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Thermal Analysis & Rheology

RHEOLOGY APPLICATIONS NOTE

THE PRINCIPLES AND APPLICATIONS OF THE COX-MERZ RULE

Principle of the Cox-Merz rule

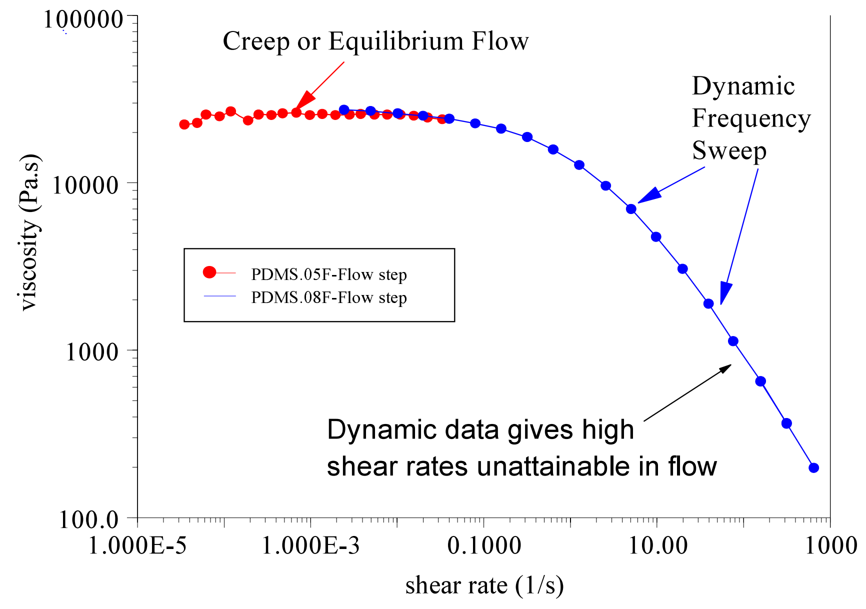
The so-called Cox-Merz "rule" is empirical relationship which has been found to be of great use in rheology. It was observed by Cox and Merz [1] that for many polymeric systems correspondence occurred between the steady state shear viscosity, η, plotted against shear rate, $\dot{\gamma}$, and the magnitude of the complex viscosity, $|\eta^*|$, plotted against angular frequency, ω. The complex viscosity is defined by:

$$\eta^* = G^* / i\omega \qquad (1)$$

where G^* is the complex modulus. So $|\eta^*| = |G^*| / \omega$

Figure 1 shows the procedure for a poly (vinyl alcohol) solution

Figure 1



Use of the rule

It is important in the application of the rule to ensure that the appropriate values for $\eta\ (\dot{\gamma})$ and $|\eta^*(\omega)|$ are used. For example, in both cases it is the steady state values which are required, i.e. any transient effects due to flow or oscillation start-up, inertia, or thixotropy must have fully decayed. Also important is that geometries are used for which the viscosity calculation is exact. This normally means cone and plate.

If applied correctly, the Cox-Merz rule can be of great value in polymer rheology, and there are several circumstances in which it might be used.

(I) The principle use is probably to predict $\eta\ (\dot{\gamma})$ from oscillatory measurements. For many polymeric systems the steady state viscosity is difficult to measure at high shear rates, because of sample fracture, secondary flows and so forth. Data obtained from oscillatory experiments are usually more reliable.

(ii) The rule can also be used to predict $|\eta^*(\omega)|$ from steady state viscosity data, for example in circumstances in which the oscillatory operating mode is not available.

(iii) The rule can also be used in an analytical sense. A good deal can be learned about the microstructure of materials from the degree to which they adhere to the rule.

Applicability of the rule

The applicability of the Cox-Merz rule has recently been reviewed in detail [2]. It has been found to hold for almost all polymer melts, and concentrated and semi-dilute solutions. Deviations from the rule occur at high frequencies, and the oscillatory data can either over- or under estimate the steady state data. Instances of polymeric systems for which it has been found not to apply are Boger fluids and certain other dilute solutions, and cross-linked or gelled systems. The rule also fails for most particulate dispersions.

Theoretical basis

Until very recently it could confidently be stated that no sound theoretical basis for the Cox-Merz rule had yet been provided, and indeed some workers felt that the correspondence was merely fortuitous. Recently, however, several, admittedly partial, justifications have been offered [3,4].

A starting point is a requirement of continuum mechanics that the dynamic viscosity and the steady state viscosity are related in the low frequency and shear rate limits, i.e.:

$$\eta'(\omega)|_{\omega\to 0} = \eta(\dot{\gamma})|_{\gamma\to 0} \qquad (2)$$

where $\eta'(\omega) = G''(\omega)/\omega$. In the limit the two experimental modes are effectively identical. This equality can be used as a check on the reliability of oscillatory and steady state data.

