



Master curve of viscoelastic solid: Using causality to determine the optimal shifting procedure, and to test the accuracy of measured data



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ABSTRACT

Viscoelastic solids such as rubber exhibit a complex elastic modulus $E(\omega)$, which depends on the frequency ω of the applied stress or strain. The modulus $E(\omega)$ can often be determined in a wide frequency range by performing measurements in a limited frequency range for many different temperatures, and then shift the frequency segments horizontally along the frequency axis to obtain a continuous master curve. We show that one can use the spectral representation of $E(\omega)$ (or $1/E(\omega)$), which obeys causality, to determine the optimal shifting procedure, and to test the accuracy of the measured data and the calculated master curve.

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1. Introduction

If an oscillatory strain is applied to a linear viscoelastic solid the oscillatory stress

$$\sigma(\omega)e^{-i\omega t} = E(\omega)\varepsilon(\omega)e^{-i\omega t}.$$

In general $E(\omega)$ is complex which gives rise to a phase shift between the oscillatory strain and stress; this phase shift is due to energy dissipation in the solid. To obtain the viscoelastic modulus $E(\omega)$ in a large frequency range it is often possible to measure $E(\omega)$ in a very limited frequency interval, e.g. from 0.1 Hz to 10 Hz, at many different temperatures, say from -100 °C to 100 °C (in temperature steps of typically 5 °C), and then shift the frequency segments along the frequency axis to obtain a continuous master curve. The shifting function a_T and the master curve $E(\omega)$ make it possible to obtain the viscoelastic modulus for any relevant temperature and frequency using $E = E(\omega a_T)$. The fundamental reason for why the viscoelastic modulus depends on the frequency ω and the temperature T via the product ωa_T follows from the theory of activated processes: the probability per unit time, w , for a thermally activated process to occur is given by the Boltzmann factor $w = w_0 \exp(-\Delta U/k_B T)$, where ΔU is the activation barrier. During the time period $t_\omega = 2\pi/\omega$ the probability to go over the barrier is $w t_\omega = (2\pi w_0/\omega) \exp(-\Delta U/k_B T)$.

Thus we expect E to depend on frequency and temperature as ωa_T with $a_T \sim \exp(\Delta U/k_B T)$ (Arrhenius equation). In reality the temperature dependency is often more complex because the barrier height ΔU depends on temperature due to thermal expansion (which (usually) makes the structure more “open” with increasing temperature, which reduces the activation barrier ΔU necessary for a local rearrangement of a polymer segment in the rubber).

For simple rubber materials the shift factor a_T is often well approximated by the Williams–Landel–Ferry (WLF) expression [1]

$$\log_{10} a_T = -A \frac{T - T_g}{B + T - T_g} \quad (1)$$

where T_g is the rubber glass transition temperature, and the standard values $A = 17.44$ and $B = 51.6$ °C. Thus one procedure to construct the master curve is to shift the frequency segments using the WLF expression for a_T with either the standard values for A and B , or optimized values [2–6]. However, in many cases this does not result in a smooth master curve. For example, in some cases (or for some temperature interval) the shift factor a_T is more accurately described by the Arrhenius equation given above with ΔU independent of the temperature.

A more general procedure is to do unrestricted shifting, where the shift function a_T is determined numerically so as to give as smooth master curve as possible [7]. In this case there exist several possible shifting procedures: (a) a_T is determined to give as smooth as possible master curve for $\text{Re}E(\omega)$. After having determined a_T this way, the same shift function is used to construct the master curve

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for $\text{Im}E(\omega)$. (b) The same procedure is used as in (a), but for $\text{Im}E$. (c) Some combination of $\text{Re}E$ and $\text{Im}E$, e.g. $\tan \delta = \text{Im}E/\text{Re}E$ is shifted. For “simple” unfilled rubber the different procedures (a)–(c) usually give nearly identical results. However, for more complex materials, such as tread rubber for tires, or as a result of poor measurements, the different shifting procedures may give rather different master curves, and in this note we will address the fundamental question of how to determine the best or optimal shifting procedure, and to test the accuracy of the measured viscoelastic modulus data.

2. Linear response, causality and spectral representation

When a body is exposed to weak external forces it usually responds in a linear way. For example, a weak electric field \mathbf{E} may induce an electric current \mathbf{J} which is linearly related to \mathbf{E} . If the driving field oscillates in time as $\cos(\omega t)$ the induced current will in general be phase shifted due to energy dissipation in the solid. This is conveniently described using complex numbers. If the external field oscillates as $\exp(-i\omega t)$ the induced current will be related to the driving force via $\mathbf{J}(\omega)\exp(-i\omega t) = \sigma(\omega)\mathbf{E}(\omega)\exp(-i\omega t)$. To account for the phase shift (due to the energy dissipation) between \mathbf{J} and \mathbf{E} , the linear response function $\sigma(\omega)$ must be complex. However, causality requires that $\text{Re}\sigma(\omega)$ and $\text{Im}\sigma(\omega)$ are not independent but related to each other. We note that causality in the present context just means that there can be no response (here the electric current) before the stimuli (here the applied electric field).

