Rheol Acta (2009) 48:241–243
DOI 10.1007/s00397-008-0329-5

SHORT COMMUNICATION

Three views of viscoelasticity for Cox–Merz materials

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Received: 24 July 2008 / Accepted: 30 October 2008 / Published online: 3 December 2008

Abstract A slight rearrangement of the classical Cox and Merz rule suggests that the shear stress value of steady shear flow,$\tau(\dot{\gamma})$, and complex modulus value of small amplitude oscillatory shear, $G^*(\omega) = (G'^2 + G''^2)^{1/2}$, are equivalent in many respects. Small changes of material structure, which express themselves most sensitively in the steady shear stress, τ, show equally pronounced in linear viscoelastic data when plotting these with G^* as one of the variables. An example is given to demonstrate this phenomenon: viscosity data that cover about three decades in frequency get stretched out over about nine decades in G^* while maintaining steep gradients in a transition region. This suggests a more effective way of exploiting the Cox–Merz rule when it is valid and exploring reasons for lack of validity when it is not. The $\tau - G^*$ equivalence could also further the understanding of the steady shear normal stress function as proposed by Laun.

Keywords Rheology · Cox–Merz rule · Viscoelasticity · Mechanical spectroscopy · Steady shear

Introduction

Fifty years ago, Cox and Merz (1958) reported that the shear rate dependence of the steady shear viscosity, $\eta(\dot{\gamma})$, and the frequency dependence of the complex viscosity $\eta^*(\omega)$ of a polystyrene melt are "similar". Within the accuracy of their experiments, the two function values were practically identical. This behavior has since been found for many polymeric liquids (here referred to as "Cox–Merz materials") which are mostly linear homopolymers. A detailed explanation for the origin of the Cox–Merz rule of congruent $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ and its range of applicability is still missing (nor will it be attempted here).

This paper is motivated by the well-known, high sensitivity of the stress to variations in material structure. Small changes in a material often magnify in a plot of shear stress as one of the axes. For the steady shear viscosity, material differences can be viewed much more clearly when plotted as $\eta(\tau)$ instead of $\eta(\dot{\gamma})$. It therefore is desirable to find an equally sensitive representation of dynamic mechanical experiments in which ω is replaced by some sort of stress.The search for a suitable stress measure led to G^* as independent variable, as will be shown below. From the famous Booij and Palmen (1992) plots of linear viscoelasticity, we already know that G^* is an advantageous variable for detecting small variations between material samples.

Data rearrangement

The following view of the Cox–Merz rule was chosen in order to emphasize the shear stress dependence of rheological material functions. We obtain stress values by multiplying the steady shear viscosity with the shear rate

$$\eta\left(\dot{\gamma}\right)\dot{\gamma} = \tau\left(\dot{\gamma}\right) \tag{1}$$

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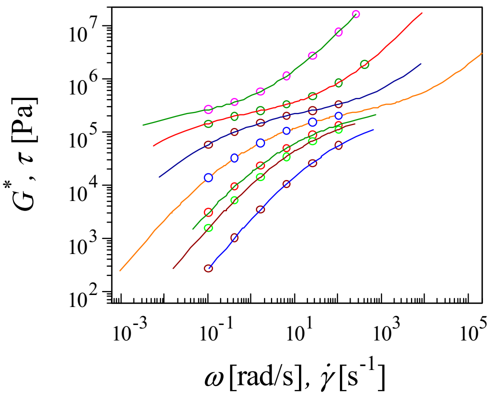

Fig. 1 Flow curves $\tau(\dot{\gamma})$ and $G^*(\omega)$. Overlay of linear (*dots*) and non-linear (*lines*) viscoelastic data of a commercial polystyrene (received from Monsanto in 1982) which is known to qualify as Cox–Merz material since a similar polymer was used in the original paper in 1958. Isotherms at T = 132, 145, 161, 181, 205, 219, and 269°C. Time–temperature shifting (Ferry 1980) of all curves onto the T= 181°C isotherm results in the large master curve. Data of Winter and Mours (2006). For the purpose of this plot, $G' - G''$ data were converted into "steady shear" data

The validity of the Cox–Merz plot is maintained by multiplying the complex viscosity value with the frequency

$$\left|\eta^*(\omega)\right|\omega = \left(\frac{|G^*|}{\omega}\right)\omega = \left|G^*(\omega)\right| \qquad (2)$$

Frequency, ω[rad/s], and shear rate, $\dot{\gamma}$[1/s], are set equal for this representation. The absolute value signs are omitted throughout the text. Figure 1 shows an overlay of $G^*(\omega)$ and $\tau(\dot{\gamma})$ for a Cox–Merz material. This gives new meaning to G^*, which became the linear viscoelastic equivalent of the steady shear stress, τ.

