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ORIGINAL ARTICLE

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Time–stress correspondence in viscoelastic materials: an equation for the stress and temperature shift factor

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Abstract Stress–time correspondence principle discovered experimentally by O'Shaughnessy already in 1948 [1] is considered. Using the Doolittle formula for the viscosity as a function of free volume [2], an equation for the generalized temperature–stress shift factor $a_{T,\sigma}$ is obtained. An equation for the stress-dependent shift factor a_σ follows as a special case. The equation for the temperature shift factor a_T already derived in 1985 [3] and successfully used since also follows from the $a_{T,\sigma}$ formula.

Keywords Viscoelasticity · Temperature shift factor · Stress shift Factor · Polymer property prediction · Polymer reliability · Polymer mechanical properties · Time–stress correspondence · Time–temperature correspondence · Thermal mechanical analysis · Equation of state · Hartmann equation · Creep compliance

Introduction and scope

Large amounts of mechanical, rheological and other properties of viscoelastic materials as functions of time are continuously being determined experimentally. The reason for this activity is the need to evaluate long-term performance and reliability of polymeric materials and components from short term tests – and also the belief that the properties in question are still far from sufficiently understood. Thus, we need the understanding not only for intellectual satisfaction but also for the development of predictive methods – so as to be able to save dramatically the time required for the experiments.

While certain predictive tools exist, they are often underestimated. An important such tool, the time–temperature correspondence principle, eloquently presented by Ferry and coworkers [4] has been used to advantage by others [3, 5–12]. Now we shall examine a tool of potentially comparable importance, namely the time–stress equivalence principle. One needs to point out the following: both principles are clearly based on the fact that in a viscoelastic material under load we have variations of free volume v^f with time t, with temperature T and with stress σ. Therefore, a generalized time-temperature stress correspondence principle should exist also. This situation behooves us to formulate a quantitative relation which would embrace t, T and σ together.

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Previous work: the existence of time–stress equivalence

In 1948 O'Shaughnessy [1] reported on work he started in 1945: compliance values of rayon from creep experiments for different levels of stress σ will fall on a single locus when plotted against time or a function of time. One notices the careful language of O'Shaughnessy. This was followed in 1953 by a similar study of nylon [13], with similar results. Later on more studies have been performed, including those by Gruntfest and coworkers [14] in 1957, by Urzhumtsev and Maksimov [15] in 1968 and others – as discussed in a book by Goldman in 1994 [9].

In spite of this long history, the stress somehow does not have *equal rights* with temperature and frequency in formulating correspondence-type relations while the utility of such relations is evident. Thus, we need a formula for the stress shift factor a_σ that would allow us – as O'Shaughnessy did using experimental data only – to move curves obtained at different stress levels to create a single master curve. Before doing this, we shall consider the temperature shift factor a_T. We shall need it to obtain later the combined temperature–stress shift factor $a_{T,\sigma}$.

Temperature shift factor

We recall first the time–temperature correspondence principle [4, 9, 16]: from mechanical measurements made at several temperatures one can create a master curve for a chosen temperature T_{ref} extending over several decades of time. Shifting of individual curves to produce the master curve is performed using the temperature shift factor ln a_T. For a property such as the creep compliance D we have

$$D(T,t) = D(T_{ref}, t / a_T) \tag{1}$$

$$a_T = \eta T_{ref} v / (\eta_{ref} T v_{ref}) \tag{2}$$

where η is the viscosity and v the specific volume (for instance in $cm^3 g^{-1}$). The reduced volume $\tilde{v}$ and other reduced parameters are defined as follows:

$$\tilde{v} = v / v^*; \quad \tilde{T} = T / T^*; \quad \tilde{P} = P / P^* \tag{3}$$

where v^*, T^* and P^* are the characteristic (hard-core) parameters for a given material. The free volume v^f can then be calculated as

$$v^f = v - v^* \tag{4}$$

where v^f and v^* are in the same units as v.