The statement above holds for any linear response function. In the present context because of causality, the Young’s modulus $\text{Re}E(\omega)$ is related to $\text{Im}E(\omega)$. Thus, for example, because of causality the real and imaginary part of $E(\omega)$ satisfies the Kramers–Kronig relation, which in the present case takes the form

$$\text{Re}E(\omega) = E(\infty) + \frac{2}{\pi} P \int_0^{\infty} d\omega' \frac{\omega' \text{Im}E(\omega')}{\omega'^2 - \omega^2}. \quad (2)$$

Here we will instead use that causality requires that $E(\omega)$ can be represented using the following spectral decomposition

$$E(\omega) = E(\infty) - \int_0^{\infty} d\tau \frac{H_1(\tau)}{1 - i\tau\omega} \quad (3)$$

where $H_1(\tau)$ is a real (and positive) valued function of the relaxation time τ . Alternatively one may write

$$\frac{1}{E(\omega)} = \frac{1}{E(\infty)} + \int_0^{\infty} d\tau \frac{H_2(\tau)}{1 - i\tau\omega} \quad (4)$$

where $H_2(\tau)$ is a real and positive. These spectral representations are also very important in many practical calculations (see below).

3. Using the spectral representation to test accuracy of master curves

The real and imaginary part of any linear response function must be related via the Kramers–Kronig relation (2) or, equivalently, can be expressed in terms of a single real-valued (positive) spectral density $H_1(\omega)$ [or $H_2(\omega)$] as in (3) [or (4)]. In numerical studies one must use discretized versions of (3) and (4):

$$E(\omega) \approx E(\infty) - \sum_n \frac{H_1(\tau_n)}{1 - i\tau_n\omega} \quad (5)$$

and

$$\frac{1}{E(\omega)} \approx \frac{1}{E(\infty)} + \sum_n \frac{H_2(\tau_n)}{1 - i\tau_n\omega} \quad (6)$$

where $n = 1, 2, \dots, N$. It is usually enough to choose $N \approx 100$ (or less) and $\tau_{n+1} \approx 3\tau_n$. We determine $E(\infty)$ and $H_1(\tau_n)$ [or $1/E(\infty)$ and $H_2(\tau_n)$] by minimizing the difference between the measured function $E(\omega)$ [or $1/E(\omega)$] and the fit function given by (5) [or (6)]. The minimization uses the Monte Carlo (MC) method. The quantity we minimize is the effective “potential” or error V . For the case where we fit the expression (5) to the measured master curve $E(\omega)$ we define

$$V = \frac{1}{\omega_1 - \omega_0} \int_{\omega_0}^{\omega_1} d\omega \left(\frac{a^2 + b^2}{c^2 + d^2} \right)^{1/2} \quad (7)$$

where

$$a = \log[\text{Re}E(\omega)] - \log[\text{Re}\tilde{E}(\omega)],$$

$$b = \log[\text{Im}E(\omega)] - \log[\text{Im}\tilde{E}(\omega)],$$

$$c = \log[\text{Re}E(\omega)], \quad d = \log[\text{Im}E(\omega)],$$

where $E(\omega)$ is the measured master curve and where $\tilde{E}(\omega)$ now denotes the fit-function (5). Note that $V = 0$ corresponds to $E(\omega) = \tilde{E}(\omega)$, i.e., perfect fitting. We have found that fitting $1/E(\omega)$ with the representation (6) requires 10–100 times less MC steps as compared to fitting $E(\omega)$ with (5), and the former procedure (which typically require less than 1 min on a PC) is therefore more convenient if the only aim is to test if a measured viscoelastic master curve obey causality.

4. Vertical shifting

We have developed a shifting procedure based on unrestricted horizontal shifting to obtain as smooth master curves as possible. Results will be presented both without and with vertical shifting. If T_0 denotes the reference temperature we write

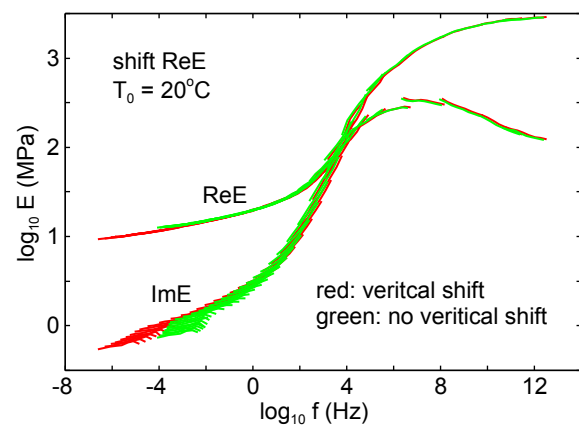


Fig. 1. The viscoelastic modulus master curves for a rubber tread compound resulting from shifting $\text{Re}E$. The green and red curves have been obtained without vertical shifting (i.e. $b(T) = 1$) and including vertical shifting according to Eq. (8). The reference temperature $T_0 = 20^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

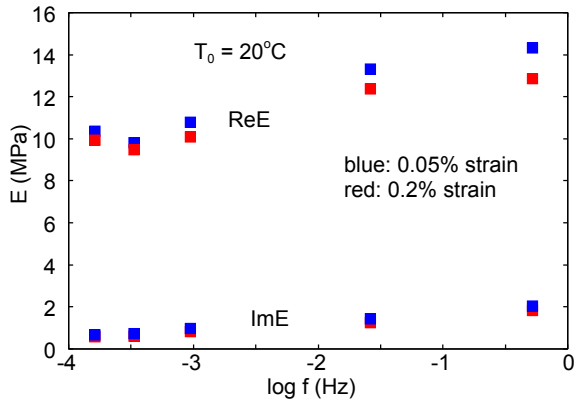


Fig. 2. Measured viscoelastic modulus for two different strain amplitudes. For the temperature $T_0 = 20^\circ\text{C}$.

