g_{J'}(u)/g_{J'}(-u) = e^{-2u} \cosh(x + u)/\cosh(x - u) \qquad (A15)$$

and, from Equation A6

$$g_{J''}(u)/g_{J''}(-u) = \cosh(x + u)/\cos(x - u) \qquad (A16)$$

Consequently, it follows that $f_e = 0$, which implies, according to Equation A14, that $f = 0$. All this proves Equation 20 of the text.

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Received 3 February
and accepted 24 August 1989