The elastic contribution to $\eta'(\omega)$ disappears in the low frequency limit, and Equation 2 can be rewritten as:

$$|\eta^*(\omega)|_{\omega\to 0} = \eta(\dot{\gamma})|_{\gamma\to 0} \qquad (3)$$

This sets a limiting condition for the rule. Milner [3] has used the Doi-Edwards reptation model to provide a theoretical basis for the rule, but his analysis is partly heuristic, and applies only to polymers with a broad distribution of molecular weights.

The rule of Al-Hadithi, Barnes and Walters

The usefulness of the Cox-Merz rule has led other authors to seek similar correspondences between other rheological functions [2,5]. These include the relationship proposed by Al-Hadithi, Barnes and Walters, who were concerned with the prediction of the first normal stress difference, N1, from oscillatory data. A second requirement of continuum mechanics is given by Equation 4:

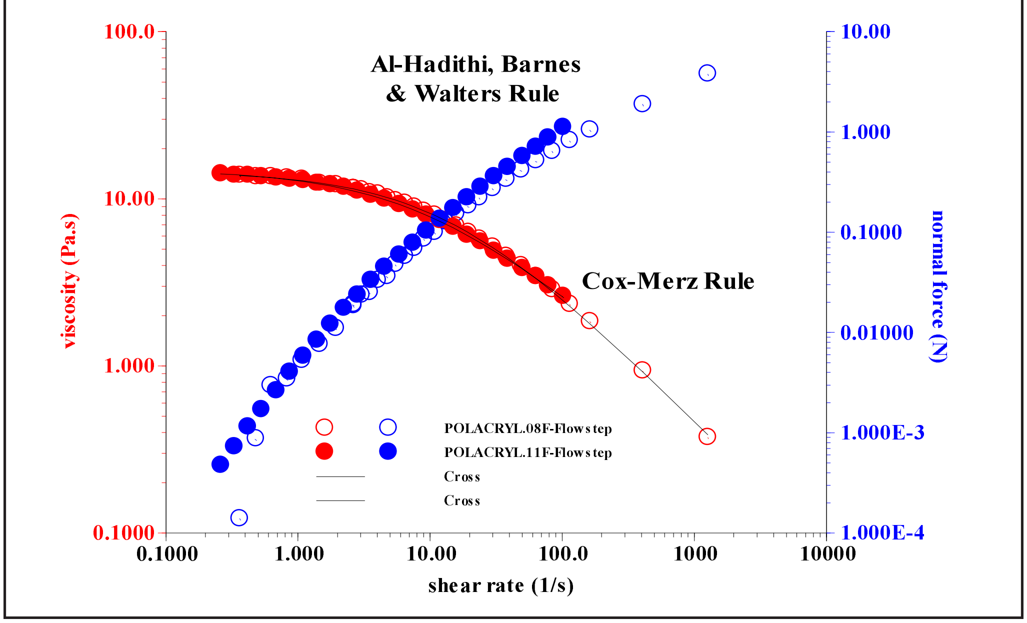
$$\left.\frac{G'(\omega)}{\omega^2}\right|_{\omega\to0} = \left.\frac{N_1(\dot{\gamma})}{2\dot{\gamma}^2}\right|_{\dot{\gamma}\to0} \qquad (4)$$

Taking this and Equation 2 as starting points, and after what they described as much trial and error, the authors arrived at the expression:

$$G_c = G'\left[\frac{(\eta_0+\eta')G'}{2\omega\eta'^2}+1\right]^{1/2} \qquad (5)$$

where η_0 is the low shear rate limiting viscosity. It is proposed that a plot of G_c. against ω will coincide with that of $N_1/2$ against $\dot{\gamma}$ when plotted on the same axes. Equally G_c against ω^2 should coincide with $N_1/2\ \dot{\gamma}^2$ plotted against $\dot{\gamma}$. Figure 2 shows the procedure for the poly (dimethyl siloxane) solution.

Figure 2



The authors suggest that their expression should be applicable to at least those systems for which the Cox-Merz rule holds, and provide example of polymeric systems for which this is the case. It is an acknowledged weakness that a value for η_0 has to be inserted, or at least determined parametrically. In the case above this was arrived at by fitting a Williamson model, $\eta = \eta_0 / [1 + (K\dot{\gamma})^m]$, to the oscillatory data in Figure 1.

References

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2. T.S.R Al-Hadithi, H.A. Barnes and K.Walters, *Colloid and Polymer Science*, 270, 40 (1992).
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4. G. Marrucci and G. Ianniruberto, Proceedings of the Royal Society - Unilever - Indo/UK Forum on the Dynamics of Complex Fluids, Cambridge, UK, June 1996.
5. H.M. Laun, *Journal of Rheology*, 30, 459 (1986).

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