$$E(\omega, T) = b_T E(a_T \omega, T_0)$$

where $a_T = a(T)$ and $b_T = b(T)$ are the horizontal and vertical shift factors with $a(T_0) = b(T_0) = 1$. In the rubbery region the viscoelastic modulus $E \sim T$ and for this reason it is often assumed $b(T) = T/T_0$. However, the origin of the linear T -dependency of E in the rubbery region (i.e., high temperatures and low frequencies) is the entropic contribution to the elasticity resulting from the thermal motion of the rubber segments between the cross-link points. At high frequencies (or low temperatures) in the glassy region this thermal motion is frozen and the large elastic modulus of rubber in the glassy region has a different physical origin. To take this into account we use an interpolation procedure where $b(T) \sim T$ at very low frequencies (in the rubbery region) and $b(T) = 1$ at very high frequencies (in the glassy region). There is no unique way to do this interpolation but we have found that the exact way to perform the interpolation is not very important. Here we use

$$b(T) = 1 + \left(\frac{\text{Re}E(\omega_{\min}, T_{\max})}{\text{Re}E(\omega_{\min}, T)} \right)^{1/2} \left(\frac{T}{T_0} - 1 \right) \quad (8)$$

where T_{\max} is the highest temperature (in Kelvin) in the frequency sweep data, and ω_{\min} the lowest frequency point. Note that in the rubbery region $\text{Re}E(\omega_{\min}, T_{\max})/\text{Re}E(\omega_{\min}, T) \approx T_{\max}/T \approx 1$ so that $b(T) \approx T/T_0$ in the rubbery region. In the glassy region $\text{Re}E(\omega_{\min}, T)$ is typically 1000 times higher than $\text{Re}E(\omega_{\min}, T_{\max})$ and hence $b(T) \approx 1$ in the glassy region.

In Fig. 1 we show the viscoelastic modulus master curve for a rubber tread compound resulting from shifting ReE. The experimental frequency sweep data was obtained as described in Sec. 5.1. The green and red curves have been obtained without vertical shifting (i.e. $b(T) = 1$) and including vertical shifting according to Eq. (8). The reference temperature $T_0 = 20^\circ\text{C}$. It is clear that including the vertical shifting gives a smoother curve for ImE for the lowest frequencies. However, both cases gives master curves which obey the causality condition equally well (not shown) (the error V is ≈ 0.0144 in both cases), so causality cannot be used to determine which vertical shifting procedure is best. In the following analysis, unless otherwise stated, we will always include vertical shifting according to Eq. (8).

5. Numerical illustrations

We will now present some results for different rubber compounds and different measurement conditions to illustrate how the causality condition can be used to test the accuracy of the measured data or the shifting procedure.

5.1. Tread compound: linear response

We have performed DMA measurements (Q800, TA instruments) on a tire tread compound in elongation mode at 0.2% strain amplitude, where the rubber to a good approximation behaves as a linear viscoelastic solid, as shown by performing strain sweeps (see Fig. 2). The measurements were performed at frequencies between 0.25 Hz and 28 Hz and for temperatures between -50°C and 120°C in temperature steps of 5°C . The frequency segments for ReE and ImE were shifted using procedures (a) and (b) described above. In both cases we use the vertical shift function b_T given by Eq. (8). In Fig. 3 (a) and (b) the noisy blue and red curves show the resulting master curves (at the reference temperature $T_0 = 20^\circ\text{C}$), and in Fig. 4 the corresponding shift factors. If we define the glass transition temperature T_g as the temperature where $\tan \delta(T)$ (for the frequency $\omega_0 = 0.01 \text{ s}^{-1}$) is maximal, then $T_g = -35^\circ\text{C}$ and $T_g = -40^\circ\text{C}$ for shifting procedures (a) and (b), respectively. Also shown in Fig. 4 (green line) is the WLF result (with $T_g = -35^\circ\text{C}$) given by (1). It is clear that the results of using procedures (a) and (b) give about equally smooth master curves but they differ strongly. The question is: which shifting procedure is best? Causality results in a relation between $\text{Re}E(\omega)$ and $\text{Im}E(\omega)$ and we will now show that this relation is best satisfied using the shifting procedure (a).

Let us now study how well one can fit the measured master curves using the spectral representation (5). The variation of the error V [see (7)] with the number of MC steps is shown in Fig. 5. Note that the error function V after many MC steps converges to a much smaller value when the master curve was constructed using procedure (a) than for procedure (b). This is also illustrated in Fig. 3 which shows the original and fitted [Eq. (5)] master curve for both