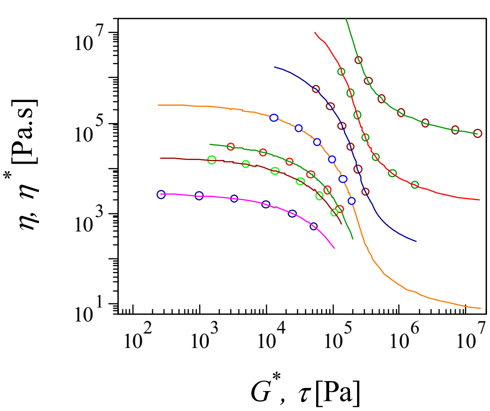

Fig. 2 Same data as in Fig. 1, however, plotted as $\eta^*(G^*)$ and $\eta(\tau)$. The *lines* represent the artificial viscosity data as defined in the text. The *dots* belong to the complex viscosity data

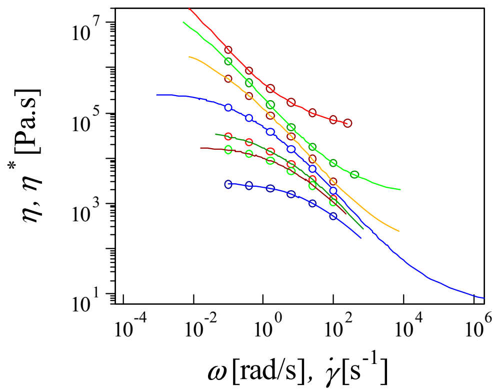

Fig. 3 Classical Cox–Merz plot (same data as in Fig. 1)

By elimination of the frequency, the data can be further transformed into an overlay plot for $\eta^*(G^*)$ and $\eta(\tau)$. This is shown in Fig. 2 which demonstrates the sensitivity of G^* as independent variable. For comparison, the classical Cox–Merz plot is shown in Fig. 3. The equivalent pairs of material functions are listed in Table 1. Figures 1, 2, and 3 demonstrate the full agreement between linear viscoelastic and steady shear data for this group of materials ("Cox–Merz materials").

The different views of the Cox–Merz relation give valuable insight in viscoelasticity and allow direct comparison with flow curves $\tau(\dot{\gamma})$. Of all three representations of the data, the $\eta^*(G^*)$ plot (Fig. 2) visualizes differences between material states most clearly. This has previously been overlooked, as far as we know.

Applications beyond Cox–Merz

When normal stress data become available, together with the corresponding dynamic mechanical data, it will be interesting to apply the τ-G^* equivalence to Laun's (1986) empirical rule that estimates the fist normal stress difference in steady shear, N_1, from dynamic mechanical data

$$N_{1,\mathrm{Laun}}\left(\dot{\gamma}\right)=2G'(\omega)\left\{1+\left(\frac{G'}{G''}\right)^2\right\}^{0.7}=\frac{2G^*}{\tan\delta}\left(\frac{G^*}{G''}\right)^{0.4} \qquad (3)$$

Table 1 Equivalent rheological material functions for Cox–Merz materials, all of them evaluated at $\omega = \dot{\gamma}$

Linear viscoelasticity		Steady shear
$\eta^*(\omega)$	$\leftrightarrow$	$\eta(\dot{\gamma})$
$\eta^*(G^*)$	$\leftrightarrow$	$\eta(\tau)$
$G^*(\omega)$	$\leftrightarrow$	$\tau(\dot{\gamma})$

Comparison is made for the absolute value of these variables

This suggests a plot of $N_{1,\mathrm{Laun}}(G^*)$ for estimating $N_1(\tau)$ of steady shear. G^*, G'', and $\tan\delta = G''/G'$ should be evaluated at $\omega = \dot{\gamma}$. It is unclear whether Laun's rule applies to Cox–Merz materials only or whether it goes beyond.

For materials that fail the Cox–Merz rule, such as many complex materials, the plotting of linear viscoelastic data as $G^*(\omega)$ and $\eta^*(G^*)$ was found to be also valuable. It visualizes structural change, yield stress, liquid-to-solid transition, and structural ripening, to name a few. Differences between viscoelasticity of gelation and glass transition show clearly. $G^*(\omega)$ and $\eta^*(G^*)$ plots, together with their respective counterparts (see Table 1), help to bridge between linear viscoelasticity and large strain behavior. In these functions, $G^*(\omega)$ and $\eta^*(G^*)$ are meaningful compliments to the powerful Booij–Palmen plot of the loss angle $\delta(G^*)$.

Lin et al. (1988) and Doraiswamy et al. (1991) proposed an extension of the Cox-Merz plot into the nonlinear domain by applying large-amplitude oscillatory shear and then rescaling the complex viscosity with an average shear rate per period. The $\tau - G^*$ equivalence might not apply to such extension.

Acknowledgements The work is supported by NSF through CBET-0651888. The appreciation for $G^*(\omega)$ and $\eta^*(G^*)$ plots evolved when working with Rheo-Hub (Winter and Mours 2006; Winter 2007).

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