We also need the Doolittle equation [2] relating the viscosity to free volume:

$$\ln \eta = \ln A' + Bv^* / v^f \tag{5}$$

where A′ and B are materials constants. Ferry [4] noted that Eq. (5) is empirical, but we now have a better understanding of its physical significance and the reasons why it works well. The second term is fairly obvious: more free volume leads to lowering of viscosity. Creation (or partial annihilation) of v^f can be accomplished by varying for instance the temperature. The first term is also a material constant which take cares of the factors which do not depend on free volume and the molecular packing directly. For instance, there exist collective small amplitude motions of adjacent torsions, seen in molecular dynamics simulations of isoprene, where constrains created by the environment play a role [17].

By applying Eqs. (5) and (4) to the definition (2), one obtains [3, 6] the following formula:

$$\ln a_T = A + \ln[T_{ref} v / (T v_{ref})] + B / (\tilde{v} - 1) \tag{6}$$

where A is a constant characteristic for a given viscoelastic material and related to A′. Various special cases can be obtained from Eq. (6), including the well-known Williams–Landel–Ferry (WLF) equation [18, 4]. However, Ferry warns [4] that the WLF equation serves at most in the temperature range of 50 K, namely from the glass transition temperature T_g to T_g + 50 K. Therefore, van Krevelen [19] recommends using below T_g an Arrhenius type equation, as espoused by Glasstone, Laidler and Eyring [20] in their theory of rate processes developed in the 1930s. Clearly we are better served – both fundamentally and practically – by using a single equation.

A simplification of Eq. (6) is possible. It has been proven numerically for low-density polyethylene [6] that variations of the $T_{ref}v/(Tv_{ref})$ term with the temperature are insignificant. Thus, one can assume

$$d[T_{ref} v / (T v_{ref})] / dT \approx 0 \tag{7}$$

so that

$$\ln a_T = A_T + B / (\tilde{v} - 1) \tag{8}$$

Equation (8) has been used with success for an adhesive, polyethylenes, polyurethanes and a PLC [3, 6–8, 12, 21, 22].

For predrawn materials, with the draw ratio $\lambda = \varepsilon + 1$, where ε is the engineering strain, Eq. (8) was generalized further [10] to the form

$$\ln a_T = 1 / [a + c\lambda] + B / (\tilde{v} - 1). \tag{9}$$

Here the first parameter in Eq. (8) is now $A_T = 1/[a+c\lambda]$; a and c are constants characteristic for a given material but independent of the degree of orientation and of temperature. Clearly parameters a and c do not affect the shape of the $a_T(T)$ curve. The denominator of the first term in Eq. (9) constitutes a direct measure of the orientation.

Equations (6), (8) and (9) are only usable in conjunction with an equation of state. Good results have been obtained repetitively [8, 10, 21, 12, 22] with the Hartmann equation which is valid for both polymer solids and melts [23–25]:

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v}. \tag{10}$$

A convincing and straightforward derivation which leads to the $T^{3/2}$ term was presented by Litt in 1976 and discussed again in 1978 [26]. It seems that his starting point were the problems with the WLF equation. WLF happened to be working with the reciprocal free volume and they have assumed that v^{f-1} varies linearly with the temperature. While for certain properties a linear expression might represent a reasonable first approximation to reality, the Litt derivation shows that this does not apply to volume. He says that the validity of the key WLF assumption can be seriously questioned and shows data for polystyrene proving how bad results the WLF equation produces. Litt also points out that the WLF equation in conjunction with the Doolittle equation predicts infinite viscosity at approximately T_g–50 K.