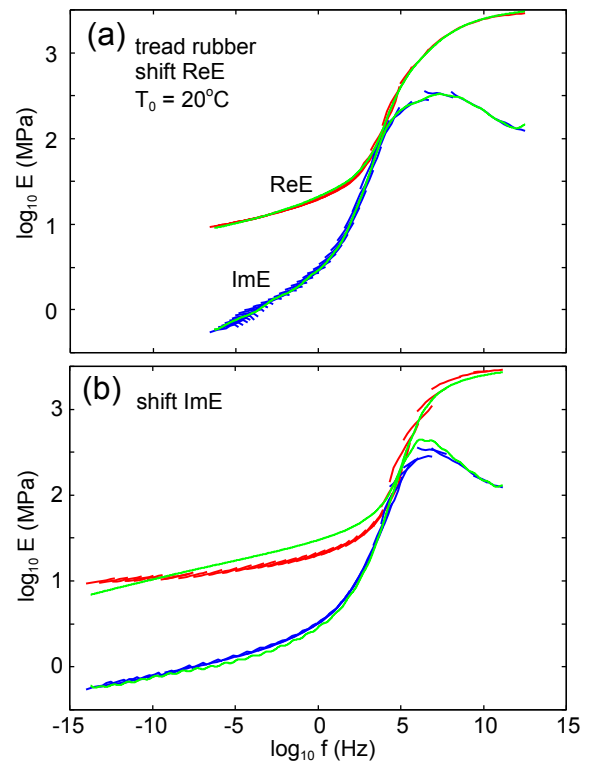


Fig. 3. The viscoelastic modulus master curves for a rubber tread compound resulting from shifting (a) ReE and (b) ImE. Also shown (green curves) are the fitting curves obtained from (5). The reference temperature $T_0 = 20^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

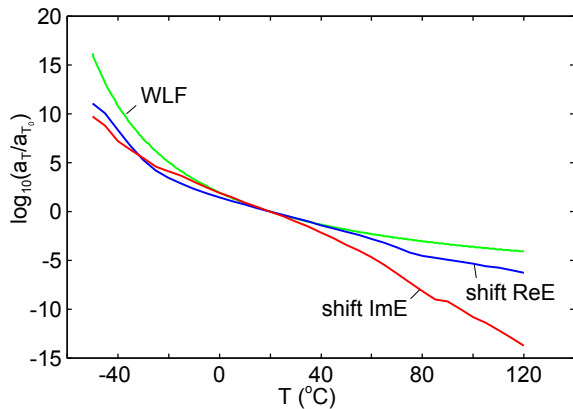


Fig. 4. The logarithm of the shift function a_T as a function of temperature T using the shift procedures (a) (blue line) and (b) (red line). Also shown is the WLF result (green line). The reference temperature $T_0 = 20^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

procedures (a) and (b). We conclude that shifting process (a) gives a master curve for $E(\omega)$ which obeys causality to a very good approximation. Using shifting process (b) gives in the present case bad results, and the same holds for the shifting process (c) (shifting $\tan \delta$).

The causality argument used in this paper assumes linear response, which requires small enough strain [4]. For our tread compound we have tested the linear response assumption by performing strain sweeps, see Fig. 2. The real part of the elastic modulus is only 5% smaller at the strain 0.2% as compared to 0.05% strain (which should be almost the same as 0% strain). The imaginary part changes slightly more but still to a good approximation, for the rubber we use, we are in the linear response region.

5.2. Tread compound: non-linear response

In many practical applications the rubber deformations are so large that the relation between the stress and the strain is non-linear. In fact, for filled rubber a linear relation is typically only observed for strain values below 0.2%. When the viscoelastic modulus is measured for large strain amplitudes (non-linear region) [8] it will not obey the Kramers–Kronig relation and it cannot be represented on the form given by (5) or (6) since these equations are only valid for linear response functions (obeying causality). To illustrate this fact, in Fig. 6 we show the viscoelastic modulus for another tread compound measured at 3% strain amplitude (in shear-mode, but this fact is irrelevant). In this case the fit by the expression (5) is very bad, and the viscoelastic modulus cannot be represented

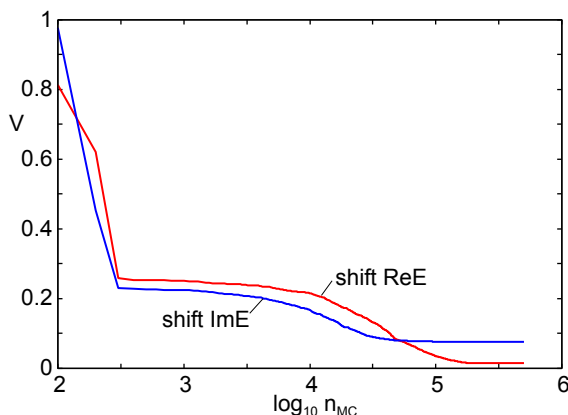


Fig. 5. The variation of the effective “potential” with the number of Monte Carlo steps.

by (5). This result is general, and we observe equally bad fits for other compounds when studied in the non-linear response region.

5.3. Unfilled and filled SB rubber

We now present the master curves for unfilled and filled (80 phr silica) SB rubber [9]. The data was measured from -35°C to 150°C at a strain amplitude of 0.2% in oscillatory shear deformation. In Fig. 7 we show the viscoelastic modulus master curves for unfilled SB rubber resulting from shifting the shear modulus $\text{Im}G$. Also shown (green curves) are the fitting curves obtained from (5). Nearly the same master curve is obtained by shifting $\text{Re}G$. In both cases the measured master curve can be rather well fitted by the expression (5).

In Fig. 8 we show the viscoelastic modulus master curves for SB rubber with Si-filler, resulting from shifting (a) $\text{Re}G$ and (b) $\text{Im}G$. Also shown (green curves) are the fitting curves obtained from (5). Note that shifting $\text{Re}G$ and $\text{Im}G$ using our software results in slightly different master curves but in both cases the master curves can be well fitted by the expression (5) i.e., both procedures result in a viscoelastic modulus which obey causality to a good approximation. Nevertheless, shifting $\text{Re}G$ results in a master curve for $\text{Im}G$ where the frequency segments do not overlap (or join smoothly) in the glassy region (high frequency), while shifting $\text{Im}G$ results in a master curve for $\text{Re}G$ where the frequency segments do not overlap in the rubbery region (small frequencies). Perhaps some other shifting procedure, which minimizes some weighted average involving the fitting error for both $\text{Re}G$ and $\text{Im}G$, would result in better master curves also in the rubbery and glassy regions. However, the aim of this study is not to present the best possible shifting procedure but to show how causality may help in testing the accuracy of the master curve independent of how it was obtained.

5.4. Viscoelastic modulus of inhomogeneous (two-phase composite) rubber

Let us consider an inhomogeneous rubber consisting of two types of rubber, say type A and B, where type B forms randomly distributed domains in the type A rubber matrix (or vice versa). This type of two-phase (or more) rubbers are very important in practical applications, e.g., tread rubber for tires often contains a small fraction of natural rubber in a SB rubber matrix (this decreases the rubber wear for reasons which does not interest us here). With

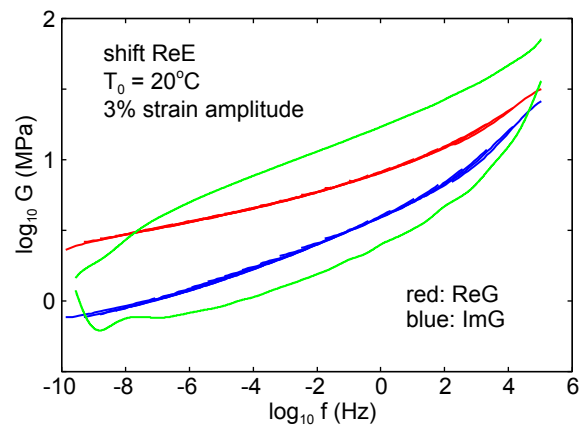


Fig. 6. The viscoelastic modulus master curves for a tread compound resulting from shifting $\text{Re}G$. Also shown (green curves) are the fitting curves obtained from (5). The reference temperature $T_0 = 20^\circ\text{C}$ and the strain amplitude in the measurements 3%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

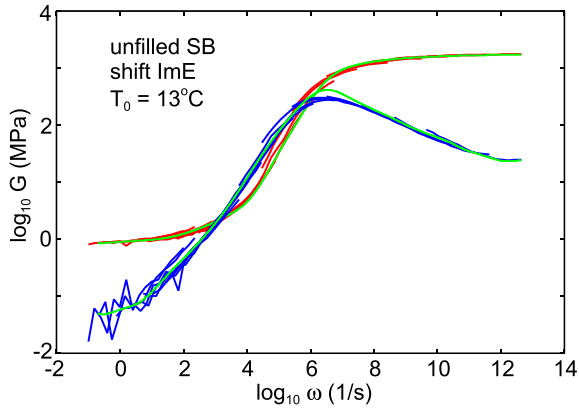


Fig. 7. The viscoelastic modulus master curves for unfilled SB rubber resulting from shifting the shear modulus $\text{Im}G$. Also shown (green curves) are the fitting curves obtained from (5). The reference temperature $T_0 = 13^\circ\text{C}$ and the strain amplitude in the measurements 0.2%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respect to deformations of the rubber which varies slowly in space on the length scale of the fluctuations in the rubber composition, we can describe the rubber with a homogeneous viscoelastic modulus $E_{\text{eff}}(\omega, T)$. We can approximately obtain $E_{\text{eff}}(\omega, T)$ using the Bruggeman effective medium theory [10]. Thus if $E_A(\omega, T)$ and $E_B(\omega, T)$ are the viscoelastic moduli of the two compounds the effective modulus of the composite is determined by Ref. [11]

$$c_A \frac{E_A - E_{\text{eff}}}{E_A + 2E_{\text{eff}}} + c_B \frac{E_B - E_{\text{eff}}}{E_B + 2E_{\text{eff}}} = 0 \quad (9)$$

where c_A and c_B are the volume fractions (with $c_A + c_B = 1$) of the rubber compound A and B.

A two component rubber is characterized by two temperature-frequency shift factors, $a_A(T)$, and $a_B(T)$. One fundamental question is to what extent the composite modulus $E_{\text{eff}}(\omega, T)$ can be approximated by a function $E_{\text{eff}}(a_T \omega)$. It is clear that this replacement cannot be exact but no theoretical study we are aware of has addressed this question quantitatively.

In Fig. 9 we show the viscoelastic modulus master curves for a tread compound A (red curve) and a syringe rubber stopper compound B (blue curve), and mixtures of the two compounds (green curves) where one compound is assumed to form domains in the second compound. The fraction of compound A decreases from the top to the bottom in the figure from $c_A = 1.0$ (red curve) to 0.9, 0.8, ... 0.1 (green curves) to 0 (blue curve). The viscoelastic modulus of the mixtures has been calculated using the Bruggeman effective medium theory, Eq. (9). The black curve has been obtained for the $c_A = 0.4$ mixture by first calculating the viscoelastic modulus using (9) for 15 frequencies between 0.01 Hz and 30 Hz, and for many different temperatures ($T = -45, -40, \dots, 20^\circ\text{C}$) and then shifting the frequency segments (shift $\text{Re}E$) to form a smooth master curve. In Fig. 10 the black curve shows the resulting shift factors while the red and blue curves are the shift factors for compound A and compound B, respectively.