Stress shift factor

In view of the discussion in the beginning of this paper, we need to derive a formula for the stress shift factor a_σ. It should serve a role similar to that of the temperature shift factor a_T. Thus, for a property such as the creep compliance D we can write

$$D(\sigma, t) = D(\sigma_{ref}, t / a_\sigma). \tag{11}$$

An attempt to calculate a_σ is described by Goldman [9]. However, it is based on the concept of the activation energy U^{act} used extensively by Eyring and his colleagues [20]. There is the limitation pointed out by van Krevelen [19] and already noted above that relations of this type can be used at low temperatures only. Moreover, according to the Eyring model, U^{act} should be a constant. However, it is not a constant even for one kind of polyethylene (PE); contrary to the assumptions made, U^{act} varies with the temperature [10]. Ohta and Yasuda [27] report for a single highly branched PE that U^{act} varies by more than 400 %, from 89 to 362 $kJ \cdot mol^{-1}$. They show a single continuous curve of $\ln a_T$ as a function of T^{-1}; an attempt to present the curve as combination of three straight lines for three different values of U^{act} produces an evidently artificial result contradicted by the experimental data. The work of Ohta and Yasuda includes a variety of PEs with various degrees of branching. In all other cases these authors have investigated U^{act} also varies widely – what vitiates the assumption made by Glasstone, Laidler and Eyring [20]. In both his thoughtful papers Litt [26] mentions the existence of the activation energy approach but finds no use for it. Still further, in 2000 Mano and his colleagues [22] report that values of U^{act} depend on the experimental procedure used. Thus, U^{act} is *not* a material property.

There is a simple explanation why the Glasstone–Laidler–Eyring model cannot possibly work. Their basic assumption is that that it takes energy to move a small unit of a material from its environment. The energy required is called the activation energy for something (diffusion, flow, chemical reaction, etc) – and this statement does make sense. However and as already noted, Glasstone and his colleagues have assumed that the activation energy is a constant. In reality the energy required for any of the processes they have considered changes with the environment, more specifically with the distance R between particles (polymer chain segments, atoms, ions). The behavior is governed by the interaction potentials, mainly by the pair interaction potential u(R). The very existence of u(R) is one of the basic tenets of molecular physics. Changes in the average R values, caused for instance by increasing the temperature of the material, are reflected in free volume changes via the equation of state. When Glasstone and his colleagues assume that U^{act} is a constant, they simultaneously assume that the average R values do not change with anything. Then the isobaric expansivity and the isothermal compressibility (see Accessibility of equation of state data below) would be always zero; equations of state would not be needed at all. Possibly in the 1930s Glasstone, Laidler and Eyring realized this, but they wanted a procedure enabling simple calculations with slide rules; computers were then nowhere in sight.

Under these circumstances, we rewrite Eq. (2) in a more general form, introducing explicitly the dependence on the stress σ while taking as before care of the shift caused by temperature changes:

$$a_{T,\sigma} = (T_{ref} / T) \cdot [(v(T,\sigma) / v_{ref}(T_{ref}, \sigma_{ref})] \cdot [\eta(T,\sigma) / \eta_{ref}(T_{ref}, \sigma_{ref})]. \tag{12}$$

Effects of the temperature (thermal energy changes) are evidently represented by the first term in Eq. (12). However, T changes affect also the specific and free volumes, hence the dependence on temperature of the remaining terms. The various effects created by varying the stress level (see above the discussion following Eq. (5)) are represented by the explicit dependence of the second and third factor an σ. We recall that, when we consider deformation of a small cubical element, it can be decomposed into a volume change (hydrostatic stress) and a change in shape (shear stress components) [28]. While in general the stress σ is a tensor with nine components [29], the simplified notation may be used when we are dealing with deformations such as uniaxial tension or compression.

Looking at the same situation from the molecular point of view, varying T we change simultaneously at least the mobility (energy) of chain segments, their capability to undergo conformational transitions jointly with their neighbors (energy barriers to overcome), and the free volume available for segmental motions. The mechanical forces applied affect all these phenomena as well. The processes in question take place at different rates; this is why formula (7) constitutes a reasonable approximation, while the η/η_{ref} ratio changes with T much faster [6].