Fig. 11 shows the viscoelastic modulus obtained for the mixture $c_A = 0.4$ ($c_B = 0.6$) at the temperatures $T = 0, 15$ and 30°C using the Bruggeman theory (blue curves) and using the master curve and shift factor given by the black curves in Figs. 9 and 10 (red curves). (Note: the shift factor in Fig. 10 is only given up to $T = 20^\circ\text{C}$, and the shift factor for $T = 30^\circ\text{C}$ was obtained by linear extrapolation.) Note that in the present case it is possible to represent the viscoelastic modulus relative accurately on the form $E_{\text{eff}}(a_T \omega)$ in spite of the two-component nature of the rubber system. Finally, we note that if

$E_A(\omega, T)$ and $E_B(\omega, T)$ are linear response functions which satisfy causality then so will the effective medium modulus obtained from (9) do.

6. Time relaxation modulus and application

The spectral representations (3) and (4) have many important applications in addition to what was discussed above. Note that if the strain is abruptly increased (at time $t = 0$) from zero to ε_0 then

$$\varepsilon(\omega) = \int_0^\infty dt \varepsilon_0 e^{i\omega t - 0^+ t} = \frac{-\varepsilon_0}{i\omega - 0^+}$$

In this case the stress at time $t > 0$ will be:

$$\begin{aligned} \sigma(t) &= \frac{1}{2\pi} \int d\omega E(\omega) \varepsilon(\omega) e^{-i\omega t} \\ &= \frac{1}{2\pi i} \int d\omega \left(E(\infty) - \int_0^\infty d\tau \frac{H_1(\tau)}{1 - i\tau\omega} \right) \frac{-\varepsilon_0}{\omega + i0^+} e^{-i\omega t} \\ &= \left[E(\infty) - \int_0^\infty d\tau H_1(\tau) (1 - e^{-t/\tau}) \right] \varepsilon_0 \end{aligned} \quad (10)$$

which describes stress relaxation in response to the change in strain. In a similar way, if the stress is abruptly changed (at $t = 0$) from zero to σ_0 we get for $t > 0$:

$$\begin{aligned} \varepsilon(t) &= \frac{1}{2\pi} \int d\omega \frac{\sigma(\omega)}{E(\omega)} e^{-i\omega t} \\ &= \frac{1}{2\pi i} \int d\omega \left(\frac{1}{E(\infty)} + \int_0^\infty d\tau \frac{H_2(\tau)}{1 - i\tau\omega} \right) \frac{-\sigma_0}{\omega + i0^+} e^{-i\omega t} \\ &= \left[\frac{1}{E(\infty)} + \int_0^\infty d\tau H_2(\tau) (1 - e^{-t/\tau}) \right] \sigma_0 \end{aligned} \quad (11)$$

which describes strain relaxation (creep) in response to the change in stress.

The representations (3) and (4) [and (10) and (11)] are useful in viscoelastic contact mechanics [12,13]. The area of real contact (neglecting adhesion) when a hard body with a nominally flat surface is squeezed against a viscoelastic material (e.g., rubber) with a constant (in time) nominal pressure σ_0 is given by

$$\frac{A(t)}{A_0} \approx \text{erf} \left(\frac{\pi^{1/2}}{2} P_1 \right)$$

where

$$P_1 = \frac{2^{3/2}}{\pi^{1/2}} \frac{1 - \nu^2}{\kappa} \frac{1}{2\pi i} \int_{-\infty}^\infty d\omega \frac{-\sigma_0}{\omega + i0^+} \frac{e^{-i\omega t}}{E(\omega)}$$

and

$$\kappa = \left(2\pi \int_0^{q_1} dq q^3 C(q) \right)^{1/2}$$

where $C(q)$ is the surface roughness power spectrum. Note that κ is the (combined) surface root-mean-square slope. Using (10) this gives

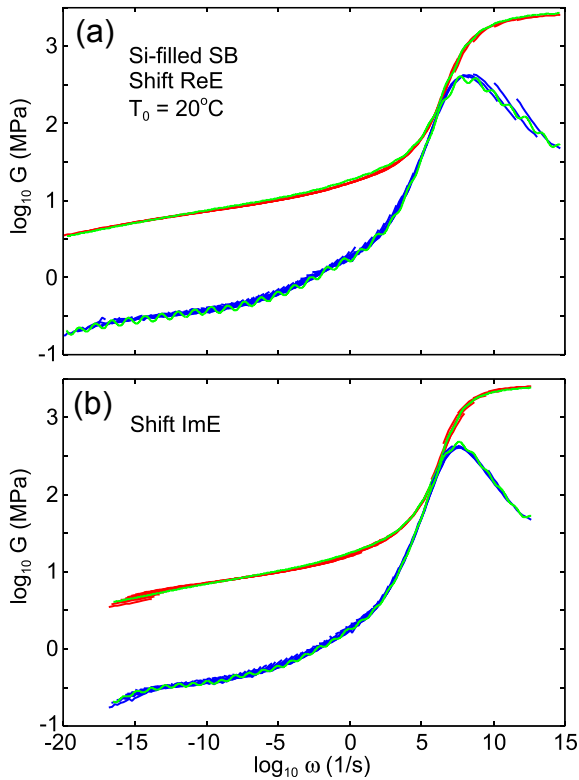


Fig. 8. The viscoelastic modulus master curves for SB rubber with Si-filler, resulting from shifting (a) ReE and (b) ImE. Also shown (green curves) are the fitting curves obtained from (5). The reference temperature $T_0 = 20^\circ\text{C}$ and the strain amplitude in the measurements 0.2%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$P_1 = \frac{2^{3/2}}{\pi^{1/2}} \frac{1 - \nu^2}{\kappa} \left[\frac{1}{E(\infty)} + \int_0^\infty dt H_2(\tau) (1 - e^{-t/\tau}) \right]$$

If instead the interfacial separation is abruptly changed at time $t = 0$ the contact area will depend directly on the relaxation modulus (10) (see Ref. [12]). Another application of (4) is crack propagation in viscoelastic solids. One can show that the viscoelastic contribution to the crack propagation energy is conveniently formulated as an integral over $H_2(\tau)$, see Refs. [14,15].

7. Discussion

We have used the spectral representation of $E(\omega)$ (or $1/E(\omega)$), which obeys causality, to determine the optimal shifting procedure for the construction of master curves. The basic idea is that since the relaxation spectrum $H_1(\tau)$ (or $H_2(\tau)$) is a (positive) real-valued function, it is in general not possible to obtain two functions, ReE and ImE, as the real and imaginary part of a complex function which depends on a single real fit-function. However, if $E(\omega)$ is a causal linear response function then ReE and ImE are related via a Kramers–Kronig relation and a complex function depending on a single real fit-function (relaxation spectrum) can exactly reproduce both ReE and ImE. We have found that for a rubber tread compound only the shifting procedure (a), where a_T is determined by shifting the measured ReE(ω) frequency segments, gives a master curve which corresponds to a linear response function which obeys causality.

The procedure outlined above can also be used to test the accuracy of the master curve, which may be inaccurate due to poor measurements. For example, if the holding time at a fixed

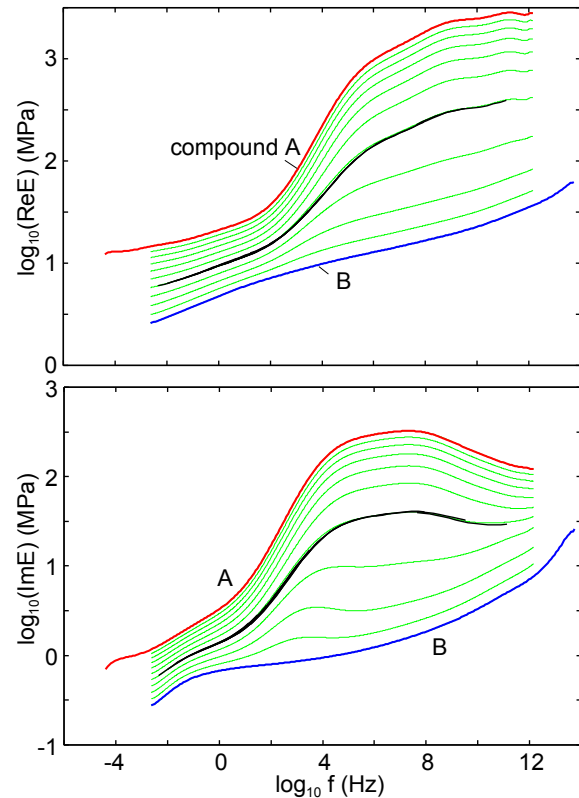


Fig. 9. The viscoelastic modulus master curves for a tread compound A (red curve) and a syringe rubber stopper compound B (blue curve), and mixtures of the two compounds (green curves) where one compound form domains in the second compound. The fraction of compound A decreases from the top to the bottom from $c_A = 1.0$ (red curve) to 0.9, 0.8, ..., 0.1 (green curves) to 0 (blue curve). The viscoelastic modulus of the mixtures has been calculated using the Bruggeman effective medium theory. The black curve has been obtained for the $c_A = 0.4$ mixture by first calculating the viscoelastic modulus using (9) for 15 frequencies between 0.01 Hz and 30 Hz, and for many different temperatures ($T = -45, \dots, 20^\circ\text{C}$) and then shifting the frequency segments (shift ReE) to form a smooth master curve. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature before the measurement of a $E(\omega)$ frequency segment is too short, the temperature inside the rubber strip may be non-uniform which will result in an error in the measured data, which may result in ReE(ω) and ImE(ω) not obeying the Kramers–

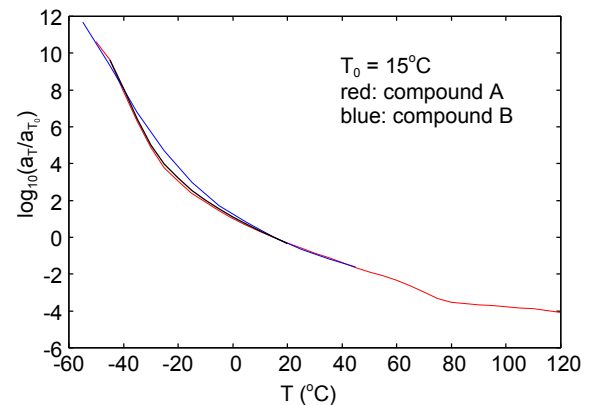


Fig. 10. The shift factor for compound A (red curve) and compound B (blue curve). The black curve is the shift factor obtained for the $c_A = 0.4$ ($c_B = 0.6$) mixture as a result of the shifting of the frequency segments which resulted in the black curve in Fig. 9. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