We now need a relation between the logarithmic viscosity η and the stress level σ, that is a generalization of the Doolittle Eq. (5). We make the simplest possible assumption, namely a linear relation between the two:

$$\ln[\eta(T,\sigma)] = \ln A'_T + B / (\tilde{v} - 1) + \ln A'_\sigma + C \cdot \sigma. \tag{13}$$

Thus, in the spirit of Arthur K. Doolittle, we have assumed that his constant B is independent of the mode of varying free volume. However, the parameters A'_T and A'_σ have to be different – representing different modes of affecting the interactions in the material when varying the temperature or the stress level. At the same time, the parameters A'_T and A'_σ are independent of the mode of performing the experiment. In general, the parameter C can be either positive or negative (recall dilatancy and pseudoplasticity in molten polymers). A negative C reflects the decrease of viscosity with increasing shear, a phenomenon typical in molten polymers [30]. Also in solid polymers a negative C implies an increase of free volume upon an increase of stress. Thus, higher σ acts similarly as higher T; the master curve will show a mechanical property under study at higher stress values corresponding to higher times.

It has been proven for a multi-phase polymer liquid crystal, namely the copolymer of poly(ethylene terephthalate) (PET) with p -hydroxybenzoic acid (PHB) containing the mole fraction of the latter equal to 0.6, that the temperature shift factor a_T values are independent of the experimental procedures such as creep or stress relaxation [12]. This testifies to the physical significance of parameters in Eqs. (5), (6), (8) and (9). We shall see whether the simple assumption of the last term in Eq. (13) and its consequences will be also verified experimentally.

Now by straigthforward arithmetic we obtain from Eq. (12) in conjuction with (13) and the definitions (3) and (4):

$$\ln a_{T,\sigma} = A_{T,\sigma} + \ln T_{ref} / T + \ln[v(T,\sigma) / v_{ref}] + B / (\tilde{v} - 1) + C(\sigma - \sigma_{ref}). \qquad (14)$$

Eq. (14) is the desired result. Given the reduced volume in the fourth member of (14), the equation is usable also only in conjunction with an equation of state. We intend to continue to use for this purpose the Hartmann Eq. (10).

We first need to verify whether Eq. (14) reduces for a constant stress level to Eq. (6) as it should. Indeed, by assuming $\sigma = \sigma_{ref}$ we recover Eq. (6).

Similarly as the temperature shift factor a_T, we shall need also a simple shift factor a_σ formula dependent an the stress level σ only for T = const = T_{ref}. Simplifying Eq. (14) accordingly, we obtain

$$\ln a_\sigma = A_\sigma + \ln v(\sigma) / v_{ref} + B / (\tilde{v} - 1) + C(\sigma - \sigma_{ref}) \qquad (15)$$

where $v_{ref} = v(\sigma_{ref}, T_{ref})$. Experimental verification of the validity of Eq. (15) will be reported in a subsequent paper [31].

Accessibility of equation of state data

It is sad that the WLF equation is still being used outside of its application range, in spite of the warning by Ferry and the important work of Litt. Developers of software which calculates the temperature shift factors a_T from the WLF equation contribute to the confusion. Some of such computation programs use the supposedly universal WLF constants, what makes the situation still worse. When the WLF equation produces dramatically wrong results, this might be the consequence of inappropriate material parameters, or too wide application range, or both. Unfortunately, some engineers conclude then that it is the TTC principle which is inapplicable. In reality, the principle generally works pretty well, but they have chosen the least reliable calculation procedure based on the principle.

Ostensibly the problem with the a_T equations (6) and (8) – which so far have always produced reliable results – is that they require the knowledge of the equation of state in the form of v(T, P). The same applies to Eqs. (14) and (15) derived in this paper. However, the experimental accuracy of determination of the equation of state is increasing, and so is the accessibility of equipment for that purpose. Moreover, the equation of state results are needed also for other purposes. For instance, once the parameters v*, T* and P* in the Hartmann Eq. (10) are determined from the P–V–T results, one can calculate the bulk modulus k_B. We apply the definition of the isothermal compressibility

$$\kappa_T = -V^{-1}(\partial V / \partial P)_T \qquad (16)$$

and differentiate Eq. (10) accordingly. If the compressibility does not change with pressure, the bulk modulus can be calculated as the reciprocal of the compressibility [29], with the result

$$k_B = P^*[1 + 5(\tilde{T}^{3/2} + \ln \tilde{v})] / \tilde{v}^6. \qquad (17)$$

Fairly often one deals with a constant pressure situation, one atmosphere in particular. Then either the volumetric isobaric expansivity

$$\alpha = -V^{-1}(\partial V / \partial T)_P \qquad (18)$$

or the linear isobaric expansivity

$$\alpha_L = -L^{-1}(\partial L / \partial T)_P \qquad (19)$$

where L is the length (or height) of the specimen, are useful. α_L can be determined with a thermal mechanical analysis (TMA) $\alpha_{L||}$ apparatus along three Cartesian coordinates, and then converted into a by simple addition. Often (for instance in extrusion) we have an orientation along the flow and the corresponding $\alpha_{L||}$ value, while the two Cartesian directions perpendicular to the flow render a single $\alpha_{L||}$ value. Then

$$\alpha=\alpha_{L||}+2\alpha_{L\perp}. \qquad (20)$$

Needless to say, the situation is still simpler in an isotropic viscoelastic material. Independently of the isotropicity – or otherwise – of the material, once the α values have been calculated, one can then use a single experimental value of the specific volume v (typically at the room temperature) to compute v(T). A simple increment algorithm

$$v(T + 1) = v(T) + \alpha(T) \qquad (21)$$

works quite well [8]. Given the v(T) results, one can substitute them into Eq. (10) and solve an overdetermined system of Hartmann equations for v* and T*. Then one can apply equations such as (6), (8) or (9).

The physical significance of v* is clear from Eq. (4). T* represents the strength of intermolecular (intersegmental, interatomic) interactions, so that large T* values correspond to high attractive configurational energies. Thus, polymers with strong orientation should have high T* values. This is indeed the case for higth density polyethylenes investigated by Mano and his colleagues [22] where the shear controlled injection molding (SCORIM) technique produces a material with a higher T* value than the conventional injection molding. A similar conclusion has been reached by Berry and coworkers [32] who have determined P–V–T relations for a series of polymer liquid crystals. Once a liquid crystal rich phase (islands) is formed, an increase of the concentration of the LC constituent in the copolymers produces necessarily more orientation – what is reflected in increasing T* values.

The third reducing parameter is P*. Its physical significance has been elucidated by connecting it to the pair interaction potential u(R) and the binary radial distribution function g(R). The result is [33]:

$$P^* = (2\pi N / 9\mu V) \cdot \overline{R} \cdot \left(du(\overline{R}) / dR\right) \cdot g(\overline{R}). \qquad (22)$$

Here μ is a geometric parameter (equal to unity for the simple cubic lattice with the coordination number z = 6), N is the number of particles in the system (hence N/V is the numerical density) while R is the average interparticle distance.

To conclude, it is worth noting that the inverse way, from mechanical properties to the equation of state, exists also. To the knowledge of this author, it has been used only once. From values of the ductile–brittle impact transition temperatures, each corresponding to a specific value of the stress concentration factor for low-density polyethylene (LDPE), values v(T) of the specific volumes as a function of temperature have been calculated [7]. The average difference between computed and experimental v values for LDPE amounted to 0.092% only. This directly supports the basic premise of the present paper advocated already by Doolittle [2]: mechanical and rheological behavior of viscoelastic materials reflect their free volume and equation of state parameters – as well as vice versa.

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