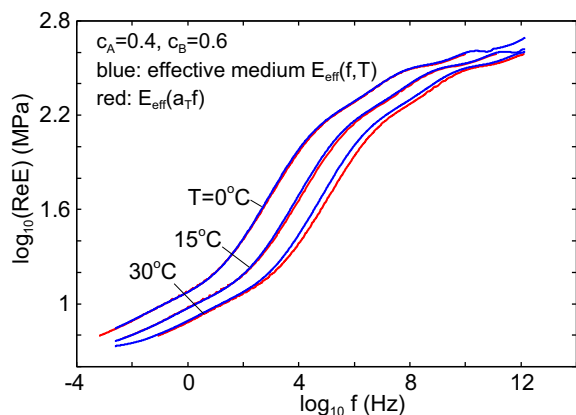


Fig. 11. The viscoelastic modulus obtained for the mixture $c_A = 0.4$ ($c_B = 0.6$) at the temperatures $T = 0, 15$ and 30 °C using the Bruggeman theory (blue curves) and using the master curve and shift factor given by the black curves in Figs. 9 and 10. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Kronig relation. That is, if there is inaccuracy in the measured $E(\omega)$ then $\text{Re}E$ and $\text{Im}E$ cannot in general be obtained from a complex function which depends on a single real function, and the error function V (after many MC step) converges to a relative large number. In this case comparing the measured $\text{Re}E(\omega)$ and $\text{Im}E(\omega)$ curves to the fit curves based on the spectral representation (as in Fig. 3) will give information about the accuracy of the measured $E(\omega)$.

The causality argument used in this paper assumes linear response, requiring small enough strain [4]. For our tread compound we have tested the linear response assumption by performing strain sweeps, see Fig. 2. The real part of the elastic modulus is only 5% smaller at the strain 0.2% as compared to 0.05% strain (which should be almost the same as 0% strain). The imaginary part changes slightly more but still to a good approximation, for the rubber we use, we are in the linear response region.

Fritzsche and Klüppel [2,3] have suggested a more complex procedure than used above to obtain the master curve of filled rubber compounds, involving measurements on both unfilled and filled compounds. In this procedure the measured data for the filled compound is shifted using the shift factor a_T (which was forced to be of the WLF-type) found for the unfilled compound. To obtain a smooth master curve for the filled compound this requires in addition performing a vertical shifting. We are not convinced that this procedure make sense because filled compounds have a distribution of activation barriers for rearrangements of the polymer chains which differ from those in the unfilled compound (e.g., the energy barriers for polymer segment rearrangements may be higher for rubber segments close to the filler particles [16,17] (however, see also Ref. [18–20])) and since the shift factor a_T reflects this distribution of activation barriers (see Section 1) there is no reason for a_T to be the same as for the unfilled compound. In addition, from a practical point of view it is often not so easy to do measurements on both filled and unfilled rubber of the same material.

In many applications, as for rubber friction in the context of tires, the strain in the asperity contact regions can be very large, say $\sim 100\%$. In our applications we take into account the non-linearity in an approximate way by first constructing the master curve for low strain, and then add information from strain sweeps up to very large strain (100% or more) at one frequency but many temperatures (see Ref. [21]).

8. Summary and conclusion

We have show that it is possible to test how accurate the master curve of a linear viscoelastic solid is by using a causality condition. How the master curve was produced is irrelevant. One can even use it to check the quality of the measurement (for a poor measurements one cannot expect $\text{Re}E$ and $\text{Im}E$ to be related by the Kramers–Kronig relation). For filled rubber already at small strain (say larger than $\sim 0.2\%$) the rubber will behave non-linearly, and in non-linear response region then again one would not expect the Kramers–Kronig relation for $E(\omega)$ to be satisfied [8].

We emphasize that when working with numerical data, which always have some uncertainty, there is not necessarily a unique shift factor from a practical point of view, and this we have indeed shown to be the case: curves in Figs. 3 and 4 gives equally smooth master curves. However, only the master curve obtained by shifting $\text{Re}E$ (Fig. 3) obey causality. In the E -shift software we have developed (see www.MultiscaleConsulting.com) we now routinely check how well viscoelastic master curves obey the causality condition.

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- [8] In the non-linear response region if the applied strain oscillates as $\varepsilon(t) = \varepsilon_0 \cos(\omega t)$ the stress will be a sum involving terms $\sim \cos(n\omega t)$ and $\sim \sin(n\omega t)$ where n is an integer. The DMA instrument we use define the modulus $E(\omega)$ in the non-linear region using only the component $f(\varepsilon_0, \omega) \cos(\omega t) + g(\varepsilon_0, \omega) \sin(\omega t)$ in this sum which oscillate with the same frequency as the applied strain. Thus $\text{Re}E(\omega) = f(\varepsilon_0, \omega)/\varepsilon_0$ and $\text{Im}E(\omega) = g(\varepsilon_0, \omega)/\varepsilon_0$. Note that with this definition the dissipated energy during one period of oscillation ($T = 2\pi/\omega$) is $\int_0^T dt \sigma(t) \dot{\varepsilon}(t) = \pi \varepsilon_0^2 \text{Im}E(\omega)$ just as in the linear response